Towards reversible and moisture tolerant aprotic lithium-air batteries

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Abstract

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 LiI 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 vs Li/Li⁺). The addition of the ionic liquid increases the oxidising 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 fuels³.

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 oxidised 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 LAB⁴⁻⁸. 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^{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 LiI as a redox mediator or Ru as a catalyst in a wet organic electrolyte¹¹⁻¹³. However, it is widely believed that LiOH is not reversible due to (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 on charge of oxidation products such as IO₃⁻^{12,14,15}, and DMSO₂¹³, which originate from the redox mediator and the solvents, respectively, and (iii) little or no oxygen evolution being observed in gas analysis experiments¹⁵. 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 decomposition¹⁵⁻¹⁸.

The electrochemical behaviour 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, 19-21}; the oxidising 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 (IL) have been shown to alter the solvation/coordination environments of this redox system, again substantially affecting the (I^-/I_3^-) redox potential¹⁹, while still allowing high ionic conductivity and reducing solvent volatility²²⁻²⁹. However, the high viscosity of ILs, which limits O_2 diffusion coefficients, and the low O_2 solubility are disadvantageous for LAB performance³⁰. The presence of water has been shown to enhance the solution-transfer of discharge products and redox mediators^{12, 31-34}, 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, 15, 35}. 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 1-butyl-1-methyl-pyrrolidinium-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^{25, 29, 30, 32, 36-38}. We find 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, and the mechanistic considerations of the oxygen evolution vs. 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.

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 tetraethylene glycol dimethyl ether (G4), a lithium conducting glass ceramic (LICGC-Ohara AG010) separating the two electrolytes, a catholyte containing 0.7 M LiTFSI, 50 mM LiI, 900 mM M Pyr₁₄TFSI 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, since redox mediator shuttling is a possible source of “artificial” capacity, the oxidised species such as I_3^- being reduced at the anode and then migrating back to the cathode to be reoxidised¹⁵. 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)¹¹. 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 (Fig. 1g-m shows similar results for a cell without Pyr₁₄TFSI for comparison). 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 O₂ of ~0.51 nmol/s (Fig. 1c), corresponding to a 4 e⁻/O₂ stoichiometry, with no significant evolution of gases indicative of parasitic reactions (Fig. 1e). The total measured O₂ consumption is 18.5 μmol, which corresponds to a 99.1% Faradaic efficiency.

Figure 1 | 4 e⁻/O₂ Formation and Removal of LiOH in water and IL-containing cells. **a, b, g, h** Galvanostatic profiles and **c, d, j, k**, online mass spectrometry analysis of O₂, and **e, f, l, m**, H₂, CO and CO₂ (m/z= 32, 28, 44 respectively) from batteries with electrolytes comprising of 0.7 M LiTFSI, 50 mM LiI and 5000 ppm H₂O in G4 with 900 mM Pyr₁₄TFSI (left) and without Pyr₁₄TFSI (right) cycled at a current of 50 μA/cm².

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 ~4 e⁻/O₂ stoichiometry (Fig. 1d). A total of 18.4 μmoles of O₂ is evolved during charge, 99.5% of the amount consumed in the discharge (Faradaic efficiency), with no significant signs of parasitic reactions as signalled by a lack of evolution of H₂, CO or CO₂ (Fig. 1f). The OER can be observed for several cycles (Supplementary Fig. 5) with a relatively high Faradaic efficiency (>80% for 7 cycles).

By comparison, in the absence of Pyr₁₄TFSI only very small amounts of O₂ (1.5 μmoles corresponding to ~8.4% Faradaic efficiency) (Fig. 1k) are detected 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 CO₂ (and O₂ and CO to lesser extent), suggesting electrode/electrolyte degradation (Fig. 1m).

Analysis of the ORR products

Analysis of the cathode after discharge with X-ray diffraction (XRD) (Fig. 2a – grey trace) is dominated by patterns corresponding to crystalline LiOH, as revealed by quantitative analysis of the diffraction pattern (Supplementary Fig. 2). All reflections associated with LiOH are absent in the diffractogram of the fully charged electrodes, confirming the removal of the crystalline discharge product (Fig. 2a – green trace). Quantification of the amount of LiOH present in the electrode was performed by acid

titration at various stages of the discharge ($\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ and full discharge) and the charge ($\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ and full charge) processes. Fig. 2b shows an increasing amount of LiOH detected in the electrode as the ORR progresses (red bars) that 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 alternative discharge product was also tested by iodometry titration (Supplementary Fig. 3); no peroxide was detected in agreement with the XRD analysis. A similar trend can be observed during different stages of the OER (Fig. 2b – green bars), indicating that LiOH is being removed according to the same $1\text{ e}^-/\text{LiOH}$ stoichiometry. *Operando* pressure monitoring during discharge (Fig. 2c) confirms a $4\text{ e}^-/\text{O}_2$ stoichiometry during ORR for cells with 900 mM $\text{Pyr}_{14}\text{TFSI}$ and 5000 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 Li_2O_2 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 – red; discharged – grey; 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; SEM characterisation (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 grey triangles and blue dots, respectively in **a**. All cells were cycled at $50\text{ }\mu\text{A}/\text{cm}^2$.

