The realization of a practical Lithium-air cell depends on understanding the oxygen reduction reaction (ORR), identifying a stable electrolyte and finding a suitable cathode. This study investigates the superoxide radical, its side reactions and correlates density functional theory (DFT) predictions of the surface activity to the experimental kinetics. The ORR on glassy carbon (GC), multi-crystalline Pt and multi-crystalline Au substrates in oxygen saturated 0.1 M Tetraethylammonium Perchlorate (TEAClO4) in Dimethyl Sulfoxide (DMSO) was studied using cyclic voltammetry and the rotating ring-disc electrode (RRDE) technique. The RRDE data was analyzed using kinetic models to understand the electrochemistry of the superoxide radical and calculate the surface reaction rate constants. The percentage of the superoxide radicals detected at the ring from GC, Pt and Au surfaces correlated linearly to the modeled activities of the substrates. Further, the modeled activity trend was found to correlate strongly with the ORR onset potential. This study validates the DFT catalyst screening approach. It also shows that side reactions involving the superoxide radical occurs in fresh, anhydrous DMSO based electrolytes.

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The present study sought to examine the oxygen reduction reaction (ORR) and identify any side reactions on glassy carbon (GC), multi-crystalline Pt and multi-crystalline Au electrodes in anhydrous 0.1 M TEAClO4 in DMSO using the Rotating Ring-Disk Electrode (RRDE) technique. The absence of lithium ensured that the electrode surface was pristine and allowed for the application of well-established kinetic models21,22 to calculate the rate constants for reactions and to identify possible side and parallel reactions.23 These techniques have been previously used by us for kinetic investigations of the H+ ORR on various surfaces such as Lead Ruthenate pyrochlores,24 Ruthenium,25 and Cobalt-Palladium.26 The measurement of the ratio of superoxide species in the solvent is challenging in the Li salt containing electrolyte due to the short half-life of the radical27 and the change in the electrode surface due to product deposition. But these constraints were overcome in the present study by the use of an unreactive TEA⁺ cation. This also allowed for the measurement of the degree of side reactions between the superoxide radical and the electrolyte and show that pristine, fresh DMSO also undergoes reactions with the superoxide radical. The ratio of superoxide radicals that are in the electrolyte was calculated and correlated with the density functional theory (DFT) modeling based activity of the substrates. The use of DFT for catalysts screening is well established28 but is also beset with challenges in the Li-air system due to the requirement to model the solvent effect and the changing substrate. Herein, we correlated the DFT predictions reported by us previously29 to the first electron transfer reaction resulting in the formation of superoxide radical, which subsequently reacts to form the peroxy product in the presence of Li⁺ via a variety of routes and possible side products due to nucleophilic attack of some electrolyte solvents. Similar to our work on the ORR in polymer electrolyte membrane fuel cells (PEMFCs),30 we found that relatively stable electrolytes and corrosion resistant materials are critical to the mechanism of the oxygen reduction reaction carried out and relatively stable electrolytes were identified.11 Further, the poorly cycle life reported in many articles can be traced to the oxygen efficiency and low power density;1 (iii) eventual ambient air operation. Li-air cells must overcome problems of (i) poor cycle life; (ii) high

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The Lithium-air cell is an attractive technology for beyond Li-ion applications due to its high theoretical specific energy of 3505 Wh Kg⁻¹ which is significantly higher than current lithium-ion cells. To achieve practical applications as a replacement for Li-ion cells, current Li-air cells must overcome problems of (i) poor cycle life; (ii) high charge and discharge overpotentials resulting in low columbic efficiency and low power density;1 (iii) eventual ambient air operation. The poor cycle life reported in many articles can be traced to the oxidative instability of the electrolyte2-4 in conjunction with electrode passivation due to irreversible product deposition and high overpotentials for decomposing Li₂O₂.5,6

