Towards Reversible and Moisture Tolerant Aprotic Lithium-Air Batteries

Israel Temprano, Tao Liu, Enrico Petrucco, James H. J. Ellison, Gunwoo Kim, Erlendur Jónsson, Clare Grey

Submitted date: 30/04/2020 • Posted date: 05/05/2020

Licence: CC BY-NC 4.0

Citation information: Temprano, Israel; Liu, Tao; Petrucco, Enrico; Ellison, James H. J.; Kim, Gunwoo; Jónsson, Erlendur; et al. (2020): Towards Reversible and Moisture Tolerant Aprotic Lithium-Air Batteries. ChemRxiv. Preprint. <https://doi.org/10.26434/chemrxiv.12221717.v1>

The development of moisture-tolerant, LiOH-based non-aqueous Li-O₂ batteries is a promising route to bypassing the inherent limitations caused by the instability of their typical discharge products, LiO₂ and Li₂O₂. The use of the I⁻/I₃⁻ redox couple to mediate the LiOH-based oxygen reduction and oxidation reactions has proven challenging to develop due to the multiple reaction paths induced by the oxidation of I⁻ on cell charging. In this work we demonstrate a reversible LiOH-based Li-O₂ battery cycling through a 4 e⁻/O₂ process with low charging overpotential (below 3.5 V vs Li/Li⁺) by introducing an ionic liquid to a glyme-based electrolyte containing Lil and water. The addition to the ionic liquid increases the oxidizing power of I₃⁻, shifting the charging mechanism from IO⁻/IO₃⁻ formation to O₂ evolution

File list (5)

Towards reversible and moisture tolerant aprotic lithium-... (600.53 KiB)	view on ChemRxiv • download file
TOC.jpg (55.04 KiB)	view on ChemRxiv • download file
TOC.png (200.33 KiB)	view on ChemRxiv • download file
SI Towards reversible and moisture tolerant aprotic lithiu... (700.98 KiB)	view on ChemRxiv • download file
TOC.bmp (1.40 MiB)	view on ChemRxiv • download file

Towards reversible and moisture tolerant aprotic lithium-air batteries

Israel Temprano¹, Tao Liu^{1,2}, Enrico Petrucco³, James H. J. Ellison¹, Gunwoo Kim¹, Erlendur Jónsson^{1,4} & Clare P. Grey^{*1}

1 Department of Chemistry, University of Cambridge, Cambridge, UK

2 Current address: Shanghai Key Laboratory of Chemical Assessment and Sustainability, Department of Chemistry, Tongji University, Shanghai, China

3 Johnson Matthey, Blounts Court, Sonning Common, Reading, RG4 9NH, UK

4 Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

Abstract

The development of moisture-tolerant, LiOH-based non-aqueous Li-O₂ batteries is a promising route to bypassing the inherent limitations caused by the instability of their typical discharge products, LiO₂ and Li₂O₂. The use of the I⁻/I₃⁻ redox couple to mediate the LiOH-based oxygen reduction and oxidation reactions has proven challenging to develop due to the multiple reaction paths induced by the oxidation of I⁻ on cell charging. In this work we demonstrate a reversible LiOH-based Li-O₂ battery cycling through a 4 e⁻/O₂ process with low charging overpotential (below 3.5 V vs Li/Li⁺) by introducing an ionic liquid to a glyme-based electrolyte containing LiI and water. The addition to the ionic liquid increases the oxidizing power of I₃⁻, shifting the charging mechanism from IO⁻/IO₃⁻ formation to O₂ evolution.

In the light of recent commitments from several European countries to ban the sale of internal combustion engine vehicles in the coming decades [1,2], the race to develop electrical storage strategies beyond the capabilities of lithium ion batteries is intensifying considerably. Amongst the many different options, Li-air batteries have attracted significant attention due to their comparable energy density to fossil fuels [3].

Non-aqueous Li-air batteries (LABs) are composed of a lithium metal anode, an organic-based lithium-ion conducting liquid electrolyte, and a porous, typically carbon based, cathode. During discharge, O₂ is reduced at the cathode (the oxygen reduction reaction, ORR), which then combines with lithium ions in solution forming insoluble discharge products that fill up the porous structure of the carbon electrode. The discharge product is oxidised during charge, with O₂ being released back to the atmosphere (the oxygen evolution reaction, OER) [4].

Despite of its potential, several fundamental challenges remain to be overcome for the successful development of non-aqueous LABs [4-6]. Amongst these challenges, the instability of the typical discharge products (LiO₂ and Li₂O₂) in the presence of moisture and CO₂ represents a fundamental stumbling block for their development [7]. Recently, it has been shown that lithium hydroxide (LiOH) can be formed as a discharge product in moisture-tolerant LABs with a high capacity and low charge overpotential using either LiI as a redox mediator or Ru as a catalyst in a wet organic electrolyte [8-10]. However, several questions surrounding the reversibility of LiOH chemistry remain, which arise from (i) the half-cell potential of the OER of LiOH under standard state (aqueous) conditions being higher than that of the Li₂O₂ OER, given the higher thermodynamic stability of the former, (ii) the detection of oxidation products originating from the redox mediator and the solvents, such as IO₃⁻ [9,11,12], and DMSO₂, [10] respectively, after charge (iii) little or no oxygen evolution being observed in gas analysis experiments [12]. These observations have given rise to doubts as to whether the

iodide/triiodide (I^-/I_3^-) redox system is capable of sustaining reversible ORR/OER chemistry via LiOH formation and decomposition [12-15].

It is now established that the (I^-/I_3^-) redox potential is solvent-dependent, and therefore that the oxidizing power of I_3^- can be tailored by means of adjusting the physicochemical parameters (i.e., dielectric constant, ionic strength, Gutmann acceptor/donor numbers, etc.) of the electrolyte [9,16-18]. Ionic liquids (IL) have been shown to alter the solvation/coordination environments of this redox system, therefore substantially affecting the (I^-/I_3^-) redox potential [16], while combining high ionic conductivity with low volatility [19-26]. However, the high viscosity of ILs, which limits O_2 diffusion coefficients, and the low O_2 solubility are disadvantageous for the performance of LABs [27]. The presence of water has been shown to help addressing some of these drawbacks by enhancing the solution-transfer of discharge products and redox mediator [28], and by affecting the solvation coordination of the electrolyte, which has also shown to have an impact in the activity of the (I^-/I_3^-) redox system during discharge [8]. Thus, the combination of LiI as redox mediator with water and an ionic liquid is a potentially good strategy for efficiently tailoring the electrolyte properties in Li- O_2 batteries.

