Proton enhanced dynamic battery chemistry for aprotic lithium–oxygen batteries

Yun Guang Zhu1, Qi Liu2, Yangchun Rong2, Haomin Chen1, Jing Yang1, Chuankun Jia1, Li-Juan Yu3, Amir Karton3, Yang Ren2, Xiaoxiong Xu4, Stefan Adams1 & Qing Wang1

Water contamination is generally considered to be detrimental to the performance of aprotic lithium–air batteries, whereas this view is challenged by recent contrasting observations. This has provoked a range of discussions on the role of water and its impact on batteries. In this work, a distinct battery chemistry that prevails in water-contaminated aprotic lithium–oxygen batteries is revealed. Both lithium ions and protons are found to be involved in the oxygen reduction and evolution reactions, and lithium hydroperoxide and lithium hydroxide are identified as predominant discharge products. The crystallographic and spectroscopic characteristics of lithium hydroperoxide monohydrate are scrutinized both experimentally and theoretically. Intriguingly, the reaction of lithium hydroperoxide with triiodide exhibits a faster kinetics, which enables a considerably lower overpotential during the charging process. The battery chemistry unveiled in this mechanistic study could provide important insights into the understanding of nominally aprotic lithium–oxygen batteries and help to tackle the critical issues confronted.

1 Department of Materials Science and Engineering, Faculty of Engineering, National University of Singapore, 117576 Singapore, Singapore. 2 X-Ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA. 3 School of Chemistry and Biochemistry, The University of Western Australia, 35 Stirling Highway Crawley, Perth, Western Australia 6009, Australia. 4 Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China. Correspondence and requests for materials should be addressed to Q.W. (email: msewq@nus.edu.sg).
The pursuit of high-energy power sources going beyond the state-of-the-art Li-ion batteries has evoked a surge of intensive studies of the lithium–air battery, as it has the potential of achieving nearly the same level of energy density as that of gasoline. Although profound studies have been carried out, several technical challenges severely hinder the development of lithium–air batteries for practical application. Taking the most studied aprotic lithium–oxygen (Li-O₂) system as an example, the formation of insoluble and insulating lithium peroxide (Li₂O₂) during the discharge process leads to surface passivation and pore clogging of the cathode, which results in low round-trip energy efficiency and limited capacity. Advances in electrocatalysts so far seem to have achieved only limited success in addressing the above issues. It remains a significant challenge that in a Li-air battery the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) take place electrocatalytically at the ‘solid–solid’ interface, which is intrinsically less favourable than those at the ‘liquid–solid’ interface in other metal-air batteries (or fuel cells). As such, soluble redox catalysts have recently been extensively investigated to transform the solid-state electrode reaction into a solution phase reaction. Among the soluble OER catalyst, iodide received the most attention owing to its relatively good stability. Another critical issue for the aprotic Li-O₂ battery is that it is in essence an open system nominally, for which not only oxygen is fed into the battery upon operation; other species in air such as moisture are also inevitably introduced into the system. The presence of water in the electrolyte is generally considered to be detrimental as it attacks lithium metal at the anode and it may become involved in the ORR reaction at the cathode. For instance, water and protons were found in one study to significantly influence the crystal growth of Li₂O₂ (refs 20,21). In other studies, lithium hydroxide (LiOH) was however identified as the main discharge product in the presence of moisture, whereas disputes persist on the oxidation of LiOH by triiodide (I₃⁻) during charging process. Moreover, water was believed to catalyse the ORR reaction in aprotic Li-O₂ battery resulting in the formation of LiOH, and good cycling performance was achieved in humid O₂ (ref. 29). Therefore, owing to the complexity of the reaction, the battery chemistry of water-contaminated aprotic Li-O₂ cell remains to be elucidated.

Here we carefully investigate the influence of water on the battery chemistry of aprotic Li-O₂ cells when LiI is used as the OER redox catalyst. With the help of a Li⁺-conducting ceramic membrane, we safely exclude any side-effects that may incur by the reactions of water and redox mediators with the lithium anode. One finding is that along with LiOH, lithium hydroperoxide (LiOOH) is detected to be one of the predominant discharge products, heralding a distinct battery chemistry for water-contaminated Li-O₂ batteries. As a rarely reported lithium compound, we study the crystallographic and spectroscopic characteristics of LiOOH both experimentally and theoretically, and find LiOOH presents much faster reaction kinetics towards I⁷⁻ as compared with Li₂O₂ and LiOH. A two-stage charging process is proposed in terms of the detailed studies to elucidate the mechanism of Li-O₂ cells involving water in the battery reactions.

