



Mechanistic Insights into the Oxygen Reduction Reaction on Metal–N–C Electrocatalysts under Fuel Cell Conditions

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Three different transition metal–C–N catalysts are tested under a range of fuel cell conditions. It is found that common features of the polarisation curve can be explained by a change in electrocatalytic mechanism. Utilising a simple model to quantify the change in mechanisms, *iR*-free results of the fuel cell experiments are fit and found to be represented by a common set of parameters. The change in mechanism is assumed to be a switch from four-electron reduction of oxygen to water to a two-electron reduction to hydrogen peroxide followed by disproportionation of the hydrogen peroxide to water and oxygen. The data is used to estimate a mass specific exchange current density towards the oxygen reduction reaction (ORR) to water in the range 10^{-11} – 10^{-13} A g^{-1} depending

on the catalyst. For the reduction of oxygen to hydrogen peroxide, the mass specific exchange current density is estimated to be in the range 10^{-2} – 10^{-3} A g^{-1} . Utilising the electrokinetic model, it is shown how the mass transport losses can be extracted from the polarisation curve. For all three catalyst layers studied, these mass transport losses reach about 100 mV at a current density of 1 A cm^{-2} . Finally a discussion of the performance and site density requirements of the non-precious metal catalysts are provided, and it is estimated that the activity towards the ORR needs to be increased by an order of magnitude, and the site density by two/three orders of magnitude to compete with platinum as an ORR electrocatalyst.

1. Introduction

Fuel cells can play a crucial role in a future sustainable world; however, these devices are currently based on platinum group metals (PGMs), which is a catalyst group of materials considered as critical raw materials.^[1] Furthermore, the oxygen reduction reaction (ORR), which is more than six orders of magnitude slower than the hydrogen oxidation reaction, requires the cathode of polymer electrolyte fuel cells (PEFCs) to utilise eight times the amount of platinum of the anode (i.e. $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}_{\text{cathode}}$ vs. $0.05 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}_{\text{anode}}$).^[2] As a sustainable alternative, non-precious oxygen reduction catalysts have been a main focus of research,^[1,3] and, in this regard, carbon-based catalysts are emerging as a viable alternative on a long-term scenario.^[4,5] They are based on naturally abundant elements, for example, C ($\geq 90\%$), N, Fe or other abundant transition metals, and we have recently shown that carbon catalysts can

also be highly selective towards the oxygen reduction reaction, with tolerance to a wide range of poisons^[6] that adversely affect PGM-based catalysts.^[7–11] Even though extremely promising, some challenges remain regarding fundamental and applied developments of carbon catalysts, for instance: (1) understanding the kinetics of the oxygen reduction reaction on these materials; (2) translation of fundamentally (e.g. RRDE) observed performances into power output in practical devices; (3) dealing with degradation of these catalysts under operational conditions that limit their ultimate lifetime. There has been progress in addressing the oxygen reduction activity of carbon catalysts;^[6,12–19] however, there is a gap in understanding the activity of the carbon catalyst cathodes, in part due to issues in appropriately determining ORR kinetics and mass transport overpotential under fuel cell conditions.

One of the first attempts to establish an ideal performance for carbon-catalysed cathodes of PEFC was set by Gasteiger et al.,^[2] aimed at promoting high practical power outputs. This proposition was based on the assumption of equivalent Tafel kinetics of carbon catalyst to platinum (a Tafel slope of 70 mV dec^{-1} at 353 K) over the entire potential window, which, in fact, may not be appropriate for carbon-based catalysts or even platinum for that matter.^[20] Current carbon-based catalyst cathodes in a PEFC are unlikely to reproduce the performance of platinum catalyst cathodes, given that the location of the active sites on Pt/C are on the surface of an extended lattice, whereas those on the carbon catalysts are individual “molecular” sites mostly located at micropores.^[21–23] This will hinder species transport; that is, oxygen to and water from the active sites.^[24] Compared with previous work utilising rotating disc

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electrode measurements (RDE) to characterise the performance of the catalysts, we have used fuel cell measurements because they allow us to operate at much higher turnover frequencies than for catalysts under RDE conditions, and also allow us to study the performance under realistic conditions. Utilising appropriate carbon-based catalysts under conditions of high mass transport or high oxygen partial pressures, the present work shows that the hypothesis of a single Tafel slope of 70 mV dec^{-1} and no debilitating mass transport effect might not be directly applicable to carbon materials. Based on the finding that the ORR proceeds on carbon catalysts with two distinct Tafel slopes, we propose a mechanism for the ORR on these catalysts. Furthermore, a methodology is proposed for quantifying the various modes of voltage losses that limit power outputs in PEFCs utilising these materials as catalyst.

2. Results and Discussion

Carbon catalysts are emerging as potential candidates to replace finite precious metals as catalysts for the oxygen reduction in a range of pH values and under various adverse conditions.^[6] Some developments have been achieved in the last few years on developing carbon catalysts with progressively increasing catalytic activities^[6,25–30] and reliable short-term practical durability.^[23] However, there has been a gap in quantifying the activity and voltage loss modes that limit the available power output of practical electrochemical devices based on the oxygen reduction reaction, that is, PEFCs. Optimising PEFCs (and generally electrochemical devices) requires a detailed understanding of the voltage losses that define the cell voltage (available power output), particularly the oxygen reduction reaction kinetics, the proton/hydroxide conduction in both catalyst layer and electrolyte, and, of great importance for carbon catalysts, the mass transport (oxygen to and oxygen reduction products from an active site). A suitably illustrative example of such development, based upon detailed knowledge of each overvoltage contributing to the total power output in practical electrochemical devices, is that of platinum catalyst on PEFCs.

Figure 1 compares the historical state-of-the-art performance of platinum-based PEFCs, in the year of 1996^[31] and a present industrial standard, which amounts to more than 25 years of development. It is clear from the data in Figure 1 that the development of both catalyst layer structure (e.g. ca. $40 \mu\text{m}$ thick E-Tek Pt/C versus ca. $10 \mu\text{m}$ Johnson Matthey Pt electrode) and catalyst activity (ΔE ca. 20 mV) has greatly promoted the development of PEFCs in terms of practical performance. At a cell potential of $0.8 \text{ V}_{\text{IR-free}}$ (i.e., corrected for ohmic losses) there are mass-transport-free current densities of approximately 0.3 A cm^{-2} for 20 wt% Pt/Vulcan versus 1.7 A cm^{-2} for the Johnson Matthey Pt/C electrode. This represents an improvement of about six times in performance, which has been obtained by properly tackling principally kinetic and mass transport overvoltage losses.

Carbon catalysts have been found to present a lower density of active sites and also lower ORR activity compared with precious metal catalysts.^[26] This feature generally leads researchers

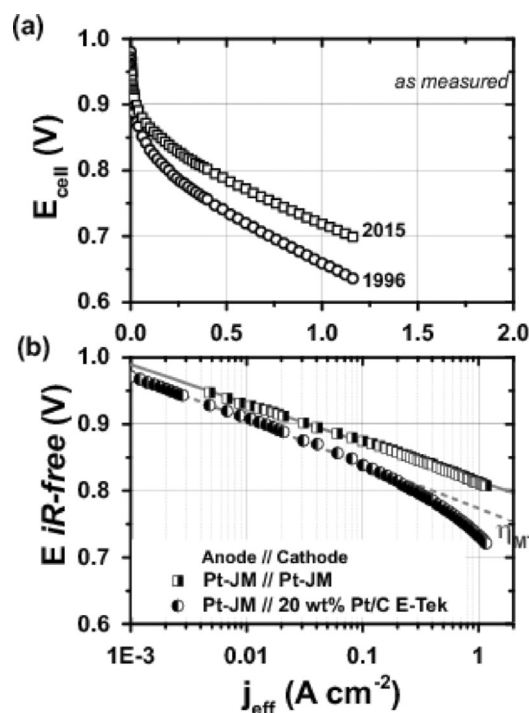


Figure 1. H_2/O_2 polarisation response of a single PEFC under galvanostatic mode a) as measured and b) resistance corrected. Cells at 80°C and gases at 100 RH%, with H_2 at 160 ccm and O_2 at 550 ccm. H_2/O_2 at a partial pressure of 100 kPa_{abs}. A NafionTM membrane NR212 was utilised as electrolyte membrane. Square: Johnson Matthey platinum electrode with a loading of $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$; circle: a catalyst layer prepared by using a method developed in 1996^[31] with a platinum loading of $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ and an ionomer to carbon ratio of 0.93. Half-filled symbols stand for resistance corrected PEFC performances, accounting for high-frequency-resistance and for proton transport resistance in the cathodic catalyst layer. Effective current density (j_{eff}) refers to hydrogen crossover corrected current densities.