In this work we report a step forward toward the realization of a viable moisture tolerant LAB, by reversibly cycling LiOH with low charging overpotentials in cells with LiI as redox mediator and H_2O and pyrrolidinium(1,4) bis(trifluoromethanesulfonyl)imide (Pyr₁₄TFSI) as additives in a low volatility electrolyte. Pyr₁₄TFSI is one of the most widely studied ILs in relation to Li- O_2 batteries, showing high stability toward superoxide species, and a relatively high Li^+ diffusion coefficient [22,26-31]. We found that the inclusion of Pyr₁₄TFSI is crucial for the reversibility of the electrochemical formation/decomposition of LiOH as demonstrated by the observation of a $4 e^-/O_2$ OER using *operando* online electrochemical mass spectrometry (OEMS). OER from LiOH decomposition is further confirmed by OEMS experiments with (electrochemically) preloaded electrodes, as well as isotopic labelling. The suppression of the side-reactions to form oxygenated iodine species (IO^- , IO_3^-), which trap the oxygen during charge is also observed.

A $4 e^-/O_2$ oxygen evolution reaction

Li- O_2 cells were constructed with a lithium metal anode, an anolyte consisting of 0.3 M LiTFSI in G4, a lithium conducting glass ceramic (LICGC-Ohara AGO10) separating the two electrolytes, a catholyte containing 0.9 M Pyr₁₄TFSI, 0.7 M LiTFSI, 50 mM LiI and 5000 ppm H_2O in G4, and a mesoporous carbon black cathode (Ensaco-P150). The LICGC serves to prevent redox shuttling (I^-/I_3^-) and reaction of catholyte additives with the Li anode. These cells were evaluated with *operando* OEMS by capacity-limiting galvanostatic cycling, in order to keep the levels of water within limits known for promoting LiOH formation during the ORR (between 1500 and 5000 ppm). Fig. 1 (system description in Supplementary Fig. 1a) shows the electrochemical profile (a, b) and gas evolution rate of O_2 ($m/z=32$; c, d), H_2 , CO and CO_2 ($m/z= 2, 28, 44$; e, f) for the discharge and charge of this cell. The electrochemical discharge profile (Fig. 1a) shows a sustained single discharge plateau at 2.6 V (vs Li/Li⁺). The discharge produces a constant consumption rate of oxygen of ~ 0.51 nmol/s (Fig. 1c), corresponding to a $4 e^-/O_2$ stoichiometry, with no significant evolution of gases indicative of parasitic reactions (Fig. 1e). The total amount of oxygen consumption detected amounts to 18.5 μ mol, which corresponds to a 99.1% Faradaic efficiency.

Figure 1| 4 Electron Formation and Removal of LiOH in Mixed Glyme/Ionic Liquid Cells. a, b, Galvanostatic profiles and c, d, online mass spectrometry analysis of oxygen, and e, f, hydrogen, carbon monoxide and carbon dioxide ($m/z = 32, 2, 28, 44$ respectively) evolution of batteries discharged (left) and charged (right) at a current of $50 \mu\text{A}/\text{cm}^2$ in an electrolyte comprising 0.9 M $\text{Pyr}_{14}\text{TFSI}$, 0.7 M LiTFSI , 50 mM LiI and 5000 ppm H_2O in G4; g, Faradaic efficiency of the OER during the first 7 cycles.

The charge profile shows an initial rapid increase in potential from 3.1 to 3.3 V followed by a relatively flat process at approximately 3.4 V (Fig. 1b). Of note, oxygen evolution is clearly observed to occur from the beginning of charge, stabilising around a rate corresponding to approximately $4 e^-/\text{O}_2$ stoichiometry (Fig. 1d). A total of $18.4 \mu\text{moles}$ of oxygen evolved during charge, 99.5% of the amount consumed in the discharge, with no significant signs of parasitic reactions as signalled by a lack of evolution of H_2 , CO or CO_2 (Fig. 1d). The Faradaic efficiency decreases steadily in subsequent discharge-charge cycles, although it remains above 80% after 7 cycles (Fig. 1g, and Supplementary Fig. 2). This indicates incomplete removal of LiOH, a small degree of degradation and/or accumulation of products from parasitic reactions.

By comparison, in the absence of $\text{Pyr}_{14}\text{TFSI}$ only a very small amounts of oxygen ($\sim 0.4 \text{ nmol/s}$) above 3.5 V, and hydrogen ($< 0.2 \text{ nmol/s}$) are detected (Supplementary Fig. 3g-m) during charge before a steep increase in potential above 3.6 V at the end of charge is observed, which is accompanied by a significant evolution of carbon dioxide (and to carbon monoxide to lesser extent), suggesting electrode (carbon)/electrolyte oxidation (Supplementary Fig. 3m).

Analysis of the ORR products

Analysis of the cathode after discharge with X-ray diffraction (XRD) (Fig. 2a – red trace) is dominated by patterns corresponding to crystalline LiOH. All reflections associated to LiOH are absent in the

diffractogram corresponding to the fully charged electrodes, confirming the removal of the crystalline discharge product. (Fig. 2a – green trace).

Operando pressure monitoring during discharge (Fig. 2b) confirms a $4 e^-/O_2$ stoichiometry during ORR for cells with Pyr₁₄TFSI, as expected for the formation of LiOH. The insert in Fig. 2b shows a bar plot of the LiOH:Li₂O₂ ratio (of 97:3±3) in the discharge product determined via an acid-base and iodometric titration [32] of the electrodes at the end of discharge. This suggests that the ORR reaction occurs almost in its entirety through the formation of LiOH, and not through Li₂O₂ chemistry under the experimental conditions shown in Fig. 1.

Figure 2| *Operando* and *ex-situ* characterization of the LiOH Formation during ORR. **a**, X-ray diffractograms at different stages of capacity-limited cycling (pristine – blue; discharged – red; fully charged – green) as represented in the electrochemical profile; **b**, *Operando* pressure monitoring experiment during discharge and representation of the percentage of LiOH (magenta) and Li₂O₂ (orange) detected by titration measurements at the end of the discharge. (Note that the presence of I_3^- in the electrolyte generates an underestimation of LiOH and overestimation of Li₂O₂ as discussed in the methods section); SEM characterisation (at different magnifications) of electrodes at the end of discharge **c**, and end of charge **d**, (scale bars shown in white). Relevant reflections due to LiOH and PTFE binder are indicated by grey triangles and blue dots, respectively in **a**. All cells were cycled at 50 $\mu A/cm^2$.

Scanning electron microscopy (SEM) images of electrodes during the first discharge are shown in Fig. 2c. The discharge product in capacity limited cells (2 mAh) present typical “flower-like” LiOH crystals, similar to those previously reported in cells containing LiI and water [9] of up to 7 μm in size. The absence of these crystalline structures in the SEM images of fully recharged electrodes (Fig. 2d) confirms the removal of the discharge product during charge without the precipitation of large quantities of by-products from parasitic reactions.

