Cycling Li-O₂ batteries via LiOH formation and decomposition

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The rechargeable aprotic lithium-air (Li-O₂) battery is a promising potential technology for next-generation energy storage, but its practical realization still faces many challenges. In contrast to the standard Li-O₂ cells, which cycle via the formation of Li₂O₂, we used a reduced graphene oxide electrode, the additive LiI, and the solvent dimethoxyethane to reversibly form and remove crystalline LiOH with particle sizes larger than 15 micrometers during discharge and charge. This leads to high specific capacities, excellent energy efficiency (93.2%) with a voltage gap of only 0.2 volt, and impressive rechargeability. The cells tolerate high concentrations of water, water being the dominant proton source for the LiOH; together with LiI, it has a decisive impact on the chemical nature of the discharge product and on battery performance.

Fig. 1. Electrochemical profiles of cells with different electrode/electrolyte combinations. (A) Discharge-charge curves for Li-O₂ cells using mesoporous SP and TiC, and macroporous rGO electrodes, with capacities limited to 500 mAh/g (based on the mass of carbon or TiC) and a 0.25 M LiTFSI/DME electrolyte. For SP and rGO electrodes, 0.05 M LiI was added to the LiTFSI/DME electrolyte in a second set of electrodes (purple and red curves). All cells in (A) were cycled at 0.02 mA/cm². The horizontal dashed line represents the position (2.96 V) of the thermodynamic voltage of a Li₂O₂ cell. (B) Galvanostatic charge-discharge curves of cells containing 0.05 M LiI and 0.25 M LiTFSI, cycled under an Ar atmosphere with different electrode/electrolyte solvent combinations with a current of 0.2 mA/cm². The crossing points (with appropriate voltages labeled) of the charge/discharge curves indicate the positions of the redox potential of Γ⁻/I⁻ in the specific electrode/electrolyte system. A direct comparison of capacities between LiI in Ar and Li-O₂ cells is given in fig. S3.
A Li-O₂ battery was prepared by using a Li metal anode, a 0.25 M lithium bis(trifluoromethyl)sulfonimide/dimethoxyethane (LiTFSI/DME) electrolyte with 0.05 M LiI additive, and a variety of different electrode structures (fig. S1). Hierarchically macroporous reduced graphene oxide (rGO) electrodes (binder-free) are used because they are light, conductive, and have a large pore volume that can potentially lead to large capacities. Mesoporous SP carbon and mesoporous titanium carbide (TiC) (36) electrodes were studied for comparison. Cyclic voltammetry (CV) measurements confirmed that rGO, SP, and TiC electrodes all exhibit good electrochemical stability within a voltage window of 2.4 to 3.5 V in a LiTFSI/DME electrolyte and can be used to reversibly cycle LiI (I₂ + 2e⁻ → 2I⁻) (37) (fig. S2).

In the absence of LiI, cells using either mesoporous TiC or macroporous rGO showed much smaller overpotentials during charge, in comparison to that obtained with the SP electrode (Fig. 1A). These decreases in overpotential are tentatively ascribed to the higher electrocatalytic activity of TiC (38) and the faster diffusion of Li⁺ and solvated O₂ within the micrometer-sized pores of the rGO electrodes (fig. S1). The addition of LiI to the SP electrode led to a noticeable drop in the overpotential over that seen with SP only, suggesting that the polarization during charge is largely caused by the insulating nature of the discharge products. The charge voltage profile is not, however, flat, but gradually increases as the charge proceeds to above 3.5 V. In contrast, when LiI is used with hierarchically macroporous rGO electrodes, a remarkably flat process is observed at 2.95 V, representing a further reduction in overpotential by -0.5 V over that seen for SP. This reduction is ascribed, at least in part, to the interconnecting macroporous network of rGO, which allows for much more efficient mediator diffusion than in the mesoporous SP electrode, even when the macropores are filled with insoluble discharged products.

