



Toward Reversible and Moisture-Tolerant Aprotic Lithium-Air Batteries

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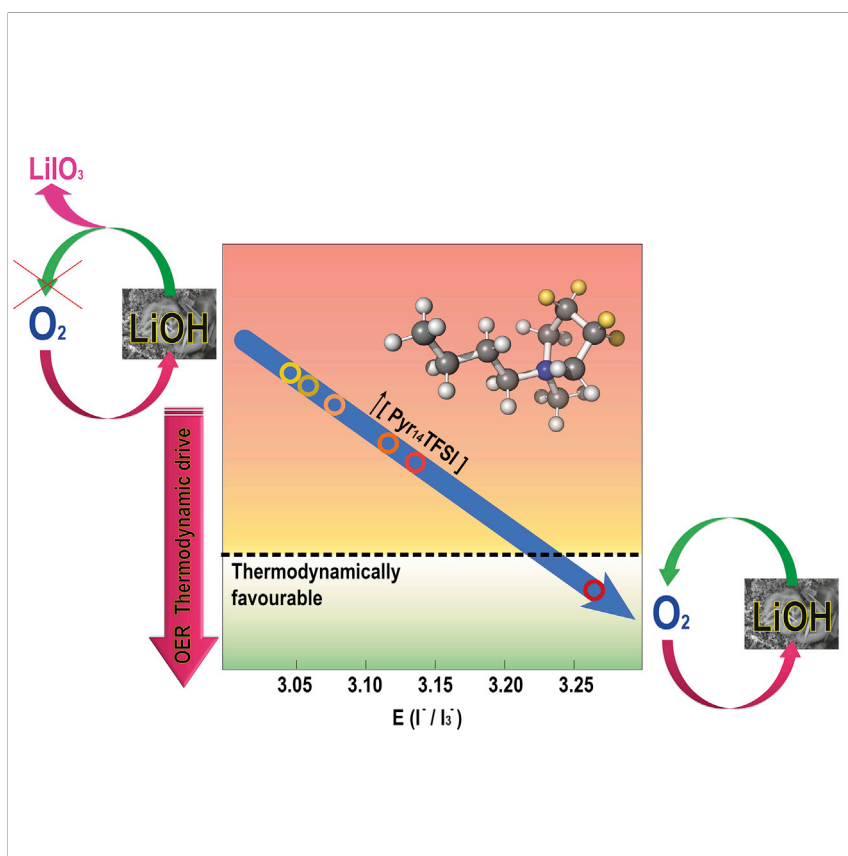
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Article

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Li-air batteries have attracted significant attention due to their very high energy density, comparable to that of fossil fuels. For their development, a stable discharge product that can be reversibly decomposed during charge needs to be developed. LiOH is a promising candidate, but questions concerning the reversibility of the charge process have been raised. Here, we report for the first time Li-O₂ cells that can reversibly cycle via LiOH by using water and an ionic liquid as additives in the electrolyte.

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HIGHLIGHTS

Iodide-mediated Li-O₂ cells can reversibly cycle via LiOH with low overpotential

Electrolyte additives can increase the redox potential of the I⁻/I₃⁻ couple

At sufficiently high I⁻/I₃⁻ redox potentials, OER from LiOH becomes favorable

Article

Toward Reversible and Moisture-Tolerant Aprotic Lithium-Air Batteries

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SUMMARY

The development of moisture-tolerant, LiOH-based non-aqueous Li-O₂ batteries is a promising route to bypass 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 due to the multiple reaction paths induced by the oxidation of I[−] on cell charging. In this work, we introduce an ionic liquid to a glyme-based electrolyte containing Lil and water and demonstrate a reversible LiOH-based Li-O₂ battery cycling that operates via a 4 e[−]/O₂ process with a low charging overpotential (below 3.5 V versus Li/Li⁺). The addition of the ionic liquid increases the oxidizing power of I₃[−], shifting the charging mechanism from IO[−]/IO₃[−] formation to O₂ evolution.

INTRODUCTION

In 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. Among 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 generally 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 oxidized during charge, with O₂ being released back to the atmosphere (the oxygen evolution reaction, OER).⁴

Despite its potential, several fundamental challenges remain to be overcome to allow the successful development of a practical non-aqueous LAB.^{4–8} Among these challenges, the instability of the typical discharge products (LiO₂ and Li₂O₂) in the presence of moisture and CO₂ represents a fundamental stumbling block.^{9,10} 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 Lil as a redox mediator or Ru as a catalyst in a wet organic electrolyte.^{11–13} However, it is widely believed that LiOH is not reversible due to (1) the half-cell potential of the LiOH OER under standard state (aqueous) conditions being higher than that of the Li₂O₂ OER, given the higher thermodynamic stability of the former; (2) the detection on charge of oxidation products such as

Context & Scale

Li-air batteries have attracted significant attention as a strategy to develop affordable and sustainable electrical storage with higher energy density than current lithium-ion batteries, having theoretical energy densities that rival those of fossil fuels and, in their simplest form, avoiding the use of resource-limited transition metal oxides. The formation of LiOH as discharge product is a promising route to bypass some of the most acute challenges this very young technology faces. However, one critical challenge is to charge the battery reversibly, evolving oxygen gas at low overpotentials. While previous studies have indicated that the I[−]/I₃[−] redox couple may not have sufficient thermodynamic drive for the oxygen evolution reaction, here we demonstrate that additives in the electrolyte (ionic liquid and water) can increase the I[−]/I₃[−] equilibrium redox potential sufficiently to enable a reversible charge process at low overpotentials.



IO_3^- ,^{12,14,15} and DMSO_2 ,¹³ which originate from the redox mediator and the solvents, respectively; and (3) little or no oxygen evolution being observed in gas analysis experiments.¹⁴ 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.^{14–17}

The electrochemical behavior of the iodide/triiodide redox system has been extensively reported in the literature, and it is by now well established that the (I^-/I_3^-) redox potential is solvent dependent^{12,18–20}: the oxidizing power of I_3^- can be readily tailored by means of adjusting the physicochemical parameters of the electrolyte (dielectric constant, ionic strength, Gutmann acceptor/donor numbers, etc.). Ionic liquids (ILs) have been shown to alter the solvation/coordination environments of this redox system, again substantially affecting the (I^-/I_3^-) redox potential,¹⁸ while still allowing high ionic conductivity and reducing solvent volatility.^{21–28} However, the high viscosity of ILs, which reduces the O_2 diffusion coefficients, and the low O_2 solubility are disadvantageous for LAB performance.²⁹ The presence of water has been shown to enhance the solution-transfer of discharge products and redox mediators,^{12,30–33} reducing the charge overpotential and therefore the level of parasitic reactions, as well as fundamentally affecting the activity of the (I^-/I_3^-) redox system during discharge.^{11,14,34} Thus, the combination of Lil 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 Lil as a redox mediator and H_2O and 1-butyl-1-methyl-pyrrolidinium-bis(trifluoromethanesulfonyl)imide ($\text{Pyr}_{14}\text{TFSI}$) as additives in a low-volatility electrolyte. $\text{Pyr}_{14}\text{TFSI}$ 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.^{24,28,29,31,35–37} We find that the inclusion of $\text{Pyr}_{14}\text{TFSI}$ is crucial for the reversibility of the electrochemical formation/decomposition of LiOH as demonstrated by the observation of a $4\text{ e}^-/\text{O}_2$ 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 labeling. The suppression of the side reactions to form oxygenated iodine species (IO^- , IO_3^-), which trap the oxygen during charge, is also observed, and the mechanistic considerations of the oxygen evolution versus iodate formation are discussed in the context of the thermodynamic driving forces for both reactions. The effects of the IL and water with respect to the activity of iodine are also investigated through molecular dynamic (MD) simulations.

RESULTS AND DISCUSSION

A $4\text{ e}^-/\text{O}_2$ Oxygen Evolution Reaction

Li-O_2 cells were constructed with a lithium-metal anode, an anolyte consisting of 300 mM LiTFSI in tetraethylene glycol dimethyl ether (G4), a lithium-ion conducting glass ceramic (LICGC-Ohara AG010) separating the two electrolytes, a catholyte containing 700 mM LiTFSI , 50 mM Lil, 900 mM $\text{Pyr}_{14}\text{TFSI}$, and 5,000 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, since redox mediator shuttling is a possible source of “artificial” capacity, the oxidized species such as I_3^- being reduced at the anode and then migrating back to the cathode to be reoxidized.¹⁴ These cells were evaluated with *operando* OEMS by capacity-limiting galvanostatic cycling, in order to keep the levels of water within limits

