



Performance measurements and modelling of the ORR on fuel cell electrocatalysts – the modified double trap model



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ABSTRACT

Experimental results for the ORR (oxygen reduction reaction) in perchloric acid for ultra low loading Pt/C electrodes have been fitted to a number of different ORR mechanisms. These were accomplished as a function of temperature (280–330 K), oxygen partial pressure ($0.01 < \frac{p_{O_2}}{p_{O_2}^0} < 1$) and potential (0.3–1.0 V vs. RHE).

A reaction exponent for oxygen of 1 ± 0.1 across the potential range 0.3–0.85 V vs. RHE is confirmed. From the experimental results it is clear that the surface becomes increasingly blocked towards the ORR as overpotential increases (i.e. as the potential decreases from 0.6 to 0.3 V vs. RHE). The double trap model [J.X. Wang, J. Zhang, R.R. Adzic, J. Phys. Chem. A, 111 (2007) 12,702] fails to account for this observation, although we have produced a modified version to include the formation of OOH_{ad} intermediates. These intermediates block the electrode at larger overpotentials and lead to a decrease in electrocatalyst performance compared to a Tafel type approximation. Furthermore these intermediates can lead to the formation of hydrogen peroxide at large overpotentials, an experimental observation which is currently poorly described by models.

The decreased activity at large overpotentials suggests that blocking of active catalyst sites may be as important to catalyst activity in an operating fuel cell as the absolute performance of the electrode in the low overpotential region as typically measured on an RDE. It may also offer an explanation to the increased losses seen in fuel cell electrodes at lower catalyst loadings – i.e. the losses, which are typically ascribed to increased mass transport losses, may instead result from decreased electrocatalytic performance at high overpotentials.

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1. Introduction

The electrochemical reduction of O_2 to H_2O is both a fundamentally and practically important reaction. In low temperature fuel cells, such as the proton exchange membrane fuel cell (PEMFC), it is the single largest source of efficiency loss while under load. The sluggishness of this reaction necessitates the use of Pt based electrocatalysts at significant monetary costs. In order for PEMFCs to achieve cost competitiveness with combustion engines, it is necessary to reduce the precious metal loading by an order of magnitude.

Although there has been much conjecture as to the mechanism of oxygen reduction in acid medium over the last fifty years, there still is not an overwhelming consensus due to the lack of suitable experimental validation techniques which can accurately identify composition and coverage of surface

intermediates formed during this reaction. In part this is because of the similarity between these intermediates and the surrounding condensed liquid phase (the product of the ORR). Although there are a large number of possible mechanisms, there are relatively few kinetic models which have been developed from those mechanisms, due to the complexity of the systems, and the large number of possible intermediates. In fact the dearth of alternative models for fitting the *orr* probably comes about because previous available electrokinetic data is confined to a limited potential range. Hence it is not possible to distinguish between different models and their predictions (or to put it another way, the results are overparameterised for the available data set). Most authors of papers involving extraction of parameters from *orr* data (e.g. rotating disk electrode results) use a Butler–Volmer type model to fit their data. Recently, some attempts have been made to develop kinetic models that explicitly account for the coverage of these intermediates. These approaches have been shown to accurately reproduce the ORR polarization curve on single crystal electrodes over the limited potential range accessible by RDE techniques [1,2].

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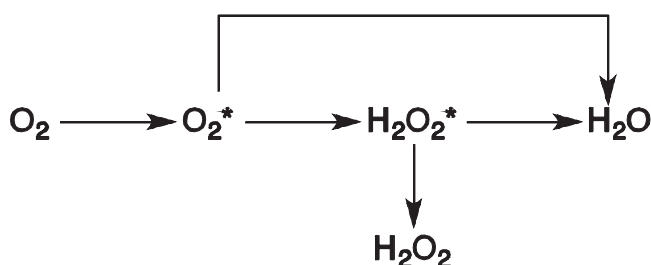


Fig. 1. Generalised oxygen reduction pathway after Wroblowa [3]. “*” denotes adsorbed intermediates.

The mechanism of the ORR is typically thought to occur by either a direct oxidation to water, or an indirect mechanism involving the formation of a peroxide intermediate (Fig. 1)[3–10].

Reduction of catalyst loading necessitates drawing higher specific current density in order to achieve the same geometric current density (assuming constant particle size and catalyst). Unfortunately, there exists a lack of kinetic studies that have accurately probed this high specific current density regime. The default technique used to characterize a catalyst's ORR performance is the rotating ring-disk electrode (RRDE). The low diffusivity and solubility of dissolved oxygen in aqueous electrolytes limits the potential range at which useful kinetic information can be determined, owing to the early onset of mass transport limitations. The result is that kinetic behaviour observed at low overpotentials is assumed to accurately describe higher overpotentials (i.e., high specific current densities). Such extrapolation can lead to inaccurate predictions. For example, Kucernak and Toyoda [11] have shown that platinum black is 10x more active than Pt/C at low overpotentials; however, this significant enhancement rapidly decreases at higher overpotentials.

Recently, Zalitis *et al* [12] have reported a new electrode for the characterization of catalysts involving gaseous reactants. In that set-up, reactants are transported to the electrocatalyst in the gas phase rather than in solution, resulting in significantly decreased transport resistances. This has allowed the kinetic current of both the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) to be measured over a wide range of overpotentials in the absence of mass transport effects. The method has achieved area specific current densities that are orders of magnitude higher than those observed in the RRDE, and has revealed fine structure in the HOR that has not been previously identified. Here, we utilize this technique to study the ORR in aqueous acid electrolyte over the potential-temperature domain relevant to PEMFCs. We then develop models to account for the variation of electrocatalytic performance with overpotential.

2. Experimental

2.1. General

Electrochemical experiments were performed in a standard jacketed 3-compartment cell that was first cleaned by soaking in acidified $KMnO_4$ overnight, rinsed with dilute acidified H_2O_2 , and then boiled in ultrapure water (Millipore Milli-Q, $18.2 M\Omega cm$). All gases used were $\geq 5.8N$ (Air Products), and electrolytes were prepared using “Suprapure” grade $HClO_4$ (VWR) and ultrapure water.

PCTE electrode working electrodes with a Pt loading of $2\text{--}4 \mu g cm^{-2}$ (HiSPEC 9100, 57 wt% Pt on Carbon, Alfa Aesar) were prepared as previously reported [12]. Before use, the electrodes were cleaned by continuously rinsing the electrode with hot ultrapure water in a soxhlet extractor for 8 hrs.

2.2. Electrochemical measurements

All electrochemical measurements were carried out using a Gamry Reference 600 potentiostat, and using 0.5 or $4 mol dm^{-3}$ $HClO_4$ electrolyte. Relatively high concentrations of acid were required to reduce the amount of iR drop correction required in the experiments (see below). The presence of small quantities of chloride is always of some concern when perchloric acid is used, as chloride is known to strongly poison the ORR. We performed RDE studies in which known amounts of chloride were added to our acid solution and we estimate that the background chloride concentration is less than $1 \mu mol dm^{-3}$. Compared to the RDE technique, the approach used in this study has the added advantage that convection of the solution is not required. This decreases the flux of contaminants to the electrode by about two orders of magnitude compared to the RDE technique, and further reduces the impact of solution phase poisons. The specific area of the catalyst deposit was calculated from the H(UPD) stripping charge assuming that one monolayer of hydrogen produces $210 \mu C cm_{Pt}^{-2}$, and all current densities are reported using the specific area of the catalyst.

Electrolytes were thoroughly purged with nitrogen before measurements, and then the cell's headspace was filled with pure oxygen to collect ORR polarization curves. The temperature of the electrochemical cell was controlled using a recirculating bath (Polyscience digital temperature controller, $\pm 0.1^\circ C$). All potentials were measured versus a purpose built reversible hydrogen electrode (RHE), and are reported versus this reference. Electrochemical impedance measurements were performed during the measurements, and the results were iR corrected post-measurement using the resistance determined from the high frequency intercept of the impedance response with the real axis of the Nyquist plot.

