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Organic Electrochemical Transistors for Neurotechnology

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DECLARATION OF ORIGINALITY

All original research presented in this thesis was undertaken by James Edward Tyrrell unless otherwise stated. The research was supervised by Professor Alasdair J. Campbell, Professor Ji-Seon Kim and Professor Martyn G. Boutelle.

James Edward Tyrrell
February 2022

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ABSTRACT

The organic electrochemical transistor is a device that has proven to provide a comprehensive insight into physiological activity. The burden of brain-related illnesses and the potential societal impact of enhancing human interaction and communication with computers motivates the advancement of technologies to provide greater insights into neural activity. This research focuses on the intersection of these fields through developing organic electrochemical transistors for neurotechnology. As such, this research reports the fabrication, characterisation, and operation of the devices to demonstrate their applicability in providing an accurate description of neural activity. In turn, pathways are offered on the optimisation and enhancement of transistor performance, informing the field on methods to maximise the efficacy of biosensing devices.

This thesis opens with the motivations to develop neurotechnology in society by considering the burden of neurological disorders and the enhancement of human-machine communication. The roles that bioelectronics and organic electrochemical transistors could take in achieving such goals are then described. The literature on organic electrochemical transistors and their applications in neurotechnology is then examined. Foundational to this research was the design and fabrication of novel transistor architectures. As such, fabrication methods are then described which provide μm -scale resolutions, facilitating the production of biocompatible, high-performance devices.

The thesis then describes an investigation with the aim to optimise the performance of organic electrochemical transistors for the maximisation of the range of electrophysiological signals that the devices can resolve and amplify. Devices are demonstrated with high amplification factors and bandwidths sufficient for transducing the full bioelectric spectrum. The devices efficaciously resolve electrophysiological inputs with a wide range of voltage and frequency characteristics, demonstrated through measuring the device response to pre-recorded signals and supported through noise quantification.

Research is then presented with aims to employ organic electrochemical transistors in a linear amplifier topology that provides precise amplification control. Circuit parameters are identified for stable amplifier operation, and the transistors are physically implemented into amplifier circuits. An equation is then formulated which models the transistor current in the linear, non-linear and saturation regimes, and this equation is used to simulate the amplifier response. Through experimentation and simulation, the amplifier is extensively characterised, providing quantitative measures on amplifier gain, linearity, bandwidth, and noise. The amplifier is then inputted with pre-recorded bioelectric signals and the linear gain of the amplifier is experimentally demonstrated.

The thesis then presents an investigation with the aim to determine the effect of electrode architecture on organic electrochemical transistor characteristics and bioelectric performance. The impacts of varying the interconnect resistance on the steady-state and transient characteristics are examined. Then, arrays of devices are fabricated, and the effects of varying the interconnect resistance and the interdigitated electrode geometry on bioelectric performance are quantified. The electrode architecture at the measurement site is then varied for a fixed site area to determine an optimal configuration for resolving bioelectric inputs. The investigation presents a pathway for the optimisation of electrode architecture for a given application.

Finally, the thesis describes research that aims to determine the relationships between the morphological properties of the organic layer and the electrical characteristics relevant to biosensing performance. Electrical characterisations and resonant Raman spectroscopy are carried out on organic electrochemical transistors that are immersed in an aqueous solution over a period of 50 days, and the temporal changes in the derived parameters are presented. Then, the effects of varying the applied voltages on the active layer morphology and the device noise are investigated, providing an insight into how the structural changes of organic polymers correlate to variations in noise.

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1. NEUROTECHNOLOGY IN SOCIETY

The development of technology that can interface with the brain and transduce neural activity can provide society with advancements in medicine, machine interaction and in our understanding of the fundamental mechanisms that constitute our consciousness. Neurotechnology can aid in the relief of the global burden of neurological disorders through the provision of medical diagnosis, prevention and rehabilitation. The potential to enhance our capabilities in communicating with computers has motivated research into the development of brain-machine interfaces. The technology implemented for such applications has also provided platforms to investigate how neuronal network architectures process information and thus determine the reality we experience. The trajectory of innovations in neurotechnology suggests that its impact on society will increase and could facilitate a revolution in human-machine and human-to-human interactions. Such developments should be considerate of ethical concerns as the recording of neural activity and the stimulation of the brain raises issues on privacy and identity.

To quantify the global impact of neurotechnology, the burden of deaths and disability caused by neurological disorders is considered. There are many disorders classified as neurological, and a subset of those that comprise a significant percentage of total cases includes Parkinson's disease, Alzheimer's disease, epilepsy, stroke, encephalitis and traumatic brain injury (TBI). The burden of neurological disorders is measured through disability-adjusted life-years (DALYs), which is defined as the sum of the years of life lost and the number of years living with a disability. In 2016, it was found that neurological disorders were the leading cause of DALYs with 276 million years lost, and were the second leading cause of death, responsible for approximately 9 million lives. With population growth and ageing, further increases in the absolute numbers of these measures are expected [1]. The COVID-19 pandemic has already shown a significant impact on neurological disorders. Following a COVID-19 infection, it was found that, within the following 6 months, the incidence of a neurological or psychiatric diagnosis was approximately 34%, with 13% receiving a first diagnosis [2]. Furthermore, individuals with pre-existing neurological disorders were found to have their symptoms significantly exacerbated by a COVID-19 infection [3].

Neurotechnology can serve to reduce the burden of neurological disorders and improve the quality of life of individuals with such conditions. Providing insight into the fundamental mechanisms of neural function better informs treatment direction. For example, electrophysiological recordings have shown how neuronal dynamics change in immune-mediated epilepsy and encephalitis, leading to suggestions for new medical

pathways [4]. The development of neurotechnology can provide faster identification of disorders. This could allow intervening measures to be introduced at earlier stages and thus potentially minimise the detrimental impacts of the disorders. For example, spreading depolarisations (SDs), which are a secondary injury of TBI and are associated with a significantly worse patient outcome, have been measured using electrocorticography and microdialysis. These technologies have provided data sets on how the physiological environment changes during the SDs. Such research could allow clinical staff to predict the onset of SDs and give insight into new treatment approaches [5, 6]. The expansion of neurotechnology to an increasing range of neurological disorders will reduce the burden on society.

Neurotechnology can aid individuals in restoring their mobility and communication, and thus in regaining a sense of independence. Recent developments in brain-computer interfaces (BCIs) have allowed a patient paralysed from the neck down to type with speeds of up to 90 characters per minute by using a neurotechnological system that decodes individual letters that the patient imagines they are writing by hand [7]. Furthermore, speech has been interpreted from neural activity by using high-density electrocorticography and decoding the recorded signals using machine learning [8]. BCIs have also been used for prosthetic arm control, with performances improved by tactile feedback facilitated by stimulation within the brain [9]. In addition to rehabilitation, BCIs can also be implemented for the enhancement of our interaction with computers. Implanted devices that allow for higher signal quality require neurosurgical operations for their insertion, which introduces a considerable level of health risk to an individual. As such, non-invasive BCIs that record neural activity from the surface of the scalp have been investigated in their abilities to decode neural signals and translate the activity into desired computational responses. For example, an electroencephalography (EEG) system with 6 electrodes was shown to provide a 93% classification accuracy into 4 classes. The BCI was connected to a virtual reality headset and was integrated into a video game with 4 different commands [10]. Nevertheless, high-density electrode arrays with 10^3 -scale channel counts that are designed to be inserted into the brain have been developed with the eventual goal of enhancing human-machine interactions by decoding neural activity [11]. With the continuing development of the technology, it is expected that interfaces with higher channel counts will combine with decoders of increasing performance to provide unprecedented degrees of control and communication with computers.

An emerging and arguably established platform upon which neurophysiological conditions can be determined and alleviated is bioelectronics. The development of organic materials in electronics has introduced properties of mixed ionic and electronic conductivity to the transduction of biological activity. The transmission of physiological

information utilises ionic fluxes, and thus such properties are ideally suited to convert neural signals into electronic outputs that can be computationally processed. Organic polymers provide a degree of biocompatibility to devices that physically interface with the brain, and their soft nature allows their incorporation into flexible structures that can conform to the non-linear geometry of the cerebral cortex [12]. This is exemplified by a device consisting of a grid of microelectrodes coated with a conductive organic material. The bioelectronic interface conformed to the cortical surface and recorded the activity of individual neurons [13].

A bioelectronic device that has received growing attention due to its continual success in transducing physiological signals is the organic electrochemical transistor (OECT). OECTs utilise an organic material whose conductivity varies with the presence of ionic species and can thus be used for the measurement of electrophysiological signals and the detection of chemical species. The OECT provides an amplification of the input signal, and investigations have shown that the devices provide superior signal qualities compared to electrodes in electrophysiology [14, 15]. Furthermore, the OECT has demonstrated its capabilities to detect chemical species relevant to neurological disorders, such as the detection of proteins associated with Alzheimer’s disease [16].

The OECT has proven itself to be a building block in high-performance bioelectronics. Nevertheless, the parameter space of their design has much to explore. Device performance is dependent on a combination of material and architectural characteristics. In the first investigation of this research, it was hypothesised that combining a range of optimisations across such characteristics would result in OECTs with amplification performances superior to those identified in the previous literature. It was further hypothesised that such performance increases would increase the range of electrophysiological signals that the OECTs could resolve and amplify. Therefore, the research aimed to explore the parameter space of such optimisations through the fabrication and characterisation of high-performance OECTs. The research then aimed to determine the capability of such devices to resolve a wide range of electrophysiological signal inputs.

Bioelectronic amplifier circuits enable the conversion of transistor currents into output voltages and the processing of physiological signals local to measurement sites. However, the amplifier circuits investigated in the previous literature do not provide a considerable degree of control over the amplification properties, and crucial characterisations relevant to amplifier performance are yet to be performed. The common-source linear amplifier is a circuit topology that provides a greater command of the amplification mechanism. It was hypothesised that the OECT could act as the amplifying element within such a circuit and provide sufficient linearity for the amplification of electrophysiological signals. As such,

the research aimed to determine the efficacy of OECTs in such an amplifying topology through the fabrication and the extensive physical and simulated characterisation of the OECT amplifier circuit.

The electrode architecture of an OECT has been shown to significantly impact biosensing performance in the previous literature. To develop a high-density OECT array for the transduction of high-frequency activity, a comprehensive investigation into the impacts of the different parameters that constitute the electrode architecture on OECT characteristics was initially required. Such a systematic investigation had not been provided in the previous literature. Therefore, the research aimed to quantify and explain the effects of varying the different components of electrode architecture on the parameters related to biosensing performance.

Extended aqueous immersion varies the properties of electronic transport in OECTs, and the previous literature showed a relationship between OECT biosensing performance parameters and the variables that describe the electronic transport. Therefore, in the final investigation, it was hypothesised that biosensing performance would vary with aqueous immersion time, and the level of this variation could be influenced by the inclusion of additives to the organic layer of the OECT. This variation would determine the efficacy of using OECTs for long-term subcutaneous electrophysiological recordings and give insights into the relationship between OECT noise and the properties associated with electronic transport. Research into improving the performance characteristics of OECTs for the maximisation of their efficacy in biosensing applications further motivates their implementation in future neurotechnologies.

2. DEVICE PHYSICS, STRUCTURES AND APPLICATIONS

2.1. Organic Layers and Electrodes

2.1.1 Charge Transport in Organic Layers

A fundamental building block of organic materials is the carbon element. Charge transport in organic polymers is facilitated by a backbone consisting of repeated units such as carbon. Such a structure of covalently bonded carbon atoms provides availability of energy states to charge carriers allowing for intramolecular mobility. An inorganic semiconductor can be considered as a covalently bonded periodic lattice where charge carriers are delocalised across its entirety. However, for organic semiconductors, the molecules or polymer chains are held together by van der Waals forces.

The formation of energy bands in the organic polymer backbone can be understood by first considering the bonding of two carbon atoms. Carbon has a ground state configuration of $1s^2 2s^2 2p^2$. When a carbon atom has the capacity for bonding, there are additional orbitals for the electrons, called hybrid orbitals, which are understood as a mixture of the s- and p- atomic orbitals. The three types of hybridised orbitals for carbon are denoted sp , sp^2 and sp^3 and provide the carbon-carbon triple, double and single bonds, respectively. In an sp^i hybridised orbital, the 2s orbital hybridises with i 2p orbitals. For $i = 3$, the 2s orbital hybridises with all three 2p orbitals, resulting in four sp^3 orbitals of equal energy. As shown in figure 2.1, an electron in the sp^3 orbital bonds with an electron from another atom (such as carbon or hydrogen), forming a σ -bond (or single bond). In $i = 2$, the s orbital hybridises with two 2p orbitals, where three electrons occupy the three sp^2 orbital states and the remaining electron occupies a 2p orbital. One sp^2 state from each carbon atom then bonds to form a σ -bond and the two remaining sp^2 orbitals bond with other orbitals. The remaining 2p orbitals from each carbon atom form a π -bond. Therefore, there is a double bond between the two carbon atoms, as illustrated in figure 2.2. For $i = 1$ there are two π -bonds and one σ -bond between two carbon atoms, resulting in a triple bond, as shown in figure 2.3. The valence electrons of the carbon atom occupy the resulting second/hybridised shell energy states such that their total energy is minimised.

For each overlap in the bonding of two carbon atoms, there are bonding and antibonding molecular orbitals. For the sp^2 hybridisation, the π bonding and π^* antibonding orbitals are more delocalised than the σ bonding and σ^* antibonding orbitals. Consequently, the energy difference between the π - and π^* - bonds is smaller than that of the σ - and σ^* - bonds. The energy levels of the π - and π^* - bonds thus define the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in the organic semiconductor. The approximate energies of the π - and π^* -

sp^3 Hybridisation

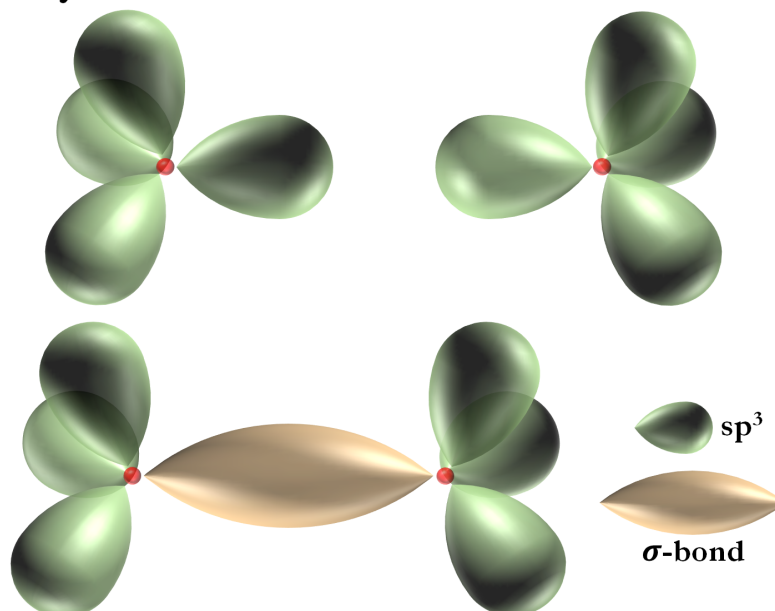


Figure 2.1: Hybridisation of two carbon atoms where, in each carbon atom, the $2s$ carbon state hybridises with three $2p$ states, forming four sp^3 states of equal ionisation energy. This results in a tetrahedral geometry. Two sp^3 states, one from each hybridised carbon atom, then join to form a σ -bond, providing a single carbon-carbon bond.

bonds can be found using the Hückel approximation, where the number of energy states is dependent on the number of carbon atoms involved in sp^2 hybridisation in a molecule or chain. The band gap between the σ - and σ^* - orbitals results in insulative material properties and thus does not contribute to semiconducting behaviour [17].

A conjugated system consists of a bonded backbone, characterised by alternating single and double bonds, with overlapping p-orbitals providing delocalised π -electrons. These π -electrons contribute to the conductivity of the conjugated polymer. The accumulation of delocalised electrons in conjugated structures leads to the formation of conduction and valence bands. Continuous bands of π -states are formed in the limit of an infinitely long chain, which can be demonstrated when taking the $n \rightarrow \infty$ limit of the Hückel approximation. As the π -states form the HOMO and LUMO bands, their convergence occurs at the Fermi level in this limit. As each state can be filled by two electrons, the π -electrons fill half of the available π -states. With no discontinuities in the first Brillouin zone, the resulting band structure is that of a metal. However, it is found that the single and double carbon bonds, and thus the expected positions of the

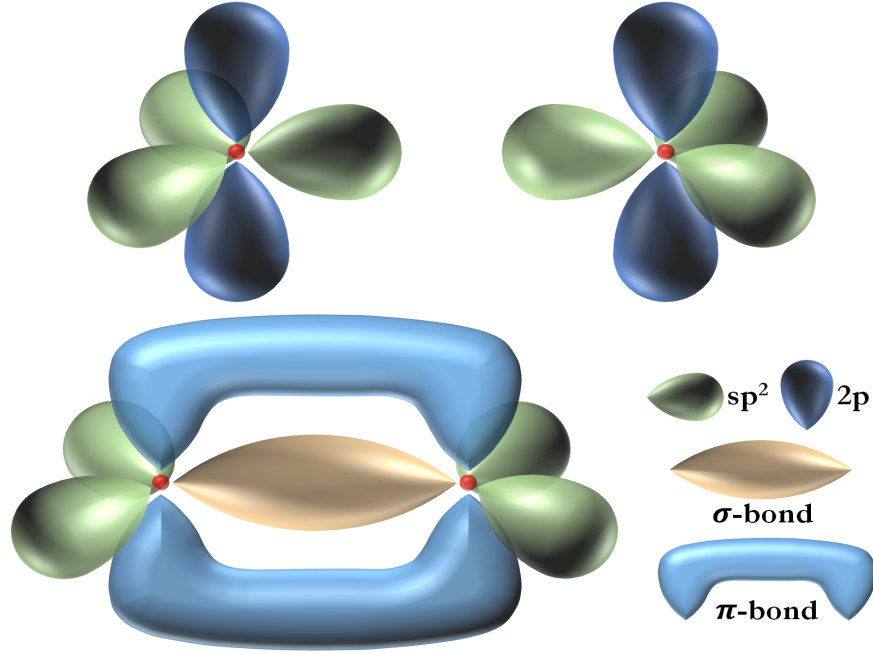
sp^2 Hybridisation

Figure 2.2: Hybridisation of two carbon atoms where, in each carbon atom, the $2s$ carbon state hybridises with two $2p$ states, forming three sp^2 states of equal ionisation energy and one $2p$ state remains. Two sp^2 states, one from each sp^2 -hybridised carbon atom, then join to form a σ -bond. Similarly, two $2p$ states join to form a π -bond, resulting in two carbon-carbon bonds.

π -electrons, have varying spatial lengths. This can be interpreted as a distortion of a periodic lattice, where the distortion doubles its periodicity. Peierl's theorem states that, under such conditions, band gaps are generated because it is energetically favourable [18]. Consequently, the band structure becomes that of a semiconductor and the Fermi level exists in the band gap. Where carbon atoms form the conjugated backbone, a simple resulting organic material is the semiconductor polyacetylene, as shown in figure 2.4. Polythiophene is a more complex conjugated polymer that develops energy bands through the build-up of a chain of thiophene monomers. Conduction and valence bands are similarly constructed in poly(3,4-ethylenedioxythiophene).

The density of states (DOS) describes the distribution of energy states for a system of a given volume. At a non-zero temperature, the number of charge carriers in the conduction band, as dependent on the product of the DOS and the Fermi-Dirac distribution, is probabilistically non-zero. The excitation of an electron to the conduction band results in the generation of a hole, a positively charged quasiparticle, in the valence

sp Hybridisation

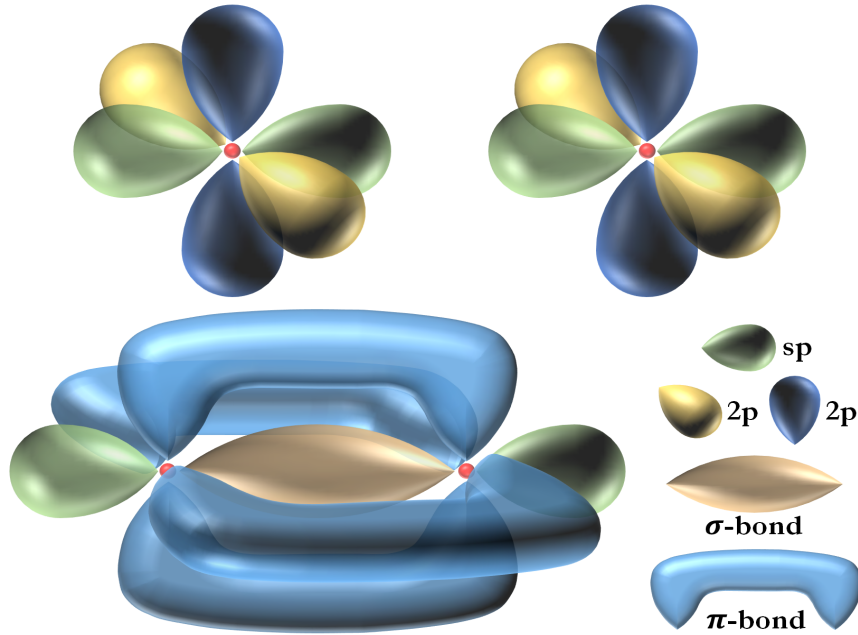


Figure 2.3: Hybridisation of two carbon atoms where, in each carbon atom, the $2s$ carbon state hybridises with one $2p$ state, forming one sp state and two $2p$ states remain. Two sp states, one from each sp -hybridised carbon atom, then join to form a σ -bond. Each of the two $2p$ states then forms π -bonds with the $2p$ states of the other carbon atom. This thus results in three carbon-carbon bonds.

band. In an organic material, the electrons and holes electromagnetically distort the surrounding molecules or chains, causing a change in its spatial, and thus energetic, configuration. Electrons and holes which cause such distortions are called polarons and have energies that exist in the semiconductor band gap [19].

The HOMO and LUMO, and thus the band gap, in organic semiconductors varies throughout its structure due to inherent sources of disorder. Charge transport is determined by the energy states available to polarons and thus by the level of energetic disorder. Sources of disorder in organic semiconductors originate on the intramolecular and intermolecular scales. Intramolecular sources include the torsion and elongation of conjugated polymer bonds. Sources of the intermolecular disorder include the variations in distances between hopping sites of adjacent conjugated chains and the differences in their relative orientations. The resulting DOS is described by a Gaussian function, where the level of disorder is described in its energetic width:

$$g(E) = \frac{N}{\sigma\sqrt{2\pi}} \exp\left(\frac{-(E - E_0)^2}{2\sigma^2}\right), \quad (2.1)$$

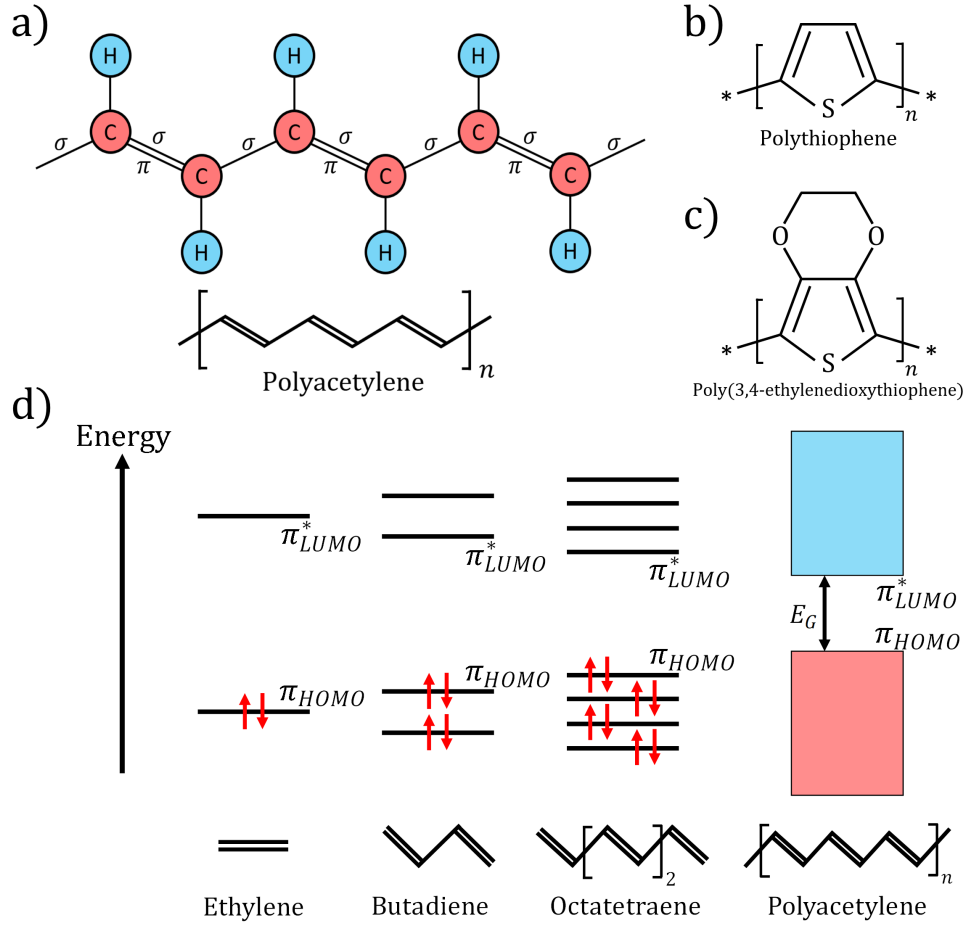


Figure 2.4: a) Chemical structure of polyacetylene with σ - and π - bonds illustrated. b) Chemical structure of polythiophene. c) Chemical structure of poly(3,4-ethylenedioxythiophene). d) Energy level diagram of increasing carbon double bond units resulting in energy bands with a band gap due to Peierl's distortion.

where $g(E)$ is the DOS at energy E which is distributed around energy E_0 with standard deviation σ and N is the total density of states [20]. Trap states are states with energies in the tail of the DOS which charge carriers have a low probability of transitioning from. Transport in organic semiconductors is predominantly limited from trap states that originate from intermolecular sources of disorder.

Charge transport between the energy states, such as those described by the Gaussian DOS shown in figure 2.5, occurs through thermally assisted hopping. Uphill hops to higher energies are thermally activated and downhill hops are independent of site energy. The rate of transitions between energy states is often described by the Miller-Abrahams hopping model, which claims that, in the absence of polaronic effects, the rate of transition from

an occupied state i to an unoccupied state j is given by

$$\nu_{ij} = \nu_0 \exp \left(-\frac{2r_{ij}}{\alpha} - \frac{(E_j - E_i) + |E_i - E_j|}{2k_B T} \right) , \quad (2.2)$$

where ν_{ij} is the transition rate from site i to site j , ν_0 is the attempt-to-escape frequency, α is the localisation length, r_{ij} is the site separation distance, E_i is the energy at state i , k_B is the Boltzmann constant and T is the temperature [21, 22]. When taking polaronic effects into account, the transfer rate can be described by the Marcus jump rate, given as

$$\nu_{ij} = \frac{J^2}{\hbar} \frac{\pi}{\sqrt{2U_b k_B T}} \exp \left(-\frac{U_b}{2k_B T} \right) \exp \left(-\frac{(E_j - E_i)}{2k_B T} - \frac{(E_j - E_i)^2}{8k_B T U_b} \right) , \quad (2.3)$$

where $J^2 \propto \exp(-2\alpha r_{ij})$ is the transfer integral between sites and U_b is the polaron binding energy. Under steady-state and in low electric fields, equations 2.2 and 2.3 give similar descriptions of transport [23].

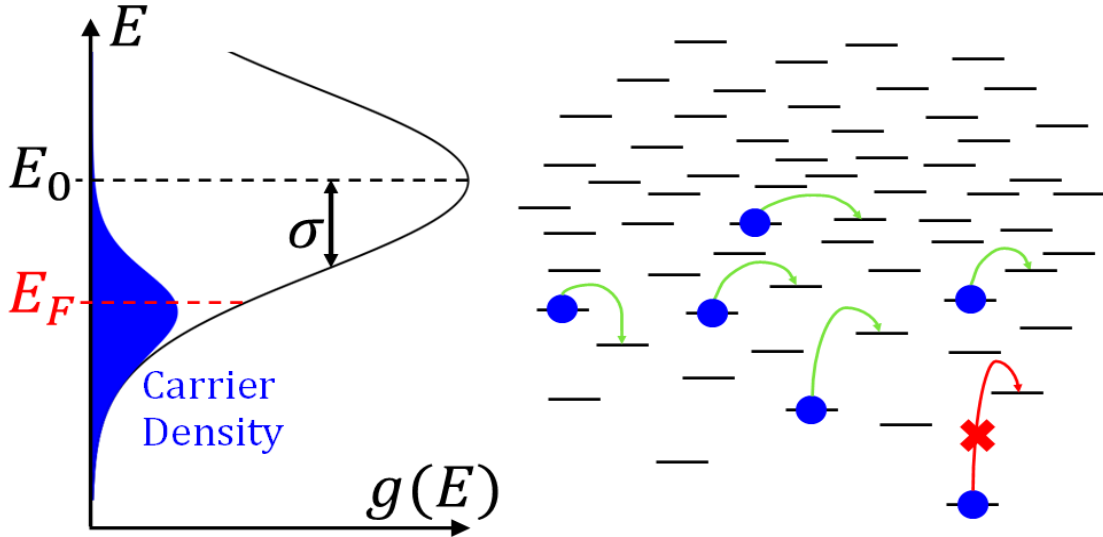


Figure 2.5: Schematic of the Gaussian DOS, $g(E)$, with energies distributed around E_0 of characteristic width σ and the carrier density as found using the Fermi-Dirac distribution and the system's Fermi energy E_F . The carrier hopping process is further illustrated with high and low probability state transitions.

The definition of charge carrier mobility, μ , provides a quantification of the ability of a charge carrier to traverse the volume of a system:

$$\mu = \frac{|\boldsymbol{\nu}|}{\boldsymbol{E}} = \frac{\sigma_{DC}}{ne} , \quad (2.4)$$

where $|\boldsymbol{\nu}|$ is magnitude of charge carrier velocity, $|\boldsymbol{E}|$ is the magnitude of an external electric field, σ_{DC} is direct-current carrier conductivity, n is the charge carrier number

density and e is the elementary charge. The charge carrier mobility is thus dependent on the properties of the disordered organic system, such as those already described. In assuming a Gaussian DOS with a Miller-Abrahams hopping model, Bässler used Monte Carlo simulations to show that the charge carrier mobility had dependencies on energetic disorder and temperature such that

$$\mu = \mu_0 \exp \left[- \left(\frac{2\sigma}{3k_B T} \right)^2 \right] , \quad (2.5)$$

where σ is the energetic width of the Gaussian DOS, k_B is the Boltzmann constant and T is temperature. It was found that mobility increased with temperature and as the energetic width, which described the level of intermolecular and intramolecular disorder, decreased [20]. The increase in mobility with temperature, contrary to what is observed in metals, is due to the thermal energy favouring the hopping process. The molecular disorder can be minimised by designing organic semiconductors with rigid, planar backbones, allowing for efficient intramolecular transport. The intermolecular transport efficiency can be increased through the consideration of crystallinity [24]. Generally, the charge transport mechanisms can be probed by considering the temperature dependence on the conductivity of a given material. The materials used in this research have been analysed in the literature using this framework, formulated by Mott, known as the variable range hopping (VRH) theory. The model states that the conductivity at temperature T is given by

$$\sigma_{DC} \propto \exp \left[- \left(\frac{T_0}{T} \right)^{\frac{1}{n+1}} \right] , \quad (2.6)$$

where T_0 is related to an activation energy which is dependent on the intersite distance and energetic barrier and n is the dimension of conduction [25]. For $n = 3$, hopping is 3-dimensional between sites. For $n = 1$ there is a favourable direction to hopping, such as the transport along 1-dimensional conjugated polymer chains [26].

2.1.2 Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)

An organic conducting polymer that has been the focus of significant investigation is poly(3,4-ethylenedioxythiophene) (PEDOT). When doped with poly(styrene sulfonate) (PSS), the resulting PEDOT:PSS exhibits a multitude of desirable attributes for a wide range of applications. Its properties include biocompatibility, high conductivity, ambient and aqueous stability, flexibility, stretchability, transparency in the visible spectrum and low fabrication cost [27].

The concept of doping organic semiconductors is similar to that of doping inorganic materials: by introducing dopants, electrons are transferred to the LUMO states (n-type)

or from the HOMO states (p-type). In n-type doping, the greater number of electrons in the conduction band results in the Fermi level increasing (the work function decreasing). Similarly, in p-type doping, the greater number of holes in the valence band results in the Fermi level decreasing (the work function increasing). For π -conjugated materials, doping results in charge carrier formation through reduction (n-type) or oxidation (p-type). The charge carriers are polarons (or bipolarons) because their generation or depletion spatially distorts the π -conjugated backbone, resulting in energetic disorder [28]. The formation of bipolarons is a result of the energy associated with geometry relaxation being greater than the coulombic repulsion between electronic charges. Relative to polaron states, bipolaron energies occupy states deeper in the bandgap [19]. At higher levels of doping, the polaronic energy states can form new bands in the band gap which overlap with the valence and conduction bands [29]. The DOS of such polymers is described by a Gaussian HOMO and LUMO with contributing (bi)polaronic bands, as shown in figure 2.6.

As described, PEDOT is a π -conjugated conducting polymer and thus facilitates charge transport along its backbone of alternating single bonds and double bonds. PEDOT is polymerised from the monomer 3,4-Ethylenedioxythiophene (EDOT) and the polyelectrolyte PSS chain contains negatively charged sulfonate ions. The doping of the two ionomers in PEDOT:PSS is oxidative and is typically at a ratio of 1:2 to 1:3 (PEDOT to PSS). The generated hole (bi)polarons that are transported along the PEDOT chain are electrostatically compensated by the sulfonate anions [30]. The oxidative doping is degenerative such that the material is defined to be a p-type conducting polymer.

The polymerisation of PEDOT results in a structure that provides a monomer to dopant ratio of 3:1, and thus approximately three EDOT monomers interact with one PSS unit to generate one hole [26]. As such, there is typically an excess of PSS in the PEDOT:PSS dispersion, and thus not all PSS is involved in doping. The excess PSS provides a number of additional properties to the organic conducting polymer. It has been shown that the presence of excess PSS provides PEDOT:PSS with a stronger adhesion to quartz substrates relative to modified PEDOT:PSS where the excess PSS has been removed [31]. Furthermore, such excess PSS also interacts with crosslinkers to facilitate the bonding of PEDOT:PSS to substrates such that delamination does not occur in aqueous environments. The removal of excess PSS can result in improvements in conductivity through increased crystallinity; however, such treatments can also result in the organic layer becoming more brittle [32, 33].

The PEDOT polymer is highly conductive, though is insoluble in water. The PSS provides the solubility of PEDOT:PSS in water, allowing the production of aqueous dispersions of the conducting polymer and thus the solution processability for device fabrication. Once processed into a thin film, the PEDOT and PSS undergo a phase

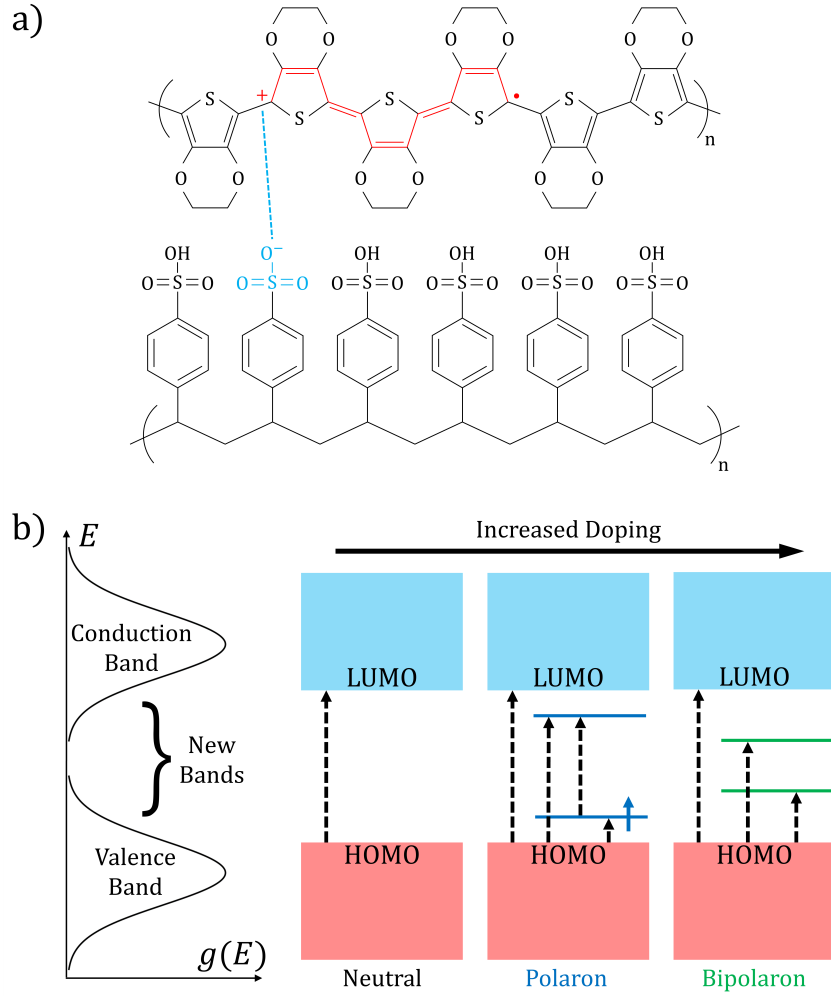
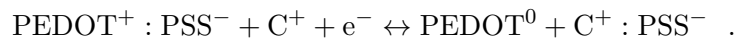


Figure 2.6: a) Chemical diagram of PEDOT:PSS. b) Gaussian conduction and valence bands with HOMO, LUMO, polaronic and bipolaronic states and optical transitions illustrated.

separation such that PEDOT chains are surrounded by a PSS-rich volume, resulting in colloidal gel particles and providing aqueous stability [34]. These gel particles, which have a PEDOT nanocrystal core and PSS-rich shell grain structure, have diameters that average between 40 nm to 60 nm [35]. Where the conjugated PEDOT backbone provides electronic transport, the PSS phase provides an ionic conduction [36]. Such mixed conductivity motivates the utilisation of PEDOT:PSS in bioelectronic applications.

Given the capability of ionic conduction, cations are able to traverse the volume of the PEDOT:PSS. The introduction of a cation, C^+ , electrostatically compensates a sulfonate anion of the PSS, PSS^- , and thus the associated hole is no longer generated [37, 38]:



This is known as electrochemical de-doping and is a reversible process that varies the conductivity of the PEDOT:PSS film. The oxidation and reduction in the electrochemical (de-)doping process vary the Fermi level of the PEDOT:PSS. The work function of pristine PEDOT:PSS has been measured to be approximately 5.0 eV [39]. The work function was reduced to 4.75 eV through reduction and increased to 5.4 eV through oxidation [40, 41]. As such, the electrochemical (de-)doping mechanism allows for the transduction of ionic fluxes in electrolytes. Other organic charge transport layers have shown ambipolar characteristics, with demonstrations including the water-stable electrochemical (de-)doping of an n-type device [42, 43].

The hydrophilic nature of the PSS, which results in a swelling of the PEDOT:PSS film, allows for ionic conduction. However, ionic hydration causes deformations in the film microstructure, and it has been found that film swelling is detrimental to electronic transport in conjugated polymers [44, 45, 46]. When interfacing PEDOT:PSS, for example as deposited on an electrode, with an aqueous solution in which an electrode is placed, applying a voltage across the electrolyte greater than that for electrolysis can cause irreversible degradation to the organic layer. As such, potential differences in such environments are typically limited to 1.2 V to avoid any damaging effects to the layer.

When using PEDOT:PSS as the transducing layer of a biosensor, additions are made to enhance its conductivity, processability and stability in aqueous solutions. As PEDOT:PSS is water-soluble, utilising the material on devices that interface with such environments, for example on a biosensor taking physiological measurements, would cause delamination. To attain mechanical stability on substrates for such applications, PEDOT:PSS has been crosslinked with (3-glycidyloxypropyl)trimethoxysilane (GOPS). It was proposed that cross-linking occurs between the excess SO_3^- of the PSS with the epoxy ring of GOPS and the methoxysilane group of GOPS bonds to glass substrates. It was found that GOPS reduces both the electronic and ionic mobility of PEDOT:PSS, which investigations suggested was caused by a morphological change between the GOPS and excess PSS. Devices which used GOPS for aqueous stability at a concentration of 0.1% v/v to 1% v/v had an electronic conductivity reduced by approximately 1 to 2 orders of magnitude, respectively [47]. However, when using polyethylene terephthalate (PET) substrates, conductivity-enhanced PEDOT:PSS films without GOPS were found not to delaminate after immersion in deionised water or phosphate-buffered saline (PBS) for 3 months [48].

In addition to maintaining lamination of PEDOT:PSS on substrates, the use of GOPS also decreases the amount of swelling in the films. It has been shown that increasing the concentration of GOPS reduces the percentage increase of swelling of PEDOT:PSS films [49]. As such, there is a trade-off between the level of morphological change in aqueous

environments and PEDOT:PSS conductivity. The effect of morphological change on performance measures such as noise level is essential to consider when using PEDOT:PSS-based devices for long-term physiological recordings.

To aid in the processing of PEDOT:PSS films, the surfactant dodecylbenzene sulfonic acid (DBSA) is used. This additive has also been shown to increase the conductivity of PEDOT:PSS films. Pristine PEDOT:PSS films from the Clevios PH1000 aqueous dispersion (PEDOT:PSS ratio of 1:2.5) without enhancement shows conductivity on the scale of 1 Scm^{-1} . Relative to a pristine PEDOT:PSS film, it was shown that a 2% v/v concentration of DBSA increased the conductivity to approximately 500 Scm^{-1} . However, a phase separation was observed at concentrations greater than 0.5% v/v, which was detrimental to film quality. Additive concentrations $\leq 0.5\%$ v/v, which still provide conductivities up to approximately 100 Scm^{-1} when mixed with unenhanced PEDOT:PSS, are commonly used in bioelectronic device fabrication [13, 50, 51, 52, 53].

With DBSA exhibiting a processing concentration threshold for conductivity enhancement and GOPS reducing such a measure of performance, further additives are utilised to increase the conductivity of PEDOT:PSS films. A number of mechanisms have been suggested for conductivity enhancement that consider morphological changes of PEDOT:PSS from additive treatments. The use of ethylene glycol (EG) at concentrations approaching 5% v/v have shown to increase the conductivity by 2 orders of magnitude [54]. It has been suggested that EG weakens the electrostatic coupling between the PEDOT core and PSS shell. As such, the PEDOT:PSS grains undergo a reorientation, resulting in a greater PEDOT crystallinity [55]. It has been shown that a higher level of crystallinity from using EG is associated with a greater conductivity [56]. In addition, it has been suggested that the primary factor for conductivity enhancement in PEDOT:PSS is the effect of the additive on the π - π stacking of PEDOT chains within the grains. Further conductivity enhancers used with PEDOT:PSS include sorbitol, glycerol and dimethyl sulfoxide (DMSO). Optimal additive concentrations for such enhancers are between 5% v/v and 10% v/v, which provide conductivity increases by 2 to 3 orders of magnitude. Furthermore, DMSO has consistently shown greater increases than EG, attributed to the relative abundance of PEDOT chain stacking [50, 54]. Conductivity enhancement has been shown to reduce the work function of PEDOT:PSS [57].

As opposed to using conductivity enhancers in the PEDOT:PSS formulation, the post-deposition treatment of pristine PEDOT:PSS in sulphuric acid has shown to increase the conductivity of the organic layer up to 4100 Scm^{-1} , which is significantly greater than that found by utilising EG and DBSA, and is approaching the orders of magnitude for highly conductive metals. The treatment requires bathing the film of PEDOT:PSS in sulphuric acid. In comparing the sulphuric acid-treated PEDOT:PSS,

Crys-P, to the EG and DBSA enhanced PEDOT:PSS, EG-P, it was found that Crys-P had greater crystallinity. The stacking organisation facilitated interchain charge transport and the PSS content was significantly reduced in Crys-P. Electrical characterisation suggested that this did not affect ionic conductivity. The superior Crys-P performance did not deviate or degrade from 3 weeks of aqueous immersion and its thickness did not swell in the environment, whereas EG-P saw significant changes [58].

The VRH model suggests that the hopping transport in PEDOT:PSS is quasi-1D, with $n = 1$ in equation 2.6. As the PEDOT:PSS conductivity is increased, the activation energy described by T_0 is observed to decrease. This indicates a reduction in the intersite energetic separation, which further implies a reduction in disorder [26, 59, 60, 61]. As conductivity is further increased, a critical limit is reached where the temperature dependence becomes weak [26, 62]. Additional increases in conductivity with sulphuric acid treatment result in a dependence that decreases with temperature, thus displaying metallic behaviour [63, 64].

The organic nature of PEDOT:PSS suggests that it provides a high degree of biocompatibility. As such, the material has been applied in physiological monitoring devices that directly interface with biological environments such as cortical structures [11, 13, 65]. It has been shown that PEDOT:PSS is non-cytotoxic and supports neural cells [66]. In addition to biocompatibility, devices such as wearable biosensors require flexible and stretchable properties [67, 68]. The intrinsic mechanical stretchability of untreated PEDOT:PSS reaches only approximately 2% before fracture [69]. However, the relative elongation can be increased to be on the scale of 10% through doping modifications, blending the PEDOT:PSS with elastomers and patterning the PEDOT:PSS into geometric patterns which support elastic strain [33].

2.1.3 Electrode Interfaces

To utilise organic conducting polymers in devices such as transistors, they are placed in contact with metal electrodes. The basic dynamics of charge transport at the metal-semiconductor interface can be described by the Schottky-Mott rules. Consider a metal with work function ϕ_M and associated Fermi level E_{FM} and a semiconductor of Fermi level E_{FS} , band gap E_G , work function ϕ_S , ionisation energy ψ (vacuum-HOMO energy), HOMO level E_V , electron affinity χ (vacuum-LUMO energy) and LUMO level E_C such that $E_G = \chi - \psi$, where energies are relative to the vacuum energy E_{VAC} . As shown in figure 2.7, in bringing the materials into contact from vacuum level alignment, there is a bending of the conduction and valence bands and a Fermi level alignment of E_{FS} with E_{FM} , resulting in a charge transfer across the interface. If $\phi_M < \psi$ or $\phi_M > \chi$ then the aligned Fermi level gets pinned at HOMO or LUMO level, respectively.

In the charge transfer, electrons tend to flow from shallower to deeper Fermi levels (as

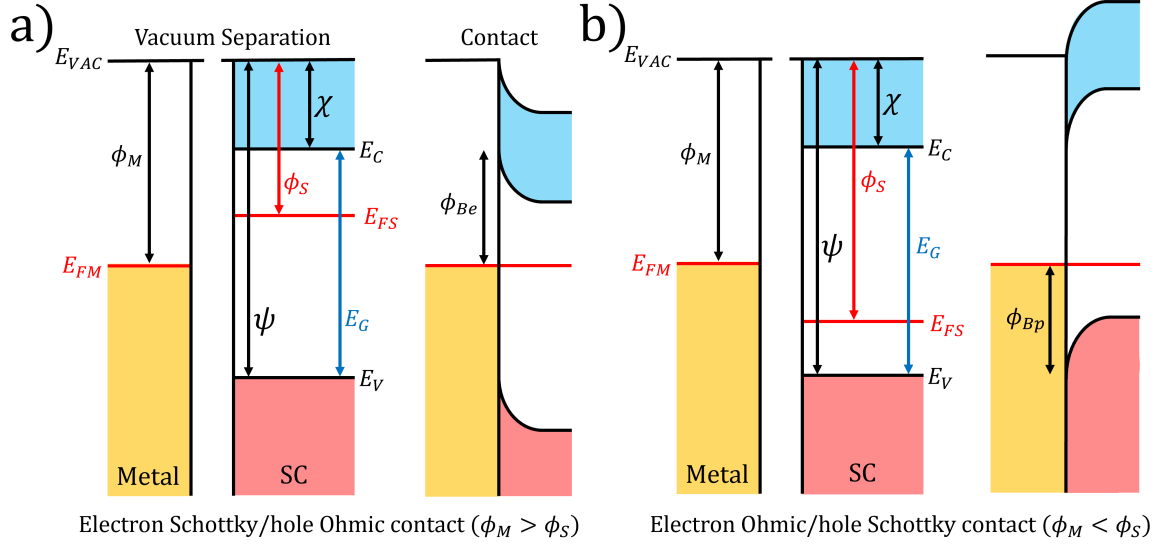


Figure 2.7: Metal-semiconductor interface energetics for a) $\phi_M > \phi_S$, b) $\phi_M < \phi_S$.

ϕ_M increases) and holes from deeper to shallower Fermi levels. As such, if $E_{FM} < E_{FS}$ (or equivalently $\phi_M > \phi_S$) in an n-type semiconductor, then the conduction band bends away from the aligned Fermi level and the electrons must overcome an injection barrier given as $\phi_{Be} = \phi_M - \chi$. Equivalently, for a p-type semiconductor with $E_{FM} > E_{FS}$ (or $\phi_M < \phi_S$), the valence band bends away from the Fermi level and the holes must overcome an injection barrier given as $\phi_{Bp} = \phi_M - \psi$. Charge separation due to the injection barrier results in a capacitive interface, and the system is defined as a Schottky contact. For the case where $E_{FM} > E_{FS}$ (or $\phi_M < \phi_S$) in an n-type semiconductor, the conduction band bends toward the aligned Fermi level and electrons are transferred from the metal to the semiconductor. Equivalently, in a p-type semiconductor with $E_{FM} < E_{FS}$ (or $\phi_M > \phi_S$), the valence band bends towards the Fermi level and holes are transferred to the semiconductor. For charge transfer to the semiconductor, the energetic barrier for carrier injection is small, defining the interface as an Ohmic contact. As such, Ohmic contacts are used when maximal efficiency is desired in device operation. To minimise injection barrier height, the Schottky-Mott rules suggest selecting a metal with a ϕ_M in close energetic proximity to the ψ for p-type semiconductors or the χ for n-type semiconductors [70].

For organic systems with a Gaussian HOMO, the ionisation energy has been defined as the energy at a number of standard deviations away from the mean. It has been suggested that the charge injection barrier is dependent on the standard deviation, where a greater deviation results in a larger injection barrier [71]. When PEDOT:PSS is used for the transduction of physiological information, gold is often used for charge injection. The work function of gold is approximately 5.1 eV, which is energetically proximal to the 5.0 eV

work function of PEDOT:PSS. The ionisation energy of PEDOT:PSS has been measured to also be approximately 5.0 eV [39]. Therefore, the hole injection barrier is small and the Fermi level could potentially be pinned to the HOMO. As such, the use of gold to interface with PEDOT:PSS follows the suggestions of the Schottky-Mott rules. This focuses the measurements of any biosensor that incorporates such materials towards the physiological environment and away from the device's internal mechanisms.

For the operation of organic transistors which utilise electrolytes such as those found in physiological environments, the electrode-electrolyte interface must also be considered. When a potential difference exists across an electrode-electrolyte interface and is transmitted through the resistive ionic liquid, the behaviour of charge carriers at the interface characterises the electrode. The type of electrode is identified to be either ideally polarisable or ideally non-polarisable and is distinguished upon the ability to allow a current to flow across the interface.

At the interface of an ideally polarisable electrode and an electrolyte across which a potential difference is applied, there is no net current. Such an interface can be modelled as a capacitor. On the surface of the charged electrode, there is an accumulation of counter ions transported from the electrolyte through coulombic forces. These layers of opposing polarity form a system with capacitive properties and form an electrical double layer. The potential distribution through the electrolyte can be described by the Stern model, which takes into consideration the Helmholtz and Gouy-Chapman models. The Helmholtz model assumes a purely capacitive interface with a linear decrease in potential. The Gouy-Chapman model uses the Poisson-Boltzmann equation to describe the diffusion of the counter ions due to thermal motion at the electrode-electrolyte interface, which predicts an exponential decrease in charge density with distance from the electrode. The resulting Stern layer screens the charge of the electrode to ions at greater distances from the electrode. The potential difference across the layer is inversely proportional to the electrode area, which is an important consideration when designing device architectures.

At the interface of an ideally non-polarisable electrode and an electrolyte across which a potential difference is applied, there is a net current. Such an interface can be modelled as a resistor and there is no frequency dependence on the potential difference in the bounds of neural activity. Furthermore, with no capacitive contribution, the behaviour is approximately independent of electrode size. A frequently used non-polarisable electrode is the Ag/Ag-Cl electrode, which undergoes a redox reaction between silver and silver chloride. The pertinent chemical reaction under the influence of a potential difference is $\text{AgCl(s)} + \text{e}^- \rightleftharpoons \text{Ag(s)} + \text{Cl}^-$. The non-polarisable interface minimises the potential difference across the electrode-electrolyte interface, which is desirable behaviour for the recording of reference signals in electrophysiology.

2.2. Organic Electrochemical Transistors (OECTs)

2.2.1 OECT Structure and Operating Principle

The organic electrochemical transistor is a device that consists of an organic layer, an electrolyte and three terminals called the gate, source and drain electrodes. The organic layer, alternatively denoted as the ‘active layer’ or ‘channel’, interfaces with the electrolyte and the source and drain electrodes. The gate electrode is immersed in the electrolyte and an encapsulation layer covers the exposed source and drain contacts, as shown in figure 2.8. The device operates by applying potential differences between the source and drain electrodes, providing electronic transport, and between the gate electrode and the channel, facilitating ionic transport. The conductivity of the organic layer is modulated by varying the number of ions transported from the electrolyte into the active layer.

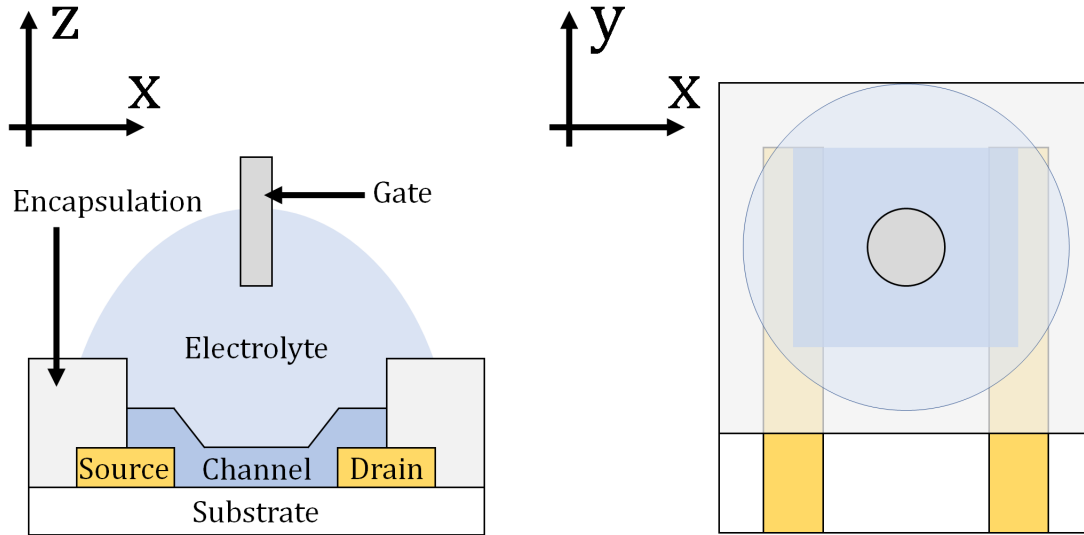


Figure 2.8: Structure of the OECT in the x - z and x - y plane.

The operation and performance of the OECT are compared to that of the organic field-effect transistor (OFET) and the electrolyte-gated organic field-effect transistor (EGOFET). The primary difference in operation between the OECT and the OFET and EGOFT is that charge carriers in the field-effect devices accumulate at the interface between the channel and the layer physically separating the channel and the gate electrode. This is opposed to the operation of the OECT, where those charge carriers permeate the electrolyte-channel interface and enter the active layer, resulting in electrical characteristics that are dependent on the volume of the organic layer.

In comparing the channel volume dependence of OECTs with the channel area

dependence of field-effect devices, a greater gate-channel capacitance, and thus a greater amplification performance, is generated in OECTs. Such greater capacitances come at the expense of slower response times. The frequency response of OECTs is typically limited by the transport of ions in the electrolyte. The upper bandwidth commonly approaches 5 kHz, which shows suitability for biosensor applications. In further comparisons to OFETs, OECTs operate at potential differences less than 1 V, whereas OFETs typically operate on the 10 V-scale. Achieving high amplification at such low operating voltages has encouraged the implementation of OECTs in voltage amplifiers [72, 73].

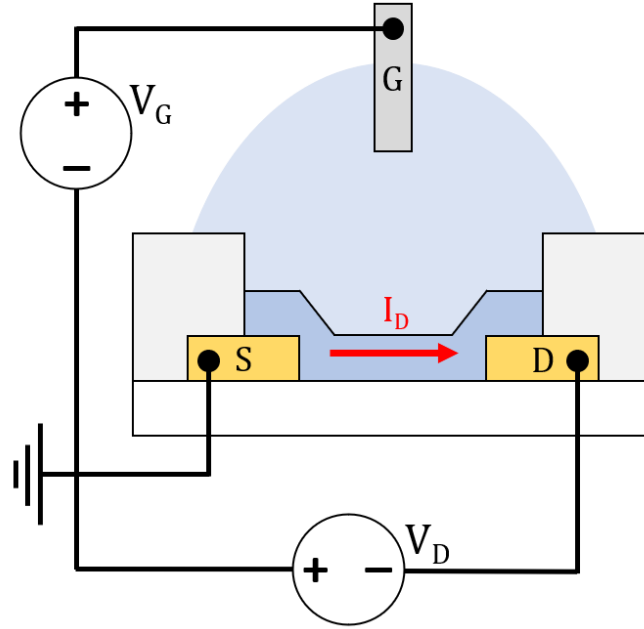


Figure 2.9: Circuit diagram of the OECT used for characterisation and application.

The OECT was first developed in the mid-1980s by the research group of Wrighton, where polypyrrole and poly(N-methylpyrrole) were used as the active layer [74]. In the subsequent development of these devices, PEDOT:PSS has traditionally been employed with modifications to suit a range of applications. The electrical circuit used to characterise OECTs is shown in figure 2.9. The source electrode is grounded and a potential difference is applied between the drain and source electrodes, V_{DS} , resulting in a current as measured at the drain, I_D . A potential difference relative to the grounded source is also applied at the gate electrode, V_{GS} , and the gate current, I_G , can be measured.

The utilisation of PEDOT:PSS as the organic layer of an OECT is motivated by its mixed electronic and ionic conduction. The metal typically used for the source and drain electrodes that interfaces with PEDOT:PSS is gold. Due to the extensive applications in biosensing, the electrolyte typically consists of ionic concentrations similar to those found

in physiological environments. The Ag/AgCl electrode is often used as the gate electrode because its non-polarisable property maximises the available voltage to facilitate cation transport into the channel. A negative V_{DS} provides hole transport from the source to the drain electrode, and a positive V_{GS} transports the cations from the electrolyte into the PEDOT:PSS, as shown in figure 2.10. Under such potential differences, cations enter the PEDOT:PSS towards the drain electrode. The current varies approximately linearly with V_{DS} for a given V_{GS} until the effect of cations compensating the sulfonate anions, thus depleting the generated holes, becomes increasingly significant. At such gate-drain voltages, $V_{GD} = V_{GS} - V_{DS}$, the dependency becomes notably sub-linear. The drain voltage for which the PEDOT:PSS is fully depleted, or saturated with cations, at the drain electrode is defined as the pinch-off voltage, V_P . At this stage of saturation, further decreases in V_{DS} do not vary I_D appreciably.

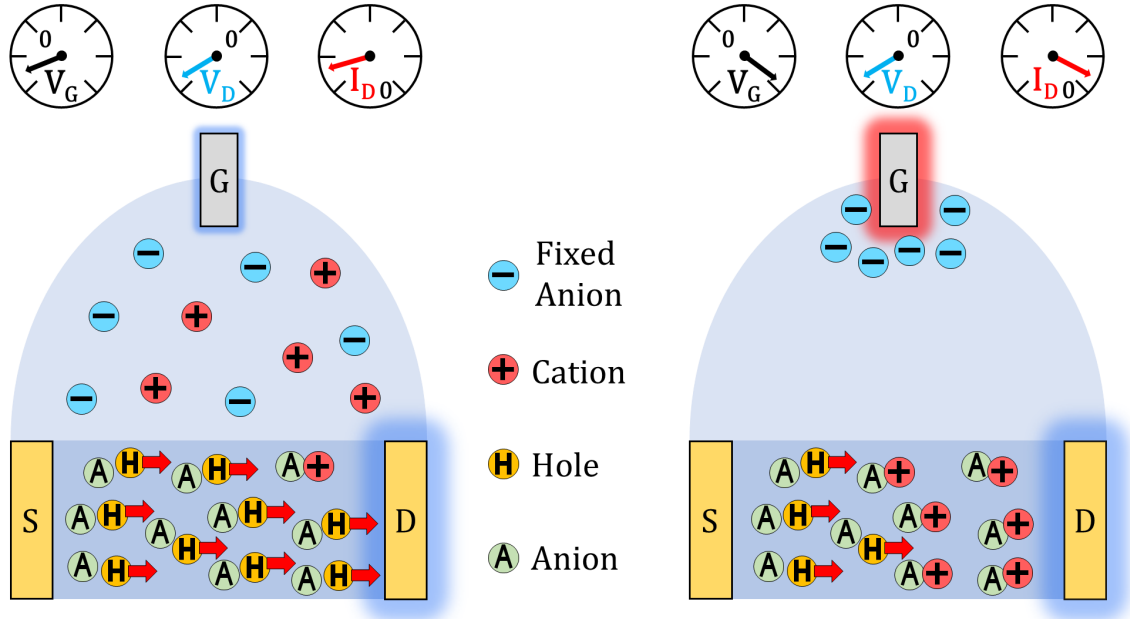


Figure 2.10: Illustration of the de-doping mechanism in an OEET where a negative drain voltage is applied and the gate voltage increases, transporting cations into the active layer.

Transistors are characterised by measuring the effect on I_D when varying V_{DS} and V_{GS} . Steady-state characteristics include the output and transfer characteristics, as shown in figure 2.11. In the output characteristics, V_{DS} is swept across a voltage range for a constant V_{GS} , and this is repeated for voltage steps in V_{GS} . For the transfer characteristics, V_{GS} is swept across a voltage range for a constant V_{DS} . The transconductance, denoted g_m , is defined as the change in drain current given a change in gate voltage, and is found through calculating the gradient of the transfer curve.

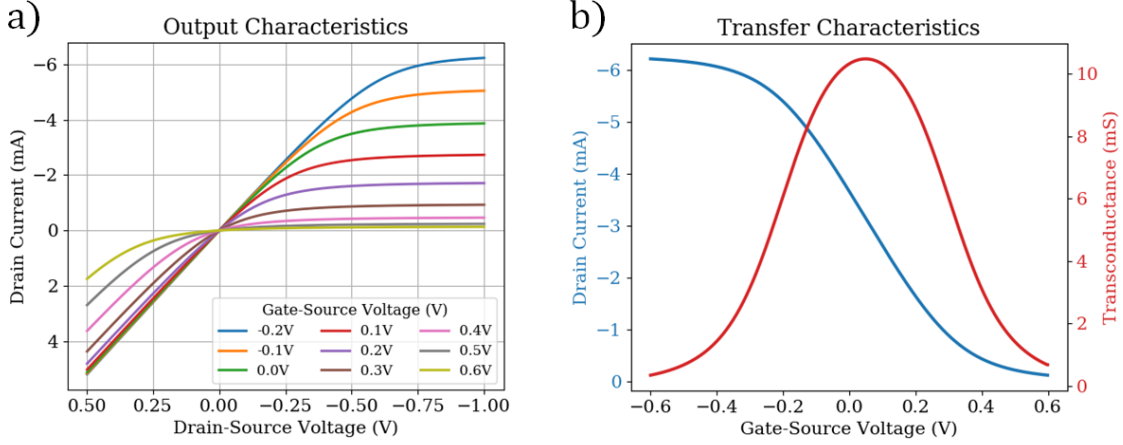


Figure 2.11: a) OEET output characteristics. b) OEET transfer characteristics.

Transient characteristics include the response time and transconductance-frequency characteristics. In the response time characterisation, V_{DS} is kept constant and V_{GS} follows a step function. The I_D is analysed and the time taken for the device to reach 90% of the final sampled I_D is found. An exponential curve fitting can be applied to the drain current measurement, giving an exponential response time constant, τ . The 90% response time, τ_{90} , is related to the exponential response time as $\tau_{90} = \tau \ln(10)$. In the transconductance-frequency characterisation, V_{DS} is kept constant and V_{GS} follows a sinusoid of increasing frequency. The sinusoidal frequency at which g_m decreases by 3 dB (or reduced to $g_m/\sqrt{2}$) is defined as the cut-off frequency, f_c . This frequency represents the upper limit of the device's bandwidth and relates to the exponential response time constant as $f_c \sim 1/2\pi\tau$.

Additional temporal device characterisations include stability and noise analyses. In the stability characterisation, V_{DS} is kept constant whilst the V_{GS} follows a square wave function. The change in g_m with time is calculated to determine the impact of gate pulsing on device performance. In the noise characterisation, V_{DS} is kept constant whilst the V_{GS} is grounded. The I_D is then analysed and the noise is calculated.

2.2.2 Models of OEET Operation

The growing utilisation of OEETs in biosensing has motivated the development of models that aim to describe the steady-state and transient device characteristics. These models have suggested how to vary architectural and material properties, such as the spatial dimensions of the OEET architecture shown in figure 2.12, to optimise characteristics for a range of applications. The models have considered OEET behaviour in terms of ionic and electronic circuits, drift-diffusion equations describing hole transport in electric fields

and the active layer conductivity resulting from organic disorder and Fermi level shifting [30, 37, 75].

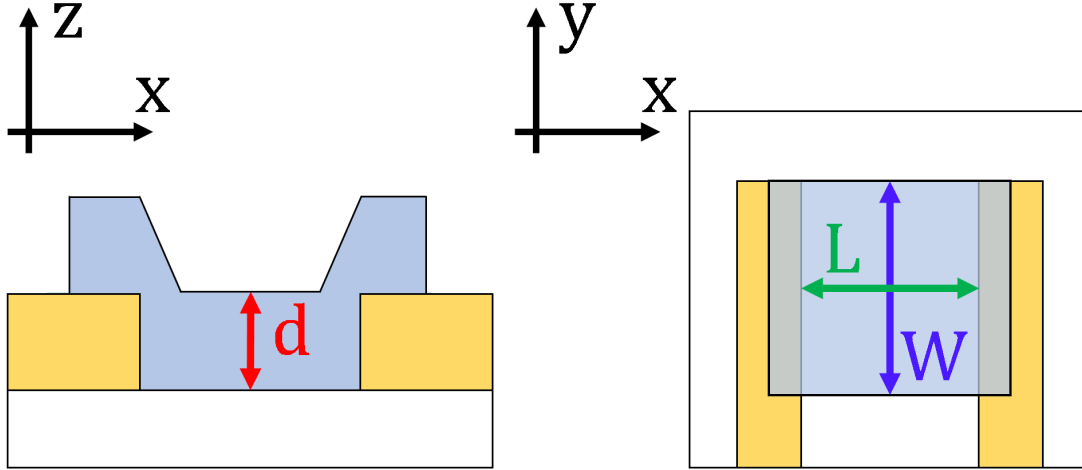


Figure 2.12: *Diagram of the OECT architecture without an encapsulation layer, electrolyte or gate electrode that shows channel width, W , length, L , and thickness, d .*

An initial model that has become well established in explaining OECT characteristics is that by Bernardis and Malliaras. The model considered the behaviour of a p-type organic film as an electronic circuit and the transport of ions in the electrolyte as an ionic circuit. The electronic circuit models the active layer current flux at position x between the source and drain electrodes of length L , $J(x)$, using Ohm's law as

$$J(x) = q\mu p(x) \frac{dV(x)}{dx} , \quad (2.7)$$

where q is the elementary charge, μ is the hole mobility, p is the hole density and dV/dx is the electric field. On gate voltage application and thus cation injection into the organic volume, the model assumed that one cation compensated one doped anion and so removed one hole. An expression was given for the hole density given the presence of cations in the organic film of volume v :

$$p = p_0 \left(1 - \frac{Q}{qp_0v} \right) , \quad (2.8)$$

where p_0 is the hole density without cation injection and Q is the total cation charge in the organic volume. The ionic circuit was formed by a resistor of resistance R_S and a capacitor of capacitance C_D in series. The resistor represented the electrolyte conductivity and the capacitor described the polarisation at the gate-electrolyte and electrolyte-channel interfaces. As such, gate voltage application exhibited the transient characteristics of a

charging capacitor:

$$Q(t) = Q_{SS} \left(1 - e^{-t/\tau_i} \right) , \quad (2.9)$$

where $Q(t)$ is charge transferred at time t , $Q_{SS} = C_D \Delta V$ is the total transferred charge across potential difference ΔV and $\tau_i = C_D R_S$ is the ionic response time. Furthermore, the cation charge in the organic active layer in a spatial slice dx at a given position x , $Q(x)$, was given as

$$Q(x) = c_d \cdot W \cdot dx \cdot (V_G - V(x)) , \quad (2.10)$$

where $C_d = c_d A = c_d W L$ for a channel of width W and length L , V_G is the gate voltage and $V(x)$ is the voltage in the channel at position x [37].

This model was revised by Friedlein *et al.*, who included the dependence of hole mobility on hole concentration as resulting from an exponentially distributed DOS near band edges in organic semiconductors. The relationship follows

$$\mu(p) = \mu_0 \left(\frac{p}{p_0} \right)^{\frac{E_0}{k_B T} - 1} , \quad (2.11)$$

where E_0 is the disorder parameter describing the energetic width of the DOS tail, k_B is the Boltzmann constant, T is temperature, μ_0 is a hole mobility independent of concentration and p_0 is the zero-field hole concentration [76].

In considering the Bernards-Malliaras model with revisions from Friedlein *et al.*, a relationship was found for the drain current in the linear and saturation regimes. In the linear regime, the model predicted

$$I_D = \frac{G V_P}{\frac{E_0}{k_B T} + 1} \left[\left(1 - \frac{V_{GS} - V_{DS}}{V_P} \right)^{\frac{E_0}{k_B T} + 1} - \left(1 - \frac{V_{GS}}{V_P} \right)^{\frac{E_0}{k_B T} + 1} \right] , \quad (2.12)$$

and in the saturation regime, where $V_{GS} - V_{DS} \geq V_P$, the model predicted

$$I_D = \frac{G V_P}{\frac{E_0}{k_B T} + 1} \left(1 - \frac{V_{GS}}{V_P} \right)^{\frac{E_0}{k_B T} + 1} , \quad (2.13)$$

where $G = q \mu_0 p_0 W d / L$ is the organic layer conductance and $V_P = q p_0 d / c_d$ is the pinch-off voltage. The transconductance of the device can be found through

$$g_m = \left. \frac{\partial I_D}{\partial V_{GS}} \right|_{V_{DS}} , \quad (2.14)$$

and thus it is found that $g_m \propto W d \mu C^* / L$ for volumetric capacitance C^* . The model provided a good fit to steady-state characterisations of OECTs [76]. It was assumed that the OECTs had sufficiently long channels to avoid short-channel effects. As the gate-drain voltage increases relative to the pinch-off voltage, the injected cations deplete dopant anions at positions closer to the source electrode and thus the effective channel length decreases.

The drain current is inversely proportional to the channel length and so its magnitude increases as the channel length decreases. This inability to saturate is thus assumed to be negligible in the model.

The initial model by Bernardis and Malliaras also provided insight into the transient behaviour of OECTs. The model considered contributions from the transport of holes in the active layer and of ions in the electrolyte. In considering Ohm's law for the active layer current with hole removal through de-doping, the model gave

$$J(t) \approx q\mu p(t) \frac{V_D}{L} + qfL \frac{dp(t)}{dt} \quad , \quad (2.15)$$

where f accounted for the spatial non-uniformity in de-doping. In using equations 2.8 and 2.9, it was found that, with a voltage step from $V_G = 0$,

$$I(t, V_G) = I_{SS}(V_G) + \Delta I_{SS} \left(1 - f \frac{\tau_e}{\tau_i} \right) e^{-t/\tau_i} \quad , \quad (2.16)$$

where $\tau_e = L^2/\mu V_D$ was the electronic transport time through the channel, $I_{SS}(V_G)$ was the steady-state I_D at V_G and $\Delta I_{SS} = I_{SS}(V_G = 0) - I_{SS}(V_G)$. The model did not consider the spatial variations in hole density and voltage and so average values were used. Thus, the behaviour only describes de-doping in the entire channel [37].