to apply high loadings of carbon catalysts onto the cathode catalyst layer of PEFCs, to reduce voltage losses associated with the oxygen reduction reaction (the catalyst effective exchange current density is dependent upon catalyst loading). However, high loadings of catalysts lead to thick catalyst layers, which may exacerbate diffusion overvoltage losses in practical devices (quantified later in this text), as indirectly evidenced in Figure 1 ($10 \mu\text{m}$ thick Pt-JM vs. $40 \mu\text{m}$ thick Pt E-Tek). Equation (1) summarises the total overpotential components, for a PEFC under operating conditions:

$$E_{\text{cell}}^{\text{meas}} = E_{\text{cell}(p_{\text{H}_2}, p_{\text{O}_2}, T)}^{\text{theor}} - \eta_{\text{HOR}}^{\text{an}} + \eta_{\text{ORR}}^{\text{cath}} - iR_{\Omega} - i(R_{\text{H}^+}^{\text{an}} + R_{\text{H}^+}^{\text{cath}}) - \eta_{\text{MT}}^{\text{an}} - \eta_{\text{MT}}^{\text{cath}} \quad (1)$$

where $E_{\text{cell}}^{\text{meas}}$ is the measured cell potential; $E_{\text{cell}(p_{\text{H}_2}, p_{\text{O}_2}, T)}^{\text{theor}}$ is the theoretical cell potential and refers to the difference between anode and cathode electrode equilibrium potentials, which follow the Nernst equation and is based on the partial pressure of the reactants in the flow field and reaction temperature; $\eta_{\text{HOR}}^{\text{an}}$ is the hydrogen oxidation reaction overpotential on the anode; $\eta_{\text{ORR}}^{\text{cath}}$ is the oxygen reduction reaction overpotential on

the cathode; R_{Ω} refers to the ohmic resistances of the system [e.g. membrane resistance, contact resistances (flow field/transport media and transport media/catalyst layer), bulk resistance of the diffusion media and the electronic resistance of the catalyst layers]; $R_{H^+}^{an}$ and $R_{H^+}^{cath}$ refer to the anode and cathode proton transport resistances within the catalyst layers, respectively; and η_{MT}^{an} , η_{MT}^{cath} refer to the mass transport overpotentials caused by reactant concentration gradients (between the flow field and the catalyst layer).

The terms in Equation (1) have different contributions to the total overvoltage of a PEFC under operation. The ORR kinetic loss (η_{ORR}^{cath}) is the most important factor contributing to the total overvoltage (easily greater than -300 mV). Ohmic resistance (iR_{Ω}) is another important term in Equation (1), with values for R_{Ω} ranging between approximately $0.06 \Omega \text{ cm}^2$ (-60 mV @ 1 A cm^{-2}) to $0.25 \Omega \text{ cm}^2$ (-250 mV @ 1 A cm^{-2}) for NafionTM membrane thicknesses between 50 and $175 \mu\text{m}$ and standard gas diffusion media.^[32–33] The proton transport resistance can also contribute remarkably to the total overvoltage of a PEFC, with $R_{H^+}^{cath}$ at about $0.10 \Omega \text{ cm}^2$ and $0.030 \Omega \text{ cm}^2$ (-100 mV and -30 mV @ 1 A cm^{-2} , respectively) for platinum-based standard catalyst layers.^[34,35] Eikerling and Kornyshev have derived analytical expressions correlating the cathode catalyst layer structure/composition with the AC impedance response of PEFCs.^[36] Among the special cases described in this model, there is the proton transport resistance signature in the EIS spectrum, which appears as a 45° straight line in the high-frequency domain, as clearly observed in the inset of Figure S2 (dashed line) and indirectly in Figure 2. Eikerling and Kornyshev also pointed out that the developed model can be approximated by using a finite transmission line equivalent circuit; therefore, experimental data can be readily fitted with this element and the proton transport resistance in the catalyst layer

obtained, as suitably carried out in the present work (for further details refer to the Experimental Section and the Supporting Information S2.2).

η_{ORR}^{cath} and η_{MT}^{cath} are the main subject of research on fuel cell technologies because of their high magnitude, particularly when carbon-based catalysts are utilised in the cathode electrode.^[6,24,37] Notably, both proton and mass transport resistances at the anode are negligible when pure and fully humidified hydrogen is utilised with optimised electrodes (i.e. η_{HOR}^{an} , η_{MT}^{an} and $R_{H^+}^{an}$ are small).^[37] This work has utilised an appropriately optimised commercial platinum electrode as anode, therefore Equation (1) can be rearranged to the form of Equation (2):

$$E_{\text{cell}}^{\text{meas}} = E_{\text{cell}(P_{H_2}, P_{O_2}, T)}^{\text{theor}} + \eta_{ORR}^{cath} - iR_{\Omega} - iR_{H^+}^{cath} - \eta_{MT}^{cath} \quad (2)$$

Understanding each loss mode in Equation (2) is crucial towards optimising power outputs of PEFCs utilising carbon catalysts. In the Supporting Information, ohmic resistances (R_{Ω} or the high-frequency resistance and $R_{H^+}^{cath}$) are discussed and determined with the aim of obtaining PEFC polarisation responses free of ohmic contributions (iR -free), which are necessary to obtain suitable estimates of $\eta_{ORR}^{cath} - \eta_{MT}^{cath}$, or of ORR kinetic polarisations. A detailed analysis of the suitable optimisation approach also utilised here, for optimising $R_{H^+}^{cath}$ on the cathode catalyst layers of PEFCs employing carbon catalysts, is given in a separate work by the present authors.^[38] In subsequent sections, an oxygen reduction electrokinetic model to describe the ORR on carbon catalysts is proposed, which uniquely opens the way for calculating ORR electrokinetic overpotentials (η_{ORR}^{cath}) and mass transport overpotentials (η_{MT}^{cath}) of carbon-based cathodes of electrochemical systems. Based on these findings,

