

Supplemental Information

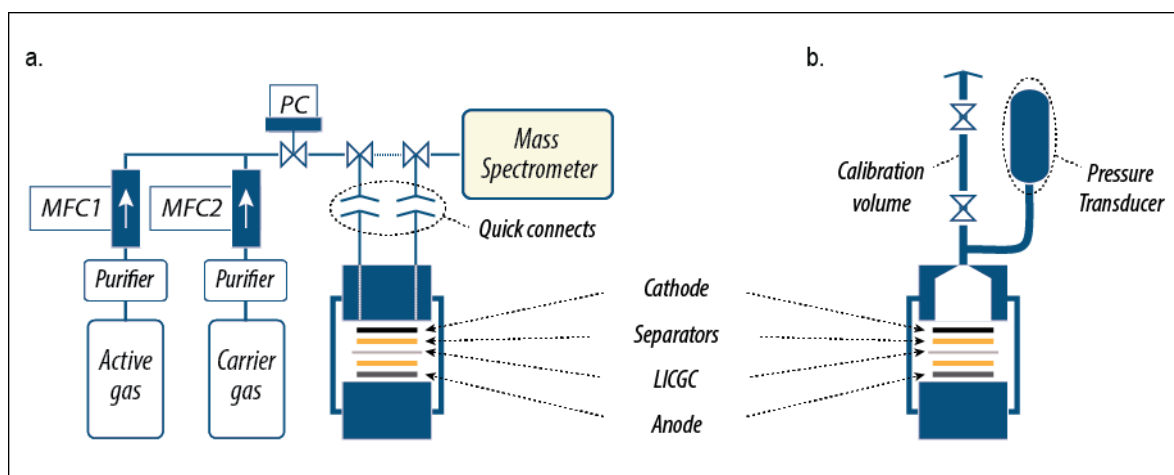


Figure S1 Schematics of the operando gas analysis systems used in this work. **a**, online electrochemical mass spectrometry (OEMS) and **b**, operando pressure monitoring. Two bespoke operando gas analysis techniques were developed in the course of this work. The OEMS system consists of a stainless-steel tube carrying gas through the electrochemical cell (described in main text) to a mass spectrometer. Mixtures of two gases can be selected from 0 to 100%, via two mass flow controllers (Bronkhorst), at any given time. For this work argon (BOC N6.0) was used as the carrier gas and O₂ (BOC N6.0) as active gas, both are connected to purifiers (Bronkhorst) before flow control. A pressure controller (Bronkhorst) was fitted ahead of entering the electrochemical cell for stability reasons. Two PEEK tube sections connect the electrochemical cell to the gas line through self-sealing quick-connects (Beswick Engineering) so the system is never exposed to air. The gas line is connected to a quadrupole mass spectrometer (Pfeiffer) through a heated capillary (120°C) to prevent condensation. A potentiostat (Ivium) controls the electrochemical operations. The pressure monitoring system consists of an all-metal assembly, with a small internal volume (~10 ml), connecting a pressure transducer (Omega) to a Swagelok-type electrochemical cell. The gas inlet incorporates a small section of tube between two valves, creating an enclosed volume of known value that is used for calibration. Gases are evacuated/introduced through a quick-connect (Swagelok).

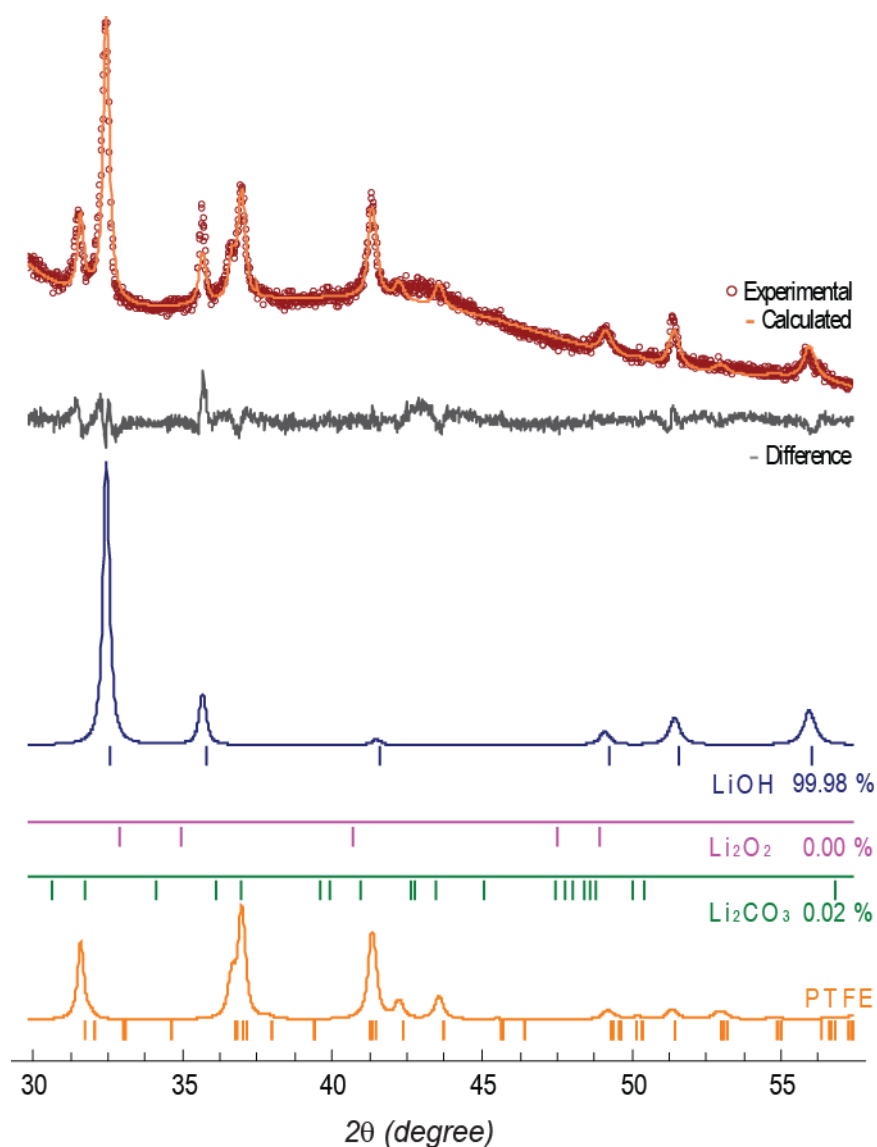


Figure S2] Refinement analysis of the X-ray diffractogram collected at the end of discharge of a cell cycled at a current of $50 \mu\text{A}/\text{cm}^2$ in an electrolyte comprising of 700mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H₂O in G4. LiOH and Li₂O₂ phases were refined using the Rietveld method, while PTFE was refined using the Pawley method to obtain a better fit the background signal from the pristine electrode. LiOH was found to form $99.98\% \pm 0.85\%$ of the crystalline discharge product, with no crystalline Li₂O₂ ($0.00\% \pm 0.50\%$) or Li₂CO₃ ($0.02\% \pm 0.69\%$) detected within the limits of this experimental setup.

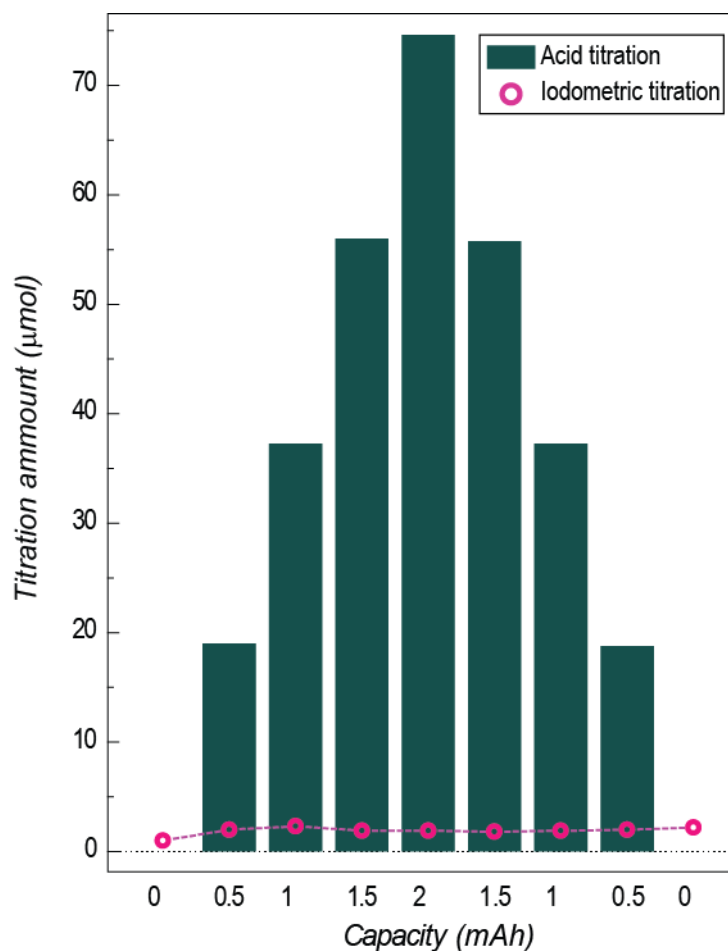


Figure S3] Quantification of the amount of HCl used to titrate the base contained in electrodes (green bars) after injection of 2 ml of Millipore water, and the amount of $\text{Na}_2\text{S}_2\text{O}_3$ used to titrate the I_2 present after generating 1 mol of I_2 /mol of Li_2O_2 , according to the reaction $\text{I}_2 + 2 \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2 \text{NaI}$ (magenta circles). The reaction $\text{LiI}_3 + 2 \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2 \text{NaI} + \text{LiI}$ also consumes $\text{Na}_2\text{S}_2\text{O}_3$. Given that I_3^- is formed during the discharge process¹, that it is consistently found in small proportion in the pristine electrolyte, and that the levels of $\text{Na}_2\text{S}_2\text{O}_3$ remain constant throughout both the discharge and charge processes (and close to the detection limit of this technique $\sim 1 \mu\text{mol}$ of $\text{Na}_2\text{S}_2\text{O}_3$), this suggest that no Li_2O_2 is formed as discharge product, in agreement with XRD and pressure monitoring data. The average amount of $\text{Na}_2\text{S}_2\text{O}_3$ consumed amounts to $1.9 \mu\text{mol}$, which would correspond to 2.6% of the (total amount of) discharge product if all consumption was due to Li_2O_2 , or to I_3^- corresponding to $\sim 12\%$ of the available I^- in the electrolyte.