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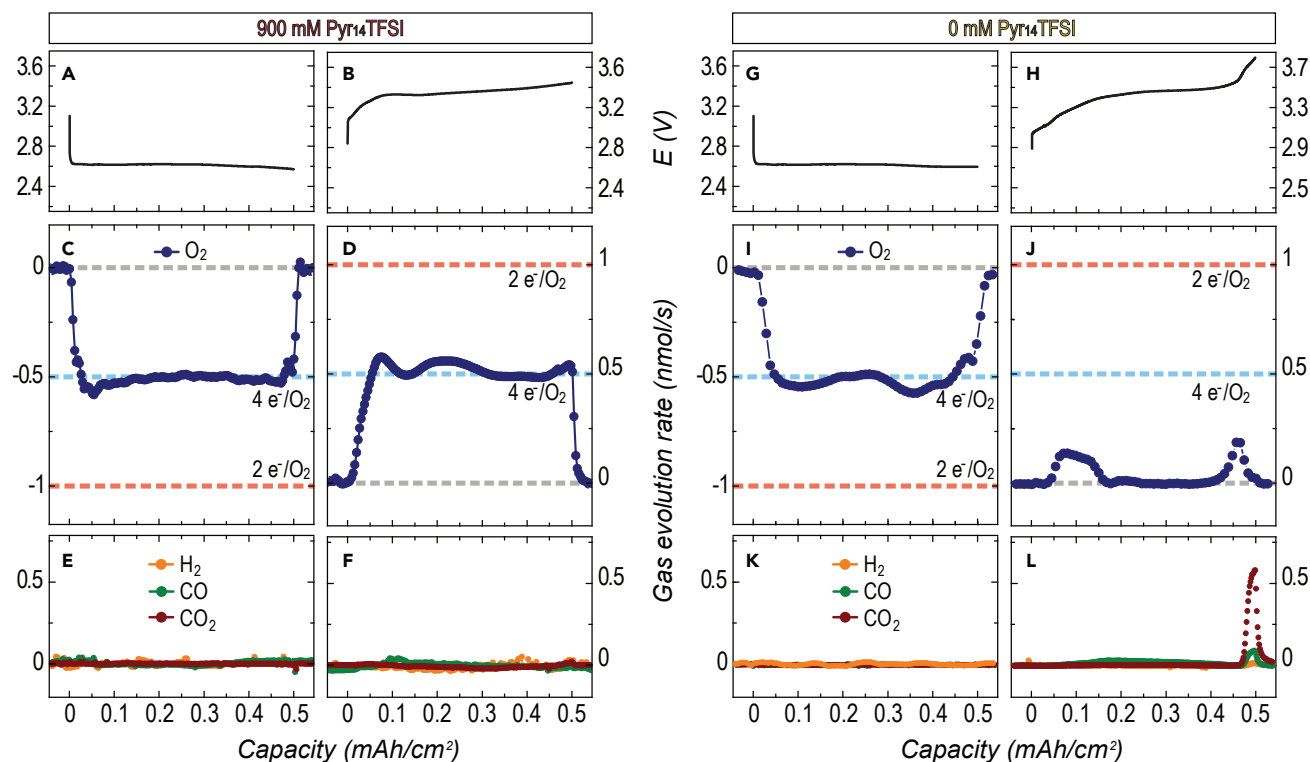


Figure 1. $4 \text{ e}^-/\text{O}_2$ Formation and Removal of LiOH in Water and IL-Containing Cells

(A, B, G, H) Galvanostatic profiles and (C, D, I, J) online mass spectrometry analysis of O_2 , and (E, F, K, L) H_2 , CO , and CO_2 ($m/z = 32, 2, 28, 44$, respectively) from batteries with electrolytes comprising of 700 mM LiTFSI , 50 mM LiI , and 5,000 ppm H_2O in G4 with 900 mM $\text{Pyr}_{14}\text{TFSI}$ (left) and without $\text{Pyr}_{14}\text{TFSI}$ (right) cycled at a current of $50 \mu\text{A}/\text{cm}^2$.

known for promoting LiOH formation during the ORR (between 1,500 and 5,000 ppm).¹¹ Figure 1 (system description in Figure S1A) shows the electrochemical profile (Figures 1A and 1B) and gas evolution rate of O_2 ($m/z = 32$; Figures 1C and 1D), H_2 , CO , and CO_2 ($m/z = 2, 28, 44$; Figures 1E and 1F) for the discharge and charge of this cell (Figures 1G–1M show similar results for a cell without $\text{Pyr}_{14}\text{TFSI}$ for comparison). The electrochemical discharge profile (Figure 1A) shows a sustained single discharge plateau at 2.6 V (versus Li/Li^+). The discharge produces a constant consumption rate of O_2 of $\sim 0.51 \text{ nmol}/\text{s}$ (Figure 1C), corresponding to a $4 \text{ e}^-/\text{O}_2$ stoichiometry, with no significant evolution of gases indicative of parasitic reactions (Figure 1E). The total measured O_2 consumption is 18.5 mmol, which corresponds to a 99.1% faradic efficiency.

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 (Figure 1B). Notably, oxygen evolution is clearly observed to occur from the beginning of charge, stabilizing at around a rate corresponding to a $4 \text{ e}^-/\text{O}_2$ stoichiometry (Figure 1D). A total of 18.4 mmols of O_2 is evolved during charge, corresponding to 99.5% of the amount consumed in the discharge (i.e., a 99.5% faradic efficiency), with no significant signs of parasitic reactions as signaled by a lack of evolution of H_2 , CO , or CO_2 (Figure 1F). The OER can be observed for several cycles (Figure S5) with a relatively high faradic efficiency (>80% for 7 cycles).

By comparison, in the absence of $\text{Pyr}_{14}\text{TFSI}$, only very small amounts of O_2 (1.5 mmols corresponding to $\sim 8.4\%$ faradic efficiency) (Figure 1K) are detected

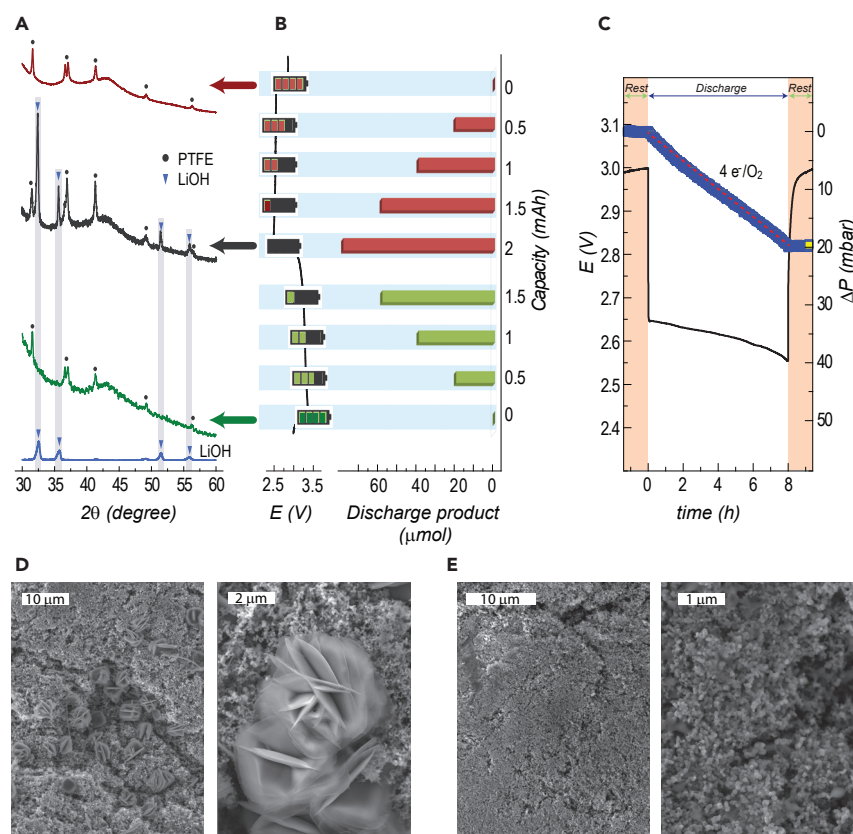


Figure 2. Operando and Ex Situ Characterization of the LiOH Formation during ORR

(A) X-ray diffractograms at different stages of capacity-limited cycling (pristine, red; discharged, gray; fully charged, green) as represented in the electrochemical profile.

(B) Quantification of LiOH present in the electrode by acid/base titration at different stages of capacity-limited cycling.

(C) Operando pressure-monitoring experiment during discharge.

(D and E) SEM characterization (at two different magnifications) of electrodes at the end of discharge (D) and end of charge (E) (scale bars shown in white).

Relevant reflections due to LiOH and PTFE binder are indicated by gray triangles and blue dots, respectively, in (A). All cells were cycled at $50 \mu\text{A}/\text{cm}^2$.

during charge to 3.5 V. A steep increase in potential above 3.6 V at the end of charge is also observed, which is accompanied by a significant evolution of CO_2 (and O_2 and CO to lesser extent), suggesting electrode/electrolyte degradation (Figure 1M).

Analysis of the ORR Products

Analysis of the cathode after discharge with X-ray diffraction (XRD) (Figure 2A, gray trace) is dominated by patterns corresponding to crystalline LiOH, as revealed by quantitative analysis of the diffraction pattern (Figure S2). All reflections associated with LiOH are absent in the diffractogram of the fully charged electrodes, confirming the removal of the crystalline discharge product (Figure 2A, green trace). Quantification of the amount of LiOH present in the electrode was performed by acid titration at various stages of the discharge ($1/4$, $1/2$, $3/4$, and full discharge) and the charge ($1/4$, $1/2$, $3/4$, and full charge) processes. Figure 2B shows an increasing amount of LiOH detected in the electrode as the ORR progresses (red bars), which matches the expected value for a $1 \text{ e}^-/\text{LiOH}$ mechanism ($4 \text{ e}^-/\text{O}_2$) at all stages of discharge. The presence of Li_2O_2 as an alternative discharge product was also tested by iodometry

titration (Figure S3); no peroxide was detected, in agreement with the XRD analysis. A similar trend can be observed during different stages of the OER (Figure 2B, green bars), indicating that LiOH is being removed according to the same $1\text{ e}^-/\text{LiOH}$ stoichiometry. *Operando* pressure monitoring during discharge (Figure 2C) confirms a $4\text{ e}^-/\text{O}_2$ stoichiometry during ORR for cells with 900 mM Pyr₁₄TFSI and 5,000 ppm of water, as expected for the formation of LiOH. These results suggest that galvanostatic cycling of this cell occurs through the formation and removal of LiOH, and not through Li₂O₂ chemistry under the experimental conditions shown in Figure 1 (Figure S6).