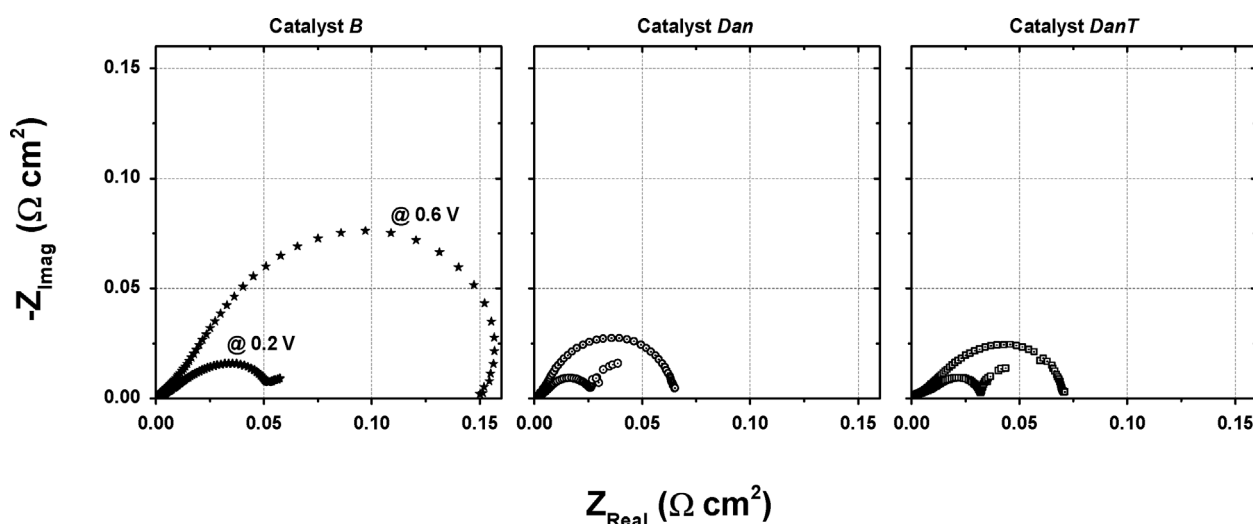


Figure 2. Complex plane impedance plot of a single PEFC cell fed with H_2/O_2 . Stars: catalyst **B**; open circles: catalyst **Dan**, and open squares: catalyst **DanT**. MEA is composed of carbon catalyst **B** at a loading of 6 mg cm^{-2} , catalyst **Dan** and **DanT** at a loading of 4 mg cm^{-2} , and at an I/C ratio of 1.5 for **Dan** and 1 for remaining catalysts. Catalysts were deposited on a Toray carbon paper THP60 with microporous layer, a NafionTM N115 as membrane and a commercial electrode as anode (Johnson Matthey, $0.4 \text{ mg}_{Pt} \text{ cm}^{-2}$). The EIS experiment was carried out under galvanostatic control at a cell potential of 0.6 V (0.09 A cm^{-2} for **B**, 0.17 A cm^{-2} for **Dan** and 0.29 A cm^{-2} for **DanT**) and 0.2 V (0.77 A cm^{-2} for **B** and 1 A cm^{-2} for **Dan** and **DanT**), with an AC perturbation of 5% of the DC current for a frequency range between 100 kHz and 0.1 Hz . Cell hardware temperature at 80°C and water humidification at $95^\circ\text{C}_{\text{anode}}$ and $85^\circ\text{C}_{\text{cathode}}$ with H_2 at 160 ccm and O_2 at 450 ccm , both anode and cathode compartments were pressurised to 210 kPa gauge (O_2 partial pressure of $244 \text{ kPa}_{\text{abs}}$).

and with an eye to the required site density mentioned previously, we assess the required electrocatalytic performance of metal-N-C catalysts to determined whether they can match PMG type catalysts.

2.1. *iR*-Free Polarisation Response of PEFCs: Evidence for Two Nernstian Tafel Regions

Experimentally determining both R_{Ω} and $R_{H^+}^{cath}$ is important towards isolating ohmic terms in Equation (2) and obtaining a true *iR*-free polarisation response of PEFCs. Such results ($E_{cell/iR-free}$ versus current density) are shown in Figure 3a for PEFCs with cathodes containing different loadings of carbon catalyst **B**. For comparison with the experimental data, a dashed line tangent to the experimental results and with a Tafel slope of $140 \text{ mV decade}^{-1}$ (i.e. $\alpha_{eff} = 1/2$ at the temperature of the experiment) is also plotted on the data. In fact, especially for the lowest loading catalyst layers, the data is well represented by such a line. At higher loadings, it is seen that there is a pronounced curvature to the data at high current densities due to the appearance of mass transport effects. It is interesting to note that the data in Figure 3 deviates from the ideal $\alpha_{eff} = 1/2$ Tafel line at low current densities, suggesting a change in mechanism at high potentials. This effect is more clearly seen in Figure 3b (catalyst **B**), in which the data, presumed to be mass-transport-free (i.e. data well away from the area of increased curvature at high current densities), is plotted for all the electrodes from Figure 3a. To allow fair comparison, the data is corrected to mass specific activity. It is compelling to see that all the data representing different catalyst loadings falls on the same curve, which strongly supports the concept that the data is mass-transport-free. Furthermore, there is a transition from a region of low Tafel slope to that of high Tafel slope as the mass-specific current density is increased. This transition does not appear to be due to a mass transport effect (as that data has been excluded from the plot); rather, it seems to be associated with a transition of mechanism.

For comparison, data for two different carbon catalysts (**Dan** and **DanT**) are also plotted in Figure 3b (in this case, mass-transport affected points were not excluded). It is interesting to note that the curve determined for catalyst **B** (see discussion below for the mathematical form of this curve) also gives a good approximation to that for **Dan** and **DanT** if the curve is offset vertically and slightly laterally as shown in Figure S3 (see below for description of fitting procedure).

Where does the change of mechanism come from? It is interesting to note that these catalysts can produce significant amounts of hydrogen peroxide.^[12, 13, 39, 40] For instance, in Figure 4, we show rotating ring disc electrode (RRDE) results for catalyst **B** in sulfuric acid electrolyte as a function of catalyst loading. It is seen that thinner catalyst layers result in increased H_2O_2 percentages detected in the ring, at less positive potentials.

The results in Figure 4 are also supported by other reported results, and we interpret the results as being due to more effective mass transport of the H_2O_2 away from the electrode surface when the mass loading of the catalyst is lower; that is,

