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Redox Probing Study of the Potential Dependence of Charge Transport Through Li$_2$O$_2$

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* Supporting Information

ABSTRACT: In the field of energy storage devices the pursuit for cheap, high energy density, reliable secondary batteries is at the top of the agenda. The Li–O$_2$ battery is one of the possible technologies that, in theory, should be able to close the gap, which exists between the present state-of-the-art Li-ion technologies and the demand placed on batteries by technologies such as electric vehicles. Here we present a redox probing study of the charge transfer across the main deposition product lithium peroxide, Li$_2$O$_2$, in the Li–O$_2$ battery using outer-sphere redox shuttles. The change in heterogeneous electron transfer exchange rate as a function of the potential and the Li$_2$O$_2$ layer thickness (∼depth-of-discharge) was determined using electrochemical impedance spectroscopy. The attenuation of the electron transfer exchange rate with film thickness is dependent on the probing potential, providing evidence that hole transport is the dominant process for charge transfer through Li$_2$O$_2$ and showing that the origin of the sudden death observed upon discharge is due to charge transport limitations.

1. INTRODUCTION

The Li–O$_2$ battery is, in theory at least, a prime candidate for the ultimate generation of beyond Li-ion chemistries, as the theoretical specific energy and energy density for a fully charged battery is 11 400 Wh/kg and 6080 Wh/L, respectively. In the Li–O$_2$ battery, the net electrochemical reaction is 2Li + O$_2$ ⇌ Li$_2$O$_2$, with the forward reaction corresponding to discharge and the reverse direction to charge. Realizing a practical specific energy of even 1000 Wh/kg with this cell chemistry still requires tremendous efforts in surmounting existing challenges.

One of the pressing problems is the lack of a fully stable electrolyte during charge and discharge, and this severely limits cycle life. Another challenge is the development of a chemically and electrochemically stable cathode since carbon has been shown to not be fully stable. In addition, the charging overpotentials are quite high, although the reasons for this are still controversial. Finally, the discharge capacity is much smaller than anticipated from complete filling of the pore volume of the cathode. To understand the last challenge requires knowledge of the mechanisms of deposition of the main discharge product, Li$_2$O$_2$.

In general, Li$_2$O$_2$ forms as either toroidal-shaped particles or conformally deposited continuous and dense films on the cathode surface and are referred to as either the solution- or the surface-based mechanism. While the surface electrochemistry always occurs on the cathode, the solution mechanism becomes important when the intermediate LiO$_2$ is soluble in the electrolyte. The solubility is described well by the electrolyte’s donor and acceptor numbers as descriptors for describing the free energy of solution of the Li$^+$ ion and superoxide, O$_2^-$, respectively. Ultimately the reaction Li$^+$ + O$_2^-$ ⇌ LiO$_2$ followed by 2LiO$_2$ → Li$_2$O$_2$ + O$_2$ takes place to form toroids. The extent to which these mechanisms dominates the cell electrochemistry has a significant impact on the discharge capacity as higher capacities have been reported when toroids are formed. It was shown by Aetukuri et al. that in a rigorously anhydrous electrolyte based on 1,2-dimethoxyethane as the solvent no toroids were formed unless some H$_2$O is added. It was suggested that this solvent does not have a high enough donor number and acceptor number to give significant solubility of LiO$_2$. On the other hand, higher donor number anhydrous solvents can produce toroids.

However, independent of the mechanism eventually a sudden drop in potential (sudden death) occurs from the increasing ohmic losses through the formed Li$_2$O$_2$. It has been argued that the origin of this sudden death is due to charge transport through the discharge product Li$_2$O$_2$ as Li$_2$O$_2$ is a high-band-gap insulator. Viswanathan et al. suggested that sudden death occurs when a hole tunneling current
through Li₂O₂ films cannot support the electrochemical current any longer. They studied the charge transport through various film thicknesses of Li₂O₂ using a ferrocene/ferrocenium redox probe and analyzed the results using a first-principles charge transport model.