Results and discussion

A schematic representation of the electrochemical cell used in this work, is shown in Fig. 2. The inset illustrates the polycarbonate track etched (PCTE) working electrode. In this set-up, gaseous reactants are transported to the catalyst layer through the hydrophobic porous membrane at rates that far exceed those observed in solution [12]. Specific current densities as high as $0.6 A cm^{-2}$ have been observed for the HOR using this set-up, and appear to be purely kinetically controlled at potentials between $0\text{--}1.2 V$ vs. RHE. The high mass transport achieved using the PCTE

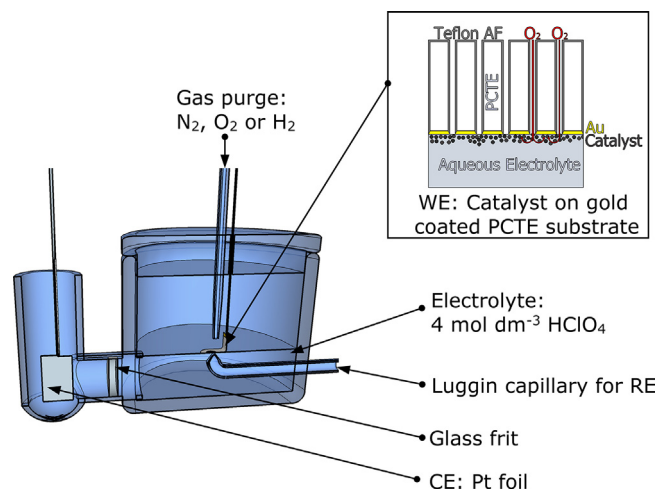


Fig. 2. Cross-section of the electrochemical cell detailing the floating electrode technique utilising ultra-low loading electrodes.

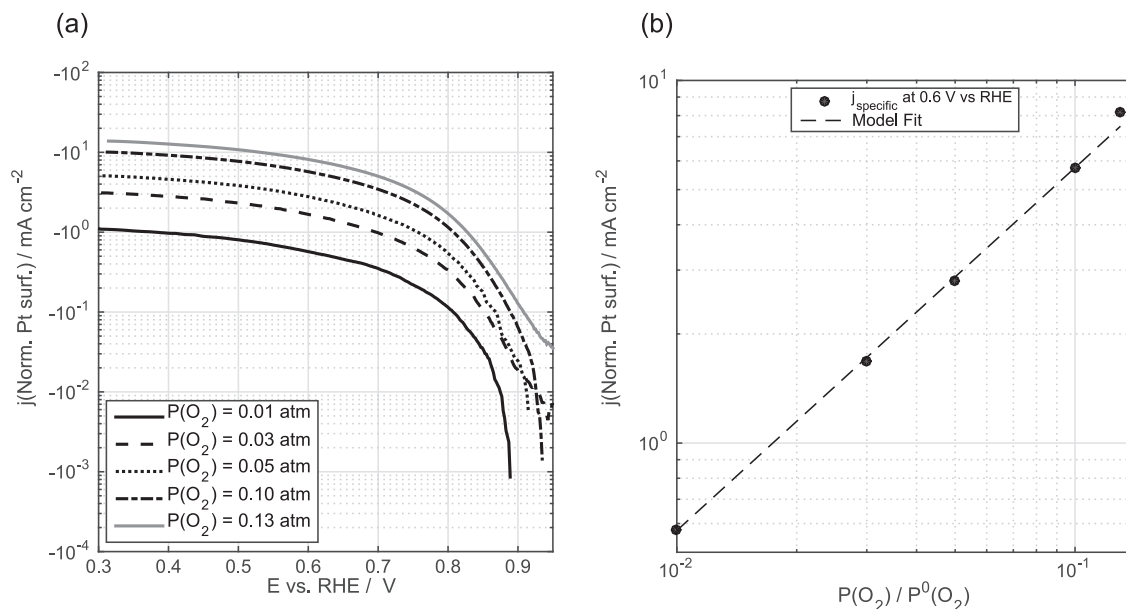


Fig. 3. (a) ORR polarization curves at room temperature obtained using the floating electrode configuration as a function of oxygen partial pressure (Nitrogen diluent), and (b) log-log plot of j_{specific} versus p_{O_2} . $3.5 \mu\text{gPt cm}^{-2}\text{Pt/C}$ (RF ≈ 3); $0.5 \text{ mol dm}^{-3} \text{HClO}_4$; $\nu = 10 \text{ mV s}^{-1}$. CE = Pt wire, RE = RHE; $T = 298\text{K}$.

electrode revealed fine structure within the HOR polarization curve that has not been previously reported, and provides a powerful data set to analyze mechanistic details of fuel cell reactions.

For the ORR, **specific** current densities as high as 185 mA cm^{-2} have been achieved using the PCTE electrode. This corresponds to a turnover frequency of 220 s^{-1} . Similar to the HOR, the polarization curves appear to be free of mass transport effects. Here, we focus on understanding the polarization curve of the ORR, with particular emphasis on modelling the transients observed at high mass-transport and overpotentials.

Partial pressure dependence

To determine the reaction order with respect to O_2 , we first assume that at large overpotentials the ORR follows the general Tafel type expression

$$j = j^0 \left(\frac{p_{\text{O}_2}}{p_{\text{O}_2}^0} \right)^\gamma e^{\alpha n F (E - E^0) / RT} \quad (1)$$

Where, j is the kinetic current density, j^0 is the exchange current density, p_{O_2} and $p_{\text{O}_2}^0$ are the partial pressures of oxygen at the operating condition and the standard state, γ is the reaction order of oxygen, α is the symmetry factor, F is Faradays constant, R is the ideal gas constant, E^0 is the equilibrium potential, E is the applied potential, and T is the temperature.

Taking the logarithm of Eq. (1) gives

$$\log(j) = \gamma \log\left(\frac{p_{\text{O}_2}}{p_{\text{O}_2}^0}\right) + C(E) \quad (2)$$

Where $C(E)$ describes the potential dependence of j ; the slope of $\log(j)$ vs. $\log(p_{\text{O}_2})$ can then be used to determine the reaction order at the operating potential. Fig. 3(a) plots the ORR polarisation curves with p_{O_2} ranging from 0.01–0.13 bar (nitrogen diluent), and Fig. 3(b) shows an example of the log-log relationship between j_{specific} and p_{O_2} at 0.6 V vs. RHE. Consistent with previous reports [13], a clear linear relationship with a slope of one is observed, indicating first order reaction kinetics with respect to O_2 .

Fig. 4 plots the reaction order of the polarisation curve as a function of potential, as well as the 95% confidence interval from the regression. We find that the reaction order remains invariant between 0.85–0.3 V vs. RHE, suggesting that no change in mechanism occurs. At potentials near the onset of the ORR, the fitted reaction order exceeds one. However, this increase is also accompanied by an expanding confidence interval with unity typically bounded within it. We thus associate this increase with experimental error at low overpotentials, rather than a change in the ORR mechanism.