The observation that the LiI/DME Li-O₂ cell charges at 2.95 V is of note, because it is slightly below the thermodynamic voltage of 2.98 V of the Li-O₂ reaction. During charge, the redox mediator is thought to be first electrochemically oxidized on the electrode (32); this oxidized form then helps to chemically decompose the discharge product. The charge voltage then reflects the redox potential (versus Li/Li⁺) of the Γ/Γ⁻ redox mediator in the electrode/electrolyte system rather than the redox potential associated with the oxidation of the solid discharge product. A low redox potential of a mediator is important for the long-term stability of the Li-O₂ cell.

To investigate factors affecting the redox potential, LiI was cycled galvanostatically in an Ar atmosphere with different electrode/electrolyte combinations (Fig. 1B). The electrolyte solvent has a larger effect on the redox potential of the Γ/Γ⁻ couple than the electrode material, with the DME electrolyte consistently exhibiting lower charge voltages than TEGDME (tetraethylene glycol diether) for all three electrodes. In addition, the voltage gaps between the charge and discharge plateaus are smaller for DME than for TEGDME electrolytes, which is consistent with the smaller voltage separations seen between the redox peaks in their respective CV curves (fig. S2). The discharge capacity is always smaller than the previous charge capacity for all cells (Fig. 1B). This indicates that some mediators, after being oxidized, have diffused into the bulk electrolyte. This observation is more prominent with DME, suggesting faster mediator diffusion in DME than in TEGDME.

The discharge overpotential for rGO-based Li-O₂ cells also decreases by 0.15 V (marked by arrows in Fig. 1A), from 2.6 V (SP/TiC) to 2.75 V (rGO), regardless of the use of LiI. Overall, the voltage gap becomes only 0.2 V (indicated by arrows), representing an ultrahigh energy efficiency of 93.2%.

X-ray diffraction (XRD) patterns (Fig. 2A) for the rGO electrodes cycled with LiI show that LiOH is the only observed crystalline discharge product; LiOH is then removed after a full charge. This is confirmed in the solid-state magnetic resonance (ssNMR) measurements (Fig. 2B), where a single resonance due to LiOH is observed at ~1.5 ppm and at 1.0 ppm in the 1H and 7Li magic angle spinning ssNMR spectra (33, 39), respectively (further corroborated by the 7Li static NMR spectrum in fig. S4). After charge, the 1H and 7Li LiOH resonances are no longer visible. We emphasize that without added LiI, the predominant discharge product for rGO electrodes is Li₂O₂ (fig. S5), the chemistry radically changing when 0.05 M LiI is added to the DME electrolyte.

Figure 2, C and D, shows optical and scanning electron microscopy (SEM) images of electrodes during the first cycle. After discharge, the electrode surface is completely covered by LiOH agglomerates, tens of microns in size, and the color of the electrode has changed from black to white. When the interior of the electrode was investigated, many crystalline “flowerlike” agglomerated LiOH particles were observed within the graphene macropores. Although these particles are more than 15 μm in diameter (fig. S6), much bigger than the Li₂O₂ toroids (fig. S5), they are in fact formed from thin-sheet primary building blocks, resulting in a more open (porous) structure. The large LiOH agglomerates efficiently fill up the pore volume available in the hierarchical macroporous electrode, leading to much larger capacities (fig. S6). When TEGDME was used as the electrolyte solvent, the discharge product, although still LiOH, now forms a thin film on the rGO electrode surface (fig. S7). After charge in DME, the hierarchically macroporous structure reappeared and the electrode turned black again (Fig. 2C). Higher-magnification SEM images revealed very small traces of residual LiOH on the electrode surface (fig. S8). We found that the reversible formation and removal of LiOH with the LiI mediator are not restricted to rGO electrodes, because mesoporous SP electrodes show similar results (fig. S9) but with larger overpotentials and lower capacities.