In this paper, we present a more extensive redox probing study of the electron conduction through thin and dense Li₂O₂ layers on glassy carbon electrodes. We set out to expand on the work by Viswanathan et al. by investigating the potential dependence of the attenuation of charge transfer through the Li₂O₂ layer in order to shed more light on the mechanism of this important process. Three different outer-sphere redox shuttles were used to probe the charge transport through Li₂O₂ at three different potentials, corresponding closely to the standard reduction potential of each redox couple. The selected redox shuttles are cobaltocene/cobaltocenium ([Co(Cp)₂]⁻/⁺), decamethylferrocene/ferrocenium ([Fe(DMCp)₂]⁻/⁺), and ferrocene/ferrocenium ([Fe(Cp)₂]⁻/⁺). These redox shuttles were used since (i) they are relatively stable and known to display facile interfacial electron exchange kinetics, yielding a reversible electrochemical response, and (ii) as illustrated in Figure 1, they ensure that a wide potential window could be probed relative to the valence (VB) and conduction band (CB) of the wide band gap of Li₂O₂. The band gap of Li₂O₂ has been estimated to lie within 5.15–6.37 eV, and as the VB of Li₂O₂ is only ~0.4 V higher than the Fermi level, the CB must therefore lie at very high energies vs Li⁰, as sketched in Figure 1. The alignment of the VB relative to the Li⁰⁰ potential is based on that suggested in refs 23 and 24.

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2. EXPERIMENTAL SECTION

2.1. Materials. Bis(trifluoromethane)sulfonamide lithium salt (LiTFSI), tetrabutylammonium perchlorate (TBAClO₄), [Fe(Cp)₂]⁻, [Fe(DMCp)₂]⁻PF₆⁻, [Co(Cp)₂]⁻, [Co(Cp)₂]⁺PF₆⁺, [Fe(DMCp)₂]⁺, dichloromethane, trifluoroacetic acid, ammonium hexafluorophosphate (99.99%), acetonitrile, and 4 Å molecular sieves were purchased from Sigma-Aldrich. 1,2-Dimethoxyethane (DME) was purchased from BASF and dried over 4 Å molecular sieves that had been dried at 230 °C under vacuum, inside a glovebox. [Fe(DMCp)₂]⁺PF₆⁺ was, to the best of our knowledge, not commercially available and therefore synthesized. This work is reported in the Supporting Information, Figure S1.

2.2. Electrochemical Experiments. All electrochemical investigations where conducted at 25 °C, and the electrochemical cells were assembled in an Ar-filled glovebox with O₂ and H₂O levels maintained below 2 ppm. Electrochemical cells were assembled with four working electrodes, a Pt counter electrode, and a dual-reference electrode consisting of a double-junction Ag/0.01 M AgNO₃—1 M LiTFSI—DME//1 M LiTFSI—DME// in parallel with a 0.1 μF capacitor connected to a second Pt wire in solution. This reference electrode maintains a stable dc potential at all times from the Ag/AgNO₃ part and thanks to the high-frequency bypass Pt-wire makes it possible to obtain high-quality electrochemical impedance also at high (f > ~100 Hz) frequencies. Use of a similar RE has previously been reported in refs 27–29. All current densities were calculated using the geometric area of the respective electrode. The electrolyte was 1 M LiTFSI—DME, where LiTFSI was dried in vacuum at 180 °C for 12 h. The cell contained three (d = 1.6 mm) working glassy carbon (GC) disk embedded electrodes and one (d = 1.6 mm) Au disk embedded electrode in polyether ether ketone (PEEK) resin from Bio-Logic, which were all polished using aqueous suspensions of 0.05 μm aluminum oxide (MicroPolish, Buehler). After assembly, the electrochemical cell was transferred out of the glovebox with minimal exposure to ambient conditions, placed in a Faraday cage, and flushed with O₂ or Ar that passed through 4 Å molecular sieves followed by dried DME before entering the cell to minimize water impurities. Increases in the H₂O and O₂ levels were monitored by examining the cyclic voltammogram of an Au electrode immersed in the electrolyte, and experiments with increasing levels of H₂O were discarded. All electrochemical experiments were performed using a SP-200 Bio-Logic potentiostat or a Gamry REF600.