The transient dynamics given by Bernardis and Malliaras in equation 2.16 show two regimes of behaviour depending on the relative values of electronic and ionic transport time. In the case that the ionic transport time, τ_i , is much greater than the electronic transport time, τ_e , the OECT shows a monotonic decay response in the drain current given a gate voltage step. On the other hand, if the OECT response is limited by τ_e , then there is a spike followed by an exponential recovery in I_D [37]. For OECTs limited by the ionic transport, the response time is dependent on $\tau_i = C_D R_S$. The OECT channel is treated as a capacitor with a capacitance that takes representation in C_D . It has been found that the channel capacitance is proportional to its volume, WLd . Measurements on PEDOT:PSS gave a volumetric capacitance of $39.3 \pm 1.3 \text{ Fcm}^{-3}$ [77]. For microelectrodes, the electrolyte resistance, R_S , has been suggested to scale as $R_S \propto 1/\sqrt{WL}$, and such a relation has been demonstrated in PEDOT:PSS-coated electrodes [78, 79]. The geometric scaling of the channel capacitance and electrolyte resistance indicates an ionic response time scaling of $\tau_i \propto d\sqrt{WL}$ [80].

As shown, the OECT transconductance is proportional to the channel thickness, d . Given that the OECT is limited by ionic transport, then the response time also scales with d . There is thus a trade-off between transconductance and response time in d . A device that responds at higher frequencies due to a reduced channel thickness would thus provide a lower amplification given a constant channel width and length. However, the geometry dependencies also suggest that transconductance can be increased whilst reducing response

time by decreasing channel length. With such dependencies on device parameters, the architecture can be tuned to maximise performance for a given application.

Further models have been produced that provide insight into the transient behaviour of OECTs [81, 82, 83]. A model by Faria *et al.* considered the ionic circuit of an OECT using a resistor to describe the electrolyte, R_S , in series with a resistor and capacitor in parallel that describes the resistance, R_D , and capacitance, C_D , of the channel, respectively. For the case of a step function in the gate voltage such that $V_G(t) = 0$ at $t < 0$ and $V_G(t) = V_0$ at $t \geq 0$, the drain current at time t was given as

$$I_D(t) = I_0 + \frac{V_0 R_D (g_m R_D - f)}{R_D + R_S} - \frac{V_0 R_D (g_m R_D + f)}{R_S (R_D + R_S)} e^{-t/\tau}, \quad (2.17)$$

where $\tau = \frac{C_D R_D R_S}{R_D + R_S}$, f described the fraction of gate current measured at the drain electrode relative to the source electrode (as similarly in equation 2.16), V_0 was the amplitude of the gate voltage at $t \geq 0$ and I_0 was the steady-state current at $t < 0$. It was noted that when $R_D \gg R_S$, $\tau \rightarrow C_D R_S$, retrieving a relation from the model by Bernards and Malliaras. This model was used to fit drain current responses of OECT devices and allowed the value of f to be determined for varying gate and drain voltages [83].

The effect of organic disorder on the steady-state characteristics was considered by Friedlein *et al.*. It was suggested that the non-monotonic transconductance is an intrinsic property of OECTs that arises from the influence of disorder on electronic transport. A model was developed which assumed a Gaussian DOS and a Miller-Abrahams hopping phenomenology. The Fermi level of the organic layer with respect to an Ag/AgCl electrode, μ , was given by $\mu = qV_G$, where q is the elementary charge. Therefore, changes in gate voltage, which corresponded to fluctuating numbers of ionic dopants in OECTs, resulted in variations in the Fermi level. The origin of the non-monotonic transconductance was interpreted in terms of how the holes fill the Gaussian DOS. The proposed model fit transconductance curves of PEDOT:PSS-based OECTs and predicted a trade-off claiming that decreasing the DOS width increases peak transconductance, conductance and mobility but narrows the gate voltage range over which the transconductance is near its peak. Given an application such as biosensing, this model suggested how the molecular structure of the organic layer could be varied to maximise device performance [75].

The injection barrier at the interface between the electrodes and the organic active layer results in additional resistances which can be observed through device characterisation. The contact resistance can dominate the total resistance of the OECT channel for highly conducting organic layers [84]. The source-channel and channel-drain resistance contributions have been measured using probes placed within the channel of an OECT such that the potential drop along the channel length can be mapped [85]. Such measurements have been performed at varying gate voltages, and the channel-drain

contact resistance is not distinguishable from the charge carrier depletion at the drain electrode. It was suggested that a gate-voltage dependence on contact resistance can result in the non-monotonic transconductance [84]. However, Friedlein *et al.* concluded that contact resistance was not the primary cause of such behaviour [75].

An alternative model to the OECT operation considers the drift and diffusion of the charge carriers in the device. Such an operating principle was explained by Szymański *et al.*, who considered the transport of holes, cations and anions in the presence of fixed ionised acceptors [86]. The charge transport was simulated in two dimensions as given by the plane illustrated in figure 2.10. The OECT model was simulated using physical parameters associated with a PEDOT:PSS-based active layer, and was able to reproduce the expected behaviours in the output, transfer and response time characteristics [86]. Using a similar approach, Kaphle *et al.* used drift-diffusion equations to claim that the channel-drain interface contributes significantly to the OECT’s operating mechanism. It was shown that in the ionic equilibrium distribution for which the ionic current in the drain-source direction is zero, the ionic concentration increases exponentially towards the drain. Consequently, the hole concentration decreases exponentially towards the drain. The model also considered the distribution of the potential in the channel. A linear change along the channel and a potential drop at the drain was simulated, which was in qualitative agreement with experimental measurements. The potential drop was explained by the accumulation of cations, and thus the channel de-doping, at the drain electrode [85].

The drift-diffusion model has also been considered by Tybrandt *et al.* when examining the electric double layer residing at the interface of the PEDOT conjugated polymer phase and the PSS polyelectrolyte phase. The model calculated the hole chemical potential using a Gaussian DOS, and the resulting quasi-electric field was included as an additional drift term in the drift-diffusion equations describing hole transport. Using this model, the simulated steady-state characteristics provided a very good fit to experimental output and transfer curves. The model further suggested that the contribution of diffusion to hole transport relative to drift was found to be small at low gate voltages (high hole concentrations) and became more significant at higher gate voltages (lower hole concentrations) [30].

2.2.3 OECT Performance Limitations

The performance of an OECT is defined in the parameters calculated from its characterisation. Frequently compared OECT parameters are peak transconductance and response time. As there is a trade-off between these parameters and it is desirable to maximise g_m^{Peak} whilst minimising τ_{90} , performance can be compared by calculating g_m^{Peak}/τ_{90} . There are parasitic contributions to OECT performance that reduce

transconductance and bandwidth. Transconductance is reduced by increasing the components of the total OECT resistance. One such component is the interconnect resistance, which can dominate the total OECT resistance when using highly conductive organic active layers. Interconnect resistance can be minimised by reducing the length, increasing the width, increasing the thickness or increasing the conductivity of the interconnect lines. The intrinsic transconductance is often calculated as the transconductance that is corrected for such parasitic contributions [87]. As indicated by Bernards and Malliaras, the bandwidth is reduced by increasing the capacitance in the ionic circuit [37]. Parasitic contributions to the capacitance which do not originate from the interaction between the gate and the active layer increase the response time without increasing the transconductance. One such contribution is the exposed overlap between the gate and the source and drain electrodes. Indeed, it was observed that the cut-off frequency decreased when the area of the overlap increased [88].

Motivations to implement OECTs for biosensing applications include the amplification mechanism offered by the transconductance. Such an amplification to a biological signal is only beneficial relative to other biosensing measurement platforms, such as electrodes, if the resulting signal-to-noise ratio (SNR) provided by the OECT is greater. Fundamentally, the OECT ideally measures variations in ionic flux and thus is well-suited to applications where such dynamics are inherent in the activity to be recorded. For example, information in a neural volume is communicated through the action potentials of neurons, which propagate electrical signals through ionic fluxes in extracellular fluids. Indeed, in interfacing the cortical surface with a biosensor consisting of OECTs adjacent to electrodes, Khodagholy *et al.* found that OECTs with a PEDOT:PSS active layer provided a superior SNR relative to PEDOT:PSS-coated electrodes [14].

The definition of the SNR is the ratio of the power of the measured signal, P_{signal} to the power of the background noise, P_{noise} . The SNR is often expressed using the logarithmic decibel scale and is given as

$$\text{SNR}_{dB} = 10 \log_{10}(\text{SNR}) \quad , \quad \text{SNR} = \frac{P_{signal}}{P_{noise}} = \left(\frac{A_{signal}}{A_{noise}} \right)^2 \quad , \quad (2.18)$$

where A_{signal} and A_{noise} are the root mean square (RMS) amplitudes of the signal and noise, respectively, for when the signal is measured in amperes or volts. For the case of measuring SNR from the cortical surface using an OECT, the signal was determined using the peak drain current value during epileptiform activity and the noise from the standard deviation of the current during periods of low biological activity [14].

The noise of an OECT can be determined in a characterisation where the drain current is measured with a fixed gate input. To calculate noise, the drain current, $I_D(t)$, is first sampled over a given time period. The frequency dependence of noise is then found by

calculating the power spectral density (PSD), $S_{I_D}(f)$. The PSD is calculated by initially determining the autocorrelation function of $I_D(t)$, $A_{I_D}(\tau)$, which describes the correlation between $I_D(t)$ and a time-delayed $I_D(t)$ as a function of time delay, τ , as

$$A_{I_D}(\tau) = \langle I_D(t + \tau) I_D(t) \rangle \quad . \quad (2.19)$$

The PSD, which describes the power of $I_D(t)$ at frequency f , is then found by taking the Fourier transform of the autocorrelation function:

$$S_{I_D}(f) = \int_{-\infty}^{\infty} A_{I_D}(\tau) e^{i2\pi f \tau} d\tau \quad , \quad (2.20)$$

where $S_{I_D}(f)$ represents the noise power per unit frequency. The power of the signal in frequency band $[f_1, f_2]$ is calculated as

$$P(f_1, f_2)_{I_D} = 2 \int_{f_1}^{f_2} S_{I_D}(f) df \quad . \quad (2.21)$$

The RMS current noise, $I_{D,RMS}$, in $[f_1, f_2]$ is then calculated as $\sqrt{P(f_1, f_2)_{I_D}}$. To compare noise between different transistors, the normalised current noise is calculated as $S_{I_D}(f)/I_D^2$. A further calculation uses the transconductance to determine the noise that would be equivalently produced in the gate input. The gate-referred voltage noise, S_{V_G} , is related to the PSD through $S_{I_D} = g_m^2 S_{V_G}$ [89]. Therefore, the gate voltage RMS noise in frequency band $[f_1, f_2]$ is

$$V_{G,RMS} = \frac{\sqrt{P(f_1, f_2)_{I_D}}}{g_m} \quad , \quad (2.22)$$

which can then be used to determine the OECT suitability to a range of applications.

The $I_D(t)$ measured in noise characterisations contains contributions from a range of sources. In any resistive device, and thus in OECTs, there are fluctuations that arise from the thermal motion of charge carriers. This thermal noise is frequency independent and thus has a constant PSD. The current noise PSD is given by $S_I = 4k_B T/R$ for a resistor R at temperature T . A further source of noise originates from the discrete nature of charge carriers and their random arrival at a point of measurement. This is called shot noise and can be modelled as a Poisson process. The associated current noise PSD is approximately given by $S_I = 2qI_{DC}$ for DC current I_{DC} , which is also frequency independent.

A prominent source of noise in electronic systems is flicker noise, which has a current noise PSD given by $S_I \propto 1/f^\alpha$ for $\alpha \approx 1$. Flicker noise is observed across many systems including OECTs, and its origin is yet to be satisfactorily defined [89, 90]. An empirical relationship between noise and frequency was proposed by Hooge, which suggested that

$$\frac{S_I}{I^2} = \frac{\alpha}{f N_C} \quad , \quad (2.23)$$

where α is the Hooge parameter and N_C is the total number of free charge carriers [91]. Given that $N_C \propto p = \sigma/e\mu$ for hole density p , conductivity σ and mobility μ , noise can be considered as originating from fluctuations in free charge carrier number or charge mobility. For organic thin-film transistors, $1/f$ noise has been suggested to originate from number fluctuations due to carrier trapping at intergrain boundaries [92]. It has been suggested that flicker noise can be minimised by reducing the level of structural disorder in organic transistors with crystalline active layers [93].

The noise was first investigated in OECTs by Stoop *et al.* who varied the geometry of the PEDOT:PSS active layer and measured the impact on current noise PSD. It was found that the flicker noise dominated at lower frequencies and frequency-independent noise sources became dominant at higher frequencies. Additionally, the S_{V_G} scaled inversely with the channel area given by $W \cdot L$ and decreased with channel thickness [89]. Further investigations into how noise scales with OECT geometry supported that thicker channels resulted in lower values of $S_{I_D}(f)/I_D^2$ [94]. Polyravas *et al.* observed that the noise is independent of the exposed overlap between the gate and the source and drain electrodes, suggesting it is independent of parasitic capacitance [88]. With thicker active layers providing higher g_m values and lower noise values, this would associate higher transconductance values with greater SNRs. However, g_m is also increased by decreasing channel length, which, by the observations by Stoop *et al.*, increases the noise. Therefore, channel geometry must be considered when making such an association.

To explain the noise in OECTs, Stoop *et al.* applied the charge-noise model. This model assumes that the fluctuating quantity resulting in the system's flicker noise is the charge carrier density and not the charge carrier mobility. The random charge fluctuations have power S_q and are coupled to the transistor using a gate capacitance C such that they are represented as fluctuations in S_{V_G} as $S_{V_G} = C^2 S_q$ [95, 96]. Therefore, the model gave

$$\frac{S_{I_D}}{I_D^2} = \frac{g_m^2 S_{V_G}}{I_D^2} = \frac{g_m^2 S_q}{I_D^2 C^2} . \quad (2.24)$$

As it is expected that $C \propto W L d$ in OECTs, $S_{I_D}/I_D^2 \propto 1/W^2 L^2 d^2$ and thus the normalised RMS current noise scales inversely with channel volume. This suggests a further trade-off between normalised current RMS noise and ionic response time.

2.2.4 OECT Materials

The material properties of the layers composing the OECT architecture can significantly affect performance and applicability. For the purposes of biosensing, an optimised response could be defined as one which maximises biocompatibility and SNR. Investigations have considered devices with different substrates, encapsulation layers, source and drain electrodes, gate electrodes, electrolytes and organic active layers.

For proof-of-concept demonstrations, glass is typically used as a substrate material. The rigidity of glass permits ease of fabrication and its optical transparency is advantageous [97]. OECTs with glass substrates have been used in electrophysiological applications. Cell cultures of cardiac-like neurons have been grown on such devices with recordings demonstrating high SNRs [98]. However, the application of OECTs with rigid substrates is restricted in subcutaneous biosensing. The implantation of a rigid device results in chronic tissue inflammation, which partly arises from the greater value of Young's modulus of the neural probe relative to the brain tissue. One component of such inflammation is the micromotion of the brain relative to the skull [99]. This leads to the formation of a wall of glial cells surrounding the implant, which degrades the SNR over time [100]. By increasing the flexibility of neural probes, the level of neural damage decreases, thus increasing the biocompatibility of the devices [101, 102]. As such, a key component of the biocompatibility of an OECT is its capacity to conform to the curved surfaces of physiological spaces.

Flexible substrate materials that have been used within the architecture of OECTs include Parylene C, PET and polydimethylsiloxane (PDMS) [14, 103, 104]. The Young's modulus is approximately 3 GPa for Parylene C, approximately 4 GPa for PET (Melinex ST506) and is on the scale of 100 kPa for PDMS [100, 105, 106, 107]. Such flexible substrates have a significantly lower Young's modulus compared to rigid neural probes incorporating silicon, which has a value of approximately 170 GPa [108]. The Young's modulus of brain tissue is approximately 1 kPa and thus the flexible substrates incorporated in OECT architectures allow sufficient biocompatibility for electrophysiological application [14, 109].

In addition to its flexibility, the substrate used in intracortical probes should ideally have the capacity to support neuronal growth. PDMS has been used in microfluidic devices which supported the growth of hippocampal neurons from rats [110]. Parylene C meets FDA guidelines for implantation and has met the ISO 10993 and USP Class VI standards. Therefore, the material has been utilised in a wide range of neural probes [11, 13, 14, 65].

The encapsulation layer of the device is required to have the same biocompatible properties as the substrate because its interfacial area is often of a similar scale. Furthermore, the encapsulation material requires patterning capabilities as it forms part of the device architecture. In addition to operating as a substrate material, Parylene C is also frequently used for the encapsulation layer because it can be patterned using photolithographic techniques. Another material used for encapsulation is the SU-8 photoresist, which has been shown to provide neuronal adhesion and support neuronal cell cultures [111, 112, 113]. Its photopatternable properties allow for rapid and high-resolution microfabrication. The Young's modulus of SU-8 is approximately 4 GPa and is thus compatible with substrates such as PET [114]. SU-8 has been used in a range

of OECT and neural probe architectures [115, 116, 117, 118]. PDMS has also been used to encapsulate OECT architectures, though optimal patterning methods are still developing and so is less commonly implemented [119].

For neurotechnological applications of OECTs, the interstitial fluid (ISF) surrounding the brain cells and the cerebrospinal fluid (CSF) can act as the electrolyte. The fluids, which are very similar in composition, would facilitate electrophysiological recordings and their chemical components could be analysed, providing insight into neural activity [120]. CSF contains approximately 147 mM Na^+ , 2.86 mM K^+ , 1.14 mM Ca^{2+} , 1.1 mM Mg^{2+} , 113 mM Cl^- and 23.3 mM HCO_3^- [121]. To emulate OECT response in neural environments, electrolytes containing ionic concentrations similar to CSF are used in characterisation. One such electrolyte is Ringer’s solution, which contains NaCl, KCl and CaCl_2 , and has been used for *in vitro* OECT characterisation [14]. Further electrolytes include PBS and solutions containing 100 mM NaCl [42, 51, 83].

For applications where OECTs can be applied externally to the physiological environment, such as in bioelectronic circuits where amplifiers are implemented, electrolyte composition can be varied to tune device characteristics [122]. In increasing the concentration of NaCl from 0.01 M to 1 M whilst using a Faradaic Ag/AgCl gate electrode, the pinch-off voltage decreased by approximately 0.2 V whereas the channel conductance and volumetric capacitance remained constant. Electrochemical impedance spectroscopy showed that the electrolyte resistance decreased as concentration increased. The shift in pinch-off voltage was modelled to result from potential difference changes at the gate-electrolyte interface described by the Nernst equation and potential difference changes at the electrolyte-channel interface described by an equation resembling the Donnan potential. The model provided a good fit to the experimentally measured shift across a wide range of chemical concentrations [123]. In addition to varying the ionic concentrations, the viscosity of the electrolyte can impact device performance. It was found that modulations in the drain current increased as viscosity decreased [124].

The implementation of OECTs as components in bioelectronic circuits ideally maintain individual gating for each device. However, in miniaturising multi-OECT architectures, using aqueous electrolytes would not permit independent device response as the ionic liquid would be shared by the devices. Given that an OECT is defined as a device in which the channel responds volumetrically to ionic interactions, then an OECT was demonstrated where the PEDOT:PSS active layer was embedded with mobile ions using D-sorbitol and was separated from the gate by Chitosan. The devices displayed faster response times relative to aqueous electrolyte-based OECTs, which was attributed to how the active layer already contained the mobile ions and thus was not limited by the ionic transport time [125]. Alternatively, elastomeric ionic gels that provide facile ion transport have been

implemented as replacements in which cations traverse the PEDOT:PSS volume as similar to when using aqueous electrolytes [126].

As previously described, gold is often used as the source and drain electrode material when interfacing with PEDOT:PSS due to their similar work functions. For applications where the devices are in contact with the physiological environment, the biologically inert properties of gold contribute to its biocompatibility. Gold has been shown to be noncytotoxic and nonimmunogenic and has been utilised in a number of neural probes [127]. It also has sufficient flexibility in electrophysiological recording devices to conform to cortical surfaces [13, 65]. Alternative source and drain electrode materials are used when printing fabrication techniques are employed. Electrode materials in such devices include PEDOT:PSS, carbon and silver [128, 129, 130, 131, 132].

The material used at the gate electrode significantly affects device response. A non-polarisable Ag/AgCl electrode provides a resistive electrode-electrolyte interface, which minimises any potential difference relative to a polarisable, capacitive gate material such as Pt. As such, the potential difference at the electrolyte-channel interface, and thus the drain current modulation, is increased [122]. By considering impedance measurements of the OEET ionic circuit, the existence of a capacitive gate-electrolyte interface was shown to reduce the de-doping of the active layer relative to a resistive interface. As input frequency increased, the potential difference across the capacitive gate-electrolyte and electrolyte-channel interfaces reduced in magnitude. As such, the response of the system with the capacitive gate-electrolyte interface tended towards that with the resistive interface. With a reducing potential difference across the electrolyte-channel interface, the de-doping decreased as frequency increased in both systems [133]. The devices are not often operated at such frequencies and thus non-polarisable electrode materials are implemented to maximise device response.

In addition to Ag/AgCl and Pt gate electrodes, other materials have been utilised to facilitate ionic transport. Such materials may have been chosen due to fabrication constraints. For example, if fabricating all electrodes in the x-y plane of figure 2.8, then it is convenient for the source, drain and gate electrodes to be composed of the same material. As such, gold has been used as the gate material, which can be described as an almost ideally polarisable electrode [134, 135]. PEDOT:PSS-coated Au electrodes have also been used as a gate electrode [136]. PEDOT:PSS has been shown to decrease the impedance of Au electrodes by increasing their effective surface area and thus increasing their capacitance [137]. For printed OEETs, the gate electrode has been made of materials including PEDOT:PSS and carbon [128, 130, 131, 138, 139, 140].

Investigations presented here consider the utilisation of PEDOT:PSS as the organic active layer in OEETs, which are p-type, depletion mode devices. Investigations in the

literature show that OECTs have been fabricated with novel organic layer materials that provide n-type operation. Furthermore, the devices have operated as accumulation (or enhancement) mode OECTs, where the transport of ions into the active layer generates electronic charges to be transported between the source and drain electrodes. To compare the performance of OECT active layers, the maximum transconductance is determined, which is proportional to the product of charge carrier mobility, μ , and channel capacitance per unit volume, C^* . The product μC^* is considered to capture the mixed electronic and ionic conductivity of the organic channel and can act as a benchmark for the material's performance [141]. The value of μC^* for PEDOT:PSS with the additive ethylene glycol has been measured to be $47 \text{ Fcm}^{-1}\text{V}^{-1}\text{s}^{-1}$ and $490 \text{ Fcm}^{-1}\text{V}^{-1}\text{s}^{-1}$ for PEDOT:PSS treated with sulphuric acid [58, 142].

Organic polymers that result in p-type, accumulation mode OECTs include p(g2T-TT), which has a μC^* value of $261 \text{ Fcm}^{-1}\text{V}^{-1}\text{s}^{-1}$ [143]. A further superior material that results in p-type, accumulation mode OECTs without the need for additives is p(gDPP-T2) with a μC^* value of $342 \text{ Fcm}^{-1}\text{V}^{-1}\text{s}^{-1}$ [144]. A material with similar performance is the ethylene glycol-functionalised polythiophene conjugated polymer p(g2T2-g3T2), with a μC^* value of $378 \text{ Fcm}^{-1}\text{V}^{-1}\text{s}^{-1}$ [145]. Such values are comparable to the highest μC^* value reported for treated PEDOT:PSS, suggesting that these novel polymers may soon overtake the dominance of the material in OECT active layers. In addition to p-type devices, an n-type, accumulation mode OECT has been demonstrated with stability in water. OECT characterisations with the material p(gNDI-gT2) showed conductance and transconductance values an order of magnitude lower than found in p-type devices [42].

2.2.5 OECT Architectures

The architecture of an OECT can contribute significantly to its performance. For the gate electrode, its position and size can impact device performance depending on the type of electrode-electrolyte interface. The geometry of the source and drain electrodes determine the channel width, W , channel length, L , and thickness, d , which further determine conductance, transconductance, response time, pinch-off voltage and noise. The interconnect resistance, which can become significantly greater than channel resistance, can also significantly impact device performance.

The impacts of the gate electrode geometry on device characteristics are examined. For non-polarisable gate materials, the potential difference across the ideally resistive interface is approximately independent of the interfacial area. Indeed, experimental measurements showed that the OECT drain current modulation was independent of the size of non-polarisable electrodes used as the gate [122]. Therefore, the area of the gate-electrolyte interface can be smaller than that at the electrolyte-channel interface without affecting

device characteristics. The capacitive dependence on the gate electrode-electrolyte interface results in a dependence on the area of the gate electrode. Modelling the gate-electrolyte and electrolyte-channel interfaces as capacitors C_{GE} and C_{EC} , respectively, then the total capacitance, C_{Tot} , is given as

$$C_{Tot} = \frac{C_{GE}C_{EC}}{C_{GE} + C_{EC}} . \quad (2.25)$$

Although C_{EC} increases with channel thickness, both C_{GE} and C_{EC} increase with their interfacial area. Given that one of the two capacitors decreases its area, the potential difference across that double layer would increase because its impedance increases. Therefore, as the gate electrode becomes smaller in size, the potential difference provided to transport the cations into the organic active layer reduces and thus the transconductance decreases [146]. Therefore, the gate electrode area must be maximised to optimise the device response when using polarisable gate electrodes.

The distance between the gate electrode and the channel has also been shown to affect the OECT response. For a 3×3 grid of PEDOT:PSS-coated gold gate electrodes, it was found that gate electrodes positioned closer to the OECT channel resulted in greater changes in drain current. This was attributed to a reduction in electrolyte resistance, which was proportional to gate-channel distance [147]. It has been suggested that the electrolyte resistance is dependent on $1/\sqrt{WL}$, and this relationship has been observed by considering OECT impedance measurements that model the electrolyte as a resistor and the electrolyte-channel interface as a resistor and capacitor in parallel. Further investigations have shown that the on-off current ratio increases as the gate-channel distance decreases and the magnitude of the on-current remained constant [148]. This suggests that if device fabrication requires placing the gate electrode in the plane of the source and drain electrodes, then device performance can be maximised by minimising the gate-channel distance and maximising channel area.

The traditional OECT structure, as shown in figure 2.12, has a ‘parallel-plate’ geometry. The conductance and transconductance are proportional to the fraction Wd/L , whereas the response time is approximately proportional to $d\sqrt{WL}$ and normalised current noise is proportional to $1/WLd$. This demonstrates that device performance can be tuned to the requirements of the application. Additionally, the observations suggest that device performance can be optimised by maximising W and d whilst minimising L . Further performance increases require the optimisation of the organic active layer. Short-channel effects begin to dominate when L becomes the same scale as the length of the charge carrier depleted region of the channel. A subset of OECT applications requires current saturation to maintain an expected operating regime, thus placing a lower limit on L .

To maximise W and minimise L for a device area that is restricted for applications such as those that require high spatial resolution of the electrical activity from the cortex,

investigations have considered a range of source and drain electrode architectures. An electrode style that is used to achieve such conditions is interdigitation. The most commonly implemented interdigitated style shapes the source and drain electrodes as interlocking ‘combs’, as shown in figure 2.13a. Alternatively, the source and drain electrodes can ‘spiral’ around each other, as shown in figure 2.13b. The use of interdigitated electrodes introduces new parameters which can be used to tune device operation. For interdigitated electrodes, the width of the device can be considered as the total length of the interface between the source (or drain) and the active layer.

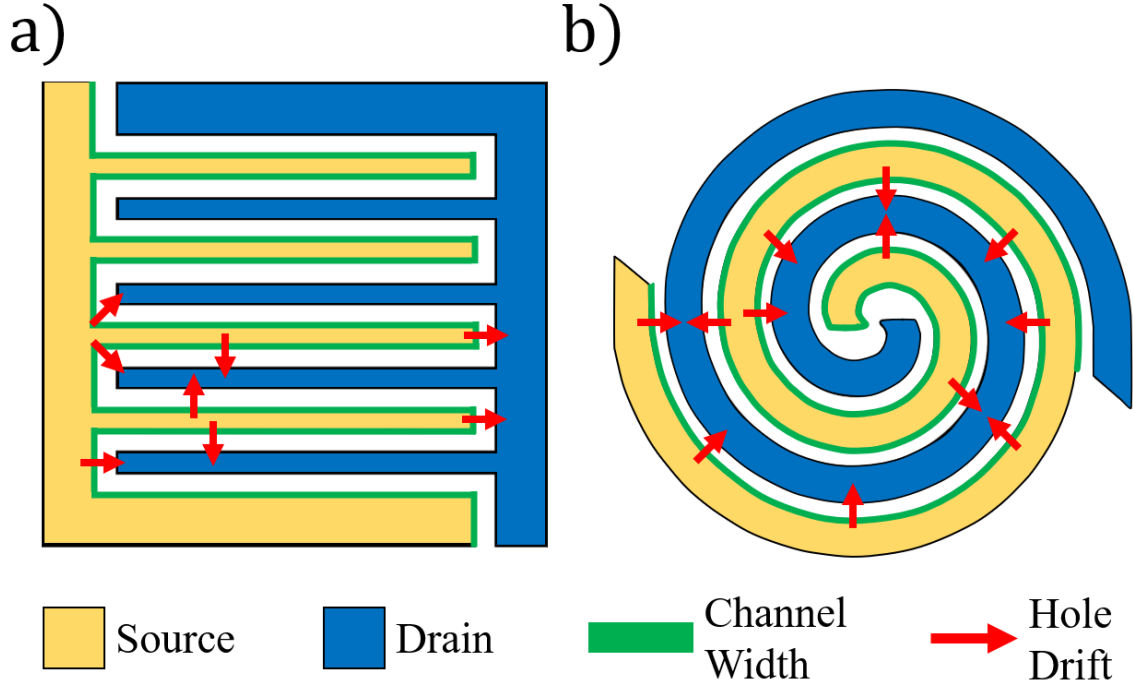


Figure 2.13: Electrode geometries for the a) Comb interdigitated electrode, b) Spiral interdigitated electrode.

The comb and spiral interdigitated electrodes have been implemented in OECT devices [98, 149]. The effect of comb parameters on OECT performance has been systematically investigated. These parameters included the number, N_f , width, W_f and length, L_f , of comb ‘fingers’, and the channel length, L , was also varied. The combination of these parameters determined the effective channel width. By individually increasing W_f and L_f , the conductance, transconductance and pinch-off voltage increased. Furthermore, it was observed that the interdigitated electrode OECTs approximately followed the temporal relationship $\tau \propto d\sqrt{WL}$, as found in parallel-plate OECT geometries [98].

OECT architectures where the source and drain electrodes are separated by the active

layer in the x-y plane as shown in figure 2.12 are labelled as planar OECTs (pOECTs). A vertical OECT (vOECT) architecture was investigated where the source and drain electrodes were separated in the z-plane, permitting channel lengths as small as 450 nm. It was found that devices could provide high transconductance values; however, the cut-off frequency was lower than expected from the $\tau \propto d\sqrt{WL}$ relationship. This was attributed to the parasitic capacitance from the unencapsulated electrode area that was required for the vOECT architecture [87].

The interdigitated electrode pOECTs and vOECTs achieved transconductance values on the 10 mS-scale. However, both investigations suggested that the values were limited by the resistance of the contact lines, also defined as a parasitic series resistance [87, 98]. Consider the resistance from the source interconnect line, R_S , and the resistance from the drain interconnect line, R_D . The circuit is powered by a supply voltage V_{DD} and has an applied gate voltage V_G which varies the conductivity of the OECT with drain current I_D and drain-source voltage V_{DS} . The supply voltage is divided across the source resistance, OECT and drain resistance as

$$V_{DD} = I_D R_S + V_{DS} + I_D R_D \quad , \quad (2.26)$$

and the gate voltage is divided across the source resistance and OECT as

$$V_G = I_D R_S + V_{GS} \quad . \quad (2.27)$$

The differential of the drain current is given as

$$dI_D = \left. \frac{\partial I_D}{\partial V_{GS}} \right|_{V_{DS}} dV_{GS} + \left. \frac{\partial I_D}{\partial V_{DS}} \right|_{V_{GS}} dV_{DS} \equiv g_{mi} dV_{GS} + g_{di} dV_{DS} \quad , \quad (2.28)$$

where g_{mi} is the intrinsic OECT transconductance and g_{di} is the intrinsic drain conductance. For a constant supply voltage, $dV_{DD} = 0$, it can be shown that the intrinsic transconductance is given by

$$g_{mi} = \frac{g_m^0}{1 - (R_S + R_D)g_d(1 + R_S g_m^0)} \quad , \quad (2.29)$$

where $g_d \equiv \partial I_D / \partial V_{DD} |_{V_G}$ is the measured conductance and $g_m^0 \equiv g_m / (1 - R_S g_m)$ [150]. This shows that parasitic series resistances decrease the intrinsic transconductance of the device to the measured extrinsic value.

Equation 2.26 shows that by increasing R_S and R_D , V_{DS} , and thus I_D , decrease in magnitude. With a decrease in V_{DS} , the electronic transport time across the channel increases. Furthermore, equation 2.27 shows that V_{GS} is dependent on R_S . Indeed, models suggest that increasing the contact resistance translates the gate voltage where the peak transconductance occurs [80, 150]. To determine the summation of the source and drain

interconnect resistances and the contact resistances, the OECT geometry is systematically varied such that the channel length decreases as all other geometry parameters remain constant. The total resistance is defined to be the resistance found at $L = 0$, determined through extrapolation. This method, known as the transmission line method, has been used to determine the intrinsic transconductance values of OECTs [87, 98]. The limits on the width and length of the interconnects that determine the interconnect resistance are dictated by the spatial requirements of the device’s application and the fabrication methods used. As previously mentioned, increasing the thickness of the interconnects reduces their resistive contribution to device behaviour and maximises the extrinsic transconductance. However, increasing the thickness increases the financial cost of the device, particularly when gold is used to interface the organic active layer.

For applications that require a spatial resolution of activity, OECTs have been fabricated into arrays where devices are separated by an approximately fixed distance, or ‘pitch’. The primary biosensing application in which OECTs are fabricated into arrays is electrophysiology. If placed into a physiological environment where the ionic fluxes in the associated electrolyte constitute the activity to be measured, such as extracellular recordings of neuronal action potentials, then only the source and drain electrodes are required on the substrate. For such two-terminal architectures, source electrodes can be shared between the OECT devices, permitted because all connect to the same ground point. Arrays of OECTs have been fabricated with both shared and individual source lines [151, 152]. Where multiplexing methods are not employed, each OECT is provided with an individual drain interconnect and thus each OECT can be simultaneously sampled. The largest OECT arrays for electrophysiology are approaching 10^2 channels [51, 153]. For comparison of array development, the largest microelectrode arrays used for similar electrophysiological applications sample with 10^4 -scale channel numbers [154]. However, increasing the channel counts of pOECT arrays with $10\ \mu\text{m}$ -scale pitch values and individual drain interconnects requires more complex interconnect designs.

To overcome scalability limitations of OECT arrays from the limited space available for interconnect lines where each OECT is provided with an individual drain line, multiplexed interconnect structures can be used [155]. For an $m \times n$ grid of OECTs, using individual drain lines and a single shared source line would require $mn + 1$ lines, whereas multiplexed structures would require $m + n$ lines. The multiplexed structure involves sequentially switching OECTs into an operating state and then switching the devices off and OECTs share source and drain lines. The OECTs are thus not simultaneously sampled and each OECT is only sampled once every sequential cycle. Furthermore, the time required to place the OECT into, and out of, an operating regime is limited by the response time of the device. As such, the multiplex structure limits the bandwidth of the

OECT array. Additionally, as OECTs share drain lines in such structures, residual signals can result in interference between device measurements, or crosstalk. This introduces additional noise to the OECT recording and thus degrades the signal. Therefore, there is a trade-off between the scalability of array size and signal quality. Traditional OECT structures provide an upper frequency already associated with high-frequency electrophysiological activity. Furthermore, the devices present noise levels that suggest that recording such activity would prove difficult and thus additional noise sources would be significantly detrimental. Therefore, the implementation of such structures is currently more suited to electrode arrays. Nevertheless, multiplexed OECT array structures have been used to measure electrophysiological activity on the cortical surface of a rat [117].

2.3. Organic Transistor Fabrication

2.3.1 Microfabrication Techniques

Owed to their high efficacy in biosensing, OECTs are being increasingly investigated as a measuring tool for a wide range of applications. As such, new methods of fabrication that are low-cost and provide a high throughput are being explored. Current high throughput techniques compromise fabrication resolution, and the choice of materials is more restricted, limiting device performance. Therefore, to demonstrate the capabilities of OECTs for a given application, lower throughput methods that provide higher fabrication resolutions and more material options are often initially utilised. Furthermore, the required device sizes for a given application may immediately limit the methods that can be used.

The two methods that are primarily used in OECT fabrication are printing and photolithography. Printing is an additive technique in that material is only deposited onto a given layer and not removed. Therefore, the deposition and patterning steps are simultaneous, and the materials need to be optimised for both performance and fabrication. On the other hand, photolithography necessarily contains subtractive steps in that material is removed to facilitate the desired patterning, leading to the separation of the deposition and patterning steps. In this case, the patterning capability is less dependent on the properties of the materials used in the architecture. Consequently, photolithography provides higher resolution and device performance than printing; however, the fabrication involves more steps, higher costs, and lower throughput.

2.3.2 Fabrication using Printing Methods

There is a range of printing methods that have been used to fabricate OECTs, which can be categorised into two types. The first category encompasses methods where the OECT materials are directly printed onto the substrate without contact and are identified as

‘direct writing’ techniques. Such methods employed for OECT fabrication include inkjet printing, aerosol jet printing and the spray-deposition technique [156, 157, 158]. The second category includes methods where a medium is used to transfer materials onto the substrate through physical contact and are designated as ‘transfer printing’ techniques. The primary transfer technique used in the fabrication of large-area OECTs is screen-printing [131].

In inkjet printing, small volumes of ink are ejected from a nozzle onto a substrate at the desired location where the liquid then spreads and dries. The area that an ink droplet occupies is dependent on the substrate surface properties and the properties of the ink, particularly the solvent and ink concentrations. Inkjet printing provides a fabrication resolution that allows for 10 μm feature sizes [159, 160]. Aerosol-jet printing and spray printing are similar techniques in which the material droplets are carried in gas and deposited on the substrate. Aerosol-jet printing is a direct writing approach whereas spray printing involves depositing the material through a mask for patterning. These techniques provide patterning resolutions on the scale of 10 μm [158, 160]. Screen printing involves pressing ink through a mask that is in contact with the surface of the substrate, providing resolutions of approximately 50 μm [131].

The printing methods require the materials they deposit to be in a liquid state. Due to the high conductivity of PEDOT:PSS, the organic material has been implemented as the active layer and the source, drain and gate electrodes in inkjet-printed OECTs [128, 156]. Additionally, silver ink has been used as interconnects to such devices [148]. Similar materials have been used in aerosol-jet printing [158]. In screen printing, carbon paste has been used in addition to silver ink to interface the PEDOT:PSS active layer and PEDOT:PSS has been used as the gate electrode [131, 161]. Such fabrication has facilitated the production of 760 OECTs with a yield of 99.7% [130].

The limitations on fabrication resolution and materials place restrictions on the applications of printed OECTs. For example, measuring the electrical activity of individual neurons requires devices with μm -scale features. However, given that the application does not restrict the device size, printing methods can be used to fabricate OECTs for neurotechnology. For example, electrolyte concentration sensing has been performed using a screen-printed differential amplifier [162]. Additionally, processing drain current values that represent physiological activity requires circuits that operate at low voltages. OECTs have been fabricated using screen-printing into advanced circuits, showing potential for their use in bioelectronic processing [131, 161].

2.3.3 Fabrication using Photolithography

Photolithography can be used to pattern the electrode, encapsulation and active layers of the OECT and has been extensively used to demonstrate the capabilities of the device.

In photolithography, a photosensitive polymer called a photoresist is selectively exposed to UV light through a mask that is placed in contact with the substrate. The type of photoresist determines if the exposed areas consequently remain or are removed from the substrate, and photoresist is removed after exposure using a solvent known as a developer. Exposed positive photoresist becomes less soluble in developer and thus remains on the substrate, whereas negative photoresist becomes more soluble and is thus removed.

Once the photoresist has been deposited onto a cleaned substrate, the structure is soft baked. This evaporates the photoresist's solvent and changes its state from a liquid to a solid. Soft baking for an insufficient time or at an insufficient temperature results in an excess of solvent in the photoresist, which can result in undesired photoresist erosion and can reduce its adhesion to the underlying layer. In contrast, excessive baking can result in photoresist degradation and cross-linking in negative resists. The mask is then aligned to the desired position and the photoresist is selectively exposed. For positive resists, overexposure results in eroded edges and decreases in feature sizes and underexposure results in dilated features and a loss of sharpness. Inversely, negative resists experience erosion for underexposure and dilation for overexposure. For negative resists, the structure is post-exposure baked, which completes the reaction produced by the UV exposure. Increasing the temperature of this bake provides more stability for the unexposed areas in development; however, there is greater cross-linking in the exposed regions and thus development becomes more difficult. The structure is then developed, removing the desired areas of photoresist. Excessive development results in photoresist erosion and small feature sizes, and insufficient development does not fully define the desired pattern and can leave residues of photoresist. Finally, the photoresist is stripped from the substrate. The photolithography process is illustrated in figure 2.14.

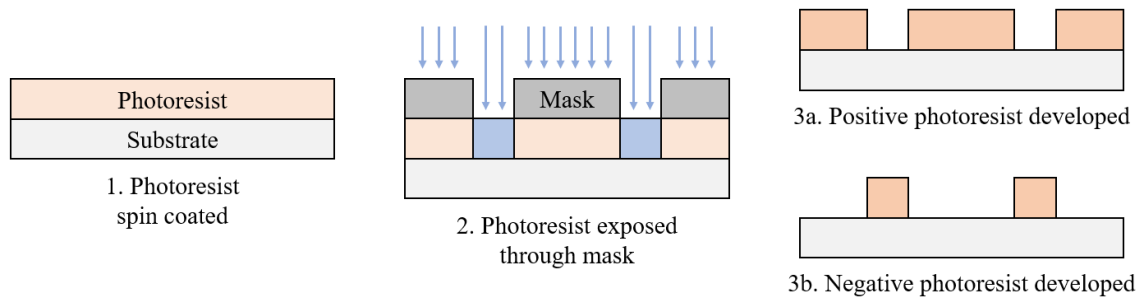


Figure 2.14: *Photolithography process for positive and negative photoresists.*

Photoresist can be used to protect underlying areas in etching processes or be used to delaminate layers deposited above the resist layer, known as lift-off. The ideal etching and lift-off processes are illustrated in figure 2.15. In lift-off, a bi-layer of photoresist

can be used to achieve optimal patterning results. Photolithography is typically used to pattern the electrode layers of organic devices. However, conventional photoresists, developers and strippers can damage the organic materials used in the active layer [163]. As such, photoresists and solvents have been developed which allow the patterning of organic materials such as PEDOT:PSS [48].

To deposit the photoresist onto the substrate, spin coating is used. In this method, the material is deposited and rotated at speeds approaching 10,000 rpm. Centrifugal forces act to spread the material across the flat substrate such that it forms a uniform, thin film, as shown in figure 2.16. Film thickness, d , varies with spin speed, ω , as $d \propto 1/\sqrt{\omega}$. In addition to the photoresist, spin coating is used to deposit the organic active layer. To deposit the metallic layers used in electrodes, thermal evaporation is used. In this process, a metal is evaporated in a near-vacuum and condenses into a solid when it reaches the surface of the substrate.

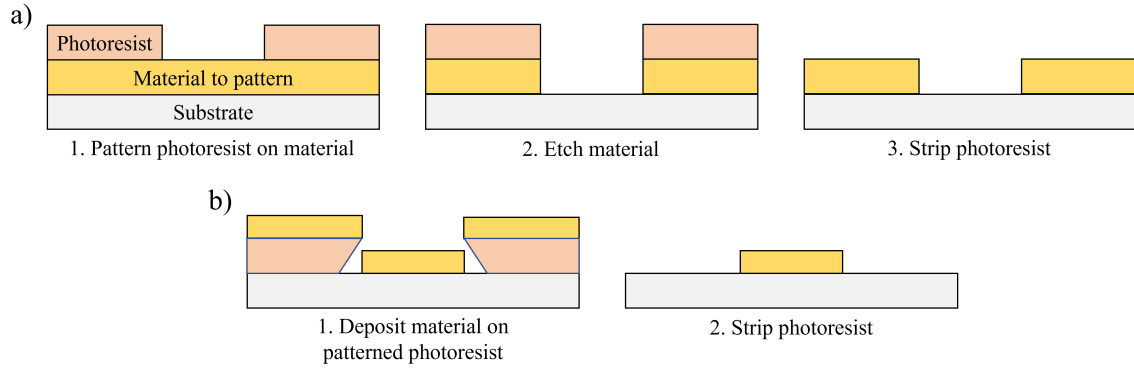


Figure 2.15: Processes of photolithographic patterning using a) etching, b) lift-off.

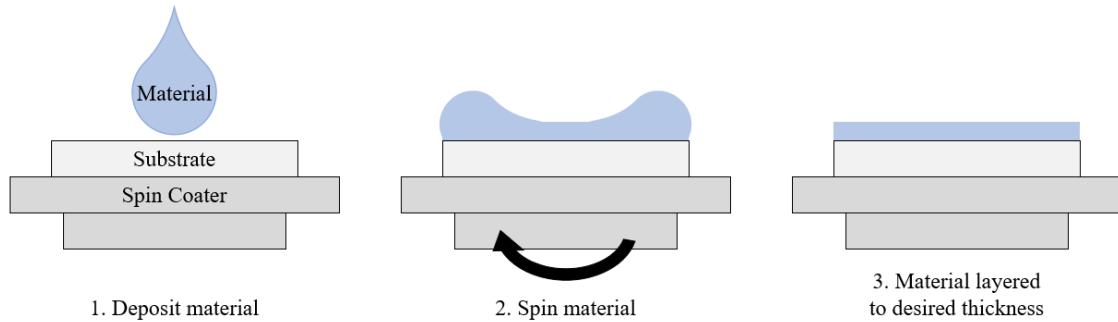


Figure 2.16: Process of spin coating a material to a desired thickness.

Investigations that utilise OECTs with photolithographic fabrication primarily use lift-off methods for the electrode patterning of gold and chromium layers. This has provided μm -scale features and high-performance devices for a range of applications in neurotechnology [14, 118, 125]. For the encapsulation layer, Parylene C has been patterned using photolithography with reactive ion etching. An alternative encapsulation that is easily fabricated is SU-8 because the layer is defined after the development step as shown in figure 2.14. Photolithographic methods have been used to pattern the active layer of OECTs and such methods have demonstrated high resolutions [48, 72].

2.3.4 Additional Fabrication Processes

A further method of patterning the organic active layer is by using a sacrificial Parylene C layer. This layer is patterned through photolithography and leaves a window over the channel. The organic layer is then spin coated and the sacrificial Parylene C is mechanically peeled off. This method has been used to fabricate OECT arrays, circuits and chemical sensors [16, 51, 53]. In comparing the Parylene C peel-off technique with the photolithographic patterning of PEDOT:PSS, the peel-off method results in greater device variability in channel conductance than when using photolithography [72]. This implies that the peel-off method results in greater variability in channel thickness. Therefore, photolithographic patterning of the active layer is preferable for device fabrication where the uniformity of characteristics is desired.

The electrodes and active layer can also be patterned using a shadow mask. A shadow mask is a thin material with the desired pattern etched away. This is such that when it is placed over a substrate there are openings to its surface only at those etched areas. Therefore, deposition through the mask onto the substrate results in the deposition of the desired pattern directly onto the substrate. The fabrication process is thus significantly faster than in photolithography. However, the patterning resolution is limited to that of the mask, and alignment to existing patterns on the substrate is less accurate. Shadow masks have been used to pattern OECT source and drain electrodes [164, 165]. They have also been used to pattern the PEDOT:PSS active layers of OECTs [85, 166].

Additional methods have been used in the fabrication of OECTs. The electromigration induced break junction technique has been used to fabricate devices with channel lengths as small as 250 nm [167]. Electron-beam lithography, which provides a higher resolution than photolithography, has been used to pattern the electrodes [168]. Nanoimprint lithography and stereolithography have also been used in OECT fabrication [169, 170].

2.4. Applications in Electrophysiology

2.4.1 Electrophysiological Measurements and Methods

Electrophysiology studies the electrical activity associated with the flow of ions in physiological volumes. The fundamental unit of electrophysiology is the neuron, within which the electrical activity is generated and propagated. Ionic fluxes are transported across the neuronal surface using ion channels and pumps, and neurons transfer ions with an extracellular fluid. In an unexcited state and an electrochemical equilibrium, the difference in ionic concentrations across the neuronal membrane results in a non-zero resting potential. During an action potential, the permeabilities of ion channels in the membrane vary, facilitating ionic transport. The concentrations of sodium, potassium, calcium and chloride temporally vary and thus the voltage changes across the neuronal surface and transmembrane currents are generated. This voltage is propagated through the neuron and is transmitted to further neurons through synaptic connections. The presence of the voltage at a synapse results in the release of neurotransmitters, which then bind to receptors in a proximal neuron. The binding events facilitate the transmission of the action potential through the connected neuron.

In measuring the potential difference of the inside relative to the outside of the neuron, the resting state takes a voltage of -70 mV. During an action potential, an inward flux of sodium drives an increase in voltage to +40 mV within approximately 1 ms. A subsequent outward flux of potassium decreases the voltage to below -70 mV in a further 1 ms. The ions then return to their resting concentrations in the subsequent 2 to 3 ms. Such events have been measured extracellularly with voltages on the scale of 100 μV at distances of 10 μm from the neuron [171]. Therefore, measuring action potentials extracellularly requires the capability to resolve μV -scale voltages at kHz-scale frequencies [172].

There are estimated to be approximately 10^{11} neurons in the brain, and it has been suggested that each neuron has approximately 10^3 synaptic connections [173, 174]. The body of a neuron in the brain has an approximate size of 10 μm and an approximate spacing of 10 μm [13, 175, 176]. The current sources and sinks from all ionic processes in the brain superpose to a total potential difference at each point in the volume, V_e , relative to a reference electrode voltage. In the conductive medium of the brain, Ohm's law gives a current flux $\mathbf{J} = \sigma \mathbf{E} = -\sigma \nabla V_e$. Therefore, for a current point source I , the voltage at distance r is given by $V_e = I/4\pi\sigma r$. As such, the measurement of V_e decays, and thus the signal-to-noise ratio decreases, with distance for the recording device.

Given that the voltage activity of multiple neurons, known as multi-unit activity (MUA), is recorded with a sufficient electrode spatial density, the measurements can be computationally analysed using spike-sorting methods to isolate the activity of individual

neurons, known as single-unit activity (SUA) [11, 13, 177]. Action potential spikes with amplitudes from $50\ \mu\text{V}$ to $250\ \mu\text{V}$ have been isolated with an RMS voltage noise of approximately $6\ \mu\text{V}$ whilst recording at a sampling frequency of $25\ \text{kHz}$ [177]. The MUA can be obtained from high-density voltage recordings by applying a high-pass filter at approximately $300\ \text{Hz}$ [178]. The summation of low-amplitude, high-frequency events such as the temporal synchrony of neuronal networks give rise to electrical waveforms with higher amplitudes and lower frequencies. The extracellular field representing this activity is known as the local field potential (LFP) and is acquired by applying a low-pass filter at approximately $300\ \text{Hz}$ [179]. The LFP power scales with frequency as $1/f^n$ for n values from $n = 1$ to $n = 2$. Therefore, LFP signals with lower frequencies have greater amplitudes which can extend to the mV-scale. This behaviour partly originates from how greater numbers of neurons can be employed in a given signal over a greater time window (or equivalently a lower signal frequency) [172]. It is noted that the scaling of LFP power is similar to that of the flicker noise in a device which could be used to record such neural activity.

The applications and capabilities of OECTs in measuring the activity associated with the ionic fluxes of the brain's electrical activity are best compared to the performance of electrodes, and thus the use of electrodes to record the activity of the brain are considered. The value of V_e can be measured to a varying degree of invasiveness, where a more invasive method is associated with higher signal quality. The least invasive measure of V_e is performed by recording activity from the surface of the scalp. This method, known as electroencephalography (EEG), records activity that has passed from the surface of the brain through intermediary physiological layers including the skull and the dura. This permeation results in an attenuation of the voltage and reduces the spatial resolution of the activity. Therefore, only the voltages with the greatest amplitudes, and thus the lowest frequencies, can be measured. The voltages measured at the scalp have amplitudes on the $10 - 100\ \mu\text{V}$ -scale for frequencies on the $1 - 10\ \text{Hz}$ -scale and become μV -scale when approaching $100\ \text{Hz}$ [180]. Investigations that measure EEG have used electrode headsets that record from up to 256 channels. In such headsets, the electrodes typically have diameters approaching $1\ \text{cm}$ and have an interelectrode spacing of approximately $2\ \text{cm}$ [181, 182]. EEG recordings have been utilised in clinical applications including in the diagnosis of epilepsy and have shown potential in providing biomarkers for Parkinson's disease dementia [183, 184]. The applications of EEG in BMIs include prosthetic hand control and computer mouse control [185, 186].

In an increasingly invasive method, electrodes are placed on the surface of the brain. This method, known as electrocorticography (ECoG), has a superior signal quality relative to EEG as the activity is not reduced from intermediary tissue. To access the surface

of the brain, neurosurgical methods are required, which result in substantial risks to the subject's physiological condition. Due to the greatly increased spatiotemporal resolution afforded by ECoG, devices with a wide range of electrode sizes and spacings have been utilised with applications in healthcare and brain-machine interfaces (BMIs). Healthcare applications include epilepsy diagnosis, and ECoG can be used in BMIs for the prediction of speech onset [187, 188]. For devices that utilise sub-mm feature sizes, the recording method is increasingly redefined as micro-electrocorticography (μ ECoG) [189]. Action potentials have been recorded from the surface of the brain using a 16×16 electrode grid with an electrode size of $10 \times 10 \mu\text{m}^2$ and an interelectrode spacing of $30 \mu\text{m}$ [13]. The ECoG methodology has been used to record spreading depolarisations (SDs), which result from traumatic brain injury and represent mass neuronal depolarisations. Events of SDs display voltage amplitudes on the 10 mV-scale and frequencies on the 10 mHz-scale [190].

The most invasive form of brain electrophysiology involves electrodes penetrating through the cortical surface and recording or stimulating from within its volume. Intracortical electrodes have isolated SUA from within the cortex, and activity has correlated with physical movements for recordings in the motor cortex [11, 177, 191]. Such devices record 10 μV -scale voltages at kHz-scale frequencies from devices with channel counts greater than 10^3 , interelectrode spacings of $\leq 100 \mu\text{m}$ and electrode sizes on the 10 μm -scale. The penetration of an intracortical electrode array results in a foreign body response (FBR) which reduces signal quality over time [192]. Therefore, efforts to minimise the FBR are needed for further development and long-term application of high-density intracortical electrodes. With a higher level of neural information at a given time, more degrees of freedom should be available for BMIs, which could be provided by intracortical electrodes for applications including restoring communication, limb motion and computer control [7]. A further use of implanting electrodes in the brain is for deep brain stimulation (DBS), in which electrical impulses regulate neural activity. The applications of DBS to healthcare include alleviating symptoms of Parkinson disease [193]. Ethical issues should be considered when stimulating or recording the brain [194].

The capabilities of OECTs to resolve bioelectric signals from different parts of the body support their capabilities to measure electrical activity from the brain. Electrical activity generated by motor neurons constitute myoelectric signals, and this activity can be measured by recording the signals of skeletal muscles in an electrophysiological method defined as electromyography (EMG). The motor unit, which consists of the signal from the motor neuron and the innervated muscle cells, generates an action potential that has an amplitude of approximately 0.5 mV and a duration from 8 to 14 ms. These parameters are measured by inserting electrodes, such as needle electrodes, into the muscle volume [195]. In a less invasive technique, EMG can be recorded from the surface of the skin (sEMG). The

frequency and voltage characteristics of sEMG signals provide amplitudes on the $100\ \mu\text{V}$ -scale with frequency components primarily up to 500 Hz [196]. In recent investigations, high-density sEMG devices identified biomarkers associated with motor neuron disease and resolved high-frequency myoelectric activity [197, 198, 199]. The technique has also captured finger motion without placing sensors on the hands or fingers [200].

During the cardiac cycle, electrical activity controls the contraction and relaxation of the heart muscles, which is measured using a technique defined as the electrocardiogram (ECG). The cells that constitute the heart muscles are cardiomyocytes, which undergo action potentials and propagate the electrical signals associated with the cardiac cycle. The action potentials associated with cardiomyocytes have a resting potential of approximately $-80\ \text{mV}$. During an action potential, the potential initially increases to $30\ \text{mV}$ within a ms-scale duration and then returns to the resting potential over approximately 200 ms [201, 202]. When measured extracellularly, the signal amplitudes are on the $0.1 - 1\ \text{mV}$ -scale [203, 204]. The ECG signal can also be recorded from the surface of the skin. Such measurements provide mV-scale amplitudes and frequencies less than 100 Hz [205, 206].

2.4.2 Applications of OECTs

Where an electrode would record the summated electric field that results from ionic fluxes, an OECT would transduce the ionic flux through its incidence on the organic active layer, causing a change in the number of electronic charge carriers flowing between the source and drain electrode. Arguably, the OECT thus provides a more fundamental measure of the ionic processes in the intracellular and extracellular spaces, permitted by the mixed ionic-electronic conductivity of the active layer. For bioelectric measurements at the surface of the skin, a gate electrode is connected to the skin and measures the voltage similar to an electrode. The gate then transmits the voltage through to the electrolyte, resulting in ionic fluxes which again cause changes in the organic active layer conductivity. For such surface measurements, the mechanism of measuring the signal is the same for electrodes and OECTs given that both use an equivalent electrode. Therefore, the signal amplitude would not be significantly different at the position of measurement. In an OECT, this voltage is then amplified through the transconductance into a current. Given that the OECT amplification introduces less noise than the voltage amplifiers typically employed in electrode recordings, then the SNR in OECTs would be greater.

A higher SNR would result in a greater number of features that could be extracted from electrophysiological recordings in a given time. Higher performances could be achieved in analytical methods that utilise feature extraction such as spike-sorting. In a BMI where the degrees of freedom are dependent on the ability to distinguish various waveforms, it is suggested that a higher SNR would provide either a greater number of degrees of freedom

or a higher performance in correctly associating waveforms with their desired behaviours. For clinical applications, a higher SNR would provide greater insights into physiological environments. This could potentially improve the ability to predict the onset of detrimental events and thus provide more time to introduce preventative measures.

OECTs have been used in the measurement of EEG, ECoG, EMG and ECG [14, 125, 207, 208]. OECTs have also been applied to the method of electrooculography in which the voltages associated with eye movement are measured [209]. In such studies, OECTs demonstrate the capability to provide either a comparable or a superior SNR compared to electrodes. The comparison of the performances of OECT BMIs and electrode BMIs for computational interactions and prosthetic control is yet to be investigated.

The EEG modality has been measured using OECTs, supporting their capability to resolve small signal amplitudes [77, 125, 209, 210]. Frequency analysis has shown the recording of the alpha rhythm with greater bioelectric power around 10 Hz, supporting that OECTs can resolve physiologically relevant signals [77, 209]. It was found that by increasing the thickness of the active layer and thus increasing the transconductance, the signal power became greater. This was at the expense of a lower bandwidth; however, EEG signals typically do not exceed 100 Hz in their frequency content, and OECTs can be fabricated to optimise their performance within such a limit. Furthermore, organic transistors that showed volumetric channel de-doping were adhered to the scalp without adhesive chemicals and, facilitated by amplification local to the recording site, provided neurophysiological signals comparable to clinical EEG electrodes. Where the clinical electrodes resulted in scalp irritation, the transistors had a smaller contact area by five orders of magnitude, resulting in no evident irritation and permitting placement between hair follicles [125].

A modality that has greatly motivated the further investigation of applying OECTs to measuring neural electrical activity is μ ECoG, in which the devices have presented superior SNRs relative to electrodes at low frequencies. In this study, OECTs with $W = 15 \mu\text{m}$ and $L = 6 \mu\text{m}$ were placed next to electrodes with areas of $12 \times 12 \mu\text{m}^2$, and the fabricated probe also allowed a penetrating silicon electrode array to be implanted through a hole in its centre. With a Parylene substrate and encapsulation layer, the total device thickness was $4 \mu\text{m}$, and the flexible probe was placed onto the cortical surface. The OECT active layer and coating of the electrodes consisted of 200 nm layer of PEDOT:PSS, EG, DBSA and GOPS. The resulting OECT characteristics showed a transconductance of 0.9 mS and a bandwidth approaching 5 kHz. All recordings were subject to a bandpass filter between 0.1 Hz and 200 Hz and a notch filter at 50 Hz. When measuring epileptiform activity in rats, the OECT recordings gave a SNR of 44 dB whereas the surface electrodes gave 24.2 dB. For neural activity providing large amplitudes between 7 – 11 Hz, the OECT provided a SNR of 52.7 dB and the surface electrode provided 30.2 dB. Although placed in

a different location, the penetrating probe provided 32 dB. In further comparisons, activity between 4 – 14 Hz gave an OECT SNR of 22.3 dB, surface electrode SNR of 13.5 dB and penetrating electrode SNR of 18.2 dB. It was claimed that this study demonstrated that OECTs could record more localised activity, which is particularly important in epilepsy measurements. The bandpass filter did not allow comparison of high-frequency activity, though it was noted that the recording of SUA could provide new neural information [14].

To resolve SUA from neural volumes, the OECT requires its transduction mechanism to volumetrically dope and de-dope the organic active layer such that changes in charge carrier density are greater than those generated by noise sources. Enhancement-mode OECTs with mobile ions embedded into the active layer, enabling μ s-scale response times, have been fabricated into linear arrays of 4 devices and placed into the intracortical layers of rats. Recordings between 250 – 2500 Hz revealed waveforms with features of cortical action potentials, supported by an analysis including the averaging of waveforms and autocorrelograms displaying refractory periods of neural firing rates. In addition to recording from deep within the cortex, the devices were also placed on the cortical surface. It was found that the devices could record high-quality LFP data including identifiable behavioural states such as activity associated with rapid eye movement. Device biocompatibility was supported by a lack of neuronal loss and tissue damage at the cortical surface. The capability of the OECT with its novel architecture and material characteristics was also shown in its application to the on-skin recordings of ECG and EMG signals. For ECG measurements, the OECT provided a SNR of 53.86 dB whereas the commercial ECG electrodes gave a SNR of 37 dB. Also, the SNR of the EMG measurements was 52.84 dB, showing validity to efficaciously record such signals [15].

In further investigations into the ECoG applications of OECTs, a 3×5 array of OECTs with a 1 mm spacing was fabricated into a probe with a thickness of 3 μ m. A focus of the investigation was to increase the transparency of the probe because the experimental method involved stimulating neurons with light. To achieve this, the Au interconnects were fabricated in a grid pattern with a 3 μ m linewidth. An additional notable aspect of the probe was its multiplexed interconnect structure. With $W = 70 \mu$ m, $L = 20 \mu$ m and $d = 150$ nm, the devices provided an average transconductance of 1.1 mS and response time of 340 μ s. However, the cut-off frequency of the device was 50 Hz, only permitting the recordings of low-frequency ECoG. In stimulating the cortical surface with light, the SNR measured by the OECT was 13 dB, which was sufficient for recording activity [117].

To demonstrate applicability to subcutaneous EMG, OECTs have been used to measure myoelectric potentials on the surface of light-stimulated muscles. The devices were integrated with OFETs into a 5×5 multiplexed array with a 1 mm-scale spacing. An individual cell consisting of an OECT and an OFET was used to measure the

ms-scale features of myoelectric potentials, provided by a kHz-scale bandwidth [207].

In addition to ECG measurements from the surface of the skin, OECTs have been used to measure the activity of cardiomyocyte cell cultures [166, 208, 209]. The activity of cardiomyocytes or other cultured cells that approximate cardiomyocyte behaviour, such as HL-1 cells, is recorded by culturing the cells onto the OECT channel and measuring the extracellular ionic fluxes generated by their action potentials. Although cardiomyocytes produce action potentials with greater amplitudes and slower temporal features relative to cortical neurons, the transduction mechanism is equivalent and thus the experimental method provides insight into the efficacy of OECTs for extracellular neural recordings. Interdigitated electrode OECTs and OECT arrays have been used to monitor action potentials and their propagation from cells resembling cardiomyocytes with SNRs up to 18. These devices have used active layers consisting of PEDOT:PSS with additives, and have successfully demonstrated the ability to measure potentials with 200 ms periods and equivalent gate voltage inputs of approximately 0.5 – 1 mV. The noise values quoted in the investigations gave equivalent gate voltage values of approximately 100 μ V [98, 153, 211, 212, 213].

2.5. Applications in Chemical Sensing

2.5.1 Functionalisation and Transduction Methods

The CSF and ISF in the brain contain ions including sodium, potassium, calcium, chloride, magnesium and bicarbonate. In addition, they also contain neurotransmitters, glucose and lactate [214]. The concentrations of these constituents represent biomarkers of physiological condition and thus monitoring their baseline levels and variations can aid in providing medical diagnostics. For example, patients who suffer from traumatic brain injury (TBI) potentially experience subsequent secondary injuries which are associated with poor patient outcomes. The spreading depolarisation occurs as a secondary injury in approximately 56% of TBI patients [215]. The high-amplitude, low-frequency electrical wave that self-propagates through neural tissue is associated with transient increases in extracellular potassium and lactate and a decrease in glucose, all with features on the 10 s-scale. Potassium concentration changes are on the mM-scale with 0.1 mM-scale features and lactate and glucose changes are on the 0.1 mM-scale with 0.01 mM-scale features [216]. Measuring such activities with microdialysis allows the location of the spreading depolarisation to be determined and thus identifies neural tissue at risk.

The concentrations of neurotransmitters found in CSF fluid can be analysed to aid in the identification of neurotransmitter disorders. For example, monoamine neurotransmitter disorders can affect motor function and can be treated given an

accurate diagnosis. More generally, neurological disorders have been associated with varying concentrations of biomolecules in the CSF [217]. The development of a platform for the analysis of neurofluids through the measurement of chemical concentrations, such as those of neurotransmitters, could aid in increasing the accuracy of medical diagnosis and thus the correct selection of treatment procedures, maximising patient outcomes and reducing the burden of neurological disorders.

The mechanism and performance of OEETs in chemical sensing is compared to that of electrodes [218, 219, 220]. To measure the concentration of chemical species in an electrolyte, electrodes are functionalised with coatings that selectively interact with those species. For example, glucose detection can be performed using electrodes coated with glucose oxidase. Interactions between glucose in a physiological fluid and glucose oxidase result in electron transfers which generate a current. To measure this current, a constant, non-equilibrium potential difference is applied between the electrode coated with glucose oxidase, more generally known as an indicator electrode for chemical measurements, and a reference electrode, which provides a stable reference potential. The Ag/AgCl electrode is commonly used as the reference electrode and is placed into an electrolyte saturated with chloride ions. The changes in current measured using this technique, known as amperometry, are proportional to the changes in concentration of the analyte. The equation describing the Faradaic current is the Butler-Volmer equation. Given that the solution is not stirred (no convection) and that charge transport is diffusion-limited, then the current for the oxidation reaction with chemical species A, $A_{Red} - ne^- \rightarrow A_{Ox}$, under the application of a voltage step can be described by the Cottrell equation:

$$I = \frac{nFSC_{A,Red}\sqrt{D_{A,Red}}}{\sqrt{\pi t}}, \quad (2.30)$$

where n is the number of electrons transferred in the oxidation reaction, F is the Faraday constant, S is the electrode surface area, $C_{A,Red}$ is the analyte concentration, $D_{A,Red}$ is the diffusion constant of species A and t is time [218, 221]. Therefore, the resulting electronic signal is used to describe chemical concentration.

When using potentiometry for measuring the concentrations of ionic species, an ion-selective electrode (ISE) can be used as the indicator electrode. An ISE contains a membrane that selectively transports the desired ion species. When the ISE is placed into an analyte, the membrane selectively transports the desired ions into the ISE until the system reaches equilibrium. The different ionic concentrations on either side of the membrane result in a potential difference, similar to the resting potential of a neuron, that is described by the Nernst equation. This potential difference at equilibrium is

measured between the ISE and the reference electrode and is given by

$$E = K + \frac{k_B T}{z_i e} \ln \left(\frac{a_i^{SOL}}{a_i^{ISE}} \right) , \quad (2.31)$$

where E is the measured potential difference, K is a summation of fixed voltages, k_B is the Boltzmann constant, T is temperature, z_i is the charge of ion i , e is the elementary charge, a_i^{SOL} is the activity of ion i in the solution and a_i^{ISE} is its activity in the ISE. The activity is the physically measurable quantity that represents concentration and accounts for the analyte's ionic strength and the ion's charge. The activity, a_i , is proportional to the concentration, C_i , through an activity coefficient, γ_i , and thus $a_i = \gamma_i C_i$. Values of γ can be calculated using the Debye-Hückel equation, and it tends to be the case that $\gamma < 1$ [222]. Therefore, measurements of the analyte tend to present lower ionic concentrations than they contain. For a singly charged ion such as potassium at 25°C, the logarithmic potential change measured per decade change in concentration is 59.2 mVdec⁻¹ (3 s.f.).

The OECT can be modified for the sensing of a desired chemical species given that changes in the electrolyte's concentration of that species result in a change in the doping level of the active layer. The traditional operation of an OECT is potentiometric, where the gate electrode and channel act as the two terminals [220]. In this operating regime, varying the gate-channel potential distribution modulates the number of ions that enter the active layer, varying the doping level, which is measurable through the drain current. Using the Ag/AgCl gate electrode, the change in ion concentration is compensated by faradaic redox reactions. The Ag/AgCl electrode provides a stable potential and acts as a pseudo-reference electrode, allowing the gate to impose a precise potential on the channel. To be analysed using the Nernst equation, the OECT must be in an equilibrium state (or steady-state) with zero gate current. By observing the change in drain current once the device reaches an approximate equilibrium, the transconductance can be used to determine the effective change in gate voltage. For a fixed V_{GS} and V_{DS} , changes in I_D can be observed for changes in the distribution of the potential across the gate-electrolyte, electrolyte and channel components, as shown in figure 2.17. For example, when a selective membrane is in the device structure, the gate-channel potential distribution varies with the concentration of that selected species [146]. This mediation in the flow of ionic species into the active layer, and thus the variation of the doping level, has been shown to provide an approximately Nernstian response in the drain current for a range of biosensors [223, 224, 225, 226]. In addition to using a selective membrane layer, immobilised layers that bind to the chemical species of interest can also be used [133, 227]. These layers can be placed on a polarisable gate electrode and are suggested to vary the fractional drop in gate-channel potential at the gate-electrolyte interface when a binding event occurs [228, 229]. The gate and channel functionalisations are illustrated in figure 2.18 in an OECT voltage amplifier circuit.

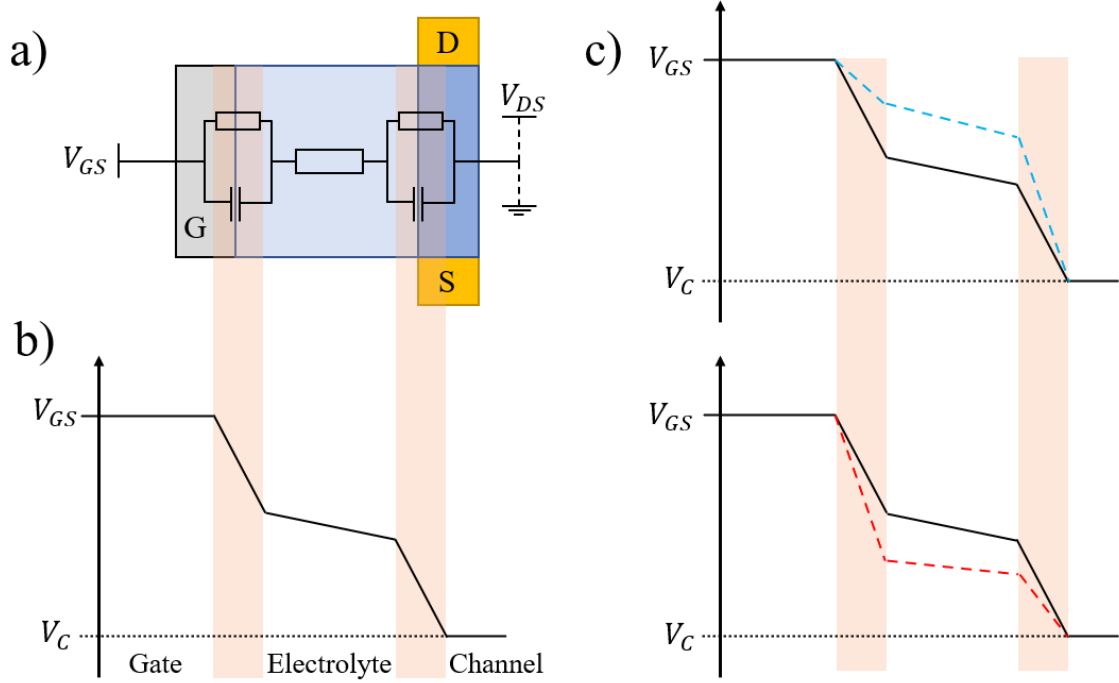


Figure 2.17: a) Circuit representation of the ionic circuit with an OEET. b) Distribution of potential difference in the ionic circuit from the gate electrode with potential V_{GS} to the channel with potential V_C where $0 \geq V_C \geq V_{DS}$. c) Change in potential difference distribution from interactions between chemical species and functionalised layers at the gate or channel.