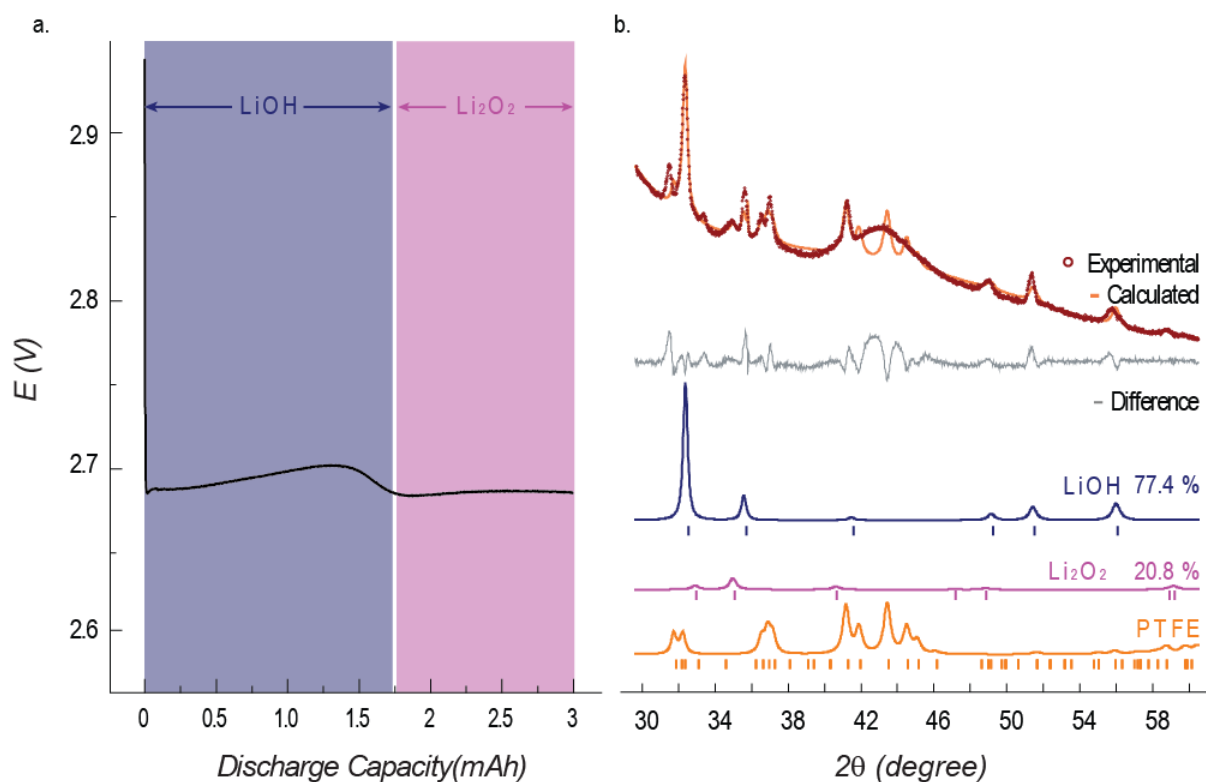


Figure S4| a, Galvanostatic discharge of a cell containing 125 μl of electrolyte, composed of 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H₂O in G4; **b**, Refinement analysis, of the X-ray diffractogram taken of the electrode at the end of discharge, showing a mixture of LiOH and Li₂O₂ generated in the presence of water and after water had been consumed, respectively¹ (LiOH and Li₂O₂ phases were refined using the Rietveld method, while PTFE was refined using the Pawley method). Two distinct plateaus can be observed during the discharge during the formation of LiOH and Li₂O₂ as the first part takes place in water containing electrolyte and the second in neat electrolyte. The charging of Li₂O₂ generated as discharge product with this electrolyte is shown in Fig. 3a.

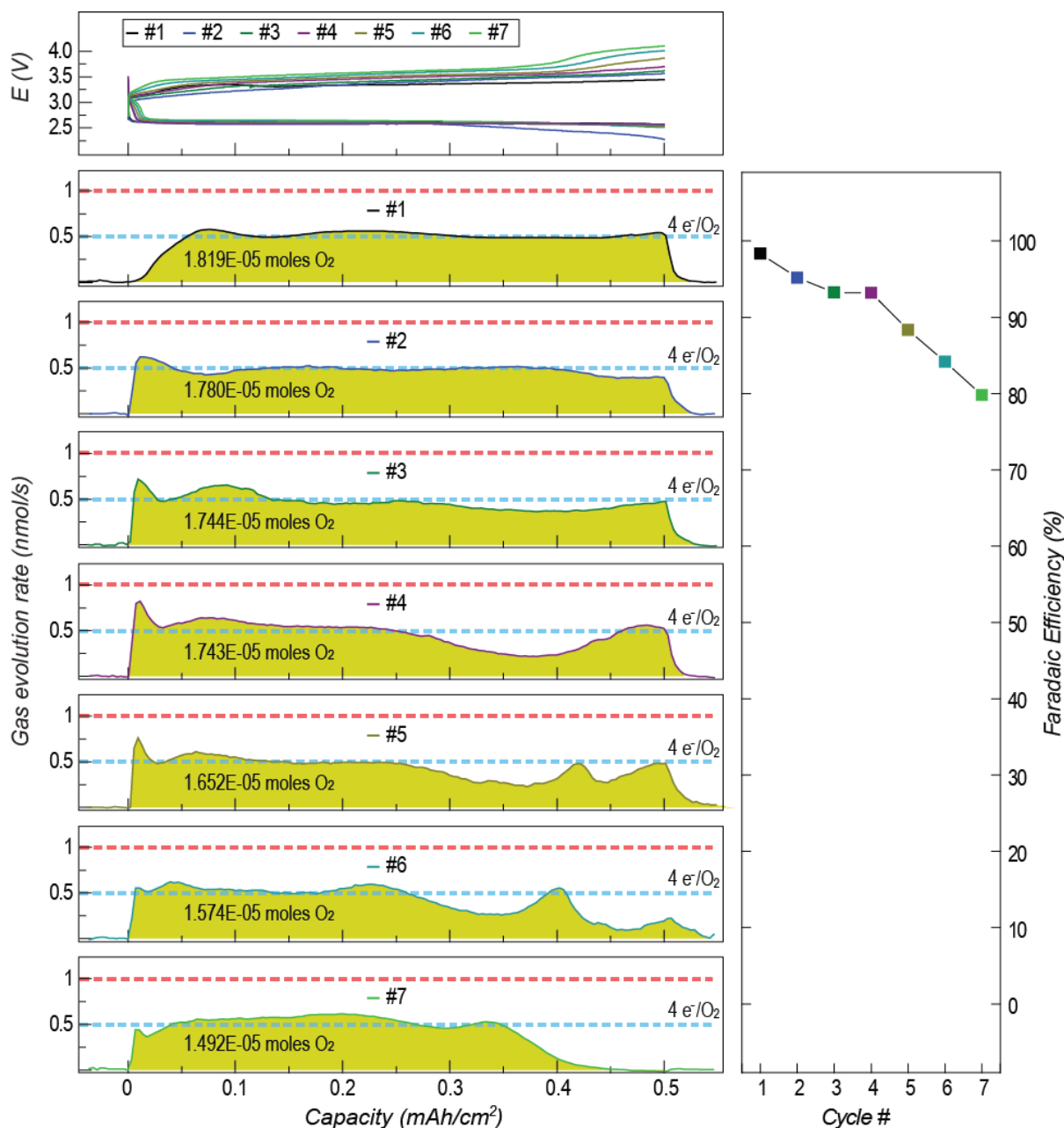
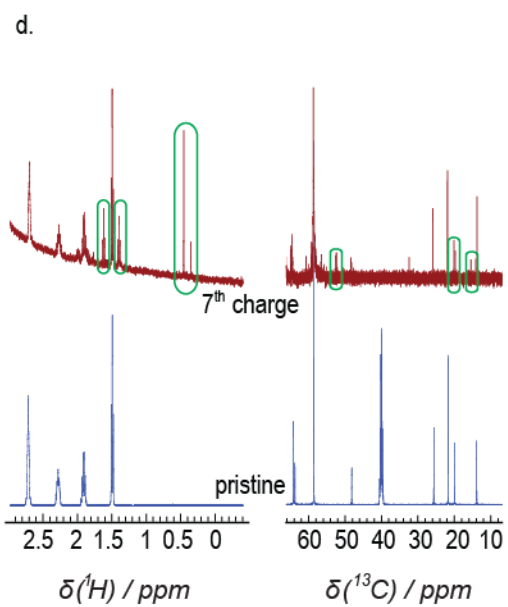
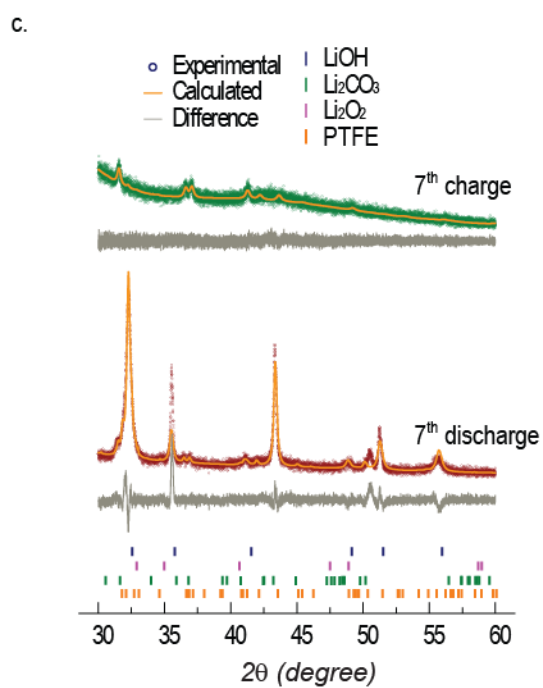
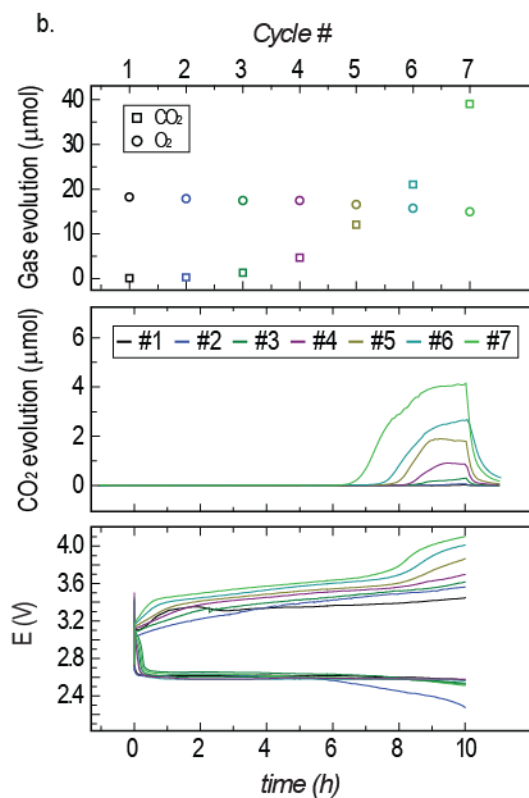
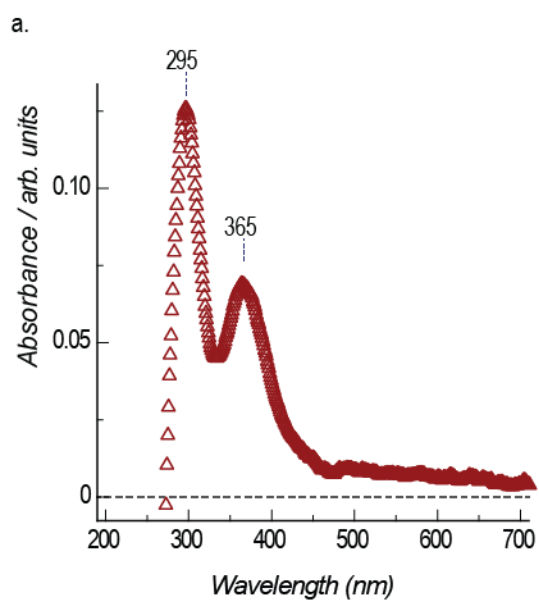


