Investigation of the Cathode–Catalyst–Electrolyte Interface in Aprotic Li–O2 Batteries

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ABSTRACT: Enabled by a unique integrated fabrication and characterization platform, X-ray photoelectron spectroscopy (XPS) studies reveal the formation of a thin solid electrolyte interphase (SEI) layer on a Li–O2 cathode after the first cycle. Subsequent cycling indicates that this SEI layer is very stable in terms of both chemistry and morphology, even after extensive cycling, preserving reversibility at the cathode/electrolyte interface. Remarkably, even after cell failure, replacement of the lithium anode resulted in recovery of the cycling behavior with the same cathode. These results demonstrate that chemical stabilization of the cathode/electrolyte interface promotes long-term operation of DMSO-based Li–O2 Ru-catalyzed batteries. Characterization of the Li anode surface reveals electrolyte decomposition, and a partial mechanism is proposed for the observed chemical composition of the cathode SEI. These studies are enabled by conformal deposition of a heterogeneous OER catalyst on a freestanding, binder-free, mesoporous, carbon-based Li–O2 cathode with high capacity and long-term cycling stability.

INTRODUCTION

Achieving the theoretical capacity of rechargeable Li–O2 batteries will require solutions to several key challenges.1−8 Issues including electrolyte stability, poor round trip efficiency,7 low cycle life, and limited power density are major deterrents to commercialization of Li–O2, all of which are inherently linked to the oxygen reduction reaction (ORR) during discharge and the oxygen evolution reaction (OER) during subsequent charging. Many recent works in the field feature porous carbons and cathode/catalyst composites,5,6 often addressing poor ORR performance by inducing formation of Li2O2 at potentials about 150−250 mV below the theoretical potential of the reaction; however, the inability to significantly decrease the potential of OER below the threshold of electrolyte and carbon oxidation is reported as a major barrier for the use of carbonaceous cathodes for Li–O2 batteries.8 Indeed, it has been demonstrated that some carbon-based cathodes in direct contact with Li2O2 will oxidize to carbonates at potentials higher than 3.5 V vs Li.8 Additionally, the electrolytes commonly applied to these systems will oxidize in the presence of oxygen, superoxides,9,10 and peroxides at potentials higher than 4 V.8

Heterogeneous catalysis is a demonstrated approach for addressing carbon stability. The focus of this work is to investigate how the chemical and morphological dynamics of the cathode–catalyst–electrolyte interface affect long-term cyclability of aprotic Li–O2 batteries. One system capable of addressing both OER/ORR reactions are cathodes decorated with Ru-based catalysts.11,13

A multiwalled carbon nanotube sponge (MWCNT) was the selected substrate for this study due to its high electronic conductivity, large surface area with mesoporosity, good chemical stability, and low intrinsic defect density which has been shown to greatly improve stability of carbon-based cathodes.14 Three-dimensional networks of carbon nanotubes exhibit considerable promise as mesoporous O2 electrodes15 as a result of an open structure with high surface area that is conducive to reduction product storage and diffusion of active species, particularly at significant depths of discharge. This MWCNT sponge has the added advantages of a freestanding,16 and offering extensive versatility as a scalable substrate platform for both practical and fundamental Li–O2 studies.

Despite the promise of sp2 hybridized carbon systems as cathode scaffolds for Li–O2 batteries, intrinsic defect sites are
conducive to parasitic side reactions.\textsuperscript{14} Atomic layer deposition (ALD) is a powerful mode of catalyst functionalization because the associated surface growth reactions are energetically favorable on these substrate defects (i.e., oxygenated functional groups).\textsuperscript{17,18} The ALD growth simultaneously augments cathode stability by selectively passivating defects in the MWCNT substrate while decorating the sponge with the Ru-based catalyst for enhanced ORR/OER activity.\textsuperscript{19} Chemically binding the catalyst to the substrate during atomic layer deposition may also improve long-term durability as compared to other Ru/RuO\textsubscript{2} decoration methods which have shown tendencies toward catalyst particle aggregation during cycling.\textsuperscript{20} Additionally, the excellent thickness control granted by ALD allows for conformal decoration of the cathode substrate while preserving the mesoporous structure of the sponge.