The issue of electrolyte instability has been extensively reported since the early attempts to fabricate a secondary lithium-air cell adopting typical lithium-ion cell electrolytes. Alkyl carbonate based electrolytes were found to undergo nucleophilic attack, form passivating films and consume the electrolyte.2 Extensive studies on a wide variety of electrolytes such as acetonitrile,3 ethers,3 dimethylformamide,4 dimethylsulfoxide (DMSO),5 and various ionic liquid9,10 have been carried out and relatively stable electrolytes were identified.5 Further, the donor number of the electrolyte solvent was found to be critical to the mechanism of the oxygen reduction reaction (ORR).5 Thus 1,2 dimethoxyethane (DME) and dimethylsulfoxide (DMSO) were extensively adopted for further study due to their high donor numbers and relative stability. Ionic liquids were also studied due to similarly favorable properties and their inherently good conductivity.9,10,13,14 Nevertheless, oxidative stability continues to be of concern. Recently, the stability of DMSO has been called into question. Sharon et al. proposed multiple schemes for the reaction of DMSO with re-

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simple DFT models showed a remarkable degree of correlation with experimental data.

**Experimental**

The 0.1 M solution of Tetraethylammonium perchlorate (TEAClO₄) (Alfa Aesar) in Dimethylsulfoxide (DMSO) (>-99.9%, Fisher) was prepared in a MBrann argon filled glove box with H₂O and O₂ levels <0.5 ppm. The TEAClO₄ salt was dried in a vacuum oven for 24 hours at 40°C and DMSO was distilled, argon purged and stored over zeolite beads in an argon filled glove box to ensure absence of moisture before use. The DMSO was opened, stored and handled in an Ar glove box with H₂O levels <0.5 ppm and data from the literature shows that the rate of water uptake at room temperature and in the absence of stirring was very low (0.05 wt% water uptake after 1-hour exposure to air at 75% relative humidity (295 K)).

In the extreme case of exposure to 98% relative humidity (295 K) air for 5 days, the mole fraction of water was 2.17. Thus, in light of the precautions taken, the water content is expected to be close to the rated value of less than 0.01%. Despite these precautions, absorption of a small amount of water is possible and its impact on the reaction is discussed in light of the “catalytic” effect reported in the literature.

The electrochemical measurements were carried out in a setup that consisted of a three-neck electrochemical cell with Teflon stoppers with openings for working, counter and reference electrodes and a gas purge line. The working electrode was a Pine instruments RRDE assembly with a Pt ring and interchangeable electrodes of glassy carbon (GC), Au and Pt polished to a mirror finish with 0.05 μm alumina suspension. The counter electrode consisted of a coiled Pt wire in a fritted glass tube (Pine instruments) and the reference electrode consisted of an Ag wire dipped in a solution of 0.1 M AgNO₃ in CH₃CN (−3.85 V vs Li/Li⁺) in 0.1 M TEAClO₄/DMSO). A gas purged bearing assembly (Pine instruments) with continuous Argon purge was used to ensure isolation from the environment during RRDE rotation. The entire setup was assembled in the glove box, sealed and then transferred to a glove-box which was kept at a positive pressure relative to the atmosphere using a continuous argon feed to prevent moisture contamination.

The electrochemical impedance spectra (EIS) were recorded using a Solartron analytical frequency response analyzer to measure the resistance of the setup prior to electrochemical measurements and was later used in iR correction of the RRDE voltammograms. The electrochemical measurements were performed using a multi-channel potentiostat (Solartron analytical).

**Results and Discussion**

Fig. 1 depicts possible pathways for the reduction of oxygen in a lithium ion containing electrolyte. There were no reports in the literature of Li₂O being detected in Li-O₂ systems and so this product of a possible 4-electron reduction was not considered in our analysis.