Scanning electron microscopy (SEM) images of electrodes during the first discharge are shown in Fig. 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 water¹². The absence of these crystalline structures in the SEM images of fully recharged electrodes (Fig. 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 (Supplementary Fig. 7).

In order to evaluate the mechanistic implications of the observed stoichiometry during the OER in Fig. 1, further OEMS experiments were performed with an electrochemically preloaded electrode with Li_2O_2 (Fig. 3 – left); the electrode was produced by discharging a cell using 0.3 M 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 minutes. This electrode was then loaded in a two-compartment cell with the same catholyte used for the cells shown in Fig. 1 (*i.e.*, 0.7 M LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H₂O in G4). In this case, the OER showed an approximately 2 e^-/O_2 stoichiometry (Fig. 3c) consistent with the oxidation of Li_2O_2 . After initially reaching an evolution rate corresponding to 2 e^-/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 particles³⁹⁻⁴¹. Preloading was similarly performed using the IL-free conditions previously shown to produce LiOH electrochemically¹¹: an electrolyte comprising 0.7 M LiTFSI, 50 mM LiI, and 5000 ppm H₂O in G4 was discharged. Switching to the IL containing electrolyte resulted in 4 e^-/O_2 , OER on charge (Supplementary Fig. 12).

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 O₂ ($m/z=32$) and e, f, H₂, CO and CO₂ ($m/z=2, 28, 44$) evolution during charge of electrochemically preloaded electrodes with Li_2O_2 (left); and of a Li-O₂ cell discharged using ¹⁷O-enriched H₂O in the electrolyte containing G4 and Pyr₁₄TFSI at 70 $\mu\text{A}/\text{cm}^2$.

Since earlier ^{17}O -ssNMR measurements have reported that both O_2 and H_2O contribute to the oxygen atoms in the LiOH formed via a LiI-catalysed electrochemical reaction in G1¹¹, a further OEMS experiment was performed using ^{17}O -enriched H_2O (Fig. 3 – right) and Pyr₁₄TFSI. A $m/z = 32$ mass spectrometer signal (Fig. 3d – blue) dominates the response on charge, which is due to ^{16}O - ^{16}O . A signal is seen at $m/z = 33$ (Fig. 3d – magenta), which corresponds to ^{17}O - ^{16}O . The signal at $m/z = 34$ (Fig. 3d – orange) corresponds to either ^{17}O - ^{17}O or ^{18}O - ^{16}O . 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 ^{17}O in O_2 gas, since the natural abundance of ^{17}O and ^{18}O are 0.04 and 0.2 %, respectively. The low enrichment of the H_2^{17}O resulted in a relatively low Li^{17}OH concentration, as observed by ^{17}O ssNMR (Supplementary Fig. 13). This explains the relatively low intensity of the $m/z = 33$ signal (from ^{16}O - ^{17}O) compared with the $m/z = 32$ signal (from ^{16}O - ^{16}O).

Pathways to LiOH removal:

The mechanisms for LiOH formation in the ORR reaction have been discussed extensively elsewhere^{11, 16, 35}, and thus we focus here on the OER reaction during charge. Two questions arise from the OEMS data (Fig. 1). 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 O_2 evolution?

The OER, during the charge of a LiOH-based Li- O_2 battery, can be described overall by:

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

and subsequently LiOH is oxidised 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 ($E^\circ_{\text{vs Li/Li}^+}$) corresponds to 3.5761 V^{19, 42}, which is sufficiently large to drive oxygen evolution. However, the reversibility of iodide-mediated aprotic Li- O_2 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)^{15-18, 20}. 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 O_2 evolution in OEMS experiments, has suggested that IO_3^- is the dominant product rather than O_2 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^{15, 16}:

or via oxidation by I_3^- to form IO^- and the subsequent disproportionation of IO^- into IO_3^- and I^- ^{14, 20}:

In this study, cells containing Pyr₁₄TFSI show clear evidence for a 4 e⁻/O₂ OER (reaction 1) commencing at ~3.2 V (Fig. 1a-f). This oxygen evolution is absent in cells without the IL (Fig. 1g-m), 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 (Fig. 4a) show the presence of features at 295 and 354 nm, corresponding to the presence of I₃⁻; no feature corresponding to I₂ (at 520 nm) is seen in either case (insert in Fig. 4a). The electrolyte of cells without Pyr₁₄TFSI (Fig. 4a – red trace) show the presence of extra features at 228 and 465 nm, assigned to IO₃⁻ and IO⁻ respectively; these are absent in cells cycled with the IL (Fig. 4a – blue trace). The presence of I₃⁻ in both samples indicates that this is the main product of I⁻ oxidation, and therefore suggest that this is the species responsible for oxidising LiOH, rather than I₂. The lack of O₂ evolution observed in OER data of cells without Pyr₁₄TFSI can be therefore explained by the formation of oxidised iodine species (IO⁻ and IO₃⁻), the oxygen effectively being trapped in the solution, as previously reported for similar electrolytes¹⁵⁻¹⁷.

The capability of I₃⁻ to oxidise LiOH during the OER was subsequently tested. A solution of I₃⁻ was injected into a mixture of electrolyte containing 0.7 M LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H₂O in G4, and commercial LiOH powder. The subsequent gas evolution was measured by mass spectrometry (Fig. 4b). Gas evolution from the LiOH powder, at m/z= 32, can be directly observed as soon as the I₃⁻ solution is injected, confirming the evolution of O₂ from this mixture and demonstrating that I₃⁻ is capable of oxidising LiOH in this electrolyte; very little O₂ evolution is observed in the absence of Pyr₁₄TFSI.

Figure 4| Spectroscopic and electrochemical analysis of the I₃⁻ oxidising power. **a**, UV spectra of catholytes collected after galvanostatic discharge and charge of cells containing 0.7 M LiTFSI, 50 mM LiI, and 5000 ppm H₂O (red trace) and with 900 mM Pyr₁₄TFSI (blue trace) in G4; **b**, Online mass spectrometry test of the reaction of I₃⁻ with LiOH. A 50 mM I₃⁻ solution is injected into a vessel containing LiOH powder immersed in electrolyte with 0.7 M LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H₂O in G4 (blue trace) and 0.7 M LiTFSI, 50 mM LiI, and 5000 ppm H₂O in G4 (red trace). The gas evolution of the ensuing reaction was recorded with a mass spectrometer (m/z=32, corresponding to O₂ evolution is displayed). A blank spectrum was collected by injecting the I₃⁻ solution into the electrolyte containing 0.7 M LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H₂O 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 ($\Delta_{\text{OER}}G$) was estimated according to reaction 1:

$$\Delta_{\text{OER}}G = 2\Delta_f G^\circ(\text{H}_2\text{O}) + \Delta_f G^\circ(\text{O}_2) + 4\Delta_f G^\circ(\text{Li}) - 4\Delta_f G^\circ(\text{OH}^-) - 4\Delta_f G^\circ(\text{Li}^+) + 2\Delta_{\text{sol}}G(\text{H}_2\text{O}) + \Delta_{\text{sol}}G(\text{O}_2) - 4\Delta_{\text{sol}}G(\text{OH}^-) - 4\Delta_{\text{sol}}G(\text{Li}^+) \quad (\text{Eq1})$$

The $\Delta_{\text{OER}}G$ can then be written as the combination of reactions 2 and 3 (the I^-/I_3^- redox pair, and the $\text{OH}^- \rightarrow \text{O}_2$ chemical reaction, respectively) giving the Gibbs free energy:

$$\Delta_{\text{OER}}G = 2\Delta_r G(I^-/I_3^-) + \Delta_r G(\text{OH}^- \rightarrow \text{O}_2) \quad (\text{Eq2})$$

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

$$\Delta_r G(I^-/I_3^-) = \Delta_f G^\circ(I_3^-) + 2\Delta_f G^\circ(\text{Li}) - 2\Delta_f G^\circ(\text{Li}^+) - 3\Delta_f G^\circ(I^-) + \Delta_{\text{sol}}G(I_3^-) - 2\Delta_{\text{sol}}G(\text{Li}^+) - 3\Delta_{\text{sol}}G(I^-) \quad (\text{Eq3})$$

and $\Delta_r G(\text{OH}^- \rightarrow \text{O}_2)$ is the Gibbs free energy of the $\text{OH}^- \rightarrow \text{O}_2$ chemical reaction, defined as:

$$\Delta_r G(\text{OH}^- \rightarrow \text{O}_2) = 6\Delta_f G^\circ(I^-) + 2\Delta_f G^\circ(\text{H}_2\text{O}) + \Delta_f G^\circ(\text{O}_2) - 4\Delta_f G^\circ(\text{OH}^-) - 2\Delta_f G^\circ(I_3^-) + 6\Delta_{\text{sol}}G(I^-) + 2\Delta_{\text{sol}}G(\text{H}_2\text{O}) + \Delta_{\text{sol}}G(\text{O}_2) - 4\Delta_{\text{sol}}G(\text{OH}^-) - 2\Delta_{\text{sol}}G(I_3^-) \quad (\text{Eq4})$$

