Cycling Non-Aqueous Lithium-Air Batteries with Dimethyl Sulfoxide and Sulfolane Co-Solvent

Evaluating influence of sulfolane on cell chemistry

Gunwoo Kim
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK; Cambridge Graphene Centre, University of Cambridge, Cambridge, CB3 0FA, UK

Tao Liu, Israel Temprano
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

Enrico A. Petrucco, Nathan Barrow
Johnson Matthey, Blounts Court Road, Sonning Common, Reading, RG4 9NH, UK

Clare P. Grey*
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

*Email: cpg27@cam.ac.uk

Despite considerable research efforts, finding a chemically stable electrolyte mixture in the presence of reduced oxygen species remains a great challenge. Previously, dimethyl sulfoxide (DMSO) and sulfolane (tetramethylene sulfone (TMS))-based electrolytes were reported to be stable for lithium air (Li-O2) battery applications. Recently lithium hydroxide (LiOH) based chemistries have been demonstrated to involve supressed side reactions in water-added ether- and DMSO-based electrolytes. Herein, we investigate the impact of DMSO-based electrolyte and sulfolane co-solvent on cell chemistry in the presence of water. We found that DMSO-based electrolyte leads to formation of a peroxide-hydroxide mixture as discharge products and the removal of both LiOH and lithium peroxide (Li2O2) on charging from 3.2–3.6 V (vs. Li+/Li) is observed. In the presence of sulfolane as co-solvent, a mixture of Li2O2 and LiOH is formed as major discharge products with slightly more LiOH formation than in the absence of sulfolane. The presence of sulfolane has also significant effects on the charging behaviour, exhibiting a clearer 3 e−/O2 oxygen evolution reaction profile during the entire charging process. This work provides insights into understanding the effects of the primary solvent on promoting LiOH formation and decomposition in lithium iodide (LiI) mediated non-aqueous Li-O2 batteries.

1. Introduction

The non-aqueous Li-O2 battery has drawn considerable scientific attention due to its higher theoretical energy density compared to the values achieved by conventional Li-ion batteries (1–3). The successful operation of a Li-O2 battery necessitates the reversible formation and decomposition of a discharge product, typically Li2O2 (4–6). However, this process is often limited by the considerable parasitic reactions caused by highly reactive reduced oxygen species, reaction intermediates (such as lithium superoxide (LiO2)) and the final product Li2O2 (7). These undesired reactions are accelerated at high charge overpotentials (8, 9) and addressing such a fundamental issue remains a major challenge hindering its commercial implementation. One promising strategy to address this issue is the formation of chemically more stable discharge products, so that fewer side-reactions occur. Recently, LiOH formation and
decomposition has been proposed as an alternative mechanism to cycle non-aqueous Li-O₂ batteries using LiI as a redox mediator, in a water-added ether-based electrolyte (10), and with ruthenium-catalysed cells with water-added DMSO-based electrolyte (11).

The search for chemically stable electrolytes against reactive reduced oxygen species with the appropriate physicochemical properties is another crucial research topic in this field. In this regard, a wide range of solvents such as carbonates, ethers and sulfones have been investigated so far (7, 12, 13). In particular, sulfur-containing solvents such as DMSO and sulfolane have shown to be promising candidates for Li-O₂ batteries because they possess high oxidation potentials (4.8 V and 5.6 V vs. Li⁺/Li, respectively), and high boiling points (189°C and 285°C, respectively) (14–16). Although initial studies have reported good reversibility of cells with either DMSO or sulfolane-based electrolytes via formation and removal of Li₂O₂, various issues related to cell performance were reported in later studies (13, 17). In the case of DMSO, its electrochemical instability with Li metal anodes has been reported as a major issue. It has been suggested that the addition of N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (PyR₁₄TFSI) ionic liquid can mitigate this issue (18) through the formation of a stable solid electrolyte interphase (SEI) via TFSI⁻ anion decompositions (19) as well as lowering the charging overpotential by stabilising superoxide species (20). Similarly, sulfolane-based electrolytes have shown to promote the reversible formation and removal of Li₂O₂ but capacity fading was observed due to the accumulation of side-reaction products such as LiOH and lithium carbonate (Li₂CO₃) (13).