The diffusion coefficients of [Co(Cp)₂]⁻/⁺, [Fe(DMCp)₂]⁻/⁺, and [Fe(Cp)₂]⁻/⁺ in 1 M LiTFSI—DME were determined by using the Randles-Sevcik method on a (d = 1.6 mm) GC electrode. These experiments were conducted in Ar-saturated electrolyte using the previously described cell.

Li₂O₂ was deposited in O₂-saturated 1 M LiTFSI—DME with a continuous flow of dry O₂ as atmosphere. The deposition was performed galvanostatically at a current density of 2.5 μA/cm². The electrodes were discharged sequentially to a given depth of discharge (~Li₂O₂ film thickness). Subsequently, dissolved oxygen was removed from the electrolyte by purging the
electrolyte with Ar until O₂ could no longer be detected on the Au electrode. A blanket of Ar was maintained over the solution after purging. Then a 1 mM stock solution of each redox shuttle pair, with a supporting 1 M LiTFSI–DME electrolyte, was added, and subsequently, the cell was purged again with Ar to ensure inert conditions. The concentration of the redox shuttle in solution was determined by the Au electrode by the peak current in a cyclic voltammogram, which ranged from 0.02 to 0.05 mM. The charge transport through Li₂O₂ deposited on each GC electrode, was probed by measuring the charge-transfer resistance \( R_{CT} \) of each redox shuttle as a function of the depth of discharge (i.e., the Li₂O₂ film thickness) by performing electrochemical impedance spectroscopy at \( E_{1/2} \) of the redox shuttle in the electrolyte. Electrochemical impedance spectroscopy (EIS) was measured using an ac amplitude of 10 mV over the frequency range from 100 kHz to 1 Hz with 12 points/decade and 2 cycles/frequency. The procedure was conducted for each of the three redox shuttles. A sketch of the experimental setup is given in Figure 2.

The electrolyte is crucial as multiple reports have shown that water is a key reactant in the formation of Li₂O₂. To ensure a pure electrolyte, a small amount of Li₂O₂ was added to the electrolyte with Ar until O₂ could no longer be detected on the Au electrode. A blanket of Ar was maintained over the solution after purging. Then a 1 mM stock solution of each redox shuttle pair, with a supporting 1 M LiTFSI–DME electrolyte, was added, and subsequently, the cell was purged again with Ar to ensure inert conditions. The concentration of the redox shuttle in solution was determined by the Au electrode by the peak current in a cyclic voltammogram, which ranged from 0.02 to 0.05 mM. The charge transport through Li₂O₂ deposited on each GC electrode, was probed by measuring the charge-transfer resistance \( R_{CT} \) of each redox shuttle as a function of the depth of discharge (i.e., the Li₂O₂ film thickness) by performing electrochemical impedance spectroscopy at \( E_{1/2} \) of the redox shuttle in the electrolyte. Electrochemical impedance spectroscopy (EIS) was measured using an ac amplitude of 10 mV over the frequency range from 100 kHz to 1 Hz with 12 points/decade and 2 cycles/frequency. The procedure was conducted for each of the three redox shuttles. A sketch of the experimental setup is given in Figure 2.

Figure 2. Schematic diagram of the experimental setup using \([\text{Co(Cp)}_2]^{0/+}\) to probe the charge transfer at three different electrodes, with each a certain thickness of Li₂O₂. WE stands for working electrode, CE for counter electrode, and RE for reference electrode.

3. RESULTS AND DISCUSSION

3.1. Electrolyte Water Content Monitoring. Ensuring a water-free environment for any nonaqueous metal–air system is crucial, as multiple reports have shown that water and different anions will replace DME in the solution shell of Li⁺, thus increasing the capacity of the cell, not only by the extra faradic route of water reduction but more importantly by activating a solution-based mechanism for Li₂O₂ formation that can be used for this purpose. In this study, a Au electrode was used to monitor changes in the water content (and other electrochemically active impurities) of the electrolyte.

