Greatly promoted oxygen reduction reaction activity of solid catalysts by regulating the stability of superoxide in metal-O₂ batteries

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ABSTRACT Oxygen reduction reactions (ORRs) with one- or two-electron-transfer pathways are the essential process for aprotic metal-oxygen batteries, in which the stability of superoxide intermediates/products (O₂^{•−}, LiO₂, NaO₂, etc.) mainly dominates the ORR activity/stability and battery performance. However, little success in regulating the stability of the superoxides has been achieved due to their highly reactive characteristics. Herein, we identified and modulated the stability of superoxides by introducing anthraquinone derivatives as co-catalysts which functioned as superoxide trapper adsorbing the superoxides generated *via* surface-mediated ORR and then transferring them from the solid catalyst surface into electrolyte. Among the studied trappers, 1,4-difluoroanthraquinone (DFAQ) with electron-withdrawing groups showed the highest adsorption towards superoxides and could efficiently stabilize LiO₂ in electrolyte, which greatly promoted the surface-mediated ORR rate and stability. This highlighted the magnitude of adsorption between the trapper and LiO₂ on the ORR activity/stability. Using an aprotic Li-O₂ battery as a model metal-O₂ battery, the overall performance of the cell with DFAQ was substantially improved in terms of cell capacity, rate capability and cyclic stability. These results represent a significant advance in the understanding of ORR mechanisms and promoting the performance of metal-O₂ batteries.

Keywords: oxygen reduction reaction, adsorption energy, superoxide, lithium oxygen battery

INTRODUCTION

Oxygen reduction reactions (ORRs) with one- (1e[−]) or

two-electron-transfer (2e[−]) pathways (M⁺+O₂+e[−]→MO₂; MO₂+M⁺+e[−]→M₂O₂) are the essential processes in aprotic metal-oxygen (M-O₂) batteries, which have been considered as one of the promising large-capacity batteries due to their high theoretical energy density [1–5]. The superoxide intermediates/products (MO₂, such as LiO₂ and NaO₂) are a kind of highly reactive agents, and their stability plays a dominant role in controlling the ORR activity/stability and overall performance of M-O₂ batteries [4–7]. In the last decade, numerous solid catalysts have been designed to improve ORR by optimizing the bond strength between the surface active sites and MO₂ [8–11]. However, ORR activity initiated from the active site is quickly lost due to the deposition of low conductive and film-like MO₂ and M₂O₂ products on the cathode, and this further results in termination of the surface-mediated ORR process at the solid catalysts [12–15], and thereby induces the low capacity and poor rate capability of the aprotic M-O₂ batteries [14,16,17]. Also, some strong oxidizing MO₂ intermediates, such as LiO₂ and NaO₂ can react with the electrolyte component *via* a nucleophilic reaction, leading to low ORR stability at the electrode surface and low cyclic stability of M-O₂ batteries [18–20]. Therefore, inhibition or stabilization of MO₂ from surface-mediated ORR is a key to improving the activity and stability of 1e[−] and 2e[−] ORR, as well as the overall performance of M-O₂ batteries.

Promoting solution-mediated 1e[−] and 2e[−] ORR with the aid of redox mediators (RMs) (RM[−]+M⁺+O₂→RM+MO₂; RM[−]+M⁺+O₂→RM+MO₂→RM+M₂O₂+O₂) [17,21–24],

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such as viologen [21], 2,5-di-*tert*-butyl-1,4-benzoquinone (DBBQ) [22] and coenzyme Q10 [23], is considered to be an effective strategy to inhibit the formation of adsorbed MO_2 from surface-mediated ORR, and thus postpone the deposition of MO_2 or M_2O_2 film on the cathode surface. However, this RM-assisted solution-mediated ORR is an indirect electron transfer process, and its reaction rate is limited by the diffusion rate of RM molecules [25–27], much lower than that of surface-mediated ORR involving a direct electron transfer pathway. Simultaneously, adsorbed MO_2 species are inevitably produced on the cathode surface, especially the catalytic cathode which has abundant active sites, and they cannot be stabilized by the reaction of RM^- and MO_2^+ : $\text{RM}^- + \text{MO}_2^+ + \text{Li}^+ \rightarrow \text{RM} + \text{M}_2\text{O}_2$ [28,29]. Hence, the stabilization of adsorbed MO_2 from surface-mediated ORR remains a significant challenge for achieving high-performance M- O_2 batteries.

In this study, modulation of MO_2 stability was achieved by introducing anthraquinone (AQ) derivatives to trap and stabilize the MO_2 generated from the solid catalyst surface and then transfer them into the electrolyte. Based on this cooperative catalysis between the solid catalyst and AQ derivatives, the ORR activity and stability of the solid catalysts were significantly enhanced. Difluoroanthraquinone (DFAQ), a trapper compound with electron withdrawing groups (two $-\text{F}$), showed the highest adsorption energy (AE) toward MO_2 and thus maximum ORR rate and stability (Fig. 1). The current densities at the defined potentials were over 10 times higher compared with the blank carbon catalysts. Taking the aprotic Li-O_2 battery as a model M- O_2 battery, DFAQ significantly boosted its discharge capacity ($4 \rightarrow 17 \text{ mA h cm}^{-2}$), cycle stability ($25 \rightarrow 171$ cycles) and rate capability (2–3 times).