Results
Identification and characterization of LiOOH. Our study started off from the assessment of the reactivity of various discharge products of Li-O₂ batteries towards oxidation by I⁷⁻. Titrations of Li₂O₂ and LiOH with I⁷⁻ were firstly conducted in dimethoxethane (DME) solutions. Despite the slightly more positive potential I⁷⁻ stays intact in Li₂O₂ suspension even after stirring for 12 h (Supplementary Fig. 1), which can be explained by the sluggish reaction between the two species in accordance with our previous computational and experimental observation. A similar phenomenon was observed here for LiOH, suggesting that in vigorously dried aprotic solution I⁷⁻ cannot be removed by Li₂O₂ and LiOH within the timescale of the titration. After adding H₂O into the above Li₂O₂ suspension, the colour of I⁷⁻ was quickly bleached as a result of rapid reduction of I⁻. In contrast, the presence of H₂O in LiOH solution did not cause an appreciable change, whereas the bleaching happened instantaneously when H₂O was added into the LiOH solution, although H₂O₂ itself was found to be stable with I⁷⁻ (Supplementary Fig. 1). To understand the above phenomena, we noticed the following two reactions for Li₂O₂ and LiOH have been reported, respectively:

\[
\text{Li}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{LiOOH} + \text{LiOH} \\
\text{LiOH} + \text{H}_2\text{O} \rightarrow \text{LiOOH} + \text{H}_2\text{O}
\]

In the presence of surplus water, the solid products of both reactions are expected to be in the hydrated form, LiOOH·H₂O and LiOH·H₂O·3H₂O. Interestingly, if not coincidentally, both reactions point to the same product—LiOOH, implying that the bleaching of I⁻ might be induced by this compound. Though its crystal structure is not known, various authors suggest it to be the intermediate when producing Li₂O₂ by reactions of H₂O₂ with Li alcoholates in the corresponding alcohol (that is, methanol, ethanol and references therein). Hence, on the basis of the above titration tests, the reactivity of LiOOH is the highest and LiOH is the lowest towards oxidation by I⁻. Whereas the comparison is arguably supported by the titrations, the formation of LiOOH, its reaction with I⁻, and more importantly the existence of the compound in Li-O₂ battery, need to be unambiguously characterized and identified.

To discern the characteristics of LiOOH from LiOH and Li₂O₂, the three compounds were concordantly characterized by synchrotron X-ray diffraction (XRD), Raman and Fourier transform infrared (FTIR) spectroscopy measurements with attenuated total reflection (ATR) mode, for which both LiOH and Li₂O₂ were used as received, whereas wet powder of LiOOH was prepared by a simple reaction between LiOH and H₂O₂ in water/DME following reaction (2).

The structures of four different Li compounds were characterized by powder XRD (Supplementary Fig. 2). The diffraction pattern of LiOOH is clearly discriminated from those of LiOH, Li₂O₂ and Li₂O. In order to figure out the structure of the obtained LiOOH, high-resolution powder XRD was performed at 11-BM, Advanced Photon Source, Argonne National Lab (Fig. 1a). As seen from the LeBail fit results in Supplementary Fig. 3, the diffraction pattern of the LiOOH phase could be well indexed to a triclinic structure with unit cell parameters:

\[
a = 6.3688 \text{ Å}, b = 6.0878 \text{ Å}, c = 3.2074 \text{ Å}, \alpha = 79.598°, \beta = 101.832°, \gamma = 102.311°, \text{volume} = 117.69 \text{ Å}^3.
\]

The goodness of indexing, F(28), is as high as 795.1 with a zero-shift as small as −0.0009°, which together indicates that the fitting result is highly reliable. LeBail fits of an additional high-resolution XRD pattern for the 2θ range up to 22° (2θ angle) showed result very close to those derived from the lower 2θ angle range.

The crystal structure of LiOOH was solved from powder data starting from a comparison of the atomic arrangements of various compounds with related chemical compositions and reduced cells, noting that the close similarity of lattice parameters a and b as well as of β and γ suggests that the structure may be seen as a distorted variant of a monoclinic C2/m or even an orthorhombic body-centred structure as originally proposed for LiOOH·H₂O by Cohen. Rietveld refinements of several of these starting
models converged to the structure shown in Fig. 2 with profile R and Chi² values ($R_p = 7.86\%$, $R_w = 6.10\%$, $\chi^2 = 2.93$) closely approximating those of the model-free LeBail fit (Supplementary Fig. 3) clarifying that for the available data quality no alternative structure model can yield a significantly closer match. Accordingly, the bond valence sums (when using soft BV parameters) of all atoms in the refined structure are close to the expectation value leading to a low global instability index of $G_I = 0.077$ underlying the plausibility of the structure model.

Geometry optimization of the result from the Rietveld refinement by DFT confirmed that this structure is metastable. Details of the structure parameters resulting from both the Rietveld refinement and the DFT geometry optimization are given in the supplementary material (Supplementary Tables 1 and 2). The refinement and the DFT geometry optimization are given in the supplementary material (Supplementary Tables 1 and 2). The structure consists of chains of H-bridged OOH ions as well as of Li⁺ ions arranged along the c-direction (O–H···O distances 1.12 and 1.46 Å from Rietveld refinement, or 1.07 and 1.46 Å from the DFT data), where each Li⁺ is tetrahedrally coordinated by O atoms of two water molecules and two HOO ions. The atomic arrangement is closely related to the one reported earlier for monoclinic LiOH·H₂O (Space group $C2/m$), as becomes more clearly visible when the primitive cell is used for that structure (see Fig. 2c). The structural similarity of LiOOH·H₂O and LiOH·H₂O also leads to similar stability. At 0 K the LiOOH·H₂O should according to the DFT calculations be marginally stable against the decomposition into LiOH·H₂O and ½ O₂, whereas at ambient conditions, the entropically more favorable decomposition of LiOOH·H₂O proceeds easily. In the presence of CO₂ from ambient air LiOH·H₂O then reacts further to form Li₂CO₃ (Supplementary Figs 4 and 5).