In order to evaluate the mechanistic implications of the observed stoichiometry during the OER in Fig. 1, further OEMS experiments using an electrode either electrochemically preloaded with Li_2O_2 (Fig. 3 - left) or discharged with partially ^{17}O -enriched H_2O (Fig. 3 – right) were performed. Li_2O_2 preloaded electrodes were first produced by discharging a cell using 3 M LiTFSI in G4 as the electrolyte (i.e., with no LiI). The cell was subsequently disassembled in the glove box and the electrode was washed 3 times with DME and dried under vacuum for 30 minutes. This electrode was then loaded in a two-compartment cell with the same electrolyte (containing 0.9 M Pyr₁₄TFSI, 0.7 M LiTFSI, 50 mM LiI and 5000 ppm H_2O in G4) used for the cells shown in Fig. 1. In this case the OER showed an approximately $2\text{ e}^-/\text{O}_2$ stoichiometry (Fig. 3c) consistent with the reversible formation and oxidation of Li_2O_2 . After reaching an evolution rate corresponding to $2\text{ e}^-/\text{O}_2$, a noticeable dip in the oxygen evolution is seen (Fig. 3c). This effect has been previously attributed to a transition between the delithiation of Li-deficient ($\text{Li}_{2-x}\text{O}_2$) species on Li_2O_2 particles [33-35]. Preloading was similarly performed using the IL-free conditions previously shown to produce LiOH electrochemically [8]: an electrolyte comprising 0.7 M LiTFSI, 50 mM LiI, and 5000 ppm H_2O in G4 was discharged at a current of $70\text{ }\mu\text{A}/\text{cm}^2$. Switching to the ionic liquid containing electrolyte resulted in $4\text{ e}^-/\text{O}_2$, oxygen evolution on charge (Supplemental Figure 6), which indicates that the presence of the ionic liquid has only a limited effect in the formation of the discharge product.

Figure 3| Operando Gas Analysis of Preloaded Electrodes and Isotopic Exchange during OER. a, b, Galvanostatic profiles (top) and c, d, online mass spectrometry analysis of oxygen ($m/z=32$) and e, f, hydrogen, carbon monoxide and carbon dioxide ($m/z= 2, 28, 44$) evolution during charge of

electrochemically preloaded electrodes with Li₂O₂ (left); and of a Li-O₂ cell discharged using ¹⁷O-enriched H₂O in the electrolyte containing G4 and Pyr₁₄TFSI at 70 μA/cm².

Since earlier ¹⁷O-ssNMR measurements have reported that both O₂ and H₂O contribute to the oxygen atoms in the LiOH formed via a Lil-catalysed electrochemical reaction in DME (G1), [8], a further OEMS experiment was performed using ¹⁷O-enriched H₂O (Fig. 3 - right) and Pyr₁₄TFSI. A m/z= 32 mass spectrometer signal (Fig. 3d – blue) dominates the response on charge, which is due to ¹⁶O-¹⁶O. A signal is seen at m/z= 33 (Fig. 3d – magenta), which is assigned to ¹⁷O-¹⁶O. The signal at m/z= 34 (Fig. 3d – orange) is assigned to either to ¹⁷O-¹⁷O or ¹⁸O-¹⁶O. Since the signal intensity of the m/z= 33 and 34 signals are similar in magnitude, this indicates that the m/z= 33 signal is not due to the ¹⁷O in O₂ gas, since the natural abundance of ¹⁷O and ¹⁸O are 0.04 and 0.2 %, respectively. The relatively low intensity of the m/z= 33 signal (from ¹⁶O-¹⁷O) compared with the m/z= 32 signal (from ¹⁶O-¹⁶O) is due to the low ¹⁷O-enrichment in the LiOH as observed by ¹⁷O ssNMR (Supplementary Fig. 6), most likely a result of the low enrichment of the H₂¹⁷O.

Pathways to LiOH removal

The mechanism for LiOH formation in the ORR reaction have been discussed extensively elsewhere [8] and thus we focus here on the OER reaction. Two questions arise from the OEMS data (Fig. 1 and Supplementary Figs. S2, S10, and S11). Firstly, what is the role played by Pyr₁₄TFSI in the promotion of oxygen evolution? Secondly, what is the mechanism for LiOH decomposition/removal in the absence of the ionic liquid when there is no O₂ evolution?

The Lil mediated OER during the charge of LiOH-based Li-O₂ batteries has been proposed to follow a two-step path where the electrochemical oxidation of I⁻ to I₃⁻ is followed by the chemical oxidation of LiOH [8-10,12,36,37]

where $E_{\text{vs Li/Li}^+}^{\circ}$ for reaction (1) corresponds to 3.5761 V under standard (aqueous) conditions. The reversibility of Li-O₂ batteries cycling through LiOH has been a much-discussed subject due to the high thermodynamic stability of LiOH and the difficulty of performing the multi electron OER process at low overpotentials [9-12,14,15,37,38].

The potential under standard conditions of the I⁻/I₃⁻ equilibrium is very close to the redox potential of the I⁻/I₂ equilibrium ($E_{\text{vs Li/Li}^+}^{\circ} = 3.5756 \text{ V}$)

and in water only a single process is seen in CV scans at close to 3.6 V, indicating that both I₃⁻ and I₂ are thermodynamically capable of decomposing LiOH to generate O₂ under standard conditions (the 2LiOH/(O₂ + H₂O) couple corresponding to 3.34 V) [16] .

The removal of LiOH upon charging in cells containing Lil in organic electrolytes with added water has been shown to produce IO₃⁻ as the dominant product rather than O₂ at ~3.5 V in ether based electrolytes [11,12], which has been proposed to form through the oxidation of I⁻ to I₂ (reaction 3) and its subsequent chemical reaction with LiOH [12]:

or via direct oxidation by I₃⁻ [11,38]:

followed by the disproportionation of IO^- into IO_3^- [11,17,38].

In this study, cells containing $\text{Pyr}_{14}\text{TFSI}$ show clear evidence for a $4\text{e}^-/\text{O}_2$ OER commencing at $\sim 3.2\text{ V}$ (Fig. 1). This oxygen evolution is absent in cells without ionic liquid (Supplementary Fig. 3 e-h) even when charging at comparable potentials (below 3.5 V for $\sim 75\%$ of charge). In order to investigate the difference in mechanism during the OER, characterization of the electrolyte after charge was performed. UV spectra of aliquots of the electrolyte of charged cells with and without $\text{Pyr}_{14}\text{TFSI}$ (Fig. 4b) show the presence of features at 295 and 365 nm , corresponding to the presence of I_3^- ; no feature corresponding to I_2 (at 520 nm) is seen in either case (insert in Fig. 4b). The electrolyte of cells without IL (Fig. 4b – red trace) show the presence of peaks at 228 and 465 nm , assigned to IO_3^- and IO^- respectively; these peaks are absent in cells with $\text{Pyr}_{14}\text{TFSI}$ (Fig. 4b – blue trace). The presence of I_3^- in both samples indicates that this is the main product of I^- oxidation, and therefore suggest that this may be the species responsible for oxidising LiOH , rather than I_2 . The lack of O_2 evolution observed in OER data of cells without $\text{Pyr}_{14}\text{TFSI}$ can be explained by the formation of oxidized iodine species (IO^- and IO_3^-) the oxygen effectively being trapped in the solution, as reported for similar electrolytes [11-13,17,38].