The initial step in the ORR mechanism was considered to be the adsorption and subsequent reduction of oxygen to the superoxide radical. Outer sphere electron transfer to form O₂⁻ and the possible subsequent adsorption of the superoxide radical was also considered. This mechanism for forming the superoxide is a possibility in light of the degradation of the electrolyte which could be caused by the highly nucleophilic superoxide radical remaining in the electrolyte. Laoire et al. show that the stability and half-life of the superoxide radical is a function of the donor number of the solvent and propose a complex formation between the tetraethylammonium cations and the superoxide radicals. Due to the consequent stability of the superoxide radical in high donor number solvents such as DMSO, its half-life could be increased greatly. The electrochemical detection of the superoxide radical was expected to be a function of this degree of stabilization. As depicted in the figure, with the stable superoxide radical, surface adsorption would be entirely dependent on the binding energy of the intermediate and would imply that disproportionation reaction on both the surface and the electrolyte is possible. Another possibility considered was the hybrid mechanism proposed elsewhere. Li₂O₂ has been observed on the surface of the cathode and has also been detected in the electrolyte. Based on observations with H⁺ ORR in aqueous systems, it is reasonable to expect a combination of these mechanisms occurring. The present system of TEAClO₄/DMSO was selected so as to have a simple system for the study of superoxide radical, its side reactions and the proportion of reduced species that is desorbed into the electrolyte. Further, the effect of the electrode material on the oxygen reduction reaction in various aprotic electrolytes was found to be reported multiple times in the literature through both experimental and theoretical methods and one part of the present study serves to examine the same in the context of the Li-O₂ cell.

**Cyclic voltammetry.**—Cyclic voltammetry allowed the identification of the potentials at which reactions occur in this model system under cathodic and anodic conditions. Parameters such as the peak voltage, reaction onset potential, the separation between the reduction and oxidation peaks allowed for the initial characterization of the system. Fig. 2 shows the cyclic voltammograms (CV) of GC, Pt and Au discs in oxygen saturated 0.1 M TEAClO₄/DMSO at scan rates of 50 mV s⁻¹, 100 mV s⁻¹ and 500 mV s⁻¹. It was evident from the voltammograms in the Ar saturated condition, in case of all three substrates, that the electrolyte was electrochemically stable within the potential window of interest. Outside this window, oxidation peaks were observed between 3.7 to 4 V as clearly seen in the slow 5 mV s⁻¹ scan CVs depicted in Fig. 3b. This was similar to the potential at which Sawyer et al. reported oxidation peaks in the presence of protons (from added HClO₄) and also close to the potential at which oxidation peaks were observed with the addition of water. The voltage range from 1.85 V to 4.35 V covered the operating range of Li-air cells wherein the discharge and charge plateaus were found to occur.

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Figure 1. Reaction scheme for the Oxygen reduction reaction in a Li-air cell. The hypothesized disproportionation reactions on the surface (black, solid arrows) and the electrolyte bulk (red, dot-dash arrows) is depicted.
at ~2.5 V and ~4 V respectively. Upon saturation with oxygen, the voltammograms showed a reduction peak below 2.45 V and oxidation peak above 2.65 V during the cathodic and anodic scans respectively on GC, Pt and Au, with a voltage separation whose magnitude suggested a degree of irreversibility. The shift in the peak position with the scan rate was found to be in agreement with the proposal of Bard and Faulkner36 of a 30 mV shift for a 10-fold increase in scan rate. Thus, the reduction and oxidation peaks were believed to correspond to the reduction of adsorbed oxygen to the superoxide radical and its subsequent oxidation to oxygen respectively. The Pt disc was found to show the highest onset potential for the ORR at 2.9 V during the cathodic scan while the Au disc showed the lowest onset potential for the oxygen evolution reaction (OER) at 2.5 V for the anodic scan. Thus, the advantages of a Pt-Au bifunctional catalyst37 was readily apparent.

Rotating ring-disc electrode (RRDE) measurements.—The rotating ring-disc electrode allowed for the characterization of the adsorption-desorption of intermediates on the disc and also allowed for the identification of the pathways of the reduction reaction occurring on the disc using a kinetic model. The ring, which was held at an oxidizing potential as identified from the CVs, allowed for the characterization of the adsorption of the reaction intermediates using binding energies. The percentage of product species transported to the ring was found to be of a different order as compared to the rate of the OER on the ring. Thus, the reaction between the near-disc environment and the ring. The creation of such a gradient would require that the product desorption rates be different for the different substrates in line with variation of intermediate binding energies. The percentage of product species transported to the ring was investigated to test this hypothesis.