We investigated the electrochemical performance of the pristine sponge and the sponge–catalyst composites with cyclic voltammetry and capacity-limited galvanostatic cycling within set voltage windows. As expected, functionalization with either Ru or RuO\textsubscript{2} nanoparticles shows considerable improvements in ORR/OER activity as compared to the pristine sponge. Observed long-term cycling motivated chemical and morphological characterization of the interface to elucidate a mechanism for continued stability. These studies indicated the presence of a nanometric chemically and morphologically stable solid electrolyte interphase (SEI). Surprisingly, even after cell failure, healthy cycling behavior was restored after replacing the anode, reinforcing the utility of this permeable and stable SEI for achieving long-term operation.

\section*{RESULTS AND DISCUSSION}

\textbf{Characterization of the As-Deposited Cathodes.} The pristine MWCNT sponge (Figure 1a–c) is a self-assembled, freestanding, three-dimensionally interconnected framework with mesoporous morphology. The individual carbon nanotubes (CNTs) have an average diameter of ∼30 nm with 10–20 walls, as shown in Figure 1C. The inherently low defect density on the surface of the CNTs results in growth characteristic of ALD nucleation, as shown in Figure 1, in which MWCNTs are decorated with discrete nanoparticles of ruthenium (Figure 1d) or ruthenium oxide (Figure 1e) after 300 cycles of the respective ALD growth process, while the open network of the sponge is preserved. The self-limiting nature of the ALD process enables controlled nucleation of catalyst particles on the CNT with morphology/size of the particles dictated by the number of process cycles.

XPS characterization of the pristine MWCNT sponge before and after the 300-cycle Ru and RuO\textsubscript{2} ALD processes is shown in Figure 2. The sharp C 1s peak of the pristine sponge, shown in Figure 2a, is characteristic of the sp\textsuperscript{2} hybridized carbon in CNTs and shows signs of very mild oxidation and/or adsorbed oxygen with some amorphous carbon, consistent with the low density of surface defects that enable nucleation growth of ALD catalyst. After ALD, the XPS spectrum collected for the RuO\textsubscript{2} ALD process is shown in Figure 2b and is consistent with bulk RuO\textsubscript{2}.\textsuperscript{21} The presence of metallic Ru and a thin native oxidized surface layer consistent with RuO\textsubscript{2} is the result from the Ru process (Figure 2c). TEM characterization of these growth processes indicates that the mesoscale morphology of the cathode is preserved, maintaining access for transport of active species while functionalizing the sponge with controlled catalyst chemistries, enabling a direct performance comparison.

\textbf{Electrochemical Characterization in a Li–O\textsubscript{2} Cell.} Cyclic voltammetry (CV) was used as an initial diagnostic of electrocatalytic ORR/OER cathode performance and to identify a reversible voltage window of operation for galvanostatic cycling studies. The CV response of the bare sponge and the decorated MWCNT cathodes are presented in Figure 3a. For the pristine MWCNT the first cycle is plotted since after this cycle the onset of OER was shifted to significantly higher potential, possibly due to oxidation of the cathode surface.\textsuperscript{14,16,18,22,23} The CV responses of the decorated cathodes were stable for all of the 10 recorded cycles, and the fourth cycle of each measurement is plotted in Figure 3a. As obtained, the onset potentials for ORR are higher for the MWCNT/Ru cathode.

In particular, the Ru-decorated cathode demonstrates superior ORR activity, shifting the onset potential for oxygen reduction from ∼2.8 V to >2.85 V. The more prominent improvement in activity is observed during the oxygen evolution reaction, with significant increases in current obtained at much lower onset potential as compared to the pristine MWCNT, approaching the theoretical value for the OER of Li\textsubscript{2}O\textsubscript{2} (3.1 V vs Li/Li\textsuperscript{+}) at low scan rates as presented in Supporting Information Figure S2. The Ru-decorated cathode demonstrated higher reversibility than the RuO\textsubscript{2}, by recovering the charge gained during the cathodic scan at lower potentials in the anodic scan. The voltage window of the CV was extended in the MWCNT and MWCNT/RuO\textsubscript{2} cathodes to identify any additional OER peaks but was not necessary with the MWCNT/Ru due to demonstration of significant reversibility below 3.5 V. Despite the enhanced OER activity exhibited by both catalyst systems, Figure 3b shows the significant decrease in charge overpotential (∼0.3 V lower compared to RuO\textsubscript{2}) after the first discharge exhibited by the MWCNT/Ru cathode.