The Raman spectrum shown in Fig. 1b for the LiOOH·H₂O sample reveals a distinct characteristic peak at around 860 cm⁻¹, assigned to the stretching of O–O bond based on the density functional theory (DFT) calculations (Supplementary Figs 6 and 7). In comparison, the O–O bond stretching of Li₂O₂ and H₂O₂ molecules is observed at ~790 and 877 cm⁻¹ (Supplementary Fig. 8), respectively, just straddling that of LiOOH·H₂O. Other fingerprint peaks for LiOOH·H₂O were also observed at 80–150 cm⁻¹, implying LiOOH·H₂O is indeed a different species from LiOH and Li₂O₂. Characteristic IR responses of LiOOH·H₂O were also detected in the FTIR measurement (Supplementary Fig. 9), where the peak at 1,643 cm⁻¹ is identified as a H₂O bending mode. Although other vibrations are not yet specified owing to a lack of reference data, the distinct spectra well evince LiOOH·H₂O as a new species relevant to Li-O₂ batteries.

**Electrochemical properties of LiOOH.** To investigate the catalytic effect of I₃⁻ on the oxidation of the above lithium compounds, rotating disk electrode (RDE) was employed to probe the reactions, in which the powders of LiOOH·H₂O, Li₂O₂, and LiOH were dispersed in LiI electrolyte. As shown in Fig. 3a, in the presence of LiOOH·H₂O suspension the limiting current for I⁻ oxidation on RDE is enhanced by nearly 10 times as compared with those with LiOH and Li₂O₂. The direct oxidation of LiOOH·H₂O on RDE could be excluded as it generated almost zero current in the absence of LiI (Fig. 3a). Thus, such a considerable enhancement is rationalized by the catalytic reaction between the formed I₃⁻ and LiOOH in the vicinity of RDE, which rapidly regenerates I⁻. In contrast, the presence of LiOH or Li₂O₂ suspension has little influence on the reaction of I₃⁻, consistent with the titration experiment.

The reactions of the various lithium compounds with I₃⁻ were substantially by battery charging test. The cell consists of a cathodic and an anodic compartment, which are separated by a piece of LAGP ceramic membrane (Supplementary Fig. 10a). The powder of LiOOH·H₂O, Li₂O₂, and LiOH were loaded on the cathode (carbon felt) before it was fabricated into the cell. The use of Li⁺-conducting membrane is crucial as it prevents I₃⁻, water and oxygen from crossing-over and parasitically reacting with the Li metal in the anodic side. As shown in Fig. 3b, the theoretical charging time of I⁺ to I₂ is ~7 h, whereas all the three cells present significantly longer charging process (>30 h), indicating the lithium compounds are involved in the reactions contributing to the charging capacity. In the absence of the above lithium compounds, the reactions of I⁻ in DME electrolyte exhibit two distinct voltage plateaus at ~3.20 and 3.70 V, corresponding to the formation of I₃⁻ and higher order polyiodide to eventually I₇⁻, respectively (Supplementary Fig. 11). In comparison, the LiOOH cell reveals only one prolonged charging plateau at ~3.20 V, which is rational in terms of the titration experiment that the formed I₃⁻ could instantaneously be reduced back to I⁻ by LiOOH for extended charging, and the cell voltage is determined by the I⁻/I₃⁻ redox reaction on the electrode. So the overall reaction on the cathode only involves I⁻/I₃⁻ mediated oxidation of LiOOH, and the capacity is limited by the quantity of material loaded. In comparison, the Li₂O₂ cell presents two charging plateaus resembling that of the pure LiI cell (Supplementary Fig. 11), but with the second plateau greatly extended. Such a phenomenon has previously been observed in redox flow lithium–oxygen battery (RFLOB) and is consistent with the titration that in aprotic electrolyte I₃⁻ is unable to rapidly oxidize Li₂O₂, which requires a stronger oxidizer such as...
I₂ formed at the higher voltage plateau. The charging of the LiOH cell is fairly similar to that of Li₂O₂, except for slightly larger overpotentials at the higher voltage plateau, presumably a result of sluggish reaction between LiOH and I₂, or more complex reactions. To eliminate the overpotentials imposed by the membrane and other cell components during the charging process, galvanostatic intermittent titration technique (GITT) measurement was performed with the cells after 20 h charging. The relaxed cell voltage is on average ~2.95 and 3.55 V for the LiOOH and Li₂O₂ cells, and is slightly higher for the LiOH cell, broadly in agreement with the respective potential of I⁻/I₃⁻ and I₋/I₂ as determined by voltammetry (Supplementary Fig. 12). The above charging tests corroborate the previous comparison of the three compounds with I₋ and that LiOOH < Li₂O₂ < LiOH in terms of oxidation capability.

Characterization of Li-O₂ battery with water contamination. In order to verify the formation of LiOOH as an oxygen reduction product in moisture-contaminated Li-O₂ battery, water was deliberately introduced into the aprotic catholyte of Li-O₂ cells. As shown in Fig. 4a, the presence of water seems to be advantageous to the reduction of overpotential during the 10 h discharging process. With increasing water content in the electrolyte, the discharging plateau shifts upwards. The charging curves for all the cells predominantly present two voltage plateaus at ~3.50 V and 3.85 V, respectively. The lower voltage plateau is assigned to the oxidation of I⁻ to I₂⁻, whereas owing to surface passivation of the electrode as generally observed in aprotic Li-oxygen batteries, the overpotential is considerably higher than that observed in Fig. 3b. The maximum charging time for I⁻ to I₂⁻ is ~4.5 h, so the extended charging would be a result of the catalytic reaction of I₃⁻ with the discharge product, in which LiOOH was identified by Raman spectroscopy when probing the electrode after 10 h discharge (Fig. 1b).