Figure S5 Galvanostatic profiles (top) with online mass spectrometry analysis of O₂ ($m/z=32$) for the first 7 cycles at a current of 50 $\mu\text{A}/\text{cm}^2$ in an electrolyte comprising of 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H₂O in G4. The total number of moles of oxygen released is given in each plot. In the first cycle 99.5% of O₂ the amount consumed in the discharge is measured in the OER during the subsequent charge (Faradaic efficiency). The Faradaic efficiency decreases steadily in subsequent discharge-charge cycles, although it remains above 80% for the first 7 cycles. The data is limited to 7 cycles due to experimental limitations derived from the OEMS set up (i.e. solvent evaporation and higher over potentials associated with the use of the LICGC). Detailed characterization of the cathode and catholyte after 7 cycles (Supplementary Fig. S6) indicates that an increase in potential at the end of charge (above 3.5 V) from the 4th cycle onwards, promotes electrode/electrolyte degradation, thus reducing the Faradaic efficiency. This degradation on charging above 3.5 V is consistent with other reports of Li-O₂ cells using G4-based electrolytes^{2,3-7}.



e.

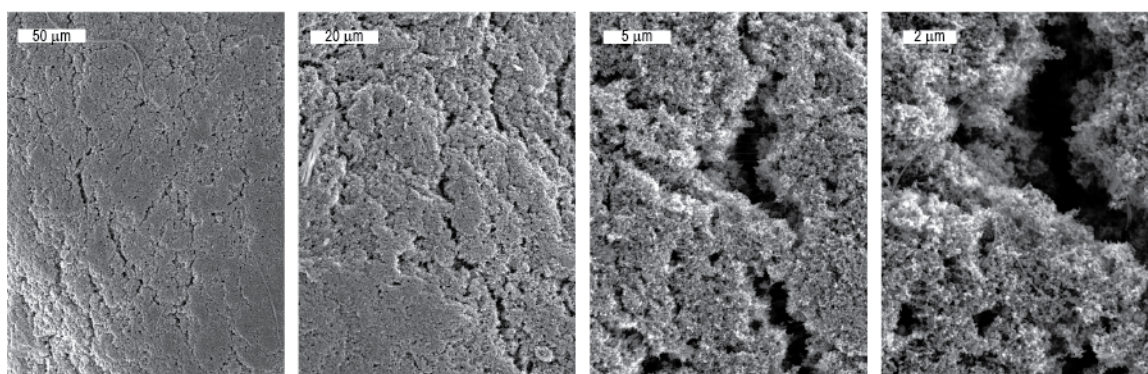


Figure S6| Analysis of the electrochemistry and electrodes during and after the first 7 charge-discharge cycles ($50 \mu\text{A}/\text{cm}^2$). **a**, UV spectra of catholytes collected after the 7th charge of a cell containing 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H₂O in G4 as catholyte; **b**, Galvanostatic profiles (bottom) with online mass spectrometry analysis of CO₂ evolution ($m/z=44$ - middle) and comparison between total amounts of CO₂ and O₂ evolved during the first 7 cycles (top); **c**, Refinement analysis of the XRD diffractogram taken on the electrode at the end of the 7th discharge (red trace) and of the 7th charge (green trace) (LiOH and Li₂O₂ phases were refined using the Rietveld method, while PTFE was refined using the Pawley method); **d**, ¹H and ¹³C solution-NMR spectra of catholytes recovered at the end of the 7th charge (red traces) compared with the pristine (blue traces); **e**, SEM images of electrodes at end the 7th charge at different magnifications.

Supplementary Fig. S6a shows the UV spectra of the electrolyte collected after the 7th charge, which is indistinguishable to the spectra observed for the 1st cycle (Fig. 4a), indicating that no substantial amount of IO₃⁻ has accumulated in the electrolyte after 7 discharge/charge cycles. This suggests that the charge process remains O₂ evolution; it has not reverted to the formation of IO₃⁻, within the detection limits of the experiment. Rietveld analysis of the XRD data of the electrodes after the 7th discharge and 7th charge (Supplementary Fig. S6c) shows that LiOH is present as the majority crystalline product present at the end of the 7th discharge ($95.2\% \pm 0.3\%$), with Li₂O₂ and Li₂CO₃ forming at $1.2\% \pm 0.2\%$ and $3.7\% \pm 0.2\%$, respectively. This indicates that the nature of the discharge product does not change dramatically over the course of the first 7 cycles. Furthermore, XRD and SEM analyses of the electrode after the 7th charge shows the efficient removal of the discharge product, with very little to no crystalline LiOH and Li₂CO₃ discernible. OEMS data (Supplementary Fig. S6b) shows the evolution of CO₂ at potentials higher than 3.5 V towards the end of charge after a couple of cycles. The extent of the CO₂ evolution increases as the potential at the end of charge increases. ¹H and ¹³C solution NMR data (Supplementary Fig. S6d) do show a few signs of electrolyte degradation at the end of the 7th charge (signalled in green). The increase in potential at the end of charge is typical of Li-O₂ cells in G4-based electrolytes²⁻⁷, where high charge potentials result in electrolyte degradation. This has been assigned to variations in the morphology of the discharge product (both LiOH and Li₂O₂) requiring different overpotentials for their removal during charge^{8, 9}. LiI has shown efficacy in reducing significantly the charge overpotential (required to remove both LiOH and Li₂O₂)^{4, 5, 10}, however, when potentials reach above 3.5V, the more corrosive I₂ is generated from the oxidation of I⁻^{7, 11}, which cause parasitic reactions as it can be seen from the reduction in O₂ evolution, causing the decline in Faradaic efficiency.

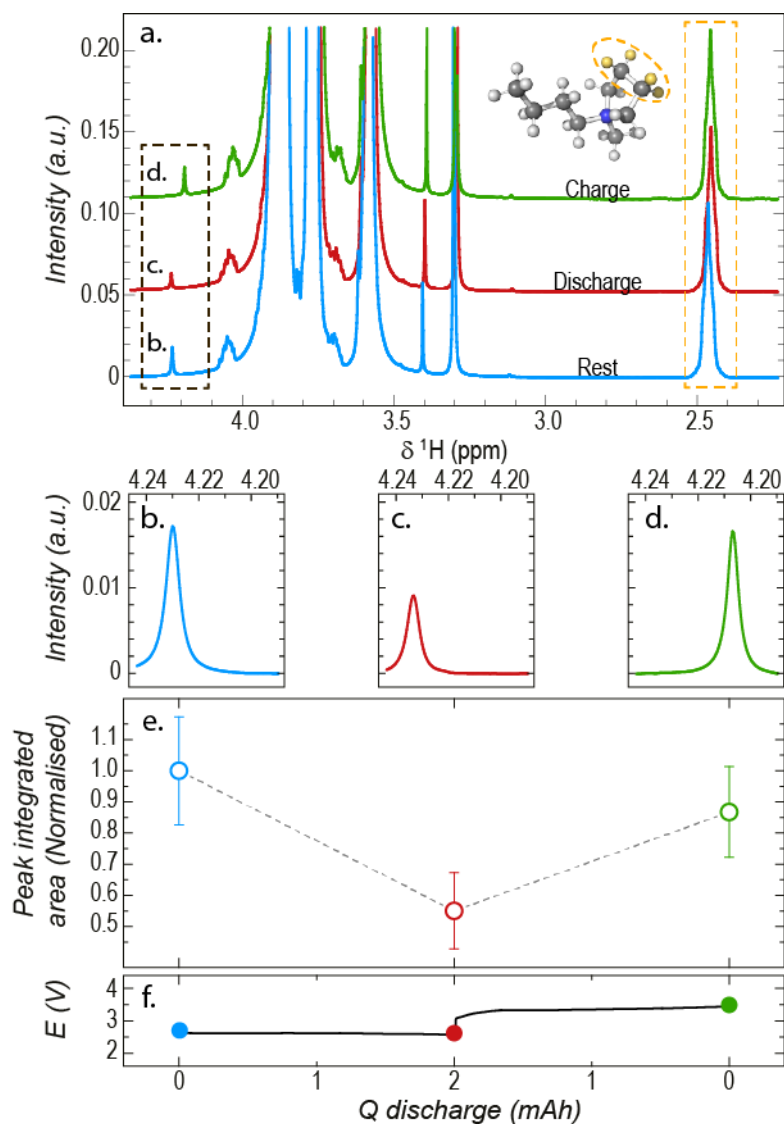


Figure S7| a, ^1H NMR data of the catholytes of cells rested at OCV for 24hs (blue), discharged to 2 mAh (red) and then charged (green). The spectra were normalized to the intensities of the CH_2 peaks of the IL (highlighted in orange) serving as an internal reference to compensate for variations in the preparation and extraction of the samples; **b, c, d,** shows the water peaks of the normalised ^1H NMR spectra that were integrated; **e,** The integration of the peaks corresponding to the end of discharge (0.55 ± 0.12 – red) and end of charge (0.87 ± 0.14) are plotted normalised with respect to the rested cell (1.00 ± 0.17 – blue) value. Error bars denote standard deviations; **f,** The voltage profile is shown for reference.