Early chemistries reported for DMSO-based electrolytes were equivocally described as promoting Li₂O₂ with significant amounts of side-reactions (17, 21). In order to increase stability the formation of LiOH as discharge product has been attempted with DMSO-based electrolytes. Ru-catalysed Li-O₂ cells cycled with LiTFSI/DMSO in the presence of added water exhibited a dominant LiOH chemistry with suppressed side-reactions, but the charging process undergoes dimethyl sulfone (DMSO₂) accumulation rather than oxygen evolution reaction (11).

In this report, we investigate the effect of sulfolane as co-solvent in DMSO based electrolytes containing LiI as redox mediator, LiTFSI salt with water and PyR₁₄TFSI as additives in non-aqueous Li-O₂ batteries. A range of ex situ and operando techniques were used to evaluate the influence of sulfolane on cell chemistry, and especially whether it promotes dominant and reversible LiOH chemistry.

2. Experimental

Electrospun carbonised polyacrylonitrile (C-PAN) electrodes were prepared using a standard recipe for preparation of carbon nanofibers with an electrode diameter of 18 mm and the typical carbon loading around 1.2 mg cm⁻². Polyacrylonitrile (Sigma-Aldrich, average M₉ = 150 k) was dissolved at 7.5 wt% in dimethylformamide (DMF) and electrospun using a custom-built device onto aluminium foil wrapped on a rotating drum at >1 kV cm⁻¹ field strength. The resulting electrospun mat was dried in a vacuum oven at 50°C for 12 h, then stabilised by heating in air at 5 K min⁻¹ up to 300°C and held for 1 h. Sections were cut to size, allowing for shrinkage, and carbonised in flowing N₂ by heating 10 K min⁻¹ to 1200°C and held for 2 h. The resulting electrodes were dried at 110°C under vacuum for 20 h in a Büchi oven and stored in a dry argon glove box for further use.

Electrodes were assembled into cells for testing in an argon glove box using EL-CELL differential electrochemical mass spectrometry (DEMS) hardware with 1.55 mm EL-CELL glass fibre separator, lithium metal anode (Alfa Aesar, 99.9% metals basis) and 360 µl of electrolyte. The electrolyte used is a mixture of 5000 ppm water, 0.9 M PyR₁₄TFSI, 0.7 M LiTFSI and 0.05 M LiI in DMSO solvent and a 1:1 DMSO:sulfolane mole ratio for the sulfolane-containing electrolyte. Added water content was carefully chosen on the basis of recent studies (10, 11) and the water content of 5000 ppm is sufficient to promote dominant LiOH formation up to the discharge capacity of 5.35 mAh. Cell temperature was controlled at 25°C and all cell testing was potential limited at 2.2–3.7 V. Exhaust gas was continuously analysed using Stanford Research Systems UGA/RGA200 with a heated capillary and channel electron multiplier (CEM) gain 200. Cell purge gas flow rate was 5 ml min⁻¹ at 1.5 bar with cell charge performed in pure argon and cell discharge in 20% oxygen in argon. Mass signal response was calibrated against standard concentrations to confirm linearity while background levels and drift were subtracted using a linear fit before and after the target dataset.
X-ray diffraction (XRD) measurements were carried out using a Panalytical Empyrean with Cu Kα radiation (λ = 1.5406 Å). Scanning electron microscopy (SEM) images were recorded with a Hitachi S-5500 in-lens field emission electron microscope. Post-mortem electrode characterisations were performed with samples to avoid air exposure during transfer and data acquisition. In the case of SEM, electrodes were exposed to air for a maximum of 20 s prior to insertion into the high vacuum chamber. For nuclear magnetic resonance (NMR), electrodes were scrapped and packed in an argon glovebox.