However, the prolonged additional 4–5 h charging time at ~3.50 V could not account for the 10 h discharge, for which around half of the discharge product seemingly remains intact with I₂⁻. When the cells were further charged to a higher voltage, where the reaction of I₃⁻/I₂ prevails, a second voltage plateau appeared at ~3.85 V with evidently extended charging for another 4–5 h. On the basis of the previous charging tests, either LiOH or Li₂O₂ may contribute to this process, whereas considering Li₂O₂ is stable in the presence of water, this extra capacity is deemed to be stemming from LiOH (or LiOH·H₂O). This is reasonable in terms of reaction (1), and that the discharge product of aprotic Li-O₂ battery, Li₂O₂, is converted into two distinct compounds co-existing in water-contaminated cells, of which LiOOH·H₂O reacts with I₂⁻ at a lower voltage, whereas LiOH·H₂O reacts with I₂ at a higher voltage in a two-stage charging process. The presence of LiOOH and LiOH in the discharge product was confirmed by ATR-FTIR measurement (Supplementary Fig. 13), in which the characteristic peaks of LiOH and LiOOH·H₂O are clearly identified upon redox-assisted ORR reaction in the presence of water.
When the charging curves in Fig. 4a are examined closely, one may notice multiple voltage steps at each voltage plateau, which is ascribed to the direct oxidation of LiOOH by H2O and LiOH·H2O on the cathode alongside the reactions with redox mediators in the electrolyte. To avoid the complexity and ambiguity, a RFLOB cell was fabricated, which employed ethyl viologen diiodide (EVI2) as a bifunctional redox mediator for both the ORR and OER reactions (Fig. 4b). One significant advantage for RFLOB over the conventional Li-O2 battery is that upon discharging O2 is fed into a gas diffusion tank (GDT) in which it is reduced by EV2+ when the catholyte circulates through (Supplementary Fig. 10c). As a result, the discharge product is chemically formed in the tank instead of being deposited on the electrode surface. Upon charging, the parallel reactions of these materials on the electrode are thus obviated. As the voltage profiles in Fig. 4c shows, the presence of water in the catholyte considerably reduces the cell overpotential, similar to that observed in static cells. The discharging process of the flow cells involves the reduction of EV2+ on the electrode and the associated ORR reaction in GDT. Upon charging, the dry cell exhibits two voltage plateaus with the first one relating to the oxidation of I− to I2−, and the second with extended capacity originating from the oxidation of I2− to I3− and the reaction between Li2O2 and I2, which is consistent with our previous study17. In comparison, although the water-contaminated flow cell also shows two clearly defined plateaus during the charging process, the capacities for both plateaus stretch nearly equally beyond that of the redox mediators, implying two distinct reactions with I2− and I3− take place at the two plateaus respectively.

The redox-targeting reactions of LiOOH with I2− and LiOH with I3− were further investigated with UV-Vis and mass spectrometry. After mixing with LiOOH·H2O suspension in DME, the characteristic absorption peak of I3− at 364 nm (extended to the visible region, Supplementary Fig. 14a) vanished. As a result, the solution became nearly colourless. Meanwhile, the mass spectrometric measurement in Supplementary Fig. 15a shows that O2 evolves instantaneously upon mixing I2− with LiOOH·H2O. In a separate test, after adding excessive LiOH into a solution of I2 in DME/H2O (10:1) and stirring for 1 h, the absorption of the I2 solution became fairly identical to that of I3− (Supplementary Fig. 14b). That is, the absorption at 400–500 nm was greatly attenuated with only the characteristic peak of I3− present, indicating the existence of I2− after reaction. We noticed IO2− was detected to be the main product of the reaction between I2 and LiOH in water-based electrolyte in the literature26. The involved reaction is, 3I2− + 6LiOH → 5LiI + LiIO3 + 3H2O. Considering both I− and IO2− are colourless, the above reaction seems unlikely to be predominant in the DME/H2O (10:1)-based electrolyte. The mass spectrometric measurement of the reaction between LiOH and I2 was conducted in two different solutions. As shown in Supplementary Fig. 15b, oxygen evolution was observed instantaneously after I2 was injected into 2 M LiOH suspension in DME/H2O (10:1), further confirming the irrelevance of the above reaction in the DME/H2O (10:1)-based electrolyte. Therefore, O2 evolution is deemed part of the reactions of LiOOH with I2− and LiOH with I2 during the charging process of water-contaminated Li-O2 cells.

Two-stage charging reactions in water-contaminated Li-O2 cells.