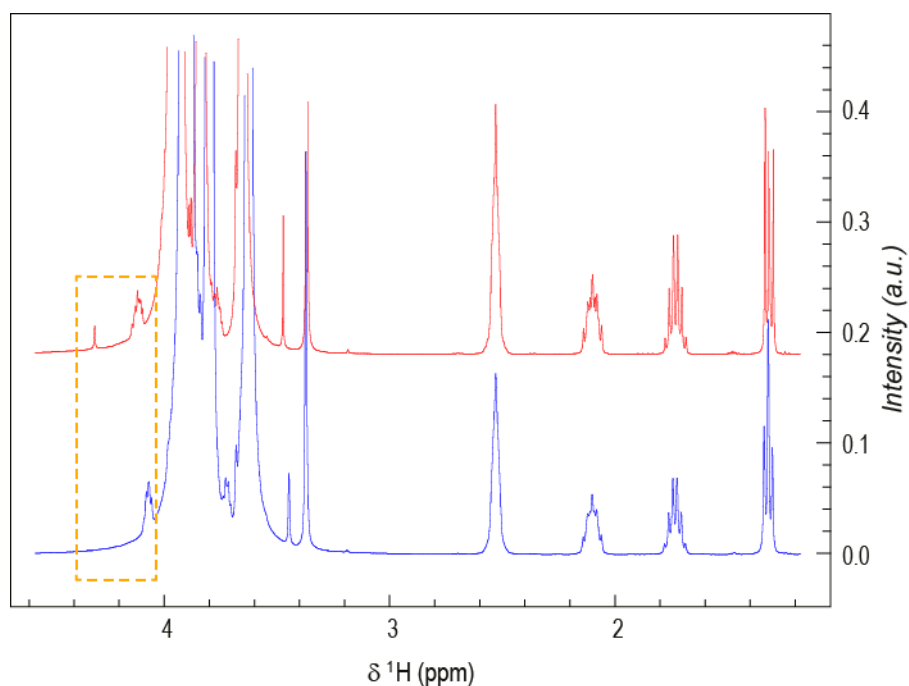


Figure S8 ^1H NMR data corresponding the catholytes of two cells discharged to 2 mAh with (red) and without (blue) the addition of 34.4 mg of LiTFSI in order to shift the water peak (highlighted in orange) at higher ppm so it would be clearly distinguishable from the TEGDME peaks.

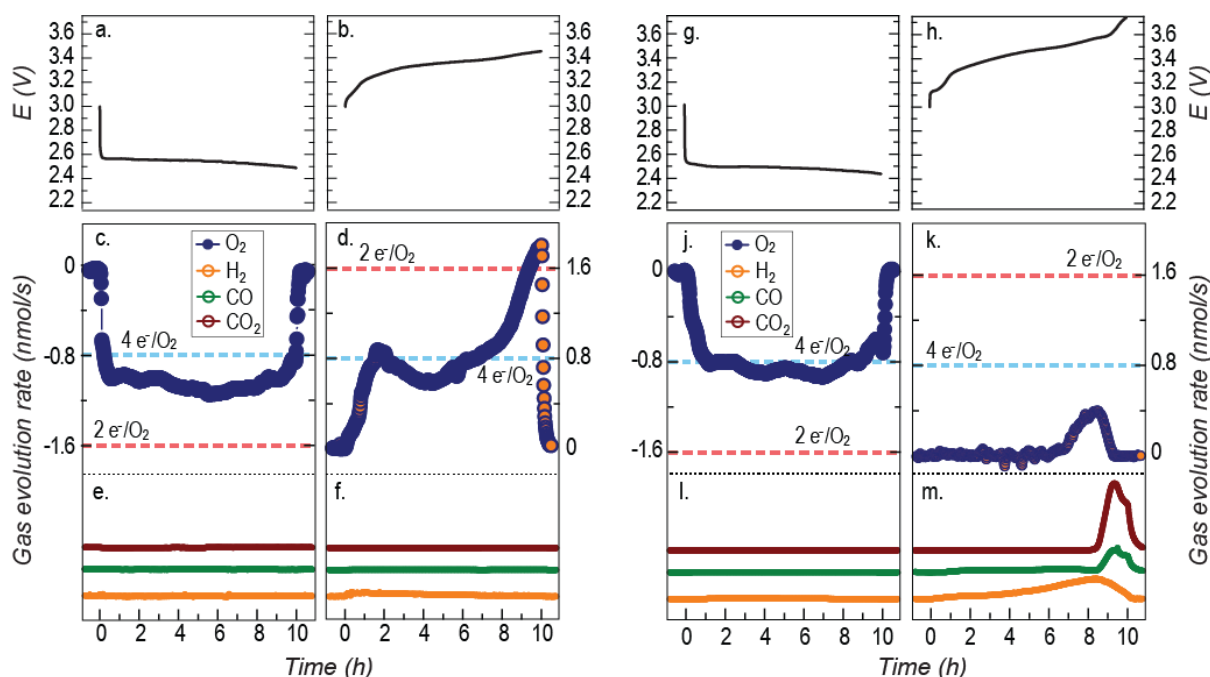


Figure S9 a, b, g, h, Galvanostatic profiles and c, d, j, k, online mass spectrometry analysis of O_2 ($m/z=32$), and e, f, i, m, of H_2 ($m/z= 2$), CO ($m/z= 28$) and CO_2 ($m/z= 44$) evolution of cells (cycled at $70 \mu\text{A}/\text{cm}^2$) in an electrolyte comprising 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H_2O in G4 (left) and 700 mM LiTFSI, 50 mM LiI, and 5000 ppm H_2O in G4 (right). An O_2 consumption corresponding to a stoichiometry of $<4 e^-/\text{O}_2$ is observed during the ORR in cells containing Pyr₁₄TFSI at this rate that can be attributed to the competing formation of LiOH and Li_2O_2 as discharge products (as indicated by Supplementary Figs. S8 and S9). The observation of a single plateau indicates the simultaneous formation of both discharge products, in contrast to the two plateaus observed in

Supplementary Fig. S5a which corresponds to the sequential formation of LiOH and Li₂O₂. The O₂ evolution profile indicates two distinctive processes during the OER, one of ~4 e⁻/O₂ between 3.15 V and 3.4 V (~70% of capacity) and a second at the end of charge of ~2 e⁻/O₂ above 3.4 V. Cells without Pyr₁₄TFSI (right) show a 4 e⁻/O₂ during discharge but no OER below 3.5 V during charge. A small O₂ evolution is observed above 3.5 V (above the I₃⁻/I₂ transition potential) followed up by the evolution of CO and CO₂, indicating electrolyte degradation at these potentials.

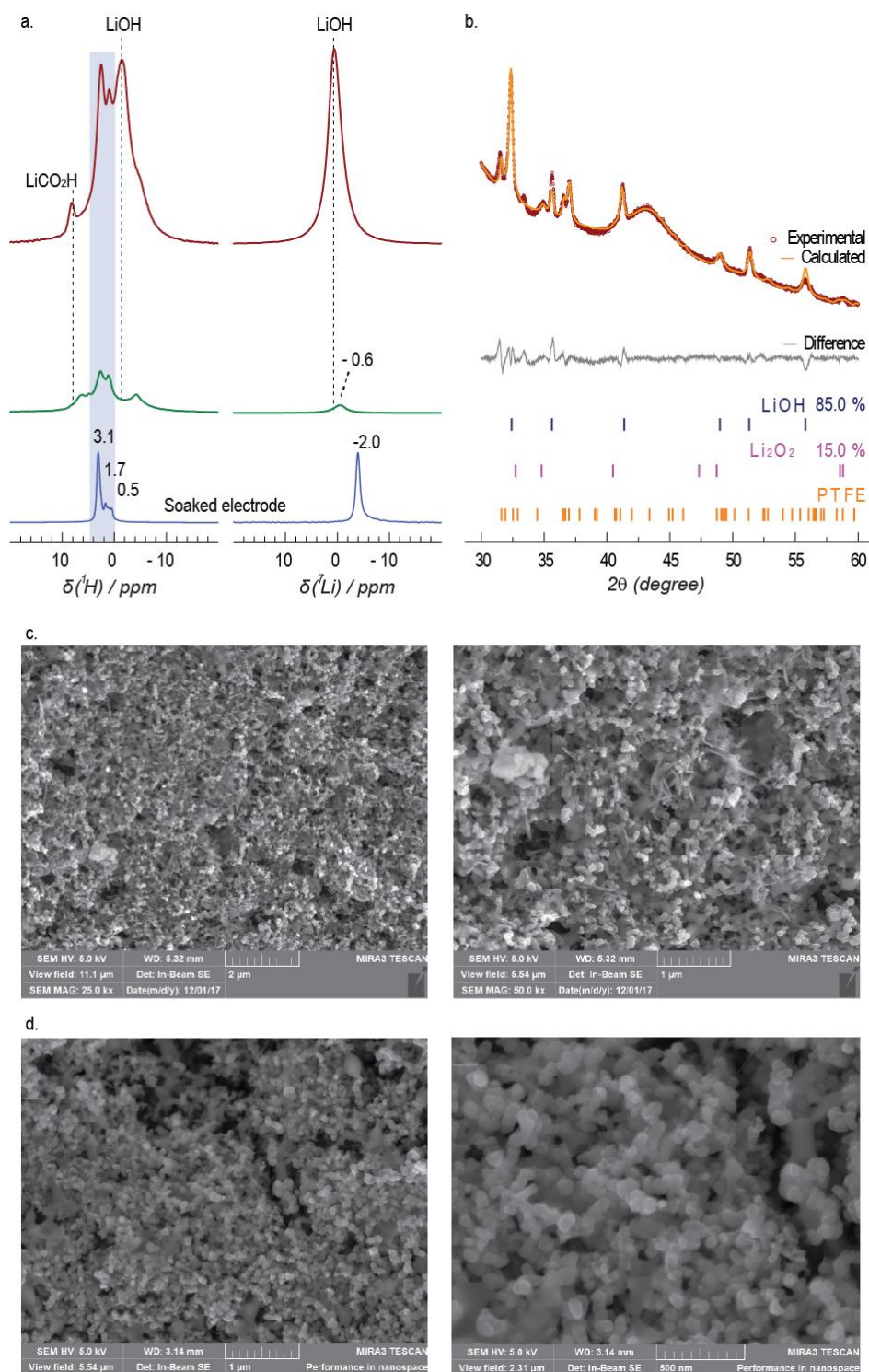


Figure S10| a. ¹H and ⁷Li solid state NMR (ssNMR) of electrodes at different stages of capacity-limited (0.7 mAh/cm²) cycling with 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H₂O in G4 at

70 $\mu\text{A}/\text{cm}^2$ (pristine – blue; discharged – red; fully charged – green); **b**, Refined X-ray diffractogram of the discharged electrode (LiOH and Li_2O_2 phases were refined using the Rietveld method, while PTFE was refined using the Pawley method); SEM images of electrodes at end of discharge **c**, and charge **d**, at different magnifications. ssNMR spectra were acquired on either a 16.4 T *Bruker Avance III* or an 11.7 T *Bruker Avance III HD* spectrometer using 1.3 mm HX (16.4 and 11.7 T) and 2.5 mm HX (11.7 T) probes.

ssNMR shows intense ^7Li and ^1H signals centred at 0.7 ppm and -1.5 ppm, respectively, indicating the predominant formation of LiOH as discharge product^{1, 10, 12, 13} (**a** – red trace). Traces of lithium formate can also be observed in the ^1H spectrum at 9 ppm, and were previously reported in the discharge product of cells containing LiI and water in G4, and were associated with electrolyte degradation during the electrochemical formation of Li_2O_2 ¹⁰. After charge, an almost complete removal of all lithium-based discharge products is observed (**b** – green trace). A broad signal is also observed in the ^1H spectrum of discharged electrodes, with maxima at 0.5, 1.7, and 3.1 ppm, which decreases noticeably in intensity in the charged electrodes. Analysis of unwashed electrodes soaked in electrolyte suggests that these signals originate from electrolyte trapped in the discharge product, which is not completely removed on washing the electrode sample with acetonitrile prior to analysis. A broad ^1H resonance at -4 ppm is assigned to protons in the electrode¹⁴. The reference NMR spectrum of a pristine electrode soaked in the electrolyte (blue) reveals ^1H NMR signals that can be assigned to the solvent in **a**. The XRD pattern of the discharged electrode (**b** – red trace) is also dominated by patterns corresponding to crystalline LiOH ($85.0\% \pm 6.0\%$), however, weak reflections from the by-product Li_2O_2 can also be observed ($15.0\% \pm 4.1\%$). Scanning electron microscopy (SEM) images of the discharged electrode show mainly dispersed collections of thin-sheets, consistent with primary building blocks of typical “flowerlike” LiOH crystals¹⁵. These small crystalline structures, of up to 1 μm in size, are indicative of LiOH electrochemically formed in an electrolyte with limited solvating properties at a relatively high rate^{16, 17}.