Kang and co-workers (34) previously reported a highly rechargeable Li-O₂ cell using carbon nanotubes and the mediator LiI (0.05 M) in a TEGDME-based electrolyte, ascribing the electrochemistry to the formation and decomposition of Li₂O₂.
Sun et al. (35) recently pointed out, however, that LiOH, rather than Li$_2$O$_2$, was the dominant discharge product when 0.05 M LiI mediator was added to the TEGDME electrolyte; LiOH was still present in the SP electrode used in their study after charge, and they suggested that LiOH could not be decomposed by the mediator. In our work, we have seen clear evidence that the discharge product is overwhelmingly LiOH and that it can be removed at low potentials of around 3 V.

In a redox-mediated Li-O$_2$ system, the effective removal of the insulating discharge products is affected by a few factors: (i) availability of bare electrode surfaces to oxidize the mediator during charge, (ii) whether the discharge product is uniformly distributed throughout the electrode, and (iii) efficient diffusion of the oxidized mediator from electrode surfaces (that supply and remove electrons) to the discharge product. TEGDME, being a more viscous solvent than DME, will lead to more sluggish I$_3^-$ and O$_2$ diffusion. When it is used with mesoporous (rather than macroporous) electrodes, the discharge product tends to concentrate on the electrode surface facing the gaseous O$_2$ reservoir, with its concentration dropping noticeably in the electrode interior [the reaction zone problem for Li-air batteries (40)]. The much more soluble LiI, however, is likely to be uniformly oxidized across the whole thickness of the electrode during charge. Consequently, for equal capacities for discharge and charge, the oxidized mediator (I$_3^-$) formed during charge may remain in excess in the electrode interior regions, where the discharge product is scarce; similarly, discharge product may be left unreacted at regions close to the O$_2$/electrolyte interface, where the discharge product is abundant. The remaining mediator in the oxidized form (I$_3^-$) will then be reduced during the next discharge, resulting in a voltage plateau at its redox potential in addition to that due to oxygen reduction. This unbalanced distribution of the mediator LiI and the discharge product LiOH across the thickness of the mesoporous electrode may be a cause of the unreacted LiOH and iodine-dominated electrochemistry observed in the work by Sun and co-workers (33). Furthermore, the thin-film morphology of the discharge product formed in the TEGDME-based electrolyte (fig. S7 and (35)) effectively passivates the electrode surface. As a result, triiodide anions may first form on bare electrode surfaces that are distant from the discharge products. They then need to diffuse to the passivated regions to remove LiOH, reducing the efficiency of LiOH removal and providing another explanation for the observed residual LiOH. We used a macroporous rGO electrode and DME, which provides faster mediator and O$_2$ diffusion, and higher LiO$_2$ solubility, leading to a more uniform Li-O$_2$ reaction during discharge and larger reversible capacities.

Figure 3 shows the electrochemical performance of the Li-O$_2$ battery. When limiting the specific capacity to 1000, 5000, and 8000 mA-h/g, the cells show no capacity fade, with little increase in voltage polarization after 2000, 300, and 100 cycles, respectively (Fig. 3, A to C). Higher capacities >20,000 mA-h/g, have also been demonstrated (figs. S5 and S11). When cycled at 1 A/gc (Fig. 3, A and C), the voltage gap is only ~0.2 V; at higher rates, the gaps widen (fig. 3D), increasing to 0.7 V at 8 A/gc. Furthermore, at this higher rate, the cell is polarized each cycle (fig. S11), and after 40 cycles the electrode surface is covered by a large number of particles (with morphologies unlike those of LiOH observed at lower currents), which do not seem to be readily removed during charge at these voltages. At these higher overpotentials, more substantial parasitic reactions probably occur, rapidly polarizing the cell by increasing its resistance and impeding the electron transfer across the electrode/electrolyte interface. A narrower operating electrochemical window within 2.95 ± 0.5 V is key for the prolonged stability of the rGO electrodes.