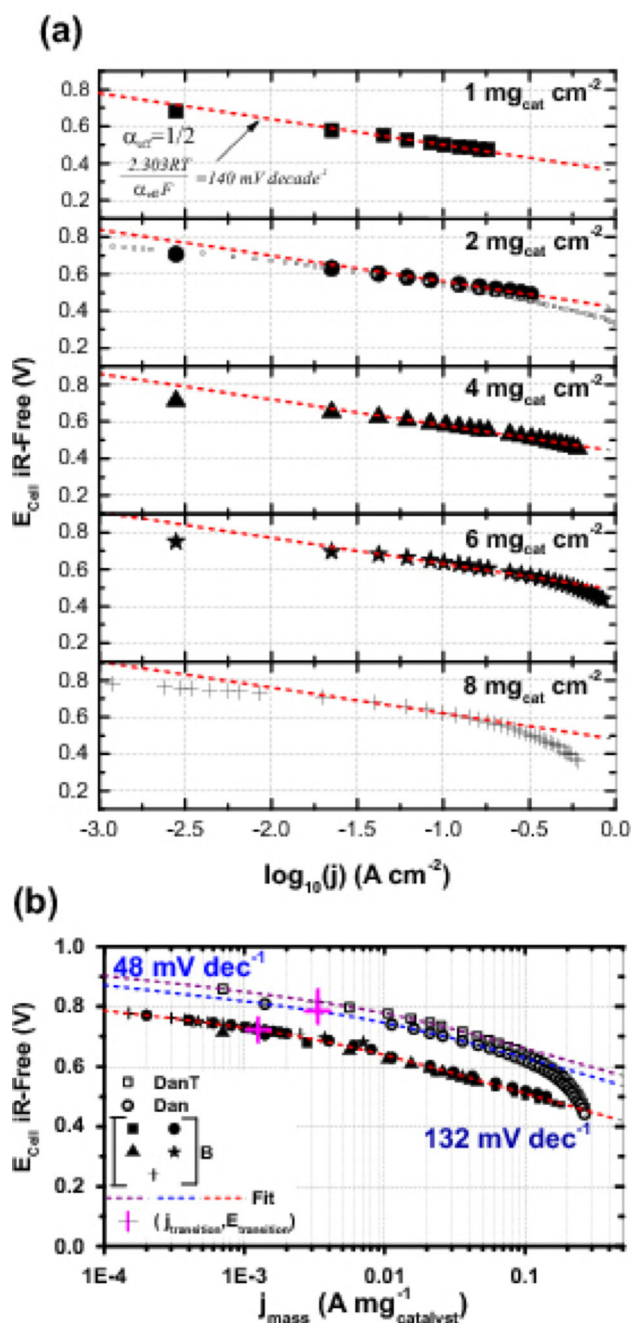


Figure 3. a) H_2/O_2 resistance corrected polarisation response of single PEFCs under galvanostatic mode for the ORR on carbon catalyst **B**. Dashed line corresponds to a Tafel slope of $140 \text{ mV decade}^{-1}$ (equivalent to an effective transfer coefficient of $1/2$ at the temperature of the experiment). Loading (■) $1 \text{ mg}_{\text{catalyst}} \text{ cm}^{-2}$; (●) $2 \text{ mg}_{\text{catalyst}} \text{ cm}^{-2}$; (▲) $4 \text{ mg}_{\text{catalyst}} \text{ cm}^{-2}$; (★) $6 \text{ mg}_{\text{catalyst}} \text{ cm}^{-2}$; and (+) $8 \text{ mg}_{\text{catalyst}} \text{ cm}^{-2}$. Experimental conditions as per Figure 2. b) Mass-specific current density with mass transport unaffected data only (1 to $8 \text{ mg}_{\text{cat}} \text{ cm}^{-2}$ catalyst **B**), data from (a) with same symbols, and complete data set for catalysts **Dan** (4 mg cm^{-2} , open circle) and **DanT** (4 mg cm^{-2} , open square) under the same experimental conditions. Fits of data to Equation (6) [(- - - - -), see Table 1 for parameters].

the likelihood of the H_2O_2 produced being autocatalytically decomposed is a function of catalyst layer thickness. For instance, Bonakdarpour et al.^[39] observed an increase in the percentage of H_2O_2 detected on the ring from 5 to 95% with a decrease in

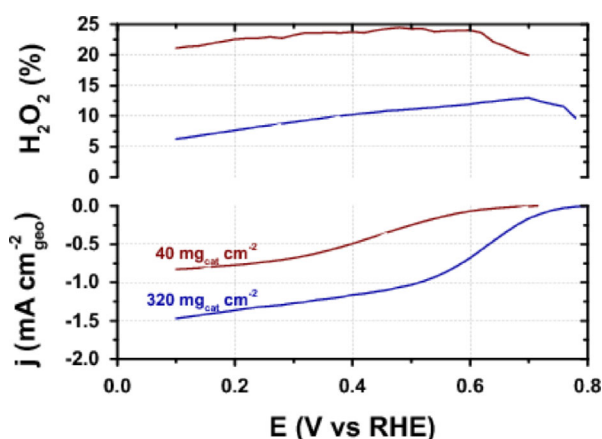


Figure 4. Steady-state oxygen reduction current densities (bottom) and H_2O_2 (top) percentage measured on carbon catalyst **B** supported on a glassy-carbon rotating ring (gold) disc electrode at 1600 rpm in 1 M H_2SO_4 at $25^\circ\text{C} \pm 0.1^\circ\text{C}$ and saturated with oxygen at 91 kPa. The blue curve was obtained with a catalyst loading of 320 mg cm^{-2} and the red curve with 40 mg cm^{-2} deposited on the disc of the RRDE electrode. Steady-state measurements were performed with a potential step of 30 mV, and hold duration of 30 s.

catalyst loading from 0.800 to 0.020 mg cm^{-2} in the disc of the RRDE.

Although there are many ways in which a mechanistic transition from one slow step to another can occur, it is modelled here as a simple system in which two different oxygen reduction processes can occur on the same active site. This ultimately leads to the formation of water or hydrogen peroxide, the latter of which can then undergo autocatalytic decomposition to oxygen and water. Hence, we ascribe a mechanism to this process as described schematically in Figure 5. Under these conditions, there is competition between the decomposition pathway and mass transport of the peroxide away from the electrode.

Based on the circumstances detailed in the last paragraph and as illustrated in Figure 5, there are two possible oxygen reduction mechanisms that can occur on carbon catalysts, each associated with its own reversible potential ($E_{\text{rev},1}$, $E_{\text{rev},2}$), ex-

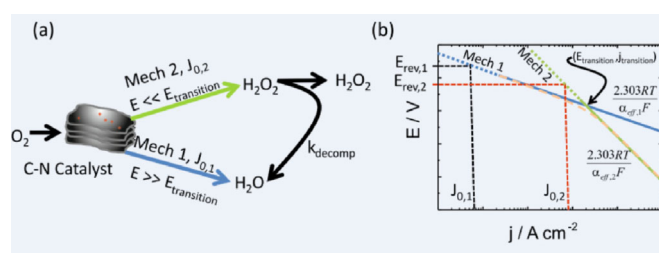


Figure 5. a) Cartoon representing the reduction of oxygen on a carbon-nitrogen catalyst through two different mechanisms leading to the formation of either hydrogen peroxide or water. The mechanisms use the same catalytic site and Mechanism 2 blocks Mechanism 1 at a high enough current density. b) Example of a Tafel plot showing what might be expected for Mechanism 1 (.....) and Mechanism 2 (-----), each with a different reversible potential, exchange current density, and α_{eff} . The combination of both mechanisms leads to the dashed line (---). For simplicity, only the reduction side of the reactions are shown, and the effect of k_{decomp} is ignored.

change current density ($j_{0,1}$, $j_{0,2}$) and effective symmetry factor ($\alpha_{\text{eff},1}$, $\alpha_{\text{eff},2}$). If it is assumed that the electrode potential is sufficiently far away from each of the reversible potentials, such that the Tafel approximation applies, then the mechanisms can be described by Equations (3) and (4):

$$\text{Mechanism 1 : } j_1(E) = -j_{0,1} \exp\left(\frac{-\alpha_{\text{eff},1} F(E - E_{\text{rev},1})}{RT}\right) \quad (3)$$

$$\text{Mechanism 2 : } j_2(E) = -j_{0,2} \exp\left(\frac{-\alpha_{\text{eff},2} F(E - E_{\text{rev},2})}{RT}\right) \quad (4)$$

As both mechanisms operate in parallel and utilise the same active site, at large overpotentials, Mechanism 2 will block Mechanism 1 (as shown in Figure 5a) and the current densities are combined as Equation (5) to represent the parallel nature of the reaction:

$$\frac{1}{j_{\text{Tot}}(E)} = \frac{1}{j_1(E)} + \frac{1}{j_2(E)} \quad (5)$$

where $j_{\text{Tot}}(E)$ is represented by the dashed line in Figure 5b.

Although Equations (3–5) could be utilised to fit the referent data in this work, there would be six possible fit parameters. This number can be reduced by one because we know the equilibrium potential for the four-electron reduction of oxygen to water under our operating conditions (see the Supporting Information, S3); however, we do not know the corresponding equilibrium potential for the oxygen reduction to hydrogen peroxide reaction, because it is unclear what the equilibrium concentration of hydrogen peroxide in the system will be, and it should be closely coupled to the magnitude of k_{decomp} . Increasing k_{decomp} (or indeed increasing mass transport of peroxide away from the catalyst layer) will drop the equilibrium peroxide concentration and thus increase the reversible potential for the oxygen/peroxide reaction, leading to a higher change-over potential. Nevertheless, the number of parameters can be further reduced by realising that the point of intersection of the Tafel slopes represents a fixed value, and the same result as Equations (3–5) can be achieved by using Equation (6):

$$j(E) = j_{\text{transition}} \left(\frac{1}{\exp\left(\frac{\alpha_{\text{eff},1} F(E - E_{\text{transition}})}{RT}\right)} + \frac{1}{\exp\left(\frac{\alpha_{\text{eff},2} F(E - E_{\text{transition}})}{RT}\right)} \right) \quad (6)$$

where $(E_{\text{transition}}, j_{\text{transition}})$ represents the point at which the two Tafel lines intercept each other; that is, the potential at which each mechanism would produce the same current.