On the basis of the above analysis, the following reactions are thus proposed to expound the discharging and the two-stage charging processes in the water-contaminated cell:

Discharging process (ORR reaction):

\[ 2\text{LiI}^+ + \text{O}_2 + 3\text{H}_2\text{O} + 2e^- \rightarrow \text{LiOOH} \cdot \text{H}_2\text{O} + \text{LiOH} \cdot \text{H}_2\text{O} \]  
(4)

Charging process (OER reaction):

\[ 3\text{I}^- \rightarrow \text{I}_2^- + 2e^- \]  
(5)

\[ 4\text{LiOOH} \cdot \text{H}_2\text{O} + 2\text{LiI}_3 \rightarrow 6\text{LiI} + 3\text{O}_2 + 6\text{H}_2\text{O} \]  
(6)

\[ \text{I}_2^- \rightarrow 3/2\text{I}_2 + e^- \]  
(7)

\[ 4\text{LiOH} \cdot \text{H}_2\text{O} + 6\text{I}_2 \rightarrow 4\text{LiI}_3 + \text{O}_2 + 6\text{H}_2\text{O} \]  
(8)

Reaction (4) indicates that equimolar amounts of LiOOH and LiOH are formed in the discharging process, which is evidenced by the identical capacity extension in the two-stage charging process in Fig. 4a,c. OOH− has been proposed in battery reactions in several studies as a result of H2O dissociation or electrolyte decomposition25,28,32,39, whereas none of them explicitly indicates LiOOH or LiOOH·H2O as a distinct discharge product, nor its structural and electrochemical properties. Besides, we have noticed that water has substantial influence on the morphology of the discharge product. When 9.1 vol.% water was added into the electrolyte, rod and cube-like
crystals with clear edges were observed after discharge, whereas crystals formed in dry electrolyte tested in separate cells are agglomerated into round-shaped particulates (Supplementary Fig. 16). Reactions (5) and (7) describe the two-stage charging process, associated with the redox-targeting reactions with LiOOH + H2O (6) and LiOH + H2O (8), respectively. Reaction (6) represents a disproportionation reaction with 3/4 of the peroxide being oxidized to O2, and the remaining 1/4 reduced to H2O. Additional 1/2 O2 is produced in reaction (8) via a 4-electron process, making up the total O2 consumption in the discharging reaction (4). A consequence of such two-step reactions is that both the voltage efficiency and energy efficiency are compromised.

This study discloses that the moisture fed into the cell does not pose immediate adverse impact to the battery operation, so long as the lithium anode is properly protected. On the basis of this new battery chemistry, a panoramic view of the ORR/OER reactions at different [H+] is conceived, which is anticipated to provide deeper insights into the mechanistic understanding of the chemistry of Li-air batteries. For that, we believe a more systematic study would be desired in future to understand the factors such as water content, [H+], type of redox mediators and so on, that influence the formation of LiOOH-H2O or other oxygen reduction products.

Methods

Materials. LiOH (98%, Sigma-Aldrich), Li2O2 (90%, Sigma-Aldrich), and H2O2 (35% (w/w) in H2O, Alfa Aesar) were used in the titration experiments. LiOH (98%, Sigma-Aldrich) and H2O2 (35% (w/w) in H2O, Alfa Aesar) were used for the preparation of LiOOH + H2O. DME(99%, Sigma-Aldrich) and dimethyl carbonate (anhydrous, > 99%, Sigma-Aldrich) were used to get the precipitation of LiOH-H2O. Diethylene glycol dimethyl ether (DEGDME, 99%, Sigma-Aldrich), DME (99%, Sigma-Aldrich), dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich) and lithium bis(trifluoromethane)sulfonimide (LiTFSI, 99.95%, Sigma-Aldrich) were used as solvent and lithium salt for electrolyte preparation. LiI (99%, Sigma-Aldrich) and EVI2 (99%, Sigma-Aldrich) were used as redox mediators in Li2O2 batteries. A Li –conducting ceramic membrane (LAGP, area 2 cm x 2 cm, thickness 0.5 mm) was used as separator in Li2O2 batteries. Prior to use, all the above chemicals were stored in an argon-filled glove box without exposure to air.

Preparation of LiOOH-H2O. 0.196 g LiOH (98%, Sigma-Aldrich) was added into 2.6 ml deionized water. Then the solution was stirred until LiOH powder was dissolved completely. With good stirring, 1.4 ml H2O2 solution (35% w/w, Alfa Aesar) were added dropwise into the above LiOH solution over 30 min, which resulted in 2 M LiOOH-H2O solution in water. In order to retrieve solid LiOOH-H2O from the solution, 2 ml DME were added dropwise into 1 ml of the above LiOOH-H2O solution with stirring for 10 min. During the process, a white LiOOH-H2O precipitate appeared and sedimentsed. In the RDE and battery measurements, 2 M LiOOH-H2O solution in water was employed directly to prepare suspension of LiOOH-H2O. For the Raman and XRD measurements, wet LiOOH-H2O particles were separated from the supernatant after centrifugation and gently dried in a vacuum oven at room temperature for 12 h.

Assembly of Li2O2 battery. Assembly of static Li2O2 battery: Lithium foil and carbon felt were used as the anode and cathode, respectively. The electrochemical cell was fabricated by sandwiching the lithium foil and carbon felt in a cell stack, in which the two electrodes were separated by a LAGP membrane mounted on a Teflon frame (Supplementary Fig. 6). The effective area of the membrane was 1 x 1 cm2. The anodic and cathodic end plates were made of stainless steel and titanium metal (with holes as O2 inlet and outlet), respectively, to prevent corrosion during the charging process makes it unsustainable. In addition, the formation of LiOOH-H2O in water- or alcohol-containing electrolytes may provide an alternative approach for reactions for water-based Li2O2 battery, in which the 4-electron process is generally considered. As water could be precluded as a reactant from the 2-electron process of LiOOH (that is, in acidic and basic conditions), it may in theory boost the energy density and energy efficiency of water-based Li2O2 cells.