Scanning electron microscopy (SEM) images of electrodes during the first discharge are shown in Figure 2D. The electrodes extracted from capacity-limited cells (2 mAh) discharged cells contain typical “flower-like” LiOH crystals of up to 7 μm in size, similar to those previously reported in cells containing LiI and water.¹² The absence of these crystalline structures in the SEM images of fully recharged electrodes (Figure 2E) confirms the removal of the discharge product during charge without the precipitation of large quantities of by-products from parasitic reactions. The consumption/regeneration of water, consistent with the reversible formation/decomposition of LiOH through the mechanism presented in Reaction 1, was also observed (Figure S7).

In order to evaluate the mechanistic implications of the observed stoichiometry during the OER in Figure 1, further OEMS experiments were performed with an electrochemically preloaded electrode with Li₂O₂ (Figure 3, left); the electrode was produced by discharging a cell using 300 mM LiTFSI in G4 as the electrolyte (i.e., with no LiI or additives). The cell was subsequently disassembled in the glove box, and the electrode was washed 3 times with ethylene glycol dimethyl ether (G1) and dried under vacuum for 30 min. This electrode was then loaded in a two-compartment cell with the same catholyte used for the cells shown in Figure 1 (i.e., 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI, and 5,000 ppm H₂O in G4). In this case, the OER showed an approximately $2\text{ e}^-/\text{O}_2$ stoichiometry (Figure 3C), consistent with the oxidation of Li₂O₂. After initially reaching an evolution rate corresponding to $2\text{ e}^-/\text{O}_2$, a noticeable dip in the oxygen evolution is seen (Figure 3C). This effect has been previously attributed to a transition from the delithiation of Li-deficient (Li_{2-x}O₂) species to stoichiometric Li₂O₂ on Li₂O₂ particles.^{38–40} Preloading was similarly performed using the IL-free conditions previously shown to produce LiOH electrochemically:¹¹ an electrolyte comprising 700 mM LiTFSI, 50 mM LiI, and 5,000 ppm H₂O in G4 was discharged. Switching to the IL-containing electrolyte resulted in $4\text{ e}^-/\text{O}_2$, OER on charge (Figure S12).

Since earlier ¹⁷O-ssNMR measurements have reported that both O₂ and H₂O contribute to the oxygen atoms in the LiOH formed via a LiI-catalyzed electrochemical reaction in G1,¹¹ a further OEMS experiment was performed using ¹⁷O-enriched H₂O (Figure 3, right) and Pyr₁₄TFSI. A $m/z = 32$ mass spectrometer signal (Figure 3D, blue) dominates the response on charge, which is due to ¹⁶O-¹⁶O. A signal is seen at $m/z = 33$ (Figure 3D, magenta), which corresponds to ¹⁷O-¹⁶O. The signal at $m/z = 34$ (Figure 3D, orange) corresponds to either 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 low enrichment of the H₂¹⁷O resulted in a relatively low Li¹⁷OH concentration, as observed by ¹⁷O ssNMR (Figure S13). This explains the relatively low intensity of the $m/z = 33$ signal (from ¹⁶O-¹⁷O) compared with the $m/z = 32$ signal (from ¹⁶O-¹⁶O).

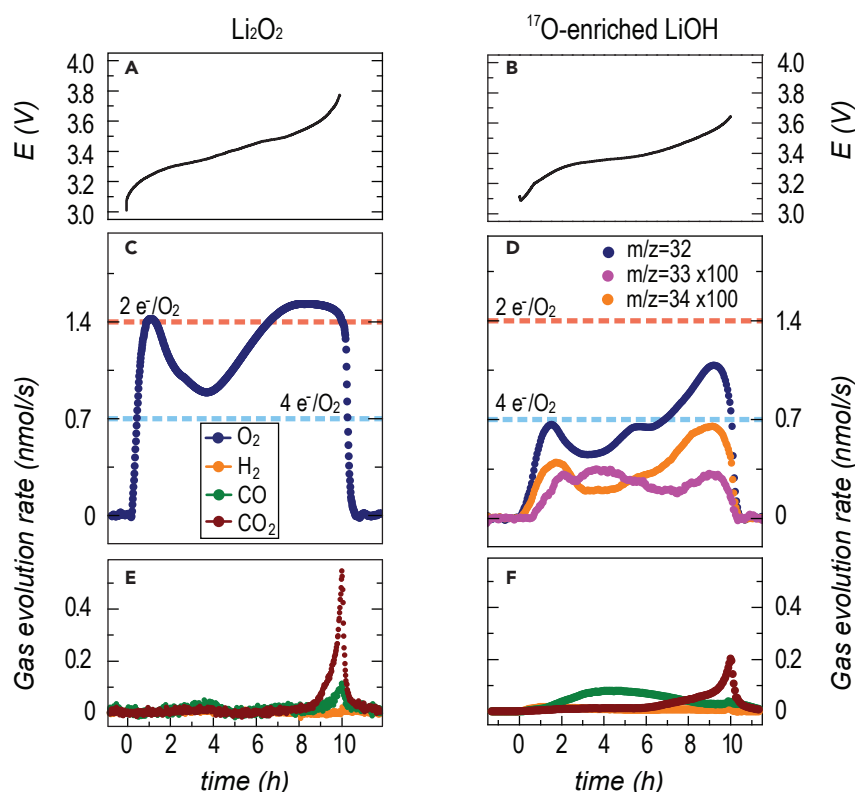
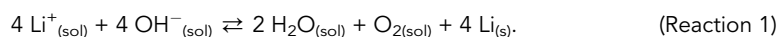


Figure 3. Operando Gas Analysis of Preloaded Electrodes and Isotopic Exchange during OER
(A and B) Galvanostatic profiles (top) and (C and D) online mass spectrometry analysis of O_2 ($m/z = 32$) and (E and F) H_2 , CO , and CO_2 ($m/z = 2, 28, 44$) evolution during charge of electrochemically preloaded electrodes with Li_2O_2 (left) and of a $\text{Li}-\text{O}_2$ cell discharged using ^{17}O -enriched H_2O in the electrolyte containing G4 and $\text{Pyr}_{14}\text{TFSI}$ at $70 \mu\text{A}/\text{cm}^2$.

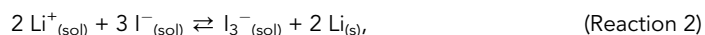
Pathways to LiOH Removal

The mechanisms for LiOH formation in the ORR reaction have been discussed extensively elsewhere,^{11,15,34} and thus we focus here on the OER reaction during charge (verification of the ORR mechanism is shown in Figure S14). Two questions arise from the OEMS data (Figure 1). First, what is the role played by $\text{Pyr}_{14}\text{TFSI}$ in the promotion of oxygen evolution? Second, what is the mechanism for LiOH decomposition/removal in the absence of the ionic liquid when there is no O_2 evolution?

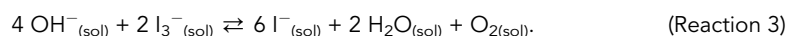
The OER, during the charge of a LiOH -based $\text{Li}-\text{O}_2$ battery, can be described overall by:



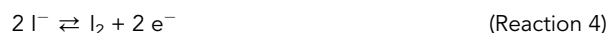
However, this reaction operates via a two-stage catalytic mechanism in which I^- is first oxidized to I_3^- (the I^-/I_3^- couple, here referenced to the Li anode [the Li/Li^+ couple]),



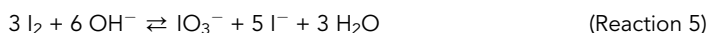
and, subsequently, LiOH is oxidized to O_2 by I_3^- with the regeneration of I^- ($\text{OH}^- \rightarrow \text{O}_2$ chemical reaction):



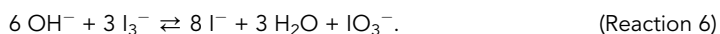
The (I^-/I_3^-) redox potential at standard (aqueous) conditions ($E^\circ_{\text{versus Li/Li}^+}$) corresponds to 3.5761 V,^{18,41} which is sufficiently large to drive oxygen evolution. However, the reversibility of iodide-mediated aprotic Li-O₂ batteries, cycling through LiOH, has been a much-discussed subject due to the difficulty of performing the OER process at low overpotentials (below 3.5 V).^{14–17,19} Alternative reaction pathways have therefore been proposed in the literature to explain the LiOH removal upon charging in LiI- and organic-electrolyte-containing cells with added water. The detection of IO_3^- in the electrolyte of charged cells, alongside the lack of O₂ evolution in OEMS experiments, has suggested that IO_3^- is the dominant product rather than O₂ at 3.5 V or below, in ether-based electrolytes. The IO_3^- formation has been proposed to form either through the oxidation of I^- to I_2



and its subsequent chemical reaction with LiOH^{14,15}:



or via oxidation by I_3^- to form IO^- and the subsequent disproportionation of IO^- into IO_3^- and I^- .^{18,42}



In this study, cells containing Pyr₁₄TFSI show clear evidence for a 4 e⁻/O₂ OER (Reaction 1) commencing at ~3.2 V (Figures 1A–1F). This oxygen evolution is absent in cells without the IL (Figures 1G–1M), even when charging at comparable potentials (below 3.5 V for ~75% of charge).