It is important to note that $E_{\text{transition}}$ is only indirectly related to the electrochemical processes occurring, and should not be assumed to be representative of a reaction itself. Nonetheless, it is interesting to note that the values of $E_{\text{transition}}$ determined are close to the standard potential of oxygen reduction to peroxide.

Utilising Equation (6) allows a suitable four-parameter fit of data ($E_{\text{transition}}, j_{\text{transition}}, \alpha_{\text{eff},1}, \alpha_{\text{eff},2}$) and this equation was utilised to fit the data in Figure 3b; indeed, the curves in Figure 3b are

the resultant fit, along with the fits for **Dan** and **DanT**. Details of the fitting procedure are provided in the Experimental Section. In this fitting procedure, it is assumed that the mechanistic slow steps remain the same for all catalysts, and thus they have a common value. It is interesting to see that a fit of only catalyst **B** also fits catalysts **Dan** and **DanT**, provided the fit is offset (i.e. $E_{\text{transition}}$ is increased), as illustrated in Figure S3. All three datasets in Figure 3b were fitted simultaneously by using a common set of values for $\alpha_{\text{eff},1}$ and $\alpha_{\text{eff},2}$ because it is assumed that the slow steps to the reactions remain the same in each region (mechanism). However, a different $E_{\text{transition}}$ is assumed for each of the catalysts and a common value of $J_{\text{transition}}$ for the **Dan** and **DanT** catalysts. A summary of the fitting parameters is provided in Table 1. It is found that the resultant fit

Table 1. Fitting parameters for Equation (6) used to fit the data for catalysts **B**, **Dan**, and **DanT** in Figure 3b, and derived exchange current densities. Common values of $\alpha_{\text{eff},1}$ and $\alpha_{\text{eff},2}$ were used for all catalysts, and a common value of $J_{\text{transition}}$ was used for **Dan** and **DanT**.

Parameter	Unit	Catalyst B	Dan	DanT
$\alpha_{\text{eff},1}$		1.45	1.45	1.45
$\alpha_{\text{eff},2}$		0.53	0.53	0.53
$J_{\text{transition}}$	[mA mg ⁻¹]	1.25	3.34	3.34
$E_{\text{transition}}$	[V]	0.722	0.784	0.816
$j_{o,1}$	[mA mg ⁻¹]	3.0×10^{-13}	1.5×10^{-11}	7.0×10^{-11}
$j_{o,2}^{\text{[a]}}$	[mA mg ⁻¹]	1.4×10^{-3}	1.1×10^{-2}	2.0×10^{-2}

[a] Calculated assuming a steady-state activity of H₂O₂ in the catalyst layer of 6.4×10^{-5} , $E_{\text{H}_2\text{O}_2}^{\text{rev}} = 0.754$ V.

produces a suitable representation of all data sets in Figure 3b with common Tafel slopes of 132 mVdecade⁻¹ ($\alpha_{\text{eff}} = 0.53$) at high current densities and 48 mVdecade⁻¹ at low current densities ($\alpha_{\text{eff}} = 1.45$). If the process occurring at high potentials is considered to be the direct four-electron reduction of oxygen to water, then the mass-specific exchange current density can be estimated under the conditions of the experiment for each of the catalysts. This is obtained by extrapolation of the Tafel line to the equilibrium potential [Eq. (7)], assuming that the overpotential losses on the anode can be neglected, as described before:

$$j_{\text{mass}}^0 = j_{\text{transition}} \exp \left(\frac{\alpha_{\text{eff},1} F (E_{\text{transition}} - E_{\text{cell}(p_{\text{O}_2}, T)}^{\text{theor}})}{RT} \right) \quad (7)$$

The values of mass-specific exchange current densities, calculated for the different catalysts, are displayed in Table 1. The mass-specific exchange current densities for the first mechanism are very low and are about five orders of magnitude below that for platinum (Figure 2, though at 100 kPa_{abs} O₂). This can be attributed to the relatively low density of active sites in the material compared with platinum. For the second process (assumed to be oxygen reduction to peroxide), the exchange current density can be estimated if we make some assumptions about the mechanism and the equilibrium activity

of hydrogen peroxide in the catalyst layer. By using an equilibrium activity of peroxide in the catalyst layer of 6.4×10^{-5} , which was calculated from the peroxide yield in the RDE experiment for the low loading electrode in Figure 4, and utilising the oxygen partial pressure, and standard potential for oxygen reduction to peroxide ($E^0 = 0.695$ V^[41]), exchange current densities for the second mechanism are calculated (Table 1). For all catalysts, the estimated exchange current density for peroxide are nine to ten orders of magnitude higher than for the reduction of oxygen to water. The absolute values of this result are dependent on the assumption of equilibrium peroxide concentration in the catalyst layer, and ultimately the applicability of the RDE results (flooded electrode) to the fuel electrode. Nonetheless, it certainly points to the fact that peroxide generation in these electrodes is significantly favoured over the four-electron reduction of oxygen to water. We have assumed in our model that the same site is responsible for both products, but it may be that a different site on the catalyst surface is responsible for peroxide formation. In principle, this configuration would give the same response as shown in Figure 5. Some support to this thesis is given by the results presented in Table 1, which show that utilising a template to increase the total surface area in catalyst **Dan** leads to an increase in both $j_{o,1}$ and $j_{o,2}$. However, they increase by different amounts. Intriguingly, the approximate five-fold increase in $j_{o,1}$ is mirrored by a fivefold increase in mesopore area (Table 2),

Table 2. BET surface area, pore analysis and median pore width of studied carbon catalysts.

Property	Unit	Catalyst B	Dan	DanT
BET surface area	[m ² g ⁻¹]	789	478	1249
micropore area	[m ² g ⁻¹]	393	362	679
mesopore area	[m ² g ⁻¹]	398	53	285
micropore volume	[cm ³ g ⁻¹]	0.11	0.14	0.21
mesopore volume	[cm ³ g ⁻¹]	0.7	0.13	0.67
median pore width	[Å]	24.8	25	23.4

whereas for $j_{o,2}$, an approximate twofold increase is mirrored by a similar increase in micropore area (Table 2). Catalyst **B** has the largest mesopore area, but performs poorly in terms of oxygen reduction to water (i.e. low value of $j_{o,1}$), suggesting that it is not just the mesopore area, but also the density of active sites in the mesopores that is important. This may suggest that the sites for the reactions occur in different parts of the catalyst, and, at least in principle, might allow some selectivity over the density of each site in the catalyst.

The high value of α in Table 1 for the reaction does not necessarily imply a highly asymmetric barrier to the electrochemical reaction. This is because for multistep electron-transfer reactions, involving adsorbed intermediates, the observed value of α is influenced by the underlying mechanism in a complex way. For instance, one of us has recently shown how effective values for α_{eff} of β , $1 + \beta$, and 2 are possible for an electro-

chemical reaction with adsorbed intermediates (where β is the true molecular symmetry factor).^[42]

Describing the existence of two Tafel slopes/oxygen reduction mechanisms is of remarkable importance for fostering appropriate advances in this research field on developing renewable catalysts, once oxygen reduction kinetic overpotentials and mass transport overpotentials can be determined in electrochemical devices, for example, PEFCs. ORR kinetics and mass transport are the major sources of overpotential limiting the performance of oxygen reduction carbon catalysed PEFCs;^[24] therefore, quantifying these losses can assist in the development of appropriate carbon catalysts and guide the design of high-performance PEFCs (see next sections), as illustrated by the historical development of platinum-based cells in Figure 1.