3.1. Double Trap kinetic model

As a first attempt to model the kinetic current of the ORR at high mass transport, we employ the double trap kinetic model published by Wang *et al* [1]. In this model, the ORR mechanism

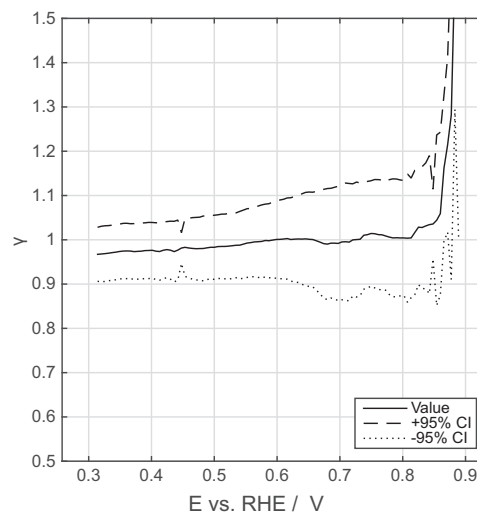
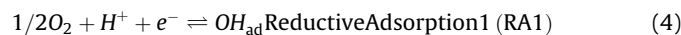
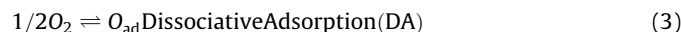


Fig. 4. Reaction order of O_2 as a function of potential, obtained by analysis of data in Fig. 3. Also plotted are the 95% confidence interval obtained from the regression of the $\log(p_{\text{O}_2})$ vs. $\log(j_{\text{specific}})$ at each measured potential. $3.5 \mu\text{gPt cm}^{-2} \text{Pt/C}$ (RF ≈ 3); $0.5 \text{ mol dm}^{-3} \text{HClO}_4$; $\nu = 10 \text{ mV s}^{-1}$. CE = Pt wire, RE = RHE; $T = 298\text{K}$.

is assumed to follow four elementary steps:



Using these expressions, the steady state coverage of O_{ad} and OH_{ad} are derived and the kinetic current is taken as calculated from the sum of the electron transfer rates. The details of this model have been thoroughly discussed previously [1], and the interested reader is referred to the original source.

Fig. 5 plots the kinetic current for the ORR using the PCTE electrode at 298 K. The figure also plots the predictions of the double trap kinetic model using the constants reported by Wang *et al* [1]. In the low overpotential region, we find that the double trap model predicts higher currents than those observed experimentally. Similar observations have been reported using Pt/C catalyst [1], and is likely associated with activity differences between single crystal Pt(111) and Pt/C.

Consistent with previous reports [1], the kinetic double trap model can be made to describe the kinetic current at low overpotentials upon invoking a scaling factor. Here, a factor of ca. 6.7 is required compared with the factor of 3 used by Wang *et al* [1], suggesting that the catalyst characterized here is less active in the low overpotential region. This may be due to differences in the catalyst itself (E-TEK vs. HiSPEC), differences in operational conditions (i.e., supporting electrolyte or O_2 concentrations), or possibly due to trace contaminants.

The double trap kinetic model diverges from the experimental data at potentials below 0.8 V vs. RHE. Specifically, the model produces a linear relationship between $\log(j)$ and potential, while clear curvature is observed using the PCTE electrode. It should be noted that the source data used to validate the data in the paper of Wang *et al*. achieves mass transport limitation at 0.7 V vs. RHE, so

observation of mechanistic effects at potentials lower than 0.8 V becomes very difficult.¹ For comparison we also plot in Fig. 5 the diffusion limited current for an RDE in 0.1 mol dm⁻³ HClO_4 at 298 K. It is clear that the experimental results significantly exceed what is possible using the RDE. In contrast, the polarization curves collected using the PCTE electrode is believed to be free of mass transport effects, and illustrate mechanistic details of the ORR that have previously not been accounted for [14].

The divergence of the double trap kinetic model result in predictions that are up to ca. three orders of magnitude greater than the experimentally measured kinetic currents reported here. This discrepancy convincingly suggests that additional and significant mechanistic details are not accounted for by the kinetic double trap model when operating at potentials below ca. 0.8 V vs. RHE.

3.2. Adsorbate blocking correction and temperature dependence

In addition to modelling the potential dependence of the polarization curve, one can also include the temperature dependence of the ORR. Here, we derive kinetic expressions for a potential-temperature-current surface rather than a polarization curve at constant temperature. The advantage to this sort of derivation lie in the concurrent fitting of both the potential dependent and temperature dependent parameters, which must then be self-consistent throughout the modelled domain.

In an attempt to account for the over-predictions of the kinetic double trap model, we first considered the blockage of the surface by adsorbed species. At potentials below 0.6 V vs. RHE, the double trap kinetic model predicts a constant coverage of OH_{ad} , (~ 0.5) and an exponential j -E relationship results. This behaviour is characteristically similar to the Butler-Volmer formulation at high overpotentials when only the cathodic branch needs to be considered. We thus attempt to model the polarization curve at high overpotentials using

$$j(E) = j^0 \left(\frac{c}{c^0} \right) (1 - \theta) e^{(E - E^0)/2RT} \quad (7)$$

Where c and c^0 are the molar concentrations of O_2 at the operating condition and standard state condition, respectively. The above expression is identical to that commonly used to model the ORR at potentials where Pt oxides are reduced and become electro-catalytically active. Here, we apply Eq. (7) to a potential region where Pt is predominantly in its reduced state, and the source of the θ term is an unidentified adsorbate. j^0 is thus the net exchange current for the complete ORR mechanism.

Due to the close proximity of the liquid electrolyte, we assume that the gaseous phase near the electrode-electrolyte interphase is saturated in water vapour. The vapour pressure of water is fitted using tabulated data [15] and assuming the Clausius-Clapeyron relationship. The partial pressure of oxygen is then calculated from

$$p_{\text{O}_2}(T) = p^* (1 - e^{-\Delta H_{\text{vap}}/R(1/T - 1/T^*)}) \quad (8)$$

Where p_{O_2} is the partial pressure of O_2 at T , and p^* is the partial pressure of O_2 in the dry gas, T^* is the boiling point of water. The partial pressure of O_2 in the gas phase is then related to the concentration of oxygen dissolved in either the Nafion film or aqueous electrolyte using Henry' law.

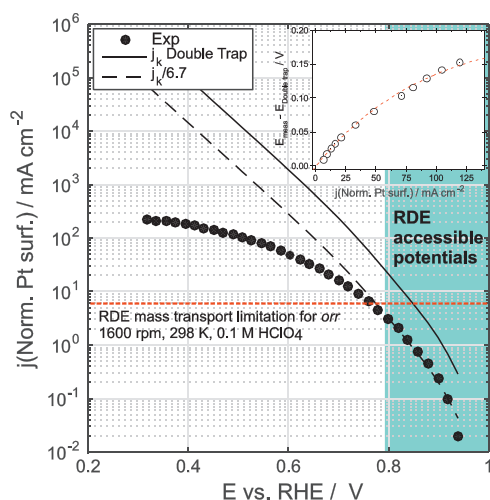


Fig. 5. Kinetic current polarization curve obtained using the PCTE electrode, and the predictions of the double trap kinetic model using the constants reported by Wang [1]. A scaled version of the model, similar to that reported by Wang [26], is also supplied. Inset is a plot of the difference in potential between the experimental data and the scaled results of Wang *et al*. as a function of specific current density. For comparison the mass transport limited current for ORR on an RDE is displayed. Experimental data: 2.2 $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ Pt/C catalyst ($\text{RF} \approx 2.8$); 4 mol dm⁻³ HClO_4 ; $\nu = 10 \text{ m V s}^{-1}$. CE = Pt wire, RE = RHE; $T = 298 \text{ K}$.

¹ Trivial back calculation of an ideal RDE curve shows that a 5% error in determining the limiting current translates into a 30% error in the extrapolated kinetic current when the measured current is 80% of the mass transport limiting value. For measured currents closed to the limiting current, the error associated with calculating the kinetic current grows very much larger than this value.