The formation of LiOH during the ORR relies on the mass transport of the species involved in the solution-based redox-mediated mechanism (redox mediator, O_2 , H_2O and Li^+). This reliance imposes a rate limitation over which competing surface-based mechanisms will occur. This is not particular to the chemistry presented in this work, but must be true for any iodide-mediated, and indeed redox-mediated Li- O_2 cell. The particular case of iodide-mediated cells containing water shows this competition clearly via the formation of two distinctive discharge products (LiOH and Li_2O_2). However, in other mediated cells, where the discharge product is not different for the redox-mediated mechanism and alternative surface mechanism this will only be reflected in the morphology of the discharge product and the capacity. The result of exceeding this limited rate, in the iodide-mediated cells containing water in this study, is therefore to form a competing discharge product without the involvement of the iodide catalytic process, *i.e.* Li_2O_2 . It is for this reason that at higher rate, the competition between a solution-based 4 e^-/O_2 mechanism producing LiOH and a surface-based 2 e^-/O_2 mechanism producing Li_2O_2 is observed. The difference between cells discharged at 70 $\mu\text{A}/\text{cm}^2$ with and without ionic liquid (Supplementary Fig. S9) show that the higher viscosity of the electrolyte containing the ionic liquid lowers this critical rate at which the surface/solution-based mechanisms competition begins.

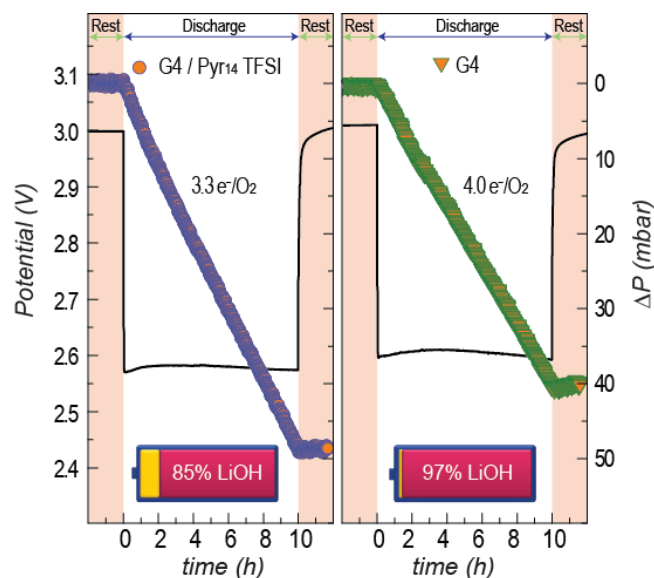


Figure S11| Pressure monitoring and titration of cells with 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H₂O in G4 (left), and with 700 mM LiTFSI, 50 mM LiI, and 5000 ppm H₂O in G4 (right) discharged at 70 $\mu\text{A}/\text{cm}^2$. Both acid-base titration and iodometric titration were considered in both cases as a substantial amount of Na₂S₂O₃ was consumed in the cell containing Pyr₁₄TFSI (above the level consistent with the presence of I₃⁻ given the amount of electrolyte).

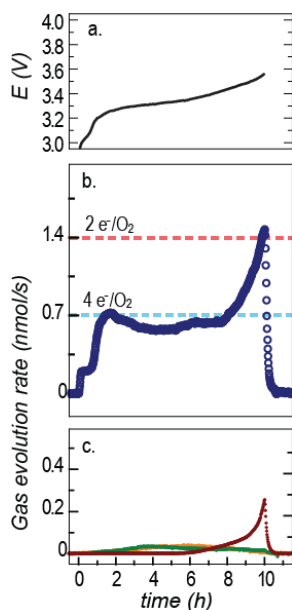


Figure S12| a, Galvanostatic profile during charge, and online mass spectrometry analysis of b, O₂ ($m/z=32$ - blue) and c, H₂ ($m/z=2$ - orange), CO ($m/z=28$ - green) and CO₂ ($m/z=44$ - red) evolution of a LiOH (electrochemically) preloaded electrode in an electrolyte comprising 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H₂O in G4 (cycled at 70 $\mu\text{A}/\text{cm}^2$). Three distinctive processes during the OER can be observed: a first small plateau at 3-3.05 V (~7.5% of capacity) showing a small O₂ evolution can be correlated with oxidation of species on the surface of LiOH crystals that may have formed during washing/drying of the electrode; a second O₂ evolution region between 3.2 V and 3.4 V shows a 4 e⁻/O₂ evolution (~73% of capacity); a third region above 3.4 V shows an increase in O₂ evolution accompanied by CO₂ evolution, indicating parasitic reactions.

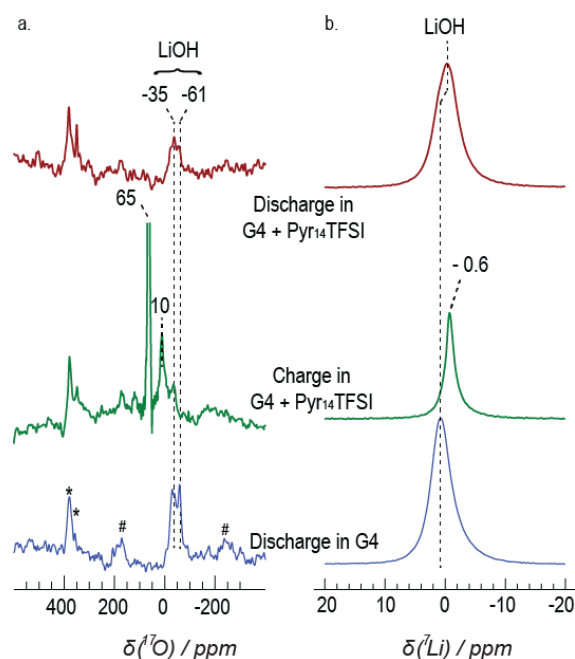


Figure S13 **a**, ^{17}O and **b**, ^7Li ssNMR spectra of the discharged (red trace) and charged (green trace) electrodes (cycled at $50 \mu\text{A}/\text{cm}^2$) in a catholyte comprising 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI in G4 with 5000 ppm H_2^{17}O , and discharged (blue trace) in a catholyte comprising 700 mM LiTFSI, 50 mM LiI in G4 with 5000 ppm H_2^{17}O . Asterisks label spinning side bands of the ZrO_2 rotor background signal. Hashtags denotes the spinning sidebands. The data was acquired on a 16.4 T Bruker Avance III 700 MHz spectrometer with a 3.2 mm triple resonance probe using a Hahn echo sequence with an RF amplitude of 55 kHz, at a MAS frequency of 20 kHz adding 29871 to 60000 transient scans with a relaxation delay of 20 s for ^7Li . ^{17}O and ^7Li were externally referenced to D_2O at 0 ppm and LiF at -1 ppm, respectively.

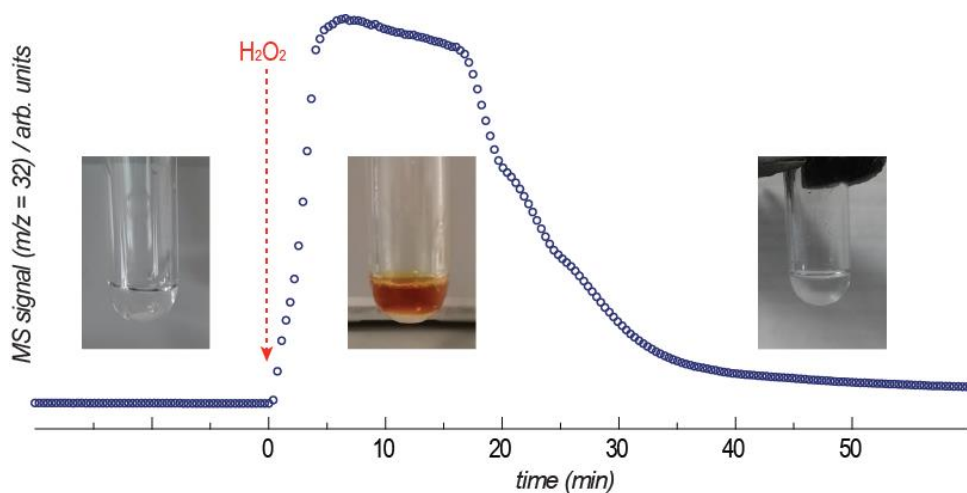


Figure S14 Online mass spectrometry chemical test ($m/z = 32$) of the reaction of H_2O_2 and I^- with 10.5 mg of LiOH in 0.5 ml of electrolyte containing 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H_2O in G4. At $t=0$, 0.2 ml of H_2O_2 (30% wt) is injected. Images of the test tube before, during, and after reaction completion are added for visual reference.

It has been recently proposed that the electrochemical formation of LiOH in I^-/I_3^- mediated cells occurs through a synergistic effect, where at $\text{H}_2\text{O}:\text{I}^-$ ratios between 0.5 and 1.5 both H_2O and I^- coordinate with Li^+ in their first solvation shells with various glyme-based solvents¹. The high proton affinity of I^- , higher than TFSI⁻ but lower than OH^- based on Pearson's Hard Soft Acid Base (HSAB) Theory¹⁸, weakens the

O-H bond of a significant portion of water molecules rendering H^+ available for the formation of LiOH, via H_2O_2 formation.