In order to test these hypotheses, a solution of I_3^- was injected into a mixture of electrolyte containing $0.9\text{ M Pyr}_{14}\text{TFSI}$, 0.7 M LiTFSI , 50 mM LiI and $5000\text{ ppm H}_2\text{O}$ in G4, and commercial LiOH powder, and the gas evolution measured by mass spectrometry (Fig. 4a). Gas bubbles can be seen evolving from the LiOH powder as soon as the I_3^- solution is injected and the $m/z = 32$ signal confirms the evolution of O_2 from this mixture, demonstrating that I_3^- is capable of oxidizing LiOH , as per reaction (2), in this electrolyte.

Solvation effects can strongly influence the electrochemistry of soluble redox mediators by altering thermodynamics and reactivity of the mediators. In particular, the oxidising power of I_3^- has been shown to depend on the solvation/coordination properties of the electrolyte [8,17,18]. Increasing the thermodynamic stability of I^- through solvation, e.g. by including additives with large Gutmann acceptor numbers (AN) and dielectric constants, has been proposed to decrease the equilibrium constant in reaction 1, driving the reaction to the left (towards I^-) and promoting an increase in the oxidising power of I_3^- [16-18]. More generally, the factors that control the relative and absolute values of the two couples are subtle, because the values are also controlled by the stability of I_3^- relative to $\text{I}_2 + \text{I}^-$, as defined by the following disproportionation reaction:

As the stability of I_3^- decreases then distinct redox process for reactions 1 and 3 are no longer seen. For example, in water, where I^- is strongly solvated and I_2 is only sparingly soluble, only one process is seen, while in acetonitrile, with its lower acceptor number (and thus weaker coordination to I^-), the two processes are separated by 0.4 V [16].

Figure 4| Spectroscopic and electrochemical analysis of the I_3^- oxidising power. **a**, Online mass spectrometry chemical test. At $t = 0$, 0.2 ml of a 50 mM I_3^- , 0.9M $Pyr_{14}TFSI$ solution in G4 is injected to 10.5 mg of LiOH in 0.5 ml of electrolyte containing 0.9 M $Pyr_{14}TFSI$, 0.7 M $LiTFSI$, 50 mM LiI , 5000 ppm H_2O in G4 (blue trace) and 0.7 M $LiTFSI$, 50 mM LiI , 5000 ppm H_2O in G4 (red trace). A blank spectrum is collected by injecting the I_3^- solution into the electrolyte containing 0.9 M $Pyr_{14}TFSI$, 0.7 M $LiTFSI$, 50 mM LiI , 5000 ppm H_2O in G4 in the absence of LiOH (green trace). Argon was used as carrier gas; **b**, UV spectra of catholytes collected after galvanostatic discharge and charge (0.7 mAh/cm²) containing 0.7 M $LiTFSI$, 50 mM LiI , 5000 ppm H_2O (red trace) and with 0.9 M $Pyr_{14}TFSI$ (blue trace) in G4; **c**, Galvanostatic charge-discharge curves of catholytes with 0.7 M $LiTFSI$, 50 mM LiI in neat G4 (light red) and G4 containing 5000 ppm H_2O (dark red) and with neat 0.9 M $Pyr_{14}TFSI$ (light blue) and $Pyr_{14}TFSI$ containing 5000 ppm H_2O (dark blue), cycled at 50 $\mu A/cm^2$ under argon. A LICGC isolated the cathode from the Li metal anode; 0.3 M $LiTFSI$ in G4 was used as the anolyte.

Galvanostatic charge-discharge curves of cells cycled under argon atmosphere show that the I^-/I_3^- couple in the 0.7 M $LiTFSI$, 50 mM LiI and 5000 ppm H_2O in G4 electrolyte is at 3.11 V (Fig. 4c – dark red trace and Supplementary Fig. S9a), slightly above of the value observed for the same neat electrolyte (0.7 M $LiTFSI$, 50 mM LiI in G4) of 3.10 V (Fig. 4c – light red trace). These values are also slightly above the ones reported for cells with 0.25M $LiTFSI$, 50 mM LiI , 5000 ppm H_2O in G4 and G1

of 3.07 V and 2.95 V respectively [9]. The addition of Pyr₁₄TFSI to these mixtures increases the I⁻/I₃⁻ redox potential to 3.20 V and 3.28 V in the wet and neat electrolytes respectively (Fig. 4c – dark and light blue traces and Supplementary Fig. S9a). The I⁻/I₂ redox potential is found above 3.7 V and 3.8 V in the absence and presence of Pyr₁₄TFSI, respectively (Supplementary Fig. S9a), with the large separation between the two iodine couples being ascribed to the poor solvation of I₂ by glymes [16,18]. This is consistent with previous work where the higher oxidative power of I₂ and I₃⁻ in pure ILs than in solvents such as acetonitrile was ascribed to the higher ionic strength of the ionic liquids, which stabilizes I⁻ (and I₃⁻ to a lesser extent) and their poor ability to solubilise I₂. The addition of water impurities to the ILs was shown to increase the oxidising power of I₃⁻, while the addition of solvents that solvate I₂ lowers the value of the I₃⁻/I₂ couple noticeably [16].

Conclusions

LiI mediated cells in the presence of water and the ionic liquid Pyr₁₄TFSI produce reversible 4 e⁻/O₂ ORR and OER at 2.6 V and 3.2-3.5 V respectively during capacity-limiting galvanostatic cycling in *operando* online electrochemical mass spectrometry (OEMS) experiments. A combination of *ex-situ* characterization methods confirm that these reactions occur through the formation/decomposition of LiOH. OEMS experiments with Li₂O₂ preloaded electrodes show that the electrolyte mixture is also capable of efficiently decomposing Li₂O₂ through a 2 e⁻/O₂ during OER. The presence of Pyr₁₄TFSI increases the I⁻/I₃⁻ redox potential shifting the mechanism of the OER from the irreversible production of IO⁻/IO₃⁻ to the evolution of O₂. The combination of an IL and water in aprotic electrolytes is an effective strategy for tailoring the electrolyte properties and reaction mechanisms in redox-mediated Li-O₂ batteries.

Methods

Materials preparation. Carbon electrodes were prepared by kneading a slurry made from 75 wt% carbon black (*Ensaco P150*, *Imerys*) and 25% PTFE binder (*Aldrich*, 60% water solution) in ethanol until a homogeneous film was obtained. Free-standing discs were cut from this film, annealed at 120°C *in vacuo* for 12 hours and transferred to the glovebox without exposure to air. The areal loading of the carbon electrode is ~ 1-2 mg/cm². Tetraethylene glycol dimethyl ether (G4, *Aldrich*, 99%) was refluxed with sodium metal under Ar for 3 days prior to fractional distillation *in vacuo*. The final water content was measured by Karl Fischer titration (*Metrohm 899*) at < 10 ppm, and then stored over 4 Å molecular sieves. Lithium bis(trifluoromethyl)sulfonylimide (LiTFSI, 3M *FluoradTM*, HQ115) and LiI (*Aldrich*, 99.9%) were dried *in vacuo* at 160°C and 200°C respectively for 12 hours before being used to prepare the electrolyte. Pyrrolidinium (1,4)-bis-(trifluoromethanesulfonyl)-imide–TFSI (Pyr₁₄TFSI, *Solvionic* 99.9%; H₂O ≤ 0,002%) was used as purchased. All materials were stored and handled in an Ar glovebox with <0.1 ppm O₂ and <0.1 ppm H₂O.