Investigations have shown that the OEET provides a current representation of the expected potentiometric response which is amplified through the high transconductance properties afforded by the volumetric doping mechanism. This has allowed the development of compact amplifying biosensors which have shown the capability to transduce a wide range of chemical species relevant to physiological conditions. For transistors that provide such a current transduction mechanism to the analyte concentration, a resistor can be placed in series with the device and an output voltage across the resistor can be measured. By choosing a sufficient resistance, the output voltage relative to the change in potential difference distribution of the transistor from analyte detection can be amplified significantly. As a result, the change in the output voltage of the transistor circuit from a change in analyte concentration can be greater than the change in potential difference measured by a homologous potentiometric system that uses electrodes and exhibits a Nernstian response [218]. Therefore, the circuit given in figure 2.18 can provide super-Nernstian outputs.

The OEET can be employed as an amperometric sensor by applying voltages that place the system out of equilibrium and observing the resulting device current. The

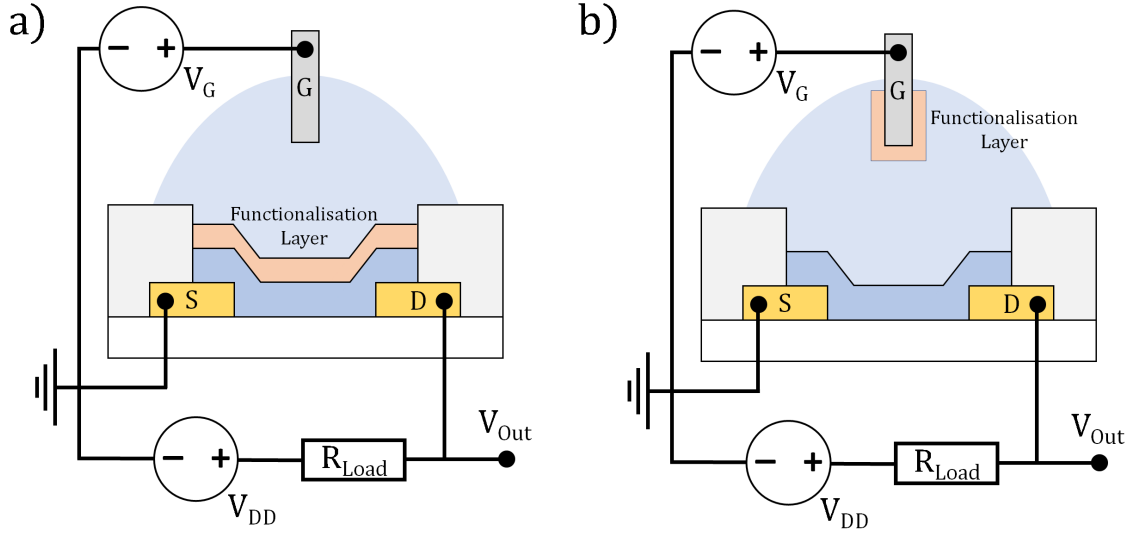


Figure 2.18: An OEET in a voltage amplifier circuit using supply voltage V_{DD} , load resistance R_{Load} and an output voltage V_{Out} with functionalised layers placed on the a) the active layer, b) the gate electrode.

non-polarisable gate electrode and channel again act as the two electrodes. Upon the application of a non-zero gate-channel potential, the gate current, I_G , peaks before decreasing in magnitude with time, t , such that $I_G \propto 1/\sqrt{t}$, similarly to that predicted by equation 2.30 [220]. This gate leakage current is the faradaic current considered in chronoamperometry, and for OEETs the measured change in drain current that is typically used as the device output is dependent on the flow of I_G . However, to maintain charge neutrality, the change in drain current as a fraction of change in gate current is approximately unity [230]. Indeed, it has been found that when utilising the traditional OEET configuration for amperometry and varying the electrolyte concentration, the fractional change in current output, determined by $(|I - I_0|/I_0)$ for current I with baseline I_0 , is greater for the gate current than it is for the drain current, whereas the absolute change in drain current is greater than that for gate current. As such, it is not clearly demonstrated that the amplification properties promoted in OEETs contribute to device performance in such a configuration. To overcome this apparent limitation, current amplifying topologies have been suggested which could provide amplification factors of the amperometric response up to 10^2 [218]. A further topology has leveraged the OEET transconductance in amperometry and has achieved current gains up to 10^3 [230].

For the continuous sampling of neurofluids for physiological monitoring, a microfluidic system can be employed to extract and transport the fluid to the biosensor and provide sufficient time for the device to optimally respond to the chosen chemical species.

Although such methods provide high selectivity, the collection process of neurofluids results in a reduction of spatiotemporal resolution. These methods are required when the functionalisation material is not biocompatible, such as when using valinomycin as a potassium membrane [231]. On the other hand, microfabricated OECTs with more biocompatible functionalisation placed within intracortical regions have provided resolutions sufficient to record neurotransmitter release on the millisecond timescale [118]. This shows the capability of OECTs to be implanted into the brain for the measurement of chemical concentrations at high spatiotemporal resolutions.

2.5.2 Devices with Active Layer Functionalisation

Methods for active layer functionalisation primarily concern the mediation of ionic flow into the active layer. This can be achieved by covering the active layer with an ion-selective membrane, typically constituted by a polyvinyl chloride (PVC) matrix containing ionophores. Interactions with target ions are selective and reversible and incorporate ionic sites that promote the exchange of the desired ions and prevent counter ions from entering [232]. Therefore, the membrane acts to mediate ionic flow between the gate and the channel. This has resulted in a logarithmic dependence between the OECT response and the chemical concentration, attributed to the Nernstian equation describing the phase boundary potential at the interface between the membrane and the analyte. The logarithmic behaviour has been identified in both the absolute values of the drain current and the shift in the gate voltage dependence of the transfer curve resulting in an effective gate voltage [226]. The structure of devices with ion-selective membranes involves placing an ionically conducting layer between the channel and the membrane with the analyte situated between the membrane and the gate electrode [224].

It is first observed that the drain current changes with electrolyte concentration when no membrane is present. The electrolyte conductivity increases with its ionic concentration, and thus differences in device response can be attributed to varying the potential difference across the resistor representing the electrolyte in figure 2.17 [233]. This highlights the importance of control experiments in which the concentrations of interferent species are varied when employing a membrane for concentration measurements of a desired species. For PEDOT:PSS OECTs it was found that increasing electrolyte concentration decreased the magnitude of the drain current, which was attributed to an increased effective gate voltage. The shifts in gate voltage followed a near-Nernstian relationship with electrolyte concentration [223]. Without a membrane, however, it would be difficult to determine the concentration of a desired species with interferents present. For membrane-free, selective sensing of ions in mixtures, OECTs have been implemented with impedance analysis. The gate voltage shifts gave information on the electrolyte concentration and the impedance

analysis provided further insight into cation type through measuring diffusion properties [234]. The OECTs with no membranes have provided limits of detection approaching 1 mM; however, lower limits have been reached using ion-selective membranes.

Primary cations in the CSF include potassium and sodium, and performance tables often compare the sensitivity and limit-of-detection for different biosensor technologies on measuring such cation concentrations [235]. For OECTs where an electrolyte has separated the membrane from the channel, potassium concentrations have been measured using membranes with potassium ionophores and control experiments have shown selectivity of potassium over interferents such as sodium. Therefore, for mixed electrolytes, such investigations have shown the capability of OECTs to transduce the concentration of the desired cation type [224]. This architecture has been implemented in OECT circuits, achieving super-Nernstian voltage shifts on the $100 - 1000 \text{ mVdec}^{-1}$ -scale for potassium sensing and a limit-of-detection on the $10 \text{ }\mu\text{M}$ -scale [164, 235].

Devices have been fabricated where a spin coatable polyelectrolyte film has separated the membrane and the channel, facilitating the miniaturisation and thus the portability of the devices. The polyelectrolyte films are constituted by charged polymer chains and mobile counter ions. The film that interfaced with the PEDOT:PSS channel was poly(sodium 4-styrenesulfonate) (PSSNa), where the PEDOT:PSS was de-doped by mobile sodium cations in the PSSNa. The proposed mechanism was that the membrane potential at the analyte-membrane interface induced a potential at the membrane-PSSNa interface, providing a gate for the PEDOT:PSS channel through the PSSNa electrolyte. Therefore, increasing the concentration of cations in the analyte transported the sodium cations from the PSSNa into the channel. This was interpreted as a gate voltage shift with a Nernstian relationship. The device has been implemented with both a sodium membrane and a potassium membrane, achieving a limit of detection on the $10 \text{ }\mu\text{M}$ -scale in each case. Furthermore, the devices had current sensitivities on the $100 \text{ }\mu\text{A}$ -scale, demonstrated capability to provide real-time monitoring and showed characterisation repeatability [226, 236].

The active layer has been functionalised with groups that bind to a desired species. Glutamate and acetylcholine have been detected using OECTs constructed using PEDOT:PSS embedded with platinum nanoparticles. The devices were functionalised with enzymes that bind to the neurotransmitters and facilitate electron transfer events. The limits of detection were $5 \text{ }\mu\text{M}$ for both neurotransmitters, sufficient for glutamate detection in extracellular fluid [237]. In a further application to neurotechnology, an accumulation-mode OECT with a membrane that binds to amyloid- β ($A\beta$) aggregates, the protein whose accumulation is linked with Alzheimer's disease, has shown the detection of the aggregates through modulating vertical ionic flow. Using a microfluidic system, $A\beta$ could be detected from the fm-scale to the nm-scale using a $1 \text{ }\mu\text{L}$ sample of

human serum. The $A\beta$ on the membrane hindered ionic transport and increased the system's impedance. The devices demonstrated a superior performance relative to other electrochemical sensors. This was afforded by the local amplification of the OECT, which provided higher SNR values and thus higher sensitivities and limits of detection [16].

2.5.3 Devices with Gate Electrode Functionalisation

Gate electrode functionalisation involves immobilising functional groups that bind to a desired species in an electrolyte. In proof-of-concept investigations, a planar gate electrode is not required and thus gate electrode functionalisation can be performed more flexibly. In particular, the active layer does not require additional treatment and so there is no potential detriment to the organic layer's performance [238].

The binding event of the desired species results in an electron transfer event, and logarithmic behaviour has been observed in the OECT by considering gate voltage shifts in the transfer curve. The shifts are considered to be a result of a varied gate-channel potential distribution where the changes are described by the Nernst equation, which is dependent on the logarithm of the fraction of oxidised to reduced molecules. As an example, glucose concentration can be transduced using glucose oxidase immobilised on a Pt gate electrode. With the addition of glucose to the electrolyte, the reaction with the oxidase transfers an electron to the gate electrode, decreasing the fraction of gate-channel potential across the gate-electrolyte interface and thus increasing the fraction across the electrolyte-channel interface, decreasing the magnitude of the drain current. Measuring the drain current once the system has reached an equilibrium with a new effective gate voltage has defined the devices as potentiometric transducers [218, 239]. In the case where an Ag/AgCl gate electrode has been used for the transduction of the H_2O_2 concentration, a linear relationship has been observed in the drain current with sub-unity current gains relative to measured changes in gate current [230].

Investigations have involved the functionalisation of the gate electrode to transduce the presence of neurologically relevant chemical species with high sensitivities and low limits of detection. For example, correlations have been suggested between excessive cholesterol levels in the brain and the risk of Alzheimer's disease [240]. Cholesterol concentrations have been measured alongside glucose and lactate levels by functionalising the gate electrode with the related oxidase [239, 241, 242, 243, 244]. A variety of immobilisation methods have been considered, and the biocompatibility of directly interfacing such devices with cells has been investigated [245]. Limits of quantification for glucose, lactate and cholesterol have been measured at 10 μ M, 50 μ M and 10 μ M, respectively. A logarithmic dependence on concentration was found up to the mM-scale and could thus detect physiologically relevant changes in concentrations, and devices responded on the 10 s-scale [243].

Neurotransmitter concentration has also been transduced using interactions at the gate electrode of OECTs [246]. One such neurotransmitter is dopamine, which plays a critical role in a wide range of functions, particularly in cognition [247, 248]. Using needle-type OECTs, dopamine concentration was transduced with at two regions of linear device response. The lower concentration range was between 1 – 160 pM and the higher was from 2 – 700 nM; however, this initial performance was not recoverable, and the gate electrode was not functionalised towards dopamine and thus would not show specificity [249]. In a further investigation, OECTs were implemented *in vivo* to measure the release of neurotransmitters that include dopamine, noradrenaline and adrenaline. The PEDOT:PSS OECTs used a Pt gate electrode and devices were intracortically implanted. It was claimed that the concentration of neurotransmitters was transduced through their oxidation at the gate, decreasing the fraction of potential difference across the gate-electrolyte interface and thus decreasing the drain current magnitude. When characterising the device in artificial CSF with interferents, the OECT was shown to respond to changes in catecholamine neurotransmitter concentration at 30 nM. It was further claimed that the device configuration could differentiate the electrical activity from the neurotransmitter release. The devices showed a log-linear relationship between the effective gate voltage and neurotransmitter concentration up to the 0.1 mM-scale and provided real-time, multichannel monitoring of neurotransmitter release [118].

2.6. Applications in Amplifier Circuits for Biosensing

2.6.1 Bioelectronic Circuits

The OECT has transduced a wide range of physiological signals with high efficacy. The inherent and significant amplification offered by the volumetric de-doping of the organic mixed ionic and electronic conductor provides an opportunity for on-site processing, reducing the noise introduced by the otherwise required back-end electronics. Such on-site processing further allows the development of closed-loop systems, which can provide instantaneous intervention in neural regions from the detection of abnormal signals [250, 251]. OECTs can be used as the transducer of a desired physiological signal or can be used in on-site bioelectronic circuitry, supported by their biocompatible nature, to provide signal processing. Their capabilities for on-site processing are demonstrated by their implementation in a range of increasingly complex bioelectronic circuits.

A circuit topology for potential use in on-site signal processing that exemplifies the developments in bioelectronics is the neuromorphic circuit. Neuromorphic circuits are hardware systems that replicate neural network architectures to provide a platform for learning desired behaviours and performing pattern recognition. To relate the dynamics

of OECTs with those of neurons, the gate voltage provides the presynaptic stimulus, the electrolyte acts as the synaptic cleft, the resulting changes in channel current are considered as the postsynaptic activity and the active layer conductance represents the synaptic weight. Under such relationships, neuronal dynamics have been reproduced in OECTs. For short-term plasticity, these include paired-pulse depression, adaptation and dynamic filtering [147, 252, 253]. By utilising non-volatile active layer materials, properties of long-term plasticity have also been observed such as long-term potentiation and depression [254, 255]. The interconnection of OECTs into low-power synaptic circuits has also been demonstrated with the emulation of Pavlovian learning and the mapping of logic functions [255, 256, 257].

For applications where the device is utilised as the transducer of activity by facilitating local amplification through the transconductance, circuits have been considered where the resulting drain current is converted to an output voltage through a resistor connected in series. In such cases, the requirements of the OECT include biocompatibility for the desired duration of recording, sufficient bandwidth to resolve the frequencies of interest and a noise level below the amplitude of the signal to investigate. For applications where the device is used in integrated circuits local to physiological environments, the OECT is additionally required to be independently gated. Its traditional structure includes a liquid electrolyte, which enables a shared gating structure [147]. However, these architectures don't lend to the fabrication of micro-scale devices that require independent gating. Therefore, novel materials have been developed which permit such individual gating in OECTs, providing building blocks for bioelectronic circuits [125].

2.6.2 Amplifier Circuits for Electrophysiology

The use of an OECT as the primary physiological transducer with a resistor connected in series, R_{Load} , for conversion of the drain current to an output voltage has been considered for applications in electrophysiology. The technique provides a gain that is proportional to $g_m R_{Load}$ when operating the OECT in the saturation regime. The gain can be used for signal amplification at the point of transduction, alleviating the introduction of noise from intermediary wiring [258]. The conversion of drain current to an output voltage increases the compatibility of OECT technology with existing electrophysiological voltage recording equipment. A further examination of the voltage amplifier circuit provided a voltage gain of 30 when operating the OECT in the saturation regime. The circuit was used for the amplification of ECG signals, where the gate electrode was connected to the skin and the OECT was amplifying external to the body. It was claimed that the resistor value did not affect SNR [53]. The voltage amplifier circuit has also been used for the recording of EEG signals and has acquired clear neural signals in the EEG frequency bands [125].

Depletion mode OECTs operate in an on-state with a supply voltage, and the transduction of electrophysiological signals involves introducing a gate voltage to reduce the conductivity of the active layer. The devices maximise their power usage in their on-state and are typically operated in the saturation regime about their point of maximum transconductance. When operating at this point, electrophysiological signals do not have sufficient voltage amplitudes to completely de-dope the device, and thus the devices can operate at high currents for extended durations. Although the devices operate at low voltages, high-performance devices have large currents that facilitate large transconductance values for amplification. Therefore, power consumption can still be considerable. This can be dissipated as heat, which can affect surrounding tissue for implanted devices. It has thus been suggested to instead operate the device in the subthreshold regime where the device transitions from its off-state to its on-state and thus where the drain currents are significantly lower. With such smaller currents, the gain is reduced; however, the transconductance efficiency, defined as g_m/I_D , is greater because the drain current varies exponentially with gate voltage, resulting in an increased power efficiency. For PEDOT:PSS, the subthreshold regime occurs at large gate voltages that equate to gate-drain potentials approaching the hydrolysis limit. As such, OECTs have been developed with organic materials that provide enhancement-mode behaviour, which is more suitable for biasing at the subthreshold region. In comparing the performance of an enhancement-mode OECT in the voltage amplifier circuit operating in the subthreshold regime with the same device in the super-threshold regime, it was found that the subthreshold regime provided a lower power operation by a factor of approximately 370 with a consumption of 20 μ W. The subthreshold voltage amplifier was configured to supply a gain of 30 and was used to record EEG signals, providing output voltage amplitudes up to 2 mV at frequencies around 10 Hz. The electrophysiological capabilities were further validated with ECG measurements, which provided the expected waveforms with the amplifier [210]. This research shows that operating an OECT in the subthreshold regime can reduce power consumption significantly. However, with exponential relationships between drain current and gate voltage, the linearity of the input voltage is lost in the output voltage.

The voltage amplifier circuit has been employed for the measurement of neural action potentials using enhancement-mode OECTs. An enhancement-mode OECT was then placed in series with a depletion mode OECT to form a non-linear rectifier circuit, which is a system that suppresses non-target signals. The OECT-based rectifier circuit was used to accurately detect epileptic activity in the hippocampus of a freely moving rat, demonstrating the capability of OECTs to be utilised in integrated circuits local to physiological environments [15].

An amplifier circuit has been fabricated by placing a p-type OECT and an n-type OECT in series, forming a complementary inverter. An inverter is a logic gate that inverts the amplitude of the input signal and provides a high signal gain in the transition of amplitude inversion. OECTs were fabricated in a vertical structure with an ambipolar organic active layer, providing p-type or n-type behaviour depending on applied biases. Implementing such an architecture allowed the amplifier circuit to utilise the same area as a micron-scale planar OECT. The high gain in the transition region was utilised for the amplification of ECG input voltages. The complementary inverter amplifier supplied a gain of 28 and provided the expected ECG features with a low-power consumption of 57.7 nW [259].

2.6.3 Amplifier Circuits for Chemical Sensing

Amplifier circuits can be implemented to enhance the capability of an OECT to transduce the presence of a desired chemical species and its changes in concentration. Similar to the voltage amplifier circuit used for electrophysiological signals, a load resistor can be placed in series with the OECT to provide super-Nernstian voltage changes from variations in electrolyte concentration, as shown in figure 2.18. However, further circuit topologies have been investigated which amplify the ionic to electronic transduction. One such topology is the differential amplifier, which can be considered as two voltage amplifier circuits connected in parallel [162]. The output voltage is defined as the difference between the output voltages of the two voltage amplifiers. Given that one OECT is used as a known reference, then the circuit only provides a non-zero output voltage in response to a desired physiological interaction. The background subtraction provides increased sensitivity to the desired chemical species as it acts to remove the common noise between the OECTs. Differential amplifiers have been applied to transduce ionic concentration, pH level and lactate concentration [72, 162, 260].

A further circuit architecture used for chemical sensing has involved placing the OECT in series with a current source, providing a topology that resembles an inverter. An output voltage is measured between the OECT drain electrode and the current source, which varies between a supply voltage $+V_{DD}$ applied at the OECT source and $-V_{DD}$ applied after the current source. A switching voltage was defined as the input voltage required to transition the regime of OECT operation from linear to saturation regime and thus switch the output voltage from $+V_{DD}$ to $-V_{DD}$. It was observed that the switching voltage was sensitive to the electrolyte concentration. A potassium-selective membrane was implemented and the switching voltage was measured for changes in concentration. Using a supply voltage of 0.4 V, an average super-Nernstian sensitivity of 414 mV dec⁻¹ was measured. Further investigations confirmed the selectivity of potassium over the sodium interferent [164].

The sub-unity current gains in drain current relative to the gate current in amperometric applications of OECTs for chemical sensing suggests that the advantageous amplification afforded by volumetric transconductance is not fully leveraged. As such, an architecture has been suggested that initially converts the faradaic redox current into a potential difference at a separate location from the OECT by using an electrode coated with a redox-active organic layer. The change in potential in this electrochemical cell is then transferred to an Ag/AgCl gate of the separated OECT in its traditional architecture, resulting in drain current changes given the overlap of the potential changes of the electrochemical cell with the voltage regimes that de-dope the OECT. Therefore, the faradaic current in the electrochemical cell is converted into the OECT drain current. The resulting circuit provided a current gain on the order of 10^3 . Glucose, lactose and ethanol concentration measurements showed that the potential changes of the electrochemical cell could reduce the OECT drain current by a factor of 10^4 , equivalent to a large dynamic range of 40 dB. The current amplifier circuit showed superior performance in current modulations relative to OECTs in their traditional architecture. However, the response time of the amplifier circuit was comparatively slower [230].

3. DEVICE FABRICATION

3.1. Preparation of Materials

Substrate Preparation

Devices were fabricated with one of two different flexible plastics as the substrate material. The plastic most commonly used for the device's foundation was PET, chosen for its ability to support PEDOT:PSS without delamination in an aqueous solution [48]. The PET used in this research was Melinex[®] ST506 from DuPont Teijin Films with a thickness of 125 μm . Alternatively, polyimide was used as the substrate, supplied as Kapton HN Thermal Insulating Film from DuPont with a thickness of 50 μm .

Device fabrication was carried out in a cleanroom environment where there were fewer than 1000 particles with a size less than 0.5 μm per cubic foot. The substrates were prepared for fabrication with their immersion and sonication in acetone and isopropanol. Sonication in acetone was performed in an ultrasonic bath to remove organic matter from the substrate's surface. Further sonication in isopropanol acted to remove residues from the substrate. Substrates were sonicated in each solvent for 10 minutes. Finally, the substrates were subject to an oxygen plasma asher. The treatment removed any final organic residues from the substrates and facilitated film deposition. For PET substrates, setting the treatment power to 100 W caused overheating, resulting in substrate deformations. Therefore, the power for substrate cleaning was set to 60 W with a treatment time of 3 minutes. The sonicator and plasma asher used in this research are shown in figure 3.1.

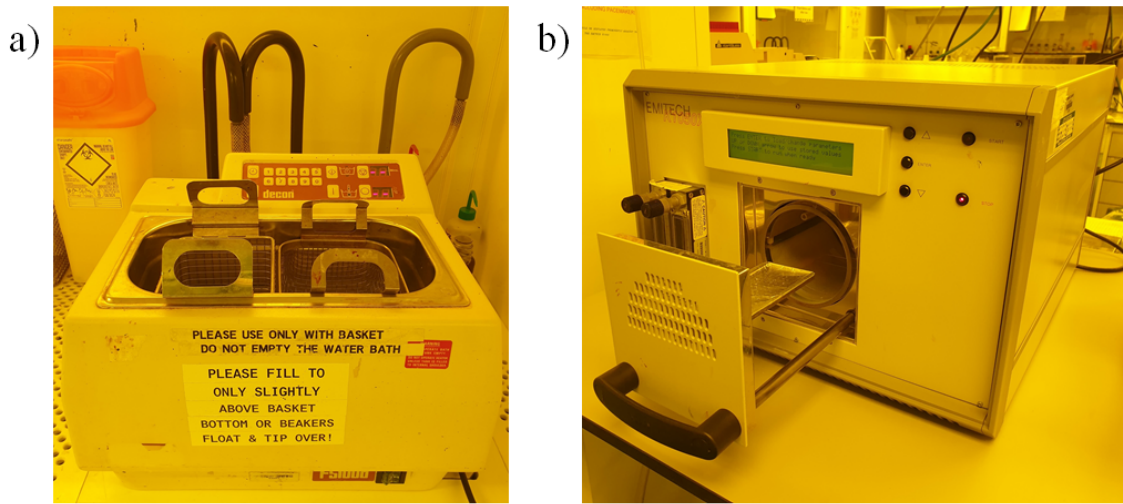


Figure 3.1: a) *Ultrasonic bath, Decon.* b) *Oxygen plasma asher, Emitech K1050X.*

Active Layer Preparation

In all devices fabricated in this research, PEDOT:PSS was the primary constituent of the active layer, chosen for its high-performance properties and proven capability to transduce physiological signals. The type of PEDOT:PSS used in this research was Heraeus CleviosTM PH1000 PEDOT:PSS, providing a PEDOT to PSS ratio of 1:2.5 by weight [261]. Additives were used to enhance desirable properties of the PEDOT:PSS. Where investigations utilised the crosslinker (3-glycidyloxypropyl)trimethoxysilane (GOPS), a 1% v/v was included [47]. This volume concentration was chosen as it has been used extensively through literature [14, 65, 262]. To facilitate film processing and enhance conductivity, dodecylbenzene sulfonic acid (DBSA) was included as an additive. To avoid phase separation effects at 0.5% v/v, the concentration was kept to 0.3% v/v [50]. The final 7% v/v with GOPS or 8% v/v without GOPS was constituted of ethylene glycol (EG), utilised to maximise the conductivity of the PEDOT:PSS. The solution comprising of PEDOT:PSS, EG, DBSA and GOPS was denoted PEDG, and was denoted PED without GOPS. To prepare the PED solution, the PEDOT:PSS, EG and DBSA were sonicated together for 20 minutes. Sonication was used to maximise the uniformity of the solution. When making PEDG, the GOPS was then added to the solution and sonicated for a further 5 minutes.

3.2. Electrode Patterning

With the substrates cleaned using solvent sonication and treatment from the oxygen plasma asher, the Cr and Au layers which defined the electrode layer were evaporated. The evaporators used in this research are shown in figure 3.2. The Cr, which acts as an adhesion layer between the substrate and the Au layer, was first evaporated to a thickness of up to 15 nm. The Au layer was then evaporated with a thickness of up to 300 nm. With the metallic layers evaporated, the devices were again cleaned with sonication in acetone and isopropanol and with treatment from the oxygen plasma asher.

Photolithography with subsequent etching was used to pattern the electrodes from the evaporated Cr and Au layers. A positive photoresist was used for all electrode patterning and thus areas exposed to the UV light were removed in the subsequent development. A range of photoresists in the MICROPOSITTM S1800 series were used for electrode patterning, with S1805 resist predominantly used. Using the spin coater shown in figure 3.3a, each photoresist was initially spin coated at 2000 rpm for 30 s and then soft baked on a hotplate at 115°C for 30 s. The photoresist was then exposed to 365 nm UV light through the mask aligner shown in figure 3.3b, which emitted an irradiance of 16.3 mWcm⁻². Intimate contact between the photomask and the substrate was ensured. For the S1805, the exposure time was 8 s. The exposure time for the S1813 was 15 s and the S1818 required a time of 20 s,

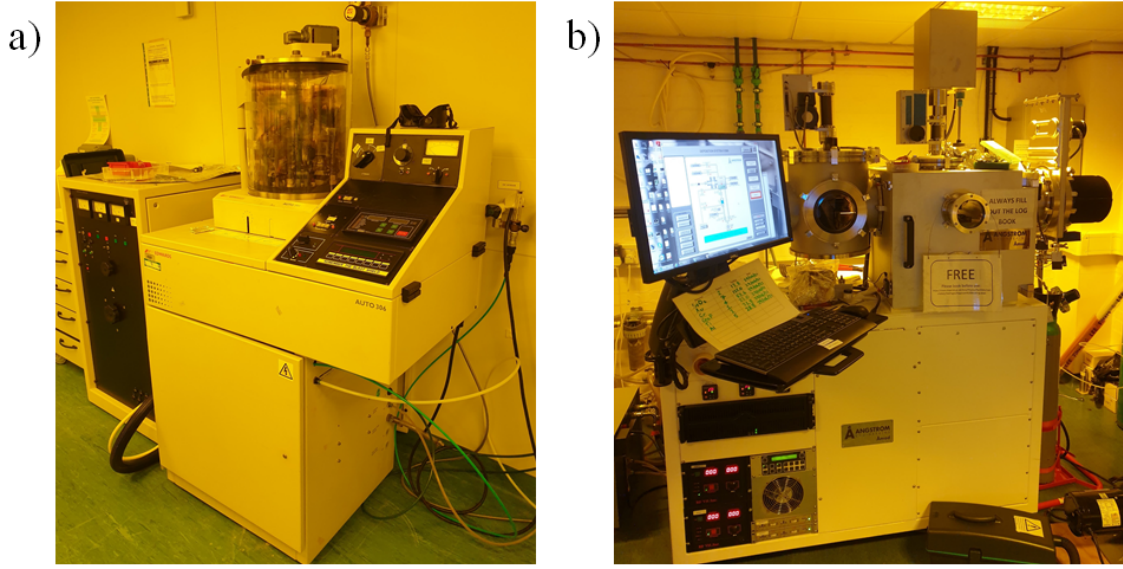


Figure 3.2: a) Thermal evaporator, BOC Edwards Auto 306. b) Thermal evaporator, Angstrom Engineering Amod System.

which was expected as thicker photoresists required longer exposure times. To develop the photoresist, the substrates were then immersed with light agitation in the MICROPOSIT MF-26A developer or the MICROPOSIT MF-319 developer. Both developers were found to facilitate the definition of patterns with equal quality. The S1805 required a development time of 5 – 10 s, the S1813 needed up to 30 s and the S1818 took up to 45 s. The photoresist was considered as sufficiently developed when no resist residue from the exposed areas could be visually identified. The substrates were then immersed in de-ionised (DI) water and isopropanol to remove photoresist and developer residues. The substrates were then blow-dried using a nitrogen gun. The quality of the patterning was then observed through an optical microscope. It was found that this methodology provided photoresist patterns with feature sizes down to 2 μm .

With the photoresist patterned into the desired electrode architecture, the unprotected metallic layers were etched. The substrates were first immersed with light agitation in the Au etchant. Immersion with the agitation was continued until the Au layer was visibly removed. The substrates were then immersed and agitated in DI water to remove etchant residue and dried using a nitrogen gun. A longer etching time was required with a thicker Au layer, and it was found that longer etching times resulted in over-etching of the smallest features. The smallest electrode features were present at the OECT channels and over-etching was found to increase the variability of the electrode geometry in those areas, contributing to deviations in expected device operation and thus

in the OECT characteristics. On the other hand, under-etching could result in thin metallic layers electrically connecting the source and drain electrodes, restricting the off-current and introducing an additional parasitic capacitance. With the Au layer etched, the substrates were then immersed into the Cr etchant. As the Cr layer was thin, the etching time was fast and took up to 5 s with light agitation. The substrates were then similarly cleaned in DI water and dried. To strip the photoresist that was protecting the desired electrode architecture, the substrate was immersed in acetone for 10 minutes and lightly agitated. To ensure the photoresist was removed, the substrates were subject to oxygen plasma ashing treatment at 60 W for 3 minutes. This also cleaned and prepared the substrate for the subsequent encapsulation patterning.

The research further investigated the ability to pattern Cr/Au electrode layers on a layer of the SU-8 negative photoresist. In such cases, SU-8 2002 was spin coated on cleaned PET substrates at 12000 rpm for 30 s. The substrates were then soft baked at 100°C for 75 s and the substrate surface was then completely exposed to UV light in a flood exposure for 15s. The post-exposure bake was a hard bake at 170°C for 1 hour. The substrates were then subject to the oxygen plasma asher at 60 W for 3 minutes. The metallic layers were then evaporated and patterned as previously described. It was found that the exposure step was imperative to the relative success of the method. Otherwise, photoresist stripping would result in a delamination of the electrodes. It was found that the success of the electrode patterning decreased as the feature size decreased and thus its reliability decreased for μm -scale features. This implied that there was a weak adherence between the electrodes and the SU-8. Also, non-uniformities in the SU-8 layers were visible in the electrode pattern.

3.3. Encapsulation Patterning

With clean substrates patterned with Cr/Au electrodes, the encapsulation layer was patterned. The encapsulation layer was itself made of the SU-8 photoresist such that the development of the layer resulted in the desired architecture. Therefore, the properties of the SU-8 provided facile processing. Such advantages in processing and its biocompatible properties motivated its choice for the encapsulation layer in this research [113].

With the substrates recently subject to treatment from the oxygen plasma asher, the SU-8 was spin coated. There were three SU-8 formulations from the SU-8 2000 series used in this research. In the first formulation, SU-8 2005 constituted 44% v/v and SU-8 2000 comprised the remaining 56% v/v. Spin coating this formulation at 1000 rpm for 30 s provided an encapsulation thickness of 1 μm . It was found that spin coating SU-8 2002 at 12000 rpm for 30 s would also produce a layer with a thickness of approximately 1 μm . Finally, SU-8 2002 was also spin coated at 2000 rpm for 30 s to produce a thickness of approximately 2.4 μm .

For the formulation containing SU-8 2005 and SU-8 2000, the pre-exposure soft bake was at 90°C for 75 s. The layer was then exposed for 10 s and the post-exposure soft bake was at 110°C for 4 minutes. The SU-8 was developed through depositing the propylene glycol monomethyl ether acetate (PGMEA) developer, sourced from Sigma-Aldrich[®], through a dynamic spin coating cycle consisting of two cycles. The first stage had a spin speed of 500 rpm and a duration of 5 s, and the second stage had a speed of 7000 rpm and a speed of 3 s. The developer was deposited during the first spin coating stage and was distributed across the given substrate, removing areas that were not exposed during development. The second stage then removed the developer, and the given substrate was subsequently dried with the nitrogen gun. The quality of the development was then observed through an optical microscope, and the development process was repeated when the layer was visibly underdeveloped. The encapsulation layer was then hard baked at 120°C for 20 minutes.

For the SU-8 2002 spin coated to produce a 1 μm layer, the pre-exposure soft bake was at 100°C for 75 s, the exposure time was 12 s and the post-exposure soft bake was at 120°C for 5 minutes. The development step was the same as that used for the formulation containing SU-8 2005 and SU-8 2000. The final hard bake was at 150°C for 20 minutes. For the 2.4 μm layer, the pre-exposure soft bake was at 100°C for 2 minutes, the exposure time was 30 s and the post-exposure bake was also at 120°C for 5 minutes. To develop the thicker SU-8 layer, the given substrate was immersed with light agitation in PGMEA for up to 10 s. The developer was then removed through substrate immersion in DI water and drying using the nitrogen gun. The final hard bake was at 150°C for 20 minutes.

All SU-8 photolithography methods were found to produce feature sizes as low as 2 μm . In sub-optimal methods, it was observed that insufficient post-exposure baking caused the entire SU-8 layer to be completely removed in the development step. Furthermore, the substrate was found to occasionally adhere to the photomask during the exposure step, increasing the difficulty of alignment. This was alleviated by providing the substrates with time to cool between the pre-exposure bake and the exposure step. When the SU-8 was over-developed, small cracks were found throughout the layer.

3.4. Active Layer Patterning

With the electrode and encapsulation layers patterned, the substrates were treated with the oxygen plasma asher at 60 W for 3 minutes to facilitate the layering of the materials used to pattern the organic active layer. The organic layer was patterned through photolithography; however, conventional solvents used in the method can deteriorate the organic materials used in OECTs [263]. Therefore, in this research, solvents compatible with PEDOT:PSS were used. The materials were the OSCoR 4001 negative photoresist, developer 103a and stripper 900, produced by Orthogonal Inc..

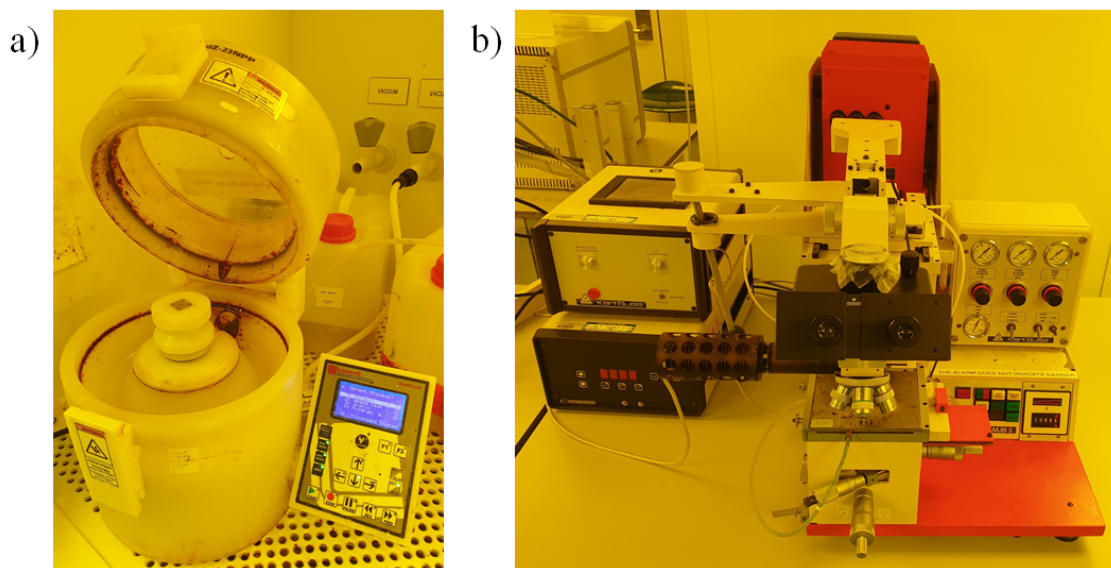


Figure 3.3: a) *Spin coater, Laurell Technologies Corporation.* b) *Mask aligner, Süss MicroTec MJB-3.*

Both etching and lift-off methods were investigated for the active layer patterning. When patterning PED, it was found that the organic layer could be etched using the oxygen plasma asher. Therefore, an etching photolithography method was used for patterning PED. On the other hand, it was found that the etching process was much less effective when patterning PEDG. Therefore, a lift-off method was developed in which the undesired regions of PEDG were removed in the stripping process.

In the etching process, the PEDOT:PSS formulation was first spin coated. To produce a 70 nm thickness, the formulation was spun at 3000 rpm for 30 s, and to produce a 35 nm layer the spin speed was increased to 12000 rpm. The organic layer was then soft baked at 100°C for 10 s. The photoresist was then spin coated at 3000 rpm for 30 s and pre-exposure soft baked at 100°C for 2 minutes. The photoresist was then exposed to UV light for 6 s and post-exposure baked at 100°C for 2 minutes. To develop the photoresist, two methods were used. In the first method, the developer was deposited onto the photoresist and was left for 45 s. The substrate was then spun at 5000 rpm for 5 s and then dried using a nitrogen gun to remove the photoresist. The quality of the patterning was observed through an optical microscope and this development process was repeated until the desired patterning was achieved. The process was typically repeated only once more until a sufficient patterning was observed. Alternatively, the substrate was immersed in the developer for up to 4 minutes, with patterning quality observed every 1 minute. It was found that sonicating the substrates whilst immersed in the developer provided sharp

edges in the intended pattern. With the photoresist covering only the areas where the PEDOT:PSS formulation was desired, the substrates were treated with the oxygen plasma asher at 70 W until there was no measurable conductivity between areas of the substrate which were considered undesirable to be electrically connected. To remove the photoresist, the substrates were immersed in the stripper and sonicated for up to 5 minutes, with observations through the optical microscope performed every 1 minute.

In the lift-off process, the photoresist was first spin coated at 3000 rpm for 30 s and pre-exposure baked at 100°C for 2 minutes. The photoresist was then exposed for 6 s and post-exposure baked at 100°C for 2 minutes. It was found that the method of developer immersion with sonication was most effective for the development step in the lift-off process. Of the two methods, the sonication provided a greater development force, implying that the photoresist adhered greater to an underlying SU-8 encapsulation layer than an underlying PEDOT:PSS layer. The PEDOT:PSS formulation was then spin coated to produce the desired thickness and was soft baked at 100°C for 10 s. The substrates were then immersed in the stripper solvent and sonicated for up to 45 minutes, with observations for photoresist removal in an optical microscope every 5 minutes after 20 minutes of sonication.

With the photoresist removed, the substrates were hard baked at 150°C for 75 minutes and immersed in DI water for the removal of excess compounds of low molecular weight [14]. At this stage, the fabrication method included the patterning of the source and drain electrodes, the encapsulation layer and the organic active layer. To complete the OECT structure, Ringer's solution was used as the electrolyte and was deposited over the active layers on the substrates. The solution contained 147 mM of NaCl, 4 mM of KCl and 3mM of CaCl in endotoxin-free water, and was chosen for its ability to accurately represent the chemical concentrations found in neurofluids, maximising the generalisability of device performance to *in vivo* physiological monitoring. Finally, a pellet Ag/AgCl electrode with a 2 mm diameter was used as the gate electrode and was immersed into the electrolyte.

3.5. Connection to Characterisation Equipment

The OECTs were electrically connected to equipment that could source and measure potential differences and currents. The characterisation equipment used in this research was the Keysight B2902A Precision Source/Measure Unit, which provided sweeping and sampling capabilities. As such, the equipment determined the output, transfer, response time, noise and stability characteristics. To connect the source measure units to the OECTs, their outputs were connected to micromanipulators which held further wires that directly interfaced to the electrodes of the OECT. Two micromanipulators were used to electrically connect to the source and drain electrodes. A further micromanipulator held the Ag/AgCl pellet electrode and immersed it into the electrolyte, as shown in figure 3.4.

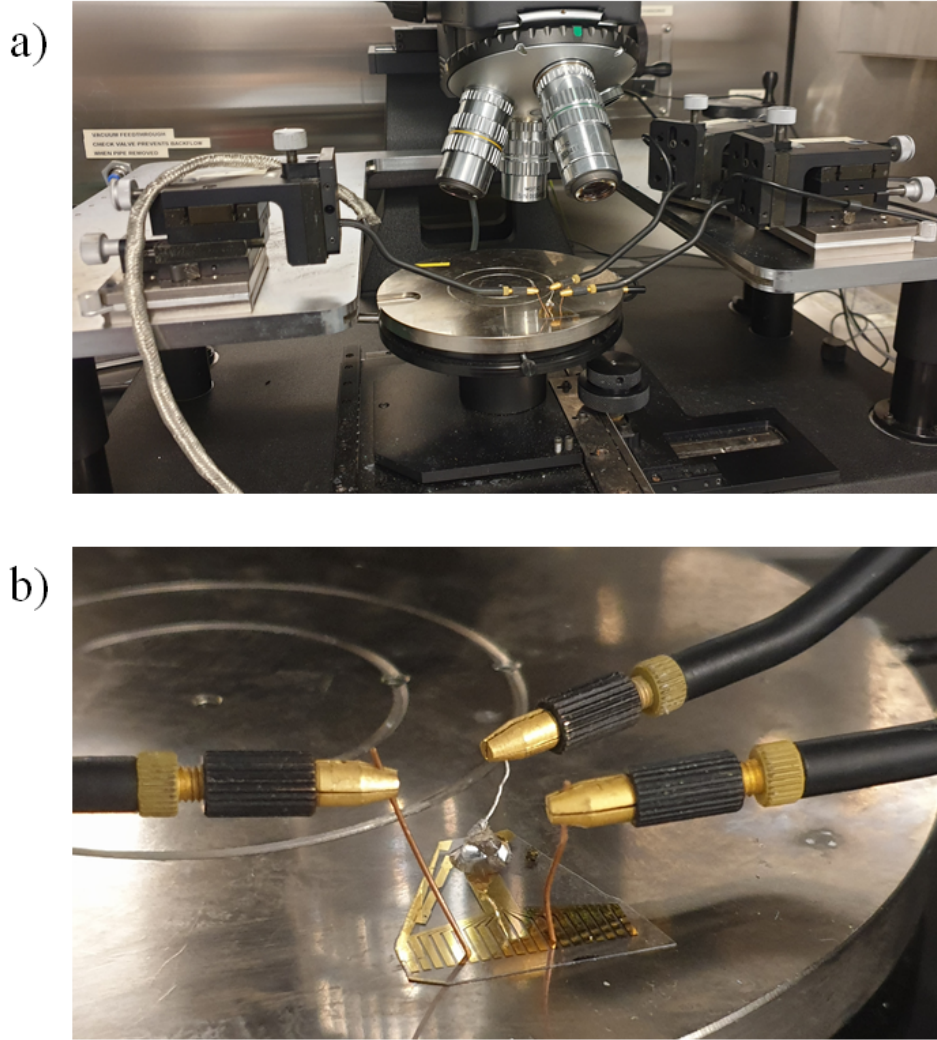


Figure 3.4: *a) Platform for the connection of the micromanipulators. b) Connection of micromanipulators to the OEET architecture.*

For the transconductance-frequency characterisations, a Keysight 33210A waveform generator produced the required frequency-varying sinusoidal voltages to the gate electrode. To determine the OEETs capability to transduce electrophysiological gate voltage inputs, a Keysight 33220A waveform generator was used to produce the voltages. To output voltages lower than 20 mV, voltage attenuators were used which reduced the amplitude by a factor of up to 10^3 . The voltages were recorded by the Keysight B2902A whilst they were inputted into the OEET gate electrode. All characterisations were managed through the Keysight B2900 Quick IV Measurement Software, which provided data sets of the characterisations. The data sets were then analysed using custom Python code.

4. MEASUREMENT OF ELECTROPHYSIOLOGICAL SIGNALS *In Vitro* USING HIGH-PERFORMANCE ORGANIC ELECTROCHEMICAL TRANSISTORS

This research was first published on the 24th September 2020 in *Advanced Functional Materials* as an open access article with a CC BY 4.0 Creative Commons Attribution License. Presented here is an adaption and extension of the work.

Tyrrell, J. E., Boutelle, M. G., Campbell, A. J., Measurement of Electrophysiological Signals *In Vitro* Using High-Performance Organic Electrochemical Transistors. *Adv. Funct. Mater.* 2021, 31, 2007086.

This research was supervised by Professor A. J. Campbell and Professor M. G. Boutelle.

4.1. Introduction

The measurement of neuronal signals has applications in brain-machine interfaces and diagnosing neurological disorders. An alternative strategy to using the voltage measurements of electrodes to transduce electrophysiological signals is to leverage the mixed ionic and electronic conductivity of OECTs [13, 14, 77, 125, 177, 207, 208, 209]. Initial *in vivo* applications of OECTs in μ ECoG yielded higher signal-to-noise ratios than microelectrodes of equivalent size for frequencies less than 200 Hz [14]. Expanding this capability to include measurements at higher frequencies is highly desirable.

Higher bioelectric frequencies are associated with smaller signal amplitudes and smaller spatial dimensions. Measuring bioelectric signals at a high spatial resolution sets a limit on the maximum device size and thus on device performance. The non-planar vOECT architecture overcomes a number of such spatial limitations, though has been shown to provide response times that are insufficient for high-frequency activity [87]. The pOECT with an interdigitated electrode style maximises the channel width-to-length ratio in the available area and has been used to transduce cardiomyocyte action potentials with mV-scale amplitudes [98, 213]. Recently, organic transistors comparable to OECTs used a parallel-plate geometry and provided sufficient spatiotemporal resolutions to resolve high-frequency activity. The devices provided a g_m^{Peak}/τ_{90} ratio of 638 S s^{-1} , and it was suggested that such a ratio surpassed the best OECT performances. The devices demonstrated the transduction of action potentials from neurons in deep cortical layers [15].

In this research, interdigitated-electrode, PEDOT:PSS-based, flexible pOECTs were fabricated and characterised, resulting in devices with state-of-the-art peak

transconductance values greater than 100 mS and response times approaching 100 μ s, achieving a g_m^{Peak}/τ_{90} of 1000 Ss⁻¹. A set of 4 $\times$ 4 OECT arrays were then characterised and sampled whilst inputting pre-recorded electrophysiological signals. The entire bioelectric frequency-voltage range was investigated, and it was demonstrated that the OECTs had the capability to resolve all inputs. This research supports that OECTs are able to resolve high-frequency bioelectric activity, and further demonstrates the resolution of the full electrophysiological spectrum.

4.2. Device Fabrication and Characterisation

Devices were fabricated as described in section 3. The substrate material was PET, chosen for its flexibility and ability to support PEDOT:PSS without the addition of the GOPS crosslinker [48]. The thermally evaporated source and drain electrodes comprised of a 200 or 300 nm gold layer with a 15 nm chromium adhesion layer and were patterned through photolithography using the MICROPOSIT S1805 photoresist. The SU-8 encapsulation, comprising of 56% v/v SU-8 2000 and 44% v/v SU-8 2005, was spin coated to a thickness of 1 μ m and patterned through photolithography. The active layer, consisting of 91.7% v/v PEDOT:PSS, 8% v/v EG and 0.3% v/v DBSA, denoted PED, was spin coated to a 35 or 70 nm thickness and was patterned using photolithography with etching. Ringer’s solution was used as the electrolyte and the gate electrode was a pellet Ag/AgCl electrode.

The Keysight B2902A was used for output, transfer, response time and stability characterisations. In all characterisations, the source electrode was grounded and the Quick-IV measurement software, available from Keysight, was used. To measure conductance, the drain-source potential was swept from -0.1 V to 0.1 V and the drain current was measured. For the output characteristics, a gate voltage was applied from -0.2 V to 0.6 V in 0.1 V steps and the drain voltage was swept from 0.6 V to -0.6 V for each step during which the drain current was measured. To measure transfer characteristics, the drain voltage was kept constant at -0.6 V, the gate voltage was swept from -0.6 V to 0.6 V and the drain current was measured. To measure response time, the drain voltage was constant at -0.6 V and a gate voltage step was applied from 0 V to 0.5 V, during which the drain current and gate voltage were sampled. To measure device stability, the drain voltage was constant at -0.6 V and a square-wave of 1 Hz frequency varying from 0 V to 0.25 V was applied to the gate, again during which the drain current and gate voltage were sampled. To measure the transconductance-frequency response, the drain voltage was kept constant at -0.6 V and the drain current was sampled. A sinusoid varying from -0.2 V to 0.2 V was produced by the Keysight 33210A and applied to the gate for frequencies ranging from 1 Hz to 10 kHz. The OECT parameter values were extracted from the measurements using custom Python code. With the aid of voltage

attenuators, the Keysight 33220A produced the voltages for testing the OECT's response to electrophysiological inputs. The Keysight B2902A sampled the output of the waveform generator and the drain current response of the OECT. The gate-drain potential difference was kept lower than the hydrolysis limit for all characterisations.

4.3. Results and Discussion

4.3.1 Device Structure

The OECTs were fabricated with four different interdigitated-electrode patterns. There were 2 styles of interdigitation: “combs” and “spirals”, as shown in figure 4.1. The interdigitated electrodes were each patterned in two sizes, denoted “small” and “large”, where the geometry dimensions are shown in table 4.1. The resulting four electrode styles had varying channel width, W , and channel length, L , and were patterned either with a 200 nm Au layer and a 70 nm active layer thickness or a 300 nm Au layer and a 35 nm active layer. These eight combinations had varying ratios of interconnect and channel resistance. The interconnects are shown in figure 4.2.

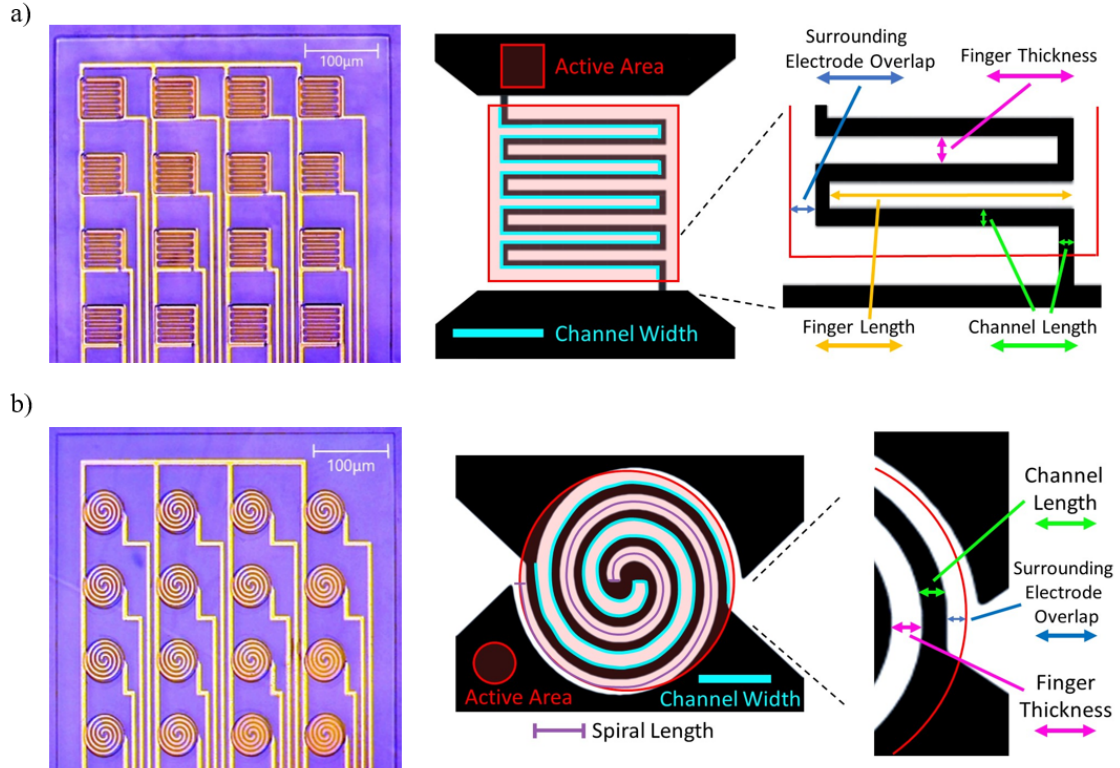


Figure 4.1: a) Small-comb array image and the “comb” geometry. b) Small-spiral array image and the “spiral” geometry. Geometry parameters are described in table 4.1.

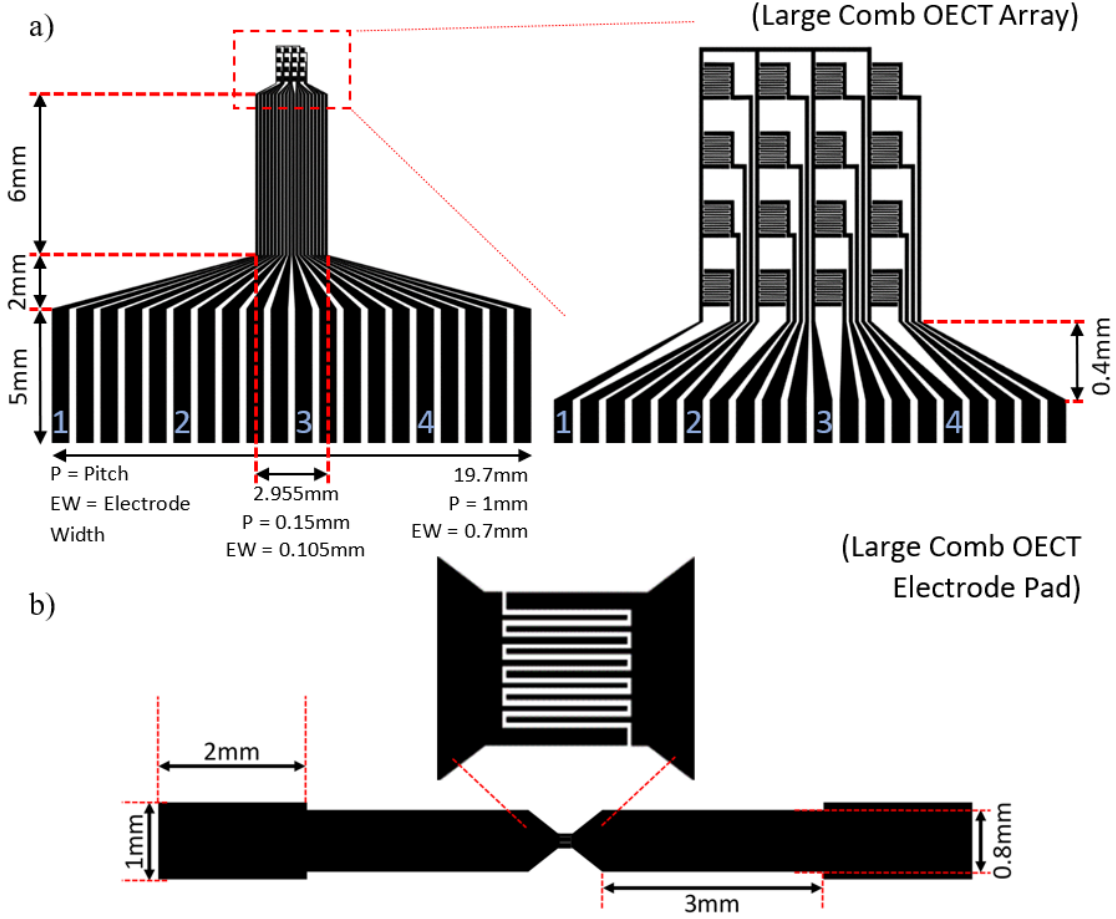


Figure 4.2: a) Interconnect design for the 4×4 large-comb OEET arrays, tailored for μ ECoG applications. The numbers on the connection wires identify the source electrode number. b) Electrode pad design, shown for the large-comb interdigitated geometry.

The interdigitated electrodes were connected to characterisation equipment either through electrode pads or the array zero-insertion-force connectors. The array interconnect resistance was minimised and the interconnects were suitable for μ ECoG testing on rats. The length of the interconnects allowed an insertion of the array from the scalp to the cortical surface of rats [264]. Previous craniotomies of rats opened a region of $2 \times 3 \text{ mm}^2$, and thus 3 mm interconnect width was chosen [13, 14]. The array output was compatible with standard zero-insertion-force connectors.

The most prominent source of variation in interconnect resistance was from the interconnect patterning. This partly originated from the photolithographic patterning of the electrode structures, giving inter-array variance. The more significant contribution to the total resistance variations within each array came from the interconnects' inherent

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Property	Small Comb (SC)	Small Spiral (SS)	Large Comb (LC)	Large Spiral (LS)
Active Area (μm^2)	86×78	$\pi(40.5)^2$	180×168	$\pi(91)^2$
Surrounding Electrode Overlap (μm)	5.0	2.5	10.0	3.0
Device Pitch (μm)	152	152	324	324
Channel Length (μm)	4	4	8	8
Finger/turn number	5	2	6	3
Finger/spiral length (μm)	72	286	152	929
Finger/spiral thickness (μm)	4	5	6	6
Channel W/L ratio	164.5	118.5	230.0	200.0

Table 4.1: Geometry parameters of the four interdigitated electrode styles characterised. The parameters are illustrated in figure 4.1.

design. It should be noted that although the “large” patterns had wider interconnects in the region of the interconnects where the OECT grid was situated, the distinction between interconnect resistance contributions between “large” and “small” arrays was not made because it was found that they were not significantly different. The two areas of the interconnect geometry which produced the variations in resistance were those where the widths of the lines were transitioning, which were the regions of length 0.4 mm and 2 mm in figure 4.2a. In these regions, the central lines were wider and shorter and thus lower in resistance, whereas the outer lines were thinner and longer. The interconnect conductance for the structures with a 200 nm metallic thickness was measured to be 17.13 ± 3.37 mS and for the 300 nm structures was 25.07 ± 5.44 mS.

4.3.2 High-Performance OECT Characterisation

To demonstrate the capability of the devices, the initial characterisation presented is from a large comb OECT with a 70 nm thick active layer and with electrode pad connections, as

shown in figure 4.2b. The OECT characteristics are shown in figure 4.3. The output and transfer characteristics showed that the devices operated in p-type depletion mode. For all electrode patterns, no short-channel effects were observed. The transfer characteristics gave a peak extrinsic transconductance of 139 mS for a drain-source potential difference of -0.6 V. To achieve this value with an active layer thickness less than 100 nm redefines state-of-the-art for OECT characteristics. The turn-off voltage was greater than the hydrolysis level, and the shift in characteristics from hysteresis was minimal.

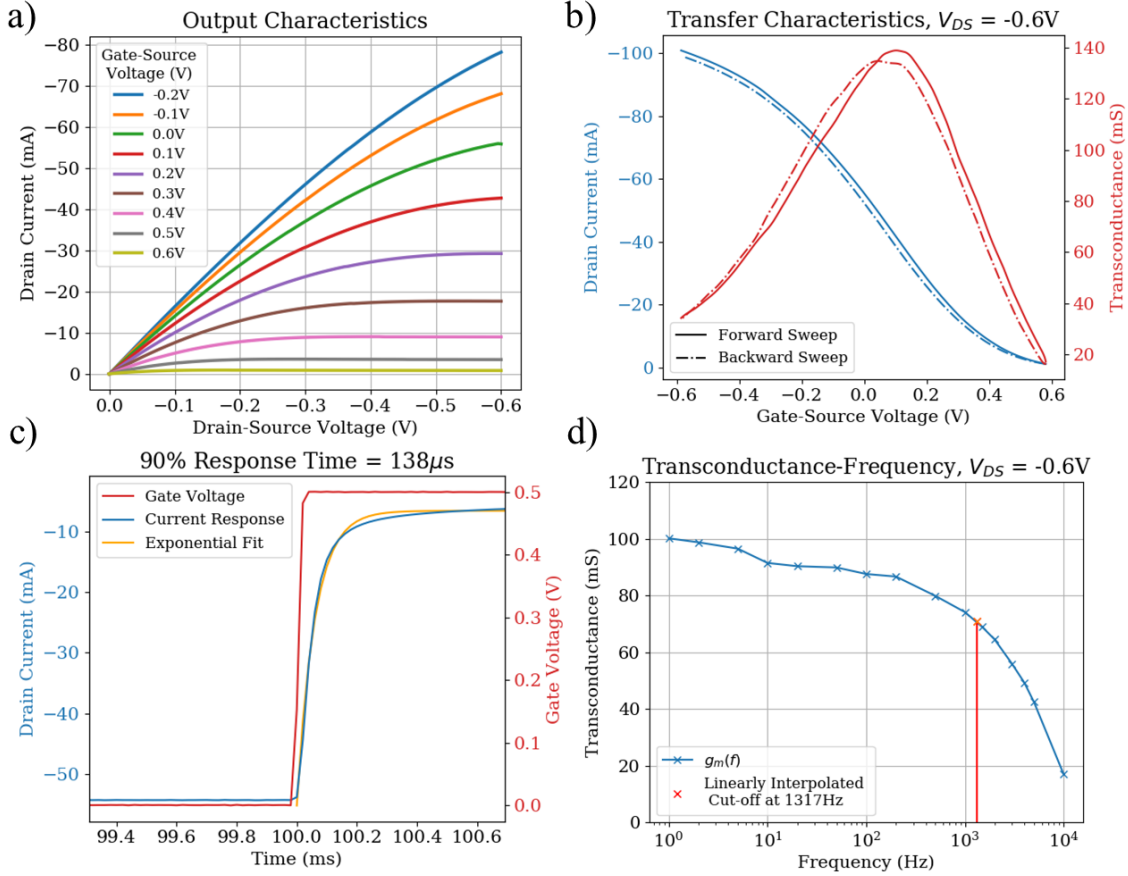


Figure 4.3: OECT characteristics for the large comb OECT electrode pad with a 70 nm active layer. a) Output characteristics shown for $V_{DS} < 0$. b) Transfer characteristics showing transconductance and hysteresis. c) Response time characteristics. d) Transconductance-frequency characteristics.

In characterising the response time, an exponential function was fitted to the data and the time required for the best-fit function to reach 90% of its final steady-state value was calculated. This analysis gave a response time of $138 \mu\text{s}$ for this device. With a peak transconductance of 139 mS, the transconductance/response time fraction was

approximately 1000 Ss^{-1} . This fraction showed that the devices provided a state-of-the-art performance and had superior properties relative to a range of other OECTs with novel architecture and material combinations [15]. The transconductance-frequency relationship was also determined. A sine wave of varying frequency with a peak-to-peak voltage of 400 mV was used at the gate with $V_{DS} = -0.6 \text{ V}$. The transconductance was found to remain substantial at 10 kHz with a value of over 15 mS. The cutoff frequency, defined as the frequency at which the transconductance decreased by 29%, occurred at over 1.3 kHz.

The devices need to maintain performance over extended time periods to be viable for brain-machine interfaces. To measure stability, the device was subject to gate pulsing. The stability characterisation was performed using a drain voltage of -0.6 V and a square wave gate input of 1 Hz frequency with an amplitude varying between $V_{GS} = 0 \text{ V}$ and $V_{GS} = 0.25 \text{ V}$. Over the 1000 s (and thus 1000 cycles of the gate input function), the change in transconductance was determined. During each test, the transconductance was reduced by 1.62% on average. To further test device stability, an OECT was immersed in Ringer's solution over a period of 8 weeks. Characterisations of the device after its extended aqueous immersion showed that the active layer was still present and that the device maintained its high performance.

4.3.3 Comparison of Array Characteristics

As predicted by Bernards and Malliaras, the conductance was proportional to the peak transconductance, as given in figure 4.4a [37]. A comparison of the characteristics for the devices with the array interconnects to those of the electrode pad design showed that the interconnect resistance was significantly greater for the devices with the array architecture.

For the case of the 200 nm interconnects with the 70 nm active layer, the device resistance could not be separated between that of the channel and the interconnects. As such, the ratio of channel resistance to interconnect resistance was increased, and it was found that the devices were not so significantly limited by interconnect resistance. With the greater resistance imposed by the μECoG array design, the peak transconductance values of the OECT arrays remained primarily above 10 mS, as shown in figure 4.4e, which still places them within state-of-the-art. With the electrode pad devices achieving values greater than 100 mS, it was evident that the implementation of an interconnect design that adheres to physiological requirements significantly decreases device transconductance. This shows that considerations of an optimal interconnect design are needed to maximise device performance for electrophysiological applications.

A comparison of the array characterisations is shown in figure 4.4, which is supported by statistical analysis in table 4.2. The peak transconductance values were consistently

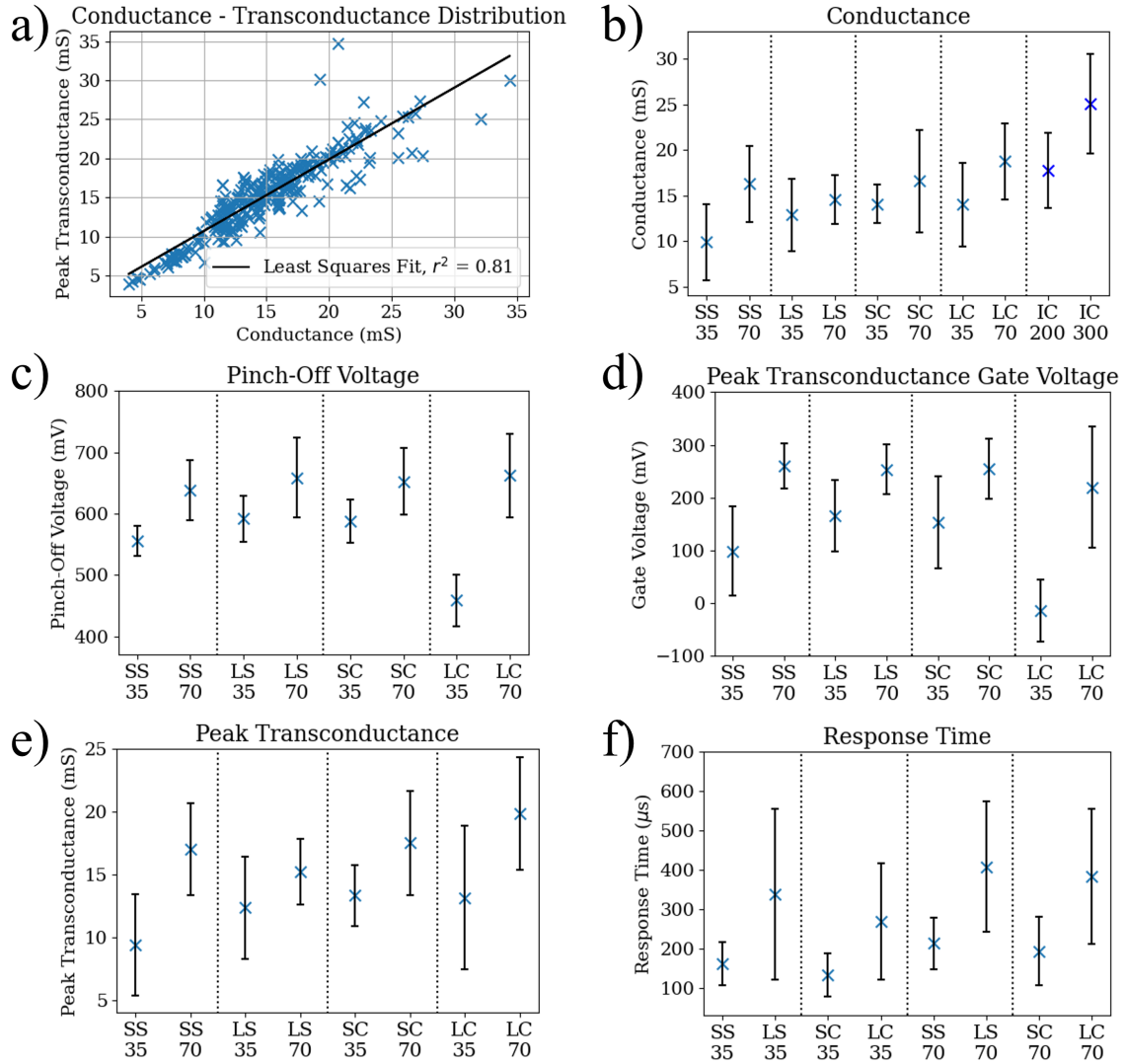


Figure 4.4: a) Conductance and peak transconductance for all devices. Mean and standard deviation values of the 8 array types for b) conductance, c) pinch-off voltage, d) peak transconductance gate voltage, e) peak transconductance and f) response time. Device characteristics are significantly different within each division, supported by the statistical analysis given in table 4.2.

significantly greater in the 70 nm devices than in the 35 nm devices, even with a thinner interconnect layer limiting the values. The active areas of the smaller patterns were approximately 25% of those of the larger patterns but provided transconductance values that were not significantly lower. Also, the pitch value of the SC and SS arrays was 47% of the pitch of the LC and LS arrays. Therefore, the smaller devices would provide a greater spatial resolution if applied to measuring bioelectric signals without a significant

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Device Number for Each Device Type							
SS 35	SS 70	LS 35	LS 70	SC 35	SC 70	LC 35	LC 70
31	29	44	51	21	39	11	43
Interconnect Cond. (Alt. Hyp. p-value)				IC 200 < IC 300 1.00×10^{-7}			
Conductance							
Alt. Hyp.	SS 35 < SS 70		LS 35 < LS 70		SC 35 < SC 70		LC 35 < LC 70
p-value	1.40×10^{-7}		1.00×10^{-2}		8.83×10^{-3}		4.98×10^{-3}
Pinch-off Voltage							
Alt. Hyp.	SS 35 < SS 70		LS 35 < LS 70		SC 35 < SC 70		LC 35 < LC 70
p-value	2.38×10^{-10}		1.44×10^{-8}		4.02×10^{-7}		6.22×10^{-12}
Peak Transconductance Gate Voltage							
Alt. Hyp.	SS 35 < SS 70		LS 35 < LS 70		SC 35 < SC 70		LC 35 < LC 70
p-value	2.95×10^{-12}		2.36×10^{-10}		3.04×10^{-5}		2.00×10^{-10}
Peak Transconductance							
Alt. Hyp.	SS 35 < SS 70		LS 35 < LS 70		SC 35 < SC 70		LC 35 < LC 70
p-value	1.80×10^{-10}		8.55×10^{-5}		5.10×10^{-6}		2.11×10^{-3}
Response Time							
Alt. Hyp.	SS 35 < LS 35		SC 35 < LC 35		SS 70 < LS 70		SC 70 < LC 70
p-value	2.56×10^{-6}		8.24×10^{-3}		4.58×10^{-8}		4.70×10^{-5}

Table 4.2: *Alternative hypotheses and p-values of Welch's t-tests for the comparison of OECT array characteristics as illustrated in figure 4.4.*

reduction in performance. The standard deviation in peak transconductance had contributions from variations in conductance which originated from the inherent array design and photolithographic patterning. The PEDOT:PSS active layer was patterned using photolithography, which has been shown to provide lower device variability than when using the Parylene C peel-off method [72]. Additional variations could have arisen from differences in the width of a Gaussian density-of-states describing the molecular disorder of PEDOT:PSS [75]. However, such variations were likely negligible for a given PEDOT:PSS thickness as the same conducting polymer solution was used in all device fabrications.

