Kinetic isotope effect in the oxygen reduction reaction (ORR) over Fe-N/C catalysts under acidic and alkaline conditions

Daniel Malko, Anthony Kucernak*

Department of Chemistry, Imperial College London, London SW7 2AZ, UK

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ABSTRACT

Heat treated Fe-N/C materials which are highly effective oxygen reduction catalysts in alkaline and acid, show a significant kinetic isotope effect (KIE). The values in acid (~ 3.4) and alkaline (~ 2.5) are much larger than the value for the metal free catalyst in acid (~ 1.8) suggesting that the rate determining step (RDS) is a proton coupled electron transfer in acid with a significant pathway involving a proton independent step under an alkaline environment.

1. Introduction

The electrochemical oxygen reduction reaction (ORR) is an important technological reaction, which is used in polymer electrolyte fuel cells (PEFCs), metal-air batteries and depolarised chlor-alkali electrolysis [1]. The most active catalysts to date are based on precious group metals such as Pt [1]. This places significant strain on the economic viability of such devices [1]. Heat treated, transition metal and nitrogen containing carbon materials (M-N/C), of which iron based variants (Fe-N/C) are the most active, have shown promising activities under acidic as well as under alkaline conditions [2]. However, in order to be used under acidic conditions, i.e. in PEFCs, their activity needs to be significantly increased [2]. Although numerous studies are concerned with the structure and nature of the active sites [3–7], few experimental studies exist that shed light on the reaction mechanism [8]. It is suggested that the proton transport properties of the active site are crucial for a high turnover frequency in acid [7,9]. A detailed understanding of this proton involvement might lead to design strategies toward a higher activity. Recently Tse et al. investigated the kinetic isotope effect (KIE) for the ORR on non-precious as well as precious metal catalysts. Although this study identified a KIE of ~ 2 in acid and alkaline, it is unclear whether the difference in equilibrium potentials for the ORR in deuterium versus the hydrogen couples was taken into account [10]. We investigate the effect on the electrochemical activity toward the ORR of changing the electrolyte from hydrogen to deuterium, both under acidic (0.45 M H_2SO_4/D_2SO_4) and alkaline conditions (1 M NaOH/NaOD) for a similar Fe-N/C catalyst with an approach to take into account the difference in equilibrium potentials.

2. Material and methods

2.1. Catalyst synthesis

The Fe-N/C and metal free N/C catalysts utilised were synthesised as per literature procedure (Fe-ODAN-1%) [11]. With the addition that the synthesised material was then subjected to a second heat treatment at 900 °C for 2 h after reaching the target temperature at a heating rate of 20 °C/min under nitrogen.

2.2. Electrochemical measurements

Measurements were conducted using an Autolab, PGSTAT20 (Metrohm) with a Rotating Ring Disk Electrode (Pine Instruments, model AFE6R1AU, with a mirror polished glassy carbon disk and rotator model AFMSRCE). The catalyst was deposited on the glassy carbon disk as per literature procedure [12]. The ink utilised consisted of 1 wt% catalyst in a 1:1 volume ratio mixture of IPA (VWR):H2O (MilliQ 18.2 MΩ cm) with the same weight of Nafion® (5 wt% solution, Sigma-Aldrich) as catalyst. This composition was found to give a uniform catalyst layer characterised under optical microscope. A custom made three compartment thermostatted double-walled glass electrochemical cell was used (25 °C). The potential was measured using a leak free Ag/AgCl electrode, (Warner Instruments) via a Luggin-Haber-Capillary. Ultrapure gases, Nitrogen and Oxygen (BIP plus-X47S, Air products) were used. Electrolytes were composed of ultrapure water (MilliQ 18.2 MΩ cm), 95% Sulphuric acid (Aristar, VWR), and NaOH pellets (VWR, ACS grade). Deuterated electrolytes were prepared using D_2O (Sigma-Aldrich, 99.9% atom % D), 96% D_2SO_4 (Sigma-Aldrich,

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99.5 atom % D) and 30 wt% NaOD solution in D_2O (Sigma-Aldrich, 99 atom % D). Although high purity D_2O was used, it was found that it contained a small contamination of hydrogen sulphide. This probably comes from the Girdler sulphide process used to produce it [13]. As sulphide is a potent poison for transition metal catalysts, we took care to remove any residual hydrogen sulphide by purging the deuterated water with ~3% Ozone in O_2 for 8 h in order to oxidise the sulphide [14] followed by stirring the solution in the presence of a platinum gauze in order to remove any residual hydrogen peroxide.