A distinct battery chemistry was discovered for water-contaminated Li2O2 battery, from which a new lithium compound—LiOOH-H2O, was identified as a predominant oxygen reduction product and structurally characterized. When iodide is used as the OER redox catalyst in the water-contaminated Li2O2 cell, the equimolar amounts of LiOOH-H2O and LiOH-H2O formed in the discharging process are oxidized stepwise by I2− and I3−, leading to a two-stage charging process.

Discussion

The above study unveils an intriguing picture of the ORR and OER reactions for water-contaminated Li2O2 batteries, for which the transfer of protons from water leads to the formation of a new compound LiOOH-H2O, while the left-over OH− prompts the formation of an equimolar amount of LiOH (or LiOH-H2O). More precisely, such a situation might be called water contamination at ‘neutral’ conditions. It would be interesting to consider the scenarios under varying proton concentrations. For instance, in weakly acidic condition, it is likely that Li+ + O2− + H+ + 2e− + H2O → LiOOH-H2O, so that LiOOH-H2O would again be the discharge product with pH-dependent equilibrium potential. However, when excessive protons present in the catholyte, it appears plausible that 2H+ + O2− + 2e− → H2O, so that, the remaining Li atom in LiOOH-H2O could be knocked out to form H2O2. At the other extreme, when extra OH− is introduced into the catholyte, the proton in LiOOH would be removed and as reported for water-based alkaline electrolytes, the formation of Li2O2 would be favoured, for which the redox potential of the overall reaction becomes pH-independent. Figure 5 illustrates the plausible battery reactions of ‘proton-contaminated’ Li2O2 cells which may predominate at different [H+]. We believe systematic studies on the impact of protons on the ORR and OER reactions would disclose deeper insights into the mechanistic understanding of the battery chemistry of Li-air batteries. Considering the LiOOH-H2O has greater reactivity towards the OER reaction, which substantially brings down the charging overpotential (Fig. 3b), it is of immediate importance to contemplate the implications of the new compound for the operation of the Li2O2 battery. However, this seems not intuitively straightforward. A formation of LiOOH-H2O during the discharging process requires protons which are not available from the anode. Although the moisture in air could be a natural source of protons, the accumulation of water in the catholyte during the charging process makes it unsustainable. In addition, the formation of LiOOH-H2O in water- or alcohol-containing electrolytes may provide an alternative approach for reactions for water-based Li2O2 battery, in which the 4-electron process is generally considered. As water could be precluded as a reactant from the 2-electron process of LiOOH (that is, in acidic and basic conditions), it may in theory boost the energy density and energy efficiency of water-based Li2O2 cells.
measurements of LiI were conducted at a variety of water contents. The electrolyte was 5 mM LiI in 0.5 M LiTFSI/DME with different water contents (DME:H2O are 100:0, 100:1, 100:5, 100:10, 100:20, 100:30, 100:50, 100:100, v/v). The working and the counter electrode were Pt disc and Pt plate electrode, respectively. The reference electrode was Ag/AgNO3 electrode. The step potential is 0.005 V and the modulation amplitude is 0.025 V. All the above measurements were performed on an Autolab electrochemical workstation (Metrohm Autolab, PGSTAT302N). The charge and discharge tests were conducted on an Arbin battery tester. The battery was tested at a constant current of 0.1 mA cm\(^{-2}\).

**Other characterizations.** Raman spectra were measured by a confocal Raman system with 532 nm laser excitation (WITec Instruments Corp, Germany). Samples for Raman spectroscopic measurement include gently dried LiOOH -H2O powder, powders of the as-purchased LiOH and Li2O2, as well as 35 % H2O2 solution. The Raman spectrum of the cathode (carbon felt) in the Li2O2 battery was also measured immediately after disassembling the fully discharged static Li2O2 cells. For the Li2O2 cells with water-free electrolyte, the cathode was washed and dried in a vacuum chamber prior to Raman measurement. All the above samples were loaded on a piece of sapphire for Raman measurement. FTIR spectra were collected via PerkinElmer Frontier MIR/FIR system by 16 scans with a nominal resolution of 0.1 cm\(^{-1}\) through an ATR mode. In the \textit{in situ} measurement of the redox-targeting reaction product between EV\(^+\) and O2, a flow cell with two inlets and one outlet (two for liquid and one for oxygen) was used. UV-Vis spectroscopic measurements were conducted on a UV-Vis spectrophotometer (Shimadzu 1800). Mass spectrometric measurements were conducted on a Hiden analytical QGA (HAS-301-1376A)). There are one outlet and two inlets of the reactor for carrying gas and injecting reactant.