Solid-state NMR data were acquired at 11.7 T on a Bruker Avance™ III HD spectrometer using a 2.5 mm HX probehead. A rotor synchronised Hahn-echo pulse sequence was used to acquire ¹H and ⁷Li magic angle spinning (MAS) spectra with a spinning speed of 30 kHz, with recycle delays of 150 s and 20 s for ¹H and ⁷Li, respectively. Radiofrequency (RF) field strength was 100 kHz and either 256 transients for ¹H or 128 transients for ⁷Li were acquired. ¹H and ⁷Li chemical shifts were externally referenced to solid adamantane at 1.87 and Li₂CO₃ at 0 ppm, respectively.

Fig. 1. Electrochemical first discharge and charge profiles of Li-O₂ batteries using C-PAN electrodes cycled with 5000 ppm water-added 0.9 M Pyr₁₄TFSI/0.7 M LiTFSI/0.05 M LiI/DMSO: (a) with; and (b) without sulfolane co-solvent, and their corresponding XRD patterns of cycled C-PAN electrodes, shown as (c) and (d), respectively. The cycling rates are all 0.1 mA cm⁻² (160 mA g⁻¹). The XRD patterns of reference LiOH and Li₂O₂ compounds (blue and green traces and also shown as blue triangles and green diamonds on the top of the XRD patterns, respectively) are also shown for comparison.
3. Results and Discussion

Figures 1(a) and 1(b) show the galvanostatic discharge and charge profiles of the first cycle of Li-O2 cells using the electrolyte 0.9 M Pyr14TFSI/0.7 M LiTFSI/0.05 M LiI/DMSO with 5000 ppm water added in the presence and absence of a sulfolane co-solvent, respectively. In both cases a similar discharge plateau was observed at around 2.7 V, although slightly lower (2.6 V) for the sulfolane-containing cell. The charge process was noticeably different; the cell without sulfolane charged in a single plateau from 3.4 V to 3.6 V, whereas the sulfolane-added cell showed a more sloped charge profile, starting at 3.2 V and finishing at 3.7 V. The observed oxygen reduction voltages are consistent with the values generally reported in the literature (13, 22) as well as the charging voltages with that of LiI-mediated oxygen evolution reaction, essentially the redox potential of $\Gamma^-/\Gamma_3^-$ (3.5 V versus Li/Li+) in DMSO-based electrolytes. In the absence of the LiI mediator, the cell charging voltages in the cells DMSO or sulfolane-based electrolyte usually exceed 4.0 V (16, 22).

The XRD patterns of electrodes after the first discharge in the presence and absence of sulfolane are shown in Figures 1(c) and 1(d), respectively. Both cases indicate the formation of a mixture of LiOH and Li2O2 as discharge product. Similarly, SEM images (Figures 2(a) and 2(c)) of the corresponding discharged electrodes reveal two distinct morphologies, suggesting a mixture of discharge products. As previously reported, distinguishing LiOH and Li2O2 mixtures by morphologies is possible if the grown particle size is large enough; electrochemically produced LiOH typically presents various morphologies, including cones, discs, large sheets and flowers (10, 23), whereas Li2O2 typically displays toroidal and platelet shapes (5). After charging, XRD patterns in both cases (Figures 2(c) and 2(d)) show that the intensity of reflections corresponding to LiOH and Li2O2 decreases significantly, more distinctly in the sulfolane-containing case, indicating that most
of the crystalline discharge products are removed. The SEM images of the charged electrodes indicate that some solid residues remain adsorbed on the surface of the carbon electrode as particles and thin films. In the sulfolane-absent case (Figure 2(b)), most of the discharge products appear to be removed from the carbon fibres of C-PAN electrodes, whereas sulfolane-containing cells (Figure 2(d)) display electrode surfaces more noticeably covered by particles and thin films after charging.