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



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



To test whether the ORR in cells containing Pyr₁₄TFSI follows this mechanism, the gas evolution after injecting H_2O_2 to a tube containing LiOH in an aliquot of the electrolyte was tested in an online mass spectrometry chemical test (Supplementary Fig. S12). Upon injection of H_2O_2 , the initially transparent electrolyte turned dark red, indicating the formation of I_3^- as per reaction 2. Almost immediately bubbles started forming from the LiOH precipitate and O_2 was detected by the mass spectrometer. After a time, the solution cleared again and the bubbling stopped, indicating that the formed I_3^- was being reduced again to I^- by the oxidation of OH^- , in agreement with reaction 3.

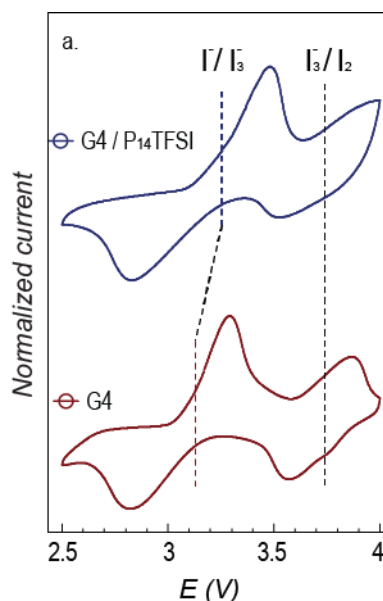


Figure S15] Cyclic voltammograms of cells with catholytes containing 700 mM LiTFSI, 50 mM LiI, 5000 ppm H_2O in G4 (red trace) and with 900 mM Pyr₁₄TFSI (blue trace) collected at 1 mV/s.

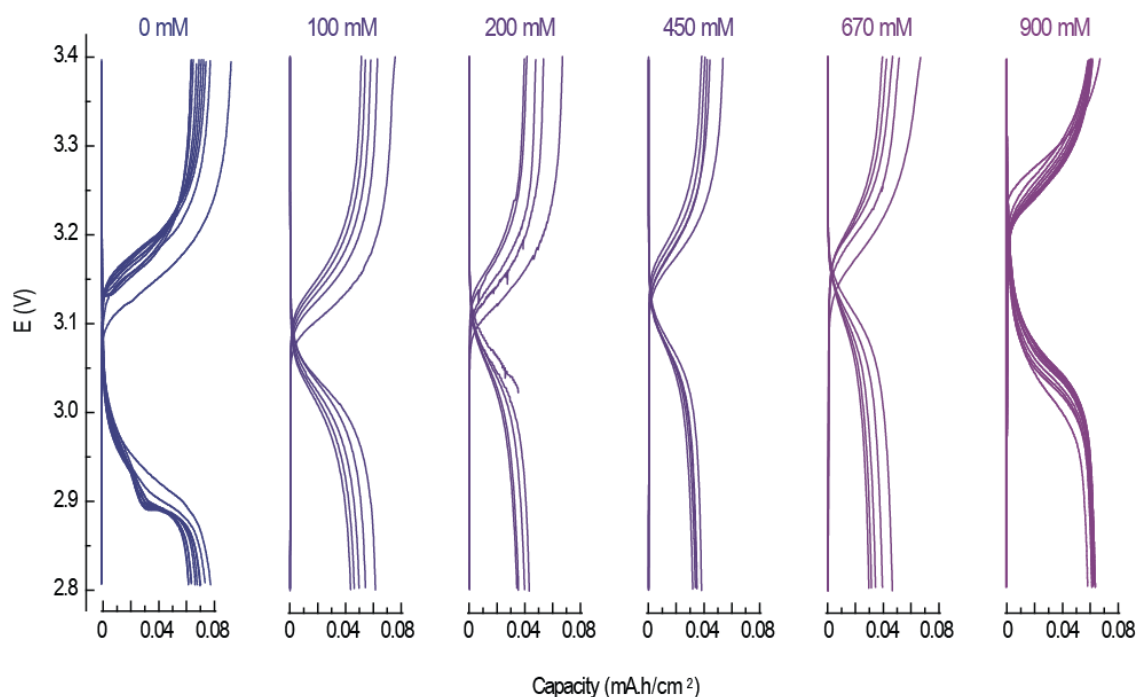


Figure S16] First few galvanostatic discharge/charge cycles of cells containing increasing amounts of Pyr₁₄TFSI in the catholyte. Cells used a LICGC to isolate the catholyte from the Li metal anode. 0.3 M LiTFSI in G4 was used as anolyte. All cells were cycled under argon at 50 $\mu\text{A}/\text{cm}^2$.

Typically, the reduction and oxidation potentials for reactions are defined by a voltammetric method rather than a galvanostatic method. If using a galvanostatic (step) method, as shown in the main text (Fig. 5), the process must be a truly reversible reaction whereby the Tafel slopes are extrapolated to intersection. The cyclic voltammograms (Supplementary Fig. S13) show good agreement with the galvanostatic cycling results shown in Fig. 5, even though the potential crossover in observed in Fig. 5 are likely reactant species diffusion/concentration dependent values. The potential crossovers and the overall capacity show negligible change over several cycles.

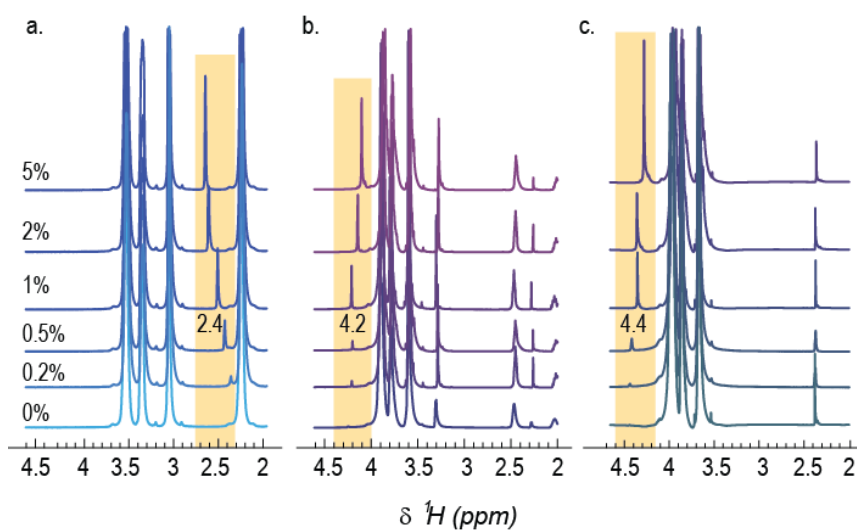


Figure S17 Solution ^1H NMR of electrolytes with increasing amounts of water with **a**, 50 mM LiI in Pyr₁₄TFSI **b**, 700 mM LiTFSI, 50 mM LiI and 900 mM Pyr₁₄TFSI in G4 and **c**, 700 mM LiTFSI and 50 mM LiI in G4

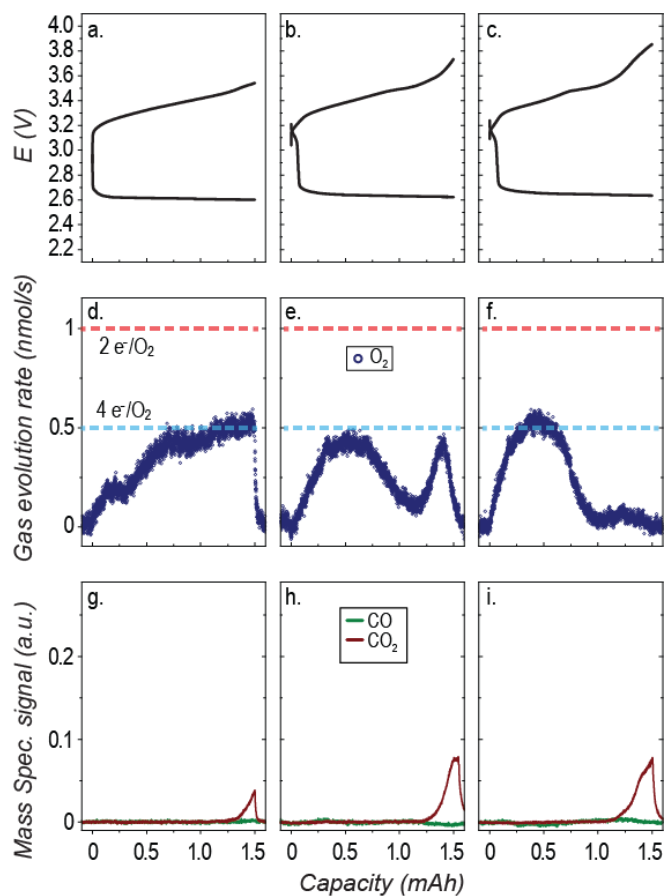


Figure S18 **a-c**, Galvanostatic profiles with online mass spectrometry analysis of **d-f**, O_2 ($m/z=32$) and **g-f**, CO and CO_2 ($m/z= 28$ and 44 , respectively) evolution of cells with an electrolyte containing 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H_2O in G4 during the first three charges. Cells were assembled in an *ECC-DEMS* cell (*EL-CELL*) without LICGC protecting the anode and cycled at $70 \mu\text{A}/\text{cm}^2$.

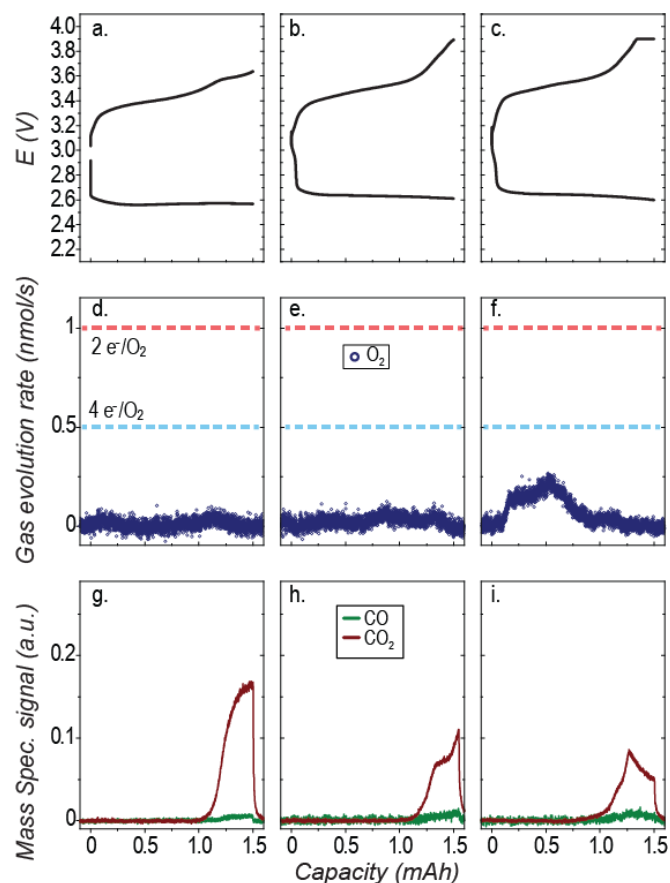


Figure S19 a-c, Galvanostatic profiles with online mass spectrometry analysis of d-f, O_2 (m/z=32) and g-f, CO and CO_2 (m/z= 28 and 44, respectively) evolution of cells with an electrolyte containing 700 mM LiTFSI, 50 mM LiI, 5000 ppm H_2O in G4 during the first three charges. Cells were assembled in an ECC-DEMS cell (EL-CELL) without LICGC protecting the anode and cycled at $70 \mu A/cm^2$.