Two different sets of galvanostatic cycling parameters were used to investigate the long-term stability of the cathodes. We first tested the cycling stability of our ALD-Ru@MWCNT cathode with round trip cycle duration of 180 min (90 per discharge) and a current density of 200 mA g\textsuperscript{−1}. As indicated by the stable cycle profile overlay in Figure 4c, the cathode was...
able to deliver the discharge capacity for 300 cycles under these conditions (Figure 4d). While these cycling conditions suggest the stability of our cathodes under high current densities and relatively short round-trip durations, a recent investigation suggested that the absolute exposure time of the Li2O2 discharge product to DMSO is a crucial factor in the evaluation of the chemical stability of the deposited peroxides on the surface of the MWCNT.10 Accordingly, a second set of galvanostatic conditions with longer cycle durations were used to test the chemical stability of the system under extended exposure of the solvent and cathode to Li2O2 and O2− (conditions outlined in Supporting Information). The round-trip cycle duration was 64 h (32 h discharge), and full recovery of the capacity was obtained at voltages below 4 V for more than 20 consecutive cycles. The pristine MWCNT cathode demonstrated limited stability, unable to cycle with a total cell current of 20 μA with 0.1 M LiTFSI/DMSO reproducibly for more than 10 cycles before irreversibly exceeding the cycling voltage window (2−4.0 V). However, under similar conditions, the Ru-decorated cathode demonstrated a healthy cycle profile for more than 24 cycles until the voltage of the discharge exceeded the 2 V lower limit without reaching the capacity limit. Mass spectroscopy is frequently used as a mode of tracking formation and evolution of Li2CO3 as a result of parasitic side reactions in Li−O2 cells,2,8,24 which have been shown to evolve CO2 (g) during charge. Prior to failure, the cell showed no early signs of performance degradation, so we collected a mass spectrum of the cell headspace after the prolonged cycling, as shown in Supporting Information Figures S3 and S4, in an attempt to diagnose the cause of cell failure. Remarkably, oxygen was still the dominant gaseous species in the cell, and negligible amounts of CO2 or H2O were detected. The cell was then reopened inside the glovebox, and only the anode was replaced. Surprisingly, after reclosing the cell and continuing the galvanostatic cycling program, the cathode showed full recovery of the voltage profile and continued cycling with the same healthy voltage profile observed before cell failure, as shown in Figure 4b. The consistency of the voltage profile before and after anode replacement strongly suggests similar surface chemistry/electrochemistry. Similar behavior was also demonstrated with the previously discussed cathode cycled to a

Figure 2. High resolution XPS spectra of the C 1s/Ru 3d region of the (a) pristine, (b) RuO2 functionalized, and (c) Ru functionalized MWCNT foam. Red open circles indicate raw data, and blue lines show the fitted envelope. The spectra are normalized to the same arbitrary intensity. The spectrum in (a) is typical of high quality carbon nanotubes. The spectra in (b) and (c) are dominated by a signal from the Ru 3d orbital, as its photoelectron cross section is over 15 times larger than that of the C 1s. (b) supports the deposition of nearly pure RuO2 while (c) shows the deposition of metallic Ru which is covered by a thin native oxide. The “Ru4+ sat.” peak refers to a conduction band screening final state effect commonly observed in conductive ruthenium oxides.37

Figure 3. (A) Cyclic voltammetry of bare MWCNT sponge (first cycle shown) and sponges loaded with 300 cyc ALD Ru and 300 cyc ALD RuO2 (fourth CV cycles shown). The scan rate is 0.5 mV s−1. (B) Comparison of first galvanostatic charge/discharge profile with a 20 μA total cell current for sponges loaded with catalyst. Despite little difference in ORR behavior, Ru exhibits significantly lower charge voltage for full capacity recovery.
lower capacity at higher currents from Figure 4c,d. These results, when taken together, strongly suggest that in our cells the cathode is not the limiting factor for cell lifetime.