2.2. Carbon Catalyst on PEFC Cathodes: Electrokinetic and Mass Transport Overpotential

The electrokinetic model developed in Section 2.1 [i.e. Eq. (6)] may now be used to determine the overpotential losses for oxygen reduction on carbon-based catalysts (i.e. oxygen reduction kinetics) and, from that, determine the remaining mass transport losses. This finding allows researchers to determine how different catalyst synthesis approaches are beneficial or detrimental to oxygen reduction kinetics and mass transport.

For instance, Figure 6b presents the expected area-specific oxygen reduction overpotential loss (calculated by using the parameters in Table 1), and mass transport loss (calculated by successive removal of the electrokinetic overpotential from the iR -free results for all three catalysts at a loading of 4 mg cm^{-2}) for data in Figure 6a.

For all three catalyst layers, which have the same loading and close to the same thickness and density (see S1 for further details), mass transport losses are similar and approach 100 mV at current densities of 1 A cm^{-2} . Of the catalyst layers, **DanT** has slightly higher losses, and this is correlated with the fact that it is the thickest of the catalyst layers. Furthermore, the mass transport overpotential difference between catalysts **Dan** and **DanT** is corroborated by comparing the start of a Warburg type feature seen on electrochemical impedance spectroscopy results in Figure S4. This result further supports the conclusion that the electrokinetic model proposed in Section 2.1 is suitable and can be used as a guide to correct quantifications of mass transport phenomena within the cathode catalyst layer with carbon-based catalysts.

It is clear that the majority of the losses experienced by the catalyst layer are predominantly electrokinetic in form, especially because the systems are operated under pure oxygen. Operating such systems under lower partial pressures of oxygen is expected to lead to significantly greater mass transport losses. An example of this is shown in Figure 7 where, at lower oxygen partial pressures (e.g. 100 kPa), mass transport losses are significantly increased. Figure 7 shows the performance of an electrode composed of catalyst **B** (2 mg cm^{-2}) under different partial pressures of oxygen. These data have been corrected for iR losses, and fitted to Equation (6) by using

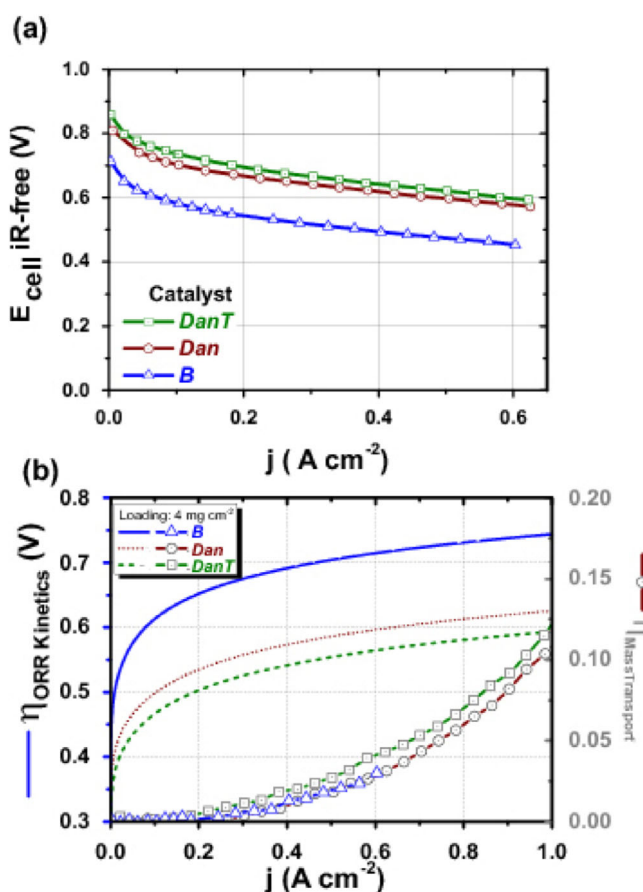


Figure 6. a) H_2/O_2 resistance corrected area-specific polarisation response of single PEFCs under galvanostatic mode employing various carbon catalysts as cathode at 4 mg cm^{-2} . The ionomer to carbon (I/C) ratio employed are, 1.0 for catalyst **B**, 1.5 for catalyst **Dan**, and 1.0 for catalyst **DanT**. b) Comparison of area-specific performance of catalysts **B**, **Dan** and **DanT** with the breakdown of cathodic overpotential and mass transport overpotentials at a loading of 4 mg cm^{-2} for all catalysts. Overpotential for ORR kinetics calculated from the fitting results to Equation (6) by using the parameters in Table 1. Experimental conditions as per Figure 2.

common values of $\alpha_{\text{eff},1}$ and $\alpha_{\text{eff},2}$, but independent values of $j_{\text{transition}}$ and $E_{\text{transition}}$. The α_{eff} values at 1.37 and 0.47 are close to those determined for the other catalysts (Table 1). Figure 7b illustrates the mass transport losses for the catalyst layer in Figure 7, determined by subtracting the experimental iR -free polarisation curve (symbols in Figure 7a) from the extrapolated electrokinetic curve (lines in Figure 7a). At low current densities, the voltage gain (21 mV) experienced upon varying the oxygen partial pressure from 244 to 100 kPa fits quite well the theoretical value (22 mV) for ORR to water. However the experimental value (ca. 36 mV) at high current densities is somewhat less than that expected for oxygen reduction to H_2O_2 (54 mV), suggesting that the reaction is operating in a rather complex kinetic regime, probably complicated by the autocatalytic decomposition of the hydrogen peroxide.

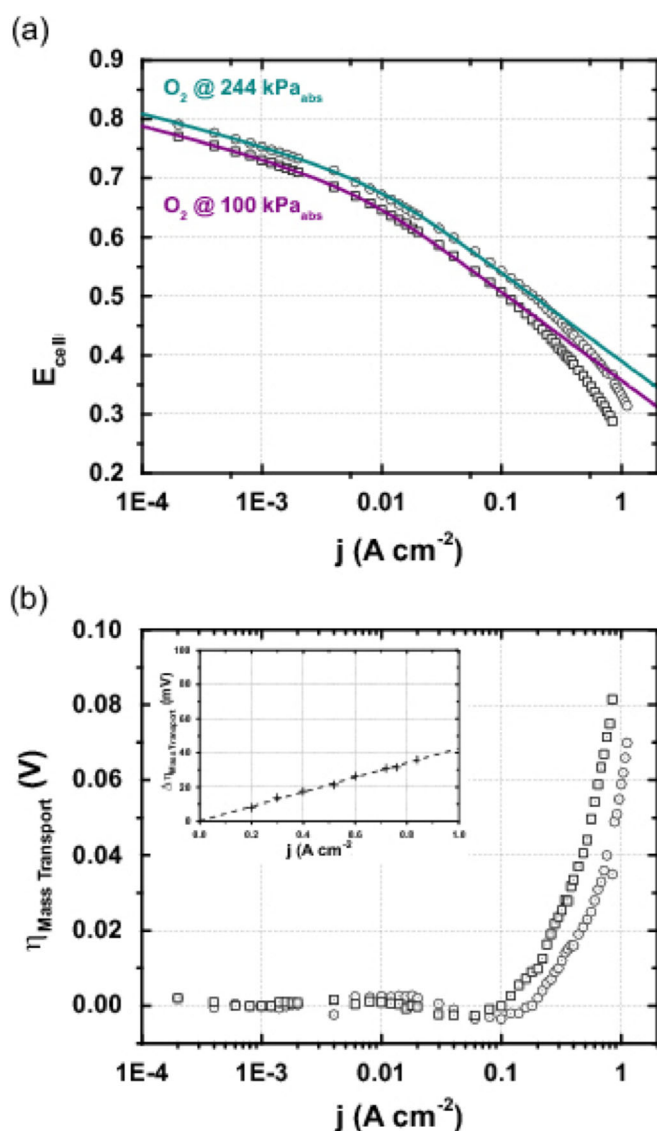


Figure 7. a) *iR*-free results for catalyst **B** (2 mg cm^{-2}) as a function of oxygen partial pressure (squares: $100 \text{ kPa}_{\text{O}_2}$, circles: $244 \text{ kPa}_{\text{O}_2}$). Lines on the points represent the best fit line to Equation (6) with $\alpha_{\text{eff},1} = 1.37$, $\alpha_{\text{eff},2} = 0.47$, $E_{\text{transition}} = 0.705$ (100 kPa), 0.718 (244 kPa), and $j_{\text{transition}} = 1.19 \text{ mA mg}^{-1}$ (100 kPa), 1.60 mA mg^{-1} (244 kPa). b) Plot of mass transport losses for the systems studied in (a), where the mass transport losses are calculated as the difference between the data and the fitted electrokinetic curve. Inset: mass transport difference between $100 \text{ kPa}_{\text{O}_2}$ and $244 \text{ kPa}_{\text{O}_2}$ calculated from main data. Other experimental conditions as per Figure 2.