$\Delta_{\text{OER}}G$ depends on the Gibbs free energy of formation of H_2O ($\Delta_f G^\circ(\text{H}_2\text{O})$), O_2 ($\Delta_f G^\circ(\text{O}_2)$), Li ($\Delta_f G^\circ(\text{Li})$), OH^- ($\Delta_f G^\circ(\text{OH}^-)$), and Li^+ ($\Delta_f G^\circ(\text{Li}^+)$) at standard conditions, and their Gibbs free energy of solvation, ($\Delta_{\text{sol}}G(\text{H}_2\text{O})$), ($\Delta_{\text{sol}}G(\text{O}_2)$), ($\Delta_{\text{sol}}G(\text{Li})$), ($\Delta_{\text{sol}}G(\text{OH}^-)$) and ($\Delta_{\text{sol}}G(\text{Li}^+)$) which are solvent specific. $\Delta_f G^\circ(\text{H}_2\text{O})$ and $\Delta_f G^\circ(\text{O}_2)$ are tabulated values⁴², whereas by definition, $\Delta_f G^\circ(\text{Li}) = 0$. Using the Nernst equation for the I^-/I_3^- redox couple, and assuming that the dissolved oxygen ($\text{O}_{2(\text{sol})}$) is at equilibrium with oxygen gas ($\text{O}_{2(\text{g})}$) at a pressure (P_{O_2}) and that the oxygen can be treated as an ideal gas over the range of temperature concerned (see SI), the above expression can be written as:

$$\Delta_r G(\text{OH}^- \rightarrow \text{O}_2) = 2\Delta_f G^\circ(\text{H}_2\text{O}) - 4\Delta_f G^\circ(\text{LiOH}) + 2nFE(I^-/I_3^-) + 2\Delta_{\text{sol}}G(\text{H}_2\text{O}) + kT \ln\left(\frac{P_{\text{O}_2}}{P^\circ}\right) \quad (\text{Eq5})$$

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 ($\Delta_{\text{sol}}G(\text{H}_2\text{O})$), and the oxygen partial pressure (P_{O_2}). The redox potential of the iodide/triiodide redox system is solvent-dependent¹⁹⁻²¹, the couple varying by over 0.5 V¹⁹, whereas variations in the solvent activity and gas partial pressure are of smaller magnitude (estimated to be ~0.17 and ~0.08 eV respectively – Supplementary Table 2). The variability in the values of the $E(I^-/I_3^-)$ is strongly influenced by stabilizing (donor-acceptor) interactions of I^- species in solution^{19, 21}, since $\Delta_r G(I^-/I_3^-)$ is proportional to the difference in $\Delta_{\text{sol}}G$ of I^- and I_3^- :

$$\Delta_r G(I^-/I_3^-) \propto \Delta_{\text{sol}}G(I_3^-) - 3\Delta_{\text{sol}}G(I^-) \quad (\text{Eq6})$$

The OEMS results presented in Figs. 1, 3 and 4 suggest that the addition of Pyr₁₄TFSI (alongside small amounts of water) is capable of increasing the oxidising 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 rationalise 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:

(i) Effect of the additives on the coordination of I^- and on the OER: It has been recently shown that water and ILs are amongst the media in which $E(I^-/I_3^-)$ has the highest values, due to the very strong coordination of I^- by these solvent molecules¹⁹: 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 (Fig. 5). The addition of 5000 ppm of water to an electrolyte with no IL (0.7M LiTFSI, 50 mM Lil in G4) increases $E(I^-/I_3^-)$ by only ~ 0.01 V (Fig. 5d). 1H -NMR spectra of the same electrolyte with increasing amounts of water (Fig. 5f) are consistent with prior work¹¹: 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 fewer $H_2O:I^-$ interactions per water molecules. In previous work¹¹: 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 to towards the position of bulk water.

