Understanding LiOH Chemistry in a Ruthenium Catalyzed Li-O2 Battery


Abstract:

Non-aqueous Li-O2 batteries are promising for next generation energy storage. New battery chemistries based on LiOH, rather than Li2O2, have recently been reported in systems with added water, one using a soluble additive LixLi and the other using solid Ru catalysts. Here, we focus on the mechanism of Ru-catalyzed LiOH chemistry. Using nuclear magnetic resonance, operando electrochemical pressure measurements and mass spectrometry, we show that on discharging LiOH forms via a 4 e⁻ oxygen reduction reaction, the H in LiOH coming solely from added H2O and the O from both O2 and H2O. On charging, quantitative LiOH oxidation occurs at 3.1 V, with O being trapped in a form of dimethyl sulfone in the electrolyte. Compared to Li2O2, LiOH formation over Ru incurs hardly any side reactions, a critical advantage for developing a long-lived battery. An optimized metal catalyst-electrolyte couple needs to be sought that aids LiOH oxidation and is able stable towards attack by hydroxyl radicals.

Non-aqueous Li-O2 batteries possess a high theoretical energy density, 10 times higher than that of the current lithium ion batteries.[1] There have been considerable efforts from academia and industry in the past decade to understand and realize the battery system. Despite of the much research investment, significant challenges remain. One of the most fundamental problems concerns the side reactions that occur during cell cycling.[2] During battery discharge, O2 is reduced to form Li2O2 via an intermediate LiO2,[3] on charging Li2O2 decomposes releasing O2.[4] Both the superoxide and peroxide (either as solvated ions or solid phases) are highly reactive and their formation/decomposition can cause electrolyte and electrode decomposition,[5] especially in the presence of high overpotentials. As a result, many groups have been searching for new Li2O2 battery chemistries.[6,7]

Recently, has been identified as the major discharge product in a couple of Li-O2 battery systems and reversible electrochemical performance has been shown.[1,7] One case is published by some of the authors,[7] concerns the use of a soluble catalyst LixLi, which catalyzes the LiOH formation with its H source solely coming from added H2O in the electrolyte; a subsequent study[9] confirmed the proposed 4 e⁻ oxygen reduction reaction (ORR) on discharging. It was also shown on charging the LiOH can be removed with the aid of Li2O at around 3.1 V.[7] The other case employs a Ru-based solid catalyst in a water-added dimethyl sulfoxide (DMSO) or tetraglyme electrolyte.[6] Ru was proposed to catalyze LiOH formation and decomposition in a tetraglyme electrolyte with 4600 ppm water.

In the DMSO case, it was suggested that at low water contents (~150 ppm), a mixture of Li2O2 and LiOH was formed on discharge, and that on charging, Li2O2 is first converted to LiOH, the latter then giving decomposed by Ru catalysts at voltages of as low as ~3.2 V. At higher water contents (~250 ppm), LiOH formation appeared to be dominant on discharge.[10] It is clear that understanding the formation and decomposition of LiOH is not only critical in helping realize a LiOH-based Li-O2 battery, but fundamental insight into LiOH based chemistries may also aid in the development of Li2O2-based batteries that operate utilizing air (or moist oxygen), where LiOH inevitably forms.

In this article, we develop a mechanistic understanding of the Ru-catalyzed oxygen chemistry. Using quantitative nuclear magnetic resonance and operando electrochemical pressure and mass spectrometry measurements, we show that on discharging, a total of 4 electrons per O2 is involved in LiOH formation, this process incurring fewer side reactions compared to Li2O2. On charging, the LiOH is quantitatively removed at 3.1 V, with the oxygen being trapped in the form of soluble dimethyl sulfone in the electrolyte.

The preparation of the Ru/Super P (SP) carbon electrode is described in the Supplementary Materials. Microscopy and diffraction experiments show that Ru crystals of less than 5 nm are well dispersed on the SP carbon substrate (S1). Fig. 1A shows typical electrochemical profiles of Li2O2 batteries prepared using Ru/SP electrodes with various concentrations of added water in 1 M LiTFSI/DMSO (lithium bis(trifluoromethane) sulfonimide in dimethyl sulfoxide) electrolyte. In the nominally anhydrous case, discharge and charge plateaus are observed at 2.5 and 3.5 V respectively, where an electrochemical process involving two-electrons per oxygen molecule and Li2O2 formation dominates process on discharging (S2). As the water content increases, it is clear (Fig. 1A) that the voltage gaps between discharge and charge reduce considerably. With 50,000 ppm water, the cell discharged at 2.85 V charges at 3.1 V, although further increasing the water content then widens the voltage gaps (S3). Fig. 1B shows the electrochemistry of cells made using various metal catalysts and 1 M LiTFSI/DMSO electrolyte with 4000 ppm water. Although the discharge voltages are all similar, and close to 2.7 V, clear differences are observed on charging, where Ir, Pd, Pt all show charging voltages beyond 3.5 V while for Ru it is only 3.2 V, demonstrating the crucial role of metal catalyst on the charging process.
morphologies were observed before for LiOH crystals. Indeed, both X-ray diffraction (XRD) and Raman measurements suggest that in the current Ru-based system, LiOH is the only discharge product observed with 4000–50,000 ppm added water; no evidence of other chemical species commonly observed in Li-O2 batteries, such as Li2O, Li2CO3, and HCOOLi, is seen by XRD and Raman spectroscopy (Fig. 1E,F). Ir, Pd catalysts also invariably lead to LiOH formation (S4).

