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Redox-flow Li-O\textsubscript{2} battery addresses surface passivation and pore clogging problems of the cathode by using a pair of redox catalysts.
A redox flow lithium-oxygen battery (RFLOB) by using soluble redox catalysts with good performance was demonstrated for large-scale energy storage. The new device enables the reversible formation and decomposition of Li₂O₂ via redox targeting reactions in a gas diffusion tank, spatially separated from the electrode, which obviates the passivation and pore clogging of cathode.

With the increasing demand for high-density energy storage, various electrochemical energy storage technologies have been proposed, of which lithium-oxygen (Li-O₂) battery is believed to be one of the most promising solutions. Li-O₂ battery “breathes” oxygen from the air as reactant, which greatly enhances the gravimetric energy density and reduces the cost of the cell. Therefore, Li-O₂ batteries have recently attracted considerable attention from all over the world. Despite the great promises, Li-O₂ battery confronts several critical issues before it becomes a credible solution for next generation energy storage, for instance, stability of aprotic electrolyte and electrode in the presence of O₂, radical, effectiveness of catalyst with the passivation of Li₂O₂, microstructures of cathode to accommodate Li₂O₂, while allowing the access of O₂ and Li⁺, and cyclability of lithium anode upon prolonged cycling, etc. While profound studies have been done in searching stable electrolytes and efficient oxygen electrocatalysts, challenges relating to surface passivation and pore clogging by the insoluble Li₂O₂ in the gas diffusion cathode remain. This severely impairs the round-trip energy efficiency and limits the achievable capacity of the cell. Recently, redox catalysis was introduced to mitigate the overpotentials for oxygen reduction or evolution reactions by utilizing redox mediators dissolved in the electrolyte. The soluble redox active species could either reduce O₂ forming Li₂O₂ in the presence of Li⁺ in the electrolyte, or oxidize Li₂O₂ releasing oxygen. Since the “catalysts” exist in the electrolyte, the adverse effect of surface passivation is alleviated. By contrast, these redox-catalyzed reactions towards O₂ in essence resemble the “redox targeting” reactions recently proposed for lithium-ion battery materials.

In the presence of suitable redox mediators in the electrolyte, battery materials could be charged and discharged through reversible chemical lithiation and delithiation without attaching to the current collector, which intuitively results in a novel battery system — redox flow lithium-ion batteries (RFLOB). Notice a Li-air fuel cell system with circulating catholyte has been demonstrated by H. Zhou and co-workers. The same group also proposed a flow system using soluble catalyst in an aqueous catholyte for the oxygen reduction reaction, which in principle, results of a redox flow Li-O₂ primary cell.

Fig. 1. Schematic illustrates the configuration and working process of a redox flow lithium-oxygen battery (RFLOB). The cell stack constitutes a lithium metal anode and carbon felt cathode, separated by a membrane. A gas diffusion tank (GDT) is connected to the cathodic compartment through a pump. During discharge process, oxygen flows into the tank and is reduced to form Li₂O₂ while electrolyte fluid containing redox mediators and Li⁺ circulates between GDT and cell. The photo in the lower right corner shows a RFLOB single cell powering three light-emitting diodes.

Here we demonstrate a new implementable solution — rechargeable redox flow Li-O₂ battery (RFLOB) to tackle the critical issues confronted by non-aqueous Li-O₂ batteries. As illustrated in Figure 1, the RFLOB has a gas diffusion tank (GDT) connected to the...
electrochemical cell stack. Electrolyte fluid is circulated between the tank and cell by a peristaltic pump, in which for the first time we concurrently introduced two different redox mediators to catalyze the O₂ reduction and evolution reactions during discharging and charging processes, respectively. As a result, the use of conventional electrocatalysts on the cathode has been completely avoided. The GDT tank is filled with porous material allowing the easy access of redox fluid and O₂, in which the O₂ pressure is kept constant through a gas inlet and outlet. During discharging process, redox mediator RM₁ is reduced at cathode and flows into the GDT tank where it is oxidized to O₂ in the presence of Li²⁺:

\[ \text{RM}_1^{\text{red}} + e^- \rightarrow \text{RM}_1^{\text{ox}} \]  
(1)

\[ \text{Li}^+ + \text{RM}_1^{\text{red}} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{RM}_1^{\text{ox}} \]  
(2)