2.3. Preconditioning of the electrode

Prior to the experiments the deposited catalyst layer was preconditioned in order to reach a stable baseline activity and minimise contributions of degradation. The procedure consisted of extensive cycling, alternating between N_2-saturated electrolyte at 100 mV/s (20 cycles) and 10 mV/s (10 cycles) and O_2-saturated electrolyte at 5 mV/s (6 cycles), in the potential window 0.75 to − 0.55 V vs Ag|AgCl in acid and − 1.0–0.050 V vs Ag|AgCl in alkaline respectively. This was repeated until stable non changing oxygen reduction performance and cyclic voltammograms under nitrogen were achieved (3–4 times). Experiments under the respective acidic and alkaline conditions were conducted from the same catalyst layer, in order to prevent errors due to the variation of the amount of deposited catalyst. The electrode tip with the catalyst layer was immersed into ultrapure water or into D_2O for 10 min under a rotation of 300 rpm prior to transferring it into the respective H or D containing solutions to avoid cross contamination and to ion exchange the Nafion® binder. Where iR free potentials ($E_{iR-free}$) are reported the potential (E) was corrected to be $E_{iR-free} = E − I * R$, where I is the measured current and R the solution and lead resistance, as determined by electrochemical impedance spectroscopy (FRA module, Autolab, PGSTAT20) as described in literature [15]. The measurements have furthermore been corrected for the capacitive background, i.e. subtracted from the equivalent measurement in N_2-saturated electrolyte. The potential of the Ag|AgCl reference electrode was determined using lab constructed reversible hydrogen/deuterium electrodes (RHE/RDE) in the respective electrolytes in order to correct for the different environments. Using an Ag|AgCl reference electrode avoids the possibility of drift in the RHE/RDE during ORR measurements due to oxygen reduction occurring simultaneously on the hydrogen electrode. Furthermore, Fe-C/N catalysts are quite insensitive to chloride [11].

2.4. Determination of overpotentials for each reaction

As the equilibrium potentials for the D_2/D^+ reaction, and the O_2/D_2O electrochemical reactions are different from their equivalent reactions in H_2O, results were corrected to the RHE (in H_2O) and RDE (in D_2O) scales before being converted into overpotentials. This corrects for the different activities of D^+ and H^+ (see discussion in [16]), although the different activities will also have an effect on the kinetics, we assume that this aspect is small and will be subsumed into the Kinetic Isotope Effect value. All experimental results were performed using an Ag/AgCl(H_2O) reference electrode. To correct for any junction potential, and the change in solvent composition the potential of this reference electrode was measured against the RHE and RDE in the appropriate electrolytes. The different free energy of formation ($\Delta_{formation}G$) of H_2O (− 237.18 kJ/mol) vs D_2O (− 243.49 kJ/mol) leads to different equilibrium potentials of 1.229 V_{SHE} vs 1.262 V_{SDE} (SDE = standard deuterium electrode) respectively [17], and hence the ORR results utilised these values as the equilibrium potential for calculations using RHE/RDE corrected data[†] Fig. 1(a).

[†] Hence measuring the rate of the ORR reaction at the same potential versus the RHE and RDE reference electrodes is **not** the same as measuring at the same overpotential for the ORR.

3. Results and discussion

Since the kinetic current is directly correlated with the rate constant it can be used to estimate the KIE [18–20]. In order to be able to compare the kinetic currents of the hydrogen and deuterium measurements, values need to be determined at the same overpotential, η, as described above. Due to the relevance of the ORR in PEFCs, which operate in an acidic environment, the catalyst was subjected to the low pH and pD electrolytes, 0.45 M H_2SO_4/0.45 M D_2SO_4. Cyclic voltammetry was conducted in nitrogen saturated solution. In order to validate whether a significant kinetic isotope effect (KIE) would be discernible under the utilised experimental conditions, the hydrogen evolution reaction was used to estimate how a primary KIE could electrochemically manifest itself. The electrochemical isotope effect for the HER is well investigated due to its technological relevance [18,21–23].