Electrochemical methods. All Li-O₂ cells were assembled inside an Ar-filled glove box on bored-through stainless-steel *Swagelok* unions by staking a Li disc (*PI-KEM*, 99.99%), 1 piece of pressed borosilicate glass fibre separator (*Whatman*) wetted with 0.3M LiTFSI / G4 (anolyte), a disk of lithium-ion conducting glass ceramic (*Ohara AG01*), 1 piece of pressed borosilicate glass fibre separator wetted with 210 µl of the active catholyte, and *Ensaco P150* cathode. Stainless steel mesh (details) was used as current collector. Electrochemical tests were performed on either a *Biologic SP-300* or an *Ivium Vertex* potentiostat/galvanostat. Due to the significant resistance of LICGC disk, the resistance was measured by impedance spectroscopy. Ohm's Law was then applied to obtain the Ohmic overpotential (Supplementary Fig. 12), which was then subtracted in the load curves. A newly designed Online Electrochemical Mass Spectrometry (OEMS) system was developed for this work and it is described in detail in the supplementary information (Supplementary Fig. S1a). The cell

design consists in a 1" Swagelok union with inlet and outlet tubes (1/16") welded to the top plunger (with ~ 0.83 cm³ headspace) and capped with self-sealing quick-connects (*Beswick Engineering*) to isolate the cell from the atmosphere between assembly in the glove box and connection to the OEMS system. Galvanostatic discharge and charge were carried out under 20% O₂, and 0% O₂ in Ar respectively. A newly designed pressure monitoring cell assembly was also developed for this work and it is also described in detail in the supplementary information (Supplementary Fig. 1b). A pressure transducer was connected to a 1" *Swagelok* cell and sealed in the glove box. The cell assembly was then pumped down and subsequently filled up with pure O₂. The total internal volume of the setup was measured independently for each test using a reference volume and the measured change in pressure was then converted to number of moles of gas consumed using the Ideal gas law.

Characterization methods. Characterization of electrodes after electrochemical tests was performed by first disassembling the cell inside the glove box, rinsing the cathode twice in dry DME, then drying them *in vacuo*. Powder X-ray diffraction measurements were performed with the electrode placed in an air-tight sample holder in a *Panalytical Empyrean* diffractometer, in reflection mode with Cu K α 1 radiation ($\lambda=1.5406$ Å). Ultraviolet spectra were acquired on samples in an air tight quartz cuvette in a *LAMBDA TM 25/35, PerkinElmer* spectrometer. G4 was used for dilutions, and pristine electrolyte was used as reference. Scanning electron microscopy was obtained in a *Tescan MIRA3* microscope (5keV; 7pA) with samples transported from the glove box sealed in a *Kammrath & Weiss* transfer module. Titration experiments were performed following the method previously reported by McCloskey *et al.* [32]. Cathodes were extracted from cells inside the glove box and placed in a sealed vial unwashed. 2ml of ultrapure water (Millipore) were injected into the vial using a syringe and then titration of the base was done with a standardized 0.01 M HCl solution, using phenolphthalein as end-point indicator while vigorously stirring. After acid-base titration 1ml of KI (2 wt %), 1 ml of H₂SO₄ (3.5 M) and 50 ml of a molybdenum-based catalyst solution were added. The I₂ generated is then quickly titrated using 0.01N NaS₂O₃ solution using a starch indicator. The quantification of electrochemically generated LiOH during cell discharge is done by subtracting the amount of LiOH generated by the reaction of Li₂O₂ with H₂O (Li₂O₂ + 2H₂O → 2LiOH + H₂O₂). The amount of LiOH generated from electrochemically generated Li₂O₂ during cell discharge is then calculated from the amount of I₂ generated from H₂O₂ (H₂O₂ + 2KI + H₂SO₄ → I₂ + K₂SO₄ + 2H₂O), which is measured during the iodometric titration (I₂ + 2Na₂S₂O₃ → Na₂S₄O₆ + 2NaI). It is important to note that the presence of I₃⁻, formed during discharge, acts as false positive in the iodometric titration, increasing the amount of Li₂O₂ detected. Since the quantification of electrochemically generated LiOH is subsequently calculated from the subtraction of the amount of Li₂O₂ detected, this has therefore an effect of decreasing the calculated amount of LiOH. The LiOH/Li₂O₂ ratio obtained must be treated therefore as an underestimation of LiOH content in the discharge product.

Acknowledgements

This research was enabled by funding support from Innovate UK (132220) and the EPSRC (EP/M009521/1 DJR00640). The authors wish to acknowledge experimental contributions to this work by C. Brackstone for help with titration, Dr Y. Jin with ssNMR, and S. Engelke with cyclic voltammograms.

References

- ¹ Bose Styczynski, A. & Hughes, L., Public policy strategies for next-generation vehicle technologies: An overview of leading markets. *Environmental Innovation and Societal Transitions* 31, 262-272 (2018).