In this process, Li₂O₂ is formed and deposited in the porous matrix of the GDT tank. The regenerated RM₁ then flows back to the cell for a second round of reactions. During charging process, another redox mediator RM₂ is oxidized at cathode and flows into the GDT tank where it is reduced by Li₂O₂ releasing O₂:

\[ \text{RM}_2^{\text{red}} \rightarrow \text{RM}_2^{\text{ox}} + e^- \]  
(3)

\[ \text{Li}_2\text{O}_2 + \text{RM}_2^{\text{ox}} \rightarrow \text{Li}^+ + \text{RM}_2^{\text{red}} + \text{O}_2 \]  
(4)

As the formation of Li₂O₂ occurs in the tank, surface passivation and pore clogging of the cathode are essentially avoided. In theory, the capacity of the cell would just be limited by the size of GDT tank since most of EV²⁺ can be oxidized to Li₂O₂. However, noting the thermal stability of Li₂O₂, the oxidation of I²⁻ to higher order polyiodides and eventually to iodine is an issue. The extended capacity at the high voltage indicates the reaction between iodine and Li₂O₂ was efficient which resulted in the oxidation of the latter and releasing O₂.

In theory, the above discharge process could carry on until Li metal in the anode is used up and reaches the theoretical specific energy of the cell. For instance, in a non-constrained discharge process close to 80% lithium was converted into Li₂O₂ with relatively low overpotential loss in the presence of 10 mM EV²⁺ (Figure 2c), which paves a way of making low-cost and extremely high-energy density LiO₂ primary cells.

During the charging process, two voltage steps appeared at ~3.55 and 3.75 V (Figure 2b). The oxidation of EV²⁺ was not observed since most of EV²⁺ have been oxidized to EV³⁺ by the surplus O₂ in the tank. Hence the cell voltage shoots directly up to that for the oxidation of I²⁻ to I³⁻ upon charging, at which there seemed very limited reaction between I²⁻ and Li₂O₂ since the capacity extension at this voltage is rather small. Thereafter the voltage rises steadily until it reaches the second voltage plateau. Brown color was built up gradually in the electrolyte, indicating more and more polyiodides was produced. The high voltage plateau corresponds to the further oxidation of I³⁻ to higher order polyiodides and eventually to iodine. The extended capacity at the high voltage indicates the reaction between iodine and Li₂O₂ was efficient which resulted in the oxidation of the latter and releasing O₂.

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from the direct reduction of dissolved \( \text{O}_2 \) on the cathode, the cell was also tested in the absence of both redox mediators (Figure S2). It is obvious that given the extremely low capacity, the reaction of dissolved \( \text{O}_2 \) on the cathode has negligible contribution to the overall cell capacity. In general, one should note that these two molecules would not chemically react with each other upon operation. During discharging, both of the molecules will subsequently be reduced to \( \text{I}^- \) and \( \text{EV}^2^- \) in the cell. Similarly during charging, both of molecules will subsequently be oxidized to \( \text{EV}^- \) and \( \text{I}_2 \). So it is unlikely that both \( \text{I}_2 \) and \( \text{EV}^- \) co-exist in the catholyte causing reaction between the two.

The above results are very encouraging that, since the deposition of \( \text{Li}_2\text{O}_2 \) mainly occurs in the GDT tank, which intrinsically obviates the passivation and pore clogging of cathode in the cell, very stable voltage profiles with relatively low overpotentials were achieved in the first three cycles, even in the absence of catalysts. To prove the formation and decomposition of \( \text{Li}_2\text{O}_2 \) in the GDT tank, X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical states of \( \text{Li} \) and \( \text{O} \) for species formed in the tank at the end of discharge and charge. The signal associated with \( \text{Li}-\text{F} \) bond (56.6 eV) presents in all the samples (Figure 3), presumably from the remained LiTFSI. The peak of \( \text{Li}-\text{O}-\text{O}-\text{Li} \) (55.0 eV) is clearly seen in the Li 1s spectra after discharging while nearly disappeared after charging. The existence of \( \text{Li}_2\text{O}_2 \) is further corroborated by O 1s spectra, where two large peaks assigned to the O1s (532.3 eV) from LiTFSI and Li–O–O–Li (531.2 eV) in \( \text{Li}_2\text{O}_2 \) are evidently observed.

The latter then vanished after charging, in agreement with the Li 1s spectra. In order to confirm the formation of \( \text{Li}_2\text{O}_2 \) on Ni foam in the GDT tank, XRD measurement was carried out with the sample after full discharging. As the diffraction pattern shown in Figure S4, the characteristic peaks of \( \text{Li}_2\text{O}_2 \) such as (101), (100) are clearly seen. These peaks are relatively broad in width in contrast to those from the Ni substrate, indicating the nanocrystalline nature of the formed \( \text{Li}_2\text{O}_2 \). In addition, some minor peaks, which may be assigned to \( \text{LiOH} \) and \( \text{Li}_2\text{CO}_3 \) phases, are also visible. These by-products may plausibly be introduced during sample transfer and/or XRD measurement, which were conducted in air. The XPS and XRD results were further substantiated by scanning and transmission electron microscopic measurements.