To further characterise the chemical nature of reaction products formed during cell cycling, solid-state $^1$H and $^7$Li NMR measurements (Figure 3) were performed on the cycled electrodes characterised by XRD and SEM. In both sulfolane-absent and present cases, the $^7$Li NMR spectra of discharged electrodes (red and orange traces, respectively, in Figure 3(b)) show a single broad resonance centred at 0.7 ppm, consistent with the presence of a mixture of Li$_2$O$_2$ (0.4 ppm) and LiOH (1.1 ppm). The corresponding discharged $^1$H NMR spectra exhibit a major resonance at −1.5 ppm, assigned to lithium hydroxide, more dominant and intense in cells containing sulfolane, and a minor one at 8.3 ppm, assigned to formate (10, 24). Other distinct resonances are present in the range 1−4 ppm, with the resonances at 2.5 ppm and 1−2 ppm attributed to DMSO and Pyr$_{14}^+$ of residual electrolyte, in agreement with the literature (25). Despite rinsing the electrodes after cell disassembly with acetonitrile and overnight drying under vacuum, the highly viscous nature of the ionic liquid-containing electrolyte inevitably results in severe adsorption of Pyr$_{14}^+$ cations onto the C-PAN electrode after cycling, showing significant contributions on the $^1$H NMR spectra. Furthermore, decomposition of Pyr$_{14}^+$ cations by superoxide attack is known to generate various $^1$H resonances in a 4−6 ppm range (highlighted in magenta in Figure 3(a)) (25). After charging, the $^7$Li NMR spectra of both cases (Figure 3(b)) are consistent with the removal of Li-containing species from the electrodes, whereas the $^1$H NMR spectrum shows that the intensity of the LiOH peak is significantly reduced. These observations are consistent with the formation and removal of a mixture of LiOH and Li$_2$O$_2$ from the electrodes during cell discharge and charge, respectively. The comparison of the

![Fig. 3. Solid-state: (a) $^1$H; and (b) $^7$Li MAS NMR spectra of the cycled C-PAN electrodes from cells using 5000 ppm water-added 0.9 M Pyr$_{14}$TFSI/0.7 M LiTFSI/0.05 M LiI/DMSO electrolyte with and without sulfolane co-solvent. The magenta-shaded areas on the $^1$H spectra indicate the $^1$H shifts of Pyr$_{14}^+$ ions and their related decomposed chemical species and residual water. A broad $^1$H resonance at −4 ppm is assigned to protons in the C-PAN electrode.](image-url)
charged $^1$H NMR spectra of both sulfolane present and absent cases suggest a higher extent of parasitic reactions occurring in the former case, in good agreement with the SEM data.

In order to investigate the charging mechanism involved in removing the LiOH and Li$_2$O$_2$ mixture, *operando* DEMS experiments were performed. The Faradaic efficiency profiles of the oxygen evolution reaction (OER) during galvanostatic charging of LiI-mediated cells with and without sulfolane are shown in Figures 4 and 5, respectively. In both cases, oxygen evolution is observed from the beginning of charge at approximately 3.4 V with an $e^-$/O$_2$ molar ratio at around three for the first half of the charge capacity. This oxygen evolution rate is consistent with the decomposition of equivalent amounts of Li$_2$O$_2$ through a two-electron and LiOH through a four-electron mechanism, respectively (Equations (i)–(iv)):

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\begin{align*}
3I^- & \rightarrow I_3^- + 2e^- \\
\text{Li}_2\text{O}_2 + I_3^- & \rightarrow 2\text{Li}^+ + 3I^- + \text{O}_2 \uparrow \\
6I^- & \rightarrow 2I_3^- + 4e^- \\
4\text{LiOH} + 2I_3^- & \rightarrow 4\text{Li}^+ + 6I^- + 2\text{H}_2\text{O} + \text{O}_2 \uparrow 
\end{align*}
\]

Beyond the midpoint of charge capacity, the DEMS profiles in both cases are noticeably different; in the sulfolane-absent case, the oxygen evolution rate is reduced continuously as the cell voltage rises above 3.5 V. This suggests that the charging process deviates from the aforementioned desirable oxidation reactions and side reactions involving less or no O$_2$ evolution pathways may occur, such as the formation of iodo-oxygen species (26, 27), and dimethyl sulfone (DMSO$_2$) (11). In the case of cells containing sulfolane the oxygen evolution rate is maintained at an overall Faradaic efficiency.
3.7 V. In both cases, the DEMS profiles are reproducible for the second charge with no significant CO₂ evolution detected. The observation of a 3 e⁻/O₂ OER process rather than a 2 e⁻/O₂ expected for Li₂O₂ decomposition, alongside the absence of CO₂ evolution and consistency in charging DEMS profiles might be associated with the partial removal of LiOH during the OER in cells containing sulfolane as co-solvent but further work is required to understand the charging mechanisms.