The sensitivity of the cell to water was explored by either deliberately adding ~45,000 parts per million (ppm) of H$_2$O (37 mg per 783 mg of DME) to the electrolyte or cycling cells under a humid O$_2$ atmosphere. In both cases, no appreciable change in the electrochemical profile was observed (fig. S12), compared to that using a nominally dry electrolyte. Furthermore, the added water was found to promote the growth of even larger LiOH crystals (>30 μm (fig. S13)). Although a certain level of scattering in the total capacity is observed, probably due to variations in the electrode structure, the cell capacity is typically within 25,000 to 40,000 mA-h/gc (i.e., 2.5 to 4.0 mA-h/gc) range for an rGO electrode of 0.1 mg and 200 μm thick. After discharge, the weight of an electrode removed from the stainless steel mesh was about 1.5 mg (2.7 V, 3.2 mA-h), giving a specific energy of 5760 Wh/kg (see section 13 of the supplementary materials).

The mechanism of O$_2$ reduction in aprotic Li-O$_2$ batteries has been extensively discussed. Many authors (5, 41, 42) have shown that the ability of an electrolyte to solvate O$_2$ (characterized by the Gutman donor number, DN) is important in governing the discharge reaction mechanism. Higher LiO$_2$ solubility favors a solution precipitation mechanism leading to large toroidal Li$_2$O$_2$ crystals and thus higher discharge capacity; lower LiO$_2$ solubility tends to drive a surface mechanism where Li$_2$O$_2$ forms thin films on the electrode surface and a lower capacity. Because of its intermediate DN, solution precipitation and surface reduction mechanisms can occur simultaneously in DME (41).

With added LiI, although LiOH rather than Li$_2$O$_2$ is the prevailing discharge product, many parallel phenomena are observed: The similar discharge voltages (2.75 V, Fig. 1A) observed with and without the added LiI suggest that the first step on discharge is an electrochemical reaction, where O$_2$ is reduced on the electrode surface to form LiO$_2$. It is unlikely that O$_2$ is reduced to O$_2^-$—via two-electron electrochemical steps or even disociatively reduced to O$^-$ (or LiOH) via four-electron electrochemical steps. Subsequent conversion of Li$_2$O$_2$ to LiOH is proposed to be a chemical process that occurs via a solution mechanism. Strong support for a solution mechanism comes from the observation that LiOH grows on both the electrode and the insulating glass fiber separators (fig. S6), the latter not being electrically connected to the current collector. This process must involve the iodide redox mediator, because in its absence Li$_2$O$_2$ is formed, even in cells with high moisture contents.

A key question is the origin of the H$^+$ in the formed LiOH, potential sources being the DME
Discharge Reactions

(1) electrochemical: \(4 \text{Li}^+ + 4 \text{O}_2 + 4e^- \rightarrow 4 \text{Li}_2\text{O}_2\)

(2) chemical: \(4 \text{Li}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{LiOH} + 3\text{O}_2\)

Charge Reactions

(1) electrochemical: \(2\text{Li}^+ + 2e^- \rightarrow 2\text{Li}\)

(2) chemical: \(4\text{LiOH} \rightarrow 4\text{Li}^+ + 6\text{H}_2\text{O} + 4\text{O}_2\)

Fig. 4. Schematic mechanisms for the formation and removal of LiOH in iodide redox-mediated Li–O2 cells in the presence of water. The electron/LiOH molar ratios during discharge and charge are both equal to 1.
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**Solving the problems with Li-air batteries**

Li-air batteries come as close as possible to the theoretical limits for energy density in a battery. By weight, this is roughly 10 times higher than conventional lithium-ion batteries and would be sufficient to power cars with a range comparable to those with gasoline engines. But engineering a Li-air battery has been a challenge. Liu *et al.* managed to overcome the remaining challenges: They were able to avoid electrode passivation, turn limited solvent stability into an advantage, eliminate the fatal problems caused by superoxides, achieve high power with negligible degradation, and even circumvent the problems of removing atmospheric water. *Science*, this issue p. 530