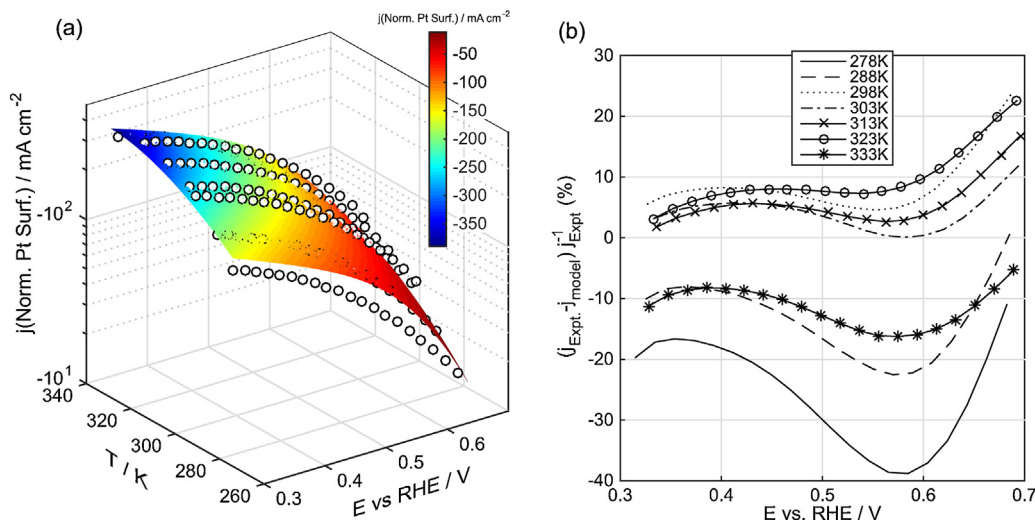


Fig. 6. (a) Modelled ORR potential-temperature-current surface assuming a simple active site blockage mechanism, and (b) percent error of the fitted surface. Experimental data: $2.2 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ Pt/C catalyst ($\text{RF} \approx 2.8$); $4 \text{ mol dm}^{-3} \text{ HClO}_4$; $\nu = 10 \text{ mV s}^{-1}$. CE = Pt wire, RE = RHE.

$$c_{\text{aq}} = k_{\text{H,cp}} p_{\text{O}_2} \quad (9)$$

We then reference the concentrations to standard temperature and pressures and with dry oxygen in the gas phase, such that

$$\frac{c_{\text{aq}}}{c_{\text{aq}}^0} = \frac{k_{\text{H,cp}} p_{\text{O}_2}}{k_{\text{H,cp}}^0 p_{\text{O}_2}^0} \quad (10)$$

The temperature dependence of the Henry's law constant is assumed to follow the van't Hoff equation, such that

$$k_{\text{H,cp}} = k_{\text{H,cp}}^0 e^{-\Delta H_{\text{solv}}^0 / R(1/T - 1/298.15)} \quad (11)$$

Combining Eq (10) and (11) then gives the temperature dependant concentration of dissolved oxygen.

$$\frac{c_{\text{aq}}}{c_{\text{aq}}^0} = p^* \left(e^{-\Delta H_{\text{solv}}^0 / R(1/T - 1/298.15)} \right) \left(1 - e^{-\Delta H_{\text{vap}} / R(1/T - 1/T^*)} \right) \quad (12)$$

It should be noted that the solvation enthalpy (ΔH_{solv}^0) is temperature dependant [16]. However, for simplicity, this dependence is neglected.

We assume that the temperature dependence of the exchange current follows the Arrhenius equation,

$$j^0(T) = j_{\text{STP}}^0 e^{-E_a / R(1/T - 1/298.15)} \quad (13)$$

Where j_{STP}^0 is the exchange current at the standard state, and E_a is the apparent activation energy.

The equilibrium coverage of the unidentified blocking adsorbate is assumed to be described by the Langmuir adsorption isotherm [17] in which the adsorbate undergoes a reductive step (i.e. coverage increases with decreasing potential). The temperature dependence of this isotherm is accounted for by fitting both the entropy (ΔS_{ad}^0) and enthalpy (ΔH_{ad}^0) of adsorption, which are assumed to be invariant over the temperature range studied here, $\frac{dE_{\text{ad}}^0}{dT} = -\frac{\Delta S_{\text{ad}}^0}{zF}$. The temperature and potential dependent surface coverage is then obtained from

$$\frac{\theta}{(1 - \theta)} = e^{\Delta S_{\text{ad}}^0 / R_e - \Delta H_{\text{ad}}^0 / RT_e - zFE / RT} \quad (14)$$

$$(1 - \theta) = \frac{1}{1 + e^{\Delta S_{\text{ad}}^0 / R_e - \Delta H_{\text{ad}}^0 / RT_e - zFE / RT}} \quad (15)$$

Where θ is the coverage of the surface by the adsorbate, and z is the charge of the adsorbing species.

Combining Eqs. (7), (12), (13), and (15) gives the final expression for the potential-temperature-current surface.

$$j(E, T) = j_{\text{STP}}^0 e^{-E_a / R(1/T - 1/298.15)} \left[p^* \left(e^{-\Delta H_{\text{solv}}^0 / R(1/T - 1/298.15)} \right) \times \left(1 - e^{-5151J / R(1/T - 1/373.15)} \right) \right] \left[\frac{1}{1 + e^{\Delta S_{\text{ad}}^0 / R_e - \Delta H_{\text{ad}}^0 / RT_e - zFE / RT}} \right] e^{(E - E^0) / 2RT} \quad (16)$$

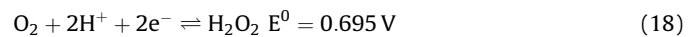
Fig. 6(a) displays the fit of Eq (14) to the experimental data set. Fig. 6(b) plots the percent error between the experimental and modelled surface. The coefficients of the modelled surface are summarized in Table 1.

Despite the simplicity of the model derived here, an absolute error of 10% is achieved over most of the potential range. Larger discrepancies between the model and data are observed at low overpotentials, but are still typically less than 20%. The larger than average percent error at high potentials may be due to neglecting other adsorbed species in the model. Indeed the kinetic double trap model shows slight potential dependence of θ_{OH} at potentials between 0.6–0.7 V vs. RHE. At potentials below 0.6 V, however, good agreement is obtained throughout the potential and temperature range studied here.

The equilibrium potential for the unidentified adsorbate is easily calculated from the ΔH_{ad}^0 , ΔS_{ad}^0 , and z using

$$E^0 = \frac{-(\Delta H_{\text{ad}}^0 - T \Delta S_{\text{ad}}^0)}{zF} \quad (17)$$

The model fits an E^0 of 0.637 V vs. RHE, with a 95% confidence interval of 0.789–0.485 V vs. RHE. It is interesting to note that the equilibrium potential for the adsorbate agrees well with the $2e^-$ -reduction of O_2 to H_2O_2 .



DFT calculations by Norskov et al [18] suggest that the ORR changes from a dissociative mechanism (O_{ad} and OH_{ad} intermediates) at

Table 1

Fitted parameters obtained for Eq. (16) based on a least-squares fit of experimental data, results shown in Fig. 6(a).

	j_{STP}^0 / $\mu\text{A cm}^{-2}$	E_a / kJ mol^{-1}	ΔH_{ad}^0 / kJ mol^{-1}	ΔS_{ad}^0 / $\text{J K}^{-1} \text{mol}^{-1}$	z
Value	2.8	40	−24	6	0.42
Std. Error	0.2	2	2	8	0.003

potentials above 0.8 V vs. RHE to one involving the formation of intermediate OOH (i.e. an associative mechanism). It seems plausible that the blocking species fitted by Eq (16) may be an intermediate in this associative mechanism, if indeed not from the formation of adsorbed OOH, as this uncharged species is known to be very unstable in the solution phase [19]. The production of H_2O_2 via the indirect mechanism is of practical importance due to its known participation in the degradation of the perfluorosulfonic acid membrane commonly used in PEMFCs [20]. The quantification of this process is most commonly achieved by detecting solution phase H_2O_2 at the ring electrode in the RRDE, and has resulted in a pervasive opinion that the indirect mechanism is a minor contributor to the ORR until potentials are in the H(UPD) region or in the absence of strong adsorbates. However, previous work in our group challenged this perception - utilizing single platinum particles, it was found that the effective number of electrons involved in the ORR is less than 4 under conditions of high mass transport [21], suggesting that the peroxide route was a significant one, but that detected peroxide concentration away from the electrode was low due to its relatively strong binding strength. Such a view has also been championed by Ke et al [22], who have demonstrated that the amount of H_2O_2 produced at moderate overpotentials and subsequently collected at the ring electrode is a function of catalyst loading. This relationship is argued to be a result of the re-adsorption of solution phase H_2O_2 onto the disk electrode, where it is further reduced to water.