- 2 Meckling, J. & Nahm, J., The politics of technology bans: Industrial policy competition and green goals for the auto industry. *Energy Policy* 126, 470-479 (2019).
- 3 Grey, C.P. & Tarascon, J.M., Sustainability and in situ monitoring in battery development. *Nature Materials* 16, 45–56 (2017).
- 4 Aurbach, D., McCloskey, B.D., Nazar, L.F., & Bruce, P.G., Advances in understanding mechanisms underpinning lithium-air batteries. *Nature Energy* 1, 16128 (2016).
- 5 Girishkumar, G., McCloskey, B., Luntz, A.C., Swanson, S., & Wilcke, W., Lithium-Air Battery: Promise and Challenges. *The Journal of Physical Chemistry Letters* 1 (14), 2193-2203 (2010).
- 6 Kwabi, D.G. *et al.*, Materials challenges in rechargeable lithium-air batteries. *MRS Bulletin* 39 (5), 443-452 (2014).
- 7 Mahne, N. *et al.*, Singlet oxygen generation as a major cause for parasitic reactions during cycling of aprotic lithium-oxygen batteries. *Nature Energy* 2, 17036 (2017).
- 8 Liu, T. *et al.*, Understanding LiOH Formation in a Li-O₂ Battery with LiI and H₂O Additives. *ACS Catalysis*, 66-77 (2018).
- 9 Liu, T. *et al.*, Cycling Li-O₂ batteries via LiOH formation and decomposition. *Science* 350 (6260), 530-533 (2015).
- 10 Liu, T. *et al.*, Understanding LiOH Chemistry in a Ruthenium Catalyzed Li-O₂ Battery. *Angewandte Chemie* 129 (50), 16273–16278 (2017).
- 11 Liu, T., Kim, G., Carretero-González, J., Castillo-Martínez, E., & Grey, C.P., Response to Comment on "Cycling Li-O₂ batteries via LiOH formation and decomposition". *Science* 352 (6286), 667d-667d (2015).
- 12 Burke, C.M. *et al.*, Implications of 4 e⁻ Oxygen Reduction via Iodide Redox Mediation in Li-O₂ Batteries. *ACS Energy Letters* 1 (4), 747-756 (2016).
- 13 Qiao, Y. *et al.*, Unraveling the Complex Role of Iodide Additives in Li-O₂ Batteries. *ACS Energy Letters* 2 (8), 1869-1878 (2017).
- 14 Shen, Y., Zhang, W., Chou, S.-L., & Dou, S.-X., Comment on "Cycling LiO₂ batteries via LiOH formation and decomposition". *Science* 352 (6286), 667-667 (2015).
- 15 Viswanathan, V. *et al.*, Comment on "Cycling Li-O₂ batteries via LiOH formation and decomposition". *Science* 352 (6286), 667-667 (2015).
- 16 Bentley, C.L., Bond, A.M., Hollenkamp, A.F., Mahon, P.J., & Zhang, J., Voltammetric Determination of the Iodide/Iodine Formal Potential and Triiodide Stability Constant in Conventional and Ionic Liquid Media. *The Journal of Physical Chemistry C* 119 (39), 22392-22403 (2015).
- 17 Leverick, G., Tulodziecki, M., Tatara, R., Bardé, F., & Shao-Horn, Y., Solvent-Dependent Oxidizing Power of LiI Redox Couples for Li-O₂ Batteries. *Joule* 3 (4), 1106-1126 (2019).
- 18 Nakanishi, A. *et al.*, Electrolyte Composition in Li/O₂ Batteries with LiI Redox Mediators: Solvation Effects on Redox Potentials and Implications for Redox Shuttling. *The Journal of Physical Chemistry C* 122 (3), 1522-1534 (2018).
- 19 Wu, S. *et al.*, A Synergistic System for Lithium–Oxygen Batteries in Humid Atmosphere Integrating a Composite Cathode and a Hydrophobic Ionic Liquid-Based Electrolyte. *Advanced Functional Materials* 26 (19), 3291-3298 (2016).
- 20 Allen, C.J. *et al.*, Oxygen Reduction Reactions in Ionic Liquids and the Formulation of a General ORR Mechanism for Li-Air Batteries. *The Journal of Physical Chemistry C* 116 (39), 20755-20764 (2012).
- 21 Elia, G.A. *et al.*, An Advanced Lithium-Air Battery Exploiting an Ionic Liquid-Based Electrolyte. *Nano Letters* 14 (11), 6572-6577 (2014).
- 22 Piana, M. *et al.*, Stability of a Pyrrolidinium-Based Ionic Liquid in Li-O₂ Cells. *Journal of The Electrochemical Society* 161 (14), A1992-A2001 (2014).

- 23 Shimizu, K. *et al.*, Structural and aggregate analyses of (Li salt + glyme) mixtures: the
complex nature of solvate ionic liquids. *Physical Chemistry Chemical Physics* 17 (34), 22321-
22335 (2015).
- 24 Elia, G.A., Bernhard, R., & Hassoun, J., A lithium-ion oxygen battery using a polyethylene
glyme electrolyte mixed with an ionic liquid. *RSC Advances* 5 (27), 21360-21365 (2015).
- 25 Amanchukwu, C.V. *et al.*, One-Electron Mechanism in a Gel-Polymer Electrolyte Li-O₂
Battery. *Chemistry of Materials* 28 (19), 7167-7177 (2016).
- 26 Mozhzhukhina, N., Tesio, A.Y., De Leo, L.P.M., & Calvo, E.J., In Situ Infrared Spectroscopy
Study of PYR₁₄TFSI Ionic Liquid Stability for Li-O₂ Battery. *Journal of The Electrochemical
Society* 164 (2), A518-A523 (2017).
- 27 Monaco, S., Soavi, F., & Mastragostino, M., Role of Oxygen Mass Transport in Rechargeable
Li/O₂ Batteries Operating with Ionic Liquids. *The Journal of Physical Chemistry Letters* 4 (9),
1379-1382 (2013).
- 28 Meini, S., Solchenbach, S., Piana, M., & Gasteiger, H.A., The Role of Electrolyte Solvent
Stability and Electrolyte Impurities in the Electrooxidation of Li₂O₂ in Li-O₂ Batteries. *Journal
of The Electrochemical Society* 161 (9), A1306-A1314 (2014).
- 29 Haskins, J.B., Yildirim, H., Bauschlicher, C.W., & Lawson, J.W., Decomposition of Ionic Liquids
at Lithium Interfaces. 2. Gas Phase Computations. *The Journal of Physical Chemistry C* 121
(51), 28235-28248 (2017).
- 30 Yildirim, H., Haskins, J.B., Bauschlicher, C.W., & Lawson, J.W., Decomposition of Ionic Liquids
at Lithium Interfaces. 1. Ab Initio Molecular Dynamics Simulations. *The Journal of Physical
Chemistry C* 121 (51), 28214-28234 (2017).
- 31 Mohzhukhina, N., Tesio, A.Y., Pozo, M.d., & Calvo, E.J., Communication-Lithium Ion
Concentration Effect in PYR₁₄TFSI Ionic Liquid for Li-O₂ Battery Cathodes. *Journal of The
Electrochemical Society* 164 (8), H5277-H5279 (2017).
- 32 McCloskey, B.D. *et al.*, Combining Accurate O₂ and Li₂O₂ Assays to Separate Discharge and
Charge Stability Limitations in Nonaqueous Li-O₂ Batteries. *The Journal of Physical Chemistry
Letters* 4 (17), 2989-2993 (2013).
- 33 Gallant, B.M. *et al.*, Influence of Li₂O₂ morphology on oxygen reduction and evolution
kinetics in Li-O₂ batteries. *Energy & Environmental Science* 6 (8), 2518-2528 (2013).
- 34 Lu, Y.-C. & Shao-Horn, Y., Probing the Reaction Kinetics of the Charge Reactions of
Nonaqueous Li-O₂ Batteries. *The Journal of Physical Chemistry Letters* 4 (1), 93-99 (2013).
- 35 McCloskey, B.D., Bethune, D.S., Shelby, R.M., Girishkumar, G., & Luntz, A.C., Solvent's Critical
Role in Nonaqueous Lithium-Oxygen Battery Electrochemistry. *The Journal of Physical
Chemistry Letters* 2 (10), 1161-1166 (2011).
- 36 Tulodziecki, M. *et al.*, The role of iodide in the formation of lithium hydroxide in lithium-
oxygen batteries. *Energy & Environmental Science* 10 (8), 1828-1842 (2017).
- 37 Torres, A.E. & Balbuena, P.B., Exploring the LiOH Formation Reaction Mechanism in Lithium-
Air Batteries. *Chemistry of Materials* 30 (3), 708-717 (2018).
- 38 Liu, T. *et al.*, Response to Comment on Cycling Li-O₂ batteries via LiOH formation and
decomposition". *Science* 352 (6286), 667b-667b (2015).