As the SEM images shown in Figure 4, after discharging the smooth surface of pristine Ni foam (Figure S5a) was covered by a layer of agglomerated particles (Figure 4a), which nearly disappeared with only little residual left after charging (Figure 4b). This is consistent with the XPS measurement should the particles be \( \text{Li}_2\text{O}_2 \). The cell in Figure 2c was also examined after full discharging, in which we expect much more product would be formed in the GDT tank. As revealed in Figure S5b, not surprisingly, a much thicker layer of particulate precipitate was observed on the Ni foam. The particles are in round shape and 10-20 nm in diameter (Figure 4c), which are crystalline in nature as revealed by the high resolution TEM. The lattice fringes of (101) and (100) crystal planes of \( \text{Li}_2\text{O}_2 \) are clearly identified (Figure 4d), with d-spacing of 0.25 nm and 0.27 nm, respectively. This unambiguously confirms the formation of \( \text{Li}_2\text{O}_2 \) upon discharging.

The above results provide compelling evidence and concertedly validate the functionality of RFLOB. The above results are very encouraging that, since the deposition of \( \text{Li}_2\text{O}_2 \) mainly occurs in the GDT tank, which intrinsically obviates the passivation and pore clogging of cathode in the cell, very stable voltage profiles with relatively low overpotentials were achieved in the first three cycles, even in the absence of catalysts. To prove the formation and decomposition of \( \text{Li}_2\text{O}_2 \) in the GDT tank, X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical states of \( \text{Li} \) and \( \text{O} \) for species formed in the tank at the end of discharge and charge. The signal associated with \( \text{Li}-\text{F} \) bond (56.6 eV) presents in all the samples (Figure 3), presumably from the remained LiTFSI. The peak of \( \text{Li}-\text{O}-\text{O}-\text{Li} \) (55.0 eV) is clearly seen in the Li 1s spectra after discharging while nearly disappeared after charging. The existence of \( \text{Li}_2\text{O}_2 \) is further corroborated by O 1s spectra, where two large peaks assigned to the O1s (532.3 eV) from LiTFSI and Li–O–O–Li (531.2 eV) in \( \text{Li}_2\text{O}_2 \) are evidently observed.

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![Fig. 3. X-ray photoemission spectroscopy (XPS) measurement of Li 1s and O 1s spectra and the corresponding peak deconvolutions. The upper and lower panels display those of the discharged and charged species in the GDT tank, respectively.](image)

Conclusions

The above results provide compelling evidence and concertedly validate the functionality of RFLOB. That is, with the assistance of redox mediators, the discharging product \( \text{Li}_2\text{O}_2 \) could be remotely formed in the GDT tank and reversibly oxidized in the charging.
process without depositing onto the cathode inside the cell. Such decoupled reactions of Li$_2$O provide great flexibility to circumvent the issues confronted by the conventional Li$_2$O batteries. The surface passivation and pore clogging of the cathode resulted from Li$_2$O precipitations, which is inevitable in conventional cells, are essentially avoided under the new operation mode. While the overpotential persists during the charging process, the intolerably large voltage hysteresis could in theory be mitigated by using suitable redox mediators even in the absence of electrocatalysts, which on the other hand is expected to also improve the cycling stability of the cell. In addition, the capacity of the cathode could be expanded by simply enlarging the size of GDT tank, which is however constrained by the pore volume of cathode and catalysts deposited on it in the conventional Li$_2$O batteries. Moreover, as the reaction of O$_2$ in GDT is far apart from the electrodes, the tolerance of the cell towards air would be enhanced as well.

While promising, to develop RFLBO into a viable device for advanced large-scale energy storage, the large voltage hysteresis would have to be further reduced. In the present study, the stagnant reaction between triiodide and Li$_2$O and resistive Li$^+$-conducting membrane represent the main causes of the large overpotential during charging process. Faster redox mediators with matched potential to the oxidation of Li$_2$O and superior chemical resistance would be the ideal option. We are currently pursuing the above aspects to develop RFLBO into a low-cost and durable alternative to the Li$_2$O batteries for large-scale energy storage applications.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Materials and methods; Fig.S1-S4, CV curves of two redox molecules under various scan rates, the charge and discharge curves of RFLBO in the absence of redox mediators in the electrolyte, XRD and SEM micrograph of the formed Li$_2$O in GDT tank. See DOI: 10.1039/c000000x/