2.3. An Idealised Performance of ORR Carbon-Based Catalyst Layers for PEFCs and Other Electrochemical Systems

From the above experimental results, it is clear that the performance of the M-C-N catalysts needs to be significantly improved to compete with platinum. The question following this would be “but by how much”? Hence, it is useful to set some benchmarks as to what is required. As has been shown in Figure 1, by moving to thinner catalyst layers with higher catalyst density, the performance of fuel cells can be improved considerably. It is fruitful to consider the number of active sites that exist within the catalyst layer of a fuel cell based on Pt/C, such as that described in Figure 1. At a loading of

$0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$, and assuming a specific surface area of the catalyst of $90 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$ (Johnson Matthey HiSPEC 9100) the number of surface platinum atoms that exist in the catalyst layer is $4.7 \times 10^{17} \text{ Pt}_{\text{surf}} \text{ cm}^{-2}$. If we reasonably assume that two platinum atoms are required for oxygen reduction, then this corresponds to $2.4 \times 10^{17} \text{ sites cm}^{-2}$ (or $2.4 \times 10^{20} \text{ sites cm}^{-3}$ of catalyst layer). If we look at the performance of the catalyst layer at 0.8 V from Figure 1, we see an extrapolated performance of about 1.69 A cm^{-2} . This corresponds to a turnover frequency of $11 \text{ electrons site}^{-1} \text{ s}^{-1}$. Recently, the turnover frequency of Metal-N-C catalysts have been measured, and at 0.8 V show values of around $1.5\text{--}1.6 \text{ electrons site}^{-1} \text{ s}^{-1}$, which is about an order of magnitude lower than that for platinum.^[5,43] However, the estimated site density is relatively low, at about $0.07 \pm 0.01 \text{ nm}^{-2}$ with respect to the mesopore surface area.^[5] Translating this to a volumetric site density using the typical values we have achieved with our catalyst layers provides a value of $3.1 \times 10^{18} \text{ sites cm}^{-3}$ of catalyst layer, which is about two orders of magnitude lower than that for the platinum catalyst layer. To match the site density of platinum in a fuel cell catalyst layer, we would need to simultaneously increase the site density to 1 active site per nm^2 and increase the mesoporous surface area to more than $500 \text{ m}^2 \text{ g}^{-1}$. Both of these aspects are feasible, although they might cause some problems because this number of sites would require about 4.5 wt% iron (or other transition metal), at which concentration there would surely be phase segregation. Furthermore, to match the performance of the catalyst layer, we would then need to increase the turnover frequency on the M-N-C catalyst by about an order of magnitude.

3. Conclusions

We have studied and analysed the performance of polymer electrolyte fuel cells utilising representative carbon-based catalysts and two distinct platinum catalysts under different conditions of oxygen partial pressure, catalyst loading and catalyst layer thickness.

Ohmic resistance corrected cell voltages versus mass-specific and geometric current densities show that oxygen reduction on carbon catalysts presents two distinct Tafel regions. A first Tafel region at low cell overpotentials presents a slope of approximately 48 mV dec^{-1} and a second Tafel region has a slope of 132 mV dec^{-1} . We believe that these two regions represent a changeover from predominantly oxygen reduction to water to that in which peroxide is the main product. It is shown that the fitted electrocatalytic curves can be used to extract the mass transport losses from the fuel cell data, and these vary as one would expect when changing the oxygen partial pressure and catalyst layer thickness.

To match the performance of platinum catalyst layers, we estimate that the intrinsic activity of the catalytic sites need to increase by about an order of magnitude, and the site density need to increase about 2–3 orders of magnitude. With these changes it would be possible to produce a catalyst layer with similar performance to those produced by using platinum today.

Experimental Section

Catalyst Synthesis

Catalyst **B** was synthesised by following a published method.^[4] In a typical route, carbon black (Ketjenblack® EC-600JD; 0.5 g) was heated to reflux in aq. HCl (1.0 mol dm⁻³, 200 mL) at 80 °C for 8 h to remove trace metals from the carbon black. Subsequently, the carbon was vacuum filtered and washed with deionised (DI) water (18.2 MΩ cm) and dried at 80 °C for 10 h. Pre-treated carbon black (200 mg) was weighted and dispersed in absolute ethanol (ca. 70 cm³) in an ultrasound bath. A separate beaker was utilised to dissolve FeCl₃ (Sigma-Aldrich; ca. 0.0583 g), Co(NO₃)₂ (Sigma-Aldrich; 0.0629 g) and *N*-ethylamine (Sigma Aldrich; 2 cm³) in absolute ethanol (30 cm³). This solution was added to the carbon black suspension and heated to reflux for 8 h at 80 °C. The resulting solids were filtered and washed with DI water and dried in an oven at 100 °C for 8 h. The dried powders were heat-treated in a tubular oven at 900 °C under a nitrogen atmosphere for 1 h using a heating ramp of 20 °C min⁻¹. Finally, the catalysts were heated to reflux in H₂SO₄ (0.5 mol dm⁻³, 100 mL) at 80 °C for 24 h to remove residual metal. This suspension was vacuum filtered, washed with excess of DI water and dried at 80 °C for 10 h.

Catalyst **Dan** was synthesised by following a published method.^[6] In a typical route, 1,5-diaminonaphthalene (97% from Alfa Aesar; 500 mg), (NH₄)₂S₂O₈ (98% from Sigma-Aldrich; 500 mg) and 1 wt% of Fe (as FeCl₂) was dissolved in absolute ethanol (VWR; 50 cm³). The dispersion was stirred for 24 h at RT, then the mixture was heated to 80 °C to evaporate the solvent. When dried, the resulting residue was transferred to an alumina boat and heat treated at 1000 °C for 2 h in a tube (quartz) furnace (from Carbolite) at a heating rate of 20 °C min⁻¹. This heat treatment was performed in an inert atmosphere, under a continuous flow of 50 ccm of nitrogen. After cooling under nitrogen atmosphere, the resulting material was removed from the alumina boat and heated to reflux in H₂SO₄ (0.5 mol dm⁻³, 100 cm³) at 80 °C for 8 h to remove residual metal. This suspension was vacuum filtered and washed with excess DI water and dried at 80 °C. The catalyst denoted **DanT** was prepared as described for **Dan**, with the addition of a 1:1 weight ratio of MgO nanopowder (Sigma-Aldrich; 5 nm) to 1,5-diaminonaphthalene in the precursor synthesis, to change the microstructure. The MgO support is removed during the acid leaching step.