EXPERIMENTAL SECTION

Preparation of CP@CNTs cathode

Carbon paper (CP) was cut into circular sheet with a diameter of 12 mm, and then soaked in acetone for 20 min to remove oil stains. After being dried at 30°C , it was treated by oxygen plasma for 5 min, and then immersed in 10 mL ethanol containing 400 mg $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ for 12 h. Self-supporting CP@carbon nanotube (CP@CNT) material was prepared with CP as substrate for the growth of CNTs, ethanol as carbon source and Ar-H_2 mixture as carrier gas at 700°C for 2 h.

Preparation of PSS-Li/GO-Li/GF separator

The preparation method of the separator refers to our previous report [30]. Briefly, lithiated graphene oxide

Figure 1 Schematic diagram of the role of Quinone-trapper in improving the oxygen reduction reaction (ORR) activity and stability. If the interaction between trapper and LiO_2 (simulated with different gesture) is stronger, the surface formed LiO_2 can be removed faster, and the surface-active sites can be regenerated more quickly. This ensures the high reaction rate of surface-mediated ORR. Simultaneously, the high interaction between Quinone-trapper and LiO_2 indicates the high stability of Quinone- LiO_2 complex and thus reduces the byproduct generated from LiO_2 , ensuring the high stability of surface-mediated ORR.

(GO-Li), lithium polystyrene sulfonate (PSS-Li) and silica were mixed in tetraethylene glycol dimethyl ether (TEGDME) solvent with a mass ratio of 4:10:15, and then the mixture was dispersed uniformly by ultrasound for 2 h. The above suspension was filtered into the glass fiber (GF) separator to form the polymer-based separator which was further filtered with the dropped 60 mL deionized water to obtain PSS-Li/GO-Li/GF separator. Finally, the separator was vacuum-dried at 60°C for 12 h.

Electrochemical cyclic voltammetry (CV)

CV was carried out on an Autolab electrochemical workstation (Metrohm) in a three-electrode system at 25°C . Carbon plates (1 cm^2) were used as the working electrodes, and lithium metal foils were used as the reference and counter electrodes, respectively.

Li- O_2 battery assembly

Li-O_2 batteries were assembled in glove boxes filled with Ar gas. CP@CNT was used as the cathode, and TEGDME dissolving 1 mol L^{-1} lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) was used as the electrolyte. Li foil and cathode were separated by the PSS-Li/GO-Li/GF separator. The cell capacities were calculated by the geometric area of cathode. All batteries were tested at 25°C .

Physical characterization

To characterize the discharged electrodes, all batteries were disassembled in an Ar-filled glove box. The electrodes

were washed by DME for three times to remove the electrolyte. The electrodes were then dried in a vacuum chamber for further characterization. X-ray diffraction (XRD) tests were carried out on a powder XRD system using Cu K α radiation (D8-ADVANCE, Bruker, Germany). Field emission scanning electron microscopy (FESEM, Nova NanoSEM 450, FEI, USA) was used to check the morphology of electrodes. Raman spectra were measured by Renishoin Via spectrometer (10 mW, 785 nm). For FTIR spectra test (VERTEX 70, Brook, Germany), the dried electrodes were scraped and pressed into a slice by mixing with KBr in the glove box. Proton nuclear magnetic resonance (^1H NMR) spectra were obtained on Bruker ADVANCE. DMSO- d_6 (dimethyl sulfide, DMSO) was used as the solvent and its chemical shift of ^1H NMR was 2.5 ppm. The quinone concentration was around 10 mmol L $^{-1}$ and the amount of KO $_2$ was excess. For the test of quinone+KO $_2$ +Li $^+$ sample, 0.1 mol L $^{-1}$ LiTFSI was added into the NMR tube containing quinone+KO $_2$. After that, the tube was quickly transformed into the NMR device.

Theoretical calculation

In order to study the adsorption energy of LiO $_2$ on different quinone molecules, the spin polarization density-functional-theory (DFT) calculations based on plane-wave were carried out using the Vienna *Ab initio* simulation software package. For confirming the exchange-correlation energy, we used the generalized gradient approximation function of Perdew-Burke-Ernzerhof (PBE). The electron-ion interaction was treated in the enhanced wave frame of the projector. The convergence criteria for electron and ion optimization were 10 $^{-5}$ eV and 0.01 eV $\text{\AA}^{-1}$, respectively, and the energy cut-off of plane wave basis set was 500 eV. The system energy was calculated at the Γ point. The interaction between adjacent atoms was eliminated by using a 30 $\text{\AA}$ $\times$ 30 $\text{\AA}$ $\times$ 30 $\text{\AA}$ box. In order to determine the local charge of atoms in the system, Bader charge analysis was used. Previous studies have shown that Bader charge analysis can correctly describe the charge states of atoms.

RESULTS AND DISCUSSION

Theoretical and experimental results for the bound state of the trapper-LiO $_2$ complex

The effect of the molecular structures of AQ derivatives on their binding strength toward LiO $_2$ was initially studied using DFT calculation. As shown in Fig. 2, the electron-donating moiety of 2-*tert*-butylanthraquinone

(TBAQ) increased the electron density of C=O, and the AE toward LiO $_2$ decreased from -1.01 to -0.98 eV compared with that of AQ (Fig. 2a and b) [29]. In contrast, the electron density of C=O in DFAQ decreased due to the electron-withdrawing effect of the fluorine group. Thus, DFAQ showed the highest LiO $_2$ AE of -1.06 eV among the three trappers (Fig. 2c).

To confirm the existence of trapper-LiO $_2$ species in the electrolyte, ^1H NMR spectroscopy was