To demonstrate that at water levels beyond 4000 ppm, LiOH is formed from O2 reduction rather than from electrolyte decomposition, we performed NMR experiments with isopropically labeled H (D2O) and O (H217O, 18O) (Fig. 2A–C). When natural abundance DMSO and H2O were used, a dominant 1H NMR resonance at -1.5 ppm attributed to LiOH was observed (Fig. 2A). Using D2O, we found a distinct 1H-order quadrupolar-broadened line shape for LiOD in the 2H NMR spectrum (Fig. 2B), when deuterated d4-DMSO and H2O were used, hardly any LOH signal was seen (Fig. 2B) and LiOH was the prevailing product (Fig. 2A). The proton in LiOH thus comes overwhelmingly from the added water in the DMSO electrolyte. Next, we 17O enriched either gaseous O or H2O to verify the O source in LiOH. In both cases, the resulting 17O NMR spectra (Fig. 2C) revealed a resonance at around -50 ppm with a characteristic 2H-order quadrupolar line shape, which is ascribed to LiOH. It is thus clear that both oxygen atoms in O2 and H2O contribute to the formation of LiOH, consistent with a 4 electron ORR.

To further verify this mechanism, operando pressure measurements show that the recorded pressure matches well with the trend line expected for 4 e- per O2. Therefore, we propose an overall discharge reaction as follows: (1) O2 + 4e- + 4Li+ + 2H2O → 4LiOH. Up to 4 electrons can be stored per O2 molecule, the theoretical capacity of the battery operating via reaction (1) being 1117 mAh/gLiOH, comparable to Li2O (1168 mAh/gLi2O). To examine the role of Ru in LiOH formation further, we discharged a SP electrode in a 1 M LiTFSI/DMSO electrolyte with 4000 ppm water. XRD and SEM show that the discharge leads to mainly Li2O2 formation with an e'/O2 ratio of 2.2 (S5), whereas discharging Ru/SP in the same electrolyte forms only LiOH. This contrasting behavior suggests that in the absence of Ru the reaction between H2O and Li2O2 (2) 2Li2O2 + 2H2O → 4LiOH + O2 is slow, even though it is thermodynamically favorable (ΔG° = -149.3 kJ/mol) but Ru clearly promoted the LiOH formation. By exposing a Ru/SP electrode discharged in a nominally dry electrolyte (where Li2O2 is the main product) to the 4000 ppm water-added electrolyte, XRD (S5) shows that all the Li2O2 was converted to LiOH in the presence of Ru after 10 hours (same time period as used for the galvanostatic discharge in the SP cell); this indicates that Ru can catalyze the reaction (2) above. It is likely that the electrochemical formation of LiOH in the Ru/SP system proceeds via first Li2O2 generation (O2 + 2e- + 2Li+ → Li2O2) and then Ru catalyzes the chemical formation of Li2O2 with H2O to eventually form LiOH. (Reaction 2); overall the reaction is O2 + 4e- + 4Li+ + 2H2O → 4LiOH. This observation also suggests that water present must be important to solubilize Li2O2, LiOH and derived species and facilitate the solid–solid phase conversion (from Li2O2 to LiOH).

Importantly, the LiOH formation during discharge involves few parasitic reactions. Quantitative 1H solid-state NMR spectra (Fig. 2E) comparing the discharged electrodes generated from an anthrahydroxy electrolyte versus those with 4000 and 50,000 ppm added water shows that the Li2O2 chemistry (at the anhydrous conditions) clearly generated Li formate, acetate, methoxide side reaction products (signified by 0–10 ppm resonances), whereas only a single resonance at -1.5 ppm was seen in the LiOH chemistry; similar results were observed with the other metal catalysts (S3). In addition, we found that soaking LiOH in dimethoxyethane (DME) and DMSO for a month showed no change in its solid state NMR spectra (Fig. 2F), indicating that LiOH is chemically inert in these solvents. 1H and 13C solution NMR measurements of the electrolytes after discharging and soaking with LiOH under O2 also show that hardly any soluble side-reaction product is detected in the electrochemical LiOH formation (S6).