The RRDE electrode was rated to have a collection efficiency (N) of 0.25 and this can be used to calculate the proportion of the ions produced on the disc that desorb and travel to the ring using the following equation:

$$\chi (\%) = \frac{i_{\text{ring}}}{i_{\text{disk}} + i_{\text{ring}}} \times 100 \quad [1]$$

The percentage of the ions produced on the disc diffusing away from the GC, Au and Pt discs were found to be 29%, 27% and 22% respectively. Thus it was found that the transient times for the various substrates were inversely proportional to the percentage of reduced species that desorbs. The case of outer sphere electron transfer was also considered where the superoxide radical formed does not adsorb on the disc but undergoes side reactions in the near disc environment. Thus, the superoxide radical detected at the ring was thought to be the unreacted superoxide. The χ (%) data showed that 88%, 83% and 81% of the superoxide radicals produced on or near the Pt, Au and GC electrodes respectively reacted further. This was found to follow the same reactivity trend as reported elsewhere.43 Thus, the analysis presented herein adequately explains the cases of both electron transfer to adsorbed oxygen on the electrode surface and also possible outer-sphere electron transfer. Further analysis of the impact of the disc material on the adsorption of the reaction intermediates using binding energies calculated from DFT is discussed in section Electrochemical reaction kinetics.

Koutecky-Levich plots.—The characteristic LSVs obtained using the rotating ring-disc electrode were well described by the classic Koutecky-Levich equation. The Koutecky-Levich equation describes the disc current of an RRDE system if the reaction kinetics is first-order with respect to dissolved oxygen. In that case, the observed currents at the rotating disk electrode are related to the rotation rate ω by the following equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_L} = \frac{1}{i_k} + \frac{1}{B \sqrt{\omega}} \quad [2]$$

Figure 2. Cyclic Voltammograms of O₂ saturated 0.1 M TEAClO₄ in DMSO on Glassy Carbon (GC), Pt and Au working electrodes. The scan rates are: 50 mVs⁻¹ (dashed line), 100 mVs⁻¹ (dotted line), 500 mVs⁻¹ (solid line). The background current in an Ar-saturated condition is shown as a solid line.
Figure 3. (a) Rotating ring-disk voltammograms on (i) Glassy carbon (GC), (ii) Pt and (iii) Au disks recorded at a scan rate of 5 mVs$^{-1}$ in O$_2$ saturated 0.1 M TEAClO$_4$ in DMSO. Ring currents recorded with the Pt ring held at 3.35 V vs Li/Li$^+$. The solid lines and dashed lines indicate cathodic and anodic scans respectively; (b) Cyclic Voltammograms of O$_2$ saturated 0.1 M TEAClO$_4$ in DMSO on (i) Glassy carbon (GC), (ii) Pt and (iii) Au disks at a scan rate of 5 mVs$^{-1}$.

where $i_k$ is the kinetic current (i.e., the maximum current attainable in the absence of any mass-transport limitation), $i_L$ is the mass transport limiting current and $B$ is a constant. They are given by:

$$i_k = \frac{i_L}{i_L - i}$$

$$B = 0.62 nFAD^2\nu^{-1/2}C_b$$

where $F$ is 96,485 C mol$^{-1}$, $n$ is the number of electrons in the overall reaction, $A$ is the disc area, $D$ is the diffusion coefficient of O$_2$, $C_b$ is the bulk concentration of O$_2$, $\nu$ is the kinematic viscosity, and $\omega$ is the rotation rate in revolutions per minute (rpm). Thus a plot of $1/i$ vs. $1/\sqrt{\omega}$ for various potentials would be expected to yield straight lines with intercepts corresponding to $i_k$ and the slopes yielding the $B$ values. Knowledge of $D$, $C_b$ and $\nu$ for a given electrolyte along with the disc area enables the calculation of the number of electrons. In the present system, $D = 3.11 \times 10^{-5}$ cm$^2$s$^{-1}$, $C_b = 2.1$ mM cm$^{-3}$ and $\nu = 9.57 \times 10^{-6}$ cm$^2$s$^{-1}$. The disc currents showed three distinct behaviors across the voltage window for reduction. Initially, the currents were independent of the rotation rate in a kinetic limited regime where the $i_k$ term in Equation 2 was zero. At more cathodic potentials, the currents entered a mixed-control regime where they began to display a rotational dependence. Finally, in the mass-transport controlled regime, the currents displayed the $i_k \propto \omega$ relationship characteristic with the $1/i_k$ intercept approaching zero. The mixed control regime was the region of interest for calculating the number of electrons using Equation 4. The Koutecky-Levich plots are shown in Fig. 4i. In the mixed control regime between 2.3 V and 2.7 V, the plots were seen to be almost parallel and showed close to one electron transfer within the experimental error of 10%. At 2.3 V the intercept was seen to be almost zero, indicative of the beginning of the mass-transport limited regime. In the kinetic controlled regime, the rate constant of the disc reaction maybe calculated from the intercept of the K-L plots using the relation $i = nF AKC_b$.

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Tafel plots.—The Tafel equation was used to elucidate the rate determining step in the multi-step reduction reaction occurring on the disc. The Tafel equation relates the kinetic current and the potential in the kinetic limited regime of the surface electrochemical reaction. It is as follows:

$$\eta = a + b \log (i_k)$$
Figure 4. (i) Koutecky-Levich plots for oxygen reduction on (a) glassy carbon, (b) Pt, (c) Au in O2 saturated 0.1 M TEAClO4 / DMSO solution during the anodic scan. The error bars show a 5% standard error.; (ii) Representative Tafel plots for oxygen reduction at 900 RPM on (a) glassy carbon, (b) Pt, (c) Au in O2 saturated 0.1 M TEAClO4 / DMSO solution during the anodic scan.

Where,

\[ a = \frac{2.3RT}{\alpha F} \log i_0 \]  \hspace{1cm} [6]

\[ b = -\frac{2.3RT}{\alpha F} \]  \hspace{1cm} [7]

Here, \( \alpha \) is the transfer coefficient and \( i_0 \) is the exchange current density in mA cm\(^{-2}\). The variable \( b \) in Equation 7 is the Tafel slope.

Fig. 4ii depicts the mass-transport corrected Tafel plots constructed from the disc current data shown in Fig. 3a. The kinetic currents were obtained from Equation 3. All three disc materials showed a Tafel slope of 120 mV dec\(^{-1}\) which was indicative of the first electron transfer step being rate determining, as would be expected for the formation of the superoxide radical. The 120 mV dec\(^{-1}\) Tafel slope was observed for over two orders of magnitude of the kinetic current which was indicative of true Tafel behavior.

Table 1. Representative comparison of Oxygen reduction reaction rate constants calculated by the Kinetic model presented herein and the intercepts of the classical Koutecky-Levich (K-L) plot, in the kinetic region (2.7 V vs Li/Li\(^+\)). The oxygen concentration was taken to be \( C_b = 2.1 \text{ mM cm}^{-3}\).

| Substrate | \( i_k \) (mA cm\(^{-2}\)) | K (cm s\(^{-1}\)) (from K-L plot) | K (cm s\(^{-1}\)) (from kinetic model) |
|-----------|------------------|-------------------------------|----------------------------------|
| GC        | 0.213            | 1.05 \times 10^{-3}          | 1.29 \times 10^{-3}             |
| Pt        | 0.568            | 2.80 \times 10^{-3}          | 3.25 \times 10^{-3}             |
| Au        | 0.447            | 2.21 \times 10^{-3}          | 1.70 \times 10^{-3}             |

N\((i/i_R) \) vs \( \omega^{-1/2} \) plots.—Damjanovic et al.\(^{25}\) provide one of the first, comprehensive discussion of the use of N\((i/i_R) \) vs \( \omega^{-1/2} \) plots to study the side reactions using a RRDE. This treatment was later used in the works of Wroblowa et al.\(^{22}\) and Hsueh et al.\(^{21}\) to study the ORR in aqueous systems.