Towards reversible and moisture tolerant aprotic lithium-... (600.53 KiB) [view on ChemRxiv](#) • [download file](#)

TOC.jpg (55.04 KiB)

[view on ChemRxiv](#) • [download file](#)

TOC.png (200.33 KiB)

[view on ChemRxiv](#) • [download file](#)

Supplementary Information

Towards reversible and moisture tolerant aprotic lithium-air batteries

Supplementary Figure 1 | Schematics of the operando gas analysis systems used in this work. a, online electrochemical mass spectrometry (OEMS) and b, operando pressure monitoring. Two bespoke operando gas analysis techniques were developed in the course of this work. The OEMS system consists of a stainless-steel tube carrying gas through the electrochemical cell (described in main text) to a mass spectrometer. Mixtures of two gases can be selected from 0 to 100%, up to a maximum flow rate of 1120 $\mu\text{L}/\text{s}$, via two mass flow controllers (*Bronkhorst*), at any given time. For this work argon (*BOC N6.0*) was used as carrier gas and O_2 (*BOC N6.0*) as active gas, both are connected to purifiers (*Bronkhorst*) before flow control. A pressure controller (*Bronkhorst*) was fitted ahead of entering the electrochemical cell for stability reasons. Two PEEK tube sections connect the electrochemical cell to the gas line through self-sealing quick-connects (*Beswick Engineering*) so the system is never exposed to air. The gas line is connected to a quadrupole mass spectrometer (*Pfeiffer*) through a heated capillary (120°C) to prevent condensation. A potentiostat (*Ivium*) controls the electrochemical operations. The pressure monitoring system consist in an all-metal assembly, with a small internal volume (~ 10 ml), connecting a pressure transducer (*Omega*) to a *Swagelok*-type electrochemical cell. The gas inlet incorporates a small section of tube between two valves, creating an enclosed volume of known value that is used for calibration. Gases are evacuated/introduced through a quick-connect (*Swagelok*)

Supplementary Figure 2 | Galvanostatic profiles (top) with online mass spectrometry analysis of oxygen ($m/z=32$) for the first 7 cycles at a current of 50 $\mu\text{A}/\text{cm}^2$ in an electrolyte comprising 0.9 M Pyr₁₄TFSI, 0.7 M LiTFSI, 50 mM LiI, and 5000 ppm H₂O in of tetraethylene glycol dimethyl ether (G4).

Supplementary Figure 3 | **a, c, e, g**, Galvanostatic profiles and **b, d, f, h**, online mass spectrometry analysis of oxygen ($m/z=32$), hydrogen ($m/z= 2$), carbon monoxide ($m/z= 28$) and carbon dioxide ($m/z= 44$) evolution of cells cycled at a current of $70 \mu A/cm^2$ in an electrolyte comprising 0.9 M Pyr₁₄TFSI, 0.7 M LiTFSI, 50 mM LiI, and 5000 ppm H₂O in G4 (left) and 0.7 M LiTFSI, 50 mM LiI, and 5000 ppm H₂O in G4 (right). An oxygen consumption corresponding to a stoichiometry of $< 4 e^-/O_2$ is observed in cells containing Pyr₁₄TFSI at this rate and correlates with two distinctive processes during the OER, one of $\sim 4 e^-/O_2$ between 3.15 V and 3.4 V ($\sim 70\%$ of capacity) and a second at the end of charge of $\sim 2 e^-/O_2$ above 3.4 V. Cells without Pyr₁₄TFSI (right) show a $4 e^-/O_2$ during discharge but no oxygen evolution below 3.5 V during charge. A small O_2 evolution is observed above 3.5 V followed up by the evolution of CO and CO_2 , indicating electrolyte degradation at these potentials.

Supplementary Figure 4 | **a**, ^1H and ^7Li solid state NMR (ssNMR); **b**, X-ray diffractograms, and of electrodes at different stages of capacity-limited (0.7 mA/cm^2) cycling with $0.9 \text{ M Pyr}_{14}\text{TFSI}$, 0.7 M LiTFSI , 50 mM LiI , and $5000 \text{ ppm H}_2\text{O}$ in G4 at $70 \text{ }\mu\text{A/cm}^2$ (pristine – blue; discharged – red; half charged – amber; fully charged – green); **c**, SEM images of electrodes at end of discharge (different magnifications). ssNMR spectra were acquired on either a $16.4 \text{ T Bruker Avance III}$ or an $11.7 \text{ T Bruker Avance III HD}$ spectrometer using 1.3 mm HX (16.4 and 11.7 T) and 2.5 mm HX (11.7 T) probes. ssNMR shows intense ^7Li and ^1H signals centred at 0.7 ppm and -1.5 ppm , respectively, indicating the predominant formation of LiOH as discharge product [8-10,26] (**a** - red trace). Traces of lithium formate can also be observed in the ^1H spectrum at 9 ppm , and were previously reported in the discharge product of cells containing LiI and water in G4, associated to the electrochemical formation of Li_2O_2 [9]. After charge an almost complete removal of all lithium-based discharge products is observed (**b** – green trace). A broad signal is also observed in the ^1H spectrum of discharged electrodes, with maxima at 0.5 , 1.7 , and 3.1 ppm , which decreases noticeably in intensity in the charged electrodes. Analysis of unwashed electrodes soaked in electrolyte suggests that these signals originate from electrolyte trapped in the discharge product, which is not completely removed on washing the electrode sample with acetonitrile prior to analysis. A broad ^1H resonance at -4 ppm is assigned to protons in the electrode [27]. The reference NMR spectrum of a pristine electrode soaked in the electrolyte (blue) reveals ^1H NMR signals that can be assigned to the solvent in **a**. XRD patterns of the discharged electrode (**b** – red trace) is also dominated by patterns corresponding to crystalline LiOH, however weak reflections from the by-product Li_2O_2 can also be observed. At half charge (**b** – amber trace), the reflections associated to LiOH appear reduced with respect to the fully discharged cell whereas the weak reflection associated to Li_2O_2 remains at similar intensity. All reflections associated to both discharge products are absent in the diffractogram corresponding to the fully charged electrodes (**b** – green trace). Scanning electron microscopy (SEM) images of the discharged electrode show mainly dispersed collections of thin-sheets, consistent with primary building blocks of typical “flowerlike” LiOH crystals [24]. These small crystalline structures, of up to $1 \text{ }\mu\text{m}$ in size, are indicative of an electrolyte with limited solvating properties, as expected for highly viscous mixtures [23,25].

Supplementary Figure 5 | Pressure monitoring and titration of cells containing **a**, Pyr₁₄TFSI/G4, and **b**, G4 discharged at 70 $\mu A/cm^2$.