3.2. Voltammetry of the Redox Shuttles. The half-wave potentials, reversibility, and diffusion coefficients of the redox shuttles used in this study were determined using cyclic voltammetry. The diffusion coefficients were used to make concentration determinations in conjunction with the redox probing experiments reported later in this manuscript. The voltammetry of the redox shuttles in 1 M LiTFSI in DME was studied using GC electrodes. All voltammograms where recorded in Ar-saturated 1 M LiTFSI–DME and have been IR corrected. Note that only one of the redox shuttles was present in solution at any given time.

Figure 3. Cyclic voltammograms recorded at a scan rate of 100 mV/s of the three different redox shuttles, \([\text{Co(Cp)}_2]^{0/+}\), \([\text{Fe(DMCp)}_2]^{0/+}\), and \([\text{Fe(Cp)}_2]^{0/+}\), and including a blank scan. All four voltammograms were recorded in Ar-saturated 1 M LiTFSI–DME and have been IR corrected. Note that only one of the redox shuttles was present in solution at any given time.

The half-wave potentials, reversibility, and diffusion coefficients of the redox shuttles used in this study were determined using cyclic voltammetry. The diffusion coefficients were used to make concentration determinations in conjunction with the redox probing experiments reported later in this manuscript. The voltammetry of the redox shuttles in 1 M LiTFSI in DME was studied using GC electrodes. All voltammograms where recorded in Ar-saturated 1 M LiTFSI–DME and have been IR corrected. Note that only one of the redox shuttles was present in solution at any given time.

The electrochemical reversibility of the three redox shuttles was evaluated in the scan rate interval of 10 to 1000 mV/s based on the peak potential separation between the anodic and the cathodic peak potentials \( \Delta E_p \). Figure 4 depicts the voltammograms of \([\text{Co(Cp)}_2]^{0/+}\) as a function of scan rate \( \nu \), and the Randles-Sevcik plot \( (I_{peak} \text{ vs } \nu^{1/2}) \) was used to determine the diffusion coefficients for the two species, e.g., the neutral and positive species of the redox shuttle in solution. For \([\text{Co(Cp)}_2]^{0/+}\), \( \Delta E_p \) ranged from 51 to 64 mV with an average of 57.14 ± 4.43 mV, which is in close agreement with the theoretical value of 56.50 mV for a one-electron process. The corresponding plots for \([\text{Fe(DMCp)}_2]^{0/+}\) and \([\text{Fe(Cp)}_2]^{0/+}\) are illustrated in Figure S3, where \( \Delta E_p \) ranged from 62 to 72 and 61 to 72 mV, respectively. A detailed report of the electrochemical reversibility is given in Tables S1–S3.

The diffusion coefficients of \([\text{Co(Cp)}_2]^{0/+}\), \([\text{Fe(DMCp)}_2]^{0/+}\), and \([\text{Fe(Cp)}_2]^{0/+}\) were determined by the Randles-Sevcik equation, eq 1, that describes the relationship between peak currents \( I_p \) and scan rate \( \nu \) of a reversible electrochemical reaction under semi-infinite linear diffusion conditions.
Figure 4. (A) Cyclic voltammogram of [Co(Cp)]0/1 in 1 M LiTFSI–DME on a GC macroelectrode at ν from 10 to 1000 mV/s. (B) Randles-Sevcik plot of peak current vs ν1/2 for the voltammograms in A.

\[
I_p = 0.4463 \frac{F^3}{RT} \cdot n^{3/2} \cdot A \cdot D_{ox}^{1/2} \cdot C_{ox} \cdot \nu^{1/2}
\]

where \( n \) is the number of electrons, \( F \) is Faraday’s constant, \( A \) is the electrode area, \( R \) is the gas constant, and \( T \) is the temperature, while \( C_{ox} \) and \( D_{ox} \) are the bulk concentration and diffusion coefficient of the species, respectively. The presented diffusion coefficients in Table 1 were determined using the Randles-Sevcik equation. The presented diffusion coefficients for each redox shuttle could be calculated.