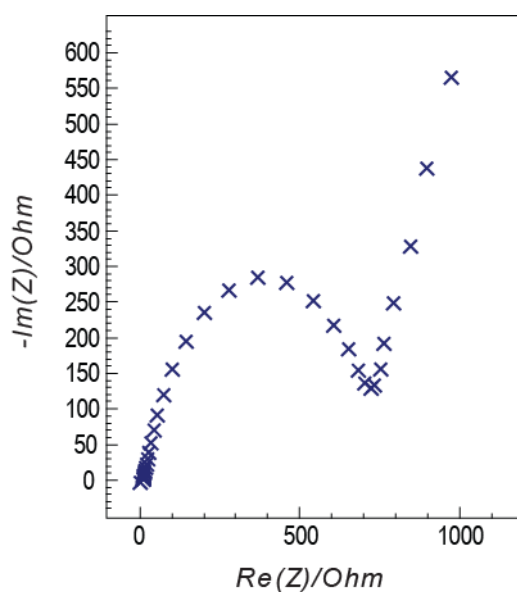


Figure S20 Electrochemical impedance spectroscopy (EIS) of cells with 700 mM LiTFSI, 50 mM LiI, 900 mM Pyr₁₄TFSI and 5000 ppm H_2O in G4. EIS was normally collected before every electrochemical operation.

Estimation of the activity of water in an electrolyte

Raoult's law can be applied to calculate the Gibbs free energy change of mixing $\Delta_{\text{mix}}G$, assuming ideal solution conditions:

$$\Delta_{\text{mix}}G = nRT(X_1 \ln(X_1) + X_2 \ln(X_2))$$

Since the mixtures under evaluation cannot be considered ideal solutions, the excess Gibbs free energy ($\Delta_{\text{ex}}G$) can be estimated using the Margules activity model. This model is used to derive an expression for the activity coefficients of a compound (γ_i) in a liquid, which is a measure for the deviation from ideal solubility.

$$\frac{\Delta_{\text{ex}}G}{RT} = X_1X_2(A_{21}X_1 + A_{12}X_2) + O(X_2^2)$$

$A_{12} = \ln(\gamma_1^\infty)$ and $A_{21} = \ln(\gamma_2^\infty)$ are the activities at infinite dilution, where only the first terms of the Margules activity model are considered. This approximation will produce high accuracy at low water concentration, as is the case in the electrolytes under discussion, but may lose accuracy at higher concentration when the other terms may become significant.

In order to estimate the water activity at infinite dilution in the electrolytes used in this work (γ_w^∞), we turned to the modified separation of cohesive energy density model (MOSCED). The MOSCED is a framework that allows the quantitative estimation of multicomponent phase equilibria based upon the modification of the solubility parameter approach, and it has been reported to be particularly suitable for the estimation of infinite dilution activity coefficients¹⁹. This model provides quantitative predictions of the activity of molecular species at infinite dilution (γ_x^∞) by parametrising their activities into molar liquid volume (v); dispersion parameter (λ); induction parameter (q); polarity parameter (τ); hydrogen-bond acidity parameter (α); and hydrogen-bond basicity parameter (β):

$$\ln \gamma_2^\infty = \frac{v_2}{RT} \left[(\lambda_1 - \lambda_2) + \frac{q_1^2 q_2^2 (\tau_1^T - \tau_2^T)^2}{\psi_1} + \frac{(\alpha_1^T - \alpha_2^T)(\beta_1^T - \beta_2^T)}{\xi_1} \right] + d_{12}$$

Using this approach, an estimation of the activity of water at infinite dilution in G4 (A_{21}) is -1.95 ± 0.8 , and the activity of G4 in water at infinite dilution (A_{12}) is 5.65 ± 1.1 .

	v	λ	τ	q	α	β
Water	26.60	6.53	14.49	1.00	45.34	12.81
G4	221.10	16.08	6.73	1.00	0.00	13.53

Table S1 Values of the parameters used in the MOSCED model for calculating the activity at infinite dilution of H₂O in G4 (A_{21}) and G4 in H₂O (A_{12}); v = Molar liquid volume (cm³/mol); λ = Dispersion parameter; q = Induction parameter; τ = Polarity parameter; α = Hydrogen-bond acidity parameter; β = Hydrogen-bond basicity parameter

With these values fed into the Margules activity model, it is then possible to calculate the Gibbs free energy of solvation of water in different solvents ($\Delta_{\text{sol}}G(\text{H}_2\text{O})$):

$$\Delta_{\text{sol}}G(\text{H}_2\text{O}) = \Delta_{\text{mix}}G(\text{H}_2\text{O}) + \Delta_{\text{ex}}G(\text{H}_2\text{O})$$

This leads to a variation of the energy of solvation of water from 0 eV at standard conditions to -0.13 eV (± 0.02) in G4 at 5000 ppm and -0.17 eV (± 0.02) at 1500 ppm (estimated water concentrations at the beginning and end of charge respectively).

	$\Delta_r G(\text{OH}^-/\text{O}_2)$ (eV/e ⁻)	$E(\text{I}^-/\text{I}_3^-)$ (V)	$kT \ln \left(\frac{P_{\text{O}_2}}{P^\circ} \right)$ at 0.05 bar (eV)	$\Delta_{\text{sol}} G(\text{H}_2\text{O})$ (eV)
0 mM Pyr ₁₄ TFSI+5000 ppm H ₂ O	0.16	3.07	-0.08	-0.13
900 mM Pyr ₁₄ TFSI+5000 ppm H ₂ O	-0.01	3.24	-0.08	-0.13
0 mM Pyr ₁₄ TFSI+1500 ppm H ₂ O	0.14	3.07	-0.08	-0.17
900 mM Pyr ₁₄ TFSI+1500 ppm H ₂ O	-0.03	3.24	-0.08	-0.17
Error +/-	0.04	0.02	0.04	0.02
Error source		in CV	1.2 - 0.001 bar	A ₂₁ , A ₁₂ [20]

Table S2| Values used in the calculation of $\Delta_r G(\text{OH}^-/\text{O}_2)$. The associated error values and sources are described for reference.

With the calculated values of the Gibbs free energy of solvation of water, the estimated values for the driving force for the OER (5000 ppm H₂O) are $\Delta_r G(\text{OH}^-/\text{O}_2) \approx -0.03$ eV (± 0.24) in the case of the electrolyte containing 900 mM Pyr₁₄TFSI ($E(\text{I}^-/\text{I}_3^-) = 3.24$ V), and $\approx +0.99$ eV (± 0.24) for the electrolyte without IL ($E(\text{I}^-/\text{I}_3^-) = 3.07$ V). However, if the conditions at the beginning of the charge process are considered (1500 ppm H₂O) these values are reduced to ≈ -0.15 eV (± 0.24) and $\approx +0.87$ eV (± 0.24) respectively.

Considering the wide range of potentials the I^-/I_3^- redox equilibrium can have depending on the media^{11, 21, 22, 23, 24}, $\Delta_r G(\text{I}^-/\text{I}_3^-)$ can be regarded as the dominant parameter for the feasibility of reversible decomposition of LiOH via OER. To illustrate this point, we have plotted the $\Delta_r G(\text{OH}^-/\text{O}_2)$ as a function of the $E(\text{I}^-/\text{I}_3^-)$ reported in several relevant articles in the literature (Supplementary Fig. S19).

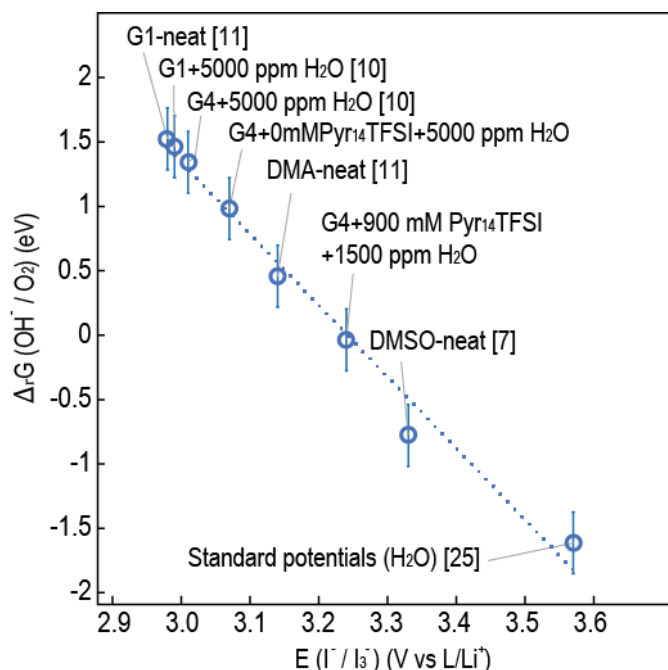


Figure S21| Driving force for the oxygen evolution reaction ($\Delta_r G(\text{OH}^-/\text{O}_2)$) as a function of the I^-/I_3^- redox pair potential ($E(\text{I}^-/\text{I}_3^-)$) of the electrolytes used in this work and some notable examples from the literature. G1-neat and DMA-neat corresponds to cyclic voltammograms of a 0.5 M LiTFSI+10 mM LiI solutions in G1 and DMA respectively¹¹; G1+5000 ppm H₂O and G4+5000 ppm of H₂O correspond to galvanostatic charge-discharge curves of 0.25 M LiTFSI+50 mM LiI+5000 ppm H₂O in G1 and G4 respectively¹⁰; DMSO-neat corresponds to cyclic voltammograms of a 1 M LiTFSI+10 mM LiI solution in DMSO⁷; G4+0 mM Pyr₁₄TFSI+5000 ppm H₂O and G4+900 mM Pyr₁₄TFSI+5000 ppm H₂O correspond

to both galvanostatic charge-discharge curves (Fig. 5 and Supplementary Fig. S14) and cyclic voltammograms (Supplementary Fig. S13) of solutions containing 700 mM LiTFSI+50 mM LiI+5000 ppm H₂O and 900 mM Pyr₁₄TFSI+700 mM LiTFSI+50 mM LiI+5000 ppm H₂O in G4 respectively, presented in this work. Standard potentials (H₂O) correspond to tabulated values²⁵.