The response time characteristics showed that there were contributions from the parasitic capacitance and the active layer thickness. With short channel lengths and high drain voltages, the device response time, τ_{90} , was limited by the ion transport time,

which is dependent on the electrolyte resistance and the capacitance of the system [37]. The parasitic contribution significantly increased the response time of the larger interdigitated patterns such that their capability to measure high-frequency bioelectric events was greatly reduced. This was supported by the significant differences found between the small and large device architectures for a constant channel thickness. The fastest devices were the 35 nm small comb electrode OECTs with a mean value of 134 μ s, thus showing suitability to temporally resolve the entire electrophysiological spectrum.

The devices with the 35 nm active layers had significantly lower pinch-off voltages and peak transconductance gate voltages than the 70 nm devices, as shown in figures 4.4c and 4.4d, respectively. This supported the prediction by Bernards and Malliaras that pinch-off voltage decreases as active layer thickness decreases [37]. The decrease implied that the devices began de-doping at smaller gate-drain potentials, as illustrated in figure 4.5. The additional decrease in pinch-off voltage for the 35 nm large comb devices was thought to originate from inter-array fabrication variation relative to the other 35 nm devices.

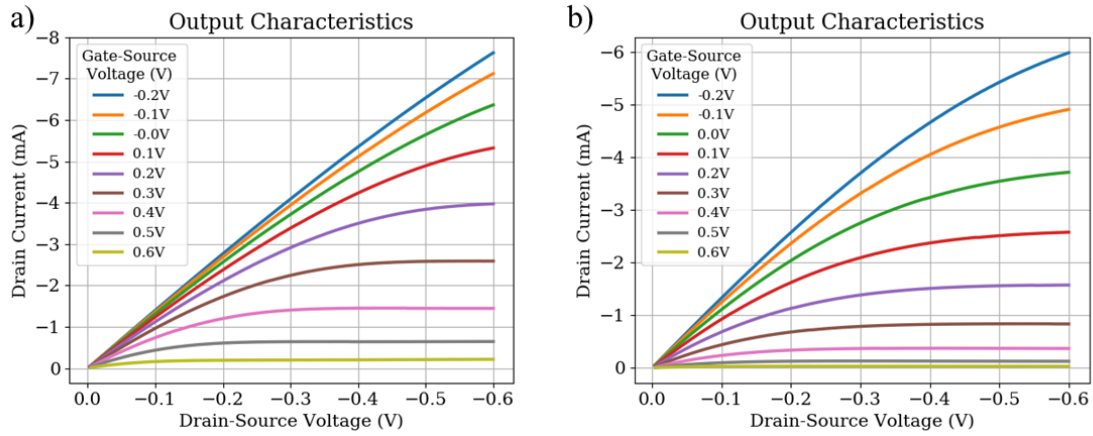


Figure 4.5: Large spiral OECT array output characteristics for a) 70 nm devices, b) 35 nm devices.

To compare the performance of the array devices, the fraction of peak transconductance to response time was found. From this measure, the comb-electrode interdigitation provided superior performance when compared to the spiral-electrode interdigitation, and the small interdigitated patterns provided greater performance than their large counterparts. The two device types which provided the greatest ratios were the 35 nm and 70 nm small comb-electrode OECT arrays, with a fraction of approximately 100 Ss^{-1} . Therefore, both device types were used for bioelectric testing.

4.3.4 Analysis of OECT Output for Electrophysiological Signal Input

Pre-recorded electrophysiological signals were inputted into the gate electrode of the chosen OECTs and the drain current was sampled with a drain voltage of -0.6 V. The types of bioelectric signals tested were local field potentials (LFP), ECoG, spreading depolarisations (SDs), surface electromyography (EMG), and EMG fasciculations. All electrophysiological recordings were performed using approved wired instruments and were taken from raw anonymised data. The device responses for the 35 nm devices are shown in figure 4.6.

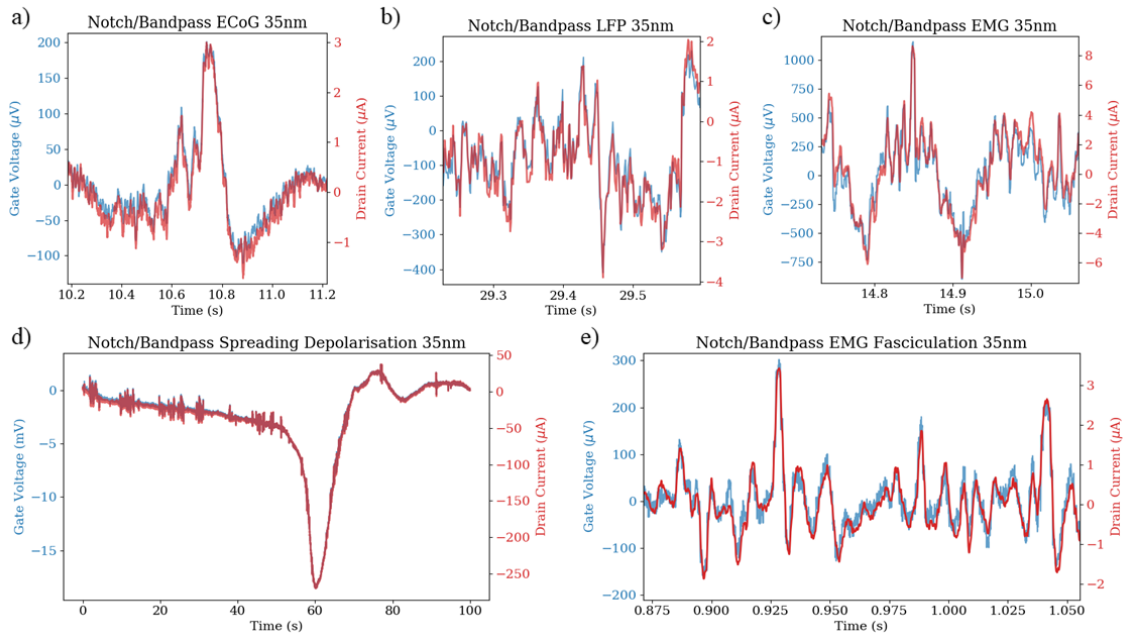


Figure 4.6: Bandpass-filtered gate voltage input and bandpass- and notch-filtered OECT current output for the electrophysiological recordings of a) ECoG, b) LFP, c) Surface EMG, d) spreading depolarisation, e) EMG fasciculation.

For each data type, a bandpass filter was applied to the gate input and drain output to investigate device efficacy in a desired frequency band. Notch filters were then applied to only the drain output. The Q-factor of the notch filters, which is a parameter describing the width of the filter attenuating the amplitude in frequency space, was set to 50. The frequency filters applied to each signal are presented in table 4.3. The effects of the bandpass and notch filters are illustrated in figure 4.7 for the ECoG and EMG fasciculation inputs, showing that the noise sources at 50 Hz and further odd harmonics were significant and detrimental to resolving the gate voltage input. All filters were computationally applied after the data acquisition.

Spreading depolarisations occur as a result of traumatic brain injury and represent the

4 MEASUREMENT OF ELECTROPHYSIOLOGICAL SIGNALS *IN VITRO* USING HIGH-PERFORMANCE ORGANIC ELECTROCHEMICAL TRANSISTORS

Signal Type	Sampling Rate (kHz)	High-pass Frequency (BW Order)	Low-pass Frequency (BW Order)	Notch Filters (Higher Harmonics)
SD	1.00	1.0 mHz (1)	None	50 Hz (Odd)
LFP	1.00	1.0 Hz (3)	None	50 Hz (Odd), 62.5 (All)
ECoG	1.67	1.0 Hz (3)	None	50 Hz (Odd), 62.5 (All)
Surface EMG	5.00	1.0 Hz (3)	None	50 Hz (Odd)
EMG Fasciculation	50.00	10.0 Hz (3)	5 kHz (20)	50 Hz (Odd)

Table 4.3: Frequency filter parameters including the Butterworth (BW) orders for the electrophysiological signals shown in figure 4.6.

mass depolarisation of cells [216]. A pre-recorded SD was inputted into the gate electrode and the drain current was sampled. Both transistor types were able to measure the 10 mHz-scale, 20 mV depolarisation. Using OECTs to measure such activity with high SNRs may provide new insights into the dynamics of SDs and guide their intervention and treatment.

Low-frequency ECoG data and LFP recordings were inputted and sampled, and frequency spectra showed that the primary recorded events had frequencies less than 200 Hz, which was expected of such signal types [172]. The ECoG and LFP signals had voltage changes from 0.1 – 1 mV-scale, and both 35 nm and 70 nm devices were able to reproduce the features of the inputs.

In surface EMG, electrode measurements give voltage changes up to 10 mV with frequency components up to 150 Hz depending on the observed muscle [265]. EMG measurements have extensive uses in rehabilitation such as their implementation in controlling robotic prostheses [266]. Both 35 nm and 70 nm devices were successful in reproducing the EMG input.

Fasciculations are the electrical events associated with muscle twitches, and their recordings are important in the diagnosis of motor neuron diseases such as amyotrophic lateral sclerosis (ALS). Fasciculations are associated with the discharges of motor units and have voltage and frequency characteristics similar to MUA. Their recorded amplitudes are on the scale of 100 – 300 μ V and show a full potential cycle within 10 ms [267]. The devices successfully reproduced the features of the EMG fasciculations. Gate electrode changes with magnitudes of 50 μ V and durations of 5 ms were resolvable in the OECT drain current. This capability was seen in both 35 nm and 70 nm devices.

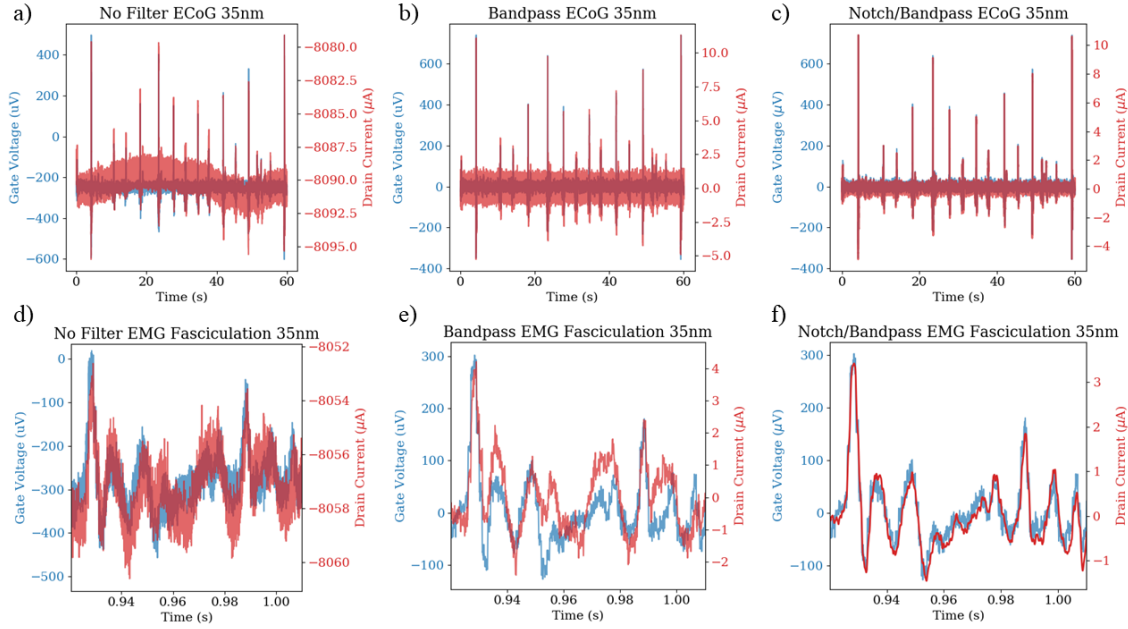


Figure 4.7: Gate voltage input and drain current output for the electrophysiological inputs of a) ECoG with no filter, b) ECoG with bandpass filter, c) ECoG with bandpass-filtered gate and bandpass- and notch-filtered drain current, d) EMG fasciculations with no filter, e) EMG fasciculations with bandpass filter, f) EMG fasciculations with bandpass-filtered gate and bandpass- and notch- filtered drain current.

Cortical neurons share the same voltage and frequency characteristics, suggesting they would be resolvable by the OECTs.

4.3.5 Quantification of OECT Noise Using Electrophysiological Voltage Input and Current Output

Quantifications of the devices' capabilities to reproduce the bioelectric inputs were made for the ECoG, SD and EMG fasciculation signals. Traditional methods of determining transistor noise require a constant gate-source voltage whilst sampling the drain current. For OECTs, the resulting power spectral density has previously revealed a dominant contribution from $1/f$ noise, considered to originate from charge fluctuations local to the active layer [89]. Analysis of the noise level is crucial in determining the feasibility of applying the devices to the different frequency-voltage regions within electrophysiology. Furthermore, considerations of frequency filtering can help to optimise future experimental methods in the analysis of bioelectric readout. Presented here are three quantifications of noise that compare the gate voltage input with the drain current output. For each input, the effects of applying bandpass and notch filters are examined.

In each case, noise values sharing resemblance to gate voltage RMS noise, $V_{G,RMS}$, were found. The novel quantifications are then compared to noise values calculated using traditional methods.

Prior to quantifying the noise, the OECT recordings were compared to an equivalent, ideal OECT response using the residual sum of squares (RSS), and the effect of filter application was considered. In the first analysis of the noise, the error between the recorded and ideal response with the change in gate voltage was examined. The second noise quantification involved the relationship between the recorded transconductance values and the changes in gate voltage. Finally, a Gaussian noise source was added to the ideal response and the resulting relationship between the transconductance and the change in gate voltage was compared to that which was measured.

Changes in the Residual Sum of Squares with Filter Application

The ideal OECT response is a linear amplification of the gate voltage input to a drain current output through the transconductance. The OECT transconductance for the measured data, g_m , was found and used to determine the ideal response. The transconductance varies for different values of gate voltage, as seen in the transfer curve. For this analysis, the changes in gate voltage from neural signals were assumed to be sufficiently small such that the transconductance remained constant for all gate voltages considered. It was further assumed that the transconductance was constant for all frequencies in the gate voltage, which held validity within the range of electrophysiological activities. The ideal OECT response for the i^{th} drain current, $I_{D,id.}^{i+1}$, is given by

$$I_{D,id.}^{i+1} = I_{D,id.}^i + g_{m,id.}(V_G^{i+1} - V_G^i) \quad , \quad (4.1)$$

where V_G^i is the i^{th} gate voltage, $g_{m,id.}$ is the ideal transconductance, which is a constant value for all changes in gate voltage, and $I_{D,id.}^0 = I_{D,rec.}^0$ for the first measured value of the drain current $I_{D,rec.}^0$. The $g_{m,id.}$ was calculated by dividing the range of sampled drain currents by the range of the sampled gate voltages. In the application of the bandpass filter, the gate voltage was filtered and inserted into equation 4.1. The same transconductance value was used and $I_{D,rec.}^0$ was given by the first value of the bandpass-filtered drain current. When applying the notch filter to the drain current, the $I_{D,rec.}^0$ was given by the first value of the bandpass- and notch- filtered drain current. The RSS was determined for the N sampled data points as

$$RSS = \sum_{i=1}^N (I_{D,id.}^i - I_{D,rec.}^i)^2 \quad , \quad (4.2)$$

and the calculations are given in table 4.4.

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Signal Type	ECoG	ECoG	SD	SD	EMG Fasc.	EMG Fasc.
Thickness	35 nm	70 nm	35 nm	70 nm	35 nm	70 nm
	RSS Values 10^{-8} (A ²) (2 d.p.)					
No Filter	26.00	4.12	47.78	22.76	63.68	5.22
Bandpass	2.60	1.94	28.78	13.80	6.37	2.77
Bandpass & Notch (I_D)	0.20	0.53	24.70	13.35	1.36	0.76

Table 4.4: *Residual sum-of-squares of the 35 nm and 70 nm device responses to ECoG, SD and EMG fasciculation (Fasc.) inputs. This is determined for the cases of no filtering, bandpass filtering on the gate input and drain output and then an additional notch filter on the drain output.*

It was found that the frequency filters decreased the RSS values. It was expected that the application of the bandpass filter would decrease the RSS value because the current drift and non-biophysical high-frequency noise contributions would be reduced. The notch filter was applied only to the drain current and consistently reduced the RSS value. Therefore, the notch-filtered drain current gave an improved representation of the ideal behaviour, implying that the noise powers at the notch-attenuated frequencies were significant.

Noise Quantification 1: Drain Current Error

The decrease in the RSS values showed that the error between the recorded and ideal drain current reduced with filter application. The relationship between the i^{th} drain current error, ε^i , and the i^{th} change in gate voltage, ΔV_G^i , was defined as

$$\Delta I_{D,rec.}^i = I_{D,rec.}^{i+1} - I_{D,rec.}^i \quad , \quad (4.3)$$

$$\Delta I_{D,id.}^i = I_{D,id.}^{i+1} - I_{D,id.}^i \quad , \quad (4.4)$$

$$\Delta V_G^i = V_G^{i+1} - V_G^i \quad , \quad (4.5)$$

$$\varepsilon^i = \Delta I_{D,rec.}^i - \Delta I_{D,id.}^i \quad . \quad (4.6)$$

The distribution of ε with ΔV_G was calculated, and contributions from noise sources would be characterised by a spread of errors for a given change in gate voltage. The distribution was found by placing the error values into μ V-scale bins of ΔV_G . It was found that there was a linear decrease with an addition of an approximately Gaussian distribution of error for all neural inputs. For example, the ε^i that were associated with ΔV_G^i such that $0 < \Delta V_G^i < 1 \mu$ V had a Gaussian distribution. The linear component and the spread of the distribution was found by calculating the mean and the standard deviation of the

errors, respectively, in each bin. The linear relationship between the error mean and the gate voltage change, $\langle \varepsilon \rangle \propto -\Delta V_G$, gave the insight that

$$\frac{\langle \varepsilon \rangle}{\Delta V_G} = \frac{\langle \Delta I_{D,rec.}^i - \Delta I_{D,id.}^i \rangle}{\Delta V_G} = \langle g_{m,rec.} \rangle - \langle g_{m,id.} \rangle, \quad (4.7)$$

where $g_{m,rec.}$ is the recorded transconductance. Given that at $\Delta V_G \approx 0$ the $\langle g_{m,rec.} \rangle \approx 0$, then $\langle \varepsilon \rangle / \Delta V_G \approx -\langle g_{m,id.} \rangle$. As ΔV_G becomes greater than the gate-referred noise floor, then $g_{m,rec.} \rightarrow g_{m,id.}$. This relationship was identified in the notch- and bandpass- filtered drain current errors. The impact of filter application on ε is shown in figure 4.8.

For small ΔV_G , the standard deviation of the Gaussian distribution describing the error around ΔV_G , σ , was found to remain approximately constant and was thus used to quantify noise. For a ΔV_G bin, 95% of the drain current errors were found within $\pm 2\sigma$ of the bin's mean. Therefore, a representation of gate-referred noise was defined as $4\sigma/g_m$ for device transconductance g_m . The resulting noise values are shown in table 4.5. Errors on the noise values were calculated from the deviations in σ for small ΔV_G .

Signal Type	ECoG	ECoG	SD	SD	EMG Fasc.	EMG Fasc.
Thickness	35 nm	70 nm	35 nm	70 nm	35 nm	70 nm
	Gate Voltage Noise Representation, $4\sigma/g_m$ (μV) (1 d.p.)					
No Filter	58.8 ± 0.5	64.9 ± 0.7	64.9 ± 2.7	70.4 ± 1.4	183.0 ± 4.0	195.0 ± 7.0
Bandpass	58.3 ± 3.1	63.5 ± 4.5	66.0 ± 2.7	70.4 ± 1.8	15.5 ± 0.2	14.8 ± 0.3
Bandpass & Notch I_D	17.6 ± 1.0	24.7 ± 1.3	27.1 ± 1.3	38.2 ± 1.4	1.9 ± 0.1	2.3 ± 0.1

Table 4.5: Gate voltage noise representations of the 35 nm and 70 nm device responses to the ECoG, SD and EMG fasciculation inputs. This is determined for the cases of no filtering, bandpass filtering and for an additional notch filter on the drain current.

It was found that the error of the 35 nm and 70 nm devices were consistently on the same scale and the noise values were reduced with filter application. The application of the bandpass and notch filters reduced the standard deviation of current error and thus the gate-referred noise values in the EMG fasciculation response, whereas only the notch filter was impactful on the ECoG and SD responses. This was expected because only the EMG fasciculation response was subject to a low-pass filter. This shows that when recording electrophysiological data, implementing physical or digital filters could significantly increase signal quality, as exemplified by the increase in quality of the EMG fasciculation output.

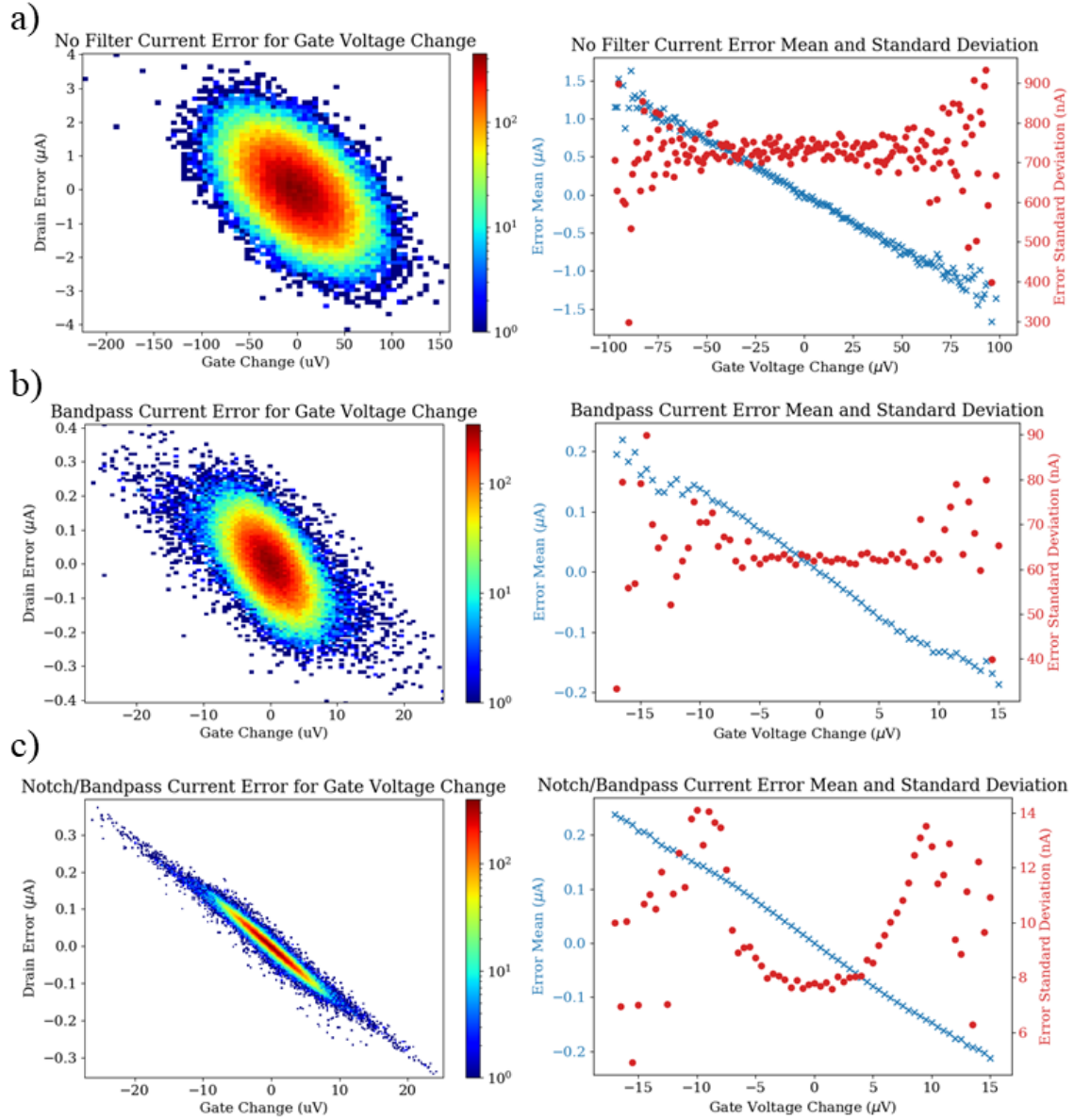


Figure 4.8: Error values and mean and standard deviation of binned error values for the 35nm EMG fasciculation gate inputs and drain outputs for a) no filter, b) bandpass filter, c) notch and bandpass filter.

Noise Quantification 2: Transconductance Distribution Analysis

For each measured datapoint there was a change in gate voltage and drain current. The recorded transconductance value for each gate voltage change, g_m^i , was found as

$$g_m^i = \frac{I_D^{i+1} - I_D^i}{V_G^{i+1} - V_G^i} . \quad (4.8)$$

As the device reaches the noise floor, the drain current can be described by a probability density function with a non-zero amplitude of current change, ΔI_D . With transconductance defined as $\Delta I_D / \Delta V_G$, then values of g_m^i increase towards an asymptote at $\Delta V_G = 0$. Therefore, the distribution of g_m with ΔV_G gave insight into the ΔV_G at which the OECT noise dominates the device response. The distribution was investigated by placing the values of g_m^i into bins of ΔV_G . Representations of the distribution are shown in figure 4.9.

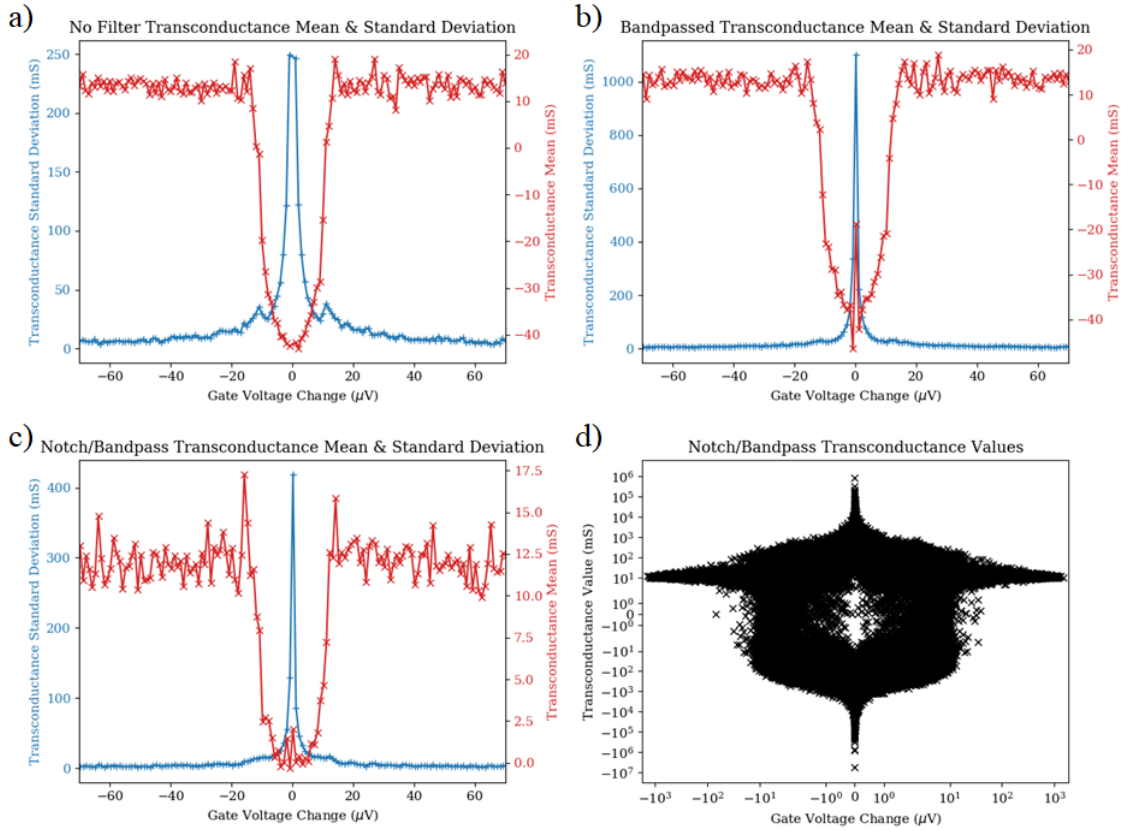


Figure 4.9: Mean and standard deviation of transconductance placed into μV -scale bins of gate voltage change for the 35 nm SD data. This is calculated for a) no filter, b) bandpass filter, c) notch and bandpass filter. d) The distribution of transconductance values with change in gate voltage of c) without bin placement.

To quantify a representation of the OECT noise, the smallest ΔV_G bin within which $g_{m,id.} - 3\sigma > 0$ was identified, where σ was the standard deviation of the g_m^i in the bin. This was found for both positive and negative values of ΔV_G , and the symmetry of the considered distribution about $\Delta V_G = 0$ provided approximately the same ΔV_G bin. The midpoint of each of the two bins was found and then their average was calculated. The resulting representations of noise are given in table 4.6.

Signal Type	ECoG	ECoG	SD	SD	EMG Fasc.	EMG Fasc.
Thickness	35 nm	70 nm	35 nm	70 nm	35 nm	70 nm
	Gate Voltage Noise Representation ± 0.7 (μV) (1 d.p.)					
No Filter	23.0	26.0	51.5	45.0	93.0	96.5
Bandpass	18.0	26.0	44.0	31.0	12.0	13.0
Bandpass & Notch I_D	14.0	16.5	20.0	19.0	1.5	2.0

Table 4.6: Average changes in gate voltage for which the difference between the expected transconductances and 3 standard deviations of transconductance values become positive. The values are found for ECoG, SD and EMG fasciculation responses for no frequency filtering, bandpass filtering and notch and bandpass filtering.

The results of this analysis were similar to those of the previous analysis with the drain current error. Both bandpass and notch filters significantly affected the values for the EMG fasciculation data, whereas only the notch filter significantly affected the transconductance properties for the analysis of ECoG and spreading depolarisation inputs. The 35 nm and 70 nm devices gave representations of noise on the same scale, implying that they had similar capabilities in resolving electrophysiological signals.

Noise Quantification 3: OECT Current Simulation

In finding that the errors were approximately Gaussian distributed, a device response was modelled as the summation of the ideal response and a Gaussian noise source of zero mean. The noise source was added to the gate input so the equivalent gate-input noise could be determined. The modelled drain current response was formulated as

$$I_D^{i+1} = I_D^i + g_{m,id.}(V_{G\sigma}^{i+1} - V_{G\sigma}^i) \quad , \quad (4.9)$$

$$V_{G\sigma}^i \sim N(V_G^i, \sigma^2) \quad , \quad (4.10)$$

where $N(V_G^i, \sigma^2)$ was the Gaussian distribution describing the i^{th} gate voltage.

The resulting response was subject to the transconductance analysis as previously described, allowing the comparison of the modelled transconductance to that which was

recorded. By varying σ in equation 4.10, the transconductance distribution varied. To find the standard deviation parameter which best reproduced the distribution of recorded data, RSS values between the simulated and recorded transconductance standard deviations were found. The noise parameter which minimised this value was considered as the best to describe the noise source. The measured and simulated transconductance distributions with the σ values best describing the noise are shown in figure 4.10.

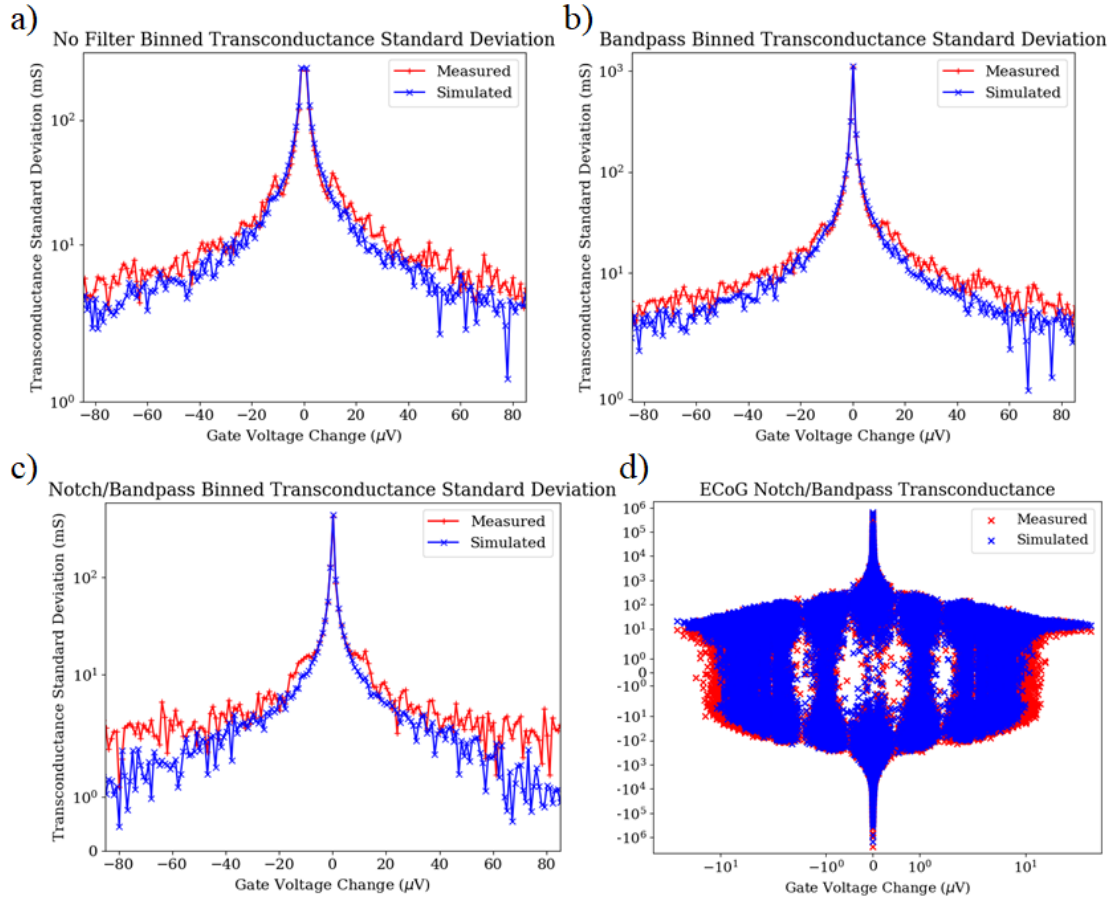


Figure 4.10: Standard deviations of the measured and simulated transconductance values placed into bins of change in gate voltage for the 35 nm SD response with a) no filter, b) bandpass filter, c) notch and bandpass filters. d) The measured and simulated transconductance distributions for the notch- and bandpass- filtered response of the 35 nm ECoG input.

The process of determining the simulated noise of the OECT was stochastic, thus introducing the possibility that a different optimal parameter value could have been found on each simulation. As such, the simulation was repeated and the mean and standard deviation of the distribution of optimal parameter values were determined. The standard

deviation was found to be negligible and so was not included in the uncertainty. The mean value, defined as σ , was such that 4σ described the width within which 95% of the gate voltages would originate to describe the noise. The value of 4σ was thus used as a representation of the magnitude of $V_{G,RMS}$. The values of 4σ are given in table 4.7, where the uncertainty originated from the resolution in σ values considered in the simulation.

Signal Type	ECoG	ECoG	SD	SD	EMG Fasc.	EMG Fasc.
Thickness	35 nm	70 nm	35 nm	70 nm	35 nm	70 nm
	Best-fit 4σ (μV)					
No Filter	44 ± 2	48 ± 2	52 ± 2	52 ± 2	136 ± 2	156 ± 2
Bandpass	44 ± 2	48 ± 2	52 ± 2	52 ± 2	10 ± 2	12 ± 2
Bandpass & Notch I_D	12 ± 2	16 ± 2	20 ± 2	24 ± 2	1.0 ± 0.5	2.0 ± 0.5

Table 4.7: *The 4σ values for which σ represents the parameter describing a noise source superposed onto the recorded gate voltage to give the recorded transconductance distribution of best fit. The values are found for ECoG, spreading depolarisation and EMG fasciculation responses for no frequency filters, a bandpass filter and notch and bandpass filters.*

The transconductance standard deviation values were successfully modelled by the Gaussian noise source at small gate voltage changes. For the neural inputs with gate voltage changes greater than $20 \mu\text{V}$, the difference between measured variance and simulated variance increased as the gate voltage change increased. This implied that additional sources of noise were operating at these scales. Therefore, the calculated noise parameters should be taken such that the noise in the system is greater than those parameters. The results of this analysis were similar to those of the previous analyses regarding the similarities between noise values of the 35 nm and 70 nm devices and the impacts of frequency filters on the different device responses.

The three methods of quantifying noise gave approximately the same value. Achieving gate-referred noise values at approximately $10 \mu\text{V}$ whilst recording kHz-scale features allowed an accurate resolution of the bioelectric inputs. Given that the superior SNR of OECTs extends from low frequencies to higher frequencies, then the device responses were limited by that of the electrophysiological recordings. In instances where the devices would measure electrical activity through the direct measurement of ionic fluctuations in physiological electrolytes, such as μECoG in cerebrospinal fluid, it is expected that the interdigitated-electrode OECT devices, arranged as presented here, would leverage the greater SNR and resolve the full electrophysiological spectrum with high efficacy *in vivo*.

4.3.6 Validation of Novel Noise Quantifications

The validity of the three presented quantifications of gate-referred voltage noise was investigated by comparing the results to the noise measured using the standard methodology. As such, OECT noise was measured by grounding the gate electrode and sampling the current with a constant drain voltage of -0.6 V. The power spectral density, $S_{I_D}(f)$, was determined and the gate-referred noise, $V_{G,RMS}$, was found by calculating

$$V_{G,RMS} = \sqrt{\frac{2 \int_0^{f_s/2} S_{I_D}(f) df}{g_m^2}}, \quad (4.11)$$

where f_s was the sampling frequency and g_m was the transconductance at $V_G = 0$ in the transfer curve. In the novel quantifications of noise, standard deviation values were identified for drain current, $I_{D,\sigma}$. In the standard methodology, the RMS value of I_D , $I_{D,RMS}$, is found. For $\langle I_D \rangle \approx 0$ and large N , then $I_{D,\sigma} \approx I_{D,RMS}$, and thus $V_{G,RMS} \approx I_{D,\sigma}/g_m$. The condition of $\langle I_D \rangle \approx 0$ can be achieved by attenuating the low-frequency components of the drain current, and indeed it was found that the standard deviation of the drain current was approximately equal to the RMS value when considering the drain current with a high-pass filter.

The OECTs were then subject to an electrophysiological signal. The noise of each method was determined without frequency filtering and then with the application of bandpass and notch filters as described previously. The value of noise predicted by novel method i on the bandpass-filtered drain current, $V_{G,Mi}$, was compared to that of the standard method, $V_{G,St}$, by taking the fraction $M_i = V_{G,Mi}/V_{G,St}$. The noise values calculated for the first noise quantification, as shown in table 4.5, were given as $4\sigma/g_m$, and in the validation the values calculated were $V_{G,M1} = \sigma/g_m$. The relationship between the standard deviation and $V_{G,M2}$ was not varied for the purposes of the validation; however, an approximately constant value of M_2 would support its implementation as a noise measure. Similarly to the first quantification, the third noise method gave values as $4\sigma/g_m$ and the validation considered $V_{G,M3} = \sigma/g_m$.

The mean and standard deviation values were found for the values of M_i calculated across 14 devices. It was found that $M_1 = 0.98 \pm 0.13$, $M_2 = 1.59 \pm 0.33$ and $M_3 = 0.67 \pm 0.13$. This showed that the first noise quantification was the most accurate in reproducing the noise value calculated using the standard methodology. The value of M_2 showed that the second noise quantification approximately provided $3\sigma/2g_m$. Finally, the third noise quantification was found to provide an underestimation of the noise, as expected, but provided a relatively constant value. The results showed that the novel methods provided noise values that were approximately a constant fraction of the standard method noise values and were on the same order of magnitude, supporting that the three

novel quantifications were providing a representation of OECT noise.

To further determine the ability of the three methods to provide a representation of noise, the fractional reduction in noise with the application of frequency filters was used as a quantitative measure. Comparison of fractional decreases in noise with frequency filters eliminated the need to consider the relationship between the standard deviation and RMS value. Results of the fractional decreases are shown in table 4.8.

Noise Method	Bandpass/No Filter (2 d.p.)	Bandpass & Notch/No Filter (2 d.p.)
Method 1	0.74 ± 0.02	0.03 ± 0.00
Method 2	0.75 ± 0.09	0.05 ± 0.01
Method 3	0.73 ± 0.09	0.02 ± 0.01
Standard Method	0.74 ± 0.05	0.22 ± 0.07

Table 4.8: *Mean and standard deviation of the fractions of noise reduction from the application of frequency filters for the noise analysis methods.*

In performing two-sided Welch’s t-tests with p-values of 0.05, it was found that there was no significant difference between each novel noise quantification and the standard methodology in the reduction of noise given the application of the bandpass filter. This further supported that all of the novel methods were capable of quantifying noise to a similar capacity as the standard method. On the other hand, with the further application of a notch filter, the same statistical tests showed that the novel methods quantified a significantly lower noise value compared to the standard method. Nevertheless, the novel methods correctly predicted that noise reduced with the notch filter.

The validation of the three novel methods of noise was found to support their capability in providing a representation of gate-referred noise in OECTs. Such results support the assumptions used in the methods. Furthermore, this analysis shows that the inherent OECT noise can be quantified from the deconstruction of the drain current response given that the gate input is known and contains a range of gate voltage changes that are smaller and greater than the gate-referred OECT noise value. Therefore, such validation provides the conclusion that the OECTs operated with a gate-referred noise value on the $10 \mu\text{V}$ -scale, supporting their capabilities to resolve low-amplitude electrophysiological signals.

4.4. Conclusions

A range of OECT devices were fabricated with the aim to maximise performance in the electrophysiological spectrum. Interdigitated electrodes and active layers of varying sizes were characterised and compared. The OECTs were organised into 4×4 grids with

interconnect lines that were of physiologically relevant length scales and connections suitable for integration with external electronics.

The capability of the interdigitated OECT style was illustrated. A state-of-the-art device was fabricated with a 100 mS-scale peak transconductance and a 100 μ s-scale response time. Multiple devices presented characteristics on this scale, showing that the fabrication method consistently allowed for high-performance devices.

The implementation of the interdigitated OECTs into the designed array structures also showed exceptional characteristics. In particular, the small comb 35 nm active layer thickness devices had response times on the 100 μ s-scale and transconductance values on the 10 mS-scale. These performance parameters were ideally suited to electrophysiological applications where the highest frequency events approach 10 kHz. The 35 nm and 70 nm active layer small-comb devices were chosen for testing their capability to resolve electrophysiological signals. The OECT arrays have shown the capability to resolve bioelectrical activity ranging from spreading depolarisations to EMG fasciculations. Such activity has ranged in voltage scales from 10 mV to 10 μ V and in frequency scales from 10 mHz to up to 10 kHz.

The capability of the OECT to resolve the electrophysiological spectrum was supported by three novel quantifications of noise, which suggested that the noise level was on the 10 μ V-scale. Both devices tested provided similar values of noise over the three measures, which was expected because the devices had similar transconductance and response time characteristics. The capability of the novel noise quantifications was supported by their comparisons to the standard methodology of measuring device noise.

The research supports the motivations to utilise OECTs for electrophysiological applications. To further improve performance, the parameters that affect OECT noise should be investigated. Such parameters include the material of the active layer, the architecture of the interconnects and the biases applied in device operation.

5. ORGANIC ELECTROCHEMICAL TRANSISTOR COMMON-SOURCE AMPLIFIER FOR ELECTROPHYSIOLOGICAL MEASUREMENTS

This research was first published on the 12th June 2021 in *Advanced Functional Materials* as an open access article with a CC BY 4.0 Creative Commons Attribution License. Presented here is an adaption of the work.

Tyrrell, J. E., Petkos, K., Drakakis, E. M., Boutelle, M. G., Campbell, A. J., Organic Electrochemical Transistor Common-Source Amplifier for Electrophysiological Measurements. *Adv. Funct. Mater.* 2021, 31, 2103385.

This research is dedicated to the memory of Professor Alasdair J. Campbell.

This research was supervised by Professor A. J. Campbell, Professor M. G. Boutelle and Professor E. M. Drakakis. Dr. K. Petkos physically constructed the amplifier circuits, collected a subset of the experimental amplifier data and verified the data analysis of the experimental amplifier data.

5.1. Introduction

Amplifier topologies play a central role in signal processing, and such circuits utilise transistors. Previous investigations into the use of OECTs as bioelectronic circuit components resulted in the development of linear and differential amplifiers [162, 258]. The investigations into using an OECT as the amplifying component in a linear amplifier have primarily considered connecting the device in series with a load resistor, where the voltage gain was determined and compared for a range of load resistances [53]. However, it is not necessarily convenient to physically vary the load resistor. An alternative method is to vary a DC bias that is applied to an AC gate voltage input and thus translate where the amplification occurs on the amplifier transfer curve. Such amplification modulation can be achieved with the common-source amplifier circuit topology. In addition, previous investigations have not given characterisations of the linear amplifier figures of merit such as those associated with distortion effects.

In this research, the implementation of OECTs into common-source amplifier circuits was investigated. Using interdigitated-electrode OECT characteristics, conditions on the voltages and resistances used in the common-source amplifier circuit were identified. It was found that the OECTs had the capacity to be utilised in the circuit. The linear amplifier circuit was then characterised with simulations and physical measurements with an emphasis on determining the performance parameters described by the figures of merit

of total-harmonic and intermodulation distortions, gain, input-referred noise, and bandwidth. The circuit was simulated through the formulation of an equation for transistor operation which showed a good fit to transistor characteristics across the linear, nonlinear, and saturation regimes. Pre-recorded electrophysiological signals of spreading depolarisations (SDs), ECoG, and EMG fasciculations were inputted at the gate electrode and amplified using the circuit.

5.2. Amplifier Fabrication, Characterisation, Formulation and Application

5.2.1 Fabrication, Circuit Topology and Characterisation

The architecture and material structure of the organic electrochemical transistors were the same as those presented in section 4, which used fabrication methods described in section 3. Comb and spiral interdigitated electrode geometries were used, each with two sizes. The resulting four geometries of the active area are described in table 4.1. The devices were constructed with interconnects of an array geometry. The devices were divided into those with an interconnect thickness of 200 nm and an active layer of 70 nm or those similarly with thicknesses of 300 nm and 35 nm, respectively. In total there were eight variations of OECT geometry initially considered in this investigation. The electrodes were composed of gold with a chromium adhesive layer and were fabricated on a 125 μm PET substrate. An encapsulation layer of SU-8 was coated with a thickness of 1 μm . The active layer consisted of the organic conducting polymer PEDOT:PSS with EG and DBSA additives (PED). Optical micrographs of the OECT source and drain electrode, encapsulation, and active layers are shown in figure 5.1.

The OECT common-source linear amplifier circuit topology is shown in figure 5.2. The amplifier is powered by a supply voltage, V_{DD} , which is used to amplify an input voltage, V_{IN} . The potential divider circuit formed with V_{DD} , R_1 and R_2 then provides a tuneable DC component to V_{AC}^{IN} , resulting in the input gate-ground voltage to the OECT. This allows the selection of the region of amplification within the OECT and thus the output gain and linearity. The supply voltage also provides a potential difference to the drain resistor, R_D , the OECT and the source resistor, R_S , in parallel with the bypass capacitor, C_1 . The amplifier gain and the range of amplifiable gate voltage inputs are dependent on the values of the source and drain resistors and the supply voltage. The bypass capacitor acts to suppress high-frequency signals that are present in the AC voltage component of the potential difference across the source resistor, drain resistor, and OECT.

In addition to the voltage divider, there is typically a contribution to the gate-ground voltage at the OECT gate from an input capacitor, which removes the DC component of V_{IN} and allows the DC gate component to be controlled entirely through varying resistors

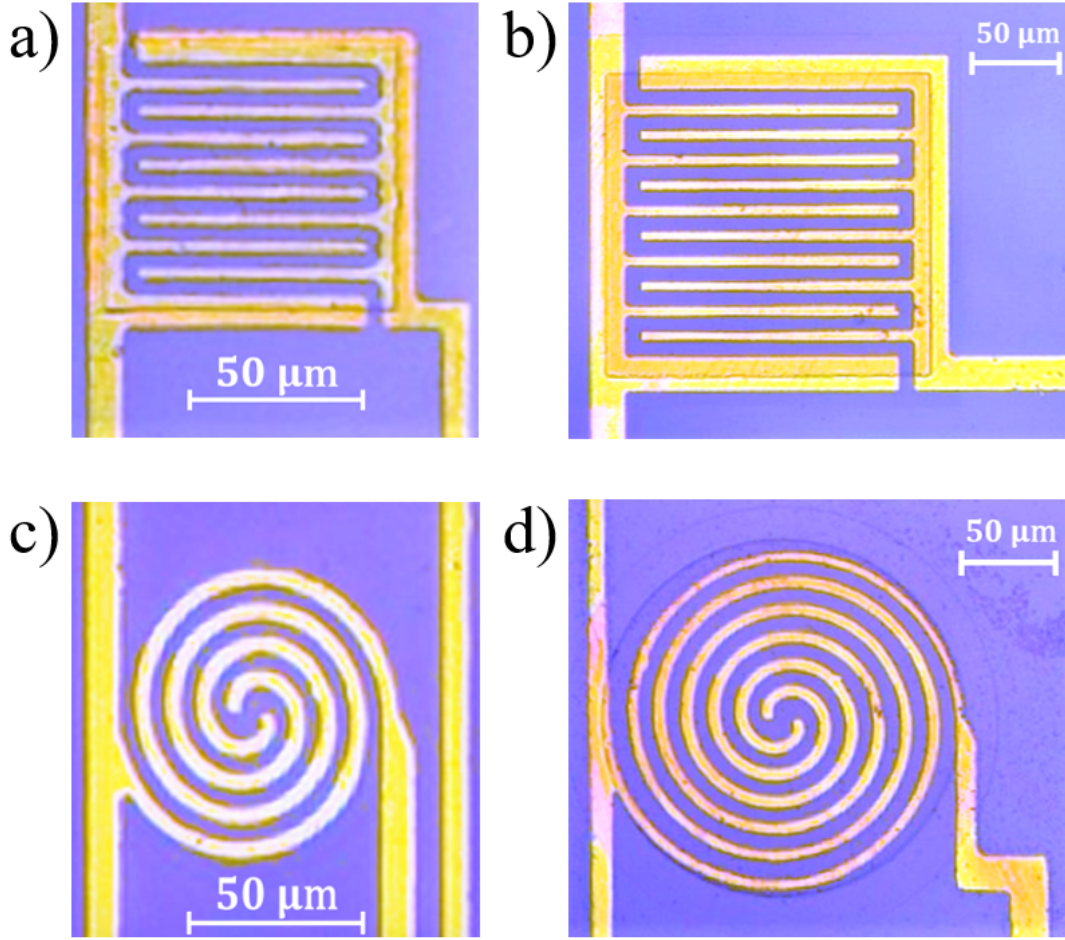


Figure 5.1: Optical micrographs of the OEETs' interdigitated source and drain electrodes for the architectures of the a) Small comb, b) Large comb, c) Small spiral and d) Large spiral.

R_1 and R_2 . This capacitor also acts as a high-pass filter to AC voltages originating from V_{IN} . However, this investigation sought to build and fully characterise a DC-coupled amplifier that could amplify a wide range of frequencies characteristic of bioelectric inputs. As such, the attenuation of low-frequency voltages from the input capacitor was not desired. Therefore, the use of an input capacitor, and thus the removal of low-frequency voltages, was avoided by using a waveform generator to produce V_{IN} , where its output voltage was equivalent to that otherwise produced if the capacitor was present. As a result, the amplifying system developed in this work was completely DC-coupled, allowing the study of its behaviour in a wide frequency range (from DC up to the 10 kHz-scale).

To characterise the linear amplifier, data acquisition was performed using the

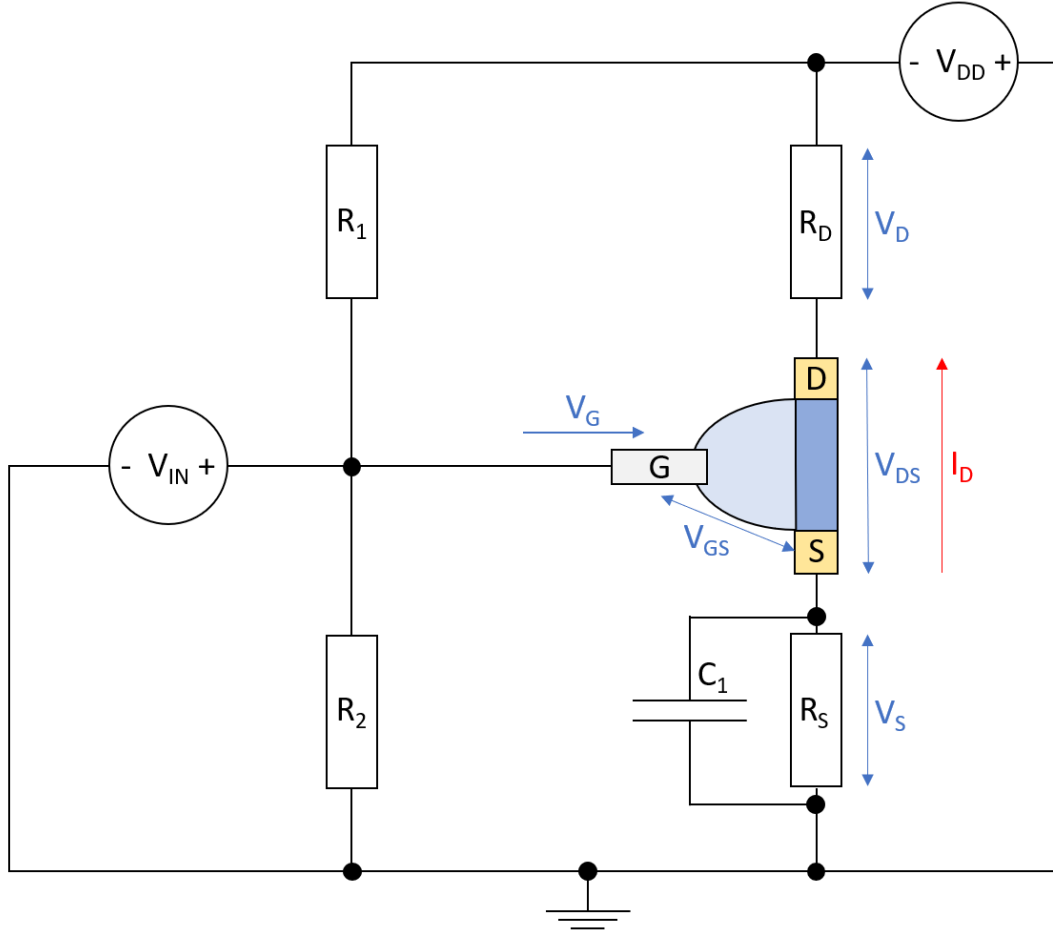


Figure 5.2: Common source linear amplifier circuit using input voltage V_{IN} , potential divider resistors, R_1 and R_2 , source resistor, R_S , drain resistor, R_D , bypass capacitor, C_1 , and supply voltage V_{DD} . The OECT is represented by the three-terminal device with gate, source, and drain labelled G, S, and D, respectively, through which a total drain current, I_D , flows.

Labchart software with PowerLab 16/35. An AC coupling filter was implemented within the LabChart software on all characterisations. For the measurement of total harmonic distortion and frequency response, the Agilent 33220A was used as the waveform generator. For the intermodulation distortion measurements, two GW INSTEK AFG-2125 waveform generators were used. For bioelectric testing, the gate electrode of the OECT in the linear amplifier configuration was connected to a Keysight 33220a waveform generator. The waveform generator was pre-loaded with electrophysiological signals and voltage attenuators were used to reduce the magnitude of the output voltage

below the minimum of 20 mV. The voltages were sampled at 100 kHz and the voltage attenuators were also utilised in amplifier characterisations when required.

5.2.2 Amplifier Formulation

The drain current of the OECT is determined by the load-line of the amplifier, which describes the dependence of drain current on the circuit topology. It can be shown that the total drain current, I_D^{TOT} , which is the summation of DC current, I_D^{DC} , and AC current, I_D^{AD} , is given by

$$I_D^{TOT} = \frac{V_{DD} - V_{DS} - I_D^{DC} \left(R_S - \left[R_S \parallel \frac{1}{2j\pi f C_1} \right] \right)}{R_D + \left[R_S \parallel \frac{1}{2j\pi f C_1} \right]} , \quad (5.1)$$

for which

$$\left| \left[R_S \parallel \frac{1}{2j\pi f C_1} \right] \right| = \frac{R_S}{\sqrt{1 + (2\pi R_S C_1 f_{IN})^2}} , \quad (5.2)$$

where $\left[R_S \parallel \frac{1}{2j\pi f C_1} \right]$ is the impedance of the resistor and capacitor in parallel and is dependent on the input frequency to the bypass capacitor, f_{IN} . Given that $2\pi R_S C_1 f_{IN} \ll 1$, then $\left| \left[R_S \parallel \frac{1}{2j\pi f C_1} \right] \right| \approx R_S$ and the load-line in equation 5.1 reduces to the DC load-line. In the regime where $2\pi R_S C_1 f_{IN} \gg 1$, then $\left| \left[R_S \parallel \frac{1}{2j\pi f C_1} \right] \right| \approx 0$ and equation 5.1 reduces to the AC load-line. In this investigation, the bypass capacitor acted to reduce noise from higher frequencies. However, in all constructed circuit topologies, the values of R_S and C_1 were set such that $2\pi R_S C_1 f_{IN} \ll 1$ at all frequencies used in the amplifier characterisation and in the *in vitro* amplification of bioelectric signals. Therefore, consideration of only the DC load-line provided approximate insights into amplifier behaviour for low-frequency AC voltage inputs. As such, application of only the DC load line is considered in the following analyses. Furthermore, the total drain current in this approximation, which is the summation of DC and low-frequency AC components, is subsequently denoted as I_D . The DC load-line, as reduced from equation 5.1, describes the distribution of supply voltage across the OECT, source resistor, and drain resistor:

$$V_{DD} = V_{DS} + I_D R_S + I_D R_D . \quad (5.3)$$

Gate voltage relations in the circuit topology presented in 5.2 are described by

$$V_{GS} = V_{GGr} - V_{SGr} = V_{IN}^{AC} + \left(\frac{R_2}{R_1 + R_2} \right) V_{DD} - I_D (V_{GS}, V_{DS}) R_S , \quad (5.4)$$

where V_{GS} is the gate-source voltage, V_{DS} is the drain-source voltage, V_{GGr} is the gate-ground voltage, V_{SGr} is the source-ground voltage and all other parameters have been previously described.

As shown in equation 5.4, the gate-source potential difference is dependent on the drain current of the OECT, which itself is dependent on gate-source voltage. As the negative gate-ground voltage increases, the drain current increases and thus the potential difference across the source resistor also increases (both decrease in magnitude toward zero). Thus, an increase in V_{GGr} leads to an increase in V_{SGr} , which stabilises V_{GS} . As the gate-ground voltage increases, the potential difference across the drain resistor also increases and the drain-source voltage decreases. However, if the device is operating in the saturation regime, then changes in drain-source voltage will not induce any further changes in drain current than those already caused by gate voltage variations. As such, the device should be operated in the saturation regime for amplification. Furthermore, short-channel effects were not desirable and were not observed.

The overlap of the load-line with the saturation region of the output characteristics shows the range of gate-source voltages where the device can be operated. As shown by the output characteristics, positive gate-source voltages are required to operate the device in this regime, where $V_{GS} - V_{DS} \geq V_P$ for OECT pinch-off voltage V_P . A condition set on the maximum difference between the applied gate-source and drain-source voltages is the hydrolysis level, which occurs at approximately 1.2 V. As the value of the supply voltage, V_{DD} , is required to be negative to operate the OECT in the saturation regime, the range of applied voltages is further restricted. This is because the voltage divider circuit can only apply a negative DC bias to the input AC signal. For negative gate-ground voltages to correspond to positive gate-source voltages, it can be seen from equation 5.4 that, in approximating low-frequency AC signals with DC behaviour, the condition $V_{SGr} \equiv I_D R_S < V_{GGr}$ is required. With negative current values in the saturation regime, the source resistor translates negative gate-ground inputs into positive gate-source voltages.

The output voltage, V_{OUT} , was defined to be the drain-source voltage across the OECT, $V_{OUT} \equiv V_{DS}$. The drain-ground voltage was also considered; however, V_{DS} decreases as $V_{SGr} \equiv I_D R_S$ increases, as can be seen on the load-line output characteristics. Therefore, the opposing voltages result in smaller changes, and thus a smaller gain, relative to considering just V_{DS} . The gain was defined as the fraction of output voltage range to gate-ground voltage input range, $\Delta V_{OUT}/\Delta V_{GGr}$. The gain is dependent on $R_S + R_D$ and has representation in the gradient of the load-line. As the gradient decreases in magnitude, there is a greater change in V_{DS} for a given change in V_{GS} . However, given the hydrolysis limit, the range of gate-source voltages that the load-line intersects in the saturation region decreases and thus the input range decreases. Therefore, there is a trade-off between gate input range and gain.

5.2.3 Applications of the OECT Amplifier in Neurotechnology

For clinical applications, the amplifier could be implemented within an electrophysiological recording device as a component that measures and amplifies bioelectric activity. Given that the amplifier is completely DC-coupled, as it was in this investigation, it could potentially be used in ECoG applications where the device directly interfaces the cortical surface. The cerebrospinal fluid would act as the OECT electrolyte and the AC voltage produced by the neuronal ionic fluxes would be superposed onto the DC potential of the potential divider and transduced into a current through the OECT. This is given that the DC potential of the cerebrospinal fluid is shifted to that of the potential divider, which could be facilitated using a voltage reference element. It has been previously shown that when applying a constant low voltage for the operation of an OECT to measure activity in a neuronal volume, there has been no measurable evoked neuronal activity or disturbance of the extracellular environment [65]. The neuronal activity would then be amplified by the circuit, producing an output voltage.

In addition to measuring and amplifying bioelectric activity, the circuit could be used to amplify a bioelectric signal measured from an electrode. The electrode's measured signal would be the V_{IN} and the low-voltage amplifier could be utilised local to the physiological environment due to its biocompatible properties. The circuit would need to use an electrolyte that is physically separated from the physiological environment to avoid the amplification of signals from other spatial locations. Alternatively, a solid-state replacement to the electrolyte could be used [125]. Such a replacement would also be needed if using multiple amplifiers taking electrode signals from a number of recording sites as each OECT would require independent gating.

Finally, the device could be used for providing a voltage output that describes the concentration of chemical species. The OECT active layer or gate electrode could be functionalised to respond to the presence of a particular species in the electrolyte. This could thus be applied to measuring and amplifying the changes in chemical concentrations of the different ionic species present in physiological electrolytes such as cerebrospinal fluid.

5.3. Results and Discussion

5.3.1 DC Load Line Analysis

Using the OECT output characteristics, values of V_{DD} , R_S , and R_D were iterated to find combinations that satisfied all OECT linear amplifier criteria. The iteration varied the supply voltage between -3.0 V to -1.0 V in 0.1 V steps and the source and drain resistors between $1\ \Omega$ to $750\ \Omega$ in $10\ \Omega$ steps. Each combination (of 112500) resulted in a DC load line passing through the output characteristics, and the analysis was applied to a number of

transistors of each OECT geometry. For combinations that satisfied the criteria, the values of the range of input gate-ground voltages and the corresponding changes in drain-source voltage were found. For each OECT, the values of V_{DD} , R_S , and R_D which maximised the gain were identified and the associated gate-ground range was found. As such, for OECTs of a given geometry, the mean and standard deviation values were found for the percentage of successful parameter combinations, maximum gain values, and the associated gate-ground ranges. Results of this DC load-line analysis are shown in table 5.1 alongside the mean and standard deviation of the pinch-off voltage for each OECT geometry. Although the analysis was restricted by the voltage range and resolution of the output characteristics, it was still indicative of the suitability of the different OECT types to be applied to the linear amplifier circuit. Given in table 5.2 are the alternative hypotheses and p-values of one-tailed Welch's t-tests for comparing the results of the different geometries.

Device	Success % (2 d.p.)	V_{GGr} Range (mV)	Gain (3 d.p.)	OECT V_P (mV)
SS 35	1.20 ± 0.34	199 ± 19	2.105 ± 0.234	511 ± 21
SS 70	0.09 ± 0.12	293 ± 64	1.067 ± 0.276	626 ± 30
LS 35	2.98 ± 1.18	201 ± 6	2.191 ± 0.142	514 ± 12
LS 70	0.09 ± 0.05	267 ± 32	1.227 ± 0.144	611 ± 44
SC 35	0.22 ± 0.35	264 ± 40	1.380 ± 0.292	543 ± 38
SC 70	0.02 ± 0.01	330 ± 56	0.946 ± 0.175	601 ± 15
LC 35	6.02 ± 4.44	167 ± 25	3.124 ± 0.478	445 ± 39
LC 70	0.01 ± 0.01	328 ± 52	0.855 ± 0.143	642 ± 26

Table 5.1: Mean and standard deviation values of performance characteristics of a common source linear amplifier circuit using an OECT transistor for eight OECT geometry configurations. Statistical results are given in table 5.2

Supported by table 5.2, it was found that the 35 nm devices provided significantly greater gain values and were significantly more likely to satisfy the implementation conditions within the iterated circuit parameters. The 70 nm devices had significantly greater gate-ground input ranges; however, the gate input range for the 35 nm devices was still significantly greater than the limits of extracellular bioelectric voltages. As the pinch-off voltage decreased, which was observed in the 35 nm devices relative to the 70 nm devices, the gain increased. For a given load-line with defined gradient and fixed gain, the gate-source voltage range would increase if the device entered the saturation region at a lower magnitude of drain-source voltage. Similarly, for a fixed gate-source voltage range, the drain-source voltage range, and thus gain, would increase given saturation at a lower magnitude of drain-source voltage. Such performance improvements require lower

5 ORGANIC ELECTROCHEMICAL TRANSISTOR COMMON-SOURCE AMPLIFIER FOR ELECTROPHYSIOLOGICAL MEASUREMENTS

Device Number for Each Device Type							
SS 35	SS 70	LS 35	LS 70	SC 35	SC 70	LC 35	LC 70
9	12	11	10	11	6	11	10
Success %							
Alt. Hyp.	SS 35 > SS 70		LS 35 > LS 70		SC 35 > SC 70		LC 35 > LC 70
p-value	3.29×10^{-6}		7.63×10^{-6}		4.84×10^{-2}		4.23×10^{-4}
V_{GGr} Range							
Alt. Hyp.	SS 35 < SS 70		LS 35 < LS 70		SC 35 < SC 70		LC 35 < LC 70
p-value	2.18×10^{-4}		6.97×10^{-5}		2.36×10^{-2}		3.67×10^{-7}
Gain							
Alt. Hyp.	SS 35 > SS 70		LS 35 > LS 70		SC 35 > SC 70		LC 35 > LC 70
p-value	2.27×10^{-8}		4.99×10^{-12}		1.42×10^{-3}		9.24×10^{-7}

Table 5.2: *Alternative hypotheses and p-values of Welch’s t-tests for the comparison of linear amplifier characteristics as given in table 5.1.*

values of pinch-off voltage, which has been shown to be proportional to the thickness of the organic active layer [37]. The pinch-off voltage can also be modulated through varying other OECT parameters including interconnect resistance. In a systematic investigation of varying interdigitated electrode parameters for the ‘comb’ style and thus varying the channel area, it was found that the pinch-off (or threshold) voltage decreased by decreasing the number and thickness of the ‘comb fingers’ and by increasing the channel length [98]. The channel thickness dependence suggests that the gain of an OECT common-source linear amplifier can be increased using a thinner charge transport layer. It has also been shown that the OECT response time, which determines the amplifier bandwidth, is proportional to active layer thickness [37]. Therefore, in decreasing the thickness, it is further suggested that the gain and bandwidth can be simultaneously increased under this amplifier configuration. However, a thinner active layer would result in greater amplifier noise. These insights show that a common-source amplifier topology, as implemented for bioelectric recordings using OECTs in this configuration, would have to consider such trade-offs in performance parameters for its optimisation towards a given electrophysiological modality.

It was found that the gate-source voltage range that frequently satisfied the conditions were $0.1 \text{ V} < V_{GS} < 0.2 \text{ V}$. In this range, the transfer characteristics showed that there was an approximately linear relationship between drain current and gate voltage. This allowed a further analysis to determine the gain values if the gate-source voltage range

was reduced from 100 mV to the mV-scale, as suitable for a range of bioelectric signals. The relationship between the original gate-source voltage range δ with gain G and the new range $\delta' = \gamma\delta$, $\gamma > 0$ with gain of G' , can be analytically determined when assuming a linear current-voltage relationship in the range of δ . The relationship is derived with the aid of figure 5.3.

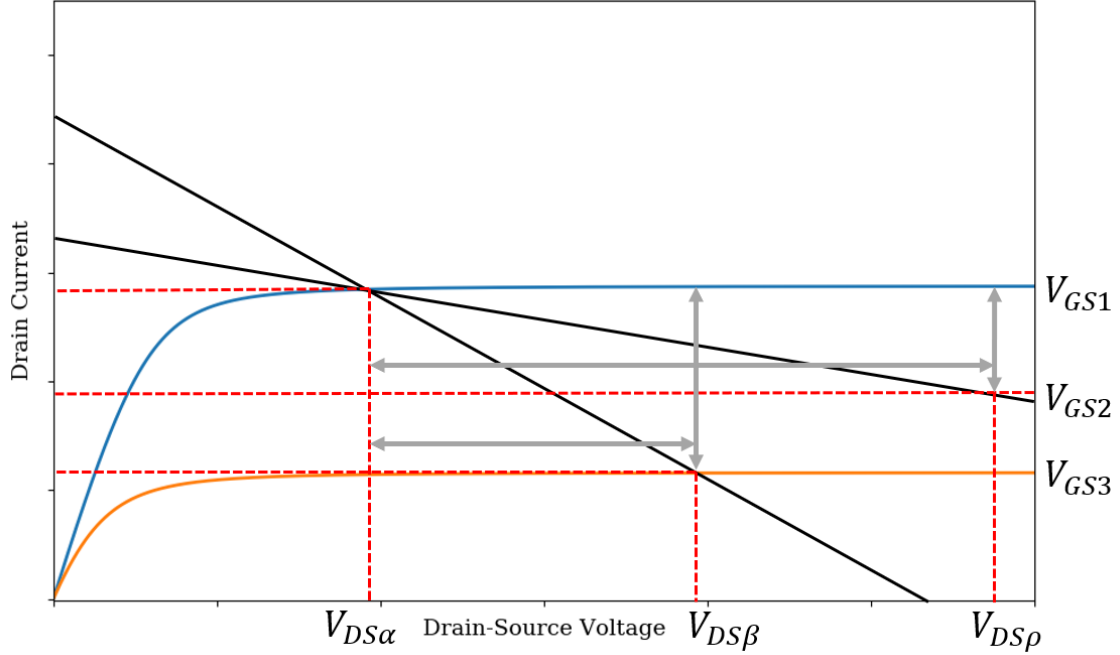


Figure 5.3: Diagram showing output characteristics of a transistor with two DC load lines. One has a greater gate-source voltage but a lower drain-source voltage (and thus gain) and the other has a lower gate-source voltage but a greater drain-source voltage.