Table 1. Diffusion Coefficients for the Six Redox Shuttles Used to Probe the Charge Transfer Through Li2O2 on GC Electrodes in 1 M LiTFSI–DME at 25 °C

<table>
<thead>
<tr>
<th>Redox Species</th>
<th>Diffusion Coefficient [cm²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(Cp)]0/1</td>
<td>4.83 × 10⁻⁶</td>
</tr>
<tr>
<td>[Co(Cp)]0</td>
<td>5.61 × 10⁻⁶</td>
</tr>
<tr>
<td>[Fe(DMCp)]0/1</td>
<td>6.67 × 10⁻⁶</td>
</tr>
<tr>
<td>[Fe(DMCp)]0</td>
<td>6.97 × 10⁻⁶</td>
</tr>
<tr>
<td>[Fe(Cp)]0</td>
<td>6.54 × 10⁻⁶</td>
</tr>
<tr>
<td>[Fe(Cp)]0/1</td>
<td>7.90 × 10⁻⁶</td>
</tr>
</tbody>
</table>

All diffusion coefficients are in the range of 5–8 × 10⁻⁶ due to their relatively similar size, and all positively charged forms have lower values compared to their respective neutral forms due to the increased drag from the TFSI⁻ counterion cloud making the diffusion of the positively charged species diffusion slower. The lowest diffusion coefficients were observed for [Co(Cp)]0/1, which was approximately 18% lower than that of [Fe(Cp)]0/1, which is in line with observations made in ionic liquids reported by Rogers et al.³² To the best of our knowledge, no previous reports are available on the diffusion coefficients of these redox shuttles in 1 M LiTFSI–DME, so in order to verify the diffusion coefficients, one of the most studied redox shuttles, [Fe(Cp)]0/1, was used for comparison with literature values in different nonaqueous solvents. In Figure 5 the diffusion of [Fe(Cp)]0/1 is illustrated as a function of the viscosity of the solution, and here a power decay is observed where the diffusion decreases as the viscosity increases. The diffusion coefficient of [Fe(Cp)]0/1 measured in 1 M LiTFSI–DME aligns into this relationship, thus supporting the validity of the values reported in Table 1.

3.3. Redox Probing of Li2O2 Surfaces. To investigate the limiting charge transport mechanism as a function of the Li2O2 thickness, the charge-transfer resistances of the redox shuttles were measured using EIS. Multiple authors³³,¹³,¹⁷ have reported that only conformal films of Li2O2 grow in strictly anhydrous 1 M LiTFSI–DME, especially on flat small surface area GC disks. Since we carefully excluded water in our experiments, we claim that only dense thin films of Li2O2 are formed on the GC in our experiments. Our discharge capacities are also similar to those of Viswanathan et al.¹⁸ in anhydrous DME, indicating that no toroids or higher capacity structures form. The GC electrodes were therefore coated with various thicknesses of Li2O2 layers prior to the impedance measurements. This was performed by a series of galvanostatic discharges onto different GC electrodes as illustrated in Figure...
experiments with [Fe(DMCp)2]0/+ and [Fe(Cp)2]0/+ are illustrated in Figures S4 and S6, respectively. The Li2O2-coated GC electrode surfaces were probed by EIS in Ar atmosphere at E1/2 of each of the redox shuttles. The Nyquist plots for three different depth of discharges using [Co(Cp)2]0/+ are illustrated in Figure 7, while the Nyquist plots for [Fe(DMCp)2]0/+ and [Fe(Cp)2]0/+ are illustrated in Figures S5 and S7.

These figures illustrate the R_CT varies in the impedance spectra as a function of depth of discharge (∼Li2O2 thickness) and how it greatly increases close to sudden death. To illustrate the dependency of R_CT as a function of depth of discharge (∼Li2O2 thickness), we were interested in quantifying the rate of electron transfer through Li2O2 using the heterogeneous rate constant (kθ) since this also made it possible to correct the measured R_CT for concentration variations of the redox shuttle in solution. These variations occurred since 5–6 GC electrodes were needed to obtain a sufficient mapping of the discharge. The electrochemical cell, as sketched in Figure 2, contained only three GC electrodes; thus, two separate experiments were performed, giving rise to small concentration deviations between the two experiments.