**XPS Diagnostic of Cathode Interface Chemistry.** Semi in situ XPS characterization of Li–O₂ cathodes directly from realistic cells, and in particular direct comparisons of discharged and charged cathodes, is uncommon in the literature but is important for understanding the chemistry of surface layers developed during operation. We characterize cathodes after one discharge, one charge, and the 40th charge, as well as the anode and cathode from a cell cycled over 350 times. We identify a thin solid electrolyte interphase formed during the first discharge/charge cycle, which appears to be subsequently very stable in terms of chemistry and morphology upon charging, as well as after extensive cycling in a limited capacity window. This characterization was facilitated by a vacuum transfer system allowing for the strict exclusion of air exposure (Supporting Information Figure S5). We first made a comparative XPS analysis of an ALD Ru-decorated MWCNT sponge after the first discharge and the first charge. Figure 5 shows the survey scans from 0 to 650 eV, which demonstrate the relative change in the quantities of oxygen and lithium. As expected, the charging process liberates a majority of the oxygen and lithium from the cathode, though a significant quantity of oxygen remains present after charge when compared to the pristine cathode. The high-resolution spectra in Figure 6 help elucidate the chemical identity of both the discharge products and the residual surface film. The discharged C 1s/Ru 3d spectrum (Figure 6a) demonstrates the near-complete suppression of the Ru signal at 280 eV, which implies that the cathode has been covered in a layer of discharge products. The primary intensity of the discharged O 1s (531 eV) and the Li 1s (54.6 eV) spectra (Figure 6c,e) match extremely well with the locations expected for Li₂O₂, as compared to both literature values and our own measurements of a Li₂O₂ commercial powder standard (Supporting Information Figure S6). This confirms that the dominant discharge product is Li₂O₂. However, the C 1s spectrum confirms the formation of a variety of C-containing side products. The primary peak at 284.8 eV contains a signal from
the nanotubes, but is dominated by non-sp² carbon and hydrocarbons as is clear from the symmetry of the peak, which points to the presence of a polymer-like material interspersed with the Li₂O₂. The C 1s also demonstrates the formation of a small amount of lithium carboxylates (HCO₂Li or CH₃CO₂Li) and carbonates (Li₂CO₃) upon first discharge, which are possibly due to the reaction of residual amorphous carbon and hydrocarbons on the surface of the pristine CNTs. This process would be expected to be self-limiting, and indeed the amounts of these products change only slightly with further cycling (Supporting Information Table S1). After the first charge, the intensities of the O 1s (Figure 6d) and the Li 1s (Figure 6f) peaks near the locations associated with Li₂O₂ are strongly suppressed, which is suggestive of healthy OER behavior. The remaining Li appears to be associated with carbonate/carboxylate species, which cannot be evolved within the typical charging potential of our cathode, as well as residual LiTFSI salt. The O 1s spectrum reveals a wide peak spread over binding energies associated with a variety of possible carbon-based moieties, but the broadness of these features precludes reliable peak fitting. We anticipate most of the residual oxygen to be bound within the polymeric surface film or involved in functionalization of the CNT surface. The first-charge C 1s/Ru 3d spectrum (Figure 6b) shows several changes. The higher detected amount of TFSI on the cathode after charge as indicated in Figure 6b is attributed to stronger electro-adsorption of the anion when higher potential was applied on the cathode upon charging the battery. More importantly, the spectrum shows the partial recovery of the Ru signal, demonstrating that either the catalyst particles are partially uncovered by the charging reaction or the thickness of any products covering them is thinned. However, the Ru signal is still dramatically suppressed relative to the as-synthesized cathode, suggesting the continuing presence of a thin SEI-type layer. Considering that the fractional Ru photoelectron intensity in Figure 6b is reduced by a factor R of approximately 80 relative to Figure 2c and that the inelastic mean free path λ of Ru 3d photoelectrons in Li, O, and C rich materials (using Li₂CO₃ as a model material) is approximately 3.1 nm, a rough calculation would predict an average overlayer thickness d of d = λ ln(R) ≈ 13 nm.