The fitted value of $z = 0.5$ is intriguing; at first glance it appears to be inconsistent with the formation of $OOH_{(ad)}$. However, this is not necessarily the case. Specifically, combining Eq. (15) and (17), substituting in z and multiplying by a hypothetical rate constant (v') gives

$$0 = v'(1 - \theta)e^{0.5(E_{ad}^0)/RT} - v'\theta \quad (19)$$

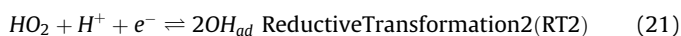
The first product of Eq. (19) is equivalent to an electrochemical adsorption following a Tafel type potential dependence ($\alpha = 0.5$), while the latter is equivalent to a non-electrochemical transformation/elimination; the full form resembles a steady state approximation for an intermediate that only has these two pathways accessible. However, it would be necessary that the fundamental rate constants describing the rate of formation and transformation/elimination be nearly identical. To investigate the possibility that the blocking adsorbate is a result of the associative pathway, we next modify the double trap kinetic model to explicitly include it.

3.3. Modified Double Trap

To account for intermediates that are likely formed during the associative ORR mechanism, we modify the double trap kinetic model to include two additional fundamental steps. The first step involves the reductive addition of a proton to an oxygen molecule as suggested by Sepa et al. as being the rds for oxygen reduction on platinum in acid [23], and also by Norskov et al [18], and used in the model by Jinnouchi et al [18]. Formally this step produces an adsorbed protonated superoxide intermediate:



The second step involves the reductive addition of a second proton, followed by dissociation into $OH_{(ad)}$ [24]



Whilst this step is written as an elementary step, it may involve intermediate steps, such as the formation of an intermediate peroxide species [24], or the intermediate formation of $O_{(ad)}$ [2].

Addition of these steps is important, as it allows the formation of solution phase hydrogen peroxide, especially at lower potentials, an aspect currently not included within the double trap model. Production of solution phase peroxide may occur through reaction with adsorbed hydrogen, $H_{(ad)}$



Or via disproportionation through a route equivalent to the solution phase reaction



The kinetics of the solution phase reaction are exceedingly fast, with the second order rate constant, $k_{obs} = 8.3 \pm 0.7 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [19]. For simplicities sake we have not included Eq (22) & (23) in the model presented in this paper. It might not be expected that a large coverage of $HO_{2(ad)}$ occurs on the surface. However, OH is also unstable in solution, but perfectly stable (and considered part of the oxide growth mechanism) on platinum. Clearly, solution phase stability may not be a good predictor of surface stability (or more precisely, the form of the surface adsorbed species may be different to that of the solution species due to electron transfer between the adsorbed species and the surface). In the model below we use the term $HO_{2(ad)}$ to represent a blocking species formed along the RA2 pathway,

With the addition of these steps, the steady state approximations becomes

$$\frac{d\theta_O}{dt} = v_{DA} - v_{RT1} = 0 \quad (24)$$

$$\frac{d\theta_{OH}}{dt} = v_{RA1} + v_{RT1} + 2v_{RT2} - v_{RD} = 0 \quad (25)$$

$$\frac{d\theta_{HO_2}}{dt} = v_{RA2} - v_{RT2} = 0 \quad (26)$$

where v_i is the rate of the i^{th} step. The rates of these additional reactions at E^0 for the ORR are defined as

$$v_{RA2} = k_{RA2}a_{O_2}a_{H^+}(1 - \theta_O - \theta_{OH} - \theta_{HO_2})e^{(E^0 - E)/2kT} - k_{-RA2}\theta_{HO_2}e^{-(E^0 - E)/2kT} \quad (27)$$

$$v_{RT2} = k_{RT2}\theta_{HO_2}a_{H^+}(1 - \theta_O - \theta_{OH} - \theta_{HO_2})e^{(E^0 - E)/2kT} - k_{-RT2}\theta_{OH}^2e^{-(E^0 - E)/2kT} \quad (28)$$

where k_i and k_{-i} are the forward and reverse rate constant of the i^{th} step at E^0 for the ORR. At the equilibrium potential, we can then define the exchange rates as

$$v_{RA2}^0 = k_{RA2}a_{O_2}^0a_{H^+}^0(1 - \theta_O^0 - \theta_{OH}^0 - \theta_{HO_2}^0) = k_{-RA2}\theta_{HO_2}^0 \quad (29)$$

$$v_{RT2}^0 = k_{RT2}\theta_{HO_2}^0a_{H^+}^0(1 - \theta_O^0 - \theta_{OH}^0 - \theta_{HO_2}^0) = k_{-RT2}(\theta_{OH}^0)^2 \quad (30)$$

Then, dividing Eqs (27) and (28) by Eqs (29) and (30) gives expressions for the kinetic rate relative to the exchange rate.

$$v_{RA2} = \frac{v_{RA2}^0}{(1 - \theta_O^0 - \theta_{OH}^0 - \theta_{HO_2}^0)} \left[\left(\frac{a_{O_2}}{a_{O_2}^0} \right) \left(\frac{a_{H^+}}{a_{H^+}^0} \right) \times (1 - \theta_O - \theta_{OH} - \theta_{HO_2})e^{(E^0 - E)/2kT} - \theta_{HO_2} \left(\frac{(1 - \theta_O^0 - \theta_{OH}^0 - \theta_{HO_2}^0)}{\theta_{HO_2}^0} \right) e^{-(E^0 - E)/2kT} \right] \quad (31)$$

$$v_{RT2} = \frac{v_{RT2}^0}{\theta_{HO_2}^0(1 - \theta_O^0 - \theta_{OH}^0 - \theta_{HO_2}^0)} \left[\left(\frac{a_{H^+}}{a_{H^+}^0} \right) \theta_{HO_2} \times (1 - \theta_O - \theta_{OH} - \theta_{HO_2}) e^{(E^0 - E)/2kT} - \theta_{OH}^2 \left(\frac{\theta_{HO_2}^0(1 - \theta_O^0 - \theta_{OH}^0 - \theta_{HO_2}^0)}{(\theta_{HO_2}^0)^2} \right) e^{-(E^0 - E)/2kT} \right] \quad (32)$$

Assuming that the Langmuir adsorption isotherm applies, the Gibb's energy of adsorption (ΔG_i^0) is related to the equilibrium coverage by

$$e^{-\Delta G_{HO_2}^0} = \frac{\theta_{HO_2}^0}{1 - \theta_O^0 - \theta_{OH}^0 - \theta_{HO_2}^0} \quad (33)$$

$$e^{-\Delta G_{OH}^0} = \frac{\theta_{OH}^0}{1 - \theta_O^0 - \theta_{OH}^0 - \theta_{HO_2}^0} \quad (34)$$