The R_CT was determined by fitting a Randles equivalent circuit to the data that describes a heterogeneous charge transfer and semi-infinite linear diffusion, and the complex nonlinear least-squares fitting was carried out using a software package written in Python.35 Data validation was carried out by using the linearized Kramers–Kronig test (KK) suggested by Boukamp.36 All data used for determination of R_CT here displayed residuals of less than ±1% using this test, indicating good adherence to the requirements of causality, linearity, stability, and finiteness of the data. The resulting Nyquist and Bode plots and the equivalent circuit model used are shown in Figure 8 for [Co(Cp)2]0/+, while the Nyquist plots for [Fe(DMCp)2]0/+ and [Fe(Cp)2]0/+ are illustrated in Figures S5 and S7.

Figure 8 depicts the EIS spectrum for the 15.97 mC/cm² discharged electrode with [Co(Cp)2]0/+ as the redox shuttle and the corresponding fitted equivalent circuit, where it is evident that the model describes charge transfer and the following diffusion well. At pristine electrodes the R_CT of the three redox shuttles could not be detected by EIS as the spectra were completely dominated by the diffusion impedance. In fact, these outer-sphere redox shuttles have very fast heterogeneous exchange rate constants causing the e⁻ transfer to be so rapid that the electronics used in measuring these systems simply is not fast enough. This is likely the reason for the lack of data in the literature of the kθ on pristine electrodes for these redox shuttles. A few authors have reported kθ’s at pristine electrode of larger and more sluggish redox shuttles, such as the 7,7,8,8-tetracyanoquinodimethane, using specialized higher harmonic techniques or steady-state voltammetry from microelectrodes.37,38 A similar study using steady-state voltammetry recorded with a microelectrode was conducted here in the hope of obtaining kθ’s of the three redox shuttles at pristine surfaces, but as Aoki et al.37 also concluded, the solution resistance and currents related to double-layer charging of the microelectrode were too great to obtain reliable results and therefore not included here. Aoki et al. suggests that [Fe(Cp)2]0/+ and similar molecules have kθ’s greater than 10 cm/s at pristine Pt surfaces.37 Assuming kθ of 10 cm/s, we can estimate that, as described in the SI, the characteristic frequency for the oxidation/reduction of [Co(Cp)2]0/+ is approximately 5 MHz and well beyond the practical frequency range of our equipment.

To illustrate the dependency of the charge transport mechanism as a function of depth of discharge (∼Li2O2 thickness) we determined the kθ for electron exchange between the glassy carbon electrode and the different redox shuttles in solution with Li2O2 sandwiched in between, Figure 1. The relationship between kθ and R_CT is given in eq 2.

$$k^\theta = \frac{R \cdot T}{n^2 \cdot F^2 \cdot R_\text{CT} \cdot A \cdot c^\text{ox1} \cdot c^\text{red} \cdot \alpha}$$  

The fourth working electrode in solution, Figure 2, was an Au electrode that was used to measure the concentration of each redox species in solution by cyclic voltammetry at 100 mV/s in Ar. From the peak currents it was possible to determine the precise concentrations by rearranging eq 1.
In eq 3, the determined diffusion coefficients were used in the determinations of $C_{\text{ox}}$ and $C_{\text{red}}$ and consequently the $k^0$'s. The concentration correction of the redox shuttles that was used in the calculation of $k^0$ clearly proved to be significant when compared to the exchange current density ($j_0$), which does not take $C_{\text{ox}}$ and $C_{\text{red}}$ into account. This is illustrated in Figure S8, where a shift in $j_0$ is clearly observed between two separate experiments, but it is also evident that this shift was caused by a concentration difference of $[\text{Co(Cp)}_2]^{0/+}$ between the experiments as this was corrected for by $k^0$.