4. Conclusions

In this report, we have investigated the effect of sulfolane as co-solvent in Li-O₂ cells cycled with LiI/H₂O/LiTFSI/Pyr14TFSI/DMSO electrolyte. A mixture of Li₂O₂ and LiOH is formed during cell discharge, with the presence of sulfolane slightly increasing the formation of LiOH as shown by solid-state ¹H NMR and SEM. On charging, the decomposition of both Li₂O₂ and LiOH is observed with oxygen evolution being monitored by DEMS measurements. The observation of residual discharge products after a full charge confirms the effect of parasitic reactions to the faradaic efficiency. Further work is required to optimise the more stable LiOH chemistry, and to understand the associated OER mechanisms for the successful commercial development of rechargeable Li-O₂ batteries.

Acknowledgements

Gunwoo Kim and Clare P. Grey thank EUHorizon 2020 GrapheneCore1-No.696656 for research funding.

References

The Authors

Gunwoo Kim is a research associate in Chemistry at the University of Cambridge, UK, and Cambridge Graphene Centre, UK. He received his PhD in Chemistry at the University of Cambridge and his current research focuses on characterising graphene-based electrodes and understanding mechanisms in metal-O₂ batteries by using various spectroscopic techniques with an emphasis on solid-state NMR spectroscopy.

Tao Liu is a research associate in Chemistry at University of Cambridge, UK, and a Junior Research Fellow of Darwin College Cambridge. He received his PhD in Chemistry at University of Cambridge and his research interests include electrocatalysis and energy storage.
Israel Temprano received his PhD in Chemistry at Université Laval, Canada, and then moved to the University of Liverpool, UK, as Marie Curie Research Fellow before joining the University of Cambridge, UK, as postdoctoral research associate. His current research focuses on the development of in situ characterisation tools for the study of Li-O₂ batteries.

Enrico A. Petrucco is currently a Senior Scientist in the Battery Materials Research department at Johnson Matthey, Sonning Common, UK. He graduated with a BSc in Physics from Rensselaer Polytechnic Institute, New York, USA, in 2004 and has 18 years’ experience in the research and development of electrochemical materials. His current research interests include oxygen evolution catalysis, graphene and energy storage and conversion materials. He currently applies multidisciplinary studies to investigate next generation battery technologies.

Nathan Barrow is currently a Principal Scientist in the Advanced Characterisation department at Johnson Matthey, Sonning Common, UK. He graduated with an MPhys in 2006 from the University of Warwick, UK, where he remained to gain a PhD in solid-state NMR. In 2010 Barrow was a Knowledge Transfer Partnership associate between the University of Warwick and Johnson Matthey, helping to install and run a solid-state NMR service. His current research focuses on applying advanced characterisation to materials such as zeolites, alumina, glasses and batteries.

Clare P. Grey is the Geoffrey Moorhouse-Gibson Professor of Chemistry at Cambridge University, UK, a Fellow of Pembroke College Cambridge and a Fellow of the Royal Society. She received a BA and DPhil (1991) in Chemistry from the University of Oxford, UK. After postdoctoral fellowships in The Netherlands and at DuPont CR&D in Wilmington, DE, USA, she joined the faculty at Stony Brook University (SBU), New York, USA, as an Assistant (1994), Associate (1997) and then Full Professor (2001–2015). She moved to Cambridge in 2009, maintaining an adjunct position at SBU. Her current research interests include the use of solid-state NMR and diffraction-based methods to determine structure-function relationships in materials for energy storage (batteries and supercapacitors), conversion (fuel cells) and carbon capture.