Now moving to battery charging, this process was characterized by ex-situ NMR and XRD measurements of electrodes after multiple cycles, as presented in Fig. 3A–C. They all consistently show that quantitative LiOH formation on discharging and LiOH removal (even at 3.7 V) on charging are the prevailing processes during cell cycling. Hardly any residual solid, side-reaction products accumulate in the electrode over extended cycles. Typically, the cells can cycle over 100 cycles at 1 mAh/cm² (0.5 mAh or 1250 mAh/gRu+c per cycle), with very consistent electrochemical profiles (S7). Although the ex-situ tests supported a highly reversible O2 electrochemistry, operando electrochemical pressure and mass spectrometry experiments suggested otherwise: very little gas was evolved on charging (Fig. 3D,E) and the pressure of cell continues to drop over extended cycles (Fig. 2F); these observations imply that oxygen must be trapped and accumulated after charging in the cell, likely in the electrolyte.

Further solution NMR measurements were performed on electrolyte samples prepared from several charged cells extracted following different cycle numbers, where 17O enriched H2O (H217O) was used in the electrolyte. Fig. 4 shows the 1H (A), 17C (B) and 13C (C), and 1H-13C heteronuclear single quantum correlation (D) solution NMR spectra of the cycled electrolytes. A common feature is that new peaks at 2.99 ppm (1H), 42.6 ppm (13C) and 169 ppm (17O) appeared and progressively intensified compared to with cycle number; these resonances consistently point towards the formation of dimethyl sulfone (DMSO2), its identity being further corroborated in the 1H-13C correlation spectrum. Of note, the 17O signal of DMSO2 is even stronger than the large amount of natural abundance (NA) DMSO used in the solution NMR experiment, suggesting that DMSO2 is likely to be 17O-enriched. Its growth in intensity is accompanied by the decrease of H217O, indicating that some 17O from H217O ended up in DMSO2 due to isotope scrambling in the charging process. Given that LiOH is quantitatively formed and then removed on charge (Fig.3), we propose that the charging reaction is initiated by electrochemical LiOH oxidation to produce hydroxyl radicals, which then chemically react with DMSO to form DMSO2: (3) LiOH → Li+ + e- + OH (hydroxyl radicals); (4) DMSO + 2'OH → DMSO2 + H2O. The overall reaction thus is: (5) 2DMSO + 4LiOH → 2DMSO2 + 2H2O + 4e- + 4Li+. It is seen that the same number
of electrons is involved in discharge (reaction 1) and charge (reaction 5), with one O reacting per two electrons (as expected for O₂ evolution reaction, OER). The electrochemical process, reaction (3), sets the voltage observed on charge, rather than the overall reaction (5). It is known that the formation of surface adsorbed hydroxyl species is the first reaction intermediate on many OER metal catalysts in aqueous media. The added water in the current electrolyte could promote LiOH dissolution, and thus facilitate the access of Ru surfaces to soluble LiOH species resulting in the formation of surface hydroxyl species. Once the radical is formed on charging, it is consumed by reacting with DMSO to form DMSO₂ and thus the battery can be continuously charged at a low voltage until all solid LiOH products are removed (see further discussion in S8). The resulting DMSO₂ is soluble in the DMSO electrolyte and will not immediately impede ion diffusion or interfacial electron transfer as other insoluble by-products would do, which is perhaps why this side reaction does not rapidly lead to battery failure.

In summary, we have shown that with added water (beyond 4000 ppm) in the electrolyte, the Ru-catalyzed battery chemistry changes from Li₂O₂ to LiOH formation, similar reactions being seen for several other metal catalysts. The cell discharge reaction consumes four-electron per reduced O₂ molecule. This LiOH formation process involves very few side reactions and LiOH itself is much more stable in organic solvents than Li₂O₂; these are the fundamental prerequisites for a long-lived Li-O₂ battery. On charging, the Ru quantitatively catalyzes LiOH removal via DMSO₂ formation rather than O₂ evolution. We propose that DMSO₂ forms by the reaction of hydroxyl radicals with DMSO, the former being generated on Ru catalyst surfaces. This work highlights the advantage of using metal catalysts to catalyze a 4 e⁻ ORR with very few side reactions, and also the unique role of a metal catalyst in promoting LiOH formation versus electrolyte decomposition. An optimized catalyst-electrolyte couple needs to be sought to satisfy both activity towards LiOH oxidation and stability against electrolyte decomposition on charge. This work provides a series of key mechanistic insights into the Ru-catalyzed Li-O₂ battery in the presence of water, which will aid the design of catalyst and electrolyte systems that can be used in more practical batteries.