This observation is supported by TEM images of MWCNT/Ru cathodes in various stages of cell cycling as presented in Figure 7 and Supporting Information Figure S10. A thin SEI layer (typically 5−15 nm in thickness) with the underlying Ru

**Figure 5.** Survey scans of the first discharge and charge of a Ru functionalized MWCNT cathode. The spectra are normalized so that the C 1s peaks have the same intensity, highlighting the relative change of the O and Li peaks. The peak heights are proportional to the total amount of each element. Inset: C:O:Li atomic ratios calculated using photoelectron cross sections.

**Figure 6.** Systematic comparison of the high resolution C 1s/Ru 3d (a,b), O 1s (c,d), and Li 1s (e,f) XPS peak regions for the first discharge and charge of a Ru functionalized cathode. All spectra are normalized to the same arbitrary peak intensity to highlight changes in peak shape and location, though the absolute quantities change significantly (Figure 5 inset). Peak locations for (a) and (b) can be found in the text. Some peaks in (b) shift slightly relative to (a), possibly due to small amounts of differential charging. Explicit peak fitting was not attempted for (c), (d), (e), and (f), though locations of possible species are highlighted, with locations based on either measured standards (LiTFSI, Li₂O₂) or literature values (all others).
Catalyst still attached to the MWCNT is observed after the first discharge (Supporting Information Figure S10), the first charge, and even after 40 cycles (Figure 7). Despite this film, the low overpotential observed in the charging process (and in all subsequent charging cycles) implies that the Ru particle surface is still available to partake in electrochemical reactions.

Conjugation of the XPS and TEM data strongly suggest that the surface film is permeable or porous, allowing the diffusion of dissolved species to reach the cathode surface during operation while still suppressing the CNT and Ru XPS signals during characterization. The nanoparticles of Li2O2 tend to form in the proximity of the Ru particles (Supporting Information Figure S10). The other features of the charged C 1s spectrum are very similar to that of the discharged with the exception of a moderate increase in epoxy-type groups. Examination of the F 1s peak region (Supporting Information Figure S9a) reveals a negligible amount of decomposition of the TFSI anion (forming LiF). Interpretation of the S 2p region (Supporting Information Figure S9b) is more complicated, as the peak from residual TFSI overlaps with several possible DMSO decomposition products, discussed below.

In order to confirm the stability of this surface film, we examined a cathode after more extensive cycling. After replacing the anode in the cell from Figure 4a and another prolonged cycling period to 40 total cycles without additional signs of failure, we reopened the cell inside the glovebox and examined the surface chemistry after the 40th charge. The C 1s region is shown in Figure 8. It is apparent that the ratio of intensities of the Ru 3d ($j = 5/2$) peak to the main C 1s peak is similar to that observed in a cathode after only a single complete cycle (Figure 6b). This implies that the thickness and morphology of the surface layer is essentially unchanged from the first cycle. If the film was progressively growing through the consumption of the electrolyte or the CNT support, one would expect the complete suppression of the Ru signal or a dramatic increase in side products. In fact, the remaining components of the C 1s spectrum are strikingly similar to those after a single cycle, still showing a dominant hydrocarbon/C−C peak at 284.8 eV and a series of small peaks associated with oxygen bonding, including carboxylates at 288.6 eV and carbonates at 290 eV. The amount of carbonate (approximately 4% of all C 1s signal) has increased somewhat relative to the single cycle cathode (approximately 1% of all C 1s signal), but this increase is far below what is typically observed in systems where the electrolyte or cathode is unstable due to either the chemical nature of the carbon or the cycling conditions.14,28

Quantification of the fit components of the C 1s spectra as well as the total atomic composition for the first discharge, first charge, and 40th charge can be found in the Supporting Information (Table S1). While the carbon chemistry remains consistent and the film thickness is stable, we noted that the amount of residual O, Li, and S relative to C on the cathode surface increased after the 40th charge relative to the first charge.

Figure 7. TEM image of the MWCNT-Ru cathode after the 1st charge (left) and the 40th charge cycle (right) showing the surface film remaining on the cathode with underlying and intact Ru catalyst.