In order to establish the reliability of the MOSCED method used for these calculations we have compared values obtained with it with known values of solubilities of various organic compounds in water. We chose two solvents to make this assessment: diethyl ether ((C₂H₅)₂O), which is structurally and chemically very similar to G4, and diethyl phthalate (C₁₂H₁₄O₄), which has MOSCED parameters amongst the closest to G4 while their experimental value of the water solubility are known, making them ideal candidates to test the use of this model on G4 (Supplemental Table 3).

	v	λ	τ	q	α	β
Diethyl ether	104.70	13.96	2.79	1.00	0.00	6.61
Diethyl phthalate	199.70	16.33	6.14	1.00	1.07	7.81

Table S3|Values of the parameters used in the MOSCED model for calculating the activity at infinite dilution of H₂O in diethyl ether, diethyl ether in H₂O, H₂O in diethyl phthalate, and diethyl phthalate in H₂O; v = Molar liquid volume (cm³/mol); λ = Dispersion parameter; q = Induction parameter; τ = Polarity parameter; α = Hydrogen-bond acidity parameter; β = Hydrogen-bond basicity parameter

The model was used to predict the solubility of diethyl ether and diethyl phthalate in water, providing values of 5.33 and 7.4 g/100g of H₂O respectively, in good agreement with their known experimental values of 6.05 and 10.8 g/100g of H₂O. At the known limit of solubility (which by definition would have a $\Delta_{\text{sol}}G(\text{H}_2\text{O}) = 0$ eV), the model predicted a Gibbs free energy of solvation of just 0.003 and 0.01 eV respectively, which are well within the errors of the model.

Furthermore, the model was tested to see if it could accurately predict the behaviour of water in G4, by calculating the Gibbs free energy of solvation of water in G4 (Supplementary Fig. S20). Experimentally, it is known that G4 is completely miscible with water, so the Gibbs free energy of solvation should be negative for all molar ratios. We observe that there is a region where the model suggests a positive Gibbs free energy of solvation, with a maximum value of +0.005 eV. However, we also note that two compounds that are chemically very similar to G4; dipropylene glycol dimethyl ether (C₈H₁₈O₃) and 1,2-diethoxyethane (C₆H₁₄O₂) are both not completely miscible in water, which suggests that water may only just be completely soluble in G4. This, in turn means that the maximum Gibbs free energy of solvation of water in G4 should be very close to 0 eV. Further the peak in the Gibbs free energy happens at high water concentrations (above 60% water content) where the Margules model is least accurate we are reassured that at lower water concentrations the model should be tracking the solvation energy with reasonable accuracy.

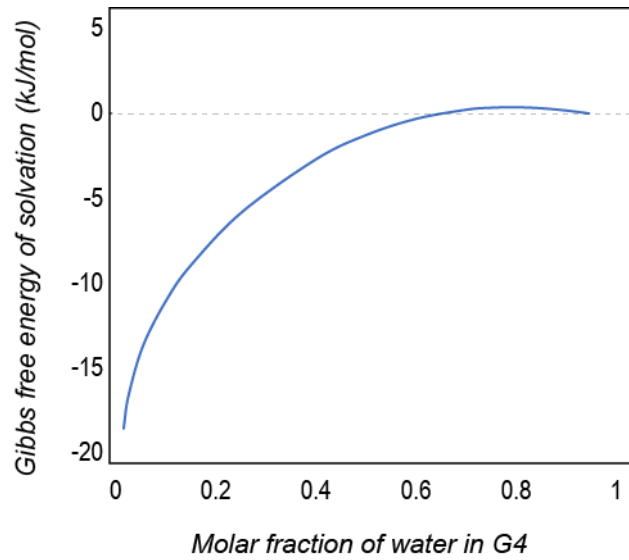


Figure S22 | Calculated Gibbs free energy of solvation of water in G4 as a function of the molar fraction using the model described here to calculate the water activity in various solvents.

The two primary sources of error in this method are the accuracy in the measurement of $E(I^-/I_3^-)$ and the water activity estimation. $E(I^-/I_3^-)$ will mainly vary depending on the concentration of I^- and I_3^- species close to the electrode surface. In cells cycled under Ar we can consider that all I^- has been converted to I_3^- near the electrode by the end of the roughly linear region of the galvanostatic cycling (end of plateau). However, the value considered as $E(I^-/I_3^-)$ is the charge/discharge cross as it arguably provides a more realistic value for regions further away from the electrode where the I_3^- concentration will have dropped and the I^- risen due to the reaction with LiOH in Li-O₂ cells.

The error in the estimation of the water activity stems partly from the assumptions in the MOSCED calculation²⁰ and partly from only considering the first-order terms of the Margules activity model²⁶. The root mean square error (RMSE) in the MOSCED calculations of $\ln(\gamma_2^\infty)$ for organics in water is estimated to be 1.090 and the average absolute error (AAE) for γ_2^∞ is 144.8%. For water in organics, the RMSE for $\ln(\gamma_2^\infty)$ is 0.771 and the AAE for γ_2^∞ is 63.2%. These values lead to variations in the $\Delta_{sol}G(H_2O)$ of ± 0.02 eV for the solvents of interest at water concentrations between 1000 ppm and 5000 ppm. Error estimates stemming from the Margules activity model are hard to quantify, although we have considered that they are negligible as we are operating at low water concentrations, where the higher-order terms become less relevant²⁶.

Thermodynamic evaluation of IO_3^- formation



The Gibbs free energy of IO_3^- formation ($\Delta_r G(OH^-/IO_3^-)$) can be calculated as the combination of the Gibbs free energy of reactions 9+10:



$$\Delta_r G(OH^-/IO_3^-) = 8\Delta_f G^\circ(I^-) + 3\Delta_f G^\circ(H_2O) + \Delta_f G^\circ(IO_3^-) - 6\Delta_f G^\circ(OH^-) - 3\Delta_f G^\circ(I_3^-) + 8\Delta_{sol} G(I^-) + 3\Delta_{sol} G(H_2O) + \Delta_{sol} G(IO_3^-) - 6\Delta_{sol} G(OH^-) - 3\Delta_{sol} G(I_3^-) \quad (12)$$

The difference between the formation of IO_3^- and the OER can be described as the following process:



$$\Delta_r G(\text{OH}^-/\text{IO}_3^-) - \Delta_r G(\text{OH}^-/\text{O}_2) = \Delta_f G^\circ(\text{IO}_3^-) - \Delta_f G^\circ(\text{I}^-) + \Delta_{\text{sol}} G(\text{IO}_3^-) - \Delta_{\text{sol}} G(\text{I}^-) - \frac{3}{2} kT \ln\left(\frac{p_{\text{O}_2}}{p^\circ}\right) \quad (14)$$

as $\Delta_f G^\circ(\text{IO}_3^-) - \Delta_f G^\circ(\text{I}^-) = -0.792 \text{ eV}^{25}$, this becomes:

$$\Delta_r G(\text{OH}^-/\text{IO}_3^-) - \Delta_r G(\text{OH}^-/\text{O}_2) = -0.792 + \Delta_{\text{sol}} G(\text{IO}_3^-) - \Delta_{\text{sol}} G(\text{I}^-) - \frac{3}{2} kT \ln\left(\frac{p_{\text{O}_2}}{p^\circ}\right) \quad (15)$$

DFT calculations with implicit solvation:

For each molecule, the structure was optimised in both the gas phase and also with an implicit solvent. In each case, the vibrational frequencies were calculated (thus also the Gibbs free energy) to ensure that a minimum had been reached in the optimisation procedure. The solvation energy term $\Delta_{\text{sol}} G()$ was calculated by subtracting the Gibbs free energy of the implicitly solvated molecule from its gas phase value. The values are found in Supplementary Table S4.

	$\Delta_{\text{sol}} G()$			$\partial \Delta_{\text{sol}} G(\text{x-Water})$		Thermo. comparison	
Species	Water	G4	IL	G4	IL	G4	IL
I^-	-2.61	-2.29	-2.42	0.32	0.19		
IO^-	-3.08	-2.69	-2.84	0.39	0.24	0.22	0.15
IO_3^-	-3.37	-2.92	-3.09	0.44	0.28	0.13	0.08

Table S4| Results of DFT calculations showing the Gibbs free energy of solvation, $\Delta_{\text{sol}} G$ for the various species in the three different solvents. The $\partial \Delta_{\text{sol}} G$ values show the free energy change going from water to G4 or pure IL. The thermodynamic comparison shows the values that were derived from a thermodynamic analysis, thus for IO^- , it is $3 \times (\Delta_{\text{sol}} G \text{ of } \text{IO}^- - \Delta_{\text{sol}} G \text{ of } \text{I}^-)$ in each solvent and thus for IO_3^- , it is $\Delta_{\text{sol}} G \text{ of } \text{IO}_3^- - \Delta_{\text{sol}} G \text{ of } \text{I}^-$. All values are in eV.

The implicit solvation calculation used experimentally derived parameters for G4 and the Pyr₁₄TFSI IL. ORCA input is as follows:

G4

```
%cpcm smd true
epsilon 7.79 # Rivas, et al., J. Chem. Thermodynamics, 38, 245-256
refrac 1.4306 # Same as soln25 below
smdsolvent "water" # Otherwise ORCA complains about the lack of SMD solvent,
parameters get overwritten
soln 1.4326 # Taken from V. Alonso et al., Thermochim. Acta, 551 (2013), 70-77
soln25 1.4306 # Taken from V. Alonso et al., Thermochim. Acta, 551 (2013), 70-77
sola 0 # Generic ether term. Taken from Abraham, Chem. Soc. Rev., 22, 77-83
solb 0.45 # Generic ether term. Taken from Abraham, Chem. Soc. Rev., 22, 77-83
solg 48.56 # Value of 33.74 mN/m (=dyne/cm) @ 298.15 taken from Manchanda et al., J.
Chem. Eng. data 2011, 56, 2669-2676, then converted into cal mol^-1 AA^-2 (*= 1.43932)
solc 0 # No aromatic carbons
solh 0 # No halogens
end
```

Pyr₁₄TFSI

```
%cpcm smd true
      smdsolvent "water" # Otherwise ORCA complains about the lack of SMD solvent,
parameters get overwritten
      # Pyr14TFSI
      epsilon 11.9 # Weingartner, Z. Phys. Chem. 220 (2006) 1395–1405
      refrac 1.42 # The literature isn't very clear on this, so it's an approximation, eg. Solvionic
data
      soln 1.43 # same
      soln25 1.42 # same
      sola 0.181 # Table 3 of Bernales et al., J. Phys. Chem. B 2012, 116, 9122–9129
      solb 0.244 # Same
      solg 47.93 # Value of 33.3 mN/m @298 and converted into cal mol-1 AA-2 (*= 1.43932)
      solc 0 # No aromatic carbons
      solh 0.1333 # There are six F in every TFSI (15 atoms) and 30 atoms in Pyr14
end
```

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