The resulting plot of $k^0$'s as a function of depth of discharge and Li$_2$O$_2$ thickness illustrated in Figure 9, and here the redox shuttles acted as the charge source/sink, Li$_2$O$_2$ as the insulator, and the GC electrode as the charge source/sink.

For $[\text{Co(Cp)}_2]^{0/+}$ and $[\text{Fe(DMCp)}_2]^{0/+}$ we see an exponential decrease in $k^0$ with a discharge capacity that mirrors the exponential sudden death in the Li$^{-}$O$_2$ with discharge capacity. This shows that the origin of the sudden death is due to charge transport limitations. Since $E_{1/2}$ of $[\text{Co(Cp)}_2]^{0/+}$ and $[\text{Fe(DMCp)}_2]^{0/+}$ both are inside the band gap of Li$_2$O$_2$ as illustrated in Figure 1, electronic conduction is likely dominated by a mechanism of hole transport. This transport could be via tunneling or via thermally excited hole polarons.

We believe that tunneling is the dominant mechanism of hole charge transport in the experiments reported here since relatively high current densities are involved in the impedance measurements (>$9 \mu$A/cm$^2$) and since this mechanism fits a wide range of experimental results, e.g., the existence of discharge sudden deaths and its dependence on current and temperature, asymmetry between discharge and charge sudden death, etc. We do note, however, that additional charge transport from hole polarons can also contribute at low current densities (<1$\mu$A/cm$^2$). A very recent extended hole polaron model by Radin et al. seems to be able to fit some of the observed aspects of sudden death.

One feature that should be noted in Figure 9 is the difference in Li$_2$O$_2$ thickness/capacity between $[\text{Co(Cp)}_2]^{0/+}$ and $[\text{Fe(DMCp)}_2]^{0/+}$, with an extended discharge capacity for $[\text{Fe(DMCp)}_2]^{0/+}$. We interpret this difference as due to the very different hole transport at 0.9 and 0.05 V relative to the VB, respectively. The predictions of charge transport at 2 $\mu$A/cm$^2$ current density as a function of the Li$_2$O$_2$ film thickness from a simple semiclassical tunneling model of charge transport and based on assuming trapezoidal barrier shapes is presented in Figure 10. Therefore, the results of Figure 9 are qualitatively

\[
C_{\text{ox}} = \frac{I_p^{\text{ox}}}{D_{\text{ox}}^{1/2} \cdot A \cdot 0.4463 \cdot n^{3/2} \cdot \nu^{1/2} \cdot \left(\frac{e^1}{R \cdot T}\right)^{1/2}}.
\]

Figure 8. Nyquist plot (A) and Bode-like plot (B) for the terminal discharge capacity of 15.97 mC/cm$^2$ with $[\text{Co(Cp)}_2]^{0/+}$ in solution corresponding to the green spectrum illustrated in Figure 7. The equivalent circuit used to model and extract $R_{\text{CT}}$ is inserted into B.

Figure 9. Heterogeneous rate constant illustrated as a function of discharge capacity and Li$_2$O$_2$ thickness (thickness was calculated assuming that the Li$_2$O$_2$ grows as a dense thin film and that the surface roughness of the electrode was a factor of 2). $k^0$'s were calculated from $R_{\text{CT}}$ obtained from the EIS. The three redox shuttles were probed at their respective $E_{1/2}$ in Ar, e.g., $[\text{Co(Cp)}_2]^{0/+}$ at 2.35 V, $[\text{Fe(DMCp)}_2]^{0/+}$ at 3.2 V, and $[\text{Fe(Cp)}_2]^{0/+}$ at 3.68 V vs Li$^{0/+}$.