The progressive addition of Pyr₁₄TFSI to the electrolyte containing 5000 ppm of water (0.7M LiTFSI, 50 mM Lil in G4) shows a similar trend in the 1H -NMR spectra (Fig. 5b), with the water peak shifting downfield even further from 4.35 to 4.1 ppm on addition of 0.9M 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 3.07 to 3.24 V (~ 0.17 V), consistent with the strong interaction between I^- and Pyr₁₄⁺ (also shown in CV data in Supplementary Fig. 15). 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 5000 ppm of water as shown in Fig. 5c and 5d. A smaller shift in the 1H resonance is observed upon increasing water concentration (between 2000 and 5000 ppm) in the presence of Pyr₁₄TFSI ($\Delta\delta = -0.03$ ppm; Fig. 5e) than in its absence ($\Delta\delta = -0.08$ ppm; Fig. 5f), which is indicative of weaker water- I^- interactions in the presence of the IL. This reduced water- I^- interaction and the higher measured $E(I^-/I_3^-)$ suggests that the Pyr₁₄⁺ 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 Pyr₁₄TFSI, compared to the mixtures shown in Fig. 5, (Supplementary Fig. 17), is in agreement with a synergistic coordination effect of both water and Pyr₁₄TFSI towards I^- . This is in agreement with the hard and soft acids and bases (HSAB) concept⁴³, since the introduction the Pyr₁₄⁺ 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.

Figure 5 | Correlation between water chemical shift and I^-/I_3^- equilibrium redox potential. Effect of Pyr₁₄TFSI concentration (0 – 900 mM) on **a**, galvanostatic charge-discharge curves, and **b**, solution 1H NMR of a 0.7 M LiTFSI, 50 mM LiI, and 5000 ppm H₂O in G4 electrolyte; Effect of water concentration (0 vs. 5000 ppm) on galvanostatic charge-discharge curves of electrolytes with **c**, 900 mM and **d**, 0 mM Pyr₁₄TFSI; Solution 1H NMR of electrolytes with increasing amounts of water with **e**, 900 mM and **f**, 0 mM Pyr₁₄TFSI. MD coordination number (CN) plots of the I^- centre of mass of to **g**, H₂O; **h**, Li⁺; **k**, G4; and **l**, Pyr₁₄⁺ as a function of distance for 5000 ppm H₂O in 0.7 M LiTFSI, 50 mM LiI, in G4 electrolyte with increasing amounts of Pyr₁₄TFSI (0 – 1350 mM); evolution of the I^- CN in the first coordination shell to **m**, H₂O; **n**, Li⁺; **o**, G4; and **p**, 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. 0.3 M LiTFSI in G4 was used as the anolyte.

In order to investigate the effects of the additives on the coordination of I^- , MD simulations were performed. Fig. 5g-l show the average coordination number (CN) of I^- to different species as a function

of distance. The increase in Pyr₁₄TFSI concentration reduces the contributions in the first I⁻ coordination shell from H₂O (Fig. 5g), Li⁺ (Fig. 5h), and G4 (Fig. 5k), while the contribution from Pyr₁₄⁺ increases (Fig. 5l). The MD results are consistent with the ¹H NMR results, the increase in the H₂O molecules in the first coordination shell of I⁻ with increasing water concentration (Fig. 5m), correlating with the shift of the water ¹H NMR peak to lower values both in the absence (Fig. 5f) and presence of the IL (Fig. 5e). The smaller chemical shift of the ¹H NMR water peak observed in the presence of Pyr₁₄TFSI is correlated with a smaller increase of H₂O molecules in the first coordination shell of I⁻, (Fig. 5m). This effect has further implications to the coordination of I⁻ by Li⁺ and G4: the number of I⁻ - Li⁺ (Fig. 5h) and G4-I⁻ (Fig. 5k) interactions in the first coordination shell of I⁻ decreases with increasing water content (up to 5000 ppm) in the absence of IL. However, the presence of IL (900 mM) reverses this effect, and both Li⁺ (Fig. 5h) and G4 (Fig. 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 (Fig. 1).

The disruptive insertion of Pyr₁₄⁺ 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 Pyr₁₄TFSI concentrations shown in Fig. 6a-d. The comparative levels of coordination of Li⁺, H₂O, G4 and Pyr₁₄⁺ ions, evaluated as a function of the concentration of Pyr₁₄TFSI (Fig. 6e) indicates a strong Pyr₁₄⁺-I⁻ interaction, to levels comparable to that of Li⁺ and H₂O at [Pyr₁₄TFSI] = 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 (Fig. 6f). In the absence of IL, I⁻ mobility is not strongly affected by increasing amounts of water (solid lines) up to 10000 ppm. The presence of 900 mM of Pyr₁₄TFSI in neat electrolytes, reduces I⁻ ion mobility compared to the electrolyte with no IL (light blue traces). However, the presence of Pyr₁₄TFSI has the effect of substantially increasing I⁻ ion mobility with increasing water content up to 5000 ppm. At higher water content the mobility is reduced to some extent due to the onset of water clusters formation¹¹. The electrolyte mixture used in the cell reported in Fig. 1 (900 mM Pyr₁₄TFSI and 5000 ppm of water) has similar average amounts of Li⁺, G4, and Pyr₁₄⁺ in the first coordination shell of I⁻ (Fig. 6e), and it has the highest measured I⁻ mobility (Fig. 6f).