Fig. 1b shows the cyclic voltammetry of the Fe-N/C catalyst in nitrogen saturated solution. The onset of the hydrogen evolution reaction is clearly visible, starting at ~ − 0.1 V vs RHE/RDE. It can also be seen that the reaction is significantly more facile in the hydrogen containing electrolyte compared to the deuterated one. From the kinetic current, as indicated in fig. 1, the KIE was estimated to be ~3.4 on the Fe-N/C catalyst. This shows, if present, a large KIE is detectable with our setup. Although we cannot be certain about the RDS in this reaction, we infer from this value that a primary KIE would at least show a value of 3. This agrees with values observed for the proton discharge being the RDS on metal electrodes (3–6) [18,22]. Since there are no data available on how a primary kinetic isotope effect would manifest itself for the ORR under these conditions, a value of 3 is taken as a reference. To confirm whether the accessible electrochemical surface area in the hydrogen and deuterium containing electrolytes are comparable, cyclic voltammetry was performed.

In order to assess whether a KIE would be expected for a "metal-free" N/C catalyst, we performed an ORR measurement on such a catalyst. The results for this measurement in the form of a Tafel plot are reported in Fig. 1(c). We find that the KIE is ~1.8. This demonstrates that in the absence of metal, there is not a significant KIE on these carbon based catalysts in acid.[‡]

Figs. 2 and 3 compare the performance of the metal containing Fe-N/C catalyst in acid and alkali respectively. It can be seen in Fig. 2a, that while the deuterated solvent shows a slightly smaller capacitance, it is not significantly different as compared to the hydrogen equivalent. The slightly smaller capacitance might be due to the larger size of the deuterium atoms or other changes in the double layer associated with the different properties, such as the dielectric constant [24]. This leads to less charged species being able to accumulate in the double layer and hence decreasing the specific capacitance of the system [25]. Nevertheless, this indicates that the accessible electrochemical surface area and hence observed activity should be comparable. A shift of ~40 mV in the reversible peak at ~0.7 V vs RHE/RDE is observed, indicating a process which involves the transfer of protons in agreement with a quinone/hydroquinone couple. Fig. 2 b shows the oxygen reduction activity of the Fe-N/C catalyst. A slight change in limiting current is undoubtedly caused by the variation in diffusion coefficient and solubility of oxygen in the deuterated solvent [26]. Correction of the results to overpotentials taking into account the different thermodynamics in D_2O versus H_2O (see Experimental section) shows that the reaction in H_2SO_4 is significantly faster than in D_2SO_4 (Fig. 2c). It can then be seen that the ratio of the kinetic currents, $i_{kin}(H)/i_{kin}(D)$ is 3.4 ± 0.1 based on three independent experiments. This value is much larger than the value determined for the metal-free catalyst in acid, 1.8, reported