Characterization of the electrolyte after charge was performed in order to establish the products formed following LiOH removal in cells with and without IL and thus investigate the difference in mechanism during the OER. UV spectra of aliquots of the electrolyte of charged cells with and without Pyr₁₄TFSI (Figure 4A) show the presence of features at 295 and 354 nm, corresponding to the presence of I_3^- ; no feature corresponding to I_2 (at 520 nm) is seen in either case (insert in Figure 4A). The electrolyte of cells without Pyr₁₄TFSI (Figure 4A, red trace) show the presence of extra features at 228 and 465 nm, assigned to IO_3^- and IO^- , respectively; these are absent in cells cycled with the IL (Figure 4A, blue trace). The presence of I_3^- in both samples indicates that this is the main product of I^- oxidation and therefore suggests that this is the species responsible for oxidizing LiOH, rather than I_2 . The lack of O₂ evolution observed in OER data of cells without Pyr₁₄TFSI can therefore be explained by the formation of oxidized iodine species (IO^- and IO_3^-), the oxygen effectively being trapped in the solution, as previously reported for similar electrolytes.^{14–16}

The capability of I_3^- to oxidize LiOH during the OER was subsequently tested. A solution of I_3^- was injected into a mixture of electrolyte containing 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI, and 5,000 ppm H₂O in G4, and commercial LiOH powder. The subsequent gas evolution was measured by mass spectrometry (Figure 4B). Gas evolution from the LiOH powder, at $m/z = 32$, can be directly observed as soon as the I_3^- solution is injected, confirming the evolution of O₂ from this mixture and demonstrating that I_3^- is capable of oxidizing LiOH in this electrolyte; very little O₂ evolution is observed in the absence of Pyr₁₄TFSI.

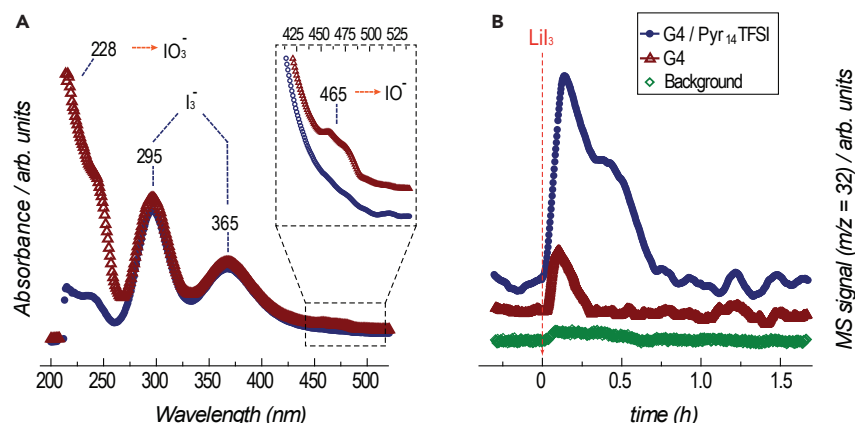


Figure 4. Spectroscopic and Electrochemical Analysis of the I_3^- Oxidizing Power

(A) UV spectra of catholytes collected after galvanostatic discharge and charge of cells containing 700 mM LiTFSI, 50 mM LiI, and 5,000 ppm H_2O (red trace) and with 900 mM Pyr₁₄TFSI (blue trace) in G4. (B) Online mass spectrometry test of the reaction of I_3^- with LiOH. A 50 mM I_3^- solution is injected into a vessel containing LiOH powder immersed in electrolyte with 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI, and 5,000 ppm H_2O in G4 (blue trace) and 700 mM LiTFSI, 50 mM LiI, and 5,000 ppm H_2O in G4 (red trace). The gas evolution of the ensuing reaction was recorded with a mass spectrometer ($m/z = 32$, corresponding to O_2 evolution is displayed). A blank spectrum was collected by injecting the I_3^- solution into the electrolyte containing 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI, and 5,000 ppm H_2O in G4 in the absence of LiOH (green trace). Argon was used as the carrier gas.

In order to assess the thermodynamic consistency of this reaction pathway, and whether the I^-/I_3^- couple provides a sufficient driving force for the OER, the Gibbs free energy of the OER ($\Delta_{OER}G$) was estimated according to [Reaction 1](#):

$$\begin{aligned} \Delta_{OER}G = & 2\Delta_f G^\circ(H_2O) + \Delta_f G^\circ(O_2) + 4\Delta_f G^\circ(Li) - 4\Delta_f G^\circ(OH^-) \\ & - 4\Delta_f G^\circ(Li^+) + 2\Delta_{sol}G(H_2O) + \Delta_{sol}G(O_2) - 4\Delta_{sol}G(OH^-) - 4\Delta_{sol}G(Li^+) \end{aligned} \quad (\text{Equation 1})$$

The $\Delta_{OER}G$ can then be written as the combination of [Reactions 2](#) and [3](#) (the I^-/I_3^- redox pair, and the $OH^- \rightarrow O_2$ chemical reaction, respectively), giving the Gibbs free energy

$$\Delta_{OER}G = 2\Delta_r G(I^-/I_3^-) + \Delta_r G(OH^- \rightarrow O_2), \quad (\text{Equation 2})$$

where $\Delta_r G(I^-/I_3^-)$ is the Gibbs free energy of the I^-/I_3^- redox couple, defined as

$$\begin{aligned} \Delta_r G(I^-/I_3^-) = & \Delta_f G^\circ(I_3^-) + 2\Delta_f G^\circ(Li) - 2\Delta_f G^\circ(Li^+) - 3\Delta_f G^\circ(I^-) + \Delta_{sol}G(I_3^-) - 2\Delta_{sol}G(Li^+) \\ & - 3\Delta_{sol}G(I^-), \end{aligned} \quad (\text{Equation 3})$$

and $\Delta_r G(OH^- \rightarrow O_2)$ is the Gibbs free energy of the $OH^- \rightarrow O_2$ chemical reaction, defined as

$$\begin{aligned} \Delta_r G(OH^- \rightarrow O_2) = & 6\Delta_f G^\circ(I^-) + 2\Delta_f G^\circ(H_2O) + \Delta_f G^\circ(O_2) - 4\Delta_f G^\circ(OH^-) \\ & - 2\Delta_f G^\circ(I_3^-) + 6\Delta_{sol}G(I^-) + 2\Delta_{sol}G(H_2O) + \Delta_{sol}G(O_2) - 4\Delta_{sol}G(OH^-) - 2\Delta_{sol}G(I_3^-). \end{aligned} \quad (\text{Equation 4})$$

$\Delta_{OER}G$ depends on the Gibbs free energy of formation of H_2O ($\Delta_f G^\circ(H_2O)$), O_2 ($\Delta_f G^\circ(O_2)$), Li ($\Delta_f G^\circ(Li)$), OH^- ($\Delta_f G^\circ(OH^-)$), and Li^+ ($\Delta_f G^\circ(Li^+)$) at standard conditions, and their Gibbs free energy of solvation, ($\Delta_{sol}G(H_2O)$, $\Delta_{sol}G(O_2)$, $\Delta_{sol}G(Li)$, $\Delta_{sol}G(OH^-)$, and $\Delta_{sol}G(Li^+)$), which are solvent specific. $\Delta_f G^\circ(H_2O)$ and $\Delta_f G^\circ(O_2)$ are tabulated values,⁴¹ whereas, by definition, $\Delta_f G^\circ(Li) = 0$. Using the Nernst

equation for the I^-/I_3^- redox couple, and assuming that the dissolved oxygen ($O_{2(sol)}$) is at equilibrium with oxygen gas ($O_{2(g)}$) at a pressure (P_{O_2}) and that the oxygen can be treated as an ideal gas over the range of temperature concerned (see [Supplemental Information](#)), the above expression can be written as:

$$\Delta_r G(OH^- \rightarrow O_2) = 2\Delta_f G^\circ(H_2O) - 4\Delta_f G^\circ(LiOH) + 2nFE(I^-/I_3^-) + 2\Delta_{sol}G(H_2O) + kT \ln\left(\frac{P_{O_2}}{P^\circ}\right). \quad (\text{Equation 5})$$

This expression indicates that three key variables dictate the driving force for the OER: the redox equilibrium potential of the I^-/I_3^- couple ($E(I^-/I_3^-)$), the water activity ($\Delta_{sol}G(H_2O)$), and the oxygen partial pressure (P_{O_2}). The redox potential of the iodide/triiodide redox system is solvent dependent,^{18–20} the couple varying by over 0.5 V,¹⁸ whereas variations in the solvent activity and gas partial pressure are of smaller magnitude (estimated to be ~ 0.17 and ~ 0.08 eV, respectively; [Table S2](#)). The variability in the values of the $E(I^-/I_3^-)$ is strongly influenced by stabilizing (donor-acceptor) interactions of I^- species in solution,^{18,20} since $\Delta_r G(I^-/I_3^-)$ is proportional to the difference in $\Delta_{sol}G$ of I^- and I_3^- :

$$\Delta_r G(I^-/I_3^-) \propto \Delta_{sol}G(I_3^-) - 3\Delta_{sol}G(I^-) \quad (\text{Equation 6})$$

The OEMS results presented in [Figures 1, 3, and 4](#) suggest that the addition of Pyr₁₄TFSI (alongside small amounts of water) is capable of increasing the oxidizing power of I_3^- and/or reducing the couple of the OER sufficiently so that it can occur below 3.5 V. We now turn to identify and rationalize the effect of the additives (water, IL) on the redox equilibrium potential of the I^-/I_3^- couple.

Modification of the I^-/I_3^- Redox Potential

Effect of the Additives on the Coordination of I^- and on the OER. It has recently been shown that water and ILs are among the media in which $E(I^-/I_3^-)$ has the highest values, due to the very strong coordination of I^- by these solvent molecules:¹⁸ water molecules, for example, solvating I^- ions via hydrogen-halogen bonds within the I^- first solvation shell. In order to investigate the effect of the additives used here, we have explored potential correlations between the ¹H-NMR chemical shift of the water peak and the I^-/I_3^- redox potential ([Figure 5](#)). The addition of 5,000 ppm of water to an electrolyte with no IL (700 mM LiTFSI, 50 mM Lil in G4) increases $E(I^-/I_3^-)$ by only ~ 0.01 V ([Figure 5D](#)). ¹H-NMR spectra of the same electrolyte with increasing amounts of water ([Figure 5F](#)) are consistent with prior work:¹¹ at low water concentrations, a peak is observed at high frequencies, consistent with strong $H_2O:I^-$ interactions. The chemical shift is slightly lower than that of bulk water, as this effect is less significant than the shift arising from H-bonding interactions between water molecules. As the water concentration increases for a fixed Lil content, the peak shifts from 4.45 to 4.35 ppm again indicating weaker $H_2O:I^-$ interactions. In previous work,¹¹ the trend was then seen to reverse at higher water concentrations of $>5\%$ H_2O (and 50 mM Lil) due to the strong hydrogen bonding interactions in between molecules in water clusters, resulting in a shift toward the position of bulk water.