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 0.7M LiTFSI, 50 mM LiI, 5000 ppm H₂O in G4 with increasing Pyr₁₄TFSI concentrations 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 5000 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 Fig. 5a) on the thermodynamic driving force for the OER assuming 5000 ppm (end of charge – blue) and 1500 ppm of water (beginning of charge – orange). The error bars are calculated based on the assumptions made in the calculations (see SI); **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 0.7 M LiTFSI, 50 mM LiI and 5000 ppm H₂O in G4 with 0 mM and 900 mM Pyr₁₄TFSI (E(I⁻/I₃⁻) = 3.07 V and 3.24 V respectively – Fig. 5a), and in standard conditions. All electrochemical reactions are scaled to 6 e⁻ so as to compare the free energies of the various reactions.

(ii) Thermodynamic analysis of the effect of additives: The measurements of the I^-/I_3^- redox potential shown in Fig. 5a, allows us to estimate the effect of the additives used in this work on the thermodynamic drive of the OER using Eq 5. Fig. 6g shows an estimation of $\Delta_r G(OH^- \rightarrow O_2)$ as a function of the I^-/I_3^- redox potential in electrolyte mixtures with increasing Pyr₁₄TFSI concentration for two levels of H₂O concentration (1500 ppm – orange and 5000 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 IO₃⁻ (Fig. 6h). It can be seen that only at a I^-/I_3^- redox potential above ~3.24 V does the OER becomes thermodynamically favourable, with $\Delta_r G(OH^- \rightarrow O_2) \approx -0.03$ eV (± 0.24) for [Pyr₁₄TFSI] = 900 mM at 5000 ppm H₂O, and ≈ -0.15 eV (± 0.24) at 1500 ppm H₂O (See SI). These values are very close to, or below, zero at equilibrium conditions, within the error margins from the assumptions made in the calculations and the measurement limitations, and thus this process is energetically feasible considering the experimental conditions (see SI). 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 the force for the OER. The high values of $E(I^-/I_3^-)$ observed in the electrolytes containing Pyr₁₄TFSI and water can therefore provide a rationale for the observation of O₂ evolution during the charge process shown in Fig. 1a-f.

OER vs IO₃⁻ formation:

Our results (Fig. 1) indicate that there is a very fine balance between the production of LiIO₃ and O₂, which we now discuss. The ability of I₃⁻ to oxidise LiOH to form LiIO₃ (via reaction 5-6) has been found to be dependent on the Gutmann acceptor number (AN) of the solvent used, with I₃⁻ in N,N-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), and 1-methylimidazole (Me-Im) being capable of oxidising LiOH (for AN > 13.6), but I₃⁻ in G1, G4, and pyridine being unable to²⁰. In the absence of water, a LiI-containing electrolyte in diethylene glycol dimethyl ether (G2) requires potentials above the I₃⁻/I₂ to remove LiOH from preloaded electrodes²⁰, whereas the formation of IO₃⁻ was reported in a LiOH-saturated G1 based electrolyte containing water (3 wt%)^{11, 14}. Electrochemically, several groups have reported the formation of IO⁻/IO₃⁻ during the charge of LiOH based Li-O₂ cells in glyme electrolytes containing water and iodide^{12, 14-16}, whereas in the absence of water, a charging plateau above the I₃⁻/I₂ redox transition was reportedly required in G2²⁰. Our studies clearly show that the addition of small quantities of water increase the I₃⁻ oxidative power and that it can oxidise LiOH under these conditions: during galvanostatic charge of cells with 50 mM LiI and 5000 ppm H₂O in G4 (Fig. 1g-m), the charge process is observed to commence below the I₃⁻/I₂ transition (from as low as 3.2 V). The detection of IO⁻ and IO₃⁻ in the UV spectra (Fig. 4a) is therefore consistent with LiOH removal via reactions 5-6.