Figure 8. High resolution C 1s/Ru 3d spectrum of a Ru functionalized cathode after the 40th charge cycle (see Figure 4). The charge spectrum from a different cathode after a single charge (Figure 6b) is almost identical. The Ru peaks can no longer be clearly resolved into metallic and oxide components, but the primary Ru 3d $j = 5/2$ intensity centered at 280 eV suggests the catalyst is still at least partially metallic.
The amount of S more than doubled, while the N and F content remained constant, suggesting a non-TFSI source of sulfur. We performed an additional experiment to identify the origin of this excess sulfur.

**Electrolyte Decomposition on the Anode.** One complication of using LiTFSI as the salt in our cells is that the S 2p peak associated with the TFSI anion overlaps with several possible oxidative decomposition products of DMSO, including Li2SO4 and DMSO2, all of which contain S atoms with a formal valence of 6+. In order to identify the origin of the excess S on the cathode observed after extensive cycling, as well as potential failure mechanisms for the anode, we assembled a cell using LiClO4 as the salt and cycled it over 350 times under conditions similar to Figure 4c. Any XPS signal from S must then originate from solid decomposition products of DMSO. After stopping the cycling program, the anode and cathode were removed and loaded into the vacuum system without rinsing.

Survey spectra, atomic quantification, and the high-resolution S 2p regions from the anode and cathode are presented in Supporting Information Figure S12. Both the anode and the cathode contained highly oxidized sulfur, confirming the decomposition of DMSO within the cell. In order to identify the origin of the excess S on the cathode observed after extensive cycling, as well as potential failure mechanisms for the anode, we assembled a cell using LiClO4 as the salt and cycled it over 350 times under conditions similar to Figure 4c. Any XPS signal from S must then originate from solid decomposition products of DMSO. After stopping the cycling program, the anode and cathode were removed and loaded into the vacuum system without rinsing.

Survey spectra, atomic quantification, and the high-resolution S 2p regions from the anode and cathode are presented in Supporting Information Figure S12. Both the anode and the cathode contained highly oxidized sulfur, confirming the decomposition of DMSO within the cell. Both anode and cathode demonstrate one S 2p peak at ~169 eV (Supporting Information Figure S12c,b), which is consistent with a variety of compounds containing S⁶⁺, indicating a chemical process oxidizing DMSO. Surprisingly, the anode surface, a nominally highly reducing environment, contains more than twice the amount of oxidized sulfur (Supporting Information Figure S12a,b) than the cathode surface. The two most likely candidates for the S species present, based on previously proposed oxidative pathways for DMSO in the presence of Li, are Li2SO4 and DMSO2. However, we note that the increase in residual S on the long-term cycled cathodes (Figure 8, Supporting Information Figure S12a) occurs simultaneously with an increase in Li relative to the first charge (Figure 6b), and the O 1s peaks for the charged cathodes (Supporting Information Figure S7a) do not support the presence of significant residual Li2O2. Because DMSO2 does not contain Li, the data therefore most strongly support the production of Li2SO4 within the cell, and that the production occurs primarily on the anode via the mechanism discussed below. However, we cannot rule out some level of DMSO2 production on the anode.

**Proposed Chemistry.** Based on our characterization, we propose a set of reactions, shown in Figure 9, which are consistent with our data and help explain the formation of the SEI on the cathode and the eventual anode-induced cell failure. Conjugation of the XPS, TEM, and cycling data indicate that a thin SEI forms on the cathode surface and is predominantly formed during the first cycle. The carbon-involved components of the SEI are stable over long-term cycling, and the SEI does not grow in thickness. One possible implication of a largely self-limiting cathode SEI is that some of the chemical precursors to its formation exist in limited quantities in the cell to begin with, and SEI growth stops when they are consumed. Assuming the cells initially contain trace (ppm level) amounts of H2O and CO2, reactions I, II, and III show how chemical reactions with Li2O2 produced during the first cycle or direct electrochemical formation could lead to the detection of lithium carbonate and lithium formate due to trace contaminants and amorphous/adventitious carbon. Lithium sulfate generated on the anode can also diffuse throughout the electrolyte and accumulate on the cathode surface.