Combining Eqs (29)–(34) then gives rate expressions related to the forward rate constant and the Gibb's energy of adsorption of the intermediates at E^0

$$v_{RA2} = k_{RA2} a_{O_2}^0 a_{H^+}^0 \left[\left(\frac{a_{O_2}}{a_{O_2}^0} \right) \left(\frac{a_{H^+}}{a_{H^+}^0} \right) \times (1 - \theta_O - \theta_{OH} - \theta_{HO_2}) e^{(E^0 - E)/2kT} - \theta_{HO_2} e^{\Delta G_{HO_2}^0/kT} e^{-(E^0 - E)/2kT} \right] \quad \text{Eq. 35}$$

$$v_{RT2} = k_{RT2} a_{H^+}^0 \left[\left(\frac{a_{H^+}}{a_{H^+}^0} \right) \theta_{HO_2} (1 - \theta_O - \theta_{OH} - \theta_{HO_2}) e^{(E^0 - E)/2kT} - \theta_{OH}^2 e^{-(\Delta G_{HO_2}^0 - 2\Delta G_{OH}^0)/kT} e^{-(E^0 - E)/2kT} \right] \quad \text{Eq. 36}$$

Assuming that concentration polarization is negligible (i.e., $a_i = a_i^0$), and defining $j = Fv$, the intrinsic exchange currents for the forward and reverse processes at E^0 can then be defined as

$$j_{RA2}^0 = Fk_{RA2} a_{O_2}^0 a_{H^+}^0 \quad (37)$$

$$j_{-RA2}^0 = j_{RA2}^0 e^{\Delta G_{HO_2}^0/kT} \quad (38)$$

$$j_{RT2}^0 = Fk_{RT2} a_{H^+}^0 \quad (39)$$

$$j_{-RT2}^0 = j_{RT2}^0 e^{-(\Delta G_{HO_2}^0 - 2\Delta G_{OH}^0)/kT} \quad (40)$$

Combining Eqs 35–40 then gives the final potential dependent expression for the two additional fundamental steps.

$$j_{RA2} = j_{RA2}^0 (1 - \theta_O - \theta_{OH} - \theta_{HO_2}) e^{(E^0 - E)/2kT} - j_{-RA2}^0 \theta_{HO_2} e^{-(E^0 - E)/2kT} \quad (41)$$

$$j_{RT2} = j_{RT2}^0 \theta_{HO_2} (1 - \theta_O - \theta_{OH} - \theta_{HO_2}) e^{(E^0 - E)/2kT} - j_{-RT2}^0 \theta_{OH}^2 e^{-(E^0 - E)/2kT} \quad (42)$$

We derive expressions for the original mechanism Eqs. (3)–(6) in the same manner as outlined above. They are identical to those originally published by Wang et al., but additionally include HO_2 coverage.

$$j_{DA} = j_{DA}^0 (1 - \theta_O - \theta_{OH} - \theta_{HO_2}) - j_{-DA}^0 \theta_O \quad (43)$$

$$j_{RA1} = j_{RA1}^0 (1 - \theta_O - \theta_{OH} - \theta_{HO_2}) e^{(E^0 - E)/2kT} - j_{-RA1}^0 \theta_{OH} e^{-(E^0 - E)/2kT} \quad (44)$$

$$j_{RT1} = j_{RT1}^0 \theta_O e^{(E^0 - E)/2kT} - j_{-RT1}^0 \theta_{OH} e^{-(E^0 - E)/2kT} \quad (45)$$

$$j_{RD} = j_{RD}^0 \theta_{OH} e^{(E^0 - E)/2kT} - j_{-RD}^0 (1 - \theta_O - \theta_{OH} - \theta_{HO_2}) e^{-(E^0 - E)/2kT} \quad (46)$$

Where the exchange currents are defined as

$$j_{DA}^0 = Fk_{DA} (a_{O_2}^0)^{1/2} \quad (47)$$

$$j_{RA1}^0 = Fk_{RA1} a_{H^+}^0 (a_{O_2}^0)^{1/2} \quad (48)$$

$$j_{RT1}^0 = Fk_{RT1} a_{H^+}^0 \quad (49)$$

$$j_{RD1}^0 = Fk_{RD1} a_{H^+}^0 \quad (50)$$

$$j_{-DA}^0 = j_{DA}^0 e^{\Delta G_O^0/kT} \quad (51)$$

$$j_{-RA1}^0 = j_{RA1}^0 e^{\Delta G_{OH}^0/kT} \quad (52)$$

$$j_{-RT1}^0 = j_{RT1}^0 e^{(\Delta G_{OH}^0 - \Delta G_O^0)/kT} \quad (53)$$

$$j_{-RD}^0 = j_{RD}^0 e^{-\Delta G_{OH}^0/kT} \quad (54)$$

The potential dependence coverage of all species was solved symbolically in MATLAB from the steady state approximation Eqs (24)–(26) using Eqs. (41)–(46) and $j_i = Fv_i$. Although the steady state approximation can be solved, the solution to this problem is too complex to reproduce here owing to the second order dependence of Eq. (42) on θ_{OH} . However, the derived MATLAB function is supplied in the supplemental information for reference.

Fig. 7 plots the ORR polarization curve at 298K, and the model fit using the parameters supplied in Table 2. Excellent agreement between the experimental data and the model is achieved over the full potential range, with a percent error of only ca. 4% across the entire range of potentials studied -0.9 to 0.3 V. Although one cannot definitively identify the adsorbed blocking species through the mechanistic modelling presented here, it is impressive that modifying the double trap kinetic model to include an additional intermediate at high overpotentials enables it to replicate the polarization behaviour over a range of 0.6 V (i.e., ca. 11 orders of magnitude change in rate constants).

The model converges on adsorption energies for O_{ad} and OH_{ad} that agree reasonably well with those reported by Wang et al. However, we find that the rate of DA and RT1 are significantly higher. It has been previously reported that step edges are more active towards the cleavage of the O—O bond than terrace sites [25]. Given that nanoparticles have a significantly higher density of

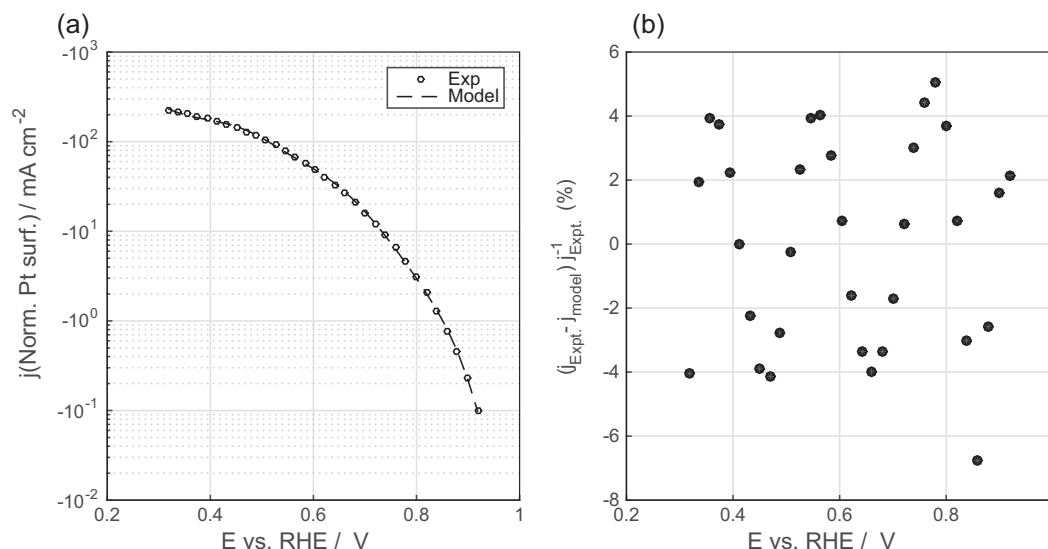


Fig. 7. (a) Polarization curve for the ORR at 298K and the modelled curve using the modified double trap kinetic model, and (b) percent error between the model and experimental data. Experimental data: $2.2 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ Pt/C catalyst ($\text{RF} \approx 2.8$); $4 \text{ mol dm}^{-3} \text{ HClO}_4$; $\nu = 10 \text{ mV s}^{-1}$. CE = Pt wire, RE = RHE; $T = 298 \text{ K}$.

edge sites than well prepared Pt(111), we suspect that the large difference between these two values may be associated with the edge site density. These differences may be the source of the scaling factor needed in Fig. 5, as presented originally by Wang *et al* [26].