RDE Analysis

Measurements were conducted with a rotating ring disc electrode (Pine Instruments, model AFE6R1AU, with a mirror polished glassy carbon disc and rotator model AFMSRCE). To prepare the electrode, catalyst (10 mg) was dispersed ultrasonically into ethanol (1 mL), H₂O (0.9 mL) and 5 wt% Nafion solution (Sigma-Aldrich; 0.1 mL). The respective amount of ink was drop coated onto the disc of the RRDE tip, which was mounted upside down onto the rotator. While drying, the rotator was set to 700 rpm thus obtaining a uniform catalyst distribution across the electrode surface. The disc electrode was scanned cathodically at a rate of 1 mVs⁻¹ and the ring potential was set constant at 1.5 V vs. RHE.

Membrane Electrode Assembly Preparation, PEFC Test Conditions and Data Fitting

Membrane electrode assemblies (MEA) were prepared by using a method developed by Paganin et al.^[31] Briefly, considering the desired ionomer to carbon ration (I/C, specified in the figure cap-

tions), the desired amount of catalyst was mixed with Nafion™ ionomer solution (Aldrich; 5 wt%, 1050EW) in isopropanol (IPA; 1.5 cm³). For Pt/C catalyst from E-Tek, the lot number was 0820623 with a platinum loading of 20.3 wt%. The solution of catalyst, Nafion™ ionomer and IPA was homogenised in an ultrasonic bath for 15 min, followed by complete evaporation of the solvents at RT. The dried solids were dissolved in isopropanol and quantitatively deposited on a gas transport medium (Toray paper TGP 60 with microporous layer, Alfa Aesar). As anode electrodes, commercial Johnson Matthey platinum electrodes were utilised (platinum loading of 0.4 mg_{Pt} cm⁻², from Alfa Aesar). The MEAs were obtained by hot-pressing anode and cathode electrodes on both sides of a pre-treated Nafion™ membrane (H⁺, DuPont) at 145 °C and 400 kg cm⁻², for 3 min. Nafion™ 115 was used in MEAs for carbon-catalyst containing cathodes and Nafion™ NR212 was used for Pt/C containing cathodes. A thicker Nafion™ 115 membrane was deliberately chosen rather than thinner Nafion™ membranes (211) to categorically avoid any Pt crossover from the anode. Single PEFC tests were performed by using 5 cm² electrode area and single serpentine flow fields (PEFC hardware from Fuel Cell Technologies, Inc.). During PEFCs tests, the cell hardware was maintained at 80 °C and humidification water bottles temperature were maintained at 80 °C (80 °C dew points) for MEAs with NR212 membranes and at 95 °C_{anode} and 85 °C_{cathode} for MEAs with N115 membranes. During PEFC tests, pure hydrogen (White Martins, 99.999) at a flow rate of 160 ccm and pure oxygen (White Martins, 99.999) at a flow rate of 550 ccm were utilised. Notably, 550 ccm O₂ was chosen because below 450 ccm the catalyst layer is not completely utilised due to an improper distribution of oxygen.^[44] Anode and cathode operated at a gauge backpressure of approximately 210/210 kPa (H₂ and O₂ partial pressure at ca. 217 and 244 kPa_{abs} taking into account water vapour) or 65/65 kPa (H₂ and O₂ partial pressure at ca. 100 kPa_{abs} taking into account water vapour), where the ambient pressure was approximately 91 kPa. PEFCs activation and polarisation curves were obtained under galvanostatic mode with a fuel cell test station from Fuel Cell Technologies, Inc. Polarisation curves were also recorded with a galvanostat, Autolab model 302N; the results were in agreement with experiments performed with the fuel cell test station. The dwell time at each current density prior to recording the cell voltage was either 60 s for current densities below 5 mA cm⁻² or 10 s for the remaining window based on a potential change of less than 1 mV after the respective waiting time, measured during preliminary chronoamperometry experiments.

Hydrogen crossover from the anode to the cathode occurs in a PEFC due to the low, albeit finite, solubility and diffusivity of H₂ in Nafion™. Upon crossing to the cathodic compartment, H₂ can be oxidised on an active electrode, for example, Pt. This process generates a parasitic current, which is generally referred to as hydrogen crossover current density. This was determined experimentally by purging the cathode compartment with argon and polarising the cathode at 0.4 V vs. the anode by using a potentiostat, while the anode was purged with hydrogen. At this potential, the resulting hydrogen oxidation current is purely limited by the H₂ permeation rate. Backpressures and gas flow rates were as in the experiments under fuel cell mode. For PEFC tests in which platinum catalyst was utilised as cathode, the effective current density (*j*_{eff}) reported refers to H₂-crossover corrected current densities (*j*_{eff} = *j* + *j*_{Hydrogen crossover}); where the latter was measured to be 0.8 mA cm⁻² for NR212 membranes. It is noteworthy that carbon catalysts are inactive towards the hydrogen oxidation reaction; therefore, PEFCs employing this catalyst as cathode did not have current densities corrected for hydrogen crossover.

Electrochemical impedance spectroscopy (EIS) experiments were carried out with the aforementioned potentiostat. These experiments were carried out under galvanostatic mode, with current densities selected that would produce cell potentials (without iR corrections) of 0.600, 0.470, 0.400 and 0.200 V for carbon catalyst based PEFCs and of 0.900, 0.850, 0.800, 0.750, 0.700, 0.650 and 0.600 V for platinum catalyst based PEFCs. An AC perturbation was superimposed on top of this DC current, as 5% of the DC current magnitude. Meticulous care was taken to reduce the effect of cable inductance.^[35] Cells were conditioned at the desired DC current for 60 s prior to EIS experiments. The linearity of the current/potential response was verified for every measurement. Towards ensuring proper signal to noise ratio, every data point was collected for five integration cycles with an integration time of 0.125 s per cycle. To further ensure validity of the collected data, collection was performed from high to low frequency, and from low to high frequency, for selected cells with several hours of operation between. No significant deviation was detected. Data were checked for Kramers–Kronig conformity according to an improved method developed by Schoenleber et al.^[45,46] No drift in the spectra was detected. EIS spectra were analysed and fitted with the use of the software ZView™ (Scribner Associates, Inc.). Fitting was carried out utilising an equivalent circuit composed of a resistor in series with a transmission line-open circuit terminus; the last component represents the catalyst layer and the former the high frequency resistance (the sum of the RH dependent membrane resistance and RH independent electronic and bulk resistances).

Multi-parameter fits of performance curves (iR -free) were performed in Microsoft Excel by utilising the GRG nonlinear solver module to simultaneously fit multiple datasets using Equation (6).

BET Measurements

BET analyses were carried out in a Micromeritics TriStar 3000 surface area and porosity analyser. The adsorbent was N_2 at a temperature 77.2 K. The Rouquerol method was used to determine the best region for the linear fit. The molecular cross-sectional area for nitrogen used was 0.1620 nm². The BJH method was used to determine the pore-size distribution from the desorption branch of the isotherm. BET measurements for the three catalysts studied are shown in Table 2.

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Keywords: carbon • fuel cells • oxygen reduction • platinum • thin films

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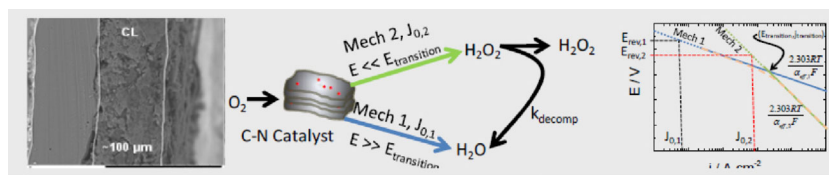
ARTICLES

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Mechanistic Insights into the Oxygen Reduction Reaction on Metal–N–C Electrocatalysts under Fuel Cell Conditions



Carbon vs. platinum in fuel cells:
Mechanistic insights into the oxygen reduction reaction points the way forward

to the improvements required to equal the performance of platinum-based catalyst layers in fuel cells.