Supplementary Figure 6| a, Galvanostatic profile during charge, and online mass spectrometry analysis of b, oxygen ($m/z=32$) and c, hydrogen ($m/z=2$), carbon monoxide ($m/z=28$) and carbon dioxide ($m/z=44$) evolution of a LiOH (electrochemically) preloaded electrode in an electrolyte comprising 0.9 M Pyr₁₄TFSI, 0.7 M LiTFSI, 50 mM LiI, and 5000 ppm H₂O in G4 cycled at a current of 70 $\mu\text{A}/\text{cm}^2$. Three distinctive processes during the OER can be observed: a first small plateau at 3-3.05 V ($\sim 7.5\%$ of capacity) showing a small oxygen evolution can be correlated with oxidation of species on the surface of LiOH crystals that may have formed during washing/drying of the electrode; a second OER region between 3.2 V and 3.4 V shows a $4 e^-/O_2$ evolution ($\sim 73\%$ of capacity); a third region above 3.4 V shows an increase in O_2 evolution accompanied by CO_2 evolution, indicating parasitic reactions.

Supplementary Figure 7 | **a**, ^{17}O and **b**, ^7Li ssNMR spectra of the discharged (red trace) and charged (green trace) electrodes cycled at a current of $50\ \mu\text{A}/\text{cm}^2$ in a catholyte comprising 0.9 M $\text{Pyr}_{14}\text{TFSI}$, 0.7 M LiTFSI , 50 mM LiI in G4 with 5000 ppm H_2^{17}O , and discharged (blue trace) in a catholyte comprising 0.7 M LiTFSI , 50 mM LiI in G4 with 5000 ppm H_2^{17}O . Asterisks label spinning side bands of the ZrO_2 rotor background signal. Hashtags denotes the spinning sidebands. The data was acquired on a 16.4 T *Bruker AvanceIII* 700 MHz spectrometer with a 3.2 mm triple resonance probe using a Hahn echo sequence with an RF amplitude 55 kHz, at a MAS frequency of 20 kHz adding 29871 to 60000 transient scans with a relaxation delay of 20 s for ^7Li . ^{17}O and ^7Li were externally referenced to D_2O at 0 ppm and LiF at -1 ppm, respectively.

Supplementary Figure 8 | Online mass spectrometry chemical test of the reaction of H_2O_2 and I^- with 10.5 mg of LiOH in 0.5 ml of electrolyte containing 0.9 M $\text{Pyr}_{14}\text{TFSI}$, 0.7 M LiTFSI , 50 mM LiI , 5000 ppm H_2O in G4. At $t=0$, 0.2 ml of H_2O_2 (30% wt) is injected. Images of the test tube before, during, and after reaction completion are added for visual reference.

It has been recently proposed that the electrochemical formation of LiOH in I^-/I_3^- mediated cells occurs through a synergistic effect, where at $\text{H}_2\text{O}:\text{I}^-$ ratios between 0.5 and 1.5 both H_2O and I^- coordinate with Li^+ in their first solvation shells with various glyme solvents [8]. The high proton affinity of I^- , higher than TFSI^- but lower than OH^- based on Pearson's Hard Soft Acid Base (HSAB) Theory, weakens the O-H bond of a significant portion of water molecules rendering H^+ available for the formation of LiOH (reaction 1).

Whereas at higher $\text{H}_2\text{O}:\text{I}^-$ ratios a water clustering effect significantly reduce the average I-H interaction attenuating this synergistic action. In this scenario the ORR mechanism proceeds through an iodide catalytic effect in which the electrochemically formed O_2^- chemically reacts with H_2O to form H_2O_2 (reaction 1), which subsequently oxidizes I^- to form I_3^- and LiOH (reaction 2).

I^- is regenerated via a chemical reaction in which O_2 is evolved (reaction 3) making the overall mechanism formally a $4 \text{e}^-/\text{O}_2$ process following the ensuing reaction pathway:

To test whether the ORR in cells containing P_{14}TFSI follows this mechanism the gas evolution after injecting H_2O_2 to a tube containing LiOH in an aliquot of the electrolyte was tested in an online mass spectrometry chemical test (Fig. 7). Upon injection of H_2O_2 , the initially transparent electrolyte turned dark red, indicating the formation of I_3^- as per reaction 2. Almost immediately bubbles started forming from the LiOH precipitate and O_2 was detected by the mass spectrometer. After a time the solution cleared again and the bubbling stopped, indicating that the formed I_3^- was being reduced again to I^- by the oxidation of OH^- , in agreement with reaction 3.

Supplementary Figure 9 | **a**, Cyclic voltammograms of cells with catholytes containing 0.7 M LiTFSI, 50 mM LiI, 5000 ppm H₂O in G4 (red trace) and with 0.9 M Pyr₁₄TFSI (blue trace) collected at 1 mV/s; **b**, First 10 galvanostatic discharge/charge cycles) of cells of the same composition; **c**, charge capacity registered during galvanostatic cycling shown in b. Cells used a LICGC to isolate the cathode from the Li metal anode. 0.3 M LiTFSI in G4 was used as anolyte. All cells were cycled under argon at 50 $\mu\text{A}/\text{cm}^2$.

Typically, the reduction and oxidation potentials for reactions are defined by a voltammetric method rather than galvanostatic method. If using a galvanostatic (step) method, as shown in the main text, the process must be a truly reversible reaction whereby the Tafel slopes are extrapolated to intersection. The cyclic voltammograms (Supplementary Fig. 9a) show good agreement with the galvanostatic cycling results shown in Fig. 4c, even though the potential crossover in observed in figure 4c are likely reactant species diffusion/concentration dependent values. The potential crossovers and the overall capacity show negligible change over several cycles (Supplementary Fig. 9c).

Supplementary Figure 10 | **a-c**, Galvanostatic profiles with online mass spectrometry analysis of **d-f**, oxygen ($m/z=32$) and **g-f**, carbon monoxide and carbon dioxide ($m/z= 28$) evolution of cells with an electrolyte containing 0.9 M Pyr₁₄TFSI, 0.7 M LiTFSI, 50 mM LiI, 5000 ppm H₂O in G4 during the first three charges. Cells were assembled in an *ECC-DEMS* cell (*EL-CELL*) without LICGC protecting the anode and cycled to 70 $\mu\text{A}/\text{cm}^2$ under 20% O₂ in Ar and 0% O₂ in Ar during discharge and charge respectively.

Supplementary Figure 11 | **a-c**, Galvanostatic profiles with online mass spectrometry analysis of **d-f**, oxygen ($m/z=32$) and **g-i**, carbon monoxide and carbon dioxide ($m/z= 28$) evolution of cells with an electrolyte containing 0.7 M LiTFSI, 50 mM LiI, 5000 ppm H_2O in G4 during the first three charges. Cells were assembled in an *ECC-DEMS* cell (*EL-CELL*) without LICGC protecting the anode and cycled to $70 \mu A/cm^2$ under 20% O_2 in Ar and 0% O_2 in Ar during discharge and charge respectively.

Supplementary Figure 12 | Example of electrochemical impedance spectroscopy (EIS) of cells tested in this work used to offset overpotential caused to increased resistance by using LICGC. EIS was normally collected before every electrochemical operation.

SI Towards reversible and moisture tolerant aprotic lithiu... (700.98 KiB) [view on ChemRxiv](#) • [download file](#)

Other files

TOC.bmp (1.40 MiB)

[view on ChemRxiv](#) • [download file](#)