Unsurprisingly, there is a high degree of coupling between the rates of RT2, and RA2 that allows the fitted values to vary significantly without changing the accuracy of the resulting fit. The rate constants for RT2 and RA2 are identical within their fitted errors, which is consistent with the steady state approximation derived from the simple adsorbate blocking mechanism Eq. (19). Clearly, the two models have converged on qualitatively identical solutions for the adsorbate isotherm. Similar to the adsorbate blockage model discussed previously, any value for j_{RA2} and j_{RT2} (i.e., any ν') will sufficiently describe the kinetic behaviour at high overpotentials as long as their ratio is near unity, as illustrated by the wide range of values in Table 2 for these fitted values.

The current generation is well described by the sum of j_{RA1} , j_{RT1} , and j_{RD} (Fig. 8). This behaviour suggest that the ORR over Pt/C predominantly occurs via rapid dissociative adsorption to form $\text{O}_{(\text{ad})}$, followed by stepwise reduction of $\text{O}_{(\text{ad})}$ to water. At higher over-potentials, site blocking by an intermediate that is formed via an electron transfer reaction then hinders the overall rate of the ORR. Hence the surface becomes poisoned at high overpotentials

by an alternate pathway which opens up at lower potentials and which ultimately can lead to formation of soluble peroxide, Fig. 9.

Despite the coupling of the rates involving the adsorbed blocking species, it is still possible to determine the equilibrium potentials for the fundamental steps by equating the forward and reverse reactions and solving for the potential. These potentials are tabulated in Table 3. We find that the equilibrium potentials for RA2 and RT1 agree reasonable well with *ab initio* calculations reported in the literature; however, somewhat greater variation in the fitted potentials of RA1, RT2, and RD is observed. It appears that the model adequately captures the passivation of the ORR by strongly bound oxides and the onset of the associative mechanism, but there appears to be discrepancies with the equilibrium potentials that describe the transitions between intermediates. There is also a larger spread in the values for these steps without significantly altering the goodness of fit, suggesting that the model is less governed by these steps.

The value calculated for RA2 is $E^0 = 0.46 \text{ V}$. This is close to the value of 0.40 V calculated in the paper of Tian and Anderson [27], and 0.46 as reported by Siahrostami *et al* [28]. In contrast, the solution phase reduction of oxygen to the superoxide acid, equivalent to the solution phase version of reaction RA2



Table 2

Examples of trial fits that well-describe the ORR polarization curves using the modified double trap kinetic model. Note that uncertainties are supplied in brackets, and fits using the unmodified double trap model for Pt(111) is provided for comparison. Fit is presented in Figure 7(a).

Fit #	J_{DA}^0 / A cm^{-2}	J_{RA1}^0 / A cm^{-2}	J_{RA2}^0 / A cm^{-2}	J_{RT1}^0 / A cm^{-2}	J_{RT2}^0 / A cm^{-2}	J_{RD}^0 / A cm^{-2}	$J_{\text{RA2}}^0/J_{\text{RT2}}^0$	ΔG_{O}^0 /eV	ΔG_{OH}^0 /eV	ΔG_{HO2}^0 /eV
1	0.03 (0.02)	3×10^{-8} (2×10^{-8})	1.85×10^{-60} (0.08×10^{-60})	0.2 (2)	1.9×10^{-60} (0.2×10^{-60})	4×10^{-7} (1×10^{-7})	0.97	-0.3 (0.1)	0 (0.1)	0.77 (0.03)
2	0.03 (0.03)	3×10^{-8} (2×10^{-8})	0.9×10^{-16} (2.0×10^{-16})	0.5×10^{-7} (5.0×10^{-7})	0.9×10^{-16} (2.4×10^{-16})	0.2×10^{-5} (9.2×10^{-5})	1	-0.5 (0.1)	-0.1 (0.1)	0.77 (0.03)
3	0.03 (0.02)	3×10^{-8} (2×10^{-8})	5.7×10^{-36} (0.1×10^{-36})	0.4×10^{-4} (5.0×10^{-4})	6.0×10^{-36} (0.5×10^{-36})	4×10^{-7} (1×10^{-7})	0.95	-0.6 (0.1)	-0.3 (0.1)	0.77 (0.03)
4	0.03 (0.02)	2×10^{-8} (2×10^{-8})	1.38×10^{-18} (0.06×10^{-18})	0.3×10^{-4} (2.8×10^{-4})	1.4×10^{-18} (0.2×10^{-18})	4×10^{-7} (1×10^{-7})	0.99	-0.61 (0.01)	-0.28 (0.07)	0.77 (0.03)
Literature [1]	4.3×10^{-5}	1.7×10^{-8}	–	3.3×10^{-9}	–	2.0×10^{-8}		-0.477	-0.120	–

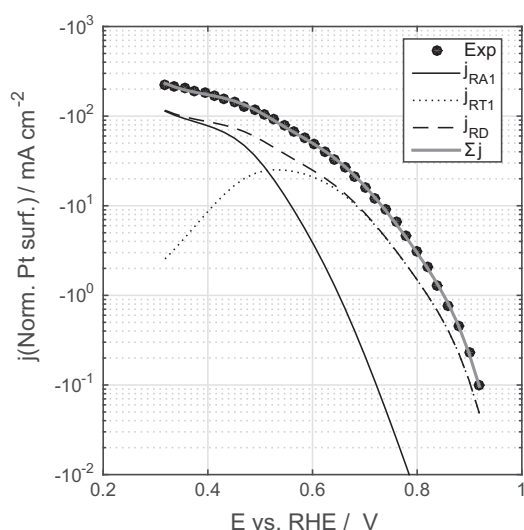


Figure 8. Component analysis for the current densities of the fundamental steps in the modified kinetic double trap model for the result given in Fig. 7. Note that j_{RA2} and j_{RT2} are omitted due to the low current densities.

Similarly we find a number of differences between the solution phase and adsorbed phase potentials of relevant reactions in Table 3. In fact this is not so strange. For instance the formation of $\text{OH}_{(\text{aq})}$ and $\text{OH}_{(\text{ad})}$ on platinum differs by about 2.1 V, demonstrating that stabilisation of Redox species by adsorption on a surface can significantly alter the equilibrium potentials from their solution phase values.