The progressive addition of Pyr₁₄TFSI to the electrolyte containing 5,000 ppm of water (700 mM LiTFSI, 50 mM Lil in G4) shows a similar trend in the ¹H-NMR spectra ([Figures 5A, 5B, and S16](#)), with the water peak shifting downfield even further from 4.35 to 4.1 ppm on addition of 900 mM Pyr₁₄TFSI, suggesting either reduced $H_2O:I^-$ interactions and/or reduced H_2O H-bonding. In both scenarios, this indicates an increased “solvation” of the water and I^- by the IL. This increase in Pyr₁₄TFSI concentration also has a large associated increase in the I^-/I_3^- redox potential, from

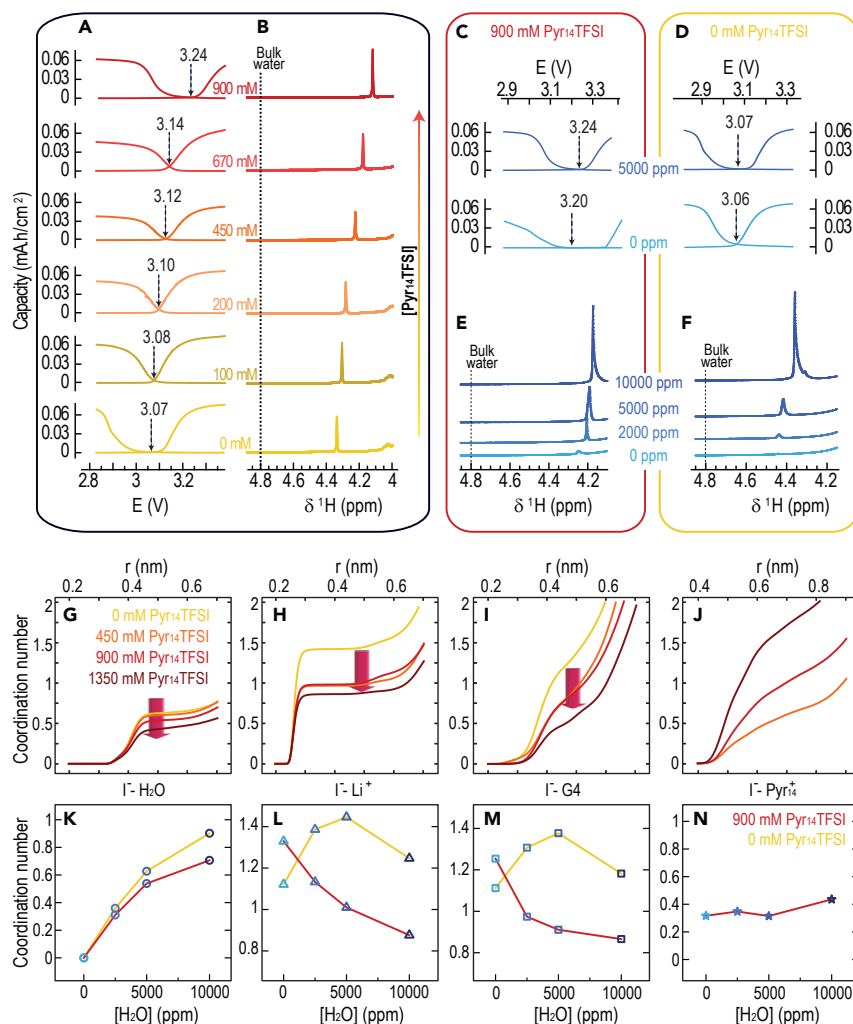


Figure 5. Correlation between Water Chemical Shift and I^-/I_3^- Equilibrium Redox Potential

(A and B) Effect of Pyr₁₄TFSI concentration (0 – 900 mM) on (A) galvanostatic charge-discharge curves, and (B) solution 1H -NMR of 700 mM LiTFSI, 50 mM LiI, and 5,000 ppm H₂O in G4 electrolyte. (C and D) Effect of water concentration (0 versus 5,000 ppm) on galvanostatic charge-discharge curves of electrolytes with (C) 900 mM and (D) 0 mM Pyr₁₄TFSI. (E and F) Solution 1H -NMR of electrolytes with increasing amounts of water with (E) 900 mM and (F) 0 mM Pyr₁₄TFSI. (G–J) MD coordination number (CN) plots of the I^- center of mass to (G) H₂O, (H) Li⁺, (I) G4, and (J) Pyr₁₄⁺ as a function of distance for 5,000 ppm H₂O in 700 mM LiTFSI, 50 mM LiI, in G4 electrolyte with increasing amounts of Pyr₁₄TFSI (0–1,350 mM). (K–N) Evolution of the I^- CN in the first coordination shell to (K) H₂O, (L) Li⁺, (M) G4, and (N) Pyr₁₄⁺ (measured at 0.5 nm for H₂O, Li⁺, and G4 and at 0.7 nm for Pyr₁₄⁺) as a function of [H₂O] in electrolytes with 0 mM Pyr₁₄TFSI (yellow lines) and 900 mM Pyr₁₄TFSI (red lines). All galvanostatic cycling was performed at 50 $\mu A/cm^2$ under argon in cells containing a LICGC. 300 mM LiTFSI in G4 was used as the anolyte.

3.07 to 3.24 V (~ 0.17 V), consistent with the strong interaction between I^- and Pyr₁₄⁺ (also shown in CV data in Figure S15). The largest value of $E(I^-/I_3^-)$ is observed when Pyr₁₄TFSI is present, the effect on the I^-/I_3^- coupling of adding Pyr₁₄⁺ being stronger than the addition of 5,000 ppm of water as shown in Figures 5C and 5D. A smaller shift in the 1H resonance is observed upon increasing water concentration (between 2,000 and 5,000 ppm) in the presence of Pyr₁₄TFSI ($\Delta\delta = -0.03$ ppm; Figure 5E) than

in its absence ($\Delta\delta = -0.08$ ppm; Figure 5F), which is indicative of weaker water- I^- interactions in the presence of the IL. This reduced water- I^- interaction and the higher measured $E(\text{I}^-/\text{I}_3^-)$ suggest that the Pyr_{14}^+ cation may be a stronger coordinating agent for I^- ions than water under the conditions used here. The larger ^1H shifts of the water peak observed in pure $\text{Pyr}_{14}\text{TFSI}$, compared to the mixtures shown in Figure 5 (Figure S17), is in agreement with a synergistic coordination effect of both water and $\text{Pyr}_{14}\text{TFSI}$ toward I^- . This is in agreement with the hard and soft acids and bases (HSAB) concept,⁴² since the introduction of the Pyr_{14}^+ cation, a softer Lewis base than Li^+ and H^+ (the other cations present in the electrolyte), would be expected to have a strong impact on the coordination of I^- , which is a soft Lewis acid.

In order to investigate the effects of the additives on the coordination of I^- , MD simulations were performed. Figures 5G–5L show the average coordination number (CN) of I^- to different species as a function of distance. The increase in $\text{Pyr}_{14}\text{TFSI}$ concentration reduces the contributions in the first I^- coordination shell from H_2O (Figure 5G), Li^+ (Figure 5H), and G4 (Figure 5K), while the contribution from Pyr_{14}^+ increases (Figure 5L). The MD results are consistent with the ^1H -NMR results, the increase in the H_2O molecules in the first coordination shell of I^- with increasing water concentration (Figure 5M) correlating with the shift of the water ^1H -NMR peak to lower values in both the absence (Figure 5F) and the presence of the IL (Figure 5E). The smaller chemical shift of the ^1H -NMR water peak observed in the presence of $\text{Pyr}_{14}\text{TFSI}$ is correlated with a smaller increase of H_2O molecules in the first coordination shell of I^- (Figure 5M). This effect has further implications on the coordination of I^- by Li^+ and G4: the number of I^- - Li^+ (Figure 5H) and G4- I^- (Figure 5K) interactions in the first coordination shell of I^- decreases with increasing water content (up to 5,000 ppm) in the absence of IL. However, the presence of IL (900 mM) reverses this effect, and both Li^+ (Figure 5H) and G4 (Figure 5K) are on average increasingly present in the first coordination shell of I^- with increasing water content. This indicates a fundamentally different contribution of the IL to the solvation of I^- compared to water and corroborates the complex interplay between the two additives used in the electrolyte capable of undergoing OER during LiOH oxidation (Figure 1).