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[‡] It should be noted, as is common of all so-called "metal-free" catalysts that there is nonetheless a trace amount of metal (60 ppm) present and this could be responsible for the observed KIE, while the "true" metal free mechanism in acid might indeed be proton independent.
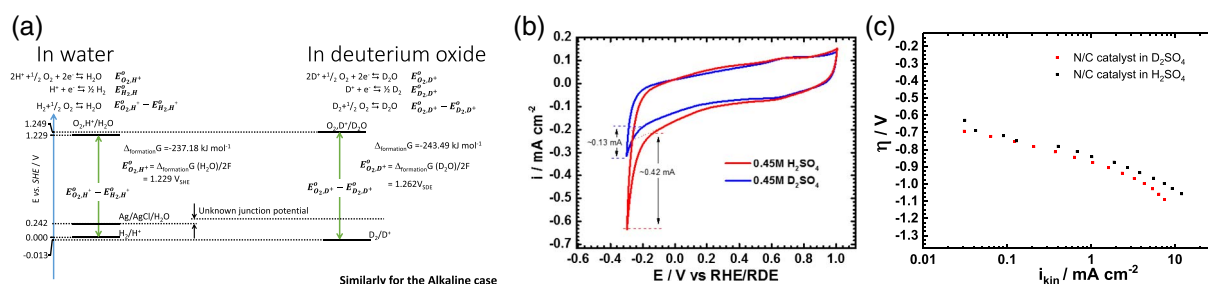
Fig. 1. (a) Energy level diagram comparing the ORR reaction in water versus that in D$_2$O for the acid case. (b) Rotating disk electrode (RDE) measurements of Fe-N/C catalyst in N$_2$-saturated electrolyte. 1600 rpm, 5 mV/s; Loading 270 μg cm^{-2}; (c) Tafel plot of rotating disk electrode (RDE) measurements of metal-free N/C catalyst, in O$_2$-saturated H$_2$SO$_4$ and D$_2$SO$_4$. 1600 rpm, loading 270 μg cm^{-2}; 0.45 mol dm^{-3} electrolyte concentration. *T* = 298 K.
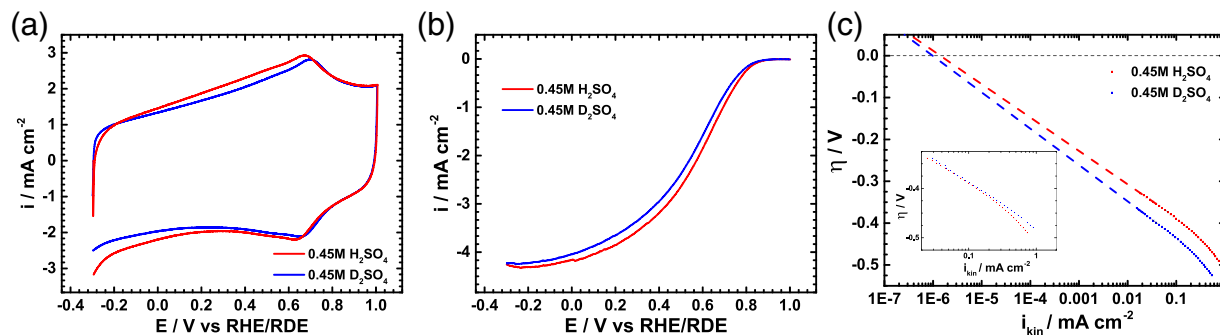

Fig. 2. Rotating disk electrode (RDE) measurements of Fe-N/C catalyst, 1600 rpm, loading 270 μg cm^{-2}. a) 50 mV/s, N$_2$-saturated electrolyte, b) background corrected, 5 mV/s O$_2$-saturated electrolyte, c) Tafel plot, where the potentials have been converted to overpotential, corresponding to the measurement in b). Inset: Current in D$_2$SO$_4$ multiplied by 3.4 (KIE factor) to show overlap of two responses. Electrolytes used were 0.45 M H$_2$SO$_4$/0.45 M D$_2$SO$_4$.

above. The currents have been compared in the region of low overpotential (< 0.1 mA cm^{-2} i.e. < 10% limiting current). This should eliminate mass transport effects, although as the results are performed on the same electrode, these should be very similar. It can be seen in Fig. 2c inset, if multiplied with 3.4, the kinetic current in D$_2$SO$_4$ overlaps with the measurement in H$_2$SO$_4$ validating the determined value. The Tafel slopes have been determined to be ~80 mV/dec and ~85 mV/dec for hydrogen and deuterium respectively, which shows no significant difference and indicates a constant KIE across a wide potential range. Although formally it would be more appropriate to compare the exchange current densities, doing so is associated with a large error, due to the extrapolation to zero overpotential being made over 4 orders of magnitude in current density. We determine a KIE of 3.4 which would be indicative of a primary kinetic isotope effect. This suggests that a proton transfer is directly involved in the rate determining step (RDS). A slight decrease in activity could also be attributed to non-mechanistic sources such as due to the lower overall accessible electrochemical surface area. This contribution should be small however, especially as electrochemical double layer capacitance seems very similar (see above). This large KIE in acid is in agreement with mechanistic suggestions present in literature, which emphasise the importance of the proton transport capabilities of the active site [7,10]. This suggests that the RDS might be for example the reductive adsorption of oxygen to the active site with a concerted proton transfer. This is different to metal surfaces where reductive adsorption is assumed to be the RDS [27]. The non-negligible KIE in the Fe-N/C catalyst however, indicates that a proton in the vicinity of the active site might contribute to stabilising the transition state that leads to this intermediate as suggested by Herranz et al. [7]. We have recently shown that this same catalyst may be reversibly poisoned by nitrite and nitric oxide [28,29]. Furthermore, these poisoning species may be removed by reductive stripping allowing us to count the number of active sites in the catalyst. We find that under acid conditions, ~80% of the current is generated by a site which is poisoned by nitrite, suggesting that this KIE result is broadly applicable to one active site in the