The high-energy XRD measurements were performed on the beam line 11-ID-C at the Advanced Photon Source, Argonne National Laboratory. A monochromator with a Si (113) single crystal was used to provide an X-ray beam with the energy of 115 keV. High-energy X-ray with a beam size of 0.2 mm × 0.2 mm and wavelength of 0.10725 Å was used to obtain two-dimensional diffraction patterns in the transmission geometry. X-rays were collected with a Perkin-Elmer large-area detector placed at 1,800 mm from the sample. The obtained two-dimensional diffraction patterns were calibrated using a standard CeO2 sample and converted to one-dimensional patterns using Fit2D software. In order to figure out the structure of the obtained LiOOH -H2O sample, the high-resolution X-ray powder diffraction pattern of LiOOH -H2O was taken at 11-BM, Advanced Photon Source, Argonne National Lab, whereas the wavelength of the X-ray is 0.41423 Å. The samples were measured in air without protection. For the stability test, XRD measurements were carried out on a Bruker D8 with Cu Kα1 radiation (λ = 0.154059 nm). The samples were measured in air without protection.

**Theoretical calculations.** DFT calculations were carried out with B3LYP hybrid exchange-correlation functional in combination with the quadruple-zeta polarized valence basis set augmented with diffuse functions, aug-cc-pVQZ, using the Gaussian 09 programme suite[41,42]. The scaled quantum mechanics force field procedure was used to analyse vibrational bands of all fundamentals. The calculated frequencies were scaled by a factor of 0.9852 for frequencies below 2000 cm\(^{-1}\) (ref. 43). Scaling harmonic vibrational frequencies is an effective way to facilitate comparison with experimentally observed frequencies. A scaling factor of 0.9852 was recommended for the B3LYP/aug-cc-pVQZ level of theory for which the corresponding root mean square error relative to the experimental frequencies was report to be 2 cm\(^{-1}\) (ref. 43). The calculated scaled frequencies for the O–O stretch are: 838.0 (LiOOH -H2O), 827.6 (LiOOLi), 934.9 (HOOH) cm\(^{-1}\). The 4-electron process shown in dotted line is neutral and \((\text{H}^+)\) basic conditions. The calculated scaled frequencies for the O–O stretch are: 838.0 (LiOOH -H2O), 827.6 (LiOOLi), 934.9 (HOOH) cm\(^{-1}\).

**Data availability.** The authors declare that data supporting the findings of this study are available within the paper and its supplementary information file or from the corresponding author on reasonable request.
References

1. Girishkumar, G., McCloskey, B., Luntz, A., Swanson, S. & Wäcke, W. Lithium-air battery: promise and challenges. J. Phys. Chem. Lett. 1, 2193–2203 (2010).

2. Abraham, K. M. & Jiang, Z. A polymer electrolyte-based rechargeable lithium/oxygen battery. J. Electrochem. Soc. 143, 1–5 (1996).

3. Read, J. Ether-based electrolytes for the lithium/oxygen electrolyte battery. J. Electrochem. Soc. 153, A96–A100 (2006).

4. Ogasawara, T., Debart, A., Holzapfel, M., Novák, P. & Bruce, P. G. Rechargeable LiO2 electrode for lithium batteries. J. Am. Chem. Soc. 128, 1390–1393 (2006).

5. Ottakam Thotiyl, M. M., Freunberger, S. A., Peng, Z. & Bruce, P. G. The carbon electrode in nonaqueous LiO2 cells. J. Am. Chem. Soc. 135, 494–500 (2012).

6. Li, Y. C. et al. Platinum-gold nanoparticles: a highly active bifunctional electrocatalyst for rechargeable lithium-air batteries. J. Am. Chem. Soc. 132, 12170–12171 (2010).

7. Liu, S. et al. Direct growth of flower-like 5-MnO2 on three-dimensional graphene for high-performance rechargeable LiO2 batteries. Adv. Energy Mater. 4, 1301960 (2014).

8. Thotiyl, M. M. G. et al. A stable cathode for the aprotic LiO2 battery. Nat. Mater. 12, 1050–1056 (2013).

9. Li, F. et al. Superior performance of a Li P2 battery with metallic RuO2 hollow spheres as the carbon-free cathode. Adv. Energy Mater. 5, 1500294 (2015).

10. Chen, Y., Freunberger, S. A., Peng, Z., Fontaine, O. & Bruce, P. G. Charging a LiO2 battery: redox mediator. Nat. Chem. 5, 489–494 (2013).

11. Bergner, B. J., Schürmann, A., Peppler, K., Garsuch, A. & Janek, J. TEMPO: a mobile catalyst for rechargeable LiO2 batteries. J. Am. Chem. Soc. 136, 15054–15064 (2014).

12. Lim, H. D. et al. Superior rechargeability and efficiency of lithium-oxygen batteries: hierarchical air electrode architecture combined with a soluble catalyst. Angew. Chem. Int. Ed. 53, 3926–3931 (2014).

13. Sun, D. et al. A solution-phase bifunctional catalyst for lithium-oxygen batteries. J. Am. Chem. Soc. 136, 8941–8946 (2014).

14. Feng, N., He, P. & Zhou, H. Enabling catalytic oxidation of Li2O2 at the liquid–solid interface: the evolution of an aprotic LiO2 battery. ChemSusChem 8, 600–602 (2015).

15. Kwas, W.-J. et al. Understanding the behavior of Li-oxygen cells containing LiI. J. Mater. Chem. A 3, 8855–8864 (2015).