The disruptive insertion of Pyr_{14}^+ ions into the first coordination shell of I^- can be clearly visualized in snapshots of the final state of the simulations of electrolytes with increasing $\text{Pyr}_{14}\text{TFSI}$ concentrations shown in Figures 6A–6D. The comparative levels of coordination of Li^+ , H_2O , G4, and Pyr_{14}^+ ions, evaluated as a function of the concentration of $\text{Pyr}_{14}\text{TFSI}$ (Figure 6E), indicate a strong Pyr_{14}^+ - I^- interaction, to levels comparable to that of Li^+ and H_2O at $[\text{Pyr}_{14}\text{TFSI}] = 900$ mM, in agreement with previous MD studies.^{16,18} This complex interplay is also reflected on the mobility of I^- ions (their mean squared displacement) in the electrolyte (Figure 6F). In the absence of IL, I^- mobility is not strongly affected by increasing amounts of water (solid lines) up to 10,000 ppm. The presence of 900 mM of $\text{Pyr}_{14}\text{TFSI}$ in neat electrolytes reduces I^- ion mobility compared to the electrolyte with no IL (light blue traces). However, the presence of $\text{Pyr}_{14}\text{TFSI}$ has the effect of substantially increasing I^- ion mobility with increasing water content up to 5,000 ppm. At higher water content, the mobility is reduced to some extent due to the onset of water clusters formation.¹¹ The electrolyte mixture used in the cell reported in Figure 1 (900 mM $\text{Pyr}_{14}\text{TFSI}$ and 5,000 ppm of water) has similar average amounts of Li^+ , G4, and Pyr_{14}^+ in the first coordination shell of I^- (Figure 6E), and it has the highest measured I^- mobility (Figure 6F).

Thermodynamic Analysis of the Effect of Additives. The measurements of the I^-/I_3^- redox potential shown in Figure 5A allow us to estimate the effect of the additives

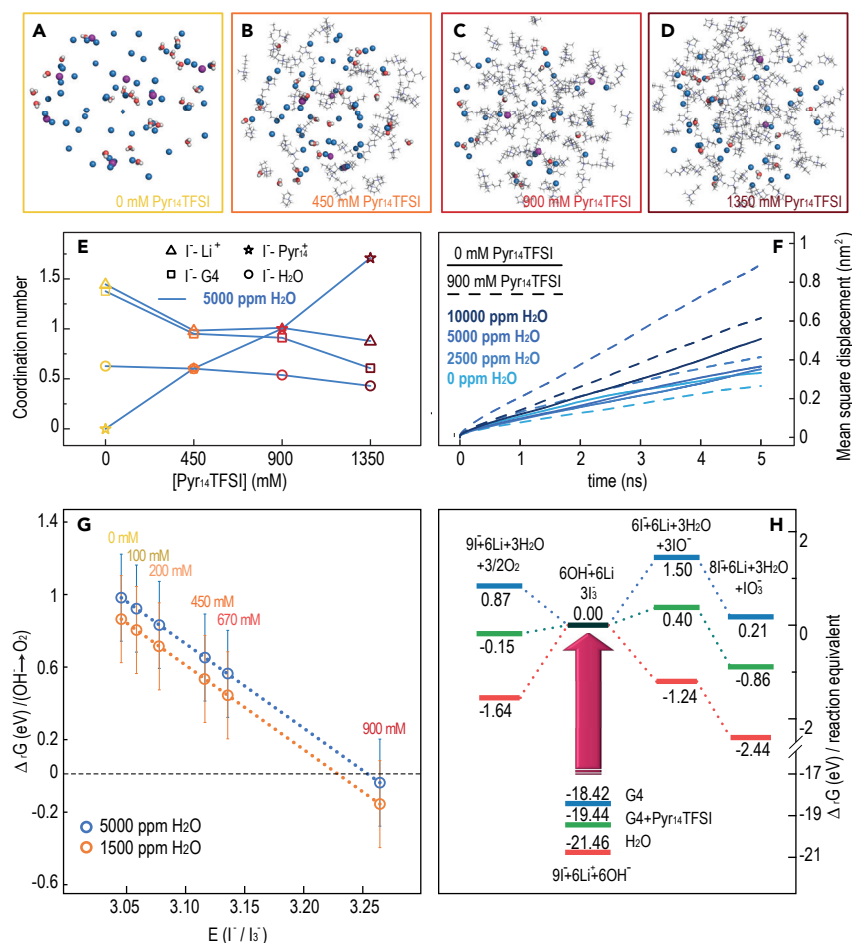


Figure 6. MD Simulations of Electrolytes with Varying Levels of Additives; Implications for the Thermodynamic Drive for the OER

(A–D) Snapshots of the final state of the simulations of electrolytes containing 700 mM LiTFSI, 50 mM LiI, and 5,000 ppm H₂O in G4 with (A) 0 mM, (B) 450 mM, (C) 900 mM, and (D) 1,200 mM Pyr₁₄TFSI showing I⁻ (magenta), Li⁺ (blue), H₂O (red/white), and Pyr₁₄⁺ (sticks). G4 molecules are omitted for clarity.

(E) Plot of the evolution of the CN in the first coordination shell of I⁻ to H₂O, Li⁺, G4, and Pyr₁₄⁺ with increasing Pyr₁₄TFSI concentration in electrolytes containing 5,000 ppm H₂O.

(F) Mean square displacement of I⁻ ions in electrolytes with 0 mM Pyr₁₄TFSI (solid lines) and 900 mM Pyr₁₄TFSI (dashed lines) with increasing water concentration.

(G) Effect of the various E(I⁻/I₃⁻) couples measured for different Pyr₁₄TFSI concentrations (shown in Figure 5A) on the thermodynamic driving force for the OER, assuming 5,000 ppm (end of charge, blue) and 1,500 ppm of water (beginning of charge, orange). The error bars are calculated based on the assumptions made in the calculations (see Supplemental Information).

(H) Free-energy diagram for the proposed mechanisms involving the iodide-mediated LiOH oxidation (O₂ evolution [left], IO⁻ and IO₃⁻ formation [right], relative to I₃⁻ formation in G4 [blue], G4 + 900 mM Pyr₁₄TFSI [green], and H₂O [red]). The Gibbs free-energy values were calculated for the electrolytes containing 700 mM LiTFSI, 50 mM LiI, and 5,000 ppm H₂O in G4 with 0 mM and 900 mM Pyr₁₄TFSI (E(I⁻/I₃⁻) = 3.07 V and 3.24 V, respectively; Figure 5A) and in standard conditions. All electrochemical reactions are scaled to 6 e⁻ so as to compare the free energies of the various reactions.

used in this work on the thermodynamic drive of the OER using Equation 5. Figure 6G shows an estimation of $\Delta_r G$ (OH⁻ → O₂) as a function of the I⁻/I₃⁻ redox potential in electrolyte mixtures with increasing Pyr₁₄TFSI concentration for two levels of H₂O concentration (1,500 ppm [orange] and 5,000 ppm [blue], representing the theoretical levels at the beginning and end of the charge, respectively). The calculation of

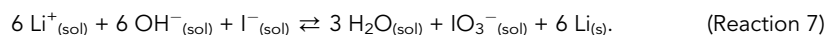
the thermodynamic drive of the OER has been scaled up to $6e^-$ (instead of the $4e^-$ process described above) in order to allow direct comparison with the formation of IO^- and IO_3^- (Figure 6H). It can be seen that only at a I^-/I_3^- redox potential above ~ 3.24 V does the OER becomes thermodynamically favorable, with $\Delta_r G(OH^- \rightarrow O_2) \approx -0.03$ eV (± 0.24) for $[Pyr_{14}TFSI] = 900$ mM at 5,000 ppm H_2O and ≈ -0.15 eV (± 0.24) at 1,500 ppm H_2O (see Supplemental Information for details). These values are very close to, or below, zero at equilibrium conditions, within the error margins arising from the assumptions made in the calculations and the measurement limitations, and thus this process is energetically feasible considering the experimental conditions (see Tables S1–S4 and Figure S22). It is of course important to note that during the charge the cell is working under non-equilibrium conditions, where the $[I_3^-]$ is higher and $[I^-]$ lower than under equilibrium conditions, providing an additional driving force for the OER. The high values of $E(I^-/I_3^-)$ observed in the electrolytes containing $Pyr_{14}TFSI$ and water can therefore provide a rationale for the observation of O_2 evolution during the charge process shown in Figures 1A–1F.

OER versus IO_3^- Formation

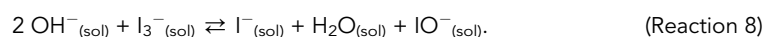
Our results (Figure 1) indicate that there is a very fine balance between the production of $LiIO_3$ and O_2 , which we now discuss. The ability of I_3^- to oxidize $LiOH$ to form $LiIO_3$ (via Reactions 5 and 6) has been found to be dependent on the Gutmann acceptor number (AN) of the solvent used, with I_3^- in *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), and 1-methylimidazole (Me-Im) being capable of oxidizing $LiOH$ (for AN > 13.6), but I_3^- in G1, G4, and pyridine being unable to.¹⁹ In the absence of water, a LiI -containing electrolyte in diethylene glycol dimethyl ether (G2) requires potentials above the I_3^-/I_2 to remove $LiOH$ from preloaded electrodes,¹⁹ whereas the formation of IO_3^- was reported in a $LiOH$ -saturated G1-based electrolyte containing water (3 wt%).^{11,43} Electrochemically, several groups have reported the formation of IO^-/IO_3^- during the charge of $LiOH$ -based $Li-O_2$ cells in glyme electrolytes containing water and iodide,^{12,14,15,43} whereas in the absence of water, a charging plateau above the I_3^-/I_2 redox transition was reportedly required in G2¹⁹ (Figure S21). Our studies clearly show that the addition of small quantities of water increases the I_3^- oxidative power and that it can oxidize $LiOH$ under these conditions: during galvanostatic charge of cells with 50 mM LiI and 5,000 ppm H_2O in G4 (Figures 1G–1M), the charge process is observed to commence below the I_3^-/I_2 transition (from as low as 3.2 V). The detection of IO^- and IO_3^- in the UV spectra (Figure 4A) is therefore consistent with $LiOH$ removal via Reactions 5 and 6.