In considering the output characteristics with the load-line as shown in figure 5.3, the device is kept within the hydrolysis limit given that

$$V_{GS3} - V_{DS\beta} = V_{GS2} - V_{DS\rho} = 1.2 \quad . \quad (5.5)$$

A fraction of gate voltage range, γ , is defined as

$$V_{GS2} - V_{GS1} = \gamma(V_{GS3} - V_{GS1}) \quad , \quad (5.6)$$

for $\gamma > 0$. It is shown that the fraction in gate-source voltage range is equivalent to the fraction in gate-ground voltage given that only the drain resistor is increased to reduce the load line gradient (the source resistor is left constant) and the OECT transfer curve is linear between $V_{GS1} \leq V_{GS} \leq V_{GS3}$. In using $V_{GS} = V_{GGr} - I_D(V_{GS})R_S$, it is found that

$$\gamma = \frac{V_{GS2} - V_{GS1}}{V_{GS3} - V_{GS1}} = \frac{(V_{GGr2} - V_{GGr1}) - R_S (I_D(V_{GS2}) - I_D(V_{GS1}))}{(V_{GGr3} - V_{GGr1}) - R_S (I_D(V_{GS3}) - I_D(V_{GS1}))} . \quad (5.7)$$

For

$$\gamma = \frac{V_{GS2} - V_{GS1}}{V_{GS3} - V_{GS1}} = \frac{V_{GGr2} - V_{GGr1}}{V_{GGr3} - V_{GGr1}} , \quad (5.8)$$

it is required that

$$I_D(V_{GS2}) - I_D(V_{GS1}) = \gamma (I_D(V_{GS3}) - I_D(V_{GS1})) , \quad (5.9)$$

which is satisfied if the source resistor is constant and the OECT transfer curve is linear between $V_{GS1} \leq V_{GS} \leq V_{GS3}$. Given the linearity, the measured gain is given by

$$G = \frac{V_{DS\beta} - V_{DS\alpha}}{V_{GGr3} - V_{GGr1}} = \frac{V_{DS\beta} - V_{DS\alpha}}{\kappa(V_{GS3} - V_{GS1})} , \quad (5.10)$$

where, by equation 5.8,

$$\kappa = \frac{V_{GGr2} - V_{GGr1}}{V_{GS2} - V_{GS1}} . \quad (5.11)$$

Using equation 5.5 with equation 5.6, it is found that

$$V_{DS\rho} = V_{GS2} - V_{GS3} + V_{DS\beta} = (\gamma - 1)(V_{GS3} - V_{GS1}) + V_{DS\beta} . \quad (5.12)$$

The G' is given by

$$G' = \frac{V_{DS\rho} - V_{DS\alpha}}{V_{GGr2} - V_{GGr1}} = \frac{V_{DS\rho} - V_{DS\alpha}}{\gamma\kappa(V_{GS3} - V_{GS1})} . \quad (5.13)$$

Substituting equation 5.12 into equation 5.13 gives

$$G' = \frac{(\gamma - 1)(V_{GS3} - V_{GS1}) + V_{DS\beta} - V_{DS\alpha}}{\gamma\kappa(V_{GS3} - V_{GS1})} = \frac{\gamma - 1}{\gamma\kappa} + \frac{V_{DS\beta} - V_{DS\alpha}}{\gamma\kappa(V_{GS3} - V_{GS1})} . \quad (5.14)$$

Using the original gain G in equation 5.11, equation 5.14 can be given as

$$G' = \frac{\gamma - 1}{\gamma\kappa} + \frac{G}{\gamma} . \quad (5.15)$$

The analysis shows that the gain can be increased by orders of magnitude given that the range of input gate voltages is reduced, highlighting a trade-off between input voltage range and output gain. In this investigation, the output characteristics gave a gate-source range of $\delta = 100$ mV with a gain value of $G \approx -2$. For a gate-source voltage range of 2 mV, then $\gamma = \delta'/\delta = 0.02$, predicting a gain of $G' \approx -126$ with $\kappa = 2$. In limiting the gate-source voltage range, the load line gradient decreases in magnitude. As such, the drain resistance values must increase to follow the relation derived here. In turn, the $|V_{DD}|$ must increase to maintain device operation in the saturation regime.

5.3.2 Simulation of OECT and Circuit Behaviour

An equation was formulated which provides a good fit to transistor output characteristics across the linear, nonlinear, and saturation regimes. This equation was developed and utilised because it provided continuity across the three regimes and thus eliminated any discontinuity that would occur from switching between equations at regime boundaries. Furthermore, an equation of this form had not been identified in previous literature and so the capabilities of this novel equation were investigated.

To derive the equation, the properties of the output characteristics were considered. The equation needed to pass through the origin and have a linear region that tended to an asymptote with a monotonic intermediary region. As such, the product of a linear variable of zero intercept with a sigmoid function was considered. It was found that the translated arctangent function provided suitable properties. Therefore, the product was parameterised with ρ and λ as

$$f(x) = \rho x \left[\arctan(\lambda x) - \frac{\pi}{2} \right] . \quad (5.16)$$

To translate equation 5.16 from $y = f(x)$ to $y' = f(x - \mu) + \nu$ whilst maintaining $y' = x = 0$, it is clear that ν is constrained as $\nu = -f(-\mu)$, and thus $y' = f(x - \mu) - f(-\mu)$. Therefore,

$$y' = f(x - \mu) - f(-\mu) = \rho(x - \mu) \left[\arctan(\lambda(x - \mu)) - \frac{\pi}{2} \right] + \rho\mu \left[\arctan(-\lambda\mu) - \frac{\pi}{2} \right] . \quad (5.17)$$

The variables and parameters in equation 5.17 were associated with OECT characteristics. The most appropriate relations for p-type depletion mode characteristics found that $y' = I_D$, $x = V_{DS}$, $\rho = -G/3$, and $\mu = \alpha V_{GS} + \beta V_P$ with $\alpha > 0$ and $\lambda < 0$. Therefore, the equation states that the drain current, I_D , varies as

$$I_D = -\frac{G}{3} \left[(V_{DS} - (\alpha V_{GS} + \beta V_P)) \left[\arctan(\lambda(V_{DS} - (\alpha V_{GS} + \beta V_P))) - \frac{\pi}{2} \right] + (\alpha V_{GS} + \beta V_P) \left[\arctan(-\lambda(\alpha V_{GS} + \beta V_P)) - \frac{\pi}{2} \right] \right] , \quad (5.18)$$

where G is the OECT conductance, V_{DS} is the drain-source voltage, V_{GS} is the gate-source voltage, V_P is the pinch-off voltage, α and β are dimensionless parameters, λ is a parameter with units of inverse voltage, and α , β and λ are identified through applying a best-fit to the output characteristics. Using equation 5.18, the transconductance of a modelled transistor at a constant drain voltage is given as

$$g_m = \left. \frac{\partial I_D}{\partial V_{GS}} \right|_{V_{DS}} = \frac{G\alpha}{3} \left[\arctan(\lambda(V_{DS} - (\alpha V_{GS} + \beta V_P))) - \arctan(-\lambda(\alpha V_{GS} + \beta V_P)) + \frac{V_{DS} - (\alpha V_{GS} + \beta V_P)}{\lambda(V_{DS} - (\alpha V_{GS} + \beta V_P))^2 + 1/\lambda} + \frac{\alpha V_{GS} + \beta V_P}{\lambda(\alpha V_{GS} + \beta V_P)^2 + 1/\lambda} \right] . \quad (5.19)$$

Temporal dynamics were also introduced by using the analyses from Bernards and Malliaras in which an exponential response in drain current was derived [37]. When assuming electronic transport time is much smaller than ionic transport time, the drain current can be described by

$$I_D(t + \delta t, V'_{GD}) \approx I_{D,SS}(t, V_{GD}) + \Delta I_{D,SS}(V'_{GD} - V_{GD})e^{(t+\delta t)/\tau} \quad , \quad (5.20)$$

where $I_{D,SS}$ is the steady-state drain current and τ is a response time constant which gives a 90% response time of $\tau \ln(10)$. The output, transfer, and transconductance-frequency characteristics as described by equation 5.18 are shown in figure 5.4a, 5.4b, and 5.4d, respectively, with the parameters of $G = 10$ mS, $V_P = 0.6$ V, $\tau = 43$ μ s (giving a 90% response time of 100 μ s), $\alpha = 1.2$, $\beta = -0.6$, and $\lambda = -3.5$ V⁻¹. A fitting of equation 5.18 was applied to the OECT output characteristics of an OECT with the 35 nm small spiral geometry, as presented in figure 5.4c. It was found that the OECT characteristics were reproduced with an accuracy sufficient for further utilisation.

Transistor characteristics can be modelled using equation 5.18. In p-type depletion mode devices, a negative drain-source voltage and a low gate-source voltage provides an on-state and increasing the gate-source voltage translates the device from an on-state to an off-state. Such characteristics can be modelled using the variables and parameters as described in equation 5.18, as shown in figure 5.5a. Similarly, the equation can model p-type enhancement mode devices, where, with a negative drain-source voltage, decreasing the gate-source voltage switches the device from an off-state to an on-state, as shown in figure 5.5b. Furthermore, n-type enhancement and depletion mode devices can be modelled using $\rho = G/3$, $V_{DS} \rightarrow -V_{DS}$, $\alpha < 0$, and $\lambda < 0$. In n-type depletion mode devices, the device is translated from an on-state to an off-state by decreasing the gate-source voltage whilst maintaining a positive drain-source voltage, as shown in figure 5.5c. This modified equation can also model n-type enhancement mode devices, where a positive drain-source voltage and a low gate-source voltage provides an off-state and increasing the gate-source voltage switches the device from an off-state to an on-state, as shown in figure 5.5d. The equation can be used to simulate the approximate dynamics of transistors under varying inputs such as the simultaneous changes in drain-source and gate-source voltages. Furthermore, circuits involving the use of transistors can be approximately simulated.

The effects of varying the α , β and λ parameters of equation 5.18, as shown in figure 5.6, were investigated and were found to be physically interpretable. A greater α value results in a smaller gate-source voltage range needed to turn off the device. Consequently, this makes the transconductance distribution narrower and of higher peak value. It has been suggested that such a scaling is possible by decreasing the width of the Gaussian density of states [75]. The β value controlled the level of doping for a given gate-source

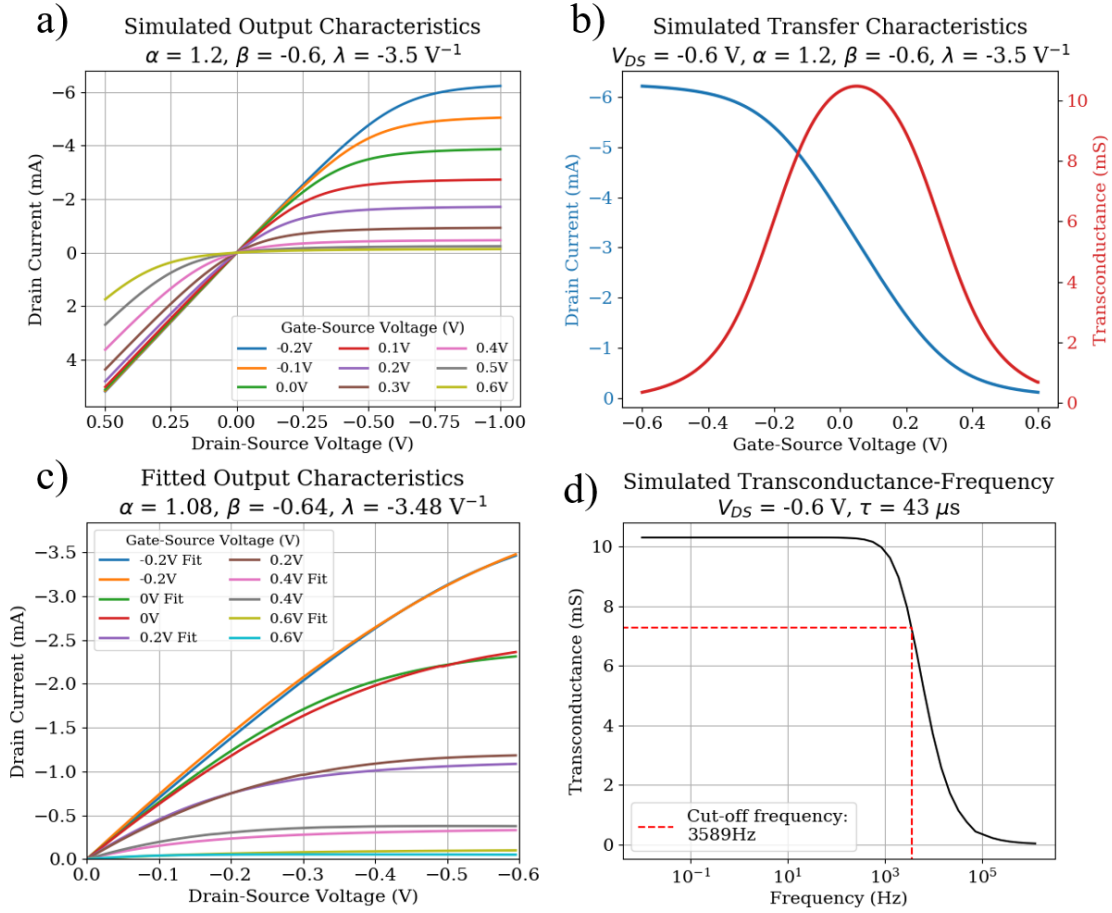


Figure 5.4: a) Simulated OEET output characteristics using equation 5.18 with $G = 10 \text{ mS}$, $V_P = 0.6 \text{ V}$, $\alpha = 1.2$, $\beta = -0.6$, and $\lambda = -3.5 \text{ V}^{-1}$, b) transfer characteristics as associated with (a), c) fitted output characteristics for the 35 nm small spiral OEET, with $G = 6.56 \text{ mS}$ and $V_P = 0.51 \text{ V}$, for $V_{DS} < 0$ giving fitting parameters of $\alpha = 1.08$, $\beta = -0.64$ and $\lambda = -3.48 \text{ V}^{-1}$, d) transconductance-frequency relationship for an OEET with a 90% response time of $100 \mu\text{s}$ and associated with (a) and (b).

and drain-source voltage. A lower λ value results in two effects. On the p-type depletion transfer curve, the transition width between the on- and off- states and the de-doping region becomes shorter and the de-doping behaviour becomes more linear. Additionally, the intervals on the output curve become more equally spaced and the transconductance peak broadens.

With equation 5.18 showing capability to reproduce the features of the output characteristics, an approximate amplifier transfer curve was determined. With the circuit parameters which provided maximum gain as found in the DC load-line analysis, the

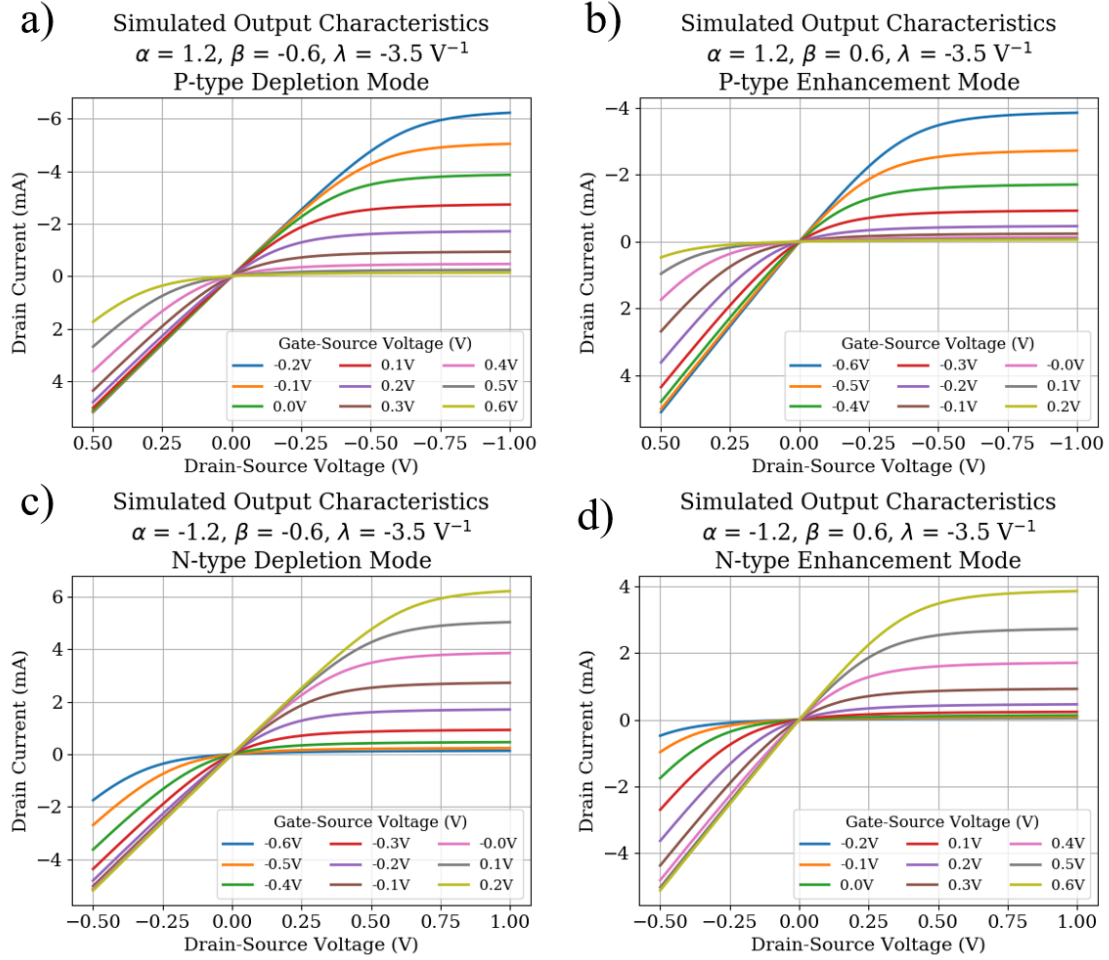


Figure 5.5: Modelled output characteristics of the transistor types: a) p-type depletion mode using equation 5.18 with $\alpha = 1.2$, $\beta = -0.6$ and $\lambda = -3.5 \text{ V}^{-1}$, b) p-type enhancement mode with $\alpha = 1.2$, $\beta = 0.6$ and $\lambda = -3.5 \text{ V}^{-1}$, c) n-type depletion mode using equation 5.18, modified by using its additive inverse and by replacing V_{DS} with $-V_{DS}$, with $\alpha = -1.2$, $\beta = -0.6$ and $\lambda = -3.5 \text{ V}^{-1}$, d) n-type enhancement mode using the equation as described in c) with $\alpha = -1.2$, $\beta = 0.6$ and $\lambda = -3.5 \text{ V}^{-1}$.

gate-ground voltage input and corresponding drain-source output voltages were calculated. Analogous to the transconductance, the gain was found by taking the derivative of the amplifier transfer curve. To find the DC transfer curve, equation 5.3 and

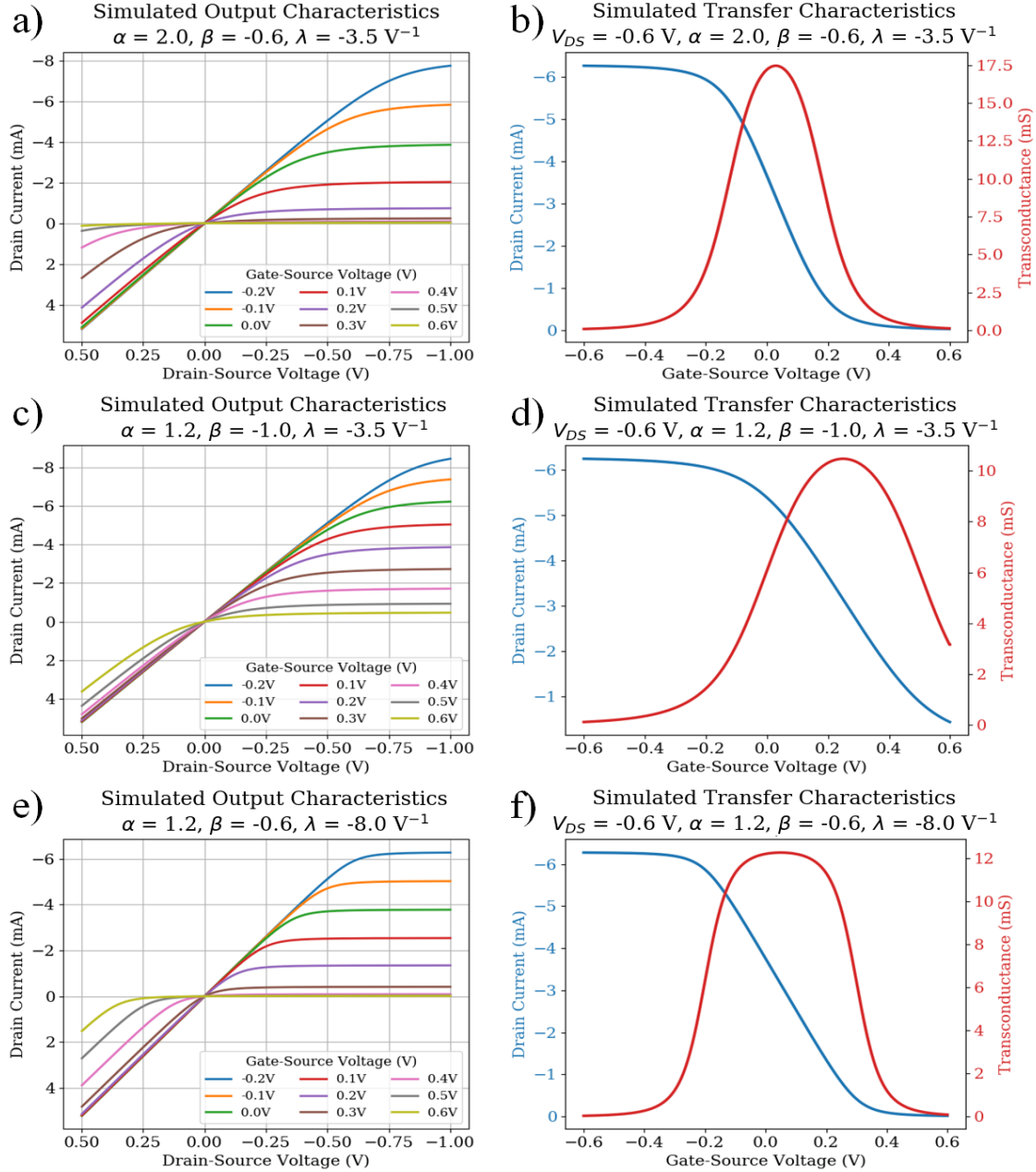


Figure 5.6: The effect on output and transfer characteristics of varying the α , β and λ parameters of equation 5.18 with $G = 10 \text{ mS}$ and $V_P = 0.6 \text{ V}$. The variations are compared to the characteristics using $\alpha = 1.2$, $\beta = -0.6$ and $\lambda = -3.5 \text{ V}^{-1}$ illustrated in figure 5.4.

equation 5.18 were computationally solved to find values of V_{GS} and V_{DS} :

$$\begin{aligned} \frac{V_{DD} - V_{DS}}{R_S + R_D} + \frac{G}{3} \left[(V_{DS} - (\alpha V_{GS} + \beta V_P)) \left[\arctan(\lambda (V_{DS} - (\alpha V_{GS} + \beta V_P))) - \frac{\pi}{2} \right] \right. \\ \left. + (\alpha V_{GS} + \beta V_P) \left[\arctan(-\lambda (\alpha V_{GS} + \beta V_P)) - \frac{\pi}{2} \right] \right] = 0 \quad . \end{aligned} \quad (5.21)$$

To computationally solve equation 5.21 to find the combinations of V_{GS} and V_{DS} , the drain-source voltage was iterated from $V_{DS} = V_{DD}$ to $V_{DS} = 0$ with a resolution of $100 \mu\text{V}$. For each drain-source voltage, the equation was calculated for gate voltages at a resolution of $10 \mu\text{V}$. A linear interpolation was performed between the two gate-source voltages for which there was a sign change. Given I_D and V_{GS} , the value of V_{GGr} was found using equation 5.4 with the value of the source resistor. The relationship between gate-source voltage and gate-ground voltage was approximately linear. The resulting combinations of V_{GGr} and V_{DS} described the amplifier transfer curve for DC amplifier behaviour.

To determine the output voltage of the amplifier simulation given a gate-ground voltage input, there were two methods that were developed which provided varying accuracy. In method 1, the closest gate-ground voltage in the amplifier transfer curve, V_{GGr}^{AMP} , was found for each gate-ground input voltage, V_{GGr}^{IN} . The V_{DS} as associated with V_{GGr}^{AMP} in the amplifier transfer curve was then assigned as the output voltage, V_{DS}^{OUT} . Therefore, the accuracy of the output voltage was limited by the $100 \mu\text{V}$ resolution used to calculate the amplifier transfer curve. In method 2, the input gate voltage was compared to the two closest gate-ground voltages in the amplifier transfer, $V_{GGr,1}^{AMP}$ and $V_{GGr,2}^{AMP}$, such that $V_{GGr,1}^{AMP} < V_{GGr}^{IN} < V_{GGr,2}^{AMP}$. The associated drain-source voltages, $V_{DS,1}^{AMP}$ and $V_{DS,2}^{AMP}$, were then identified and the drain-source voltage associated with V_{GGr}^{IN} , V_{DS}^{OUT} , was considered to satisfy $V_{DS,1}^{AMP} < V_{DS}^{OUT} < V_{DS,2}^{AMP}$. Assuming a linear behaviour in the range, the V_{DS}^{OUT} was calculated through

$$\frac{V_{GGr}^{IN} - V_{GGr,1}^{AMP}}{V_{GGr,2}^{AMP} - V_{GGr,1}^{AMP}} = \frac{V_{DS}^{OUT} - V_{DS,1}^{AMP}}{V_{DS,2}^{AMP} - V_{DS,1}^{AMP}} \quad (5.22)$$

Although the calculation of V_{DS}^{OUT} was still limited by the resolution, the interpolation provided a higher accuracy of output voltage compared to that of method 1.

The temporal response of the amplifier was thought to be limited only by that of the OEET. Inspired by Bernards and Malliaras, to simulate the approximate temporal response of the linear amplifier, the output voltage was defined as

$$V_{OUT}(t + \delta t, V_{GGr}') = V_{OUT}(t, V_{GGr}) + \Delta V_{OUT}(V_{GGr}' - V_{GGr})e^{-(t+\delta t)/\tau} \quad (5.23)$$

where V_{OUT} is the DC output voltage across the OEET, V_{GGr} is the gate-ground voltage and τ is the OEET response time constant [37]. This provided a comparison between the noise-free approximation and the physical measurement of the amplifier response during the characterisations.

To demonstrate the effects of varying resistor R_2 on the amplifier circuit, the output voltage was simulated with a 1 Hz, 20 mV amplitude sinusoidal gate input. The response of this simulation is shown in figures 5.7b and 5.7d, which illustrated that as the gate-ground

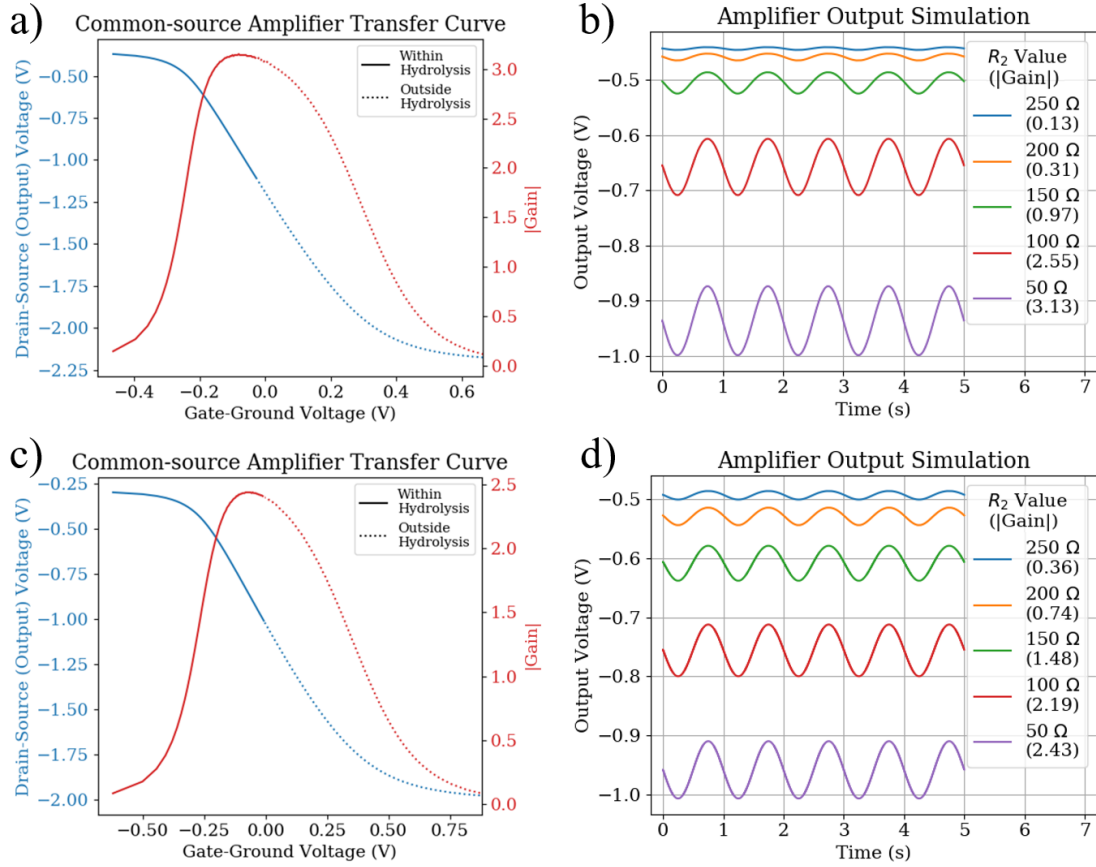


Figure 5.7: a) Simulated amplifier transfer curve using a LC 35 OECT with circuit parameters $R_1 = 1 \text{ k}\Omega$, $R_2 = 40 \text{ }\Omega$, $R_S = 90 \text{ }\Omega$, $R_D = 740 \text{ }\Omega$, $V_{DD} = -2.2 \text{ V}$, and $C_1 = 100 \text{ nF}$, transistor parameters of $G = 6.14 \text{ mS}$, $V_P = 0.45 \text{ V}$, and $\tau = 159 \text{ }\mu\text{s}$ and equation 5.18 parameters of $\alpha = 1.02$, $\beta = -0.62$, and $\lambda = -4.42 \text{ V}^{-1}$. b) Amplifier simulation of a 1 Hz, 20 mV amplitude gate input for varying R_2 values using (a). c) Simulated amplifier transfer curve using a SS 35 OECT with parameters of $R_1 = 1 \text{ k}\Omega$, $R_2 = 55 \text{ }\Omega$, $R_S = 170 \text{ }\Omega$, $R_D = 680 \text{ }\Omega$, $V_{DD} = -2.0 \text{ V}$, $C_1 = 100 \text{ nF}$, $G = 6.86 \text{ mS}$, $V_P = 0.51 \text{ V}$, $\tau = 37 \text{ }\mu\text{s}$, $\alpha = 1.08$, $\beta = -0.64$, and $\lambda = -3.48 \text{ V}^{-1}$. d) Amplifier simulation of a 1 Hz, 20 mV amplitude gate input for varying R_2 values using (c).

voltage increased from a decrease in the value of R_2 , the gain of the amplifier increased. As these simulations used the DC characteristics from the amplifier transfer curves, they again were using the DC circuit behaviour to approximate AC voltage inputs. Such an approximation had validity as the frequency of the input voltage was low.

As designed in determining the voltages and resistances in the DC load-line analysis, the gate-drain voltages within hydrolysis were associated with negative gate-ground voltages. Furthermore, the peak gain values were within the ranges expected in table 5.1,

supporting the capabilities of equation 5.18. The amplifier transfer curves in figure 5.7a and figure 5.7c highlight that the region of gate-ground voltage used can significantly affect the amplification. Within the hydrolysis limit, the gain varies greatly in the gate-ground voltage range, emphasising the importance of identifying the optimal operating point to maximise the linearity of the amplified output. The topology of the common-source linear amplifier allows for the region of amplification to be chosen through the variation of the potential divider resistors R_1 and R_2 , as illustrated in figures 5.7b and 5.7d. The simulated amplifier transfer curves suggest that, for each circuit topology in this investigation, the optimal operating point existed around the point of maximum gain.

5.3.3 Linear Amplifier Figures of Merit

Using the optimal circuit parameters found in the DC load-line analysis, five OECTs each from two geometry types were physically tested in the linear amplifier circuit. The two device types were the 35 nm small spiral and 35 nm large comb. These were used because the 35 nm devices showed a greater capability in implementation and allowed a comparison of performance with varying electrode geometry. The common-source linear amplifier circuit was physically characterised to give its figures of merit of gain, total harmonic distortion (THD), intermodulation distortion (IMD), input-referred noise, and bandwidth.

The input-referred noise represents the noise voltage which, if applied to the input of a noiseless system, would reproduce the measured level of output noise. The input-referred noise is commonly used to determine the $1/f$ flicker noise. The THD is defined as the ratio of the RMS-amplitudes of higher harmonics to the RMS-amplitude value of the fundamental input frequency. The THD calculation is thus a measure of a system's linearity. For the IMD measurements, inputting two sinusoids with different frequencies results in the generation of frequency components at linear combinations of the input frequencies, and the order of IMD is given by the sum of the coefficients of such a linear sum. Similar to the THD, the IMD is measured to a given order by finding the ratio of the RMS-amplitudes of generated frequencies to that of the fundamental frequencies. When inputting two sinusoids of frequency f_1 and f_2 , the third-order components of interest are $2f_1 - f_2$ and $2f_2 - f_1$ due to their proximity to the fundamental frequencies. Where the output powers of the fundamental frequencies increase by 1 dB, the powers of the third-order components increase by 3 dB. When considering the relationship between input and output powers of the fundamental and third-order components, the intercept point of their extrapolated behaviours defines the third-order intercept point, IP3. A greater IP3 value implies a greater linearity of the amplifier and thus defines a figure of merit [268].

The IMD characterisation was performed in addition to that of the THD because measuring the harmonic distortion produced by single-tone sinusoidal signals of various frequencies, as performed in THD, does not convey all the information required to assess the amplifier’s linearity performance when there are a number of noise sources operating at different frequencies. Therefore, it is often required that an amplifier be assessed in terms of the IMD product levels produced by two tones positioned spectrally close to each other and applied simultaneously at the input of the amplifier, allowing for the practical and meaningful assessment of linearity. The realisation of a device that can accurately record weak physiological signals for diagnostic and therapeutic purposes in the presence of strong interference originating from noise sources within the clinical environment requires the consideration of a range of challenging issues. Sources of such noise include the 50 Hz interference, high-frequency interference from radio frequencies and the operating frequencies of the medical devices used in the clinic [269]. Crucially, the transduction of interference signals by an amplifying device that is not characterised by high linearity levels may indeed result in the presence of undesired intermodulation products within the device bandwidth, degrading the quality of the recorded signals.

To assess the linearity of the proposed linear amplifier, the THD was determined for sinusoidal waves at a constant frequency of 5 Hz with a range of amplitudes from 10 μ V to 15 mV. The input dynamic range is defined here as the width of amplitudes within which the THD remained lower than 1% [268]. The input dynamic range was determined for each characterised amplifier using physical measurements and simulations. The gain was calculated by dividing the amplitude of the output voltage from the THD data by the amplitude of the input signal. The IMD was found by inputting two sinusoidal waveforms with frequencies $f_1 = 4.9$ Hz and $f_2 = 5.1$ Hz and of equal amplitude at V_{IN} . The sinusoidal waveform amplitudes were increased through the same range as those in the THD measurements. The fundamental frequencies and the $2f_{1/2} - f_{1/2}$ components were used to generate the IMD third-order intercept point, IP3. To measure the input-referred noise, the gate electrode was grounded and the output voltage was recorded for 1 minute. The output voltage was divided by the gain and the power spectral density (PSD) was calculated. The PSD was then integrated to determine the RMS voltage noise from specified frequency bands. The Bode plot was determined by inputting a sinusoidal waveform of increasing frequency into the gate and calculating the amplitude changes in the amplifier output. The input frequency was swept from 1 Hz to the 10 kHz-scale and the frequency at which the amplitude changed by -3 dB defined the upper limit of the bandwidth.

The physical characterisation of the common-source linear amplifier using the 35 nm small spiral OECT is shown in figure 5.8, in which the locations of the figures of merit are highlighted. The THD, IMD, and Bode amplifier characterisations were also simulated.

A comparison of the physical characterisations to those from the simulation using the two methods is shown in figure 5.9. The physical characterisations only considered gate inputs within electrophysiological limits and so the simulations provided the distortion levels at greater voltage inputs. Table 5.3 gives the mean and standard deviation values of the physically measured and simulated figures of merit for the two transistor geometries tested. For each property associated with the figures of merit, a t-test of independence was performed comparing the two geometries each implemented into five amplifiers. The test assumed that the variances of the underlying populations were unequal and the p-value for significance was 0.05. The results of the statistical tests are also shown in table 5.3. The device gain could have been increased with a decrease in gate voltage range. However, to ensure the stability of the OECTs throughout testing, the chosen parameter values were those found to satisfy the linear amplifier criteria in the DC load-line analysis.

The corner frequency, defined as the noise level at which flicker and thermal noise are of the same magnitude, could not be identified in the input-referred noise because there was no observed transition between a frequency-dependent and frequency-independent region. A further property that could not be determined using only the physical THD characterisation was the input dynamic range. Only the lower limit of the range was identifiable as the THD remained lower than 1% for all subsequent voltage inputs of greater amplitude within the electrophysiological limit. At the input amplitudes of greatest magnitude, THD calculations showed that the powers of higher harmonics were increasing, though a level lower than 1% was maintained. As such, table 5.3 shows only the lower 1% THD limit for physical measurements. The simulation was used to investigate the nonlinearity at voltage input amplitudes greater than those used in the physical characterisations and the upper limit at which the THD returned to 1% was identified. With physical measurements providing lower 1% THD values and simulations providing upper limits, approximate input dynamic range values were calculated.

For the physical measurements of the THD, the distortion values were lower than 1% for gate amplitudes from the 100 μ V-scale to the 10 mV-scale, and turning points were found on the mV-scale, as shown in figure 5.8a. In the simulation, if not using interpolative methods but maintaining a 100 μ V resolution as performed in method 1, the lower THD limit provided values that were not significantly different to those physically measured. This was determined by using a t-test of independence with a p-value for significance of 0.05 and assumed the sample populations had normal distributions of unequal variance. Furthermore, this resolution-limited simulation showed a non-monotonic behaviour between input and output power as observed in physical characterisations. Within this behaviour, the turning point was also recovered on the same scale as physically measured, as shown in figure 5.9c. These results suggested that

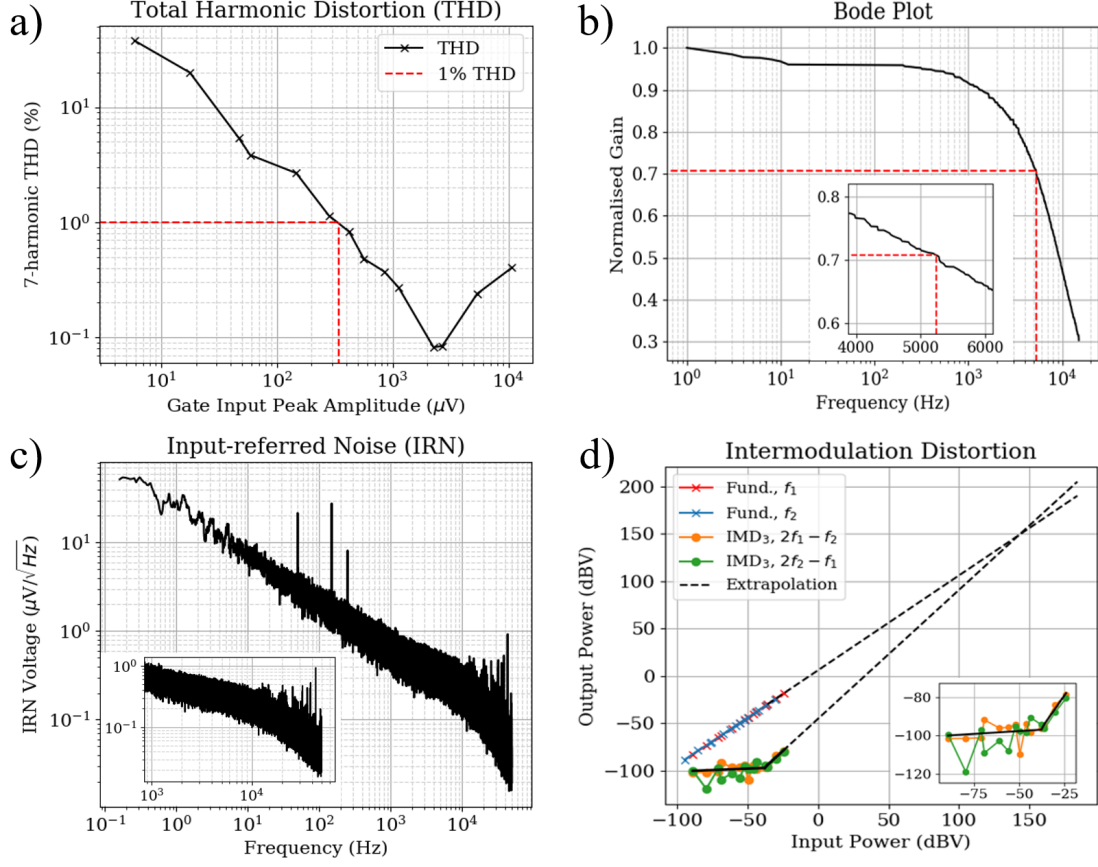


Figure 5.8: *Physical characterisations of a SS 35 OEECT amplifier with $R_1 = 1 \text{ k}\Omega$, $R_2 = 55 \text{ }\Omega$, $R_S = 180 \text{ }\Omega$, $R_D = 600 \text{ }\Omega$, $V_{DD} = -1.9 \text{ V}$, and $C_1 = 100 \text{ nF}$ and OEECT parameters of $G = 6.06 \text{ mS}$, $V_P = 0.53$, and $\tau = 32 \text{ }\mu\text{s}$. The characterisations illustrated are a) total harmonic distortion using seven harmonics with the 1% value indicated. b) Bode plot with the cut-off frequency indicated. c) Input-referred noise of the amplifier using a grounded gate input. d) Intermodulation distortion showing the first- and third-order harmonics with linear extrapolation of the first- and third-order harmonics.*

using a noninterpolated $100 \text{ }\mu\text{V}$ output voltage resolution introduced an effective noise into the simulation which was of the same scale as that in the physical amplifier. Indeed, the integrated noise showed the noise was approximately $100 \text{ }\mu\text{V}_{RMS}$ in the bandwidth of the OEECT. This supported the capability of the simulation to recover the distortion effects as presented in the physical system when using method 1.

For the physical measurements of the IP3, there were no clear increases in the output powers of third-order harmonics for input powers less than -40 dBV . The points used for extrapolation were the highest points of the $2f_{1/2} - f_{2/1}$ components where an increase in input power corresponded to an increase in output power, as illustrated in figure 5.8d.

5 ORGANIC ELECTROCHEMICAL TRANSISTOR COMMON-SOURCE AMPLIFIER FOR ELECTROPHYSIOLOGICAL MEASUREMENTS

Property	SS 35	LC 35	Ind.?
Bypass Capacitor, C_1 (nF)	100	100	N.A.
Resistor R_1 (k Ω)	1.0	1.0	N.A.
Resistor R_2 (Ω)	55	40	N.A.
Source Resistor, R_S (Ω)	170 ± 6	78 ± 12	N.A.
Drain Resistor, R_D (Ω)	610 ± 37	698 ± 66	N.A.
Supply Voltage V_{DD} (V)	-1.90 ± 0.04	-2.20 ± 0.04	N.A.
Cut-off Frequency (Hz)	5090 ± 825	1000 ± 49	Yes
Cut-off Frequency Sim. (Hz)	4500 ± 189	989 ± 2	Yes
Lower 1% THD V_G Peak Amplitude (mV)	0.58 ± 0.29	0.45 ± 0.07	No
Upper 1% THD V_G Peak Amplitude Sim. (mV)	95.10 ± 17.54	48.88 ± 15.78	Yes
Input Dynamic Range Peak Amplitude (mV)	95.10 ± 17.54	48.43 ± 15.76	Yes
OECT V_P (mV)	519 ± 7	453 ± 3	Yes
Measured Gain	1.97 ± 0.11	2.82 ± 0.21	Yes
Simulated (Sim.) Gain	2.17 ± 0.15	3.22 ± 0.12	Yes
Integrated Noise 0.5 – 40 Hz (μV_{RMS})	87.5 ± 37.9	88.5 ± 13.0	No
Integrated Noise 0.5 – 100 Hz (μV_{RMS})	95.7 ± 39.2	97.2 ± 13.4	No
Integrated Noise 0.5 – 500 Hz (μV_{RMS})	106.0 ± 42.4	108.8 ± 13.8	No
Integrated Noise 0.5 – 5000 Hz (μV_{RMS})	119.9 ± 47.7	121.3 ± 15.7	No
IP3 Input Power (dBV)	84.57 ± 44.93	60.62 ± 39.82	No
IP3 Input Power Sim. (dBV)	4.07 ± 0.44	2.68 ± 0.31	Yes

Table 5.3: *Physical and simulation measurements of the figures of merit of the common source linear amplifier with a t-test of independence of each characteristic for the small spiral 35 nm (SS 35) and large comb 35 nm (LC 35) OECT geometries.*

However, the gradient found in such a linear extrapolation did not take the expected value of 3. Due to the limited number of points that did show consistent increases, the inter-amplifier variation in the line of best fit was large and thus the standard deviation in the IP3 was high. The simulation of the IMD allowed the input of powers greater than the bioelectric limit and showed the expected behaviour with less variation, as illustrated in figure 5.9d and 5.9f. As such, the simulated IP3 points are also given in table 5.3. The intercept point of the simulation indicated that harmonics became significant at input powers less than 10 dBV, whereas extrapolation of the physical characterisations suggested such input powers approached 100 dBV. The simulation using method 1 provided the expected gradient of 3 and agreed with physical measurements in showing that there was no clear linear increase in output power of third-order harmonics for input powers less

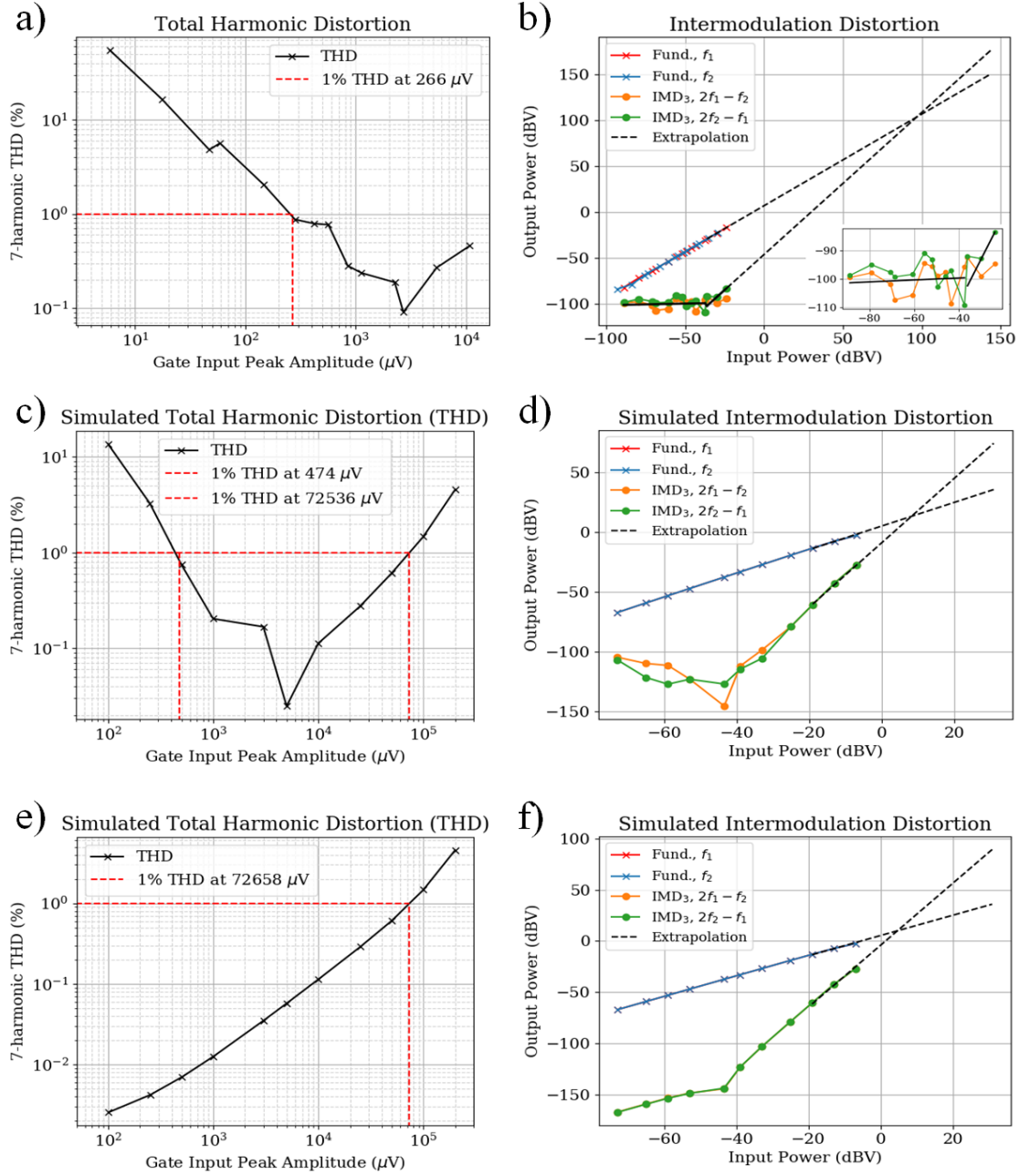


Figure 5.9: Total harmonic distortions and intermodulation distortions for the 35 nm small spiral OECT geometry in a common source linear amplifier configuration. The THD and IMD of the physical measurements are given in a) and b), respectively. The THD and IMD of the simulation using method 1 are given in c) and d), respectively. The THD and IMD of the simulation using method 2 are given in e) and f), respectively.

than -40 dBV, illustrated in figure 5.9d. However, physical measurements included input powers at -25 dBV. At this input power, all simulations predicted a linear increase in third-order harmonics with a gradient of 3, which was not physically observed. The inability to identify a clear linear increase in all physical characterisations of the 10 OEET amplifiers suggested that all circuit topologies provided an exceedingly high linearity within the range of voltages used in characterisation. As the voltages were typical of the electrophysiological spectrum, this shows that the circuit topology was ideally suited to amplify such signals. With a higher IP3 input power, an input of greater amplitude is required to equalise the third-order harmonics with the fundamental components, indicating a more linear device response. The physical measurements of the IP3 point did not give a statistically significant preference to either geometry. However, the simulations suggested that the small spiral geometry had a greater linearity to a statistically significant level.

In a noiseless system, the nonlinearity of transistor amplification provides an increasingly linear response as input voltage decreases in amplitude. This can be represented by a reduction in the powers of higher harmonics. Therefore, the THD would be described by a monotonic function that decreases with decreasing input power. The simulated THD and IMD physical characterisations using method 2 are shown in figure 5.9e and figure 5.9f, respectively. With a higher level of accuracy in simulating the output voltage for a given input voltage, the THD and IMD showed monotonic characterisations, as expected in a noiseless system. With a negligible level of noise, a lower limit for the THD could not be found. The THD increased with gate voltage input and the upper THD limit agreed with that found using method 1, which was expected because the gate amplitudes were much greater than the method 1 voltage resolution. The IMD was found to continue to decrease with decreasing input power, and the intercept point again agreed with that found in method 1, again as expected. With the greater levels of accuracy, method 2 was used to determine simulated characteristics presented in table 5.3.

It is clear that the OEET amplifier presented in this work achieves low THD levels and high IP3 values, as found in efficacious amplifiers. It is desirable in the design of high-performance and noise-robust bioelectronic recording systems to have high IP3 values. In hospital wards with multi-frequency noise sources and in applications where concurrent neural sensing and electrical stimulation is required, for example in deep brain stimulation and spinal cord stimulation setups, the nonlinearity of the amplifying system must be minimised to avoid coupling the electrophysiological measurements through intermodulation with undesired artefacts [268].

As found previously through the DC load-line analysis, the lower pinch-off values were associated with higher gain values, as presented in table 5.3. Relative to the DC load-line gain in table 5.1 and the simulated gain in table 5.3, the physically measured gain was

of the same scale and it followed that the large comb had a greater gain than that of the small spiral. In addition to ensuring device operation below the hydrolysis limit, a conservatively low gain was utilised because, in general, there is a trade-off between gain and linearity levels. When the gain value increases, the output signal level is increased and the nonlinearities innate to the device are also amplified, leading to a subsequent increase in the distortion products. Inversely, when the gain decreases, the output signal level is decreased, and the nonlinearities present in the device are weaker because the distortion amplitudes can decrease below the noise floor. Furthermore, the primary aim of this study was to maximise the achieved gain of the OECT-based amplifier whilst maintaining an approximately linear relationship between drain current and gate voltage. Indeed, the measured THD and IMD levels reported in this work indicate that the aim of providing a linear amplifying system built with high-performance OECTs has been accomplished. Nevertheless, in addition to varying the gain of the implemented circuit by changing only the potential divider resistor values R_1 and R_2 , the gain can be increased by varying the supply voltage and the source and drain resistors, as described in equation 5.15.

The results in table 5.3 suggest that an increased gain was associated with a lower bandwidth. However, as previously mentioned, higher gain values and bandwidths are still thought to be associated with a thinner OECT active layer for a constant electrode geometry. The bandwidth of the amplifier was limited by the response time of the OECT, and so was dependent on the OECT gate-channel capacitance. This capacitance is reduced with a thinner active layer, though there are parasitic contributions from the overlap of the OECT electrodes [77]. Investigations in section 4 suggested that the slower response time of OECTs with larger interdigitated electrodes was a result of the additional parasitic capacitance from the greater overlap between the gate electrode and the source and drain electrodes. Furthermore, the pinch-off voltages of these devices suggested that the dependence was primarily on channel thickness. Therefore, the lower pinch-off voltages in the large comb devices suggested that the OECT active layers were thinner than those of the small spiral. The differing thicknesses were thought to originate from the variances introduced in the photolithographic fabrication of the OECTs. These results imply that even with a thinner active layer in the large comb geometry, the bandwidth was significantly restricted by the parasitic contributions of the electrode overlap. Therefore, such contributions should be minimised in linear amplifier designs.

The amplifier’s simulated temporal response was dependent only on the OECT response time constant. Therefore, the cut-off frequency identified in the simulated Bode characterisation was dependent only on this parameter. The mean of the cut-off frequency modelled by the simulation was found to be within one standard deviation of the physical values measured across the five devices used for each geometry. This

supported that the exponential response of the OECT with response time constant τ , as associated with a cut-off frequency of $f_c \sim 1/2\pi\tau$, was sufficient to model the amplifier bandwidth. The difference between the cut-off frequencies of the two geometries was statistically significant and their values provided limits on the bioelectric signal types that could be measured. With a cut-off frequency of approximately 1 kHz, the large comb geometry could amplify bioelectric signals such as the local field potential (LFP), ECoG, EMG, and electrocardiography (ECG) [270]. The small spiral geometry, with a cut-off frequency of approximately 5 kHz, could amplify high-frequency neural activity.

The measurements of total harmonic distortion showed that the devices provided low distortion effects from inputs with amplitudes of approximately 500 μV . The difference in the lower limit of the THD between the OECT geometries was not statistically significant. The input-referred noise gave values of approximately 100 μV_{RMS} in the bandwidth of the OECT, thus the noise became considerable at amplitudes lower than 500 μV . With no significant difference in the values of input-referred noise between the geometries and such noise dominating at low amplitudes, the lower limits of THD were expected to take similar values. Furthermore, the lower limit suggests that the OECT linear amplifier would be best implemented in unipolar recordings as opposed to bipolar recordings for electrophysiology. For the simulated upper limit, and thus for the full input dynamic range, the small spiral geometry gave a greater input dynamic range to a statistically significant level. However, the values for both geometries were greater than typical extracellular electrophysiological voltages, so both would still be appropriate for such measurements.

As shown in table 5.3, the difference in RMS voltage noise between the two OECT geometries was not statistically significant when considering frequency bands between 0.5 Hz and 5 kHz. Relative to electrophysiological levels, the input-referred noise values imply that the measurable activity types are LFP, EMG, and ECG [270]. This is assuming that there is no frequency filtering applied to reduce the level of noise. The distribution of noise with frequency followed a $1/f$ relationship, as shown in figure 5.8c. The $1/f$ noise has previously been observed in OECT devices, which was suggested to originate from charge fluctuations in the bulk of the organic channel [89]. It was previously observed in section 4 and in the literature that OECTs produce noise on the scales presented in table 5.3 when not subject to frequency filtering [98, 213]. This suggests that the OECT device was the dominant source of noise in the amplifier topology. With no significant difference in noise between the OECT geometries, the results indicated that the noise was independent of the electrode overlap, supporting other investigations in the literature [88]. However, it was also previously observed that OECT noise scaled inversely to channel area, which was found using varying parallel-plate electrode geometries [89]. The channel areas varied by a factor of approximately 6, though the devices in this investigation utilised interdigitated

electrode geometries. This suggests that further investigation is needed into the noise scaling relationships of interdigitated electrode architectures.

It was observed that the input-referred noise began to reduce relative to the $1/f$ behaviour after 10 kHz, as illustrated in the subplot of figure 5.8c. When considering both DC and AC behaviour, the gate-ground voltage is dependent on the potential difference across the source resistor and bypass capacitor. For the values of R_S and C_1 used in this investigation, the AC response of the amplifier was expected to only become evident for input frequencies approaching the 10 kHz-scale, which was greater than the bandwidth of the OECTs. For such frequencies, the impedance of the source resistor and bypass capacitor reduces, varying the potential difference across the source resistor and thus shifting the gate-ground voltage. The amplifier thus operated around a different gate-ground voltage, resulting in variations in gain and thus in input-referred noise. As evident in figure 5.8c, the small spiral input-referred noise for frequencies at, and greater than, 10 kHz had values lower than those expected from extrapolating the lower-frequency $1/f$ noise. Therefore, the operating point of higher frequencies provided a lower gain, resulting in the attenuation of input voltages on the 10 kHz-scale. The bypass capacitor could thus be interpreted as a low-pass filter.

5.3.4 Linear Amplification of Neural Signals

To further test the efficacy of the amplifier for electrophysiological signals, pre-recorded bioelectric voltages were used as the gate input. The signals covered the entire extracellular electrophysiological spectrum and were previously recorded from patients (with full research ethics committee approvals) as part of other studies. Recordings were made using approved wired instruments and were taken from raw anonymised data. The signals were taken from measurements of ECoG, spreading depolarisations (SDs), and EMG fasciculations. ECoG signals are recorded in patients with severe acute brain injuries to allow the detection of slow-moving mass SDs that are associated with poor patient outcomes [271]. EMG signals are used for patients with motor neuron disease to detect high-frequency fasciculations, which are predictive of disease progression [272].

EMG fasciculations are associated with the discharge of motor units and thus have features with 10 – 100 μ V-scale amplitudes and 0.1 – 1 kHz-scale frequencies [267]. The pre-recorded ECoG data provided amplitudes of 0.1 – 1 mV with frequencies of 10 – 100 Hz. The pre-recorded SD data exhibited 10 mV-scale amplitudes and 10 mHz-scale frequencies. The EMG fasciculation recordings contained frequency components greater than the cut-off frequencies of the large comb OECTs. Therefore, the small spiral devices were used as the transistors in the amplifier circuits as their bandwidths were sufficient.

Amplified outputs of the 3 electrophysiological signals are shown in figure 5.10. The

gate input and amplified output were both subject to an identical bandpass filter, allowing signal comparison within the same frequency range. The SD signals were bandpass filtered between 5 mHz and 500 Hz, the ECoG between 1 Hz and 500 Hz and the EMG fasciculations between 10 Hz and 5 kHz. Notch filters were only applied to the amplified output and were present at 50 Hz and higher odd harmonics.

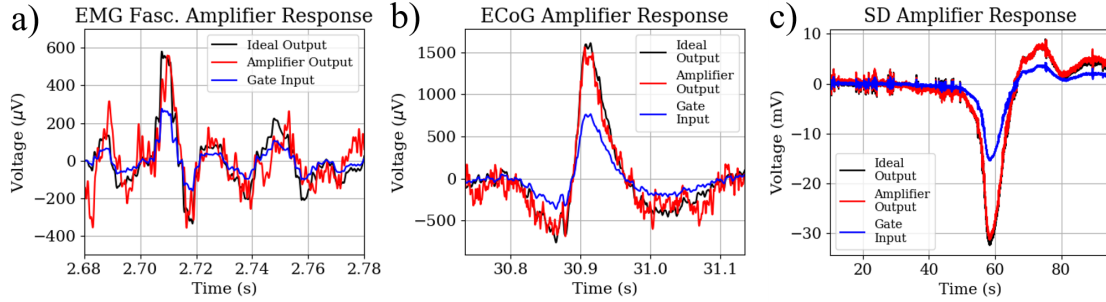


Figure 5.10: Response of a 35 nm small spiral OECT common-source linear amplifier with $R_1 = 1$ k Ω , $R_2 = 55$ Ω , $R_S = 180$ Ω , $R_D = 600$ Ω , $V_{DD} = -2$ V, and $C_1 = 100$ nF and with OECT characteristics of $G = 6.06$ mS, $V_P = 0.53$ V, and $\tau = 32$ μ s to a pre-recorded gate voltage input of a) EMG fasciculations (EMG fasc.), b) ECoG data, c) a spreading depolarisation (SD). The ideal output was given as the product of the input signal with the amplifier gain.

The amplifier response to the EMG fasciculations is presented in figure 5.10a. Incremental variations approaching as low as 100 μ V were resolvable and were amplified to 200 μ V outputs. It was evident that noise started to dominate the amplifier response at those amplitudes. Indeed, the RMS noise voltages given in table 5.3 presented values of approximately 100 μ V. Furthermore, at such amplitudes, there were significant contributions from higher harmonics, as highlighted in figure 5.8a. The utilisation of notch and bandpass filters allowed the resolution of features with amplitudes of 100 μ V.

The response from the ECoG input, as shown in figure 5.10b, was successful in resolving and amplifying the features present in the signal. This was expected because the potential differences were within the frequency bandwidth, greater than the RMS noise voltages and associated with THD values approaching 1%. The OECT amplifier was also able to accurately reproduce and amplify the features of the SD input, as illustrated in 5.10c. The low-frequency spreading depolarisation is identifiable in the amplifier output. With such large amplitudes of such events, the relative level of noise is negligible. Of the amplifier characteristics, the input dynamic range takes greater consideration for these bioelectric signals. With potential differences taking a range within 20 mV and the simulated input dynamic range having a width approaching 100 mV, the circuit was able to amplify the

input signal with high linearity.

These results show that the OECT common-source linear amplifier has the capability to amplify neural activity local to the measurement site. Therefore, noise sources that superpose onto the recorded signals would be less detrimental to the output signal compared to electrodes, which could be subject to additional noise sources in the process of external amplification. As such, the amplifier could facilitate the recording of neural activity with higher SNR values compared to electrodes, as has been shown in the literature [14, 15].

5.4. Conclusions

The linear amplifier circuit was successfully implemented with an OECT as the amplifying element. With the physical limitations of the OECT under consideration, viable combinations of voltage and resistor values were found by using the output characteristics in a DC load-line analysis. This gave sufficient information to determine amplifier parameters such as gain, which allowed the further investigation to correlate amplifier performance with OECT parameters. Using the drain-source voltage as the amplifier output, it was found that lower pinch-off voltages, which were associated with thinner OECT active layers, enabled higher gain values.

To simulate the dynamics of the amplifier, an equation was formulated which showed a good fit to OECT output characteristics across the linear, nonlinear, and saturation regimes. This allowed the determination of an amplifier transfer curve, showing the output voltage given a gate-ground input voltage. The equation was used to simulate the output of the common source linear amplifier given an arbitrary, low-frequency input.

In determining that the 35 nm devices could give greater gain values than the 70 nm devices, the 35 nm small spiral and large comb OECTs were physically implemented into a common-source linear amplifier. The voltage and resistor values were chosen based on those previously found in the DC load-line analysis. Previous literature on voltage amplification with OECTs had not included the characterisation of a number of figures of merit, and thus comprehensive testing was carried out for such an analysis. In particular, the total harmonic distortion, intermodulation distortion, input-referred noise, and bandwidth were accurately determined. Furthermore, the circuit topologies were simulated with the same inputs used to calculate the figures of merit, allowing for comparison to the physical measurements and insight into amplifier behaviour outside the electrophysiological bounds.

The figures of merit were compared between the device types based on the mean and standard deviation of 5 devices tested per type. Using a t-test of independence assuming unequal variances, it was found that the cut-off frequencies and gain values were significantly different. Physical measurements found no significant difference in the lower

bound for 1% THD, though simulations suggested that input dynamic range for the small spiral geometry was greater than the large comb geometry to a significant degree. There was no significant difference in the level of noise present in the two geometries, and the corner frequency could not be identified in the 50 kHz frequency range. The physical measurements of intermodulation distortion did not show preference between OECT types, though the simulation suggested that the small spiral geometry provided a superior linearity.

Finally, pre-recorded electrophysiological signals were inputted into the small spiral OECT amplifier. With the application of frequency filters, the primary features of EMG fasciculations could be resolved and amplified. The efficacy to amplify bioelectric signals was greater for the ECoG and SD inputs, which was expected when comparing the RMS voltage noise to the magnitude of voltage changes expected in the different signal types.

In this investigation, the OECT common source linear amplifier was comprehensively characterised to determine the figures of merit and has shown the capability to amplify electrophysiological signals. The biocompatibility of the OECT, derived from its use of organic and biologically inert materials, provides implementation into amplification local to physiological environments. With the circuit topology allowing for a more fine-tuned amplification, this work has illustrated the capabilities of bioelectronic voltage amplifiers.

6. EFFECT OF ELECTRODE ARCHITECTURE ON ORGANIC ELECTROCHEMICAL TRANSISTOR CHARACTERISTICS AND BIOELECTRIC PERFORMANCE

This research was supervised by Professor J.-S. Kim and Professor M. G. Boutelle.

6.1. Introduction

In the application of OECT arrays to measuring electrophysiological activity, the architecture of the electrodes plays a crucial role in the performance of resolving signals [87, 98, 153]. The electrode architecture encompasses the interconnects, which can be designed for convenient connection to output electronics, and the geometry of the source and drain electrodes, which could take an interdigitated form. In the case that the OECT channel is highly conductive, the dominating source of resistance can originate from the source and drain interconnects, which are also known as parasitic series resistances. These contributions vary the potential difference applied across the channel, affecting device characteristics [150, 273]. As shown in section 4, the design of the electrodes in the active area can significantly impact device performance. Therefore, the optimal electrode design in the channel area is of interest for area-limited applications. As the bandwidth and the noise level are of primary interest for biosensing devices, understanding the effect of electrode architecture on those performance parameters is of great importance.

The impacts of interconnect resistance on the transfer characteristics of OECTs have been experimentally considered. The gate voltage of peak transconductance was found to increase with interconnect resistance and the magnitude of transconductance was observed to decrease. However, the effects of independently varying the source resistor or drain resistor were not determined [262]. Furthermore, the effects on transient and noise characteristics were not measured. The impact of electrode architecture on noise has also been previously considered. It has been found that noise is independent of contact overlap, suggesting that the greater exposure in interdigitated electrode geometries relative to parallel-plate styles is not detrimental to noise performance [88]. Furthermore, the gate-referred noise has been shown to decrease as the active layer thickness increases, though this decreases bandwidth [94]. Finally, for parallel-plate electrodes, gate-referred noise was found to scale inversely to channel area [89]. However, the comparison of parallel-plate electrodes with IDEs for OECT noise has not been investigated.

In this investigation, the impacts of varying electrode architecture on device characteristics were comprehensively quantified. Firstly, the effects of independently varying the source and drain on OECT steady-state characteristics were experimentally

measured and were also simulated using an equation formulated in section 5. Then, the effects of independently varying the source and drain resistance on the response time and gate-referred noise were experimentally measured. The potential distribution within the channel was then hypothesised.

To investigate the impact of interconnect length on OECT characteristics and performance, two interconnect architectures suitable for OECT arrays were fabricated and characterised, and the results were compared to an architecture with minimal interconnect resistance. Additionally, three interdigitated styles of source and drain electrodes with varying active areas and geometries were implemented into the three interconnect architectures. The transient characteristics of each device type were experimentally measured. Of great importance in electrophysiology is the capability of the drain current to resolve gate voltage inputs or ionic fluxes in the electrolyte. Therefore, pre-recorded bioelectric signals were inputted into the gate electrode of the devices and their capabilities to resolve the recordings were quantified.

Finally, parameters of OECTs with parallel-plate and interdigitated source and drain electrodes with the same active areas were compared. A subset of the devices had an active area of $20 \times 20 \mu\text{m}^2$ and thus could be compared in the context of resolving high-frequency electrophysiological activity. This provided a direction of optimal electrode design to maximise desirable characteristics in area-limited applications.

6.2. Methodology

6.2.1 Simulation of an OECT with Interconnect Resistance

In simulating the device as shown in figure 6.1, the potential differences across the source interconnect resistor, OECT and drain interconnect resistor was described by

$$V_{DD} = V_S + V_{DS} + V_D = I_D(V_{DS}, V_{GS})R_S + V_{DS} + I_D(V_{DS}, V_{GS})R_D \quad , \quad (6.1)$$

where V_{DD} is the supply voltage, V_{GS} is the gate-source voltage, V_S is the voltage across the source resistor, V_{DS} is the voltage across the OECT, V_D is the voltage across the drain resistor, R_S is the source resistance and R_D is the drain resistance.

The OECT is subject to the gate-source voltage, but a gate-ground voltage, V_{GGr} , is applied. The transconductance that is measured is the change in drain current for a change in gate-ground voltage, V_{GGr} . The gate-source voltage is related to the gate-ground voltage through

$$V_{GS} = V_{GGr} - V_{SGr} = V_{GGr} - I_D(V_{DS}, V_{GS})R_S \quad , \quad (6.2)$$

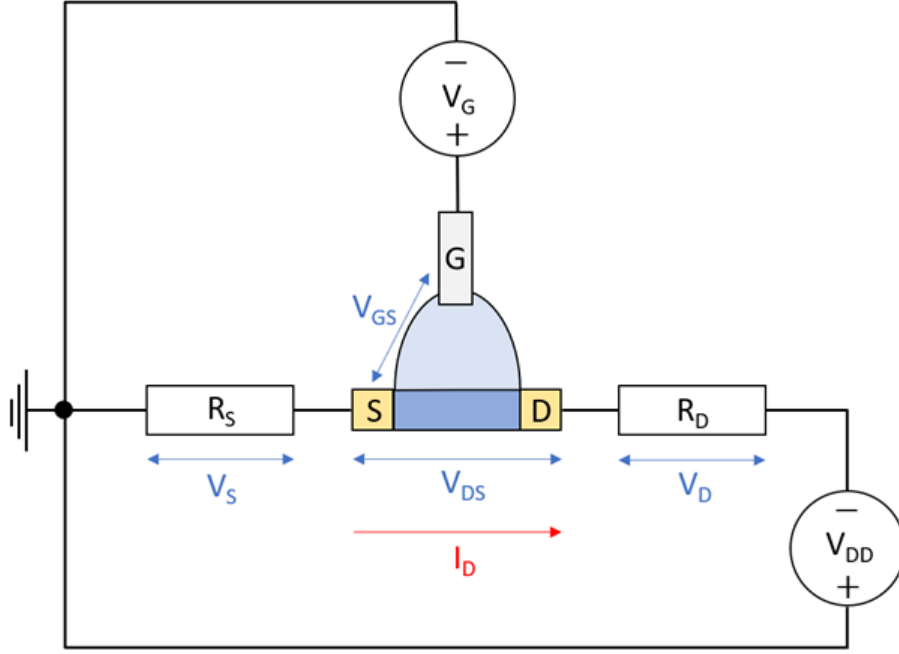


Figure 6.1: Circuit diagram showing an OECT with a gate-ground voltage, $V_G \equiv V_{GGr}$, a supply voltage, V_{DD} , and an interconnect resistance represented by a source resistor, R_S , and a drain resistor, R_D , in series with the OECT.

where $V_S \equiv V_{SGr}$. The extrinsic transconductance that is measured is given as

$$g_m = \left. \frac{\partial I_D}{\partial V_{GGr}} \right|_{V_{DD}} . \quad (6.3)$$

The function describing the relationship between I_D , V_{DS} and V_{GS} was

$$I_D = -\frac{G}{3} \left[(V_{DS} - (\alpha V_{GS} + \beta V_P)) \left[\arctan(\lambda (V_{DS} - (\alpha V_{GS} + \beta V_P))) - \frac{\pi}{2} \right] + (\alpha V_{GS} + \beta V_P) \left[\arctan(-\lambda (\alpha V_{GS} + \beta V_P)) - \frac{\pi}{2} \right] \right] . \quad (6.4)$$

The drain current, as formulated in section 5, is dependent on the parameters of the OECT. These are the conductance, G , pinch-off voltage, V_P , dimensionless constants α and β , and the constant λ with units of V^{-1} , where α , β and λ are found through a best-fit of equation 6.4 to the output characteristics.

To consider how characteristics vary with changes in only source resistance, the drain resistance was considered negligible through $R_D=0$. As such, equation 6.1 became

$$V_{DD} - I_D(V_{DS}, V_{GS})R_S - V_{DS} = 0 . \quad (6.5)$$

The supply voltage was given as $V_{DD} = -0.6$ V and the source resistance was fixed and iterated. The source resistance was given as a function of OECT resistance, $1/G$, and equation 6.5 was solved numerically. To determine the gate-ground voltage from the gate-source voltage, equation 6.2 was used. This then allowed the measurable transfer curve, as given by equation 6.3, to be determined.