16. Liu, T. et al. Cycling Li2O2 batteries via LiO2 formation and decomposition. Science 350, 530–533 (2015).

17. Zhu, Y. G. et al. Dual redox catalysts for oxygen reduction and evolution reactions: towards a redox flow LiO2 battery. Chem. Commun. 51, 9451–9454 (2015).

18. Gao, X., Chen, Y., Johnson, L. & Bruce, P. G. Promoting solution phase discharge in LiO2 batteries containing weakly solvating electrolyte solutions. Nat. Mater. 15, 882–888 (2016).

19. Zhu, Y. G., Wang, X., Jia, C., Yang, J. & Wang, Q. Redox-mediated ORR and OER reactions of low lithium oxygen batteries enabled with a pair of soluble redox catalysts. ACS Catal 6, 6191–6197 (2016).

20. Aetukuri, N. B. et al. Solvating additives drive solution-mediated electrochemistry and enhance toroid growth in non-aqueous LiO2 batteries. Nat. Chem. 7, 50–56 (2015).

21. Schwenke, K. U., Metzger, M., Restle, T., Piazza, M. & Gasteiger, H. A. The influence of water and protons on Li2O2 crystal growth in aprotic LiO2 cells. J. Electrochem. Soc. 162, A573–A584 (2015).

22. Viswanathan, V. et al. Comment on ‘Cycling Li2O2 batteries via LiO2 formation and decomposition’. Science 352, 667–667 (2016).

23. Shen, Y., Zhang, W., Chou, S.-L & Dou, S.-X. Comment on ‘Cycling Li2O2 batteries via LiO2 formation and decomposition’. Science 352, 667–667 (2016).

24. Liu, T. et al. Response to comment on ‘Cycling Li2O2 batteries via LiO2 formation and decomposition’. Science 352, 667–667 (2016).

25. Kwas, W.-J. et al. Li2O2 cells with LiBr as an electrolyte and a redox mediator. Energy Environ. Sci. 9, 2334–2345 (2016).

26. Burke, C. M. et al. Implications of 4 e–oxygen reduction via iodide redox mediation in LiO2 batteries. ACS Energy Lett. 1, 747–756 (2016).

27. Zhang, W. et al. Promoting Li2O2 oxidation via solvent-assisted redox shuttle process for low overpotential LiO2 battery. Nano Energy 30, 43–51 (2016).

28. Li, F. et al. The water catalysis at oxygen cathodes of lithium-oxygen cells. Nat. Commun. 6, 7843 (2015).

29. Wu, S. et al. A synergetic system for lithium-oxygen batteries in humid atmosphere integrating a composite cathode and a hydrophobic ionic liquid-based electrolyte. Adv. Funct. Mater. 26, 3291–3298 (2016).

30. Aurbach, D., McCloskey, B. D., Nazar, L. F. & Bruce, P. G. Advances in understanding mechanisms underpinning lithium-air batteries. Nat. Energy 1, 16128 (2016).

31. Choban, A., Yurchuk, I. & Lyavinen, A. Effect of base nature on the oxidation of dimethyl sulfoxide with hydrogen peroxide in superbasic media. Russ. J. Gen. Chem. 82, 247–250 (2012).

32. Black, R. et al. Screening for superoxide reactivity in Li2O2 batteries: effect on Li2O2/LiOH crystallization. J. Am. Chem. Soc. 134, 2902–2905 (2012).

33. Cohen, A. J. Observations on several compounds of lithium and oxygen. 14,1b J. Am. Chem. Soc. 74, 3762–3764 (1952).

34. Vol’nov, I. & Petrocelli, A. Peroxides, superoxides, and ozonides of alkali and alkaline earth metals (Springer, 1966).

35. Adams, S. Practical considerations in determining bond valence parameters (Springer, 2013).

36. Adams, S. & Rao, R. P. Simulated defect and interface engineering for high power Li electrode materials. Solid State Ion. 184, 57–61 (2011).

37. Adams, S. & Rao, R. P. High power lithium ion battery materials by computational design. Phys. Status Solidi (a) 208, 1746–1753 (2011).

38. Rehl, W. K. & Chin, D. T. Electrochemical overcharge protection of rechargeable lithium batteries i. kinetics of iodide/tri-iodide/iodine redox reactions on platinum in solutions. J. Electrochem. Soc. 135, 16–21 (1988).

39. Staszk-Jirkovsky, J. et al. Water as a promoter and catalyst for dioxygen electrochemistry in aqueous and organic media. ACS Catal. 5, 6600–6607 (2015).

40. Matsui, M. et al. A novel aqueous lithium-oxygen cell based on the oxygen-peroxide redox couple. Chem. Commun. 51, 3189–3192 (2015).

41. Frisch, M. et al. Gaussian 09, revision A. 02 (Gaussian, Inc., 2009).

42. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 98, 5648–5652 (1993).

43. Sinha, P., Boesch, S. E., Gu, C., Wheeler, R. A. & Wilson, A. K. Harmonic vibrational frequencies: scaling factors for HF, B3LYP, and MP2 methods in combination with correlation consistent basis sets. J. Phys. Chem. A 108, 9213–9217 (2004).

44. Hermansson, K. & Thomas, J. O. The experimental electron density in lithium hydride monohydrate. Acta Crystallogr. B Struct. Crystallogr. Cryst. Chem. 38, 2555–2563 (1982).