catalyst. Under certain conditions in Nitric Oxide containing solutions, we can irreversibly remove the acid activity of the catalyst whilst retaining virtually all of the alkaline activity [29].

It is known that in alkaline the ORR proceeds in a much more facile manner and several M-N/C and N/C materials have been reported which have comparable activity to Pt on the RDE (although at much greater loading) [9]. The ORR in alkaline might be interesting for alkaline fuel cells and depolarised chlor-alkali electrolysis and a different mechanism is most likely present in alkaline solutions. Therefore we extended our investigation to high pH and pD in 1 M NaOH and 1 M NaOD respectively. The cyclic voltammetry in nitrogen containing electrolyte (Fig. 3a) again reveals that the capacitance of the deuterated solvent is slightly lower.

Fig. 3b shows the ORR polarisation curves recorded in the alkaline electrolytes (1 M NaOH and 1 M NaOD) and Fig. 3c the kinetic analysis. This time the ratio i$_{kin}$(H)/i$_{kin}$(D) is ~2.5, which is smaller than under acidic conditions. The Tafel slopes are 56 mV/dec and 55 mV/dec in NaOH and NaOD respectively and a good overlap of the traces is again achieved when multiplying the kinetic current in the deuterium measurement with the KIE (Fig. 3c inset). While a small variation can again stem from various sources, this decrease in KIE is significant. The smaller KIE in alkaline might indicate a significant contribution from a second pathway, which has a proton independent RDS, as suggested by Ramaswary et al. [9]. Our nitric oxide adsorption/reductive stripping experiments suggest that under alkaline conditions there is also a metal centred active site which can undergo reversible poisoning, but this site does not seem to be responsible for the majority of the current. Indeed, we are able to irreversibly poison this site by cycling the electrode in nitric oxide containing solution such that in acid the activity approximates that of the metal free catalyst. In alkaline solution, these irreversible poisoned catalysts show very little change, affirming the idea that the active site in alkaline is quite different to that in acid [29].

The observed findings are used to suggest the RDS for both acid and alkaline. In acid, the mechanism will most likely proceed with an inner sphere electron transfer [9,25]. This means that the oxygen molecule
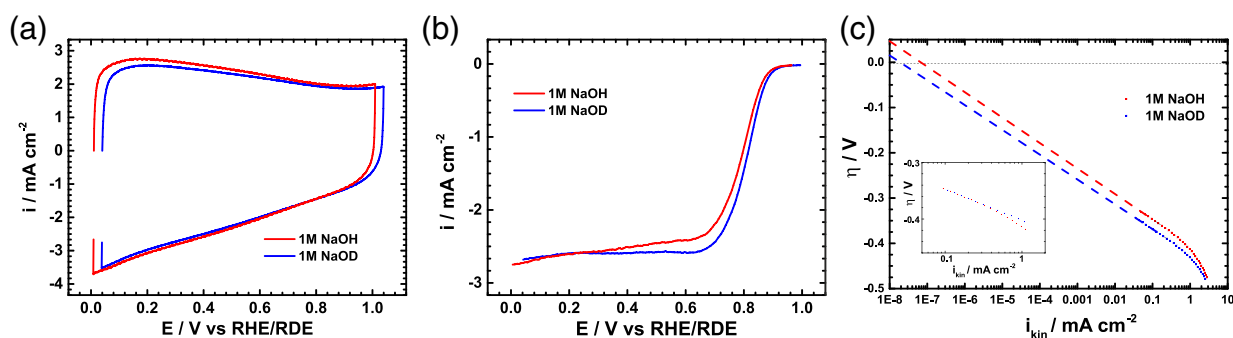
Fig. 3. Rotating disk electrode (RDE) measurements of Fe-N/C catalyst, 1600 rpm, loading 270 μg cm^{-2}. a) 50 mV/s, N$_2$-saturated electrolyte, b) background corrected, 5 mV/s O$_2$-saturated electrolyte, c) Tafel plot, where the potentials have been converted to overpotential, corresponding to the measurement in b). Inset: Current in NaOD multiplied by 2.5 (KIE factor) to show overlap of two responses.