It has recently been argued that LiIO₃ is the thermodynamic product, rather than O₂, on oxidation of Li₂O₂ by I₃⁻, even though O₂ evolution is seen. The reported lack of LiIO₃ formation was ascribed in this study to the slow kinetics of O-O dissociation needed to form IO⁻ (and subsequently LiIO₃), even in solvents with low Gutmann acceptor number (AN), such as G4, where the decomposition of Li₂O₂ is very slow²⁰. The authors similarly argued that the most thermodynamically favourable route for the oxidation of LiOH occurs through the formation of LiIO₃ (reactions 5-6) rather than the formation of O₂ (reaction 2). Our results motivate the same question as raised previously for O₂ evolution from Li₂O₂ in the presence of LiI: the presence of Pyr₁₄TFSI increases the oxidising power of I₃⁻ so that it can promote O₂ evolution, but why does it also disfavour the IO₃⁻ 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 reaction (full derivation is found in the SI):

This reaction is in fact redox-mediated, via the following two-stage catalytic mechanism, in which first I^- is oxidised 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: $\Delta_r G(\text{OH}^- \rightarrow \text{IO}^-)$):

And 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 be therefore calculated from the combination of the Gibbs free energy of these three reactions:

$$\Delta_r G(\text{OH}^- \rightarrow \text{IO}_3^-) = 3\Delta_r G'(\text{I}^-/\text{I}_3^-) + \Delta_r G(\text{OH}^- \rightarrow \text{IO}^-) + \Delta_r G(\text{IO}^- \rightarrow \text{IO}_3^-) \quad (\text{Eq7})$$

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. Whilst 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:

$$\Delta_r G(\text{OH}^- \rightarrow \text{IO}^-) - \frac{3}{2} \Delta_r G(\text{OH}^- \rightarrow \text{O}_2) = 0.40 + 3\Delta_{\text{sol}} G(\text{IO}^-) - 3\Delta_{\text{sol}} G(\text{I}^-) - \frac{3}{2} kT \ln\left(\frac{p_{\text{O}_2}}{p^\circ}\right) \quad (\text{Eq11})$$

This indicates that under standard conditions (implying Δ_{sol} terms are 0), the thermodynamic drive for the OER vs. IO^- formation is +0.40 eV (as $3\Delta_f G(\text{IO}^-) - 3\Delta_f G(\text{I}^-) = +0.40$ eV from Eq. 11 – see SI)⁴². However, the thermodynamic drive is solvent dependent due to differences in solvation energies of I^- , IO^- , and O_2 (Eq. 11). 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 SI). 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 Pyr₁₄TFSI, making $\Delta_r G(\text{OH}^- \rightarrow \text{IO}^-) - \frac{3}{2} \Delta_r G(\text{OH}^- \rightarrow \text{O}_2) +0.63$ eV and +0.55 eV in G4 and

pure Pyr₁₄TFSI respectively. *I.e.*, the formation of IO⁻ is thermodynamically unfavourable in comparison to the OER regardless of the presence or absence of IL.

A similar thermodynamic analysis of the formation of IO₃⁻ can be performed (see SI):

$$\Delta_r G(\text{OH}^- \rightarrow \text{IO}_3^-) - \frac{3}{2} \Delta_r G(\text{OH}^- \rightarrow \text{O}_2) = -0.79 + \Delta_{\text{sol}} G(\text{IO}_3^-) - \Delta_{\text{sol}} G(\text{I}^-) - \frac{3}{2} kT \ln\left(\frac{P_{\text{O}_2}}{P^\circ}\right) \quad (\text{Eq12})$$

The formation of IO₃⁻ is more thermodynamically favourable than the OER under standard conditions (-0.79 eV)⁴², and the thermodynamic balance between the formation of IO₃⁻ and O₂ 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 IO₃⁻ in G4 and Pyr₁₄TFSI is less favourable than in water by very similar amounts as 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 IO₃⁻ over O₂ (Eq12), being reduced to -0.627 eV and -0.557 eV in G4 and pure Pyr₁₄TFSI, respectively. *I.e.*, IO₃⁻ formation is always favoured over the OER in all solvents.