The case of an ideal system with no side reactions or loss of products was considered where the ring current would be equal to the collection efficiency of the system times the disc current. This implied that, subject to the physical constraint of the collection efficiency of the system, all the reduction products would be oxidized at the ring.
Thus, a plot of \( N(i_{D}/i_{R}) \) vs \( \omega^{-1/2} \) would result in a single straight line and the plots at various potentials would overlap. The occurrence of side or parallel reactions and the deposition of the product on the disc or its precipitation would result in deviation from the ideal described previously.

The second case examined was that of disc products that react further. In the absence of convection (no rotation) the ring current would depend on the rate of product desorption and diffusion to the ring which would be independent of the potential and hence the \( N(i_{D}/i_{R}) \) vs \( \omega^{-1/2} \) plots converge to a single intercept value at \( \omega^{-1/2} = 0 \). It was seen that as the rotation rate increased, the movement of product to the ring was no longer transport limited and hence the \( N(i_{D}/i_{R}) \) plots diverged from their common intercept.

In the case of parallel reactions where the products do not react further, the net rate of reaction was thought to be potential dependent as each reaction would be a function of potential. But as the products do not react further, the concentration in the near electrode environment would be only a function of the rate of desorption and transport to the ring. Thus the \( N(i_{D}/i_{R}) \) vs \( \omega^{-1/2} \) plots would be a series of straight lines parallel to the x-axis and the intercept would be a function of potential.

A fourth case analyzed was that of parallel reactions producing products that can react further. Similar arguments as for the third case were found to apply. But now the \( N(i_{D}/i_{R}) \) vs \( \omega^{-1/2} \) plots were expected to show a dependency on the convection rate due to the competition between further reaction of the product and its transport to the ring.

The \( N(i_{D}/i_{R}) \) vs \( \omega^{-1/2} \) plots shown in Fig. 5 were found to be of the fourth case. The plots values were taken from the mass transport limited region as then the transport and kinetics are at steady state. These plots indicated that the superoxide radical does undergo further reaction. The reaction was thought to consist of nucleophilic reaction with DMSO and reaction with any traces of water present. Further studies with techniques such as in-situ XPS are required to identify the exact products produced.

\[
i_{L}/(i_{L}-i_{D}) \text{ vs. } \omega^{-1/2} \text{ plots.—Following the work of Wroblowa et al.}^{22} \text{ which was extended by Hsueh et al.}^{21} \text{ the rate constants for the formation of the superoxide radical were calculated. The equations given in the above studies were adopted for the present case as follows:}
\]

\[
\frac{i_{L}}{i_{L}-i_{D}} = 1 + \frac{k_{1}}{Z} \omega^{-1/2} \quad [8]
\]

Where \( Z = 0.62 D_{O_{2}}^{-1/2} \nu_{DMSO}^{-1/2} \) in which \( D_{O_{2}} \) represents the diffusion coefficient of oxygen and \( \nu_{DMSO} \) is the viscosity.

Thus the slope of the \( i_{L}/(i_{L}-i_{D}) \) vs. \( \omega^{-1/2} \) plots shown in Fig. 6 were used to calculate the rate constants for superoxide formation. The model predicted that the intercept was 1 and this was borne out in the case of all the substrates. The model was applied in the kinetic region of the disc voltammograms of Fig. 3a. Beyond the kinetic region the model would be unphysical as it would track the disc current increase and predict a constantly rising rate constant whereas the increase in the disc current is attributable to the improved mass transport with the kinetics reaching its steady state.