3.4. Relevance to fuel cell catalysis

If blocking by oxygenated species at low overpotentials is the reason for increased losses at high overpotentials then the consequences are rather severe. As can be seen from the inset of Fig. 5, there is a strong nonlinear correlation of the overpotential loss which increases with specific current density. At a cathode potential of ~ 0.7 V, the “effective overpotential loss” (i.e. that due to assuming Tafel like behaviour versus the true performance) is 30 mV. At 0.6 V, that value increases to 80 mV. The reduction in performance towards the oxygen reduction reaction at large overpotential implies that oxygen reduction catalysts will not function as efficiently under high fuel cell loads as previously expected based on rather simplistic models relying on Tafel-like behaviour, see below. This will appear as an added loss in cell

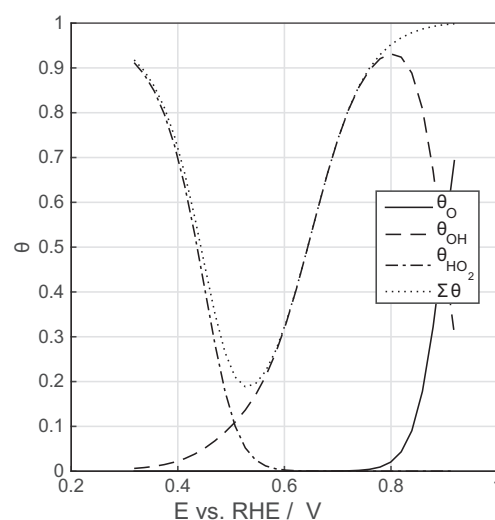


Fig. 9. Surface coverage of adsorbed species obtained from the modified double trap kinetic model for the example given in Fig. 7.

potential at large current densities when compared to standard kinetic models which assume Butler-Volmer or Tafel-type kinetics e.g. see inset in Fig. 5.

The standard approach for assessing losses in fuel cells involves successive removal of the different losses. Starting with the open circuit potential of the cell, resistive effects, which are proportional to the cell current density are removed (i.e. removal of Ohmic potential drop). Next the non-linear activation overpotential of the electrodes is estimated based upon a (typically unsophisticated) electrokinetic model usually based on a Tafel type approximation. Typically this assumes a Tafel slope for the ORR kinetics of around 60 to 70 mV/decade, although sometimes there is specific modification for the region associated with oxide coverage on platinum. Finally, the difference between the real operating fuel cell voltage, and the one calculated previously is assumed to be the losses due to mass transport effects. This approach is taken as it is somewhat difficult to estimate mass transport losses which will vary significantly on the cathode due to the effects of water condensation within the porous structure. Recent attempts at reducing electrocatalyst loading on fuel cell electrodes have been confounded by a supposed increase in mass-transport losses as loading is decreased [30,31]. As loading is decreased, the effective utilisation of catalyst increases – that is the mass activity and specific activity in the kinetic region

Table 3

Equilibrium potentials for the ORR determined from the modified kinetic double trap model using the adsorption energies in Table 2. Standard potentials are given for the aqueous phase reactions and for the reactions leading to adsorbed intermediates on platinum. The values for the adsorbed intermediates are calculated using DFT for Pt(111) whereas the experimental values (fit) are for polycrystalline samples. (state) refers to either aqueous or surface adsorbed.

Reaction	$E^0_{\text{fit}} / \text{V}$ Fit 1	Fit 2	Fit 3	Fit 4	$E^0_{\text{calc}} / \text{V}$ (adsorbed, Pt)	E^0 / V (aqueous)
RA1 : $\frac{1}{2}\text{O}_2 + \text{H}^+ + \text{e}^- \rightleftharpoons \text{OH}_{(\text{state})}$	1.229	1.329	1.529	1.509	1.86 ^a	0.079 ^c
RA2 : $\text{O}_2 + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HO}_{2(\text{state})}$	0.459	0.459	0.459	0.459	0.46 ^b	-0.125 ^c
RT1 : $\text{O}_{(\text{state})} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{OH}_{(\text{state})}$	0.929	0.826	0.929	0.899	0.83 ^d	2.48 ^e
RT2 : $\text{HO}_{2(\text{state})} + \text{H}^+ + \text{e}^- \rightleftharpoons 2\text{OH}_{(\text{state})}$	1.999	2.129	2.599	2.559	3.26 ^f	0.281 ^f
RD : $\text{OH}_{(\text{state})} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{H}_2\text{O}$	1.229	1.129	0.969	0.949	0.6 ^d	2.38 ^g

(state) = adsorbed or aqueous

^a Calculated using E^0 of the ORR, and $\text{OH}_{(\text{ad})} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{H}_2\text{O}$.

^b From Siahrostami et al. [28]

^c From Bard et al [29]

^d From Tian and Anderson [27]

^e Calculated from $\text{O} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}$ [29] and $\text{OH} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{H}_2\text{O}$.

^f Calculated from $\frac{1}{2}\text{O}_2 + \text{H}^+ + \text{e}^- \rightleftharpoons \text{OH}_{(\text{state})}$ and $\text{O}_2 + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HO}_{2(\text{state})}$.

^g From Stanbury [34]

improves [32]. This effect comes about because the catalyst is more favourably disposed within the catalyst layer, leading to less “shielding” of catalyst particles by one another. However, it might be expected that mass transport effects should be reduced under these circumstances. Hence, increased mass transport effects with reduced loading are somewhat counterintuitive and remain the subject of some discussion. For instance Yoon and Weber contend that some of the effect is due to a sub-unity oxygen stoichiometry in the kinetic equation ($\gamma = 0.8$), along with severe limitations in diffusion of oxygen through the perfluorosulfonic acid ionomer covering the platinum particles [33]. An intriguing possibility of the work in this paper is that the supposed increase in mass transport overpotential is an artefact of the way that the measurements are made and a more sophisticated electrokinetic model of the type developed within this paper would eliminate the extra mass transport losses seen at low catalyst loading.

4. Conclusion

The reduction of O_2 to water under electrokinetic control has been studied at overpotentials not typically accessible by conventional methods due to the onset of mass transport limitations. We have tried to use the double trap kinetic model to fit our experimental data [26]. However, considerable deviation from the model occurs at potentials in the double layer region. In this region the experimental current densities were lower than the values predicted by the standard double-trap model. The experimental data on which the double trap model is validated is realistic only under electrokinetic control at potentials above 0.8 V, so it is hardly surprising that the standard double trap model is unable to capture the true electrokinetic behaviour of the ORR in the potential regime less than 0.8 V. By introducing a simple model which includes an adsorbate binding to the surface at low potentials, we find good fits to our experimental dataset with a relative accuracy of 10% over temperature (280–330 K) and potential ranges of 0.3 to 0.7 V vs. RHE. At low overpotentials there are somewhat larger deviations as this simple model does not include the formation of oxide blocking species on the surface. The model does however imply a blocking species on the surface with increasing coverage as overpotential is increased (i.e. as potential is decreased down to 0.3 V vs. RHE). The adsorption isotherm of this adsorbate agrees with the formation of hydrogen peroxide.

Aided by this simple model, we have modified the double trap kinetic model to include the formation and decomposition of adsorbed $HO_2(ad)$. By including this species we were able to model the polarization curve within 4% error between 0.3 and 0.9 V vs. RHE. The fitted model suggests that the predominant path for the ORR is rapid dissociative adsorption to form $O(ad)$, followed by subsequent reduction to H_2O . This mechanism is hindered by the formation of an additional surface species at potentials in the double layer. Although the model cannot unequivocally identify the species, the presented model appears to be consistent with the formation of a surface species via the associative pathway. The extra species allow for the possible formation of hydrogen peroxide (although this aspect is currently missing in our model), something which is known to occur on real catalysts but is not catered for by the double trap model. This addition has the effect of adding extra blocking species to the platinum surface, and this blocking increases as the overpotential increases. The net result is that the ORR on platinum underperforms compared to standard models which assume Tafel-like behaviour at large overpotentials. We further note that the structure of the fitted isotherm is consistent with a step involving a free site, and the removal of this species in a steady state type relationship.

These results suggest limits to the performance of catalysts in fuel cells, and also suggest that studying the performance of

catalysts in the so-called kinetic regime (i.e. 0.9 V vs. RHE) and extrapolating this performance to that at fuel cell relevant potentials (ca. 0.7 V vs. RHE) may give an incomplete picture as to the performance in a fuel cell. Control of the blocking species on the catalyst may be just as important as pushing the absolute performance of the catalysts on RDE electrodes at 0.9 V vs. RHE.

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