![Figure 9. Proposed mechanisms of formation for species observed with XPS (blue boxes) on cathode and anode surface. (Left): Decomposition of DMSO at the anode surface proceeds via stepwise nucleophilic attacks of the methyl groups by highly basic O2⁻⁻ (green box) to formation of lithium sulfate. Formaldehyde is formed as a leaving group (red boxes) in the process. (Right): Cathode surface reactions outlining formation of lithium carbonate and lithium formate due to trace contaminants and amorphous/adventitious carbon. Lithium sulfate generated on the anode can also diffuse throughout the electrolyte and accumulate on the cathode surface.](attachment:image.png)
formate in the SEI. Li2CO3 can also be produced by a direct reaction between Li2O2 and C (Reaction V). Residual amorphous carbon from the growth process (Figure 2a) or surface bound hydrocarbons could provide an exhaustible initial source of C. We have previously shown that the Li2O2/DMSO interface is chemically stable in the absence of a proton source and in similar operating voltages; hence, continued growth of this type of Li−O2 cathode/electrolyte interlayer, observed in a recent work, could be attributed to cell operation outside of the voltage stability window of the cathode/electrolyte, leading to parasitic side reactions and decomposition products. While these cycling conditions will initially yield higher capacity, long-term cycling stability is compromised by continuous growth and evolution of the SEI layer. We demonstrate that achieving long duration cycling and a stable cathode/electrolyte interface depends on selection of an appropriate cycle capacity and potential limitations.

However, the increase in sulfur content observed on the cathode surface along with the observation of even higher amounts of oxidized sulfur on the anode surface suggests that the Li/DMSO interface is unstable. We believe that cell failure is ultimately caused by degradation at the Li/DMSO interface, which is supported by the recovery of the cell after anode replacement (Figure 4a). On the basis of the observation of Li2SO4 on the anode surface, we propose that DMSO is primarily decomposed through the formation of the dimsyl anion via reaction with O2− produced on the Li anode surface at voltages < 2.05 vs NHE. The dimsyl ion can then undergo base-catalyzed autoxidation to form lithium sulfate, producing formaldehyde as an intermediate leaving group. Generated formaldehyde can diffuse to the cathode and form lithium formate, as shown in Reaction IV. This mechanism is based on one proposed by Sharon et al. but supposes O2− to be the primary involved base because of the higher degree of reaction observed on the anode and due to low acidity of the DMSO proton. The discharge potential of the cathodes (>2.6 V vs Li/Li+) is likely too high to produce O2−, and previous work has demonstrated DMSO to be stable against the superoxide anion during the discharge process. Additionally, Roberts et al. have shown that dissolved O2 affects the coulombic efficiency of Li stripping and plating in DMSO, suggesting that reduced O2 on the anode side plays an important role in this system, though further work is needed to elucidate the precise nature of oxygen electrochemistry in the presence of the lithium SEI. Finally, we note that because Li2SO4 is soluble in DMSO, we propose at least some of the oxidized S observed on the cathode is due to a spillover process involving diffusion and redeposition of the sulfate produced on the anode. The slow accumulation of sulfate on the cathode side does not seem to compromise the stabilizing effect of the SEI formed on the first discharge.

While we have shown that it is possible to obtain long-term reversibility and stability on the cathode, Li−O2 cells will remain out of reach if cathode-friendly electrolytes like DMSO degrade the Li anode to the point of cell failure. The cathode is usually considered to be the point of failure in the Li−O2 chemistry, but our work highlights the more pressing need for effective anode protection systems, such as solid electrolytes, engineered carbon coatings, or conformal thin film treatments, which help stabilize the anode/electrolyte interface.

**CONCLUSIONS**

Chemical and morphological characterization of the cathode—catalyst—electrolyte interface indicate that these composite electrodes exhibit formation of a stable SEI, primarily forming during the first cycle and without significant evolution after prolonged cycling. Cycling studies of the MWCNT/Ru system showed excellent stability over long discharge/charge durations, and cell failure was found to be related to electrolyte decomposition on the anode. These results demonstrate that chemical stabilization of the cathode/electrolyte interface, enabled by heterogeneous catalysis, is capable of promoting long-term operation of DMSO-based Li−O2 batteries.

**REFERENCES**


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