To determine how characteristics varied by changing only the drain resistance, the source resistance was similarly assumed negligible with $R_S = 0$ and $V_{DD} = -0.6$ V. The characteristics were determined using equation 6.4 with

$$V_{DD} - I_D(V_{DS}, V_{GS})R_D - V_{DS} = 0 \quad . \quad (6.6)$$

With $R_S = 0$, the gate-source voltage is equal to the gate-ground voltage and thus equation 6.2 was not needed to determine the measurable transfer curve. Equation 6.6 was numerically solved, and the transfer characteristics were found.

Finally, to simulate how the characteristics varied with increasing both the source and drain resistances, this process was repeated with

$$V_{DD} - I_D(V_{DS}, V_{GS})(R_S + R_D) - V_{DS} = 0 \quad . \quad (6.7)$$

Equation 6.7 was solved numerically. Equation 6.2 was used to determine the gate-ground voltage and the transfer curve was then found using equation 6.3.

For a comparative analysis of the extrinsic transfer curves found computationally and experimentally, the parameters extracted from the transfer characteristics showing the (V_{GGr}, I_D) included the on-current magnitude, peak transconductance, the fraction of peak transconductance to the on-current magnitude and the gate-ground voltage of peak transconductance. The fraction of peak transconductance to the on-current magnitude gave a measure of the broadness of the transconductance curve. In more quantitative terms, it was a representation of the change in gate-ground voltage required to turn the device from its on-state into its depleted off-state.

6.2.2 OECT Characterisation

For experimental data, OECT characterisation parameters were measured and processed using custom python code. The conductance was calculated by taking the gradient of a linear region of the output characteristics where a positive V_{DS} was applied. The pinch-off voltage was also calculated from the output characteristics using the transition from the linear to the saturation regime. The transfer characteristics provided the values of the on-current, peak transconductance and the gate voltage at which it occurred. The transient characteristics gave a response time from an exponential fit and information on the contribution of the gate current. The current noise was measured by connecting the

gate electrode to the ground and measuring the drain current for a fixed supply voltage. The gate-referred noise, $V_{G,RMS}$, was calculated using

$$V_{G,RMS} = \frac{\sqrt{2 \int_0^{f_s/2} S_{I_D}(f) df}}{g_m} , \quad (6.8)$$

for sampling frequency f_s , transconductance g_m and drain current power spectral density $S_{I_D}(f)$. For the noise sampling, the drain current resolution was chosen such as to provide the greatest current accuracy.

For the measurement of the response time, gate and channel current contributions were recorded. Where a change in gate voltage from 0 V to 0.5 V would result in an increase in channel current, the gate current also increases. As the drain current can be modelled as the difference between channel and gate current, as shown in equation 6.9, these opposing currents can result in an initial decrease in the drain current before increasing due to the de-doping of the active layer forming the channel current. The contribution of the total gate current to the drain current is described by the f factor. The measured current at the drain electrode, as described by Faria *et al.*, is given by

$$I_D(t) = I_0 + \Delta I_{Ch}(t) - f I_G(t) , \quad (6.9)$$

where it has been suggested that f describes the proportion of the gate current that enters the device at the drain electrode [83]. For a positive gate voltage, a positive gate current is produced. Therefore, if $f I_G > \Delta I_{Ch}$ at the potential step, then the drain current initially decreases before then increasing towards zero with de-doping.

For an initial drain current I_D at $t = 0$, $I_{D,0}$, which changes to a reacted drain current $I_{D,R}$ from the application of a gate voltage at $t_0 > 0$, a reaction fraction, δ , is defined as given in equation 6.10 and is illustrated in figure 6.2. The reacted drain current is given by $I_{D,R} = I_{D,0} - f I_{G,R}$ for gate current $I_{G,R} = I_G(t = t_0)$ [80]. Therefore, it is found that, for a negative V_{DS} ,

$$\delta = \frac{I_{D,R}}{I_{D,0}} = \frac{I_{D,0} - f I_{G,R}}{I_{D,0}} = 1 - \frac{f I_{G,R}}{I_{D,0}} = 1 + \frac{f I_{G,R}}{|I_{D,0}|} . \quad (6.10)$$

The magnitude of the reaction is thus dependent on the f factor and the relative sizes of the reacted gate current and initial drain current. The δ value is calculated in each response time characterisation. In using a Faradaic gate electrode, the gate current response can be modelled similarly to the Cottrell equation, where $I_G(t) \propto 1/\sqrt{t}$.

The measurement of the noise is dependent on the current accuracy of the characterisation equipment. When the device response presents features on the scale of the equipment resolution, a noise source is introduced from the equipment in the approximation of the feature. This approximation is independent of frequency and is thus

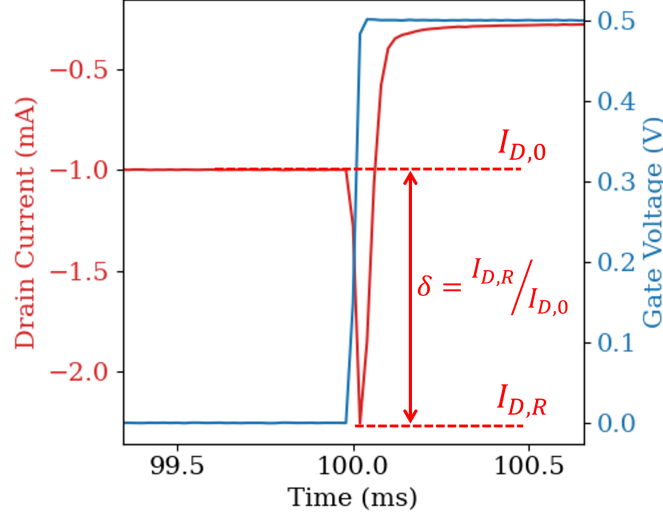


Figure 6.2: Response time characteristics with an illustration of the definition of the δ value.

represented by a constant value in the frequency space as shown in the power spectral density. In OECTs, the noise has a characteristic $1/f$ behaviour. Where the amplitude of the noise from the OECT becomes lower than that of the equipment, a corner frequency would be identified. Integrating across all frequencies would then calculate a noise value which would depend on equipment accuracy as well as the OECT properties. Therefore, the equipment must provide the highest accuracy allowable for the OECT drain current output to obtain the most accurate calculation of noise. The impact of using an unoptimised relative to an optimised equipment accuracy is illustrated in figure 6.3. For the example given, the same OECT is measured using two accuracies and the noise calculation in equation 6.8 gives a difference in magnitude by a factor of 5.

For bioelectric measurements, a signal was inputted into the gate electrode and the drain current was measured. This was repeated for a range of supply voltages. The gate voltage input and drain current output was bandpass- and notch- filtered. For each bioelectric response, the effective transconductance was calculated. In addition, the ratio of the peak amplitude to the background activity was compared between the frequency-filtered gate voltage input, $V_{G,P}/V_{G,Bg}$, and OECT drain current output, $I_{D,P}/I_{D,Bg}$, as illustrated in figure 6.4. The ‘Recovery Fraction’, R , was given by

$$R = \frac{I_{D,P}}{I_{D,Bg}} \bigg/ \frac{V_{G,P}}{V_{G,Bg}} . \quad (6.11)$$

The recovery fraction was a representation of the fraction of OECT drain current signal-to-noise ratio (SNR) to gate input SNR. As $R \rightarrow 1$ the OECT drain current recovered the

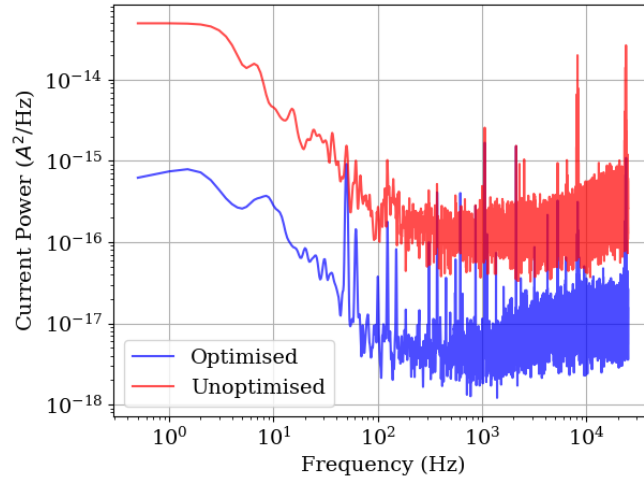


Figure 6.3: Current power spectral density for an unoptimised and optimised equipment accuracy.

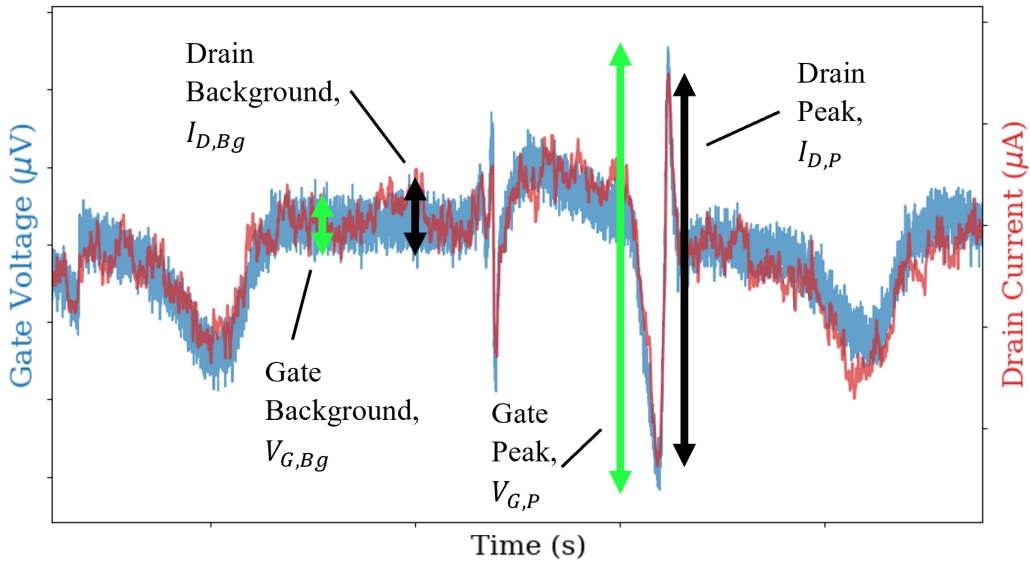


Figure 6.4: Bioelectric gate voltage input and drain current output with an illustration of the parameters used in the recovery fraction.

input gate voltage with a better performance and thus higher values of R were more desirable. With all calculated parameters, an analysis was performed which determined how the properties of the electrode architecture related to greater values of R . In particular, the impact of array interconnect length on signal quality was examined.

6.3. Results and Discussion

6.3.1 Independent Variations in Source and Drain Interconnect Resistance

Fabrication and Characterisation of a High-Performance OEET with Low Interconnect Resistance

To experimentally determine the impact of varying a gate-independent source and drain resistance (or equivalently the source and drain interconnect length) on steady-state and transient characteristics, a high-performance OEET with a minimal interconnect resistance was fabricated. The architecture of the OEET is shown in figure 6.5.



Figure 6.5: a) Geometry of the large comb (LC). b) Geometry of the short interconnects (SI).

Device fabrication followed the procedures in section 3. The OEET was fabricated on a PET substrate with a 10nm Cr and 200 nm Au metallic layer for the electrodes, which were patterned through photolithography. A 1 μm layer of SU-8 was used as an encapsulation layer and was patterned through photolithography. Finally, a 70nm layer of PEDOT:PSS (91.7%) with EG (8%) and DBSA (0.3%) (PED) was deposited. The resulting interdigitated electrode OEET had an active area of $180 \times 168 \mu\text{m}^2$, a channel width of 1840 μm and a channel length of 8 μm, as described as ‘LC’ in table 4.1. The interconnects were designed to minimise resistance from the position of voltage application to the active layer and their geometry was described previously in figure 4.2. The device characteristics are presented in figure 6.6. The best-fit simulated steady-state characteristics, from fitting equation 6.4 to the output characteristics in figure 6.6, are shown in figure 6.7. The device was connected in series with a variable resistor placed at the source or drain electrode, as illustrated in figure 6.1. Electrical characterisations revealed that the device gave a peak transconductance, g_m^{Peak} , of 101 mS and a response time, τ_{90} , of 101 μs, resulting in a $g_m^{\text{Peak}}/\tau_{90}$ value of 1000 Ss^{-1} , as previously reported with this device architecture in section 4.

The supply voltage is distributed across the source resistor, channel and drain resistor, $\{V_S, V_{DS}, V_D\}$. The distribution of the potential is dependent on the relative resistances and thus the source and drain resistors are compared to the OEET resistance. Generally,

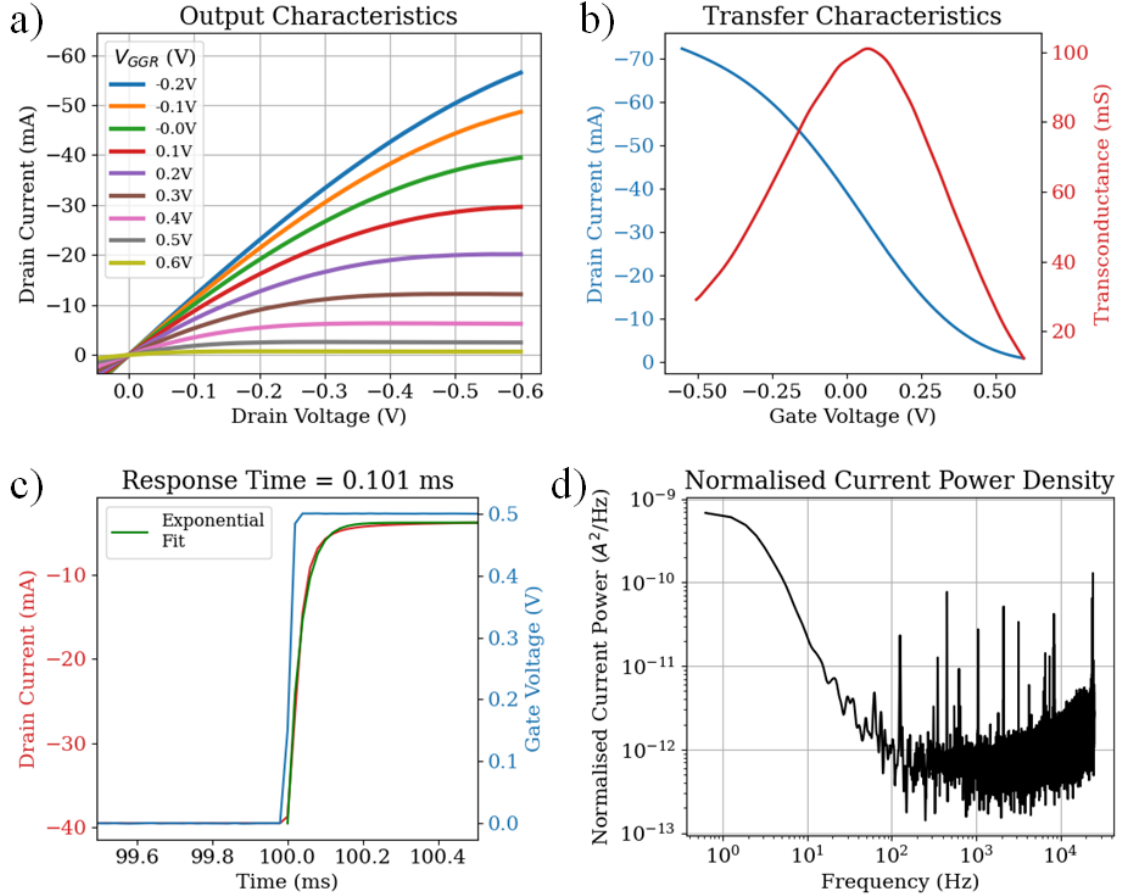


Figure 6.6: a) Output, b) transfer, c) response time and d) noise characteristics of a device with a geometry as shown in figure 6.5.

the potential is distributed as $\{0 \rightarrow \alpha V_{DD}, \alpha V_{DD} \rightarrow \beta V_{DD}, \beta V_{DD} \rightarrow V_{DD}\}$ for $0 \lesssim \alpha < \beta \lesssim 1$. In the case where the interconnect resistance is small relative to the on-state resistance of the OECT, such as for the characteristics shown in figure 6.6, $\alpha \approx 0$ and $\beta \approx 1$. Consequently, $V_{DS} \approx V_{DD}$ and $V_{GS} \approx V_{GGr}$. When the gate-ground voltage is increased, the resistance of the OECT increases and thus an even greater proportion of the supply voltage is across the channel. The changes in V_S and V_D are insignificant and the distribution remains approximately constant. Therefore, the changes in the drain current are determined entirely by the dynamics of the OECT channel and not by the influences of interconnect resistance. As such, minimisation of interconnect resistance is desirable when comparing the characteristics of OECTs with different active layer materials.

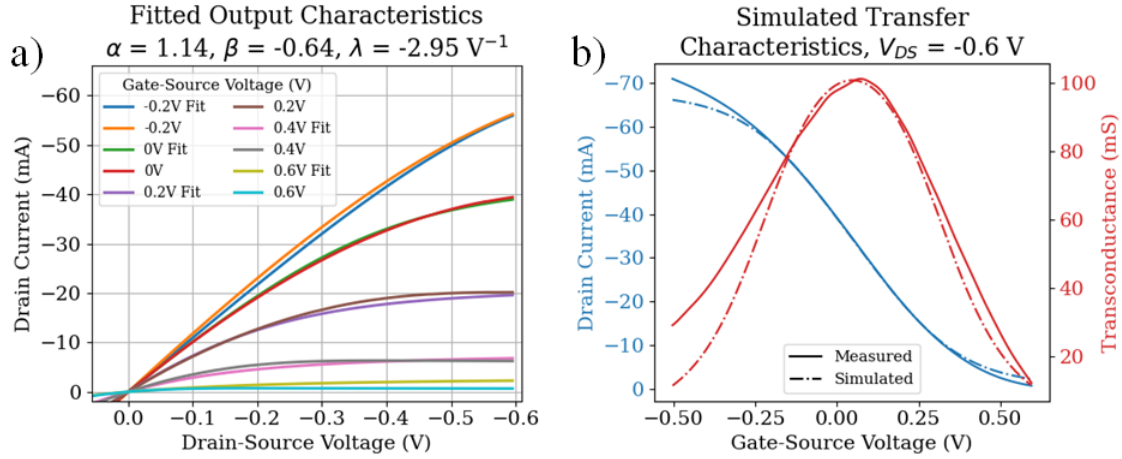


Figure 6.7: Best-fit simulated steady-state characteristics of the output characteristics in figure 6.6 with $R_S = R_D = 0 \Omega$. Parameters are $\alpha = 1.14$, $\beta = -0.64$, $\lambda = -2.95 \text{ V}^{-1}$, $G = 109.0 \text{ mS}$ and $V_P = 0.55 \text{ V}$.

The Effect of Varying Source Resistance on Steady-state Characteristics

The OECT was placed in series with a resistor that was situated between the source electrode and the ground, equivalent to $R_D = 0$ in figure 6.1. The value of R_S was increased and the transfer characteristics were determined for each resistance. The transfer characteristics were both simulated and measured experimentally. In presenting the results, the applied resistance was given as a fraction of OECT resistance. The OECT resistance was defined as that associated with the on-state, measured by applying a positive drain-source voltage such that cations were minimally present in the channel, leaving it in its most doped state. The simulated transfer characteristics are given in figure 6.8 and those experimentally measured are shown in figure 6.9.

In addition to p-type depletion mode devices, the equation used to simulate the circuit has been shown to also model the characteristics of p-type accumulation, n-type depletion and n-type accumulation characteristics, as shown in section 5. The equation was not specific to OECT behaviour. As such, the results could be applied more generally across all p-type depletion mode transistors. Furthermore, by changing the parameters of the equation, the impact of interconnect resistance on the steady-state characteristics of other operating modes could be explored.

Properties of the transfer characteristics for the simulated and experimental results were extracted and are presented in figure 6.10. The transfer curves showed that the peak on-current decreased as source resistance increased. The simulation accurately reproduced this behaviour for all source resistances, as illustrated in figure 6.10a. With

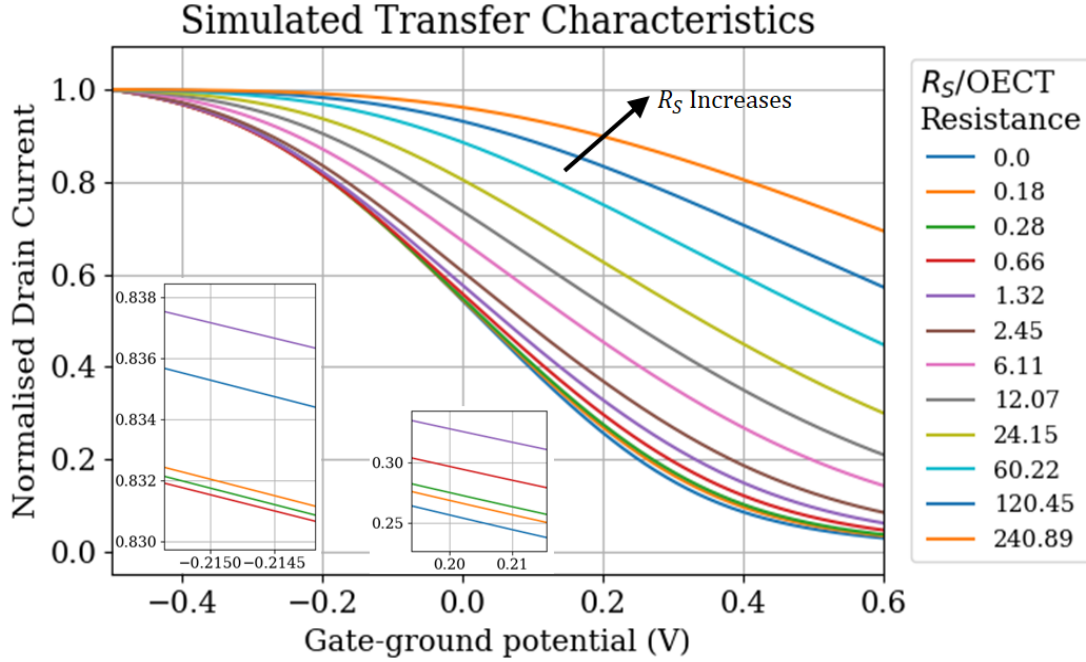


Figure 6.8: Simulated, normalised transfer curves for changes in source resistance as a fraction of OECT resistance. The simulation used parameters of $R_D = 0 \, \Omega$, $V_{DD} = -0.6 \, \text{V}$, $\alpha = 1.14$, $\beta = -0.64$, $\lambda = -2.95 \, \text{V}^{-1}$, $G = 109.0 \, \text{mS}$ and $V_P = 0.55 \, \text{V}$.

transconductance and on-current both dependent on the total circuit conductance, the peak transconductance, as given in figure 6.10b, followed a similar trend. Experimental measurements showed that the fraction of peak transconductance to on-current magnitude did not change significantly as source resistance increased, as shown in figure 6.10c. The simulation reproduced the experimental results at low series resistances; however, at higher resistances, the simulation deviated and suggested that this fraction decreased with source resistance. With a lower fraction at higher source resistances, the simulated transfer curve was broader than that experimentally measured. Finally, as shown in figure 6.10d, the gate-ground voltage of peak transconductance initially decreased with increasing source resistance until the source resistor and OECT had a resistance on the same order of magnitude. This behaviour was captured both experimentally and in the simulation. Subsequently, the gate-ground voltage at peak transconductance then increased with source resistance, found in both the experimental and simulation results. However, the functions of the subsequent increases were different for the experiment and simulation. In general, these results support that the simulation was capable of reproducing experimental behaviour for source resistances up to an order

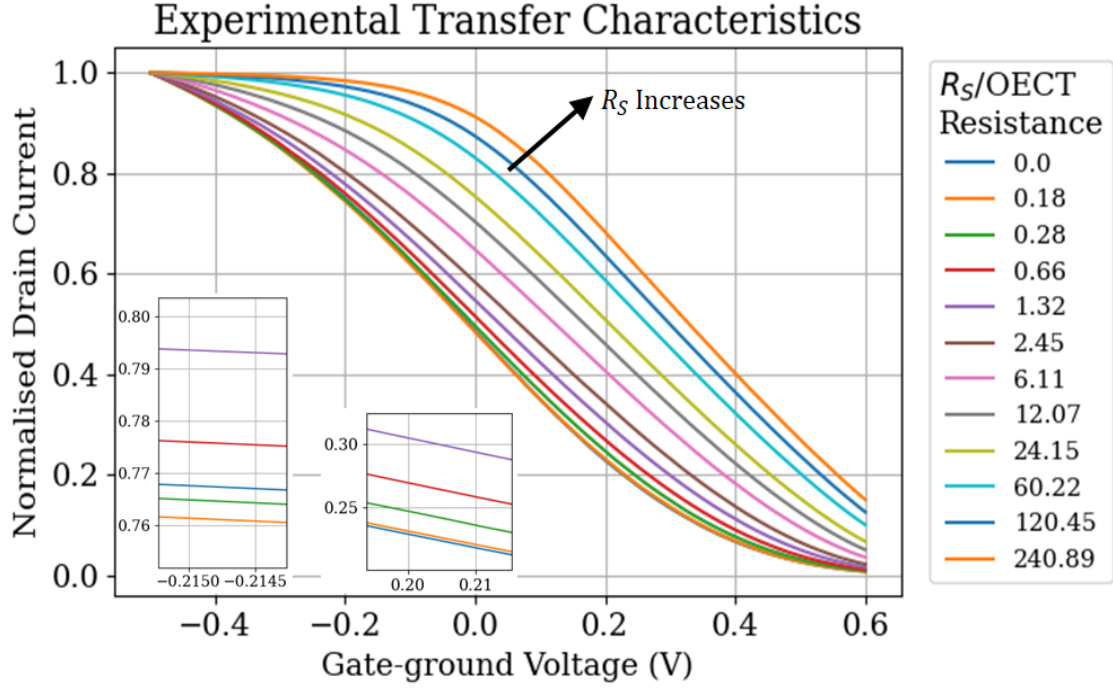


Figure 6.9: *Experimental, normalised transfer curves for changes in source resistance as a fraction of OECT resistance.*

of magnitude greater than the OECT resistance. However, deviations became significant at larger source resistances. This suggested that either the capabilities of the equation were reached or that there were additional mechanisms that contributed significantly to the device behaviour at such operating regimes.

An interesting feature of the characteristics was the initial decrease in gate-ground voltage of peak transconductance. This is because it could provide a tuning of peak transconductance around $V_{GGr} = 0$, which has previously been the subject of investigation [258, 274]. Consider an increase in source interconnect resistance which changes the potential distribution from $\{0 \rightarrow 0.1V_{DD}, 0.1V_{DD} \rightarrow V_{DD}, V_{DD} \rightarrow V_{DD}\}$ to $\{0 \rightarrow 0.5V_{DD}, 0.5V_{DD} \rightarrow V_{DD}, V_{DD} \rightarrow V_{DD}\}$. With a negative supply voltage, the V_{GS} would increase from $V_{GGr} - 0.1V_{DD}$ to $V_{GGr} - 0.5V_{DD}$. Although the V_{DS} decreases, the I_D would not decrease if the device was still operating in the saturation regime. Therefore, with a negative shift in $V_S \equiv V_{SGr}$ resulting in an increase in $V_{GS} = V_{GGr} - V_{SGr}$, a lower V_{GGr} would be required to de-dope the active layer. Thus, the applied gate voltage V_{GGr} required to bias the device to the point of maximum transconductance reduces. As the source resistance is further increased, the V_{DS} reduces into the linear regime. In the linear regime, changes in gate voltage at low values result in

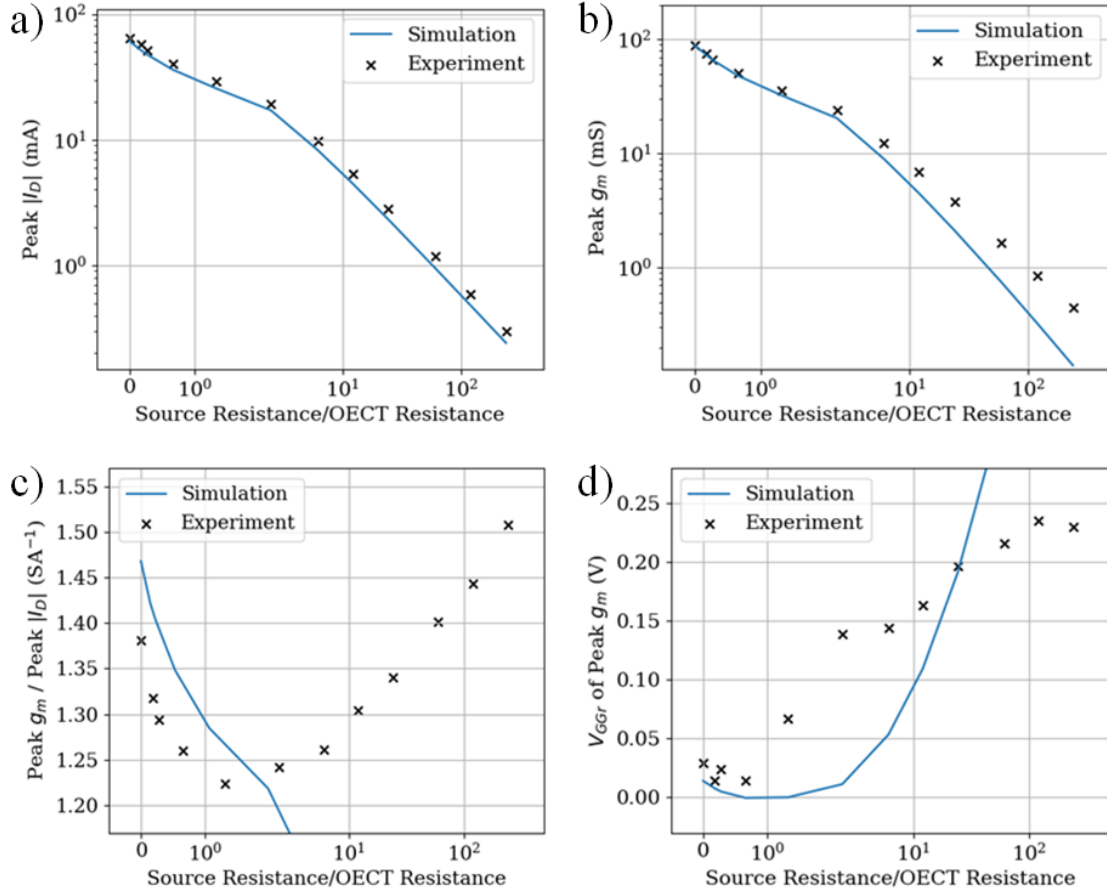


Figure 6.10: Simulated and experimental properties of transfer characteristics for a range of source resistances, presented as a fraction of OECT resistance. a) Change in magnitude of on-current. b) Changes in peak transconductance. c) The fraction of peak transconductance to on-current. d) The gate-ground voltage of peak transconductance.

significantly smaller fractional changes in drain current than at higher gate-source voltages in the saturation regime. Therefore, more significant de-doping occurs at greater gate-source voltages. As such, the gate-ground voltage of peak transconductance increases with further increases in source resistance. As the gate voltage increases for a given source resistance, smaller values of I_D result in the decrease in magnitude of $V_S = I_D R_S$. Therefore, the gate-ground voltage tends towards the gate-source voltage.

The Effect of Varying Drain Resistance on Steady-state Characteristics

In a similar manner to varying the source resistance, the effect of varying the drain resistance was investigated by placing the OECT in series with a resistor between the drain electrode and the supply voltage, equivalent to $R_S = 0$ in figure 6.1. The simulated transfer characteristics are given in figure 6.11 and those experimentally measured are shown in figure 6.12.

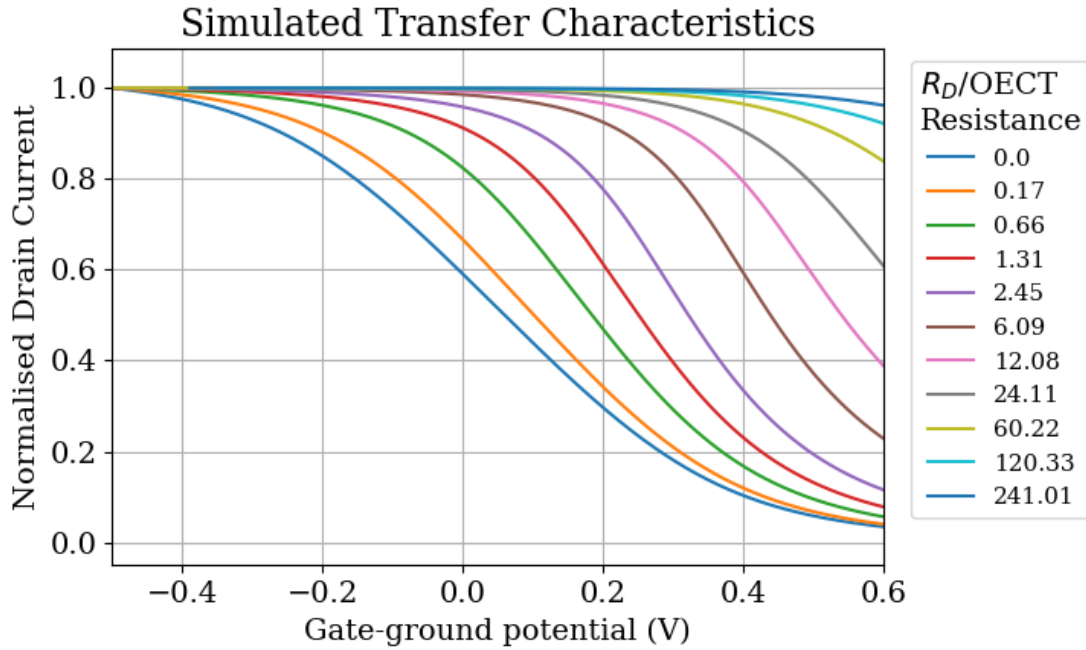


Figure 6.11: *Simulated, normalised transfer curves for changes in drain resistance as a fraction of OECT resistance. The simulation used parameters of $R_S = 0 \Omega$, $V_{DD} = -0.6 \text{ V}$, $\alpha = 1.14$, $\beta = -0.64$, $\lambda = -2.95 \text{ V}^{-1}$, $G = 109.0 \text{ mS}$ and $V_P = 0.55 \text{ V}$.*

It was found that the peak on-current decreased as drain resistance increased, as was found with increasing source resistance. Again, the simulation reproduced this behaviour well, as illustrated in figure 6.13a. The peak transconductance also decreased as drain resistance increased. However, the decrease was again smaller than when simulated for higher drain resistances, as shown in figure 6.13b, owed to the increase in the fraction of peak transconductance to peak on-current magnitude. The increase in this fraction was captured in the simulation at drain resistances up to a magnitude greater than the OECT resistance, highlighted in 6.13c. The simulation predicted that subsequent increases in drain resistance would reduce the fraction; however, experimental data showed that it increased significantly, demonstrated by sharper decreases in drain current in figure 6.12.

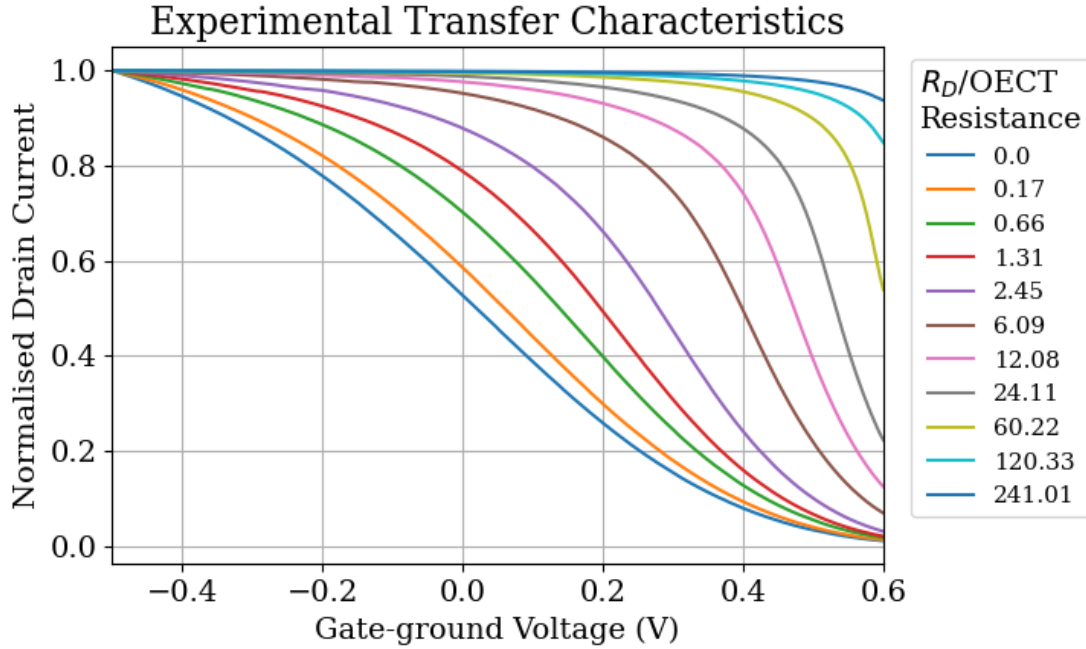


Figure 6.12: *Experimental, normalised transfer curves for changes in drain resistance as a fraction of OECT resistance.*

Experimental characterisations did not subject the OECT to gate-drain potentials greater than that of hydrolysis, and so the decrease in the fraction at the highest drain resistances was a result of the true peak transconductance being outside the hydrolysis range. Finally, it was found that the gate-ground voltage of peak transconductance increased as drain resistance increased. This was captured by the simulation at drain resistances up to a magnitude greater than the OECT resistance, illustrated in figure 6.13d. The gate-ground voltages were increased up to 0.6 V, contributing to the tendency of that property to that value. This limit was chosen to ensure that the gate-drain potential remained lower than that required for hydrolysis. As found when increasing source resistance, the simulation of increasing drain resistance recovered the experimental data well for low resistances, and deviations became evident at higher resistances and higher gate-ground voltages.

To provide a greater insight into the impact of drain resistance on OECT behaviour, the load-lines for varying drain resistances overlayed onto the output characteristics are shown in figure 6.14. The importance of considering the distribution of drain-source voltage is highlighted in equation 6.7, which can be re-arranged to give

$$I_D = \frac{V_{DD}}{R_S + R_D} - \frac{V_{DS}}{R_S + R_D} \quad . \quad (6.12)$$

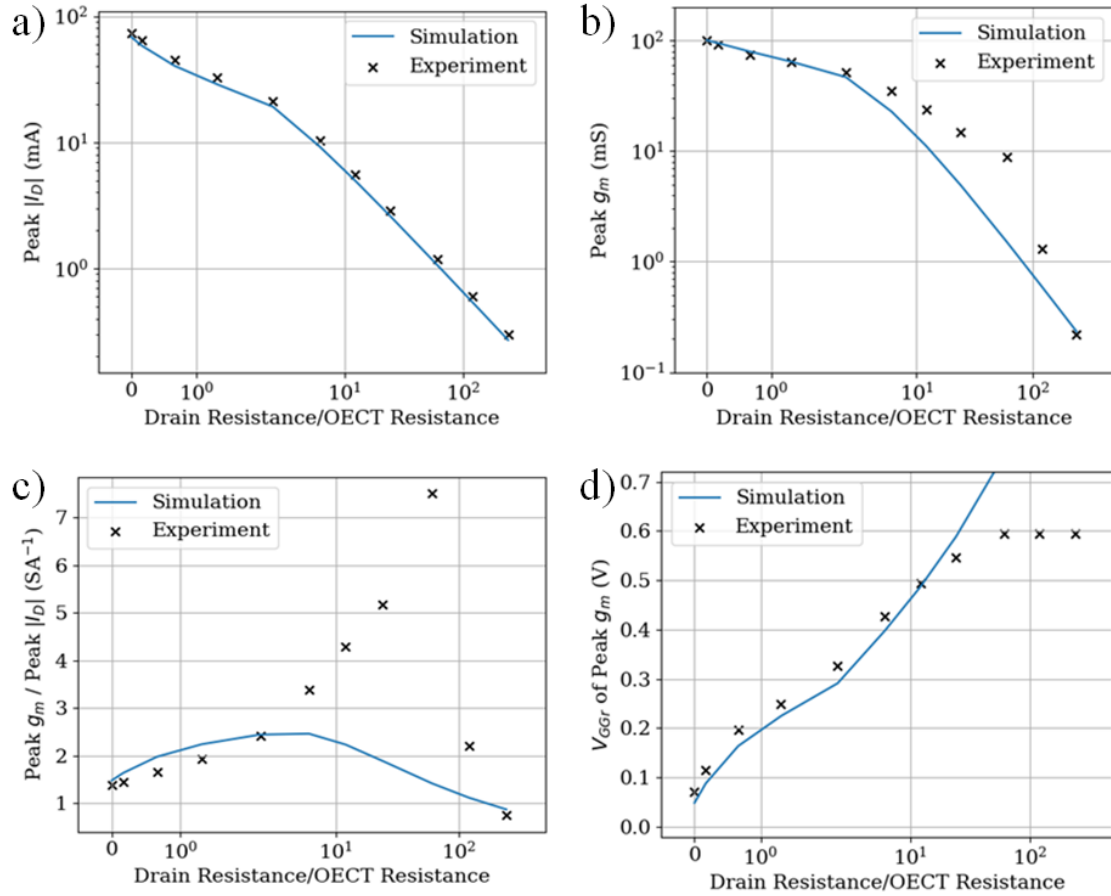


Figure 6.13: Simulated and experimental properties of transfer characteristics for a range of drain resistances, presented as a fraction of OECD resistance. a) Change in magnitude of on-current. b) Changes in peak transconductance. c) The fraction of peak transconductance to on-current. d) The gate-ground voltage of peak transconductance.

The intersection of the load-line with the output characteristics determines the drain current for a given gate voltage. For a system with no interconnect resistance, the transfer curve would be found by taking the intersection of $V_{DS} = V_{DD}$ with all output lines. For increases in only the drain resistance, the vertical line on the output curve would rotate anti-clockwise and take a gradient of $-1/R_D$. The transfer curve would then again be found by the intersection of this load-line with the output characteristics. As the drain resistance increases, the load-line becomes shallower, and in all regimes the drain current is proportional to the drain-source voltage. Where there are also changes in the source resistance, the OECD output curve changes with each source resistance because the lines of constant gate-source voltage would be shifted through equation 6.2.

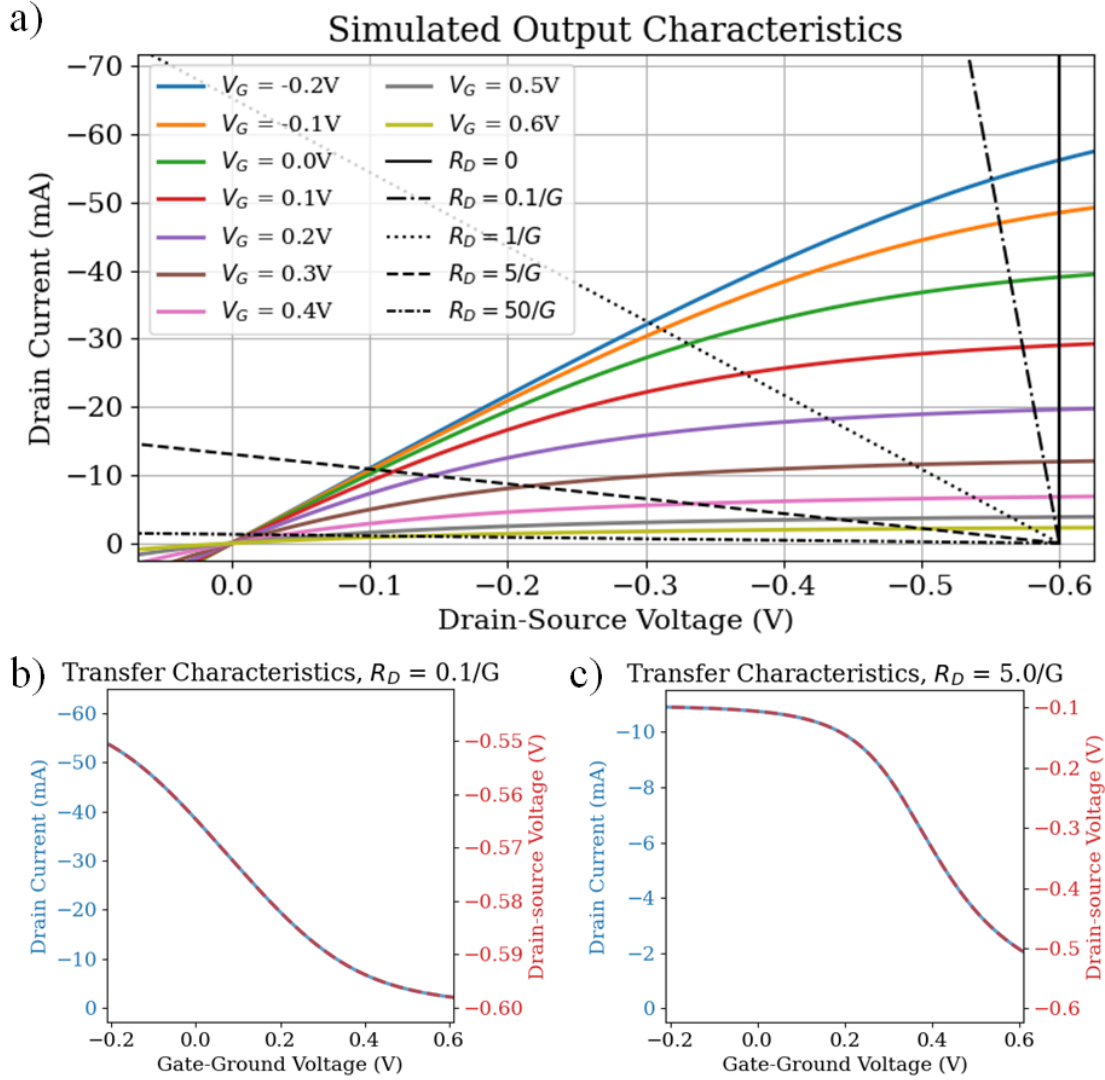


Figure 6.14: a) Simulated output characteristics using the parameters of $R_S = 0 \Omega$, $V_{DD} = -0.6$ V, $\alpha = 1.14$, $\beta = -0.64$, $\lambda = -2.95 \text{ V}^{-1}$, $G = 109.0 \text{ mS}$ and $V_P = 0.55 \text{ V}$ with load-lines for a range of drain resistances. Transfer curves for the simulated OECT with b) $R_D = 0.1/G$, c) $R_D = 5.0/G$.

As illustrated in figure 6.14, the intersection of the load line with the output characteristics results in the increased fraction of peak transconductance to peak on-current magnitude. For higher drain resistances, the device enters the saturation regime at higher gate voltages and the additional gate voltage required to turn off the device is lower. Therefore, in the saturation regime, the fractional change in drain current with gate voltage increases. This insight can also explain the increase in gate-ground

voltage of peak transconductance. As the drain resistance increases, the magnitude of the drain-source voltage decreases and the average gate-channel potential decreases. With sufficient drain resistance, the OECT transitions into the linear regime for a given gate voltage. In the linear regime, a greater gate-source voltage is required to provide significant fractional changes in the drain current and de-dope the active layer. Therefore, a greater gate-ground voltage is needed to reach the peak transconductance. This is represented in the load-line by observing that at high drain resistances, and thus a shallower line, higher gate voltages are required to transition the device into the saturation regime in which the drain current decreases most significantly.

Simulation of Varying Source and Drain Resistance on Transfer Properties

The transfer curve properties were simulated for a parameter grid of source and drain resistances. Resistances up to $R_{S/D} = 5/G$ were chosen as they provided a satisfactory reproduction of the experimental characteristics. The properties for the considered source and drain resistances are presented in figure 6.15. The simulation suggested that there were no additional notable features of the transfer properties from having both a source and drain resistance beyond those features found when individually increasing the resistances. For the gate-ground voltage of peak transconductance, the increase caused by significant increases in the drain resistance, as shown in figure 6.13c, was greater than the decrease caused by increasing the source resistance.

Equal increases in both source and drain interconnect resistance results in a voltage distribution of $\{0 \rightarrow \alpha V_{DD}, \alpha V_{DD} \rightarrow (1-\alpha)V_{DD}, (1-\alpha)V_{DD} \rightarrow V_{DD}\}$ for $\alpha < 0.5$. As the interconnect resistance increases, $\alpha \rightarrow 0.5$, $|V_{DS}|$ decreases and V_{GS} increases whilst V_{GD} decreases. Similarly, as the interconnect resistance decreases, $\alpha \rightarrow 0$, $|V_{DS}|$ increases, V_{GS} decreases and V_{GD} increases. Therefore, the voltages that transport cations towards the source and drain electrodes change in magnitude. It is noted that the average gate-channel voltage would remain approximately constant. For transient measurements, modulating the potential distribution towards the drain electrode results in a varied contribution of the gate current to the drain current, as described by the f factor [83].

Simultaneously increasing the source and drain resistance is equivalent to increasing the length of the source and drain interconnect lines. This could be required when placing OECTs in a physiological environment with the application of voltages for device operation external to the body. An example is a brain-machine interface where the recording sites measure activity from a region of the brain, and voltage applications and current measurements take place external to the scalp.

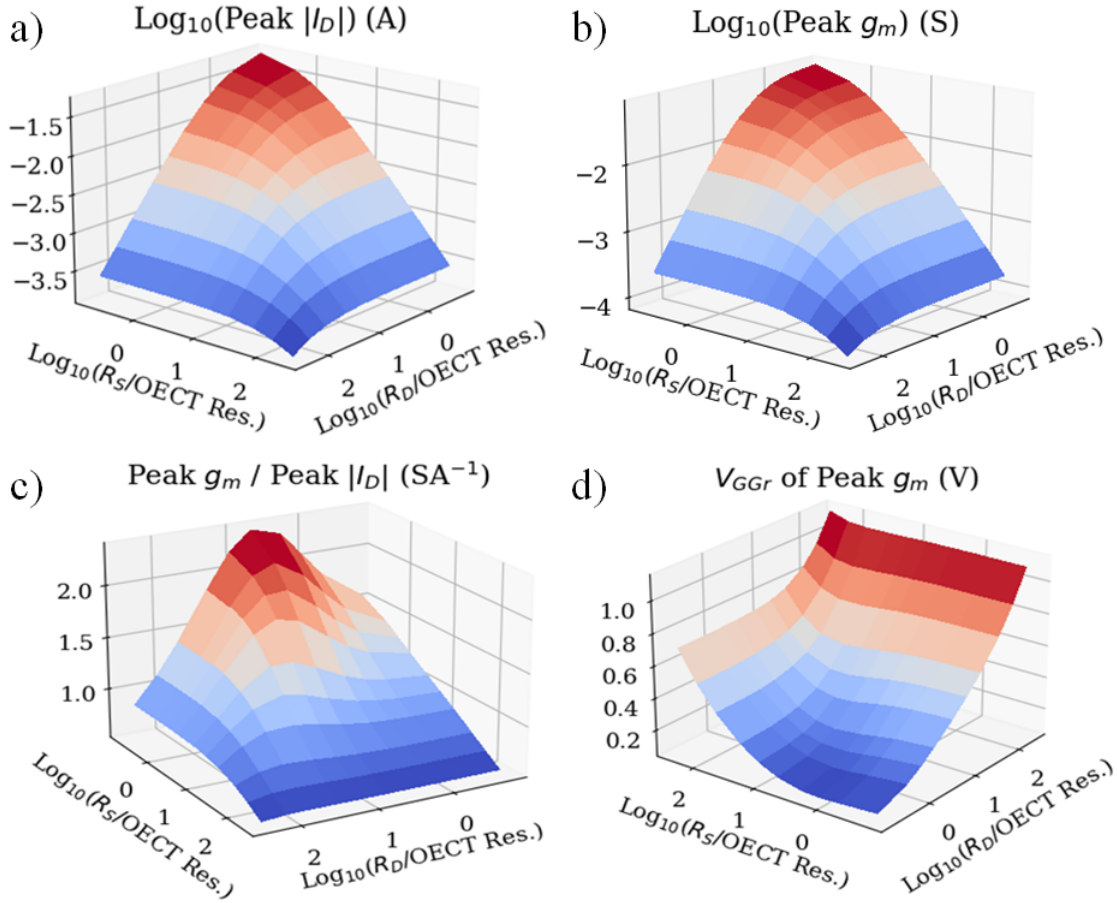


Figure 6.15: Simulation of changes in transfer properties for variation in source and drain resistance using the parameters of $V_{DD} = -0.6$ V, $G = 109.0$ mS, $V_P = 0.55$ V, $\alpha = 1.14$, $\beta = -0.64$ and $\lambda = -2.95$ V⁻¹. a) The magnitude of on-current. b) The magnitude of peak transconductance. c) Fraction of peak transconductance to on-current. d) Gate voltage of peak transconductance.

Steady-state Potential Distribution within the Channel

This investigation has focused on the distribution of potential differences across the source interconnect resistor, drain interconnect resistor and the resistor representing the channel. Within the channel, it has been observed that the potential is non-linear, particularly at the drain electrode [85]. It is found that the potential difference and changes in potential at the drain electrode are significantly greater than those in the regions of the channel towards the source electrode [84].

Numerical modelling suggests that ions that enter the organic layer are not locally trapped and can move freely [275]. Therefore, it is suggested that the distribution of

cations in the channel can be considered similar to that of an electric double layer. The cations form a capacitive interface at the drain electrode and then form a diffusive layer at greater distances. In approximating such behaviour with only the diffusive layer, there is an exponential distribution of positively charged ions at the negatively charged drain electrode. An exponential distribution has been previously found in 2D drift-diffusion OECT models in which the ionic current between the source and drain electrodes is in equilibrium [84]. Assuming that the number of holes decreases and thus the resistance increases with the number of cations, then the resistance increases exponentially through the channel:

$$\frac{dR}{dx} = \alpha R \quad , \quad (6.13)$$

where R is the resistance at position x in the channel of length L such that $0 \leq x \leq L$, and α describes the rate of increase of cation number in the channel as $x \rightarrow L$. Solving equation 6.13 using $R = R_c$ at $x = L$ for channel resistance R_c gives

$$R(x) = R_c e^{\alpha(x-L)} \quad , \quad (6.14)$$

Therefore, the steady-state potential difference at position x , as normalised by the drain-source voltage, is found through

$$\frac{V(x)}{V_{DS}} = \frac{\int_0^x R(x') dx'}{\int_0^L R(x') dx'} = \frac{e^{\alpha x} - 1}{e^{\alpha L} - 1} \quad , \quad (6.15)$$

and thus the potential at position x , $V(x)$, is given by

$$V(x) = V_{DS} \left(\frac{e^{\alpha x} - 1}{e^{\alpha L} - 1} \right) \quad . \quad (6.16)$$

The potential distribution is shown in figure 6.16 for $V_{DS} = -0.6$ V and channel length $L = 10 \mu\text{m}$ for a range of α values. The potential distribution presents similarities to those found in the literature that model OECT behaviour using drift-diffusion equations [30, 84, 85]. With comparison to the literature, the results suggest that the resistance increases towards the drain electrode with an α value between $1 \times 10^5 \text{ m}^{-1}$ to $1 \times 10^6 \text{ m}^{-1}$.

As the α value increases, the proportion of potential difference dropping at the drain electrode increases. With a negative V_{DS} and a positive V_{GS} , cations enter towards the drain electrode. Given that the active layer is modelled as resistors in series, then the resistors near the drain electrode increase in resistance. Therefore, the potential in the channel is redistributed such that there is a greater potential difference towards the drain and a lower potential difference towards the source. With a greater potential difference at the drain, more cations are attracted to that region, further increasing the resistance and

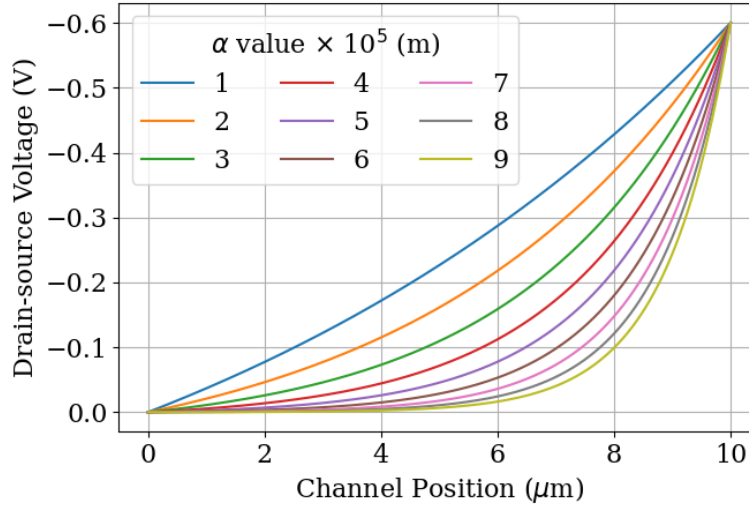


Figure 6.16: Potential distribution with a channel length of $L = 10 \mu\text{m}$, $V_{DS} = -0.6 \text{ V}$ and a range of α values.

thus the potential difference towards the drain. This effect becomes increasingly dominant as the gate-source voltage increases.

An exponential distribution of voltage is seen in figure 6.16, and thus it is suggested that the α value increases as gate voltage increases. Therefore, $\alpha = f(V_{GS})$, and at low gate voltages and thus low α values, the potential is approximately linear, providing agreement with experimental data in the literature [30, 276]. The total V_{DS} across the channel does not vary and so represents the case where there is no interconnect resistance. In cases where interconnect resistance becomes significant, the value of V_{DS} would increase in magnitude with gate-ground voltage and thus $V_{DS} = f(\alpha, V_{DD})$. Additional contributions to the potential distribution between the source and drain electrodes include the potential differences at the source-channel and channel-drain interfaces where there are charge injection and extraction barriers. Potential differences at these interfaces have been observed in OEETs [276].

To experimentally determine the validity of equation 6.16, a set of electrodes lines can be placed within the channel of an OEET at which the voltage profile can be measured, as shown in the literature [75, 85]. To increase the insight afforded by such structures, electron-beam lithography could be employed to reduce the width and increase the density of the electrode probes. This would improve the spatial resolution of the voltage profile in the channel. Characterisations can be performed in the different regimes of behaviour to determine how α could change with the applied voltages.

The Effect of Varying the Source and Drain Interconnect Resistance on OECT Transient Characteristics

The response time, δ value and gate-referred RMS noise were calculated for OECTs with varying source and drain series resistances. For increases in source resistance, it was found that the response time tended to increase, as shown in figure 6.17a. However, relative to the bandwidth of bioelectric responses, the increases were not significantly detrimental. Increases in source resistance also resulted in significant increases in the δ value when those resistances reached an order of magnitude greater than the OECT resistance, as illustrated in figure 6.17b. The response time calculation accounted for the initial decrease in drain current from the increase in gate current and thus the fast response times occurred even with the significant gate current contributions. For increases in drain resistance, the response time increased significantly and showed a non-monotonic dependence, as shown in figure 6.17c. As with increases in source resistance, the largest δ value was found at the largest drain resistance, as shown in figure 6.17d. However, the increases in δ value were significantly smaller than for those observed when increasing source resistance and the contribution of gate current to the initial drain current response appeared negligible.

This analysis shows that an increasing source resistance results in an increase in the impact of gate current on the initial drain current response, signified by a significant increase in δ value; however, there is no significant impact on response time. On the other hand, increasing the drain resistance results in an increase in the response time, though the data suggests that the impact of gate current on the initial drain current response is negligible. Therefore, the effects on transient response are approximately mutually exclusive. To illustrate the impact on response time, the drain current response is given in figure 6.18a and figure 6.18b where the source and drain resistance is approximately a factor of 10 greater than the OECT resistance.

In general, exponentially increasing interconnect resistance results in an exponential decrease in the channel current, as shown in the steady-state results. On the other hand, such increases don't exponentially decrease the gate current, and I_G remains on the same order of magnitude at the voltage step. Therefore, the ratio of $I_G^{Peak}/|I_{D,0}|$ increases significantly and thus the greater δ values were expected. For increases in source resistance, it was found that the $I_G^{Peak}/|I_{D,0}|$ values at the voltage step took the same relationship as the δ values. This indicated that the f value was approximately constant and that the significant increases in the δ value could be attributed to the relative magnitude of the gate current to the channel current.

With an increased δ value implying a reduced value of $|I_{D,0}|$, then it further implied a reduced value of $|V_{DS}|$ and thus a reduced electronic transit time. The response time has contributions from both the electronic and ionic transit times. The electronic transit

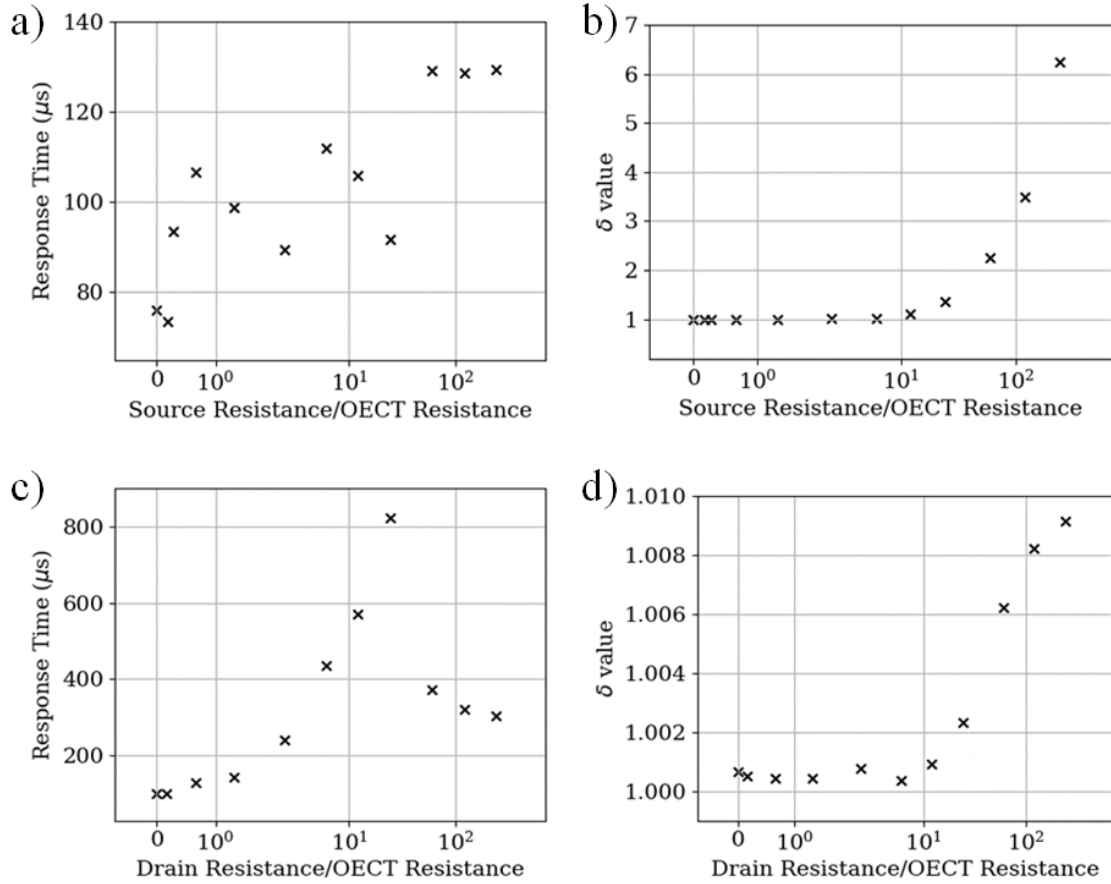


Figure 6.17: a) 90% response time calculated through exponential fitting for changes in source resistance. b) δ values for changes in source resistance. c) 90% response time calculated through exponential fitting for changes in drain resistance. d) δ values for changes in drain resistance.

time, τ_e , is given by $\tau_e = L^2/\mu V_{DS}$. Increasing the series resistance reduces the $|V_{DS}|$ and thus increases τ_e . At $V_{GGr} = 0.5$ V, the V_{DS} was approximately -0.6 V for $R_S = 0$ and the V_{DS} was -0.43 V for the highest R_S . Assuming a hole mobility for EG-modified PEDOT:PSS of approximately $3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and with a channel length of $8 \text{ }\mu\text{m}$, the τ_e values were expected to be less than $1 \text{ }\mu\text{s}$. This suggests that the $10 \text{ }\mu\text{s}$ -scale increases in response time for increases in source resistance did not originate from the increases in τ_e . The increases can instead be considered as the time taken to compensate the relatively larger magnitudes of gate current to provide an overall decrease in drain current.

Similarly to the increases in source resistance, it was expected that the δ values would also increase exponentially for exponential increases in drain resistance. Indeed, the $I_G^{Peak}/|I_{D,0}|$ increased exponentially on a similar scale to that found when increasing

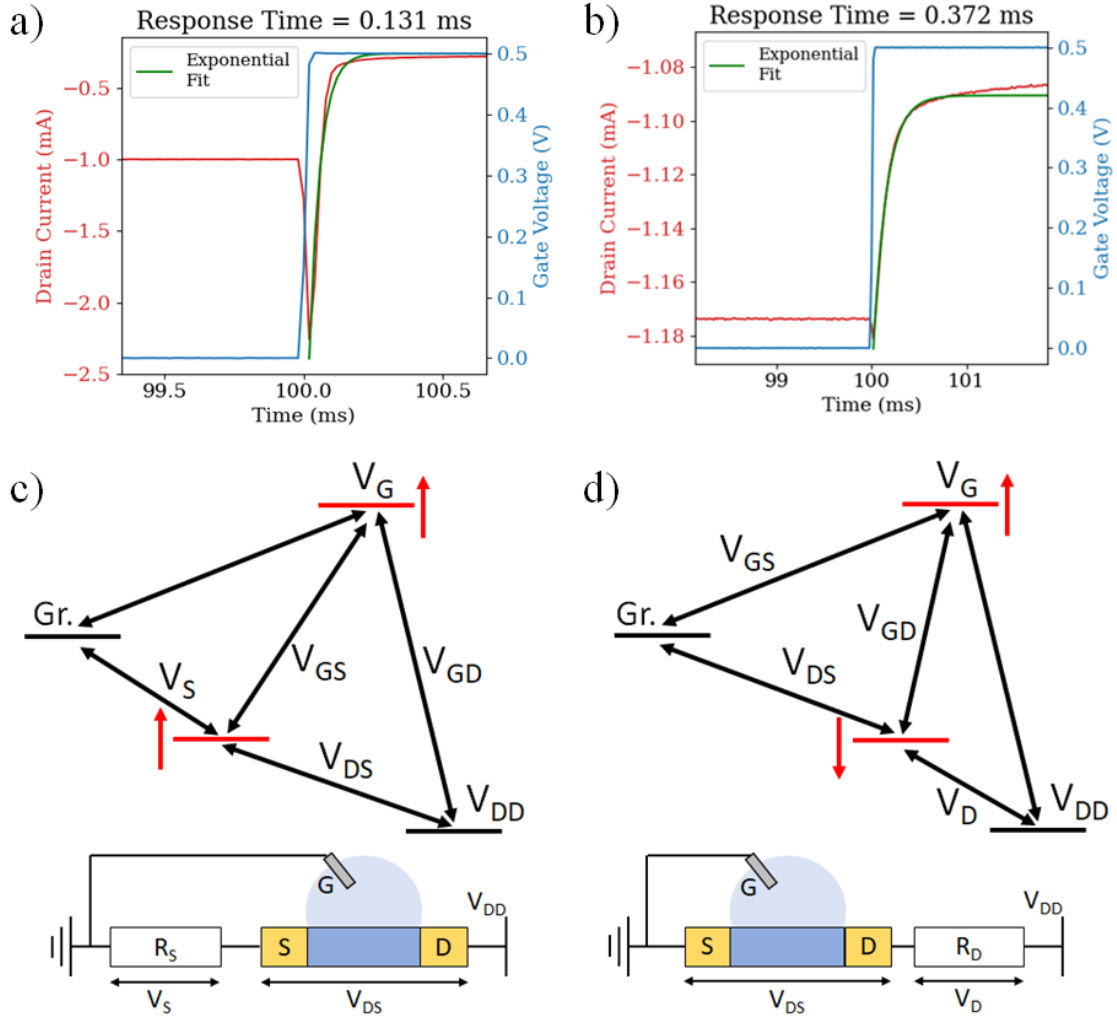


Figure 6.18: Response time characteristics for (a) $R_S = 503$, $R_D = 0$, (b) $R_S = 0$, $R_D = 503$.
c) Potential distribution for a source resistance. d) Potential resistance for a drain resistance.

source resistance. The increase was smaller for drain resistance increases than for source resistance increases. This was understood by how the V_{GD} was smaller for changes in drain resistance, as illustrated in figure 6.18, resulting in smaller gate currents. Although the δ value increased with drain resistance, the increases were negligible. This showed that the f value, and thus the contribution of the gate current to the drain current, was low at high drain resistances. Indeed, as $V_{GD} \rightarrow V_{GS}$, de-doping is less focused at the drain electrode and is more uniform throughout the channel. This is supported by results from the literature that show that the change in channel potential with channel distance becomes more linear and that the f value decreases as $V_{GD} \rightarrow V_{GS}$ [83, 85].

The response time was found to increase significantly with drain resistance. The scale of increase in response time implied an origin in ionic transport as opposed to electronic transport. This was supported by how the $|V_{DS}|$ decreased monotonically, whereas the response time was non-monotonic. Furthermore, the τ_e for the smallest $|V_{DS}|$ was estimated to be approximately 10 μs , whereas the response time was on the 100 μs -scale. As shown in figure 6.12, the fastest response times were associated with the OECT operating in the saturation regime for both $V_{GGr} = 0$ V and $V_{GGr} = 0.5$ V in the characterisation. The response time increased significantly as the device operation changed from the linear regime at $V_{GGr} = 0$ V to the saturation regime at $V_{GGr} = 0.5$ V. The turning point in the response times occurred at the highest drain resistance for which such a regime change occurred. The response times then decreased with further increases in drain resistance, which was associated with the device operating in the linear regime through the entire response time characterisation.

Considering the changes in response time for increasing source resistance, the transfer curves in figure 6.9 showed that the OECT was operating in the saturation regime through the entire characterisation for all source resistances, afforded by how the pinch-off voltage did not vary significantly. Indeed, the response times for increasing source resistance were all fast and did not deviate significantly. This implies that the response time can increase significantly given that a regime transition occurs during the characterisation. Therefore, the response time values could be used to determine the pinch-off voltage. The faster response times for increases in source resistance can also be understood by considering the potential distribution changes during the characterisation. As shown in figure 6.18c, increasing R_S does not vary the $|V_{GD}|$ and thus the potential difference across the primary ionic transport pathway does not vary. On the other hand, increasing R_D results in a decrease in $|V_{GD}|$, as shown in figure 6.18d. Therefore, the ionic current to the drain electrode is reduced, which corresponds to the increase in response time.

When experimentally determining the impact of increasing source or drain resistance on gate-referred noise, it was found that there was an apparent decrease in noise as the resistance approached approximately a factor of 5 greater than the OECT resistance, as shown in figure 6.19. For DC drain currents greater than 10 mA, the limit of measurable currents was set to a value of 100 mA in the Keysight B2902A, whereas that limit could be set to 10 mA for currents lower than 10 mA. The 100 mA setting had a lower accuracy whilst the 10 mA setting had a higher accuracy. Therefore, the two sets of values were treated individually. It was found that within each optimisation category the gate-referred noise increased as the source or drain resistance increased. Contrary to that presented in figure 6.19, this suggests that the noise values at lower source and drain resistances were lower than the values at higher resistances.

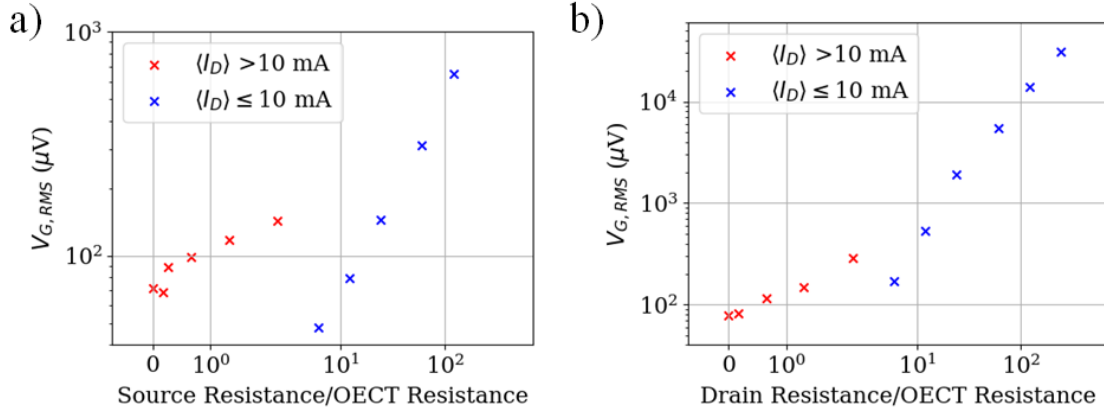


Figure 6.19: Gate-referred noise for changes in a) source resistance, b) drain resistance.