Fig. 6h shows free energy diagrams comparing the thermodynamic drive to form O₂ (Eq 5) vs IO⁻ (Eq 11) and IO₃⁻ (Eq 12) in electrolytes with and without IL, and in standard conditions. The value of E(I⁻/I₃⁻) used for the calculations is the one measured for the electrolytes containing 0.7 M LiTFSI, 50 mM LiI and 5000 ppm H₂O in G4 with 0 mM and 900 mM Pyr₁₄TFSI (E(I⁻/I₃⁻) = 3.07 V and 3.24 V respectively – Fig. 5a), while the solvation energy terms were calculated for implicit solvents (in pure G4, Pyr₁₄TFSI, and water respectively). The overall thermodynamic analysis indicates that the introduction of Pyr₁₄TFSI (Fig. 6h) to G4 has two effects: (1) oxidation of OH⁻ by I₃⁻ becomes thermodynamically favourable ($\Delta_r G(\text{OH}^- \rightarrow \text{O}_2) < 0$). (2) IO⁻ formation is never favourable vs. the OER, while IO₃⁻ is always more thermodynamically favourable. This suggests that the kinetics associated with IO₃⁻ formation must also play a role in the observed switch from IO⁻/IO₃⁻ formation to OER during charge. Given that the formation of IO₃⁻ is the thermodynamic product, and that it requires 3 equivalents of IO⁻ (reaction 12), 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 unfavourable, it occurs because there is no alternative competing OER reaction; its formation is likely driven by the driving force for IO₃⁻ formation. The introduction of Pyr₁₄TFSI changes this equilibrium as the OER is now favourable. While IO₃⁻ remains the thermodynamic product, the kinetics of its formation involving the reaction of three IO⁻ molecules is unfavourable, 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 fields⁴⁴, 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 [IO⁻]^{44, 45}.

Our MD and ¹H NMR results confirm that the introduction the (soft Lewis base) Pyr₁₄⁺ cation to the electrolyte has a strong impact on the coordination of the (soft Lewis acid) I⁻, replacing H₂O, Li⁺, and G4 to some extent in the environment of I⁻ (Fig. 6e), in agreement with previous studies^{19, 21}. This suggests that the fast kinetics, of the IO⁻ formation in water-containing electrolytes, are disturbed by the introduction of Pyr₁₄TFSI due to efficient donor-acceptor interactions. Furthermore, as the MSD plot (Fig. 6f) shows, there is a synergistic interaction between water and the Pyr₁₄⁺ 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 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 as monitored 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 LiOH OER from the irreversible production of IO⁻/IO₃⁻ to the evolution of O₂. 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-O₂ 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 continue to understand all the intricate mechanistic details of this chemistry, as well to improve the overall performance of the cell, especially with regards to rate and long term reversibility.

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*) 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 hours 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 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 (LICGC; *Ohara*), 1 piece of pressed borosilicate glass fibre separator wetted with the active catholyte (90 µl in ½" 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 (Supplementary Fig. 20), 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. 1a). 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 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 *Swagelok*-type 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 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 K α 1 radiation ($\lambda=1.5406$ Å). 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 glove box sealed in a *Kammrath & Weiss* transfer module. Solution ¹H NMR spectra were acquired using an 11.7 T *Bruker Avance III HD* spectrometer with a single 30° flip angle pulse sequence (10.5 μ s), 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 glove box 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 0.01 M HCl solution, using phenolphthalein as end-point indicator while vigorously stirring. The LiOH content is calculated based 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, is 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 (Supplementary Fig. 4). 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 5000 ppm of water). The cells were then filled with O₂ (after 2 pumping/filling cycles) and then investigated after resting, discharging and charging to 2 mAh. Subsequently the gas in the cells was evacuated by pumping for 30mins before introducing the cells into the glove box 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 34.4mg LiTFSI to bring its concentration up to 700mM. (LiTFSI was added since its addition results in a shift of the water peak at higher ppm and into a range that does not overlap with the G4 peaks – see Supplementary Fig. 8), stirred for 2mins and left to rest for 24hrs. 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 $\Delta_{sol}G()$ terms, density functional theory (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 SI).

Molecular dynamics simulations. The simulation boxes were setup, using Packmol⁴⁸, to be congruent with the experimental concentrations (0.7M LiTFSI, 50 mM Lil in G4 with 5000 ppm of H₂O as starting point). Furthermore, water concentration was varied (0, 2500 and 10000 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 1350 mM). The full list of values is presented in the SI (Supplementary Table 2). Time step in each simulation was 2 fs as the C-H bonds were fixed utilising LINCS. The forcefield used was OPLS-AA, with additional parameters for Pyr₁₄TFSI from CL&P⁴⁹. 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 298K 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 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 2000 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 used⁵⁰. 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 centre of mass of each molecule.

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 and UV spectroscopy, V. Kunz with water quantification, Dr Y. Jin with ¹⁷O-ssNMR characterization, and S. Engelke with cyclic voltammograms. T. Liu acknowledges support from the Schlumberger Fellowship, Darwin College and Thousand Talent Recruitment Programme. E.J. acknowledges support from the Swedish Research Council in the form of an International Postdoc fellowship. Via our membership of the UK's HEC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202, EP/R029431), this work used the ARCHER UK National Supercomputing Service (<http://www.archer.ac.uk>).

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