Figure 10. Tunneling charge transport Li$_2$O$_2$ films as a function of film thickness $d$ assuming the energy levels given in Figure 1. Since the absolute value of $k^0$ at $d = 0$ depends on the exchange current densities of the two different redox species (and is unknown), it is simply scaled to be in rough agreement with experiment.
consistent with hole tunneling. We anticipate that if hole polarons were the dominant charge transport mechanism, there should be much larger differences between the [Co(Cp)_2]^{0+/1} and the [Fe(DMCp)_2]^{0+/1} capacities (at which the charge-transfer attenuation becomes significant) since the polaron population and hence conductivity depends exponentially on the energy of the polaron relative to the VB. Since the bulk polaron energy is required to be the same as the electrochemical Fermi energy, i.e., the [Co(Cp)_2]^{0+/1} and [Fe(DMCp)_2]^{0+/1} redox potentials, we would anticipate significantly larger differences. Of course, bending at the interfaces of the thin films could lessen this effect.22

In this figure, the barrier thickness is given by a nearly uniform Li_2O_2 film thickness d (Gaussian roughness of 0.5 nm). This is in reasonable qualitative agreement with the experimental observations in Figure 9, although the difference between [Co(Cp)_2]^{0+/1} and [Fe(DMCp)_2]^{0+/1} is overemphasized. We suspect this may be due to uncertainties in the exact barrier heights for tunneling or due to contributions from hole polaron charge transport. The experiments with [Fe(Cp)_2]^{0+/1} need a different explanation. The relationship between k^0 and the thickness of Li_2O_2 (or discharge capacity) almost exhibit a linear relationship. The electronic conduction through Li_2O_2 at this potential (3.68 V vs Li^{0/1}) can therefore not be assigned to hole tunneling, since the potential of [Fe(Cp)_2]^{0+/1} (3.68 V vs Li^{0/1}) is well inside the VB of Li_2O_2 (3.25 V vs Li^{0/1}), and thereby there is no need for hole tunneling, since electron (hole) conduction though Li_2O_2 should be possible via the VB. Instead, we hypothesize that the observed relationship between k^0 and discharge capacity (~Li_2O_2 thickness), in the case of [Fe(Cp)_2]^{0+/1}, is a consequence of the increasing R_{CT} as the Li_2O_2 layer thickens but that the difference in k^0 attenuation and lack of exponential decay (which is the case for tunneling) is due to the charging potential at which [Fe(Cp)_2]^{0+/1} was probed. At this potential, Li_2O_2 was oxidized for the entire duration of the EIS measurement (approximately 3.5 min) while probing the surface. Note that, Viswanathan et al.18 suggested that [Fe(Cp)_2]^{0+/1} probed hole tunneling, but with better knowledge of energy level alignments provided here, this is unlikely. Therefore, the k^0 for [Fe(Cp)_2]^{0+/1} is a mixture of both hole transport through Li_2O_2 via some ohmic process, Li_2O_2 oxidation and possibly LiRCO_3 electrochemical formation, which has been shown to form at these potentials in this specific electrolyte.42–44

4. CONCLUSION

In this paper, we performed detailed electrochemical experiments to probe the fundamental limiting processes of e^- transfer through the main deposition product in the Li–O_2 battery, Li_2O_2. The experiments utilized three outer-sphere redox shuttles to probe the charge transfer through electrochemically grown Li_2O_2 on glassy carbon electrodes. The results show (i) the attenuation of the heterogeneous rate constants for [Co(Cp)_2]^{0+/1} and [Fe(DMCp)_2]^{0+/1} displays an exponential decay caused by hole charge transport at the potentials probed as a function of the Li_2O_2 thickness (discharge capacity) and (ii) a clear dependency on the potential probed and the Li_2O_2 thickness (discharge capacity) obtained. We suggest that this results from different hole tunneling barriers at which the charge transfer through Li_2O_2 was probed; hence, the smaller the hole tunneling barrier (or the greater the polaron/hole conductivity), the greater the thickness at which significant attenuation of the heterogeneous exchange rate takes place. The findings reported here thus further confirm that sudden death in the Li–O_2 battery occurs when the charge transport can no longer support the applied electrochemical current.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b08757.

Synthesis and characterization of [Fe(DMCp)_2]^{0+/1}, supporting figures and tables including voltammetry results of the three redox shuttles, water impurities, impact of redox shuttle concentration on j_0, and characteristic frequency for the redox shuttles on pristine electrodes (PDF)

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