**Electrochemical reaction kinetics.—** The rate constants calculated from the model described in section \( i_{L}/(i_{L}-i_{D}) \) vs. \( \omega^{-1/2} \) plots are shown in Fig. 7. These rate constants were compared with rates calculated from the classical Koutecky-Levich equation and found to be in good agreement as shown in Table 1. The rate constants were seen to increase in the order \( \text{GC} < \text{Au} < \text{Pt} \) with the values at the start of the mixed control region being 0.0013 cm s\(^{-1}\), 0.0018 cm s\(^{-1}\), 0.0034 cm s\(^{-1}\) respectively. The predicted first electron transfer activity of the carbon basal plane, Au (111) plane and Pt (111) plane from DFT calculations\(^{28} \) was compared to the experimental values and the trends were found to be in close agreement. The experimental values were for multi-crystalline electrodes but the electrochemical reactions tend to be dominant on a single plane and thus the DFT models of the most active crystal plane was seen to be in close agreement with experiments. It was hypothesized in Sankarasubramanian et al.\(^{29} \) that since the maximal surface activity is a function of the intermediate binding energy, the binding energies could serve as a good predictor of surface activity. It was seen from the calculated rate constants and the onset potentials of the ORR shown in Fig. 8 that the predicted activities of the substrates closely match experimental trends. Further, the relation between the activity, the ORR onset potential and the percentage of disc species that desorbs was examined. The \( \chi \) (%) served as an indicator of the reduced species binding energy, the degree of side reactions and it was found that the theoretical activity and the experimental onset potentials showed a linear relationship with \( \chi \) within experimental and modeling error of 10% as seen from Figs. 8ii and 8iii. Finally, the experimental data was found to closely fit the kinetic model predictions which are predicated on the reaction substrate being unchanged. Thus, it can be concluded that any side-reaction product deposits had little or no effect on the kinetics measured herein.

![Figure 5](image-url) N(iD/iR) vs \( \omega^{-1/2} \) plots for oxygen reduction on (i) glassy carbon, (ii) Pt, (iii) Au in O\(_2\) saturated 0.1 M TEAClO\(_4\)/DMSO solution. The error bars show a 5% standard error.
Figure 6. \( i_L/(i_L-i_D) \) vs. \( \omega^{-1/2} \) plots for oxygen reduction on (i) glassy carbon, (ii) Pt, (iii) Au in \( \text{O}_2 \) saturated 0.1 M TEAClO\(_4\) / DMSO solution. The error bars show a 10% standard error.

Figure 7. Rate constants for the one electron oxygen reduction reaction to form the superoxide radical in the kinetic controlled region. The values are calculated from the slopes of the \( i_L/(i_L-i_D) \) vs. \( \omega^{-1/2} \) plots depicted in Figure 8. The error bars show a 10% standard error.

Figure 8. (i) Representative ORR polarization curves on GC, Pt, and Au in \( \text{O}_2 \) saturated 0.1 M TEAClO\(_4\) in DMSO at a scan rate of 5 mV s\(^{-1}\) and RDE rotation rate of 1600 RPM; (ii) Correlation between surface activity and percentages of superoxide radicals detected at ring; (iii) Correlation between ORR onset potential and percentages of superoxide radicals detected at ring. The error bars show a 10% standard error. The DFT model surface activity values were taken from Reference 29.

Conclusions

The kinetics of the oxygen reduction reaction in 0.1 M TEAClO\(_4\)/DMSO was studied using Rotating Ring-Disk voltammetry. The cyclic voltammetry peaks for reduction of oxygen and subsequent oxidation of the superoxide radical was found to show a voltage difference that is possibly indicative of irreversibility and in agreement with reports in the literature that observe high overpotentials for charge and discharge. Only a portion of the superoxide radicals produced on or near the disc was detected at the ring indicating that both further electrochemical and chemical reduction of the superoxide radicals in the presence of Li\(^+\) or other alkali metal ions could be expected. This was also an indicator of the occurrence of possible nucleophilic reactions between the superoxide radical and the electrolyte. The disc voltammograms were analyzed using standard kinetic models and it was seen that the superoxide radical undergoes further reaction, possibly with the DMSO solvent. The rate constants for the formation of the...
superoxide radical were calculated and found to be in close agreement with prior predictions for the first electron transfer form DFT calculations. Further, it was seen that the hypothesis of the intermediate binding energy being a good predictor of substrate activity was borne out and seems to point to a possible screening method for potential catalytic surfaces for preferential electrochemical reduction of oxygen.

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