It has recently been argued that $LiIO_3$ is the thermodynamic product, rather than O_2 , on oxidation of Li_2O_2 by I_3^- , even though O_2 evolution is seen. The reported lack of $LiIO_3$ formation was ascribed in this study to the slow kinetics of O–O dissociation needed to form IO^- (and subsequently $LiIO_3$), even in solvents with low Gutmann AN, such as G4, where the decomposition of Li_2O_2 is very slow.¹⁹ The authors similarly argued that the most thermodynamically favorable route for the oxidation of $LiOH$ occurs through the formation of $LiIO_3$ (Reactions 5 and 6) rather than the formation of O_2 (Reaction 2). Our results motivate the same question as raised previously for O_2 evolution from Li_2O_2 in the presence of LiI : the presence of $Pyr_{14}TFSI$ increases the oxidizing power of I_3^- so that it can promote O_2 evolution, but why does it also disfavor the IO_3^- formation mechanism?

We now consider the thermodynamic driving force to form lithium iodate (IO_3^-) in basic media via an analogous analysis to the $LiOH$ oxidation, through the I^- -mediated OER described above. Starting with the following reaction (full derivation is found in the Supplemental Information):



This reaction is in fact redox mediated via the following two-stage catalytic mechanism in which I^- is first oxidized to I_3^- (I^-/I_3^- couple, Gibbs free energy: $\Delta_r G(\text{I}^-/\text{I}_3^-)$; [Reaction 2](#)). Subsequently, LiOH reacts chemically with I_3^- to form IO^- and H_2O (Gibbs free energy: $\Delta_r G(\text{OH}^- \rightarrow \text{IO}^-)$):



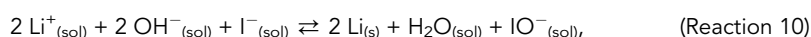
Finally, IO^- disproportionates to form IO_3^- and I^- (Gibbs free energy: $\Delta_r G(\text{IO}^- \rightarrow \text{IO}_3^-)$):



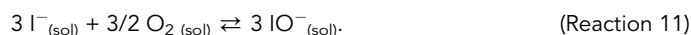
The Gibbs free energy of IO_3^- formation ($\Delta_r G(\text{OH}^- \rightarrow \text{IO}_3^-)$) can therefore be calculated from the combination of the Gibbs free energy of these three reactions:

$$\Delta_r G(\text{OH}^- \rightarrow \text{IO}_3^-) = 3\Delta_r G'(\text{I}^-/\text{I}_3^-) + \Delta_r G(\text{OH}^- \rightarrow \text{IO}^-) + \Delta_r G(\text{IO}^- \rightarrow \text{IO}_3^-). \quad (\text{Equation 7})$$

The key step in the $\text{IO}^-/\text{IO}_3^-$ route during charge is the reaction of I_3^- and OH^- to form IO^- ([Reaction 8](#)), as this reversible process is directly in competition with the OER. While the formation of IO_3^- is thermodynamically downhill with respect to IO^- , the proposed mechanisms require the formation of IO^- as an initial step. As previously discussed, the solvation of I^- strongly influences the I^-/I_3^- redox potential, and therefore also $\Delta_r G(\text{OH}^- \rightarrow \text{IO}^-)$. However, the (formally) I^+ ion in I_3^- is consumed to create IO^- , generating only two I^- ions ([Reaction 8](#)), as opposed to three I^- ions in the OER reaction ([Reaction 3](#)). The effect of this difference, and whether this is sufficient to create a thermodynamic driving force for IO^- over O_2 because of it, can be assessed by examining the overall reaction to form IO^- ([Reaction 8](#) + [Reaction 2](#)).



which competes with the formation of O_2 via the OER given in [Reaction 1](#). The competition between these two reactions is described via the following equilibrium:



The Gibbs free energy for this process can be calculated:

$$\begin{aligned} \Delta_r G(\text{OH}^- \rightarrow \text{IO}^-) - \frac{3}{2} \Delta_r G(\text{OH}^- \rightarrow \text{O}_2) &= 0.40 + 3\Delta_{\text{sol}} G(\text{IO}^-) - 3\Delta_{\text{sol}} G(\text{I}^-) \\ &- \frac{3}{2} kT \ln \left(\frac{P_{\text{O}_2}}{P^\circ} \right). \end{aligned} \quad (\text{Equation 8})$$

This indicates that, under standard conditions (implying Δ_{sol} terms are 0), the thermodynamic drive for the OER versus IO^- formation is +0.40 eV (as $3\Delta_r G(\text{IO}^-) - 3\Delta_r G(\text{I}^-) = +0.40$ eV from [Equation 8](#); see [Supplemental Information](#)).⁴¹ However, the thermodynamic drive is solvent dependent due to differences in solvation energies of I^- , IO^- , and O_2 ([Equation 8](#)). If the value of $\Delta_{\text{sol}} G(\text{O}_2)$ is assumed to be unchanging in the various electrolytes under consideration, then the thermodynamic balance between the formation of IO^- and O_2 ($\Delta_r G(\text{OH}^- \rightarrow \text{IO}^-) - \Delta_r G(\text{OH}^- \rightarrow \text{O}_2)$) hinges entirely upon the difference in the Gibbs free energy of solvation of I^- and IO^- in different electrolytes ($\Delta_{\text{sol}} G(\text{IO}^-) - \Delta_{\text{sol}} G(\text{I}^-)$).

To obtain an understanding of the magnitude of the solvation energy terms, density functional theory (DFT) calculations with implicit solvation were performed (see [Supplemental Information](#)). The calculated difference in the Gibbs free energy of solvation of I^- and IO^- ($3\Delta_{\text{sol}}G(\text{IO}^-) - 3\Delta_{\text{sol}}G(\text{I}^-)$) is +0.22 eV in G4 and +0.15 eV in pure $\text{Pyr}_{14}\text{TFSI}$, making $\Delta_rG(\text{OH}^- \rightarrow \text{IO}^-) - \frac{3}{2}\Delta_rG(\text{OH}^- \rightarrow \text{O}_2)$ +0.63 eV and +0.55 eV in G4 and pure $\text{Pyr}_{14}\text{TFSI}$, respectively; i.e., the formation of IO^- is thermodynamically unfavorable in comparison to the OER regardless of the presence or absence of IL.

A similar thermodynamic analysis of the formation of IO_3^- can be performed (see [Supplemental Information](#)):

$$\Delta_rG(\text{OH}^- \rightarrow \text{IO}_3^-) - \frac{3}{2}\Delta_rG(\text{OH}^- \rightarrow \text{O}_2) = -0.79 + \Delta_{\text{sol}}G(\text{IO}_3^-) - \Delta_{\text{sol}}G(\text{I}^-) - \frac{3}{2}kT\ln\left(\frac{P_{\text{O}_2}}{P^\circ}\right).$$

(Equation 9)

The formation of IO_3^- is more thermodynamically favorable than the OER under standard conditions (−0.79 eV),⁴¹ and the thermodynamic balance between the formation of IO_3^- and O_2 in different electrolytes again depends on ($\Delta_{\text{sol}}G(\text{IO}_3^-) - \Delta_{\text{sol}}G(\text{I}^-)$). DFT calculations similarly show that the solvation of IO_3^- in G4 and $\text{Pyr}_{14}\text{TFSI}$ is less favorable than that in water by amounts very similar to those found for IO^- and I^- ($\Delta_{\text{sol}}G(\text{IO}_3^-) = +0.44$ and +0.28 eV, respectively). This results in the difference in driving force for the formation of IO_3^- over O_2 ([Equation 9](#)) being reduced to −0.627 eV and −0.557 eV in G4 and pure $\text{Pyr}_{14}\text{TFSI}$, respectively; i.e., IO_3^- formation is always favored over the OER in all solvents.

[Figure 6H](#) shows free energy diagrams comparing the thermodynamic drive to form O_2 ([Equation 5](#)) versus IO^- ([Equation 8](#)) and IO_3^- ([Equation 9](#)) in electrolytes with and without IL, and in standard conditions. The value of $E(\text{I}^-/\text{I}_3^-)$ used for the calculations is the one measured for the electrolytes containing 700 mM LiTFSI , 50 mM LiI , and 5,000 ppm H_2O in G4 with 0 mM and 900 mM $\text{Pyr}_{14}\text{TFSI}$ ($E(\text{I}^-/\text{I}_3^-) = 3.07$ V and 3.24 V, respectively; [Figure 5A](#)), while the solvation energy terms were calculated for implicit solvents (in pure G4, $\text{Pyr}_{14}\text{TFSI}$, and water, respectively). The overall thermodynamic analysis indicates that the introduction of $\text{Pyr}_{14}\text{TFSI}$ ([Figure 6H](#)) to G4 has two effects: (1) oxidation of OH^- by I_3^- becomes thermodynamically favorable ($\Delta_rG(\text{OH}^- \rightarrow \text{O}_2) < 0$); (2) IO^- formation is never favorable versus the OER, while IO_3^- is always more thermodynamically favorable. This suggests that the kinetics associated with IO_3^- formation must also play a role in the observed switch from $\text{IO}^-/\text{IO}_3^-$ formation to OER during charge. Given that the formation of IO_3^- is the thermodynamic product, and that it requires 3 equivalents of IO^- ([Reaction 9](#)), the rate at which this intermediate is formed is of paramount importance. Our results indicate that in water-containing glyme electrolytes, while the conversion to IO^- is still thermodynamically unfavorable, it occurs because there is no alternative competing OER reaction; its formation is likely driven by the driving force for IO_3^- formation. The introduction of $\text{Pyr}_{14}\text{TFSI}$ changes this equilibrium as the OER is now favorable. While IO_3^- remains the thermodynamic product, the kinetics of its formation involving the reaction of three IO^- molecules are unfavorable, which we suggest is key here. The kinetics of iodine redox reactions have been an intensely debated subject on its own for decades, with important ramifications to many fields,⁴⁴ which lies well outside of the scope of this article. It is, however, well understood that kinetically, iodine redox reactions are heavily dependent on the media. For instance, the iodine disproportionation reaction in aqueous media is greatly

reduced (by up to two orders of magnitude) at high pHs, at which the reaction becomes first order with respect to $[\text{IO}^-]$.^{44,45}

Our MD and ^1H -NMR results confirm that the introduction of the (soft Lewis base) Pyr_{14}^+ cation to the electrolyte has a strong impact on the coordination of the (soft Lewis acid) I^- , replacing H_2O , Li^+ , and G4 to some extent in the environment of I^- (Figure 6E), in agreement with previous studies.^{18,20} This suggests that the fast kinetics, of the IO^- formation in water-containing electrolytes, are disturbed by the introduction of $\text{Pyr}_{14}\text{TFSI}$ due to efficient donor-acceptor interactions. Furthermore, as the MSD plot (Figure 6F) shows, there is a synergistic interaction between water and the Pyr_{14}^+ cation on the mobility of I^- , which could also play a kinetic role during the charge process.