has to adsorb onto the active site. The results suggest that the reductive adsorption might proceed concerted with a protonation of the adsorbed superoxide intermediate. The following mechanism for the RDS, where the transition state could be stabilised by a proton might be relevant for the first electron transfer:
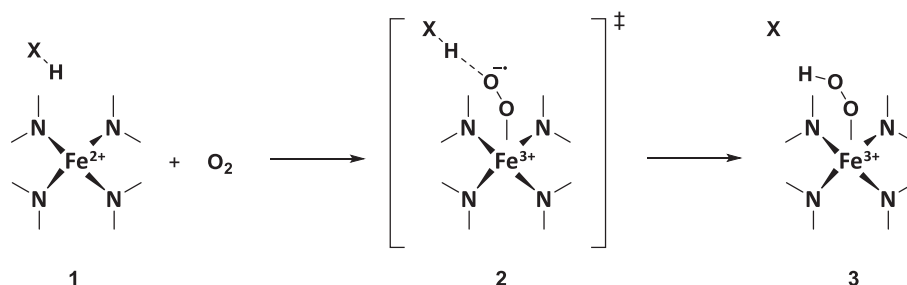
X represents a species which can carry protons, such as solvating water molecules or functional groups in the vicinity of the active site, and a transition state as represented by species 2 might be present. In alkaline on the other hand a combination of inner-sphere and outer sphere electron transfer has been suggested [9]. This gives the possibility that additional to the mechanism present under acidic conditions an outer sphere mechanism as follows is present:
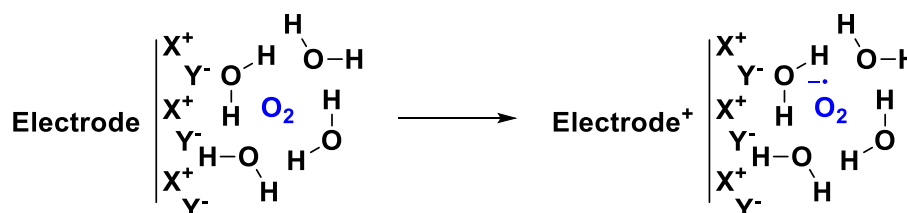
This second mechanism yields a solvated superoxide molecule which might be proton independent and then continues to adsorb to the surface for the further reduction to water or peroxide. However, detailed mechanistic considerations should be taken with caution, as numerous factors can influence the KIE. Nevertheless, the insight of a significant KIE in acid as well as alkaline is interesting and might have important implications for follow up studies.

4. Conclusion

In conclusion, we show that for the ORR on Fe-N/C catalysts the proton transfer seems to be directly involved in the RDS, both in acid and in alkaline. This is evident due to the measured values for the KIE of ~3.4 and ~2.5 respectively. In comparison, the metal free catalysts

only show a KIE of 1.8 in acid. It is likely that the mechanism in acid proceeds exclusively via an inner sphere electron transfer. This implies that the RDS could well be the reductive adsorption of oxygen onto the active site with a concerted proton transfer. In alkaline a significant outer sphere electron transfer component is suggested. The smaller KIE here indicates the occurrence of 2 parallel pathways, one of which has a proton independent RDS. These findings provide insight into the mechanism of Fe-N/C catalysts and the KIE values could be used to verify computationally proposed mechanisms.

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