Experimental Section

Experimental Details: see Supplementary Materials.

Acknowledgements

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Keywords: Li-O₂ batteries • oxygen reduction/evolution reaction • LiOH • dimethyl sulfone • ruthenium catalysis

Labeling the events: Ru catalyzed LiOH formation and decomposition reactions are demonstrated in a Li-O2 battery with added water, its mechanism being revealed via isotopic labeling.
Fig. 1 Electrochemical profiles of Li-O₂ cells with different water contents (in ppm) (A) in a 1M LiTFSI/DMSO electrolyte and using different metal catalysts (AC = activated carbon, SP = super P) (B). Characterization of discharged electrodes by SEM (C,D), XRD (E) and Raman spectroscopy (F). All cells in A use Ru/SP electrodes; All cells in B contain a water content in the electrolyte of 4000 ppm. All cells were cycled at a current of 50 μA (0.1 mA/cm²). The discharged electrodes measured in XRD (E) and Raman (F) are both prepared using the electrolyte with 4000 ppm water and Ru/SP electrodes.
Fig. 2. $^1$H (A), $^2$H (B) and $^{17}$O (C) solid state NMR spectra of discharged Ru/SP electrodes, prepared from Li-O$_2$ cells with 1 M LiTFSI/DMSO electrolyte with 4000 ppm water. The $^1$H NMR spectra (A) show that all samples, independent of the nature of isotope enrichment (as labelled), give rise to a dominant resonance at -1.5 ppm corresponding to LiOH; the small resonance at 2.5 ppm is due to residual DMSO. The $^2$H NMR spectra confirm that water is the proton source for LiOH formation. Note that the $^1$H NMR experiments in Fig. 2A are not quantitative, and the LiOH detected in the case with added D$_2$O in the DMSO-based electrolyte is likely due to H$_2$O impurities from D$_2$O. Operando pressure measurement of a Ru-catalyzed cell with 50,000 ppm water (D) and quantitative $^1$H NMR spectra (E) of 1$^{st}$ discharged electrodes prepared from Li-O$_2$ cells using 1 M LiTFSI/DMSO electrolyte with 0, 4000, and 50000 ppm water contents. 10 μmol O$_2$ consumption corresponds to 27.7 mbar pressure drop measured for 1 mAh capacity (200 μA, 5 hours). $^1$H NMR evaluating the long-term stability of LiOH in DMSO and DME solvents (F) by comparing LiOH powder with those after being soaked in DMSO and DME solvents for a month. Apart from the residual DMSO or DME solvent, no additional signals are observed, the soaked LiOH powder remaining chemically unchanged.
Fig. 3 Quantitative $^1$H (A, B), ex situ XRD measurements (C) of cycled Ru/SP electrodes prepared using 1 M LiTFSI/DMSO electrolytes with 50,000 ppm water; _operando_ electrochemical pressure (D, F) and mass spectrometry (E) measurements of a Ru-catalyzed cell with 50,000 (D) and 4000 ppm (F) water. Batteries terminated both at different state of charge (A) and fully charged following different discharge-charge cycles all show quantitative electrochemical removal of LiOH. Little O$_2$ evolution is seen during charging (D, E) and the cell pressure continues to drop over extended cycles (F). 10 μmol O$_2$ in D and F corresponds to 27.7 mbar pressure change measured for 1 mAh capacity (200 μA, 5 hours).
Fig. 4 $^1$H (A), $^{13}$C (B) and $^{17}$O (C) and $^1$H-$^{13}$C heteronuclear single quantum correlation (D) solution NMR spectra of cycled 1M LiTFSI/DMSO electrolyte with 45,000 ppm $^{17}$O enriched water from Ru-catalyzed Li-O$_2$ batteries. New resonances at 2.99 ppm ($^1$H), 42.55 ppm ($^{13}$C) and 169 ppm ($^{17}$O) signify the formation of DMSO$_2$. The heteronuclear correlation experiment was performed on a charged electrolyte at the end of the 6th cycle. The cross peak at (2.99 ppm $^1$H – 42.55 ppm $^{13}$C) further supports DMSO$_2$ formation; the other cross peak at (2.54 ppm $^1$H - 41.0 ppm $^{13}$C) is due to DMSO.