Conclusions

LiI-mediated cells in the presence of water and the ionic liquid $\text{Pyr}_{14}\text{TFSI}$ produce reversible $4\text{e}^-/\text{O}_2$ ORR and OER at 2.6 V and 3.2–3.5 V, respectively, during capacity-limiting galvanostatic cycling as monitored in *operando* OEMS experiments. A combination of *ex situ* characterization methods confirm that these reactions occur through the formation/decomposition of LiOH. OEMS experiments with Li_2O_2 pre-loaded electrodes show that the electrolyte mixture is also capable of efficiently decomposing Li_2O_2 through a $2\text{e}^-/\text{O}_2$ during OER. The presence of $\text{Pyr}_{14}\text{TFSI}$ increases the I^-/I_3^- redox potential, shifting the mechanism of the LiOH OER from the irreversible production of $\text{IO}^-/\text{IO}_3^-$ to the evolution of O_2 . This shift in redox potential can be explained by a change in the solvation conditions of I^- in the presence of both water and the IL. Our NMR and MD results indicate that 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- O_2 batteries. This study reopens the possibility of using LiOH as a viable, and water-resistant, discharge product in Li-air batteries. Further studies will be needed to understand all the intricate mechanistic details of this chemistry, as well as to improve the overall performance of the cell, especially with regard to rate and long-term reversibility.

EXPERIMENTAL PROCEDURES

Resource Availability

Lead Contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Clare P. Grey (cpg27@cam.ac.uk).

Materials Availability

This study did not generate new unique reagents.

Data and Code Availability

The solvation parameters used for implicit solvation DFT calculations are presented in the [Supplemental Information](#).

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 h, and transferred to the glovebox without exposure to air. The areal loading of the carbon electrode is $\sim 1\text{--}2\text{ mg/cm}^2$. 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) at <10 ppm and then stored over 4 Å molecular sieves. Lithium bis(trifluoromethyl)sulfonylimide (LiTFSI, 3M) and LiI (Aldrich, 99.9%) were dried *in vacuo* at 160°C and 200°C, respectively for 12 h before being used to prepare the electrolyte. 1-butyl-1-methyl-pyrrolidinium-bis-(trifluoromethanesulfonyl)-imide (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 glovebox on bored-through stainless steel Swagelok unions by staking a Li disc (PI-KEM, 99.99%), 1 piece of pressed borosilicate glass fiber separator (Whatman) wetted with 300 mM LiTFSI / G4 (anolyte), a disk of lithium-ion-conducting glass ceramic (LICGC; Ohara), 1 piece of pressed borosilicate glass fiber separator wetted with the active catholyte (90 μL in 1/2" and 210 μL in 1" cells, respectively), and Ensaco P150 cathode. Stainless steel mesh (Advent) was used as a current collector. Electrochemical tests were performed on either a Biologic SP-300 or an Ivium Vertex potentiostat/galvanostat. Due to the significant overpotential induced by the use of a LICGC disk, the resistance of the cell was measured by impedance spectroscopy. Ohm's Law was then applied to obtain the Ohmic overpotential (Figure S20), which was then subtracted in the load curves. Galvanostatic cycling was limited to a current of 50 μA/cm² due to kinetic limitations of the very viscous electrolyte (Figures S9–S11, S18, and S19). A newly designed OEMS system was developed for this work, and it is described in detail in the Supplemental Information (Figure S1A). The cell design consists in a Swagelok-type cell with inlet and outlet tubes welded to the top plunger and capped with self-sealing quick-connects (Beswick Engineering) to isolate the cell from the atmosphere between assembly in the glovebox 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 is described in detail in the Supplemental Information (Figure S1B). A pressure transducer was connected to a Swagelok-type cell and sealed in the glovebox. 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 glovebox, rinsing the cathode twice in G1, then drying them *in vacuo* at room temperature. 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 Kα1 radiation ($\lambda = 1.5406 \text{ \AA}$). Ultraviolet spectra were acquired on samples in an air-tight quartz cuvette in a PerkinElmer (LAMBDA TM 25/35) spectrometer. G4 was used for dilutions, and pristine electrolyte was used as reference. Scanning electron microscopy was obtained in a Tescan MIRA3 microscope (5 keV; 7 pA) with samples transported from the glovebox sealed in a Kamrath & Weiss transfer module. Solution ¹H-NMR spectra were acquired using an 11.7 T Bruker Avance III HD spectrometer with a single 30° (10.5 μs) flip angle pulse sequence - and with a recycle delay of 1 s. DMSO-d₆ was used as solvent. Titration experiments were performed following the method previously reported by McCloskey et al.⁴⁶ Cathodes were extracted from cells inside the glovebox and placed in a sealed vial unwashed. 2 mL of ultrapure water (Millipore) was

injected into the vial using a syringe, and then titration of the base was done with a standardized 10 mM HCl solution, using phenolphthalein as end-point indicator while vigorously stirring. The LiOH content is calculated based on this acid-base titration. Subsequently, 1 mL 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 from the reaction of Li₂O₂, alongside the I₃[−] present in the unwashed electrodes, was then quickly titrated using 0.01 N NaS₂O₃ solution using a starch indicator, in order to establish the presence or absence of Li₂O₂ in the discharge product (Figure S4). Post mortem measurement of water in electrolyte was measured in cells using Super P coated gas diffusion layer electrodes. The separator in the cathode side was wetted with 0.25 mL of electrolyte (containing 900 mM of IL and 5,000 ppm of water). The cells were then filled with O₂ (after 2 pumping/filling cycles) and investigated after resting, discharging, and charging to 2 mAh. Subsequently, the gas in the cells was evacuated by pumping for 30 min before introducing the cells into the glovebox for disassembly. The separator and electrode were then removed and stored in a vial in which 0.5 mL of G4 was used to wash the electrolyte. 0.3 mL of washed electrolyte was then collected and added to 34.4 mg LiTFSI to bring its concentration up to 700 mM (LiTFSI was added since its addition results in a shift of the water peak to higher ppm and into a range that does not overlap with the G4 peaks; see Figure S8), stirred for 2 mins, and left to rest for 24 h. ¹H-NMR of this solution was then collected, and the spectra was normalized with respect to the peak corresponding to the CH₂ groups of the IL.

Density Functional Theory Calculations

To obtain an understanding of the magnitude of the $\Delta_{\text{sol}}G(\cdot)$ terms, DFT calculations were performed. In each case, the B3LYP-D3/def2-TZVP level of theory was used. The SMD solvation model⁴⁷ was used for implicit solvation calculations. The built-in parameters for water were used, while for G4 and Pyr₁₄TFSI, parameters were derived for the calculations (see Supplemental Information).

Molecular Dynamics Simulations

The simulation boxes were set up, using Packmol,⁴⁸ to be congruent with the experimental concentrations (700 mM LiTFSI, 50 mM Lil in G4, with 5,000 ppm of H₂O as starting point). Furthermore, water concentration was varied (0, 2,500, and 10,000 ppm of H₂O) as well as the presence/absence of the IL. The role of the concentration of the IL was also explored by varying the number of Pyr₁₄TFSI molecules to be 0, 0.5, and 1.5 times the experimental concentration (0 mM, 450 mM, and 1,350 mM). The full list of values is presented in the Supplemental Information (Table S2). The time step in each simulation was 2 fs as the C-H bonds were fixed utilizing LINCS. The forcefield used was OPLS-AA, with additional parameters for Pyr₁₄TFSI from CL&P.⁴⁹ The SPC water model was used. Scaled charges (to 0.8) were also used to speed up the simulation due to the inclusion of an IL in the system. The equilibration procedure was as follows: an initial starting run of 0.2 ns NVT (Nose-Hoover thermostat set to 298 K and 1 ps) followed by two NPT runs, both 4 ns long (the first one used the Berendsen barostat, set to 1 atm and 5 ps, and the second used the Parrinello-Rahman barostat). The two-step NPT procedure was used due a simulation instability when the Parrinello-Rahman barostat was used directly. The production runs were 10 ns NVT runs, storing output every 2,000 steps.

In each case, short-range cutoffs for non-bonded interactions were set to 1.2 nm. Gromacs versions 2018.2 and 2018.3 were used.⁵⁰ Analysis of the MD trajectories were done using the Gromacs toolchain, e.g., gmx rdf and gmx msd. The coordination number plots were done using the center of mass of each molecule.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.joule.2020.09.021>.

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AUTHOR CONTRIBUTIONS

I.T. contributed to project planning, data acquisition, analysis, and article writing; T.L. contributed to project planning; E.P. contributed to project planning and preliminary experiments; J.H.J.E. and G.K. contributed to data acquisition and analysis; E.J. contributed to theoretical data and analysis; C.P.G. contributed to project planning, supervision, and article writing. All authors contributed to the discussion of the results presented and editing.

DECLARATION OF INTERESTS

C.P.G. and T.L. have a patent pending associated with lithium-air technology.

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