The increases in gate-referred noise with increases in drain resistance were significantly higher than those with source resistance increases. It was found by Stoop *et al.* that increasing the channel resistance relative to the gate-independent contact resistance by increasing gate voltage decreased the gate-referred noise. Under such conditions, the transfer curve of the circuit is dominated by the de-doping behaviour of the OEET, as shown in figure 6.14b, and not the OEET resistance trying to overcome the interconnect resistance, as shown in figure 6.14c. In the noise characterisations, $V_{DD} = -0.6 \text{ V}$ and $V_{GGr} = 0 \text{ V}$, and so the relative contributions of the channel and the interconnects to the drain current behaviour can be seen in the transfer curves for increasing source and drain resistance, shown in figures 6.9 and 6.12, respectively. For increasing source resistance, the transfer curves show that the de-doping behaviour is dominant even at high resistances, implying a lower $V_{G,RMS}$. On the other hand, the transfer curves for increasing drain resistance show that the drain current behaviour becomes quickly dominated by the parasitic series resistance, implying a higher $V_{G,RMS}$. Such observations suggest that increases in $V_{G,RMS}$ would be smaller for increases in source resistance relative to increases in drain resistance. This informs that increasing source resistance is less detrimental to SNR than increasing drain resistance. It was previously found that the response time increases significantly more with drain resistance than it does with source resistance. Therefore, the results suggest that it is more beneficial to system performance to connect a resistor between the source and the OEET than between the OEET and the voltage supply.

6.3.2 Characterisations of OEET Array Interconnect Architectures

Interconnect Architecture and Steady-state Characteristics

To investigate the impact of increasing interconnect length in an OEET array, three interconnect structures were considered. In addition to the short interconnects (SI) presented in figure 6.5b, medium interconnects (MI) and long interconnects (LI), as shown in figure 6.20c and 6.20d, respectively, were designed and fabricated. The exact geometry of the MI structure is shown in figure 4.2a. The resistance of an interconnect line, R_{IC} , of width W_{IC} , length L_{IC} , thickness D_{IC} and material resistivity ρ_{IC} is given by $R_{IC} = \rho_{IC}L_{IC}/W_{IC}D_{IC}$. For the interconnect architectures fabricated here, the ρ_{IC} and D_{IC} were constant and thus the fraction of L_{IC}/W_{IC} was varied to change the interconnect resistance. For the SI, MI and LI structures, the source and drain interconnect L_{IC}/W_{IC} fractions were approximately equal ($R_S \approx R_D$) and had a constant thickness consisting of a 10 nm Cr layer and a 200 nm Au layer. The SI was considered to have a minimal interconnect resistance. The total interconnect resistance, $R_S + R_D$, of the MI was 60 Ω and was 660 Ω for the LI.

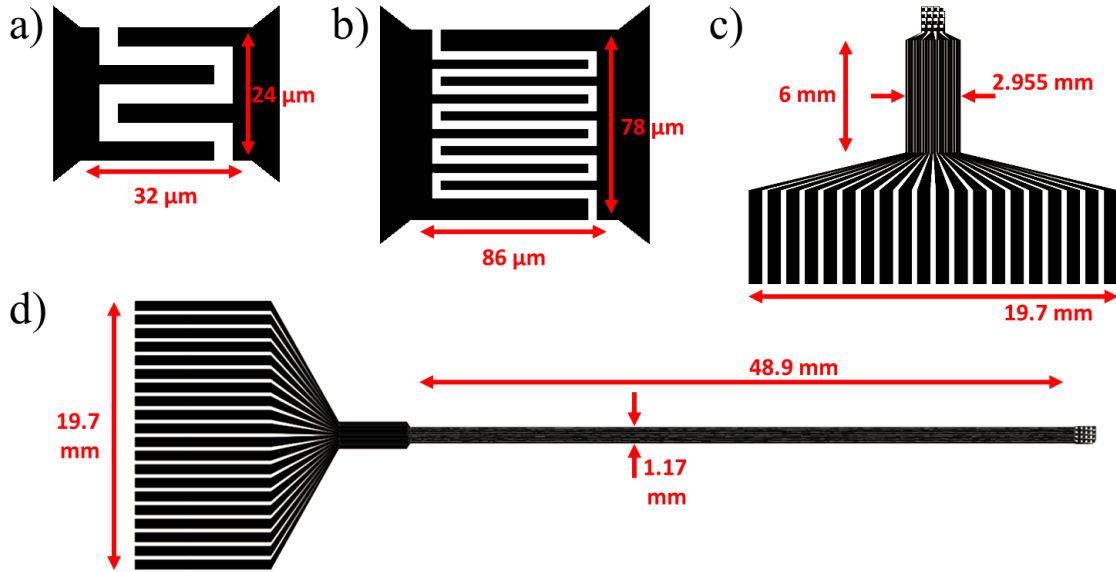


Figure 6.20: a) Small comb (SC) interdigitated electrodes. b) Medium comb (MC) interdigitated electrodes. c) Medium interconnects (MI) architecture. d) Long interconnects (LI) architecture.

The electrode geometry of the active layer was also varied, and three interdigitated electrode architectures were considered. These geometries were denoted the small comb (SC), medium comb (MC) and large comb (LC). It is noted that the ‘SC’ geometry in

section 4 is designated here as ‘MC’. The SC and MC architectures are shown in figure 6.20a and 6.20b, respectively. The LC structure was shown previously in figure 6.5a. With the SI interconnects, the SC resistance was approximately 82.9Ω , the MC resistance was 12.1Ω and the LC resistance was 6.4Ω . With three interconnect styles and three interdigitated geometries, a total of nine variations of interconnect resistance to OECT resistance could be experimentally investigated. An example of a transfer curve for each device type is shown in figure 6.21. Devices were fabricated following the procedures in section 3. The encapsulation layer of each device used a $1 \mu\text{m}$ layer of SU-8 and each channel had a PED active layer that was spin coated to a thickness of 70 nm . Each OECT was electrically characterised, and the parameters were analysed using custom python code.

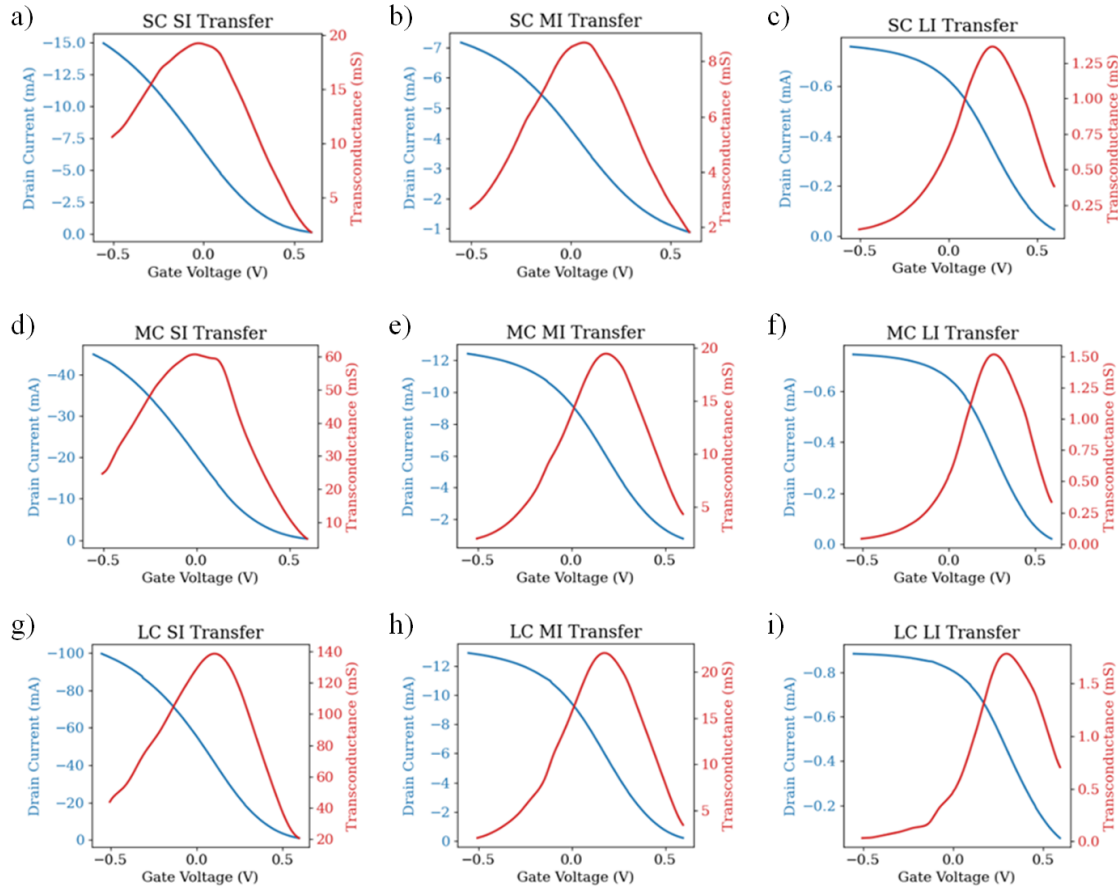


Figure 6.21: Experimental transfer curves for the devices of a) SC SI, b) SC MI, c) SC LI, d) MC SI, e) MC MI, f) MC LI, g) LC SI, h) LC MI, i) LC LI.

The comparison of the experimentally measured transfer curves presented in figure 6.22 highlights the increase in gate-ground voltage required to decrease the drain current magnitude as interconnect resistance increases. Furthermore, the narrowing of the transfer

curve is evident as interconnect resistance increases. The transfer properties were extracted for all devices and the mean and standard deviation values are presented in figure 6.22. Statistical tests that examine the differences in parameters for variations in channel and interconnect architectures are shown in table 6.1. The variations in device number was partially reflective of the relative difficulties of fabrication.

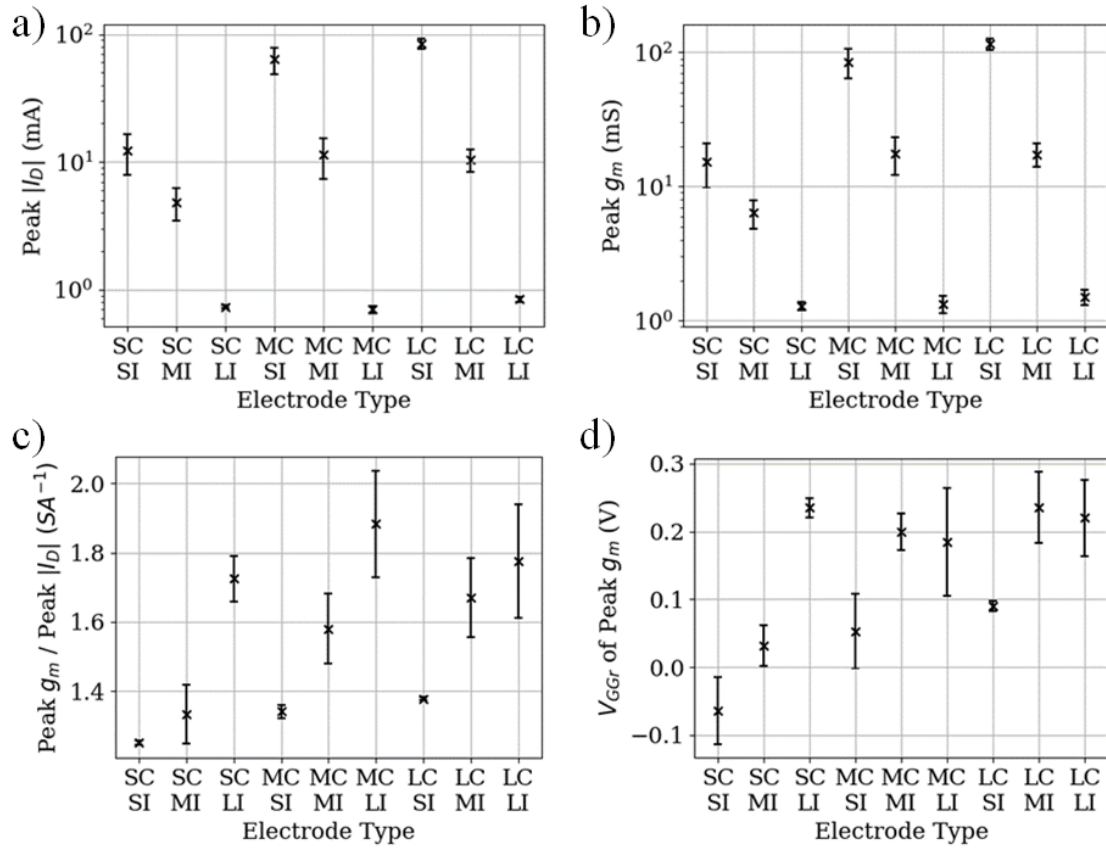


Figure 6.22: a) Peak on-current magnitude, b) peak transconductance, c) fraction of peak transconductance to peak on-current magnitude and d) gate-ground voltage of peak transconductance for each OECT architecture with statistical analysis in table 6.1.

It was found that increasing interconnect length (or resistance) from SI to LI resulted in significant decreases in peak on-current and peak transconductance, as shown in figure 6.22a and figure 6.22b, respectively. The statistical results in table 6.1 showed such significant differences when using a threshold p-value of 0.05. This supported the previous simulated and experimental results. Furthermore, increasing the channel conductance by increasing the W/L ratio resulted in increases in peak on-current and peak transconductance.

As shown in figure 6.22c, it was found that increasing the fractions of interconnect

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Device Number for Each Device Type								
SC SI	SC MI	SC LI	MC SI	MC MI	MC LI	LC SI	LC MI	LC LI
2	2	2	2	13	2	2	9	4
Peak $ I_D $								
Alt. Hyp.		SC SI>SC MI		SC MI>SC LI		SC SI<MC SI		MC SI<LC SI
p-value		1.90×10^{-1}		5.38×10^{-2}		9.99×10^{-2}		1.92×10^{-1}
Alt. Hyp.		MC SI>MC MI		MC MI>MC LI		SC MI<MC MI		MC MI<LC MI
p-value		1.08×10^{-1}		3.61×10^{-7}		7.27×10^{-5}		4.12×10^{-1}
Alt. Hyp.		LC SI>LC MI		LC MI>LC LI		SC LI<MC LI		MC LI<LC LI
p-value		4.09×10^{-2}		9.66×10^{-7}		7.21×10^{-1}		7.47×10^{-2}
Peak g_m								
Alt. Hyp.		SC SI>SC MI		SC MI>SC LI		SC SI<MC SI		MC SI<LC SI
p-value		1.99×10^{-1}		6.98×10^{-2}		1.01×10^{-1}		1.75×10^{-1}
Alt. Hyp.		MC SI>MC MI		MC MI>MC LI		SC MI<MC MI		MC MI<LC MI
p-value		1.13×10^{-1}		1.21×10^{-7}		7.41×10^{-5}		2.03×10^{-1}
Alt. Hyp.		LC SI>LC MI		LC MI>LC LI		SC LI<MC LI		MC LI<LC LI
p-value		4.01×10^{-2}		5.91×10^{-7}		4.15×10^{-1}		3.14×10^{-1}
Peak g_m / Peak $ I_D $								
Alt. Hyp.		SC SI<SC MI		SC MI<SC LI		SC SI<MC SI		MC SI<LC SI
p-value		1.27×10^{-1}		2.69×10^{-2}		4.51×10^{-3}		1.67×10^{-2}
Alt. Hyp.		MC SI<MC MI		MC MI<MC LI		SC MI<MC MI		MC MI<LC MI
p-value		6.37×10^{-7}		1.42×10^{-1}		3.74×10^{-2}		3.05×10^{-2}
Alt. Hyp.		LC SI<LC MI		LC MI<LC LI		SC LI<MC LI		MC LI<LC LI
p-value		1.79×10^{-5}		2.73×10^{-1}		2.37×10^{-1}		7.62×10^{-1}
V_{GGr} of Peak g_m								
Alt. Hyp.		SC SI<SC MI		SC MI<SC LI		SC SI<MC SI		MC SI<LC SI
p-value		1.33×10^{-1}		1.83×10^{-2}		1.19×10^{-1}		2.56×10^{-1}
Alt. Hyp.		MC SI<MC MI		MC MI<MC LI		SC MI<MC MI		MC MI<LC MI
p-value		1.07×10^{-1}		5.63×10^{-1}		3.64×10^{-2}		2.68×10^{-1}
Alt. Hyp.		LC SI<LC MI		LC MI<LC LI		SC LI<MC LI		MC LI<LC LI
p-value		4.24×10^{-4}		5.80×10^{-1}		6.83×10^{-1}		4.10×10^{-1}

Table 6.1: Alternative hypotheses and p-values of one-tailed Welch's t-tests for the comparison of OECT characteristics as illustrated in figure 6.22.

resistance to OECT resistance from equal additions in source and drain resistances resulted in increases in the fractions of peak transconductance to on-current magnitude. For a threshold p-value of 0.05, statistically significant results were found in a subset of the comparisons, supporting the observations. Previous results showed that such behaviour

originated primarily from the increase in the drain resistance, and thus these results show the significant influence of drain resistance on the transfer characteristics when both source and drain resistances are present. However, with the LI drain interconnect resistance being approximately a factor of 50 greater than the OECT resistance, previous results that considered increasing only the drain resistance would predict a fraction of approximately 6.0, as shown in figure 6.13c. However, there were no such significant changes for only source resistance increases. This shows that whilst the drain resistance is attempting to increase the fraction, the source resistance could be dampening such effects. Such a dampening was suggested by the simulation, as shown in figure 6.15c.

The gate voltage of peak transconductance was found to increase with the ratio of interconnect resistance to OECT resistance, as shown in figure 6.22d, supporting results by Han *et al.* [262]. The effect of the reduction of the gate voltage from increasing source resistance was not evident. Therefore, the results suggest that the increase from the drain resistance was greater than the reduction from the source resistance, which was also shown in the simulation. It was also found in the array structures that the increases in the peak transconductance gate voltage saturated at approximately 0.2 V. This saturation was found previously when increasing only the source resistance, as shown in figure 6.10d. This shows that the source interconnect suppresses increases in the peak transconductance gate voltage when both source and drain interconnect resistances are present. Such a saturation was accounted for in the statistical results, which only presented significant differences on a small subset of comparisons when using a threshold p-value of 0.05.

For using the OECT as an amplifier, the interconnect resistance decreases peak transconductance and thus the amplification factor decreases. Critically, if the amplification occurs at a desired gate-ground voltage, then large interconnect resistances can significantly decrease the facilitating transconductance. As such, a DC bias can be applied to the gate-ground input voltage, which can be implemented by using a common-source linear amplifier circuit topology, as demonstrated in section 5.

Transient Characteristics of the OECT Array Interconnect Architectures

The exponential response times and δ values were calculated for the three interdigitated electrode geometries across the three interconnect structures. The results are shown in figure 6.23. It was previously found that the LC MI response time was significantly greater than the MC MI response time. It was suggested in section 4 that this was due to the higher parasitic capacitance of the LC architecture arising from the greater exposed area of the source and drain interdigitated electrodes to the gate potential.

The transient characterisations in figure 6.17 showed that the δ values and response times increased as the fractions of source and drain resistance to OECT resistance increased,

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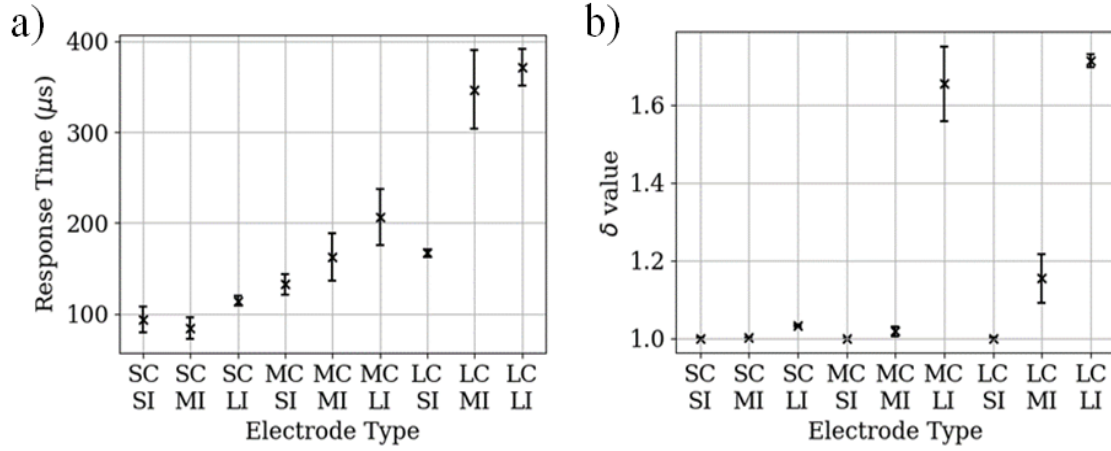


Figure 6.23: a) Exponential response times and b) δ values for each OEET array architecture, with statistical results given in table 6.2.

Response Time				
Alt. Hyp.	SC SI<SC MI	SC MI<SC LI	SC SI<MC SI	MC SI<LC SI
p-value	6.90×10^{-1}	4.96×10^{-2}	1.20×10^{-1}	1.75×10^{-2}
Alt. Hyp.	MC SI<MC MI	MC MI<MC LI	SC MI<MC MI	MC MI<LC MI
p-value	2.93×10^{-3}	1.89×10^{-1}	4.98×10^{-8}	2.46×10^{-6}
Alt. Hyp.	LC SI<LC MI	LC MI<LC LI	SC LI<MC LI	MC LI<LC LI
p-value	5.01×10^{-6}	5.09×10^{-1}	9.72×10^{-2}	4.85×10^{-2}
δ value				
Alt. Hyp.	SC SI<SC MI	SC MI<SC LI	SC SI<MC SI	MC SI<LC SI
p-value	3.89×10^{-1}	2.30×10^{-2}	7.46×10^{-1}	1.57×10^{-1}
Alt. Hyp.	MC SI<MC MI	MC MI<MC LI	SC MI<MC MI	MC MI<LC MI
p-value	2.03×10^{-4}	4.80×10^{-2}	3.20×10^{-4}	3.88×10^{-3}
Alt. Hyp.	LC SI<LC MI	LC MI<LC LI	SC LI<MC LI	MC LI<LC LI
p-value	1.60×10^{-3}	1.51×10^{-9}	4.93×10^{-2}	3.27×10^{-1}

Table 6.2: Alternative hypotheses and p-values of one-tailed Welch's t-tests for the comparison of OEET characteristics as illustrated in figure 6.23. The device numbers are the same as those given in table 6.1.

respectively. For a threshold p-value of 0.05, these observations were supported by the statistical results given in table 6.2. Therefore, the effects found in the array architectures are a combination of those found when individually increasing source or drain resistance. For a constant interconnect resistance, it was found that the MC devices had a faster response time than the LC devices, and the SC devices provided faster response times

than the MC devices. In addition to the slower response times resulting from the higher interconnect to channel resistance fractions of the larger channel geometries, the parasitic capacitance was expected to play a significant role in the increases in response time.

Given that a device architecture necessitates long interconnect lengths, for example in applications where the devices are placed deep into a neural region whilst voltages are applied externally to the scalp, then either the interconnect thickness can be increased to reduce interconnect resistance, or the channel resistance could be increased. Increasing interconnect thickness can result in more difficult and expensive fabrication techniques. With OECT active layer material development focusing on increasing the product of electronic mobility and volumetric capacitance, μC^* , and the dependency of OECT conductance on μ , it is expected that the intrinsic channel conductance values in literature will increase. Therefore, the impact of interconnect resistance will become increasingly important for applying such materials in any application.

Bioelectric Characteristics of the OECT Array Interconnect Architectures

It was found that gate-referred RMS noise decreased as supply voltage increased in magnitude, as shown in figure 6.24a. Therefore, lower noise, and thus higher bioelectric performance, was associated with greater power consumption. This was supported by concurrent increases in the recovery fraction. In a further analysis using more device types, it was found that there was a negative correlation between the recovery fraction and the gate voltage RMS noise, as presented in figure 6.24b. This supported the use of the recovery fraction as a figure of merit of bioelectric signal resolution for the OECT.

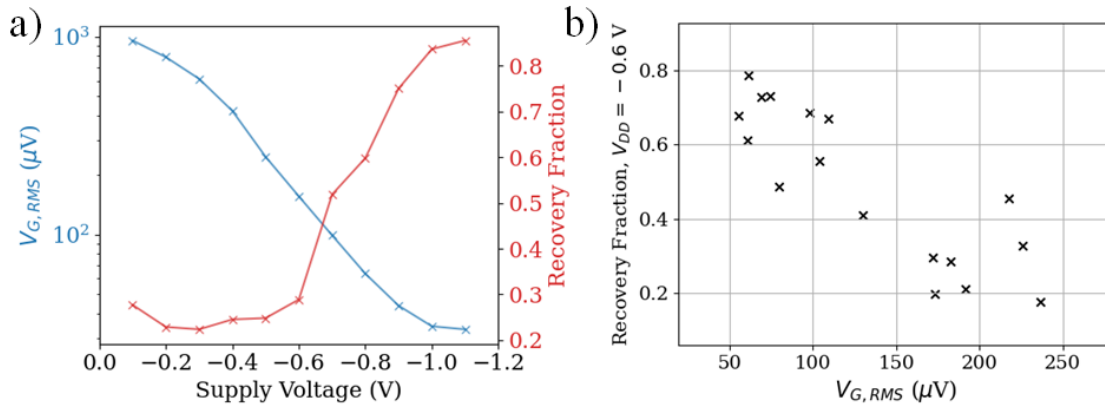


Figure 6.24: a) The variation in recovery fraction and gate-referred noise with supply voltage for an LC MI device with a pinch-off voltage of 0.73 V. b) Recovery fraction for $V_{DD} = -0.6$ V and gate-referred noise for all characterised devices.

It was observed that the recovery fraction increased significantly when the supply voltage magnitude was increased. At such supply voltages, the gate voltage RMS noise was smaller than the primary features of the signal. At the largest supply voltage magnitudes, the recovery fraction reached an upper limit, which was associated with the device entering the saturation regime and operating near maximum transconductance. This shows that supply voltage can be increased to increase the SNR of the signal. As such, the device is required to consume a greater power to resolve smaller signals. However, the OECT will only be efficacious at resolving the desired signals if the smallest noise power achieved with sufficient supply voltage is lower than the signal power. Gate-referred noise has been shown to reduce also when the active layer increases in thickness, which also results in an increase in pinch-off voltage and thus a greater supply voltage to enter the saturation regime [94]. Therefore, a greater supply voltage, and thus an increased power consumption, would be required to optimally operate the device, though smaller signal magnitudes could be resolved.

The effect of electrode architecture on the recovery fraction was investigated. Previous investigations have shown that noise decreases as the active area increases, and thus it was expected that the MC and LC devices would have lower gate-referred noise values than the SC devices [89]. Furthermore, the impact of interconnect length on the recovery fraction was considered. With a range of potential distributions for each interconnect type, it was expected that the gate-referred noise values would vary. A subset of bioelectric responses is presented in figure 6.25.

It was confirmed that a greater interdigitated electrode area with a greater W/L ratio provided reduced noise values. The bioelectric responses highlighted that although the larger electrode geometries have higher recovery fractions, the additional parasitic capacitance reduces their upper bandwidth. Indeed, in comparing figure 6.25c and figure 6.25d, the SC device captures the initial gate voltage spike, whereas the LC responds with a lower relative change in amplitude, and it would be more difficult to distinguish the event from the background. In addition, the LC response is noticeably lagged relative to the gate voltage, whereas the temporal SC response is almost indistinguishable. Therefore, there is a trade-off between low-frequency and high-frequency SNR.

In addition to showing that greater interdigitated electrode areas with higher W/L ratios provide higher recovery fractions, the effect of the interconnect length on the recovery fraction is shown in figure 6.26a. For the SC devices, the recovery fraction when connected with the LI was greater than when using the SI. The contrary effect was observed for the MC and LC, where the recovery fraction for the LI was lower than that of the SI. The MC and LC devices have significantly smaller channel resistances than the SC devices and thus the potential differences across the MC and LC device channels are lower than those of the

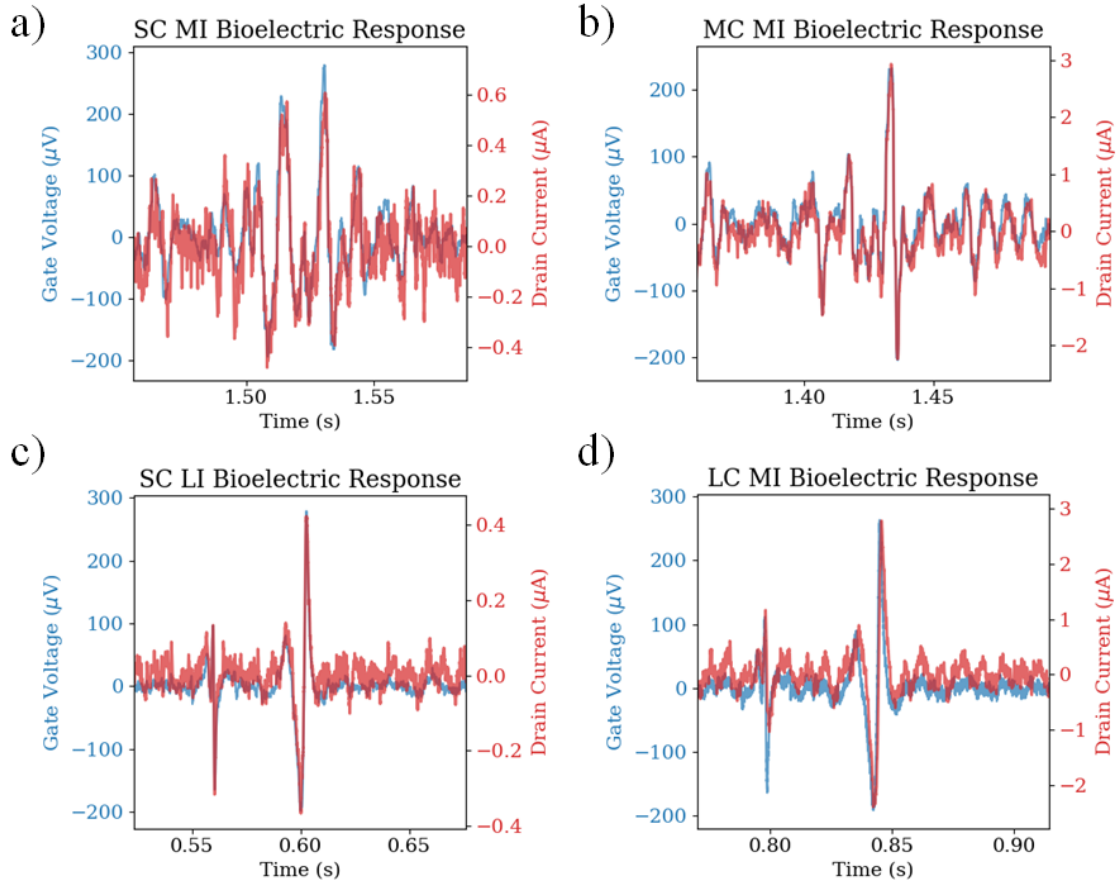


Figure 6.25: Bioelectric gate voltage input and drain current output for a) SC MI device, b) MC MI device, c) SC LI device and a d) LC MI device.

SC channels. This was supported by the higher δ values, and the significant increases in δ values for the MC LI and LC LI devices correlated with the significant decreases in their recovery fractions. In considering how gate-referred noise decreases as $|V_{DS}|$ increases, the results show that there is a trade-off between the reduction in noise as a result of increased active area (or W/L ratio) and the increase in noise as a result of a reduced potential difference across the channel. However, such relationships would also suggest that the recovery fractions of the MI devices would be lower than those of the SI devices, which is not clearly observed. The large DC currents of the MC SI and LC SI devices necessitated using lower sampling accuracies than those used for the MC MI and LC MI devices. This resulted in larger noise values, which thus contributed to the lower recovery fractions. This highlights the need for sampling with high current accuracies when recording OEECT drain currents in electrophysiological applications.

The results show that the impact of the interconnect resistance on bioelectric

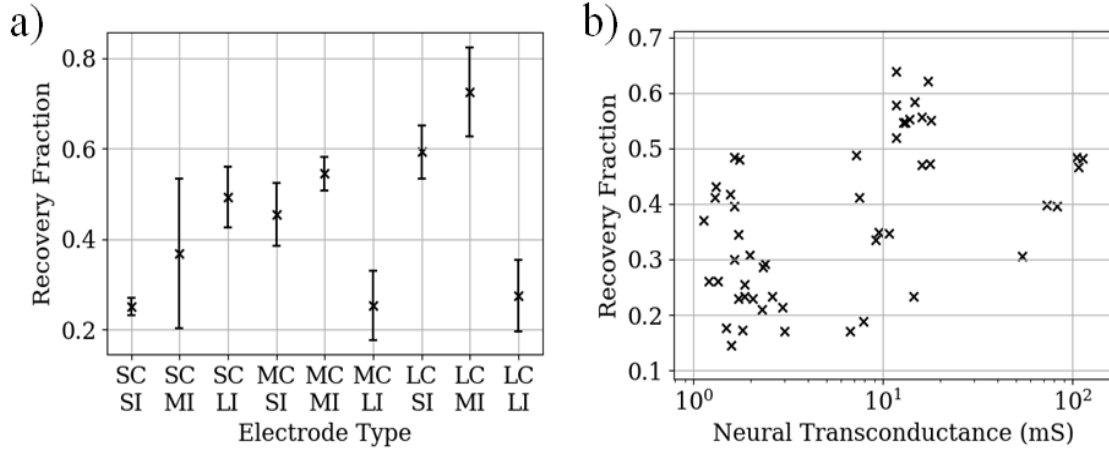


Figure 6.26: a) The mean values and standard deviations of the recovery fractions for each OEET architecture. b) The recovery fraction and neural transconductance, given by the transconductance as measured in the bioelectric signal, for all characterised devices.

performance is dependent on the channel properties and the recording configuration. For array structures, it could be argued that the results suggest minimising interconnect resistance. Furthermore, the results illustrated in figure 6.26b show that there is no direct relationship between the extrinsic transconductance of an OEET and its ability to resolve bioelectric signals. This highlights how important device performance metrics are not dependent on the parameters often used for comparison.

6.3.3 Active Area Electrode Geometry Comparison

Device Architecture and Fabrication

The optimal electrode architecture at the active area for area-limited applications was investigated. An interdigitated electrode OEET, denoted ‘IDE’ was compared to an OEET with a parallel-plate geometry and an equal active area, denoted ‘SPE’, and to a parallel-plate OEET with an equal W/L ratio, denoted ‘LPE’. Devices were fabricated following the procedures in section 3. The Cr and Au layers had thicknesses of 10 nm and 100 nm, respectively. The encapsulation layer was formed using SU-8 to a thickness of 2.4 μm . The active layers consisted of PEDOT:PSS, EG, DBSA and GOPS (PEDG) and were spin coated at 2000 rpm, producing a layer with a thickness of approximately 90 nm. The three electrode designs are illustrated in figure 6.27 and the properties are given in table 4.1.

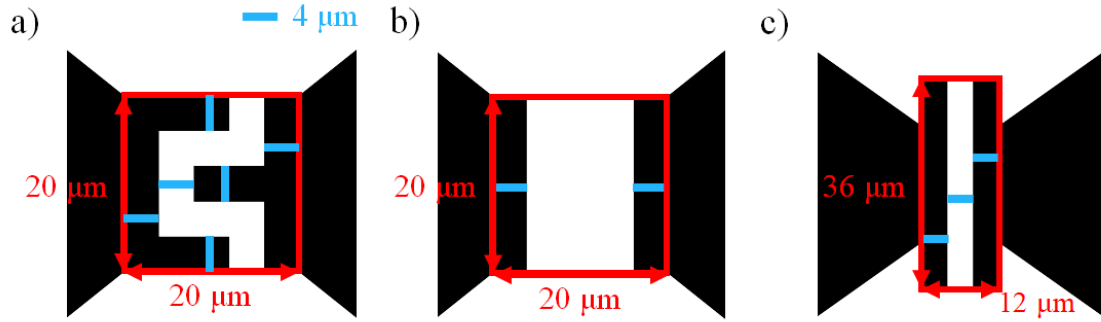


Figure 6.27: Electrode diagrams showing a) the interdigitated electrode geometry denoted as ‘IDE’, b) the parallel-plate geometry with an equal active area to a) denoted as ‘SPE’, c) the parallel-plate geometry with an equal W/L ratio to a) denoted ‘LPE’.

Property	IDE	SPE	LPE
Channel Width (μm)	36	20	36
Channel Length (μm)	4	12	4
W/L Ratio	9	1.67	9
Active Area (μm^2)	400	400	432
Electrode Overlap Area (μm^2)	256	160	288

Table 6.3: Geometrical properties of the three electrode types shown in figure 6.27.

Steady-State and Transient Device Characteristics

Devices were characterised for their steady-state and transient characteristics. The parameter values are presented in table 6.4 with statistical analysis in table 6.5. The results are further visualised in figure 6.28. It was found that the SPE and LPE device had a distinction between all parameters, whereas the IDE devices had subsets of parameters with values that were not significantly different from each of the SPE and LPE device types.

Supported by the statistical analysis, the conductance characterisations, illustrated in figure 6.28a, found that the LPE devices had the greatest conductance and the SPE devices had the lowest. This was expected as conductance is proportional to the W/L ratio, which is greater for the LPE devices. The IDE devices had a conductance between the LPE and SPE devices, which can be partly understood as the channel length increases from 4 μm at corners of the comb structure, resulting in a lower W/L value than is approximated in table 6.3. The resistances of the three devices were significantly greater than the interconnect resistance. Therefore, the transfer curve described the OECT de-doping and not the effects

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Parameter	IDE	SPE	LPE
Device Number	5	7	8
Conductance, G (mS)	14.6 ± 1.0	9.7 ± 1.4	19.4 ± 3.7
Resistance (Ω)	68.5 ± 4.7	103.1 ± 14.9	51.5 ± 9.8
Peak transconductance, g_m^{Peak} (mS)	11.3 ± 2.5	7.6 ± 0.6	15.9 ± 2.6
$V_{GGr}(g_m^{Peak})$ (V)	-0.07 ± 0.05	-0.08 ± 0.04	-0.01 ± 0.01
Pinch-off Voltage, V_P (V)	0.50 ± 0.03	0.57 ± 0.05	0.51 ± 0.02
Exponential τ_{90} (ms)	14.1 ± 2.4	10.5 ± 3.7	7.1 ± 3.7
Gate-referred Noise, Δ (μ V)	42.1 ± 8.7	59.3 ± 13.3	45.9 ± 14.8

Table 6.4: *Electrical characteristics of the three electrode types shown in figure 6.27.*

Parameter	Alt. Hyp.	p-value	Alt. Hyp.	p-value
G	IDE > SPE	2.47×10^{-4}	IDE < LPE	6.01×10^{-3}
g_m^{Peak}	IDE > SPE	1.98×10^{-2}	IDE < LPE	1.21×10^{-2}
$V_{GGr}(g_m^{Peak})$	IDE < SPE	5.80×10^{-1}	IDE < LPE	2.67×10^{-2}
V_P	IDE < SPE	8.36×10^{-3}	IDE > LPE	8.10×10^{-1}
τ_{90}	IDE > SPE	6.03×10^{-2}	SPE > LPE	6.19×10^{-2}
Δ	IDE < SPE	2.90×10^{-2}	IDE > LPE	6.78×10^{-1}

Table 6.5: *Alternative hypotheses and p-values of one-tailed Welch's t-tests for the comparison of OECT characteristics as given in table 6.4 and illustrated in figure 6.28.*

of interconnect resistance. Indeed, all devices had broad transfer curves characteristic of short interconnects. This permitted an accurate comparison of device characteristics. The transconductance is proportional to the conductance and thus took similar relative values, as shown in figure 6.28b and supported by the statistical analysis with a threshold p-value of 0.05. These results show that the higher transconductance values of the IDE devices allow greater signal amplification in area-limited applications.

The gate voltages of peak transconductance were not significantly different between the IDE and SPE devices and were significantly lower for the LPE devices, as shown in figure 6.28c. The pinch-off voltages, illustrated in figure 6.28d, were not significantly different between the IDE and LPE devices and were higher for the SPE devices. The ratios of peak transconductance to on-current were not significantly different between the IDE and LPE devices and were lower for the SPE devices, indicative of a broader transfer curve. These observations were supported by the statistical analysis with a threshold p-value of 0.05.

The response time characterisations gave values significantly greater than expected

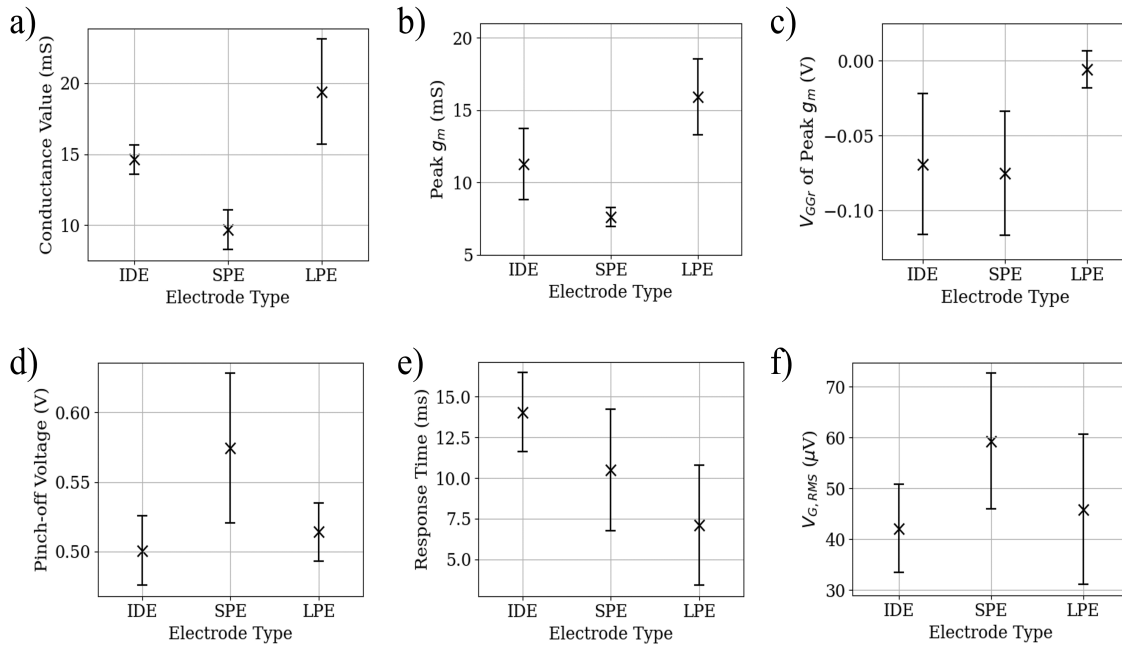


Figure 6.28: The mean values and standard deviations of the three electrode types for the OECT parameters of a) conductance, b) peak transconductance, c) gate-ground voltage of peak transconductance, d) pinch-off voltage, e) 90% response time and f) gate-referred noise. Statistical differences are given in table 6.5.

relative to previous characterisations. Nevertheless, the values for all three devices were on the same scale and thus were still considered comparable. It was found that the IDE devices had the slowest response time, and the SPE devices were faster, as shown in figure 6.28e. The LPE devices had the fastest response time whilst also having the greatest electrode overlap area, showing that parasitic capacitance was not limiting the response times. Illustrated in figure 6.28f and supported by the statistical analysis with a threshold p-value of 0.05, the gate-referred noise for the IDE devices was not significantly different from the LPE devices and was significantly higher for the SPE devices. This suggests that the geometrical properties that determine the noise of IDE OECTs also determine the noise of parallel-plate OECTs with equal W/L ratios.

For electrophysiological applications that require a high device density and thus a limited device area to resolve bioelectric signals, the greatest SNR can be achieved by minimising the system noise. Therefore, the comparison of noise was a critical aspect of this investigation. For such applications where the electrode type is restricted between an IDE and SPE geometry, the characteristics suggest that there is a trade-off between noise and response time. The SC SI geometry characterised previously had a similar electrode architecture and the response time provided a bandwidth sufficient for high-frequency

electrophysiological signals. Therefore, further reductions in response time with an SPE geometry would not yield a significantly better signal quality. As such, choosing to minimise noise by using an IDE geometry would improve the SNR. Therefore, the IDE geometry is suggested as an optimal architecture for the design of high-density OECT arrays in electrophysiology.

6.4. Conclusions

This investigation considered how varying the electrode architecture of the interconnects and the source and drain electrodes affected transistor operation and performance. It was found that increasing the source resistance showed capability in reducing the gate voltage of peak transconductance whilst increasing drain resistance impacted the broadness of the transconductance peak. It was further suggested that the potential distribution in the channel took an exponential form, which was supported by experimental data from the wider literature. The experimental steady-state characteristics were emulated by the simulation, though deviations became evident as interconnect resistance increased, particularly at higher gate-ground voltages within such high-resistance circuits. The observed changes in the behaviour of the steady-state characteristics were interpreted in terms of how the distribution of the supply voltage changes across the source interconnect, channel and drain interconnect. Transient characterisations showed that the δ value increased significantly as source resistance increased, attributed to the greater ratio of gate current to drain current, whereas the response time did not increase significantly. On the other hand, increasing the drain resistance resulted in significant increases in response time, though the δ value did not notably increase. Finally, it was found that increasing the source resistance resulted in smaller increases in gate-referred noise than when increasing drain resistance.

The steady-state characteristics of the OECT arrays confirmed that interconnect resistance behaved as though there were source and drain resistors in series with the OECT. Transient measurements of OECT arrays confirmed that interdigitated electrode OECTs have slower response times as the channel area increases with greater areas of interlocking source and drain combs. Furthermore, it was found that the response time and the δ value increased as the fraction of interconnect resistance to channel resistance increased. This suggested that decreasing interconnect resistance would maximise response time, which could be achieved by increasing channel resistance or by increasing interconnect width or thickness. Minimising response time would also maximise the SNR for high-frequency bioelectric signals. It was further found that increasing the supply voltage magnitude decreased the gate-referred noise and increased the recovery fraction. This showed that higher SNR comes at the expense of increased power consumption. It

was found that increasing the channel area with greater interdigitated electrode areas and higher W/L ratios resulted in greater recovery fractions, implying lower gate-referred noise values and thus an increased SNR. However, it was highlighted that increasing the area reduces efficacy in resolving high-frequency bioelectric signals due to parasitic capacitance. Therefore, a trade-off was identified between low-frequency and high-frequency SNR. The impact of increasing interconnect resistance varied depending on the channel resistance. The results suggested that excessive increases in interconnect resistance resulted significant decreases in the recovery fraction. This correlated with the results for the δ values, implying that the gate-referred noise increases as the magnitude of drain-source voltage decreases and thus as the hole transit time increases. Therefore, it was concluded that the optimal design electrode architecture minimises the interconnect resistance, which can be achieved by increasing the electrode thickness. However, this results in more financial expense and introduces difficulties in fabrication.

The investigation finally considered how an interdigitated electrode OECT, denoted IDE, compared to a parallel-plate OECT, denoted SPE, with a fixed active area. It was found that the IDE devices shared a subset of characteristics with the SPE devices and a further subset with OECTs that had the same W/L ratio as provided by the IDE geometry, denoted LPE. The IDE devices presented a gate-referred noise value that was proximal to the LPE devices and was lower than the SPE devices. On the other hand, the SPE devices presented a greater bandwidth than the IDE devices, implying a further trade-off between gate-referred noise and response time. However, previous results suggested that the small IDE architecture would provide sufficient bandwidth to resolve high-frequency bioelectric activity and thus the reduced noise levels suggested it had superior applicability.

As new organic conductive polymers show greater values of hole mobility, channel resistance will decrease and thus the impact of interconnect resistance will become more prominent. However, greater material performance could also correlate with reduced noise values, and therefore power consumption could decrease for a given level of noise. Alternatively, the trade-off between low-frequency and high-frequency SNR would reduce because the active area could be made thinner for a given level of noise. This investigation highlights the inherent limitations of optimising planar electrode architecture and suggests that further research should focus on how the material properties can be optimised to maximise device efficacy. Beyond improving material performance, further research could investigate the interplay and optimisation between material properties and electrode architecture.

7. IMPACT OF AQUEOUS IMMERSION AND APPLIED BIAS ON THE ELECTRICAL AND CONJUGATED POLYMER CHARACTERISTICS OF PEDOT:PSS ORGANIC ELECTROCHEMICAL TRANSISTORS

This research was supervised by Professor J.-S. Kim and Professor M. G. Boutelle. E. Tan collected the resonance Raman spectroscopy data, performed simulations using density functional theory and contributed to the data analysis and interpretations of the data.

7.1. Introduction

Biosensing over extended time periods requires operational stability of the measuring device such that the efficacy of physiological recording does not significantly degrade. The SNR, which describes biosensor performance, can be maximised by minimising the level of noise. With extended aqueous immersion, it has been shown that hole mobility decreases in OECTs [44]. In investigations utilising organic thin-film transistors, noise has shown dependencies on the film microstructure, and it is hypothesised that noise is dependent on the trap states at grain boundaries in the active layer [90, 277]. Such investigations suggest that the impact of aqueous immersion on the organic active layer morphology could be detrimental to OECT performance in the transduction of physiological activity over extended periods.

In this investigation, the effects of extended aqueous immersion on the electrical characteristics of PEDOT:PSS OECTs and their PEDOT channel structures are measured to determine the degree to which the devices remain capable of long-term biosensing measurements. In particular, the effect of aqueous immersion on OECT noise is considered, and such measurements are correlated with changes in PEDOT structure, which are explored using resonance Raman spectroscopy. Furthermore, the impact of an applied gate and drain voltage on OECT noise and PEDOT structure is considered. Devices with and without the crosslinker GOPS as an active layer additive are compared throughout the investigation to determine if crosslinker addition is beneficial or detrimental to device performance and stability. The insights gained by the research include how significant changes in OECT noise level correlate to variations in the PEDOT structure and the degree of stability of device characteristics imperative for efficacious biosensing over 50 days of aqueous immersion. The results inform the material design to minimise the noise and describe the conditions to maximise the performance of OECTs for physiological monitoring in aqueous environments.

7.2. Methodology

7.2.1 Device Architecture and Fabrication

The devices were fabricated as described in section 3. The OECTs were fabricated on Kapton HN Thermal Insulating Film substrates made of polyimide with a thickness of $50\text{ }\mu\text{m}$. The substrates were cleaned by sonication in acetone and IPA with subsequent exposure to oxygen plasma. A 5 nm Cr layer and a 100 nm Au layer were evaporated and patterned into source and drain electrodes using photolithography. The electrode architecture comprised of interdigitated source and drain electrodes which were patterned into an array style. The interdigitation had an active area of $86 \times 78\text{ }\mu\text{m}^2$ and a W/L ratio of 164.5. Specifically, the geometry is of that described as the MC MI architecture in section 6. A layer of SU-8 2002 was spin coated at 2000 rpm and was patterned using photolithography, producing a layer with a thickness of approximately $2.4\text{ }\mu\text{m}$. The two organic active layer formulations used were PED and PEDG. Each solution was spin coated at 2000 rpm, producing a layer approximately 90 nm thick, and was not patterned. The devices were baked at 150°C for 75 minutes and immersed in deionised water overnight.

7.2.2 Device Characterisation and Resonance Raman Spectroscopy

Electrical characterisations were performed on each OECT. These included the output, transfer, response time and noise characterisations, providing the parameters of conductance, peak transconductance, gate voltage of peak transconductance, pinch-off voltage, 90% response time and the gate-referred noise.

To probe how the polymer structure varied with aqueous immersion, resonant Raman spectroscopy was employed. In Raman spectroscopy, a laser is incident onto a material and the laser's photons interact with the electrons of the material. The electrons are excited to an energetic state and then de-excite with the emission of a photon. The Rayleigh-scattered photons which undergo elastic interactions with the material are not of interest. The Stokes-scattered photons which interact inelastically with the material reveal information on the energetic transitions describing the vibrational modes available to the electrons. The Raman intensity represents the number of inelastically scattered photons from the incident laser across a range of wavenumbers. Therefore, increases in Raman intensity at a given wavenumber correspond to the presence of vibrational modes [278]. In resonance Raman spectroscopy, the wavelength of the incident laser is associated with the electronic transitions of the material, providing an enhanced intensity of Stokes scattered photons [279]. In this investigation, the Raman spectra gave information on the relative intensities of the vibronic modes of the carbon single and double bonds that construct the conjugated PEDOT backbone.

The measurements were taken using a Renishaw inVia microscope with a 785 nm laser source. The laser was incident on the PEDOT:PSS active layer with penetration through the electrolyte. The Ag/AgCl gate electrode was placed to the side of the channel and was connected through the electrolyte. The variation in the electrolyte layer between measurements resulted in significant differences in Raman intensity. Therefore, the absolute value of the intensity could not be a parameter for comparison. The 785 nm laser was chosen because it was resonant with the energetic transitions associated with both the neutral and the doped polaron PEDOT states. The Raman laser was focused on the channel between the source and drain electrodes. Any contributions from the electrodes to the Raman intensity signal were considered to be small.

To determine the stability of the devices and the effects of aqueous immersion on PEDOT structure, OECTs were immersed in Ringer’s solution and were measured over a period of 50 days. The devices were analysed after fabrication, denoted as day 1, and were then immersed until the next characterisation time point on day 2. The time points used were days 1, 2, 4, 8, 16, 25, 36 and 50. For each timepoint, resonance Raman spectroscopy was initially performed on the devices and electrical characteristics were then obtained.

In the investigation of how the Raman parameters evolved with aqueous immersion time, the devices were provided with a supply voltage of -0.6 V and the gate was grounded for each Raman characterisation. The impact of increasing the magnitude of the supply voltage on OECT noise and PEDOT structure was investigated. The supply voltage was increased from -0.1 V to -1.1 V in steps of 0.1 V. Raman spectra were obtained and gate-referred noise values were then found for each supply voltage. Similarly, the effect of increasing gate voltage on noise and PEDOT structure was examined. A drain voltage of -0.6 V was applied and the gate voltage was iterated from -0.2 V to 0.5 V in 0.1 V steps. A Raman spectrum was obtained for each gate voltage. To measure noise for varying gate voltages, a constant gate bias was applied and the drain current was sampled.

7.2.3 Raman Spectroscopy Background Subtraction

The measurement of the Raman spectra provided intensity peaks that corresponded to the energy levels of vibronic modes. The peaks were superposed onto a background intensity and thus the removal of the background was desired to provide greater clarity on the peak intensities. A number of instrumental and computational methods have been developed to maximally remove the background signal. In this investigation, a novel computational method of background subtraction was formulated. Traditional computational methods include utilising frequency-domain filtering, signal derivatives and polynomial fitting. More recently, machine learning methods have been employed for the removal of the Raman background signal [280]. The novel method described here uses a combination of frequency-

domain filtering, linear interpolation, signal derivatives and non-parametric statistics.

Firstly, a low-pass filter was used to remove high-frequency components from the Raman spectra. Then, the rolling standard deviation and the rolling local minimum was found in a window of a given size for each data point. Therefore, each intensity data point had a smoothed value, a standard deviation value and a local minimum. The data set of rolling standard deviations was then analysed and a percentile was chosen based on the proportion of activity to background intensities. This provided a threshold in the data set of standard deviations. If the standard deviation at a data point was smaller than the standard deviation percentile, then the data point was considered as a point of insignificant activity and the value to subtract at that data point was the local minimum. Otherwise, the data point was designated as one at which the Raman intensity was significantly different from the background signal and required further analysis to determine its subtraction value. This method was motivated by the assumption that peaks appear in the background as extraneous events and thus the intensity fluctuates much greater than for background values. Therefore, for each Raman intensity, this analysis provided either a value to subtract or a label indicating that the Raman intensity was significantly different from the background.

The subtraction data set consisting of background points and signal points was then analysed and modified. Data points that were considered to constitute the desired signal were subject to interpolation. Such data points often occurred in groups. Interpolation was performed by taking the subtraction points considered as background activity on either side of the group of signal points and fitting a straight line between those background points. For each signal point, the underlying straight line provided a subtraction value. Following this stage, a subtraction value was determined for each intensity data point.

In the following analysis, the gradients of the background subtraction data set were used. Large gradients were identified at the boundaries previously used for interpolation which were not characteristic of the background subtraction. Therefore, the background subtraction data set was subject to a low-pass filter to remove such uncharacteristically large gradients. Then, an additional subtraction data set was formed by subjecting the background subtraction data set to a further low-pass filter with a lower frequency such as to capture the underlying trend of the subtraction. To search for regions of significant activity, the gradient of the subtraction data set was compared to the gradient of its underlying trend. For each gradient in the subtraction data set and its underlying trend, if the gradients were of opposite sign then the subtraction data point would be relabelled as one at which there was activity. The data points with labels of activity were then subject to a linear interpolation as previously described where background points on either side of the groups of activity-labelled points were used as the two points of the linear interpolation.

Although the gradient analysis was successful in identifying regions of activity, it was found that the linear interpolation was resulting in regions where the background subtraction points were greater than the intensity values, resulting in negative intensities. Therefore, the background subtraction and intensity data sets were compared and if the intensity value was found to be lower than the background subtraction, then the new subtraction data point would be equal to the intensity. Finally, the background subtraction was smoothed by applying a low-pass filter.

The measured Raman intensity was reduced by the subtraction line and normalised to the resulting peak value if desired. The method required the input of parameters for frequency filtering, rolling windows and the standard deviation percentile. Therefore, the number of turning points in the background subtraction was not limited by the order of a polynomial, and the manual selection of fitting points was not required. Furthermore, the subtraction line proved to be robust for a range of Raman measurements. An example of the subtraction line shown in figure 7.1, and variation of the degree of the background subtraction is also demonstrated. The subtraction method developed in this investigation was used in the analysis of Raman spectra to facilitate the observations of changes in spectra with the aqueous immersion of the organic active layer.

7.2.4 PEDOT Structure and Raman Spectroscopy Interpretation

A unit of the PEDOT backbone can exist in an undoped (neutral) or a doped state. Each state has a different distribution of single and double carbon bonds characteristic of conjugated polymers. The undoped state, described as having a benzoidal structure, is presented in figure 7.2a. Under oxidative doping, polaronic and bipolaronic states are induced, and thus the relative quantities of those states relative to the neutral PEDOT states are varied [281]. The doped PEDOT assumes a quinoidal structure, as shown in figure 7.2b. The distribution of neutral and doped species, or equivalently the states of the PEDOT units, is inferred by the Raman spectrum.

The three vibronic modes of interest can be identified in a Raman spectrum as shown in figure 7.3, and each corresponds to the vibrational motions of a bond. In relating the vibronic modes to the Raman peaks, the $C=C_{Sym}$ mode is associated with peak 1 and also with a peak at approximately 1510 cm^{-1} , which arose for a subset of spectra where the applied gate voltage was varied. Additionally, the $C=C_{Intra}$ mode is associated with peak 2 and the $C=C_{Inter}$ mode is associated with peak 3 [39, 282]. To determine the characteristics of these Raman features, parameters were extracted from each spectrum, as illustrated in figure 7.3, using custom python code. The wavenumbers of the three peaks between 1200 cm^{-1} and 1500 cm^{-1} were identified and their normalised relative intensities were calculated. Also, the full width at half maximum (FWHM) of peak 1 was determined.

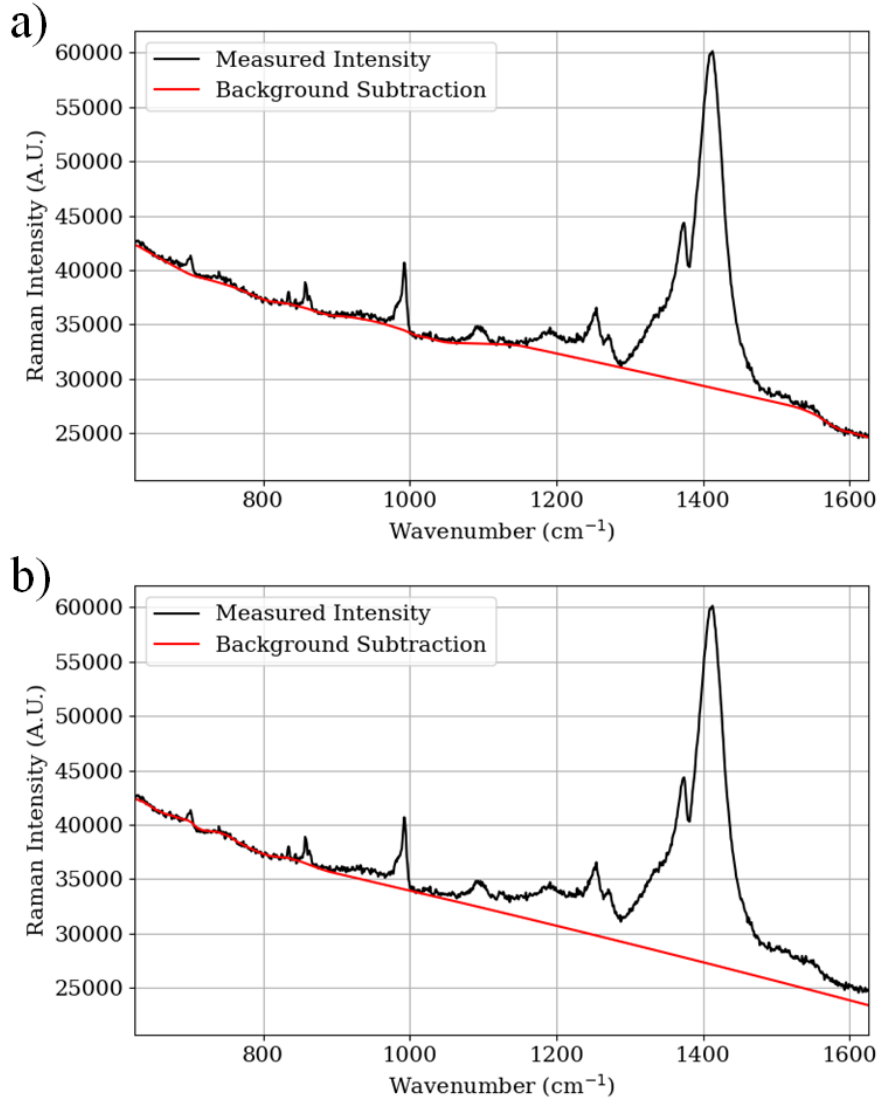


Figure 7.1: Raman spectra showing the measured intensity and the algorithmically determined background subtraction line with a fitting that is a) assuming more of the activity is the background signal, b) assuming less of the activity is the background signal.

For the neutral PEDOT, the C=C_{Sym} bond is resonant at approximately 1410 cm⁻¹ and in the doped phase is resonant at approximately 1450 cm⁻¹. Therefore, for a PEDOT volume with a mixture of both doped and de-doped units, peak 1 represents a superposition of resonances. As the doping level increases, a separation of peak 1 into the contributions of the neutral and doped states becomes increasingly evident. Under such increases, the peak 1 wavenumber can increase. Furthermore, the FWHM represents the degree of state mixing

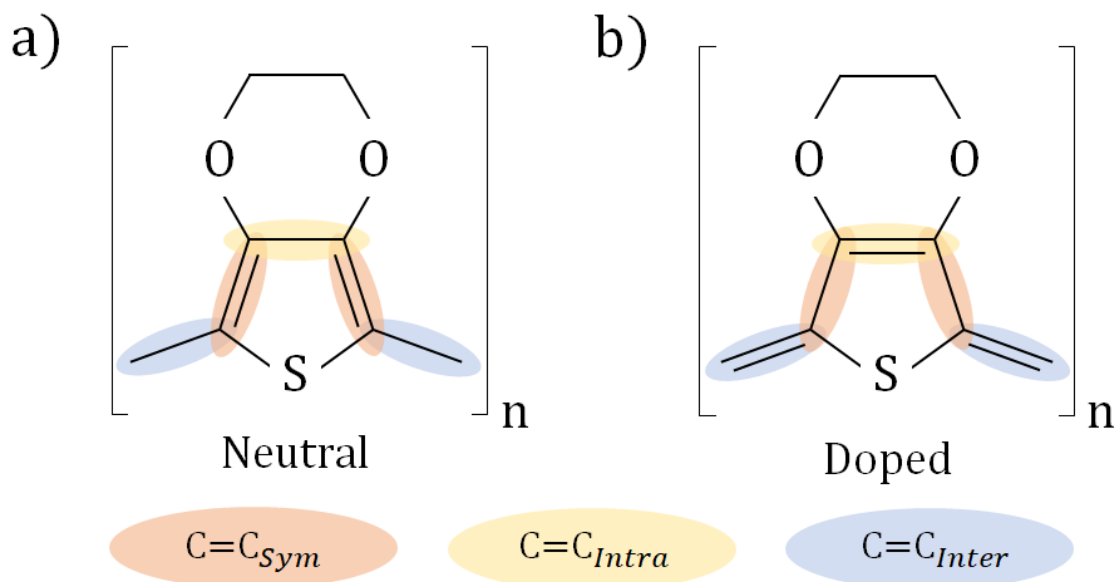


Figure 7.2: Structure of PEDOT showing the correspondence between the carbon bonds and the Raman peaks in its a) neutral form (benzoidal), b) doped form (quinoidal).

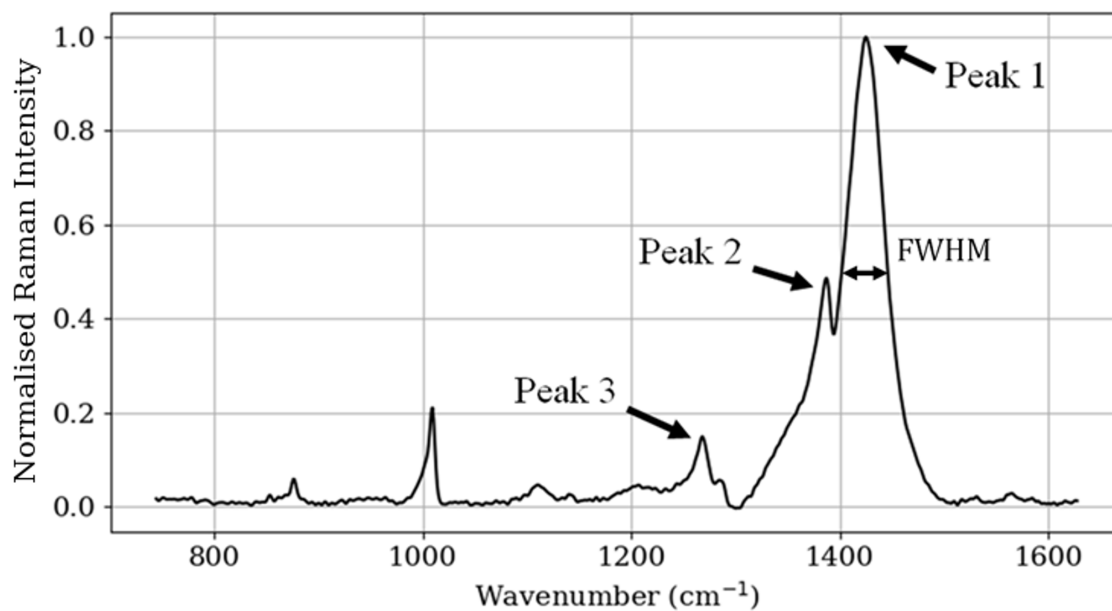


Figure 7.3: Background subtracted Raman spectrum showing the location of the three peaks associated to the carbon bonds illustrated in figure 7.2 and the location of the full width at half maximum (FWHM).

in the volume and can thus also increase. Such relations between doping level and changes in Raman spectra were confirmed using density functional theory. In transitioning from a volume of neutral PEDOT to one that contains a subset of doped units, the total fraction of benzoidal structures decreases with the introduction of the quinoidal structures. Therefore, with a more mixed set of PEDOT structures, as represented by a greater FWHM, the conformational disorder increases. For the $C=C_{Intra}$ mode, increasing the doping level has been found to decrease the intensity of the associated Raman peak at approximately 1370 cm^{-1} . Finally, for the $C=C_{Inter}$ mode, increasing the doping level is associated with an increase in the peak wavenumber at approximately 1250 cm^{-1} [283, 284].

7.3. Results and Discussion

7.3.1 Changes in Electrical Parameters through Time

The evolution of the electrical characteristics is presented in figure 7.4. The first value in each subfigure of figure 7.4 is the mean and standard deviation of the absolute value of the examined parameter. Subsequent values are the mean and standard deviation of the parameter percentage changes relative to those measured on day 1. There were three PED devices and four PEDG devices characterised throughout the aqueous immersion.

After 50 days of aqueous immersion, it was found that both PED and PEDG devices maintained their performance. The conductance values of the PED devices were greater than those of the PEDG devices, which can be attributed to the decrease in conductivity from the addition of GOPS [47]. A one-tailed Welch's t-test with an alternate hypothesis that the PED conductance was higher than the PEDG conductance on day 1 gave a p-value of 6.39×10^{-2} . Using two-tailed Welch's t-tests with a threshold p-value of 0.05, it was found that the conductance did not deviate significantly with aqueous immersion time from its value measured on day 1 for both device types. As expected from the conductance values, the peak transconductance for the PED devices was higher than that of the PEDG devices for all characterisation time points, and a similar Welch's t-test gave a p-value of 5.32×10^{-2} . However, the peak transconductance for both device types decreased with time through the 50 days of immersion by a total of approximately 10%. A two-tailed Welch's t-test with a threshold p-value of 0.05 found that this decrease was not significant.

For the pinch-off voltage, the PED devices had significantly lower values than the PEDG devices on day 1. This was confirmed with a one-tailed Welch's t-test that used an alternative hypothesis stating that the PED pinch-off voltage was lower than the PEDG pinch-off voltage and provided a p-value of 3.82×10^{-3} . This was also found in the gate voltage of peak transconductance, for which a similar Welch's t-test provided a p-value of 5.38×10^{-3} . Subsequent changes in the values followed the same relationship through

7 IMPACT OF AQUEOUS IMMERSION AND APPLIED BIAS ON THE ELECTRICAL AND CONJUGATED POLYMER CHARACTERISTICS OF PEDOT:PSS ORGANIC ELECTROCHEMICAL TRANSISTORS

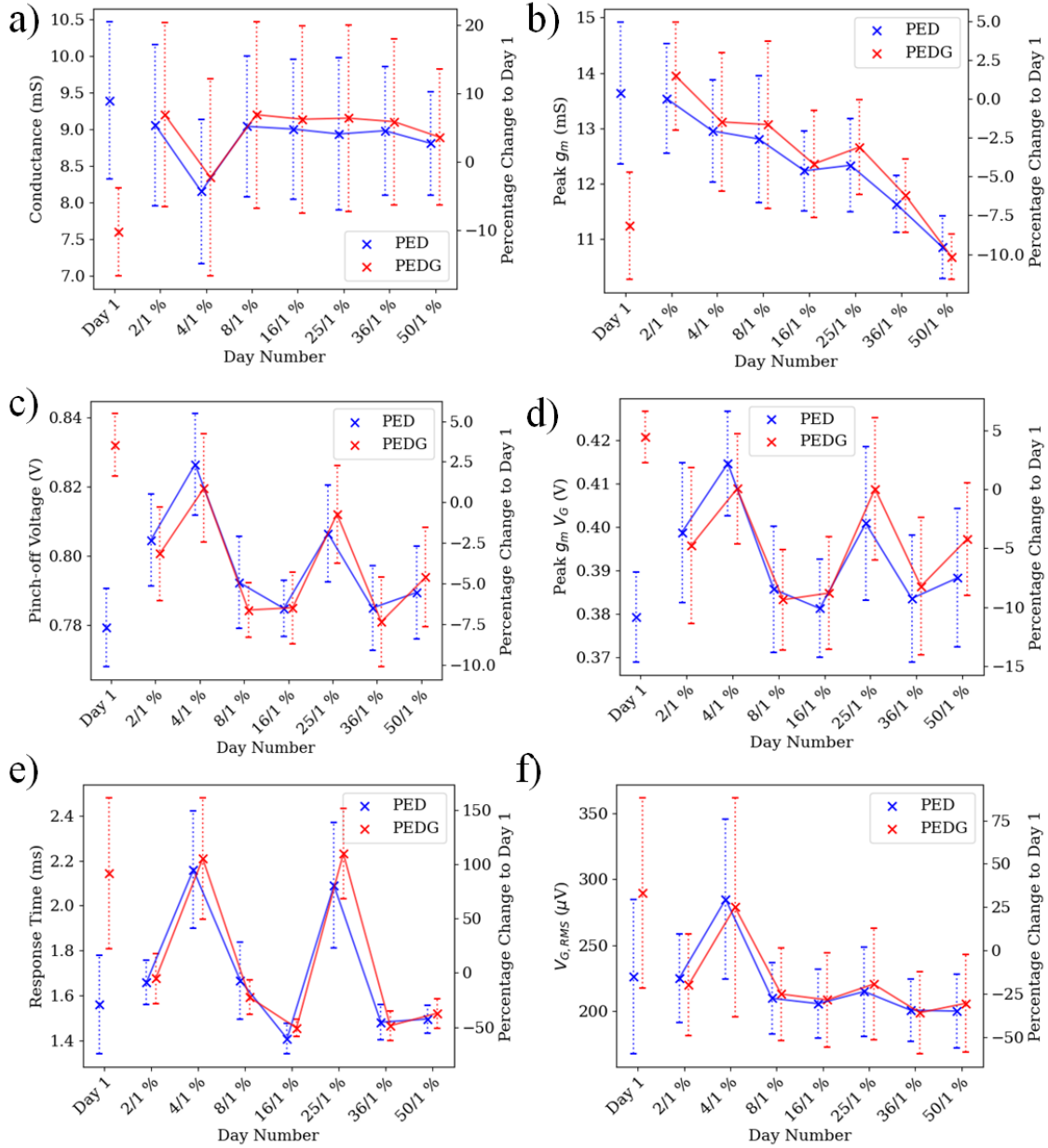


Figure 7.4: Mean and standard deviation of initial value and subsequent percentage change in electrical characteristics of PED and PEDG OECTs with aqueous immersion through time. The characteristics that presented are a) conductance, b) peak transconductance, c) pinch-off voltage, d) gate voltage of peak transconductance, e) response time and f) gate-referred noise, $V_{G,RMS}$.

time for both parameters and both device types. In comparing to the values measured on day 1, statistical analysis using two-tailed Welch's t-tests with a threshold p-value of 0.05

showed that the subsequent changes in the gate voltage of peak transconductance were not significant. Similar statistical tests found significant differences with aqueous immersion time in the pinch-off voltage. However, the final decreases in both parameters for both device types were small at approximately 5% with variations extending to 10%. Therefore, the region of amplification on the transfer curve would not be notably different through time for both device types if fabricated as described here.

The parameter which varied most significantly was the response time. The response times for the PED devices were significantly faster than those of the PEDG devices on day 1. This was confirmed with a one-tailed Welch's t-test that used an alternative hypothesis stating that the PED response time was lower than the PEDG response time and provided a p-value of 1.39×10^{-2} . For a threshold p-value of 0.05, two-tailed Welch's t-tests showed that there were significant differences in response time with aqueous immersion time for both PED and PEDG devices. The changes in the response time correlated with changes in the pinch-off voltage and the gate voltage of peak transconductance. This suggested that there were changes in the volumetric capacitance of the active layer. On day 50, the response times for both device types were significantly faster than those on day 1 with a reduction of approximately 40%. With the response time of OECTs allowing only a sufficient response time for measuring high-frequency bioelectric activity, such increases in response time could prove detrimental to performance. On the other hand, the results show that preconditioning the device with aqueous immersion for a selected time period could significantly improve device performance. In particular, with peak transconductance decreasing only 10% through the time but response time reducing by 50%, the trade-off in these parameters could be alleviated. Therefore, the g_m^{Peak}/τ_{90} ratio could be significantly increased [15].

The mean gate-referred noise was found to be lower in the PED devices than the PEDG devices. A one-tailed Welch's t-test that used an alternative hypothesis stating that the PED gate-referred noise was lower than the PEDG gate-referred noise provided a p-value of 1.95×10^{-1} . Results later in the investigation supported that the PED devices provided a lower noise than the PEDG devices. This indicated that the crosslinker was detrimental to the biosensor performance and thus its inclusion should be avoided unless required. From day 8 onwards, the mean noise was lower than on day 1 by approximately 25% for both device types and remained approximately constant. Two-tailed Welch's t-tests showed that such differences through time were not significantly different to those values measured on day 1 when using a threshold p-value of 0.05. Such observations show that the SNRs of OECTs using PED or PEDG formulations and fabricated as described here should remain sufficient for extended physiological monitoring.

7.3.2 Changes in Raman Spectra through Time

An averaged Raman spectrum for each device type was determined for each day. The novel background subtraction method was used in processing the Raman intensity, and the spectra were normalised to the intensity of peak 1. The resulting averaged spectra are shown in figure 7.5a for PED devices and figure 7.5b for PEDG devices, and the extracted parameters are shown in figure 7.6.

As with the electrical characteristics, the temporal evolution of the Raman spectra in figure 7.6 showed that the PEDOT structure remained approximately constant throughout the 50 days of aqueous immersion. This is quantified through the extracted Raman parameters. In comparing the Raman background subtraction method developed in this research to the background subtraction from a polynomial fit using Origin software, it was found that the same Raman parameter relationships were identified for all following analyses with approximately equal Raman parameter values. This supported the capability of the novel method to remove the undesired background signal.

The analysis of the extracted parameters supported the stability of the organic active layer throughout the aqueous immersion. The difference between the peak 1 wavenumbers of the PED and PEDG devices was found to not be significant using a one-tailed Welch's t-test with an alternate hypothesis that the PED wavenumber was greater than the PEDG wavenumber and a threshold p-value of 0.05. Furthermore, using two-tailed Welch's t-tests with a threshold p-value of 0.05, there were no significant changes in each of the device types from day 1 to day 50. Such statistical results were also found for the peak 3 wavenumber. For the peak 3 relative intensity, the mean values were consistently lower until day 25. However, a one-tailed t-test with an alternate hypothesis that the PED intensities were lower than the PEDG intensities and a threshold p-value of 0.05 found no significant differences for any characterisation timepoint. Additionally, a two-tailed Welch's t-test with a threshold p-value of 0.05 found no significant changes in each of the device types from day 1 to day 50.

The FWHM values of peak 1 were significantly smaller for the PED devices than those of the PEDG devices for a subset of the characterisation timepoints. This was confirmed by one-tailed Welch's t-tests with an alternate hypothesis that the PED FWHM values were lower than the PEDG FWHM values and a threshold p-value of 0.05. For each device, changes in the FWHM with aqueous immersion were not significant, supported by two-tailed Welch's t-tests with a threshold p-value of 0.05. The peak 2 wavenumbers were greater for the PED devices than those of the PEDG devices to a statistically significant degree for a subset of the characterisation timepoints. This was supported by one-tailed Welch's t-tests with an alternate hypothesis that the PED wavenumbers were greater than the PEDG wavenumbers and a threshold p-value of 0.05.

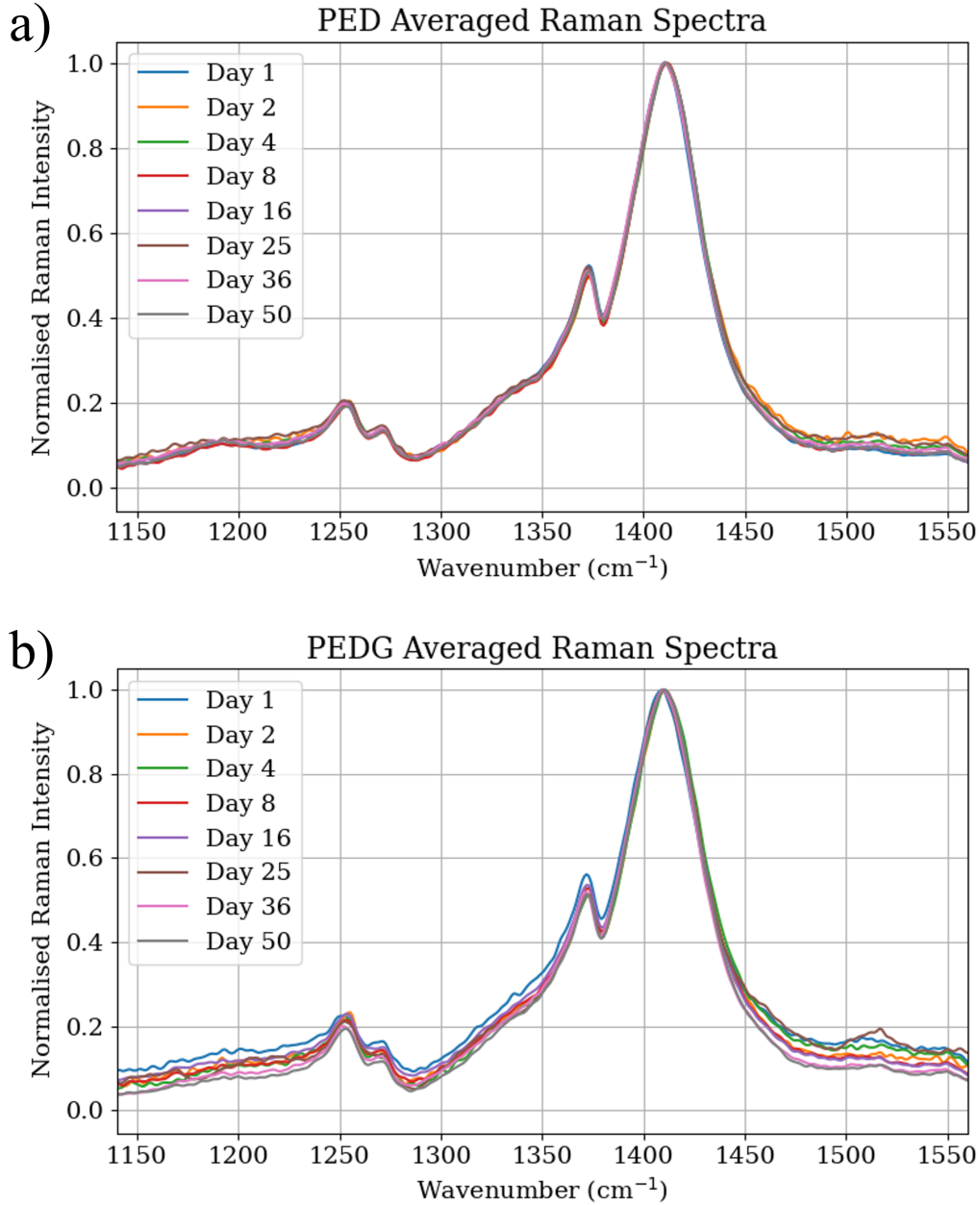


Figure 7.5: Raman spectra averaged over a set of transistors characterised on each day through an aqueous immersion time of 50 days. The devices had an active layer of a) PED, b) PEDG.

For each device, changes in the wavenumbers with aqueous immersion were found to be significant for a small subset of the characterisation timepoints, supported by two-tailed Welch's t-tests with a threshold p-value of 0.05. However, the absolute changes in the

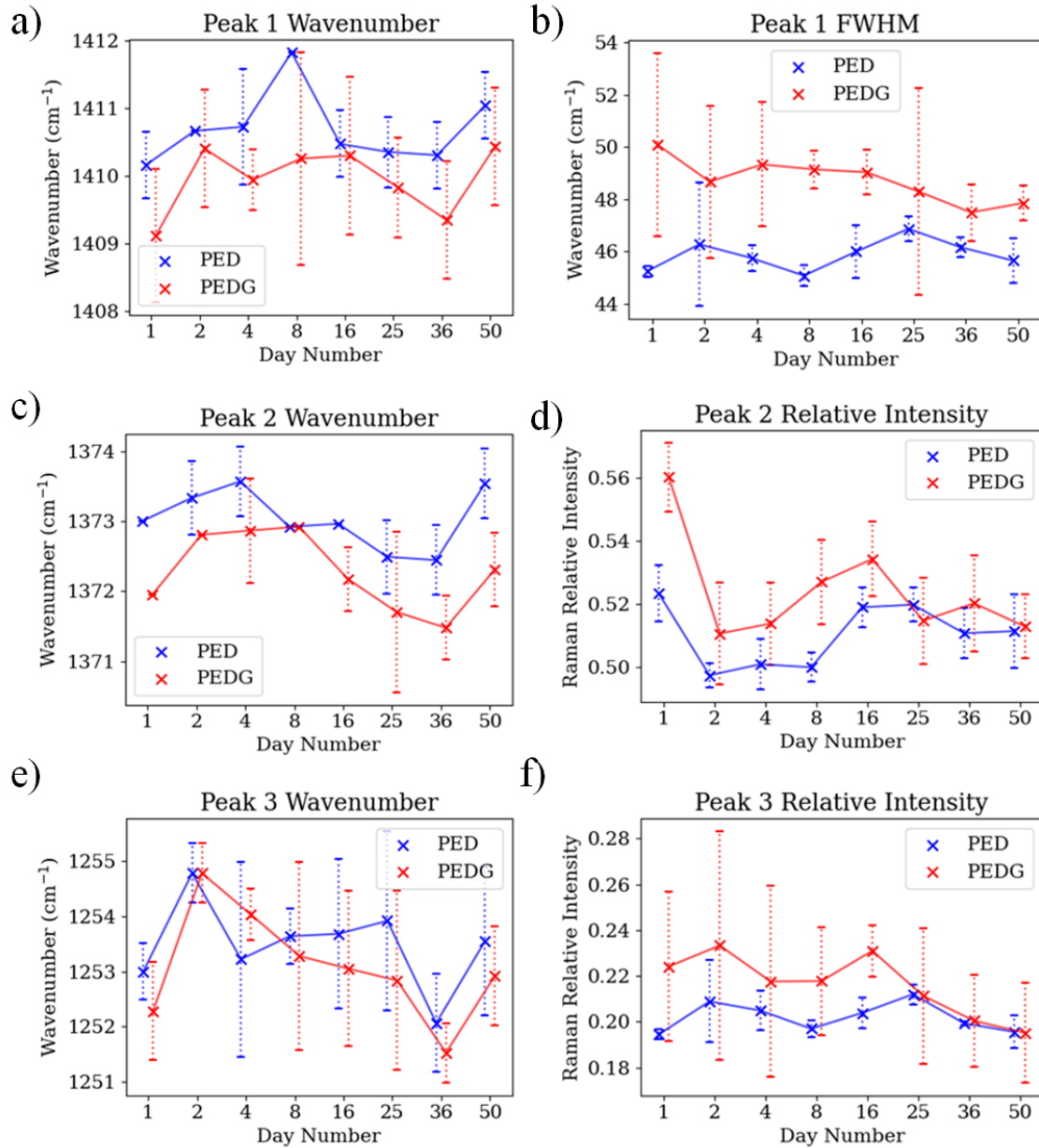


Figure 7.6: Mean and standard deviation of Raman parameters as identified in figure 7.3 for increasing aqueous immersion time of PED and PEDG OECTs. The parameters are a) peak 1 wavenumber, b) peak 1 FWHM, c) peak 2 wavenumber, d) peak 2 relative intensity to peak 1, e) peak 3 wavenumber and f) peak 3 relative intensity to peak 1.

wavenumbers were small, supporting the stability of the organic active layer throughout the aqueous immersion. The relative intensities of peak 2 were significantly lower in the PED devices than in the PEDG devices for a subset of the characterisation timepoints,

supported by one-tailed Welch’s t-tests with a threshold p-value of 0.05. For both device types, the initial change from day 1 to day 2 was statistically significant using two-tailed Welch’s t-tests with a threshold p-value of 0.05. Subsequent values in the PEDG devices maintained that significant difference with aqueous immersion time whereas the PED devices reverted towards their day 1 values. The extracted Raman parameters suggest that the vibronic modes of the PEDG PEDOT structures tended towards those of the PED PEDOT structures as immersion time increased.

The mechanism for the differences in Raman parameters for each device type was considered. For the effect of the application of biases on Raman parameters, it was found, as shown in figure 7.10 and figure 7.13, that the FWHM of peak 1 and the relative intensity of peak 3 both decrease as the device is de-doped whilst operating in the linear regime. In considering all Raman parameters measured throughout the aqueous immersion, a positive correlation was found between peak 1 FWHM and peak 3 relative intensity, as shown in figure 7.7a. This suggested that the changes in the parameters of each device through the aqueous immersion originated from differences in the doping level. This was supported by the changes in the pinch-off voltage, which implied that the doping level would have varied for a fixed gate-channel potential. Furthermore, such behaviour was considered as a contributing factor towards the lower FWHM values observed in the PED devices relative to the PEDG devices. A lower FWHM and lower peak 3 relative intensity for the PED OECTs suggested that the devices were more de-doped than the PEDG devices during the characterisation. This was supported by how the PED devices had a lower pinch-off voltage than the PEDG device, as shown in figure 7.4c, and thus the active layer would be relatively more de-doped for a given gate-channel potential.

The data set that explored how electrical and Raman characteristics varied with aqueous immersion permitted an analysis to find correlations between their parameters. Although changes in the parameters were small, relationships could still be inferred. Investigations presented later in which the applied voltages are varied further explore these relationships with greater parameter ranges. To search for parameter relationships, correlation matrices were found using the Pearson correlation methodology.

The Raman parameter with the greatest correlations to electrical parameters was the peak 1 width. As described, the relative intensity of peak 3 positively correlated with the FWHM of peak 1 and thus also showed moderate correlations to the electrical parameters. The electrical characteristics with correlations to peak 1 width were conductance, peak transconductance, pinch-off voltage, gate voltage of peak transconductance, and the gate-referred noise, illustrated in figure 7.7. In addition, a positive correlation was found between the peak 1 width and the δ value as defined in section 6. For electrical characteristics, the gate-referred noise showed a strong positive correlation with pinch-off voltage, suggesting

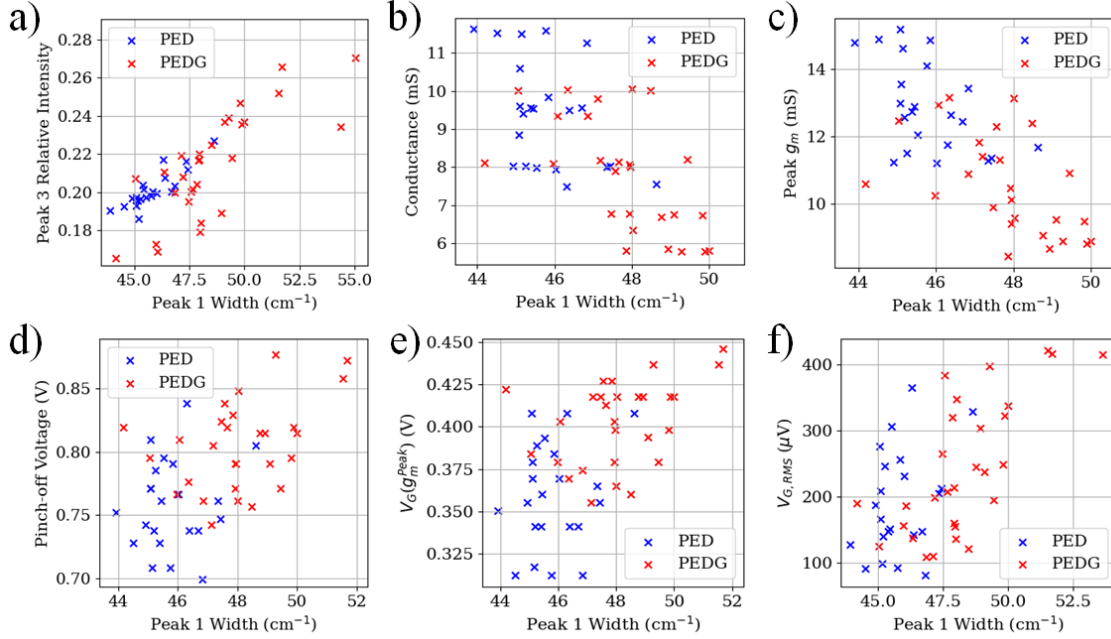


Figure 7.7: a) Correlation between peak 1 width and peak 3 relative intensity. Relationship between the width (FWHM) of peak 1 and b) conductance, c) peak transconductance and d) pinch-off voltage, e) gate voltage of peak transconductance and f) gate-referred RMS noise, for all device characterisations through 50 days of aqueous immersion.

that the capacitances of the active layers were varying.

The correlations showed that the device performance increased as the conformational disorder decreased. No clear correlation was found between peak 1 width and response time. This supports that the response time is more dependent on ionic mobilities, which are associated with the PSS units of the PEDOT:PSS as opposed to the PEDOT backbone [47]. However, the response time strongly correlated with the pinch-off voltage, which itself showed a moderate correlation to peak 1 width.

Raman characterisations were also performed on the PED and PEDG OECTs when no voltages were applied. It was found that the PEDG device had signatures of being more de-doped than the PED device, indicating that GOPS inherently reduces the doping level of PEDOT:PSS. With the applied voltages, it was found that the PED device was more de-doped than the PEDG device. Therefore, the PED device went from a more doped state to a more de-doped state than the PEDG device when increasing the magnitude of the supply voltage from $V_{DD} = 0$ V to $V_{DD} = -0.6$ V. This suggests that the de-doping efficiency, defined as the number of holes reduced per cation, was greater in the PED devices.

7.3.3 Parameter Relationships from Changes in Supply Voltage

The effect of increasing the supply voltage magnitude on the gate-referred noise and Raman characteristics was investigated. Raman spectra were obtained for each supply voltage, permitting an analysis to compare how the PEDOT structure changed as the gate-referred noise decreased. The noise was found to decrease approximately monotonically with supply voltage magnitude for both the PED and PEDG devices, supporting the results in section 6. It was found that the relationships between the supply voltage and the Raman parameters were approximately the same for both the PED and PEDG devices, though observations in their differences are noted. The Raman spectra for the PED and PEDG devices are shown in figures 7.8a and 7.8b, respectively.

The Raman spectra revealed a directional change to the extracted parameters, showing a clear dependence on the supply voltage. In comparison to the spectra in figure 7.5, the changes induced by variations in supply voltage were significantly greater than those that occurred from immersing the devices in an aqueous environment. Changes in electrical parameters for variations in supply voltage are illustrated in figure 7.9.

As previously found and as illustrated in figure 7.9a, the gate-referred noise in the PED device was lower than in the PEDG device, providing lower values at each supply voltage. With a greater conductance, the PED device was found to have a greater steady-state current at each supply voltage than the PEDG device, as shown in figure 7.9b. The devices transitioned from the linear regime to the saturation regime at supply voltages ≤ -0.8 V. At such voltages, the steady-state drain current showed that the PED and PEDG devices were transitioning from the linear to the saturation regime, and both devices were saturated at a supply voltage of approximately -1.1 V. Decreases in noise with supply voltage in the saturation regime were significantly smaller than those in the linear regime.

For both PED and PEDG devices, the peak 1 wavenumber decreased as the supply voltage magnitude increased, as illustrated in figure 7.10a. For the PEDG device, the wavenumber continued to decrease until a supply voltage of -0.6 V, at which point there were no further decreases. The initial wavenumber was higher for the PED device, and the wavenumbers for both devices decreased to the same value at a supply voltage of -1.1 V, showing a greater total change in the PED device. The width of peak 1, given in figure 7.10b, decreased for both PED and PEDG devices as the supply voltage magnitude increased. Furthermore, the width of the PED device decreased more than that of the PEDG device at higher supply voltage magnitudes. As shown in figure 7.10c, the peak 2 wavenumber decreased as the supply voltage magnitude increased for both PED and PEDG devices. The most significant changes of peak 2 were in its relative intensity, given in figure 7.10d, where the value increased for both device types as the supply voltage magnitude increased. For peak 3, the wavenumber for both PED and PEDG materials

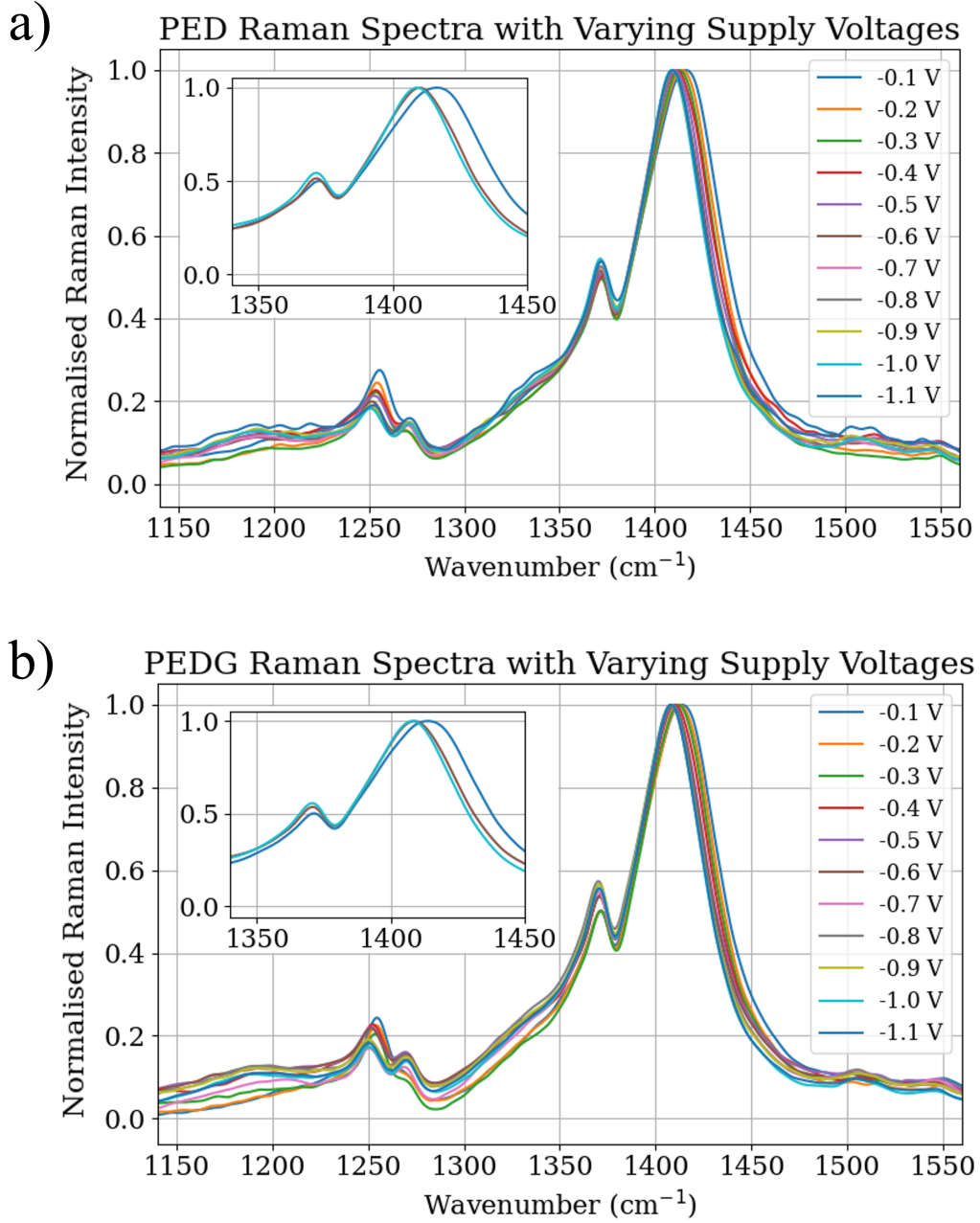


Figure 7.8: Raman spectra of OECTs for changes in supply voltage with an active layer of a) PED, b) PEDG.

also decreased as the supply voltage magnitude increased, as illustrated in figure 7.10e. This was accompanied by a decrease in relative intensity of peak 3 for both devices, as displayed in figure 7.10f, and the decrease for the PED active layer was greater than that for the PEDG active layer.

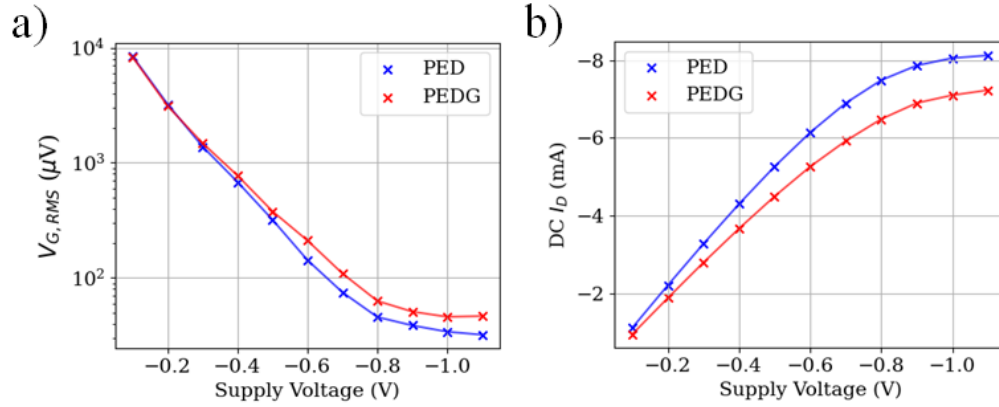


Figure 7.9: Relationship between changes in supply voltage and a) normalised drain current noise, b) steady-state drain current, for PED and PEDG OECTs.

The spectra showed that changes in the Raman parameters for the PED were greater than those for the PEDG devices. It has been suggested that GOPS acts to electrically insulate the PEDOT segments, resulting in lower electrical conductivity [47]. Therefore, the inclusion of GOPS could reduce the impact of electrostatic forces on the PEDOT backbone and result in more inhomogeneous de-doping of the PEDOT segments. This could explain the smaller changes in the vibronic mode distribution and the relative reduction in de-doping from the applied voltage.

As the supply voltage becomes more negative, there is a greater electrical field to attract the cations into the active layer, thus increasing the de-doping of the PEDOT. In de-doping the active layer, the contribution to the peak at approximately 1450 cm^{-1} associated with the doped PEDOT unit decreases and peak 1 shifts towards the contribution at approximately 1410 cm^{-1} associated with the neutral PEDOT. This can be seen in figure 7.10a, in which the peak 1 wavenumber decreased and saturated at approximately 1409 cm^{-1} . In reducing the 1450 cm^{-1} doped contribution to peak 1, the FWHM of the peak also decreased towards a lower limit, as shown in figure 7.10b. Therefore, the parameters of peak 1 supported that increasing the supply voltage magnitude resulted in a de-doping of the active layer. The de-doping caused by increasing the supply voltage magnitude was supported by variations in the parameters describing peak 2 and peak 3. The relative intensity of peak 2 increased as supply voltage magnitude increased, and such increases have previously been associated with active layer de-doping [284]. The peak 2 wavenumber was also observed to decrease with de-doping, though the decrease was small. The decrease in the wavenumber of peak 3 and its relative intensity to peak 1 was also indicative of de-doping [39].

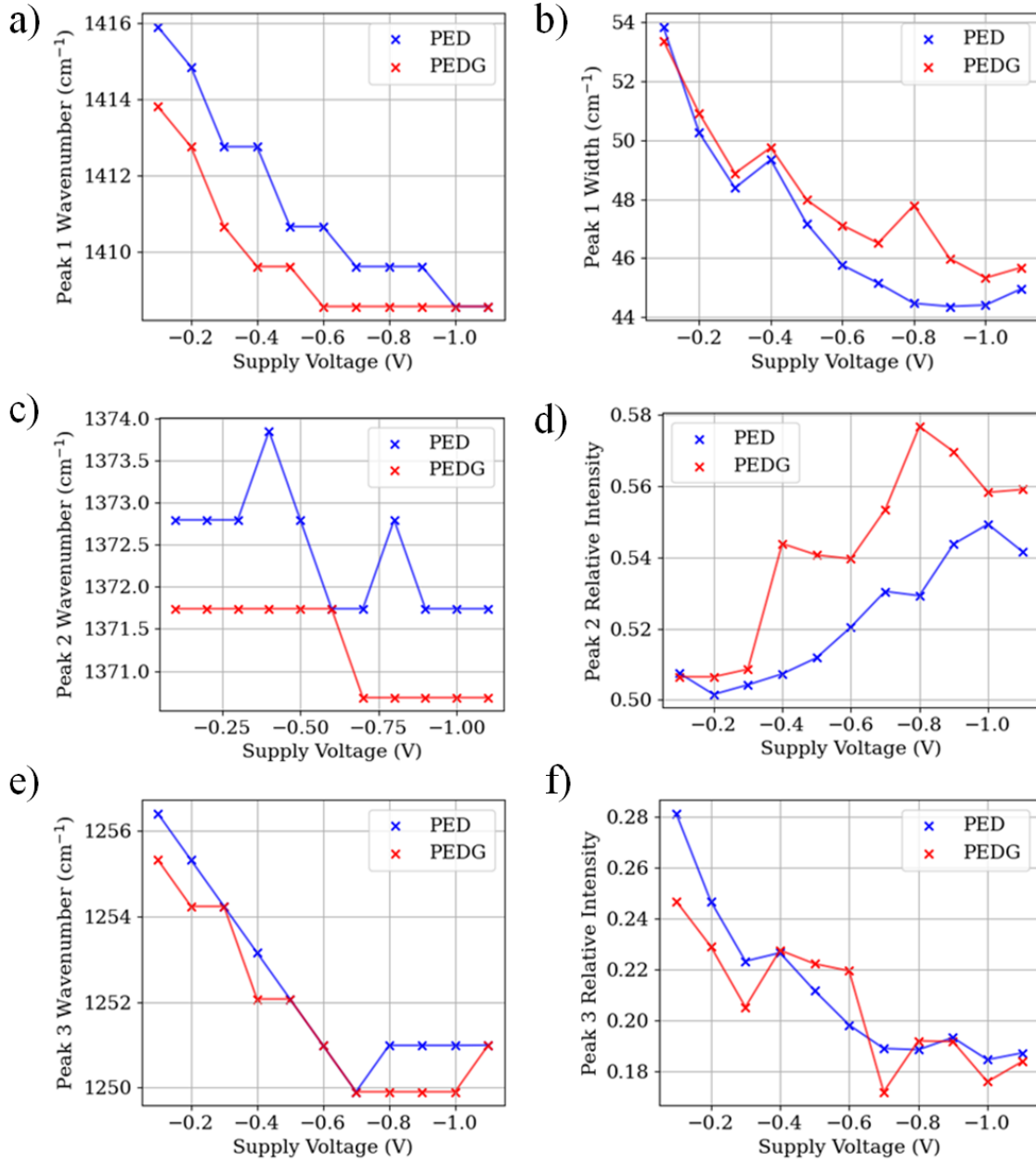


Figure 7.10: Relationships between the supply voltage and the Raman parameters of a) peak 1 wavenumber, b) peak 1 FWHM, c) peak 2 wavenumber, d) peak 2 relative intensity, e) peak 3 wavenumber, f) peak 3 relative intensity, for PED and PEDG devices.

7.3.4 Parameter Relationships from Changes in Gate Voltage

The effects of increasing the gate voltage on the gate-referred noise and the Raman characteristics were investigated. It was found that increasing the gate voltage decreased

the gate-referred noise for both the PED and PEDG devices. As with the supply voltage, Raman spectra were obtained for each gate voltage, permitting an analysis to compare how the PEDOT structure changed as the gate voltage and the gate-referred noise varied. The Raman spectra for the PED and PEDG devices are shown in figures 7.11a and 7.11b, respectively.

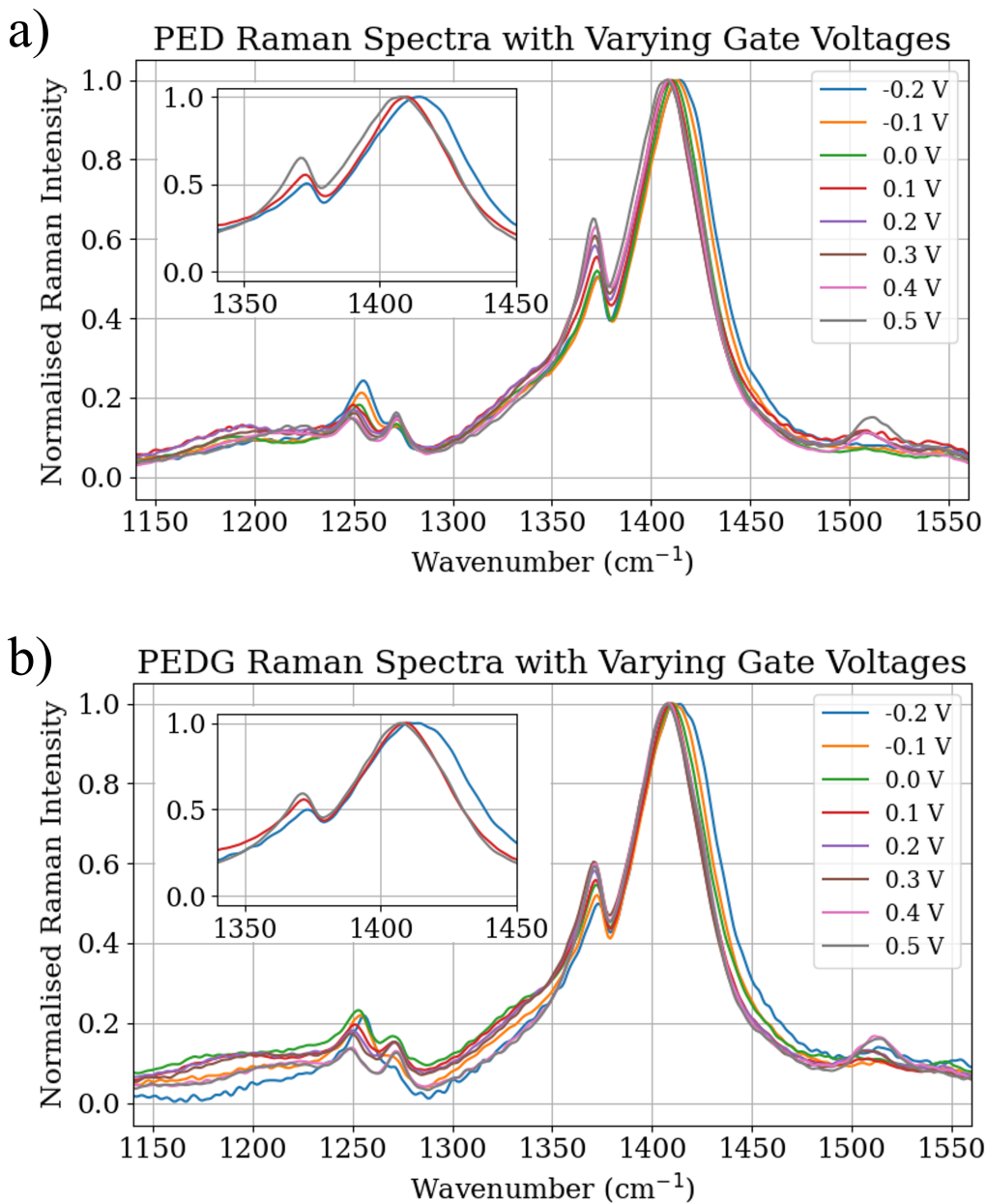


Figure 7.11: Raman spectra of OECTs for changes in gate voltage with an active layer of a) PED, b) PEDG.

For changes in the gate voltage, the Raman spectra revealed a directional change to the extracted parameters, showing a clear dependence. Similar changes in the extracted Raman parameters were found for increases in gate voltage compared to those determined for increases in supply voltage magnitude. This was expected because increasing the supply voltage with a grounded gate increases the gate-channel potential, and such behaviour has similarities to increasing gate voltage with a fixed supply voltage. Changes in electrical parameters for variations in gate voltage are illustrated in figure 7.12.

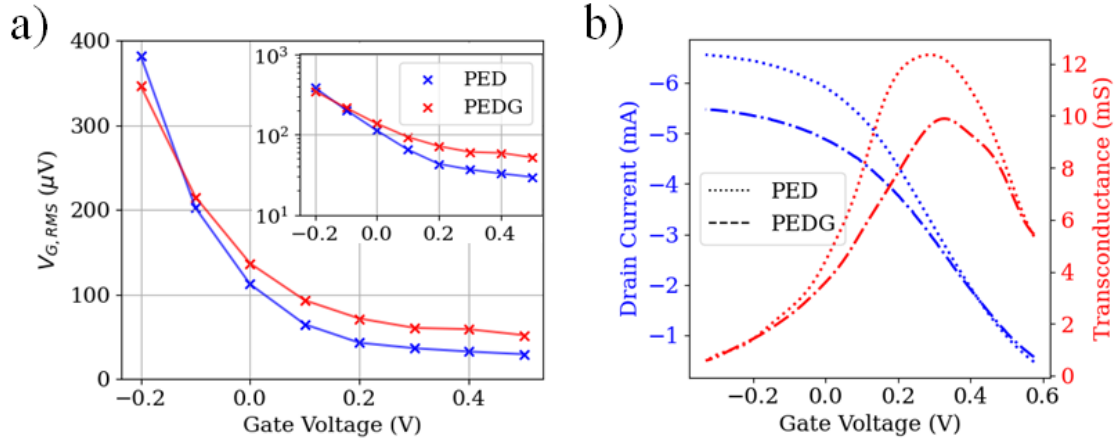


Figure 7.12: Relationships between the changes in gate voltage and a) gate-referred RMS noise, b) steady-state drain current, for PED and PEDG OECTs.

Electrical characterisations showed that the gate-referred noise decreased as gate voltage increased. Furthermore, the decrease in noise was reduced when the device entered the saturation regime. Therefore, as the PED device entered the saturation regime at a lower gate-drain potential, the noise would have been inherently lower than in the PEDG device at each gate voltage. However, it is clear in the saturation regime that the noise in the PED device is lower than a gate voltage-shifted noise profile of the PEDG device, supporting that the GOPS increased the noise of the device. Increasing the gate voltage results in an increase in the resistance of the active layer. This focuses the dynamics of the OECT on the de-doping of the active layer rather than the impacts of the gate voltage-independent interconnect resistances described in section 6. In such a regime, signified by a decrease in channel current and thus by the gate voltage of peak transconductance, the noise was lower, supporting observations from the literature [89]. It was observed that the gate-referred noise continued to decrease as gate voltage increased when the device was operated in the saturation regime. However, the decreases were smaller than in the linear regime, as found when increasing the magnitude of the supply voltage.

The transfer curves for both devices are shown in figure 7.12b, highlighting the difference in steady-state characteristics from increased conductivity. It was noted that increasing the conductivity of the active layer, and thus reducing the channel resistance, increases the ratio of interconnect resistance to channel resistance. It was previously shown in section 6 that increasing this ratio results in an increase in gate voltage of peak transconductance. Therefore, the observation of a lower $V_G(g_m^{Peak})$ in the PED OECT strongly supported that the device started to de-dope at lower gate-channel potentials.

The Raman spectra showed that the peak 1 wavenumber, extracted into figure 7.13a, decreased as gate voltage decreased. The wavenumber at $V_G = -0.2$ V was greater for the PED device and the values equated for $V_G \geq 0.1$ V, thus showing greater changes for the PED Raman spectrum. The peak 1 width, given in figure 7.13b, decreased as gate voltage increased for low gate voltages in both devices. A turning point then emerged for $V_G = 0$ V in the PED device and $V_G = 0.1$ V for the PEDG device. This corresponded with the devices entering their saturation regimes, as can be seen in their transfer curves shown in figure 7.12b. The subsequent increase in peak 1 width in the PED device was significantly greater than that in the PEDG device. The peak 2 wavenumbers, shown in figure 7.13c, were found to decrease for both device types. A much more significant change was found in the relative intensity of peak 2, which increased significantly for both devices, as illustrated in figure 7.13d. The increase was found to plateau in the PEDG device for $V_G \geq 0.3$ V, whereas the increase continued in the PED device. The peak 3 wavenumber and relative intensity, given in figures 7.13e and 7.13f, respectively, decreased as gate voltage increased for both devices, and there was no significant difference between the changes in the devices. The spectra for changes in gate voltage supported those for changes in supply voltage in that the changes in the PEDOT structure of the PED device were greater than those of the PEDG device because the Raman parameters showed greater variations.

Increasing the applied gate voltage results in a greater electric field for cations to drift into, and thus de-dope, the active layer. The de-doping mechanism was supported by the increase in peak 2 relative intensity and the decreases in peak 1 wavenumber, peak 2 wavenumber, peak 3 wavenumber and peak 3 relative intensity. Such de-doping features were also observed in increasing the magnitude of the supply voltage. In addition to the features of the three primary peaks, a further peak arose for significant de-doping at 1510 cm^{-1} , which has also been associated with the de-doping of PEDOT:PSS [39].

The parameter that clearly distinguishes the linear regime from the saturation regime in the Raman parameters is the peak 1 width. As found with the supply voltage, the FWHM of peak 1 decreased in the linear regime and then increased in the saturation regime. Operating the device deeper into the saturation regime further increased the FWHM. This behaviour can be understood by considering the contribution of peak 2. The

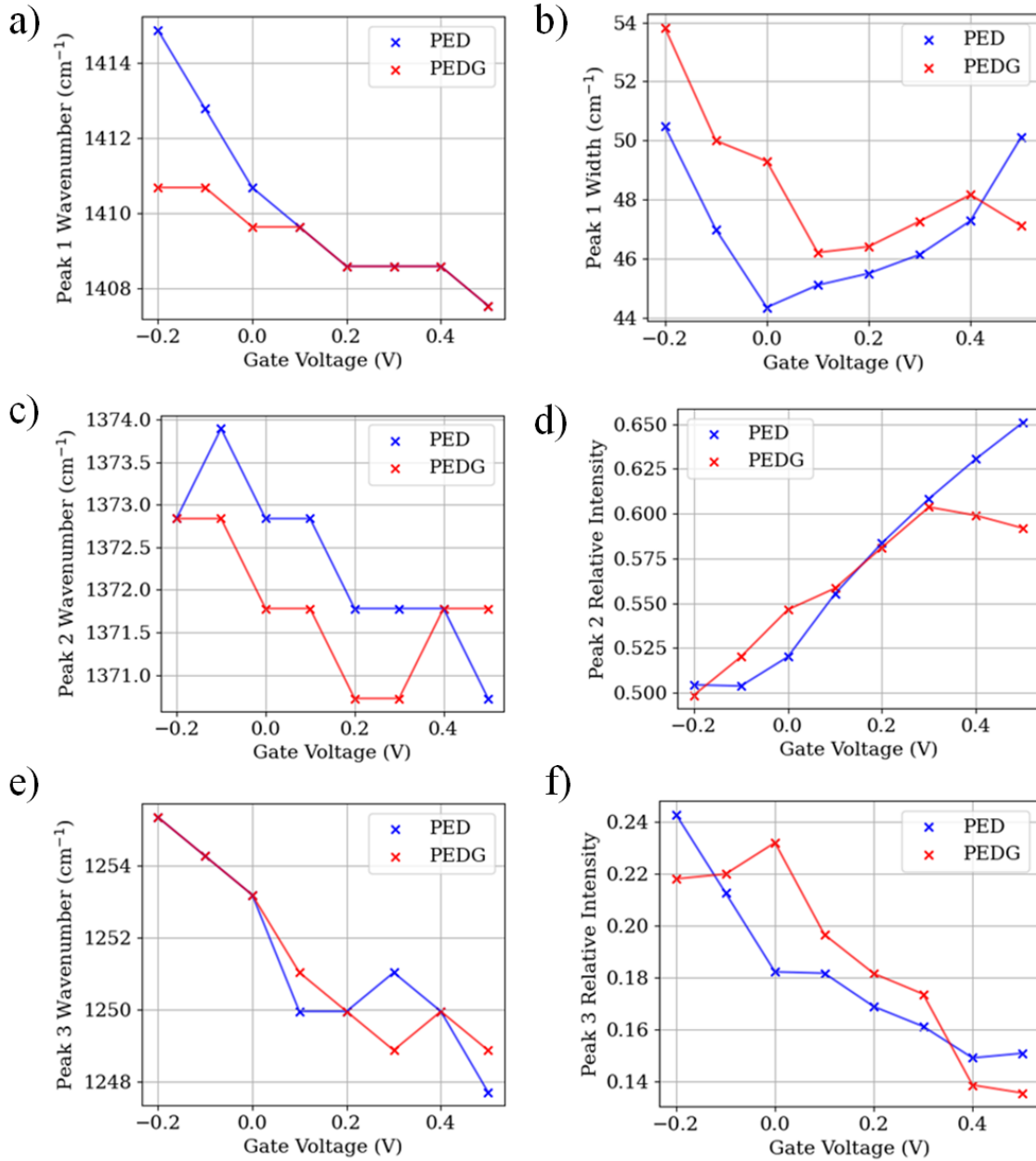


Figure 7.13: Relationship between gate voltage and the Raman parameters of a) peak 1 wavenumber, b) peak 1 FWHM, c) peak 2 wavenumber, d) peak 2 relative intensity, e) peak 3 wavenumber, f) peak 3 relative intensity, for PED and PEDG devices.

results suggest that the width of peak 2 contributes to the width of peak 1 when the peak 2 relative intensity increases and the peak 1 wavenumber and FWHM reduces through de-doping. This is supported by the changes in the shape of the Raman spectra as given

in figure 7.11. For the PED spectra, the left shoulder of peak 1 widens whereas the right shoulder remains constant, implying that the width of peak 2 is contributing to the width of peak 1. This is further supported by the Raman parameters given in figures 7.13b and 7.13d, which shows that the PED FWHM continues to increase as the PED peak 2 relative intensity increases and the PEDG FWHM starts to stabilise as the PEDG peak 2 relative intensity reaches a limiting value. Furthermore, a Gaussian fitting of the spectra showed that the FWHM increased as the peak 2 relative intensity increased when operating at higher gate voltages. Where the FWHM decreased in the linear regime, it increased in the saturation regime, and, as shown by the other parameters, the device was increasingly de-doped as the gate voltage was increased from the linear regime and through the saturation regime towards switching off the device. This shows that the peak 1 FWHM is not an accurate measure of de-doping in the saturation regime because its dependence becomes non-monotonic. The decreasing drain current shown in figure 7.12b indicated that the number of quinoidal (doped) PEDOT units continued to decrease. Under such conditions, the gate-referred noise would show a correlation to conformational disorder, where a lower disorder results in a lower noise value.

7.3.5 Variations in Noise and Structural Changes in PEDOT

It was found that the gate-referred noise decreased as the gate-channel potential increased and thus as the active layer was de-doped. The conformational disorder, or equivalently the ratio of quinoidal to benzoidal PEDOT units, decreased as the active layer was de-doped. Therefore, the noise decreased as the conformational disorder, and thus as the energetic disorder, decreased. This suggests that a more highly doped PEDOT:PSS induces a greater energetic disorder and thus a higher noise level, which can be reduced through the electrochemical de-doping of the organic layer during OECT operation. This could be further investigated by comparing the noise measurements of OECTs with different PEDOT:PSS compositions that have their ratio of PEDOT to PSS chemically varied in the active layer preparation stage of device fabrication. With the insights provided by this investigation, it is expected that the gate-referred noise of OECTs with an active layer of sulphuric acid-treated PEDOT:PSS would be lower than that of PED due to the removal of excess PSS and the increased crystallinity, which could correlate with a decreased energetic disorder [58].

The de-doping, which results in a greater proportion of benzoidal PEDOT states, was represented by an increase in peak 2 relative intensity, a decrease in the peak 3 relative intensity and, in the linear regime, a decrease in the peak 1 width. In addition to a lower disorder, this indicated that the reduction in noise was associated with a conformational change in which the π -electron density was more localised towards the thiophene ring and

away from the C_{Inter} bonds. Indeed, the thiophene ring in the benzoidal (neutral) structure has a greater double-bond character, whereas the C_{Inter} bonds have a more single σ -bond nature. This is in contrast to the quinoidal (doped) structure, for which the C_{Inter} bonds have a greater double-bond character, as shown in figure 7.2.

It was observed in the saturation regimes of behaviour, as shown in figures 7.9 and 7.12, that the minimum noise values achieved by the PED device were significantly smaller than those of the PEDG device. The functions describing the PED device noise dependence on gate and supply voltage could not be considered as translations of the functions describing the PEDG OECT. As such, the reduced noise of the PED device could not be entirely attributable to the increased de-doping. Therefore, comparisons of Raman parameters in the saturation regime gave the strongest indication of the structural differences that could result in reducing the noise. When considering the results from changes in both gate voltage and supply voltage, the FWHM value at the regime transition was lower in the PED device than in the PEDG device. Furthermore, the FWHM values which increased with gate-channel potential in the saturation regime were primarily lower in the PED device. Therefore, further to the suggestion that gate-referred noise reduces with the conformational disorder, a lower noise is also achieved with an inherently lower FWHM. In addition to the contributions to the peak 1 FWHM from the vibrational modes of the doped C_{Sym} bonds at 1450 cm^{-1} and the peak 2 width, the peak 1 FWHM is constituted by the standard deviation of the approximate Gaussian describing the energetic disorder of the vibrational modes of the neutral C_{Sym} bonds at 1410 cm^{-1} . Therefore, it is suggested that an inherently lower FWHM could be achieved by reducing the energetic disorder of the vibrational modes in the conjugated PEDOT backbone.

7.4. Conclusions

This research investigated the stability of the electrical characteristics and the evolution of the distribution of the vibrational modes in the carbon bonds constituting the conjugated polymers of PEDOT:PSS-based OECTs over 50 days of aqueous immersion. Furthermore, the impact of applied biases on OECT noise and on the structure of PEDOT was measured. To probe the structural changes such as the conformational disorder, resonance Raman spectroscopy was employed.

To aid in the analysis of the Raman spectra, a novel background subtraction method was developed. The novel method incorporated frequency-domain filtering, linear interpolation, signal derivatives and non-parametric statistics, and did not require the input of manually selected fitting points. In comparison to established background subtraction techniques, the novel method provided approximately equal parameter values.

The analysis of OECT stability with aqueous immersion over 50 days suggested that

the device maintained sufficient electrical characteristics and the Raman spectra did not vary significantly. This supported the capability of the device for long-term physiological monitoring such as the recording of neural activity on or within the cortex. The PED devices showed higher performance in their electrical parameters, with higher conductance and transconductance values, lower pinch-off voltages and peak transconductance gate voltages, faster response times and lower gate-referred noise values. Notable changes in device parameters included a reduction in peak transconductance by 10% and a reduction in gate-referred noise by 25%. Furthermore, the response time values fluctuated significantly through the immersion time. The results showed that devices could undergo aqueous immersion as a preconditioning step to increase performance characteristics.

The parameter values collected from the OECT characterisation and the Raman spectra through the aqueous immersion were subject to correlation analysis. It was found that the FWHM of peak 1, and to a lesser extent the relative intensity of peak 3, was correlated to the OECT conductance, peak transconductance, gate voltage of peak transconductance, pinch-off voltage, and the gate-referred noise. The correlation between peak 1 FWHM and peak 3 relative intensity and the variations in pinch-off voltages for both devices supported that the changes in Raman parameters were related to the differences in doping level of the PEDOT:PSS.

Increases in the magnitude of the supply voltage by an order of magnitude resulted in the gate-referred noise decreasing by a factor greater than 10^2 . The PED active layer was shown to provide a lower gate-referred noise than the PEDG layer, and decreases in noise became smaller in magnitude as the devices transitioned from the linear to the saturation regime. Raman spectra supported that the device was de-doping as the supply voltage magnitude increased. This was signified by an increase in peak 2 relative intensity and a decrease in peak 1 wavenumber, peak 1 width, peak 2 wavenumber, peak 3 wavenumber and peak 3 relative intensity.

Increasing the applied gate voltage for a fixed supply voltage resulted in the gate-referred noise decreasing. The noise decreased significantly in the linear regime and decreased less with gate voltage once in the saturation regime. This showed that the optimal amplification of an input signal occurs in the saturation regime. Additionally, the electrical characterisations further supported that the PED devices provided a lower gate-referred noise than the PEDG devices. Raman characterisations showed that the PEDOT:PSS was de-doping as the applied gate voltage increased. Both gate voltage and supply voltage variations found that the Raman parameters varied more for the PED OECT than the PEDG device, suggesting that the GOPS crosslinker restricted the structural changes and the electrochemical de-doping of the organic layer in response to applied electric fields of equal magnitude.

The reduction of gate-referred noise with active layer de-doping showed how the structure of PEDOT varied as device performance improved. The results showed that a lower conformational disorder, or equivalently a greater ratio of benzoidal to quinoidal PEDOT units, was associated with lower gate-referred noise. Therefore, the electrochemical de-doping during the OECT operation reduced the energetic disorder of the PEDOT:PSS, which resulted in lower noise values. The noise values for the devices were at the threshold of showing capability to resolve electrophysiological signals with voltage characteristics of action potentials. Therefore, this investigation suggests that the efficacy of OECTs for neurological recordings could be improved by reducing the sources of morphological, and thus energetic, disorder in the active layer. Furthermore, decreasing the noise results in lower limits of detection for chemical concentration measurements of physiologically relevant species such as potassium and sodium. Such signal improvements result in a more accurate insight into neurological conditions. In healthcare environments, this could provide better patient treatment and better inform intervening methodologies to improve patient outcomes.

This investigation has connected the vibrational properties of the conjugated backbone of organic conducting polymers to the electrical parameters relevant to long-term biosensing and, in turn, has provided insight into the fundamental sources of noise present in OECTs. The minimisation of noise is universally advantageous in the implementation of OECTs for an increasingly wide range of bioelectronic applications. To develop this work, the contribution of the PSS units to noise could be considered. In this investigation, the gate-referred noise for varying doping ratios of PEDOT to PSS could be measured, and the properties of inter-PEDOT electronic transport could be compared to the noise values. In further research which compares the performance of different organic active layers, such as that which aims to maximise the product of electronic mobility and volumetric capacitance, noise measurements could be included alongside those of output, transfer and response time characterisations. The efficacies of organic materials in physiological monitoring applications could then be quantitatively compared by considering the product of gate-referred noise and response time, where a lower value would be more desirable.

8. CONCLUSIONS, FURTHER RESEARCH AND OUTLOOK

8.1. Conclusions

Prior to this research, the application of OECTs to neurotechnology had already proven efficacious. Throughout the course of this research, novel materials and architectures had been added to the literature that further supported the capability of OECTs to measure neural activity. The primary motivators for utilising OECTs in measuring neural activity include its ionic-electronic transduction, high amplification, biocompatibility and low-voltage operation. These attributes have afforded the measurement of neural activity *in vivo* at high signal-to-noise ratios and have facilitated superior signal properties compared to electrodes. These demonstrations implore further investigations into the implementation of OECTs for measuring a greater range of neural activity, and indeed the expanse of novel literature in the field has proven that such motivations exist.

The research presented in this work has contributed to the field of bioelectronics. This research aimed to utilise OECTs for neurotechnology. As such, the research focused on exploring the parameter space and improving the device performance in OECTs to increase their efficacy in resolving the full spectrum of neural bioelectric signals and reducing their noise to improve their performance in a wider range of applications including chemical concentration measurements. Furthermore, the research considered the integration of OECTs into amplifier circuits and highlighted additional considerations when applying the devices for neurophysiological monitoring in clinical settings where a range of noise sources would be present. Finally, the research considered the relationship between the morphological structure of the organic polymer and the electrical characteristics of OECTs, which could be used to inform the material design to improve device performance through noise minimisation, thus improving the signal properties of OECTs in neural recordings.

The capabilities of interdigitated electrode architectures and additively-enhanced PEDOT:PSS was demonstrated in section 4. State-of-the-art OECTs were fabricated with transconductance values greater than 100 mS and response times approaching 100 μ s, providing g_m^{Peak}/τ_{90} values of 1000 Ss⁻¹. The incorporation of OECTs with array interconnects demonstrated efficacy in resolving bioelectric signals with frequencies on the kHz-scale and amplitudes on the 10 μ V-scale. This was facilitated through frequency-domain filtering, and the results supported that the OECTs had sufficient SNRs to resolve voltage inputs of cortical action potentials. Device noise was quantified using three novel methods, which allowed the gate-referred noise to be measured by comparing the gate voltage input and drain current output, and all methods were supported by comparison to standard methodologies of noise measurement.

The integration of OECTs into a linear amplifier topology that can be used to amplify gate voltage inputs from electrophysiological measurements was explored in section 5. The amplifier circuit was also simulated through the development of a novel equation that models transistor current in the linear, non-linear and saturation regimes. In addition to determining the gain and bandwidth of the OECT amplifiers, their linearities were parameterised through distortion measurements. Such characterisations had not previously been considered in the literature of OECT amplifiers and are of particular importance when considering operating the devices in environments with various noise sources. The amplification of pre-recorded electrophysiological signals was demonstrated using the linear amplifier, further exemplifying the capabilities of OECTs to be applied within integrated bioelectronic circuits. In addition to amplifying bioelectric signals, the circuit topology could also be implemented to amplify variations in potential distributions that arise from changes in chemical concentrations within electrolytes.

The insertion of OECTs into cortical regions with supply voltages applied externally to the scalp whilst minimising the insertion width of the device, and thus the damage to neural tissue, requires minimising the size of the interconnect electrode wires that bridge the output electronics to the OECT active areas. Increasing the length and minimising the width of the interconnects results in increasing resistances in series with the OECT, which reduces the proportion of the supply voltage across the active area. In addition, the geometry of the electrodes at the active area significantly impacts device performance. Such considerations for OECTs in neurotechnology were investigated in section 6. In both experimental measurements and simulations using the novel equation developed in section 5, it was found that the effects of source resistance on steady-state and transient device characteristics were distinct from those of drain resistance. The effects of interconnect resistance became significant when its magnitude approached the resistance of the organic active layer, and the effects were primarily detrimental to device performance. The impact of electrode architecture in the active area on OECT electrical characteristics was then investigated. Each aspect of the investigation identified a number of trade-offs pertinent to bioelectric resolution, and the research provided a comprehensive parameter space to inform optimising OECT electrode architecture for neurotechnology.

With the limits of minimising device noise through optimising electrode architecture explored in section 6, the impacts of the morphological parameters of PEDOT on the noise values and electrical characteristics of OECTs was explored in section 7. The PEDOT morphology was probed using resonant Raman spectroscopy, and electrical and resonant Raman characterisations were performed through aqueous immersion time to determine parameter stability. The effects on the morphological properties and electrical characteristics from the addition of a crosslinker and the variation of the voltages applied

to the OECTs was also investigated. In the development and utilisation of a novel Raman background subtraction method, the results indicated that the primary source of variation with immersion time was the doping level of PEDOT. Furthermore, the Raman characteristics suggested that the crosslinker acted to restrict morphological changes, and its inclusion as an additive proved detrimental to OECT performance, displaying increased noise values, slower response times and reduced de-doping efficiency. The OECT noise was found to decrease as the active layer was de-doped, which correlated with a reduction in the conformational disorder of the PEDOT units. This indicated that the OECT noise could be reduced by decreasing the sources of energetic disorder in the organic active layer. Informing material design to reduce the noise helps in the development of enhancing device performance, benefitting the implementation of the devices across a wide range of applications in neurotechnology.

8.2. Further Research

It was observed that the SC LI devices of section 6 had the capability to resolve gate voltage inputs characteristic of action potentials. This suggested that PEDOT:PSS OECTs with an active area of $20 \times 20 \mu\text{m}^2$ fabricated into an array with a device pitch less than $40 \mu\text{m}$ could detect cortical action potentials. The literature showed that enhancement mode, internal ion-gated OECTs, fabricated with spatial dimensions appropriate for resolving single-unit activity from multi-unit activity, could detect such signals from deep cortical layers [15]. However, spike-sorting methods are yet to be employed on OECT arrays.

As described in section 6, the interconnect design plays a critical role in the bioelectric performance and minimising the width of the interconnect lines to minimise neural tissue damage increases interconnect resistance. For an $m \times n$ OECT array, the total required number of output interconnect lines is $mn + 1$ given that there is only one shared source electrode. Therefore, the limited width available to the interconnects is divided into at least $mn + 1$ segments, highlighting a trade-off between interconnect resistance and channel number. To overcome such limitations, multiplexed interconnect structures, requiring only $m + n$ output interconnect lines, can be employed, and indeed have been utilised in OECT arrays [117, 155]. However, the limitations of such structures suggest that they would be unable to resolve high-frequency neural activity. Therefore, an OECT array would require using one drain electrode per device to provide a sufficient SNR and bandwidth for the resolution of action potentials within the brain.

A device architecture and a fabrication method were devised which allowed the interconnect resistance to not be entirely limited by its typical 2-dimensional area. The design would have provided an array with 8×12 interdigitated electrode OECTs, each with an active area of $20 \times 20 \mu\text{m}^2$ and a device pitch of $32 \mu\text{m}$. However, the fabrication

method proved unsuccessful when using the materials and equipment available. Nevertheless, the literature indicated that the devised architecture could be fabricated using Parylene C and reactive ion etching [259]. Given an unsuccessful fabrication, the architecture and method were formulated such that an array of size 8×4 could still be fabricated using the techniques described in section 3.

The interconnect architecture was designed with the consideration of the volumes of physiological regions and the characteristics of previous devices used to interface bioelectronic devices with the brain. The device was designed to be placed on the surface of, or inserted into, the cortical surface. The distance between the scalp and the cortex has been measured to be approximately 15 – 20 mm. As such, the interconnects were designed with a length of 25 mm [285]. Investigations in literature accessed the brains of rats through a craniotomy with a width of approximately 3 mm [13, 14]. Therefore, the interconnect width was limited to 3 mm. Furthermore, motivated by section 6, the interconnects were designed such that the interconnect resistance was approximately equal for each OECT and that the source and drain interconnect lines had the same resistance. This aided in minimising the variation in characteristics between the devices. The output interconnects were made compatible with commercially available zero insertion force connectors for the connection to external electronics.

Arrays of size 8×4 were fabricated on 50 μm Kapton HN Thermal Insulating Film from DuPont. The interconnects had a 150 nm gold layer with a 10 nm chromium adhesion layer and were patterned through photolithography. The interdigitated electrodes had the ‘IDE’ architecture as described in section 6. The electrodes were encapsulated by a 1 μm thick layer of SU-8, and patterning with photolithography exposed the $20 \times 20 \mu\text{m}^2$ OECT channels. Each array had an active layer of PED or PEDG, patterned through photolithography with lift-off or etching, respectively, and both were spin coated at 2000 rpm, producing a layer of approximately 90 nm. The characterisations and a frequency-filtered bioelectric response for a PEDG transistor are shown in figure 8.1.

The gate-referred RMS noise of the device was measured to be 56 μV . The transfer characteristics suggested that the active layer resistance was at least on the same scale as the interconnect resistance. With the inclusion of the crosslinker, which was shown to increase device noise in section 7, the devices still showed the capability to resolve large-amplitude action potentials. This provided motivation to continue with the investigation, which sought to test the *in vitro* capabilities of the OECT array using the brain slice of a rodent [286].

To acquire output signals of each OECT, a resistor would have been placed in series and the potential difference across the resistor would have been measured. The results from section 5 would have provided directions to maximise the gain through optimising

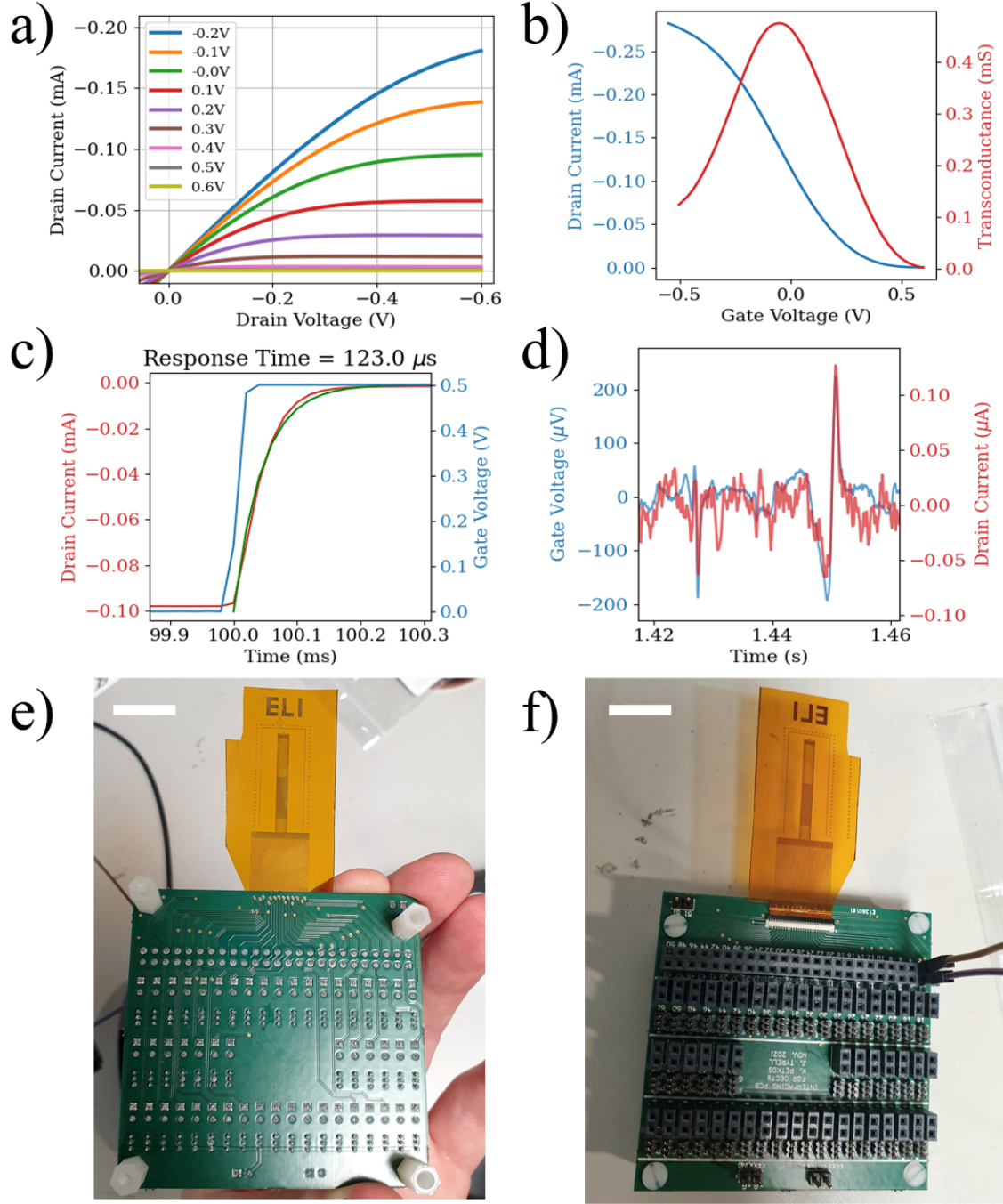


Figure 8.1: OECT Characteristics of a) output, b) transfer, c) response time, d) bioelectric performance. Front and back of OECT array, shown in e) and f), respectively, with external connector (scale bar represents 15 mm).

the supply voltage and series resistance values for the chosen range of effective gate voltage input whilst maintaining potential differences lower than the hydrolysis level. The action potentials that would have generated the ionic fluxes of the extracellular environment would have acted as the gate input, and this would have been represented by output voltages transduced by the mixed ionic-electronic conductivity of the OECT active layer. The local amplification delivered through the transconductance could have provided a highly detailed window into neural activity. Moving forward, electrical components could have been integrated more locally to the bioelectronic circuit such that the input signals could have undergone processing prior to being digitally converted. Such circuits are starting to be developed in OECTs applied for electrophysiology, and they show potential to reduce the power consumed by computational processing [15].

8.3. Outlook

The implementation of organic electrochemical transistors in neurotechnology is positioned to grow as new materials and architectures are applied in an increasing number of neurological measurements. For electrophysiological recordings, developments in OECT performance have resulted in the demonstration of their efficacy to transduce activity from a widening range of modalities. Investigations into overcoming the trade-offs presented in this research would further improve the signal quality, providing a window into neural activity with an unprecedented level of detail. Such investigations include noise and power minimisation through material engineering, the development and integration of a greater number of bioelectronic processing components local to measurement sites, and the advancement of novel fabrication techniques to enable the production of more complex device architectures. The superior signal qualities presented by OECTs suggest that they could provide a better performance relative to electrodes in human-machine, in particular brain-machine, interfaces. This could be determined through a comparison of the electrode and OECT technologies in tasks that correlate measured activity to desired computational actions. With the recent interest in the utilisation of wearable technology to enhance communication and interaction in virtual environments, such comparisons could pave the way for the significant adoption of OECT technology.

The transduction of chemical concentration facilitated by the organic mixed ionic-electronic conduction of the active layer has been utilised to monitor an expanding range of chemical species relevant to neurological conditions. The recent developments in the fundamental understanding of applying OECTs to amperometry open new directions to measure a wide range of species with increasing sensitivities and lower detection limits. Furthermore, the development of novel materials and microfluidics has enabled the

miniaturisation of devices, showing a pathway towards transducing a comprehensive set of chemical species in a compact and low-power system of devices. The utilisation of amplifier topologies in OECT chemical sensing has proven to provide high sensitivities, and their incorporation with novel materials could further improve performance. Finally, motivations to reduce the cost and increase the rate of device fabrication will drive developments in printing techniques and material engineering. The eventuality of advancements in the detection of chemical species is a low-cost, low-power, accurate, compact, portable, and comprehensive physiological monitoring device that can provide a clinically valuable description of activity, and the performances demonstrated by OECTs show that they could play a critical role in its realisation.

Beyond electrophysiological measurements and chemical concentration monitoring, OECTs are also being applied in neurotechnology to the development of neuromorphic circuits. Their capability to provide low-power operation whilst displaying dynamics analogous to neuronal behaviour has motivated their growing implementation in demonstrating the functions of neuromorphic circuits. This highlights that OECTs are being applied in an increasing number of fields related to neurotechnology. The devices continue to receive extensive attention, motivated by their demonstrated utility to society, and the future of OECTs, both in neurotechnology and in wider fields, shows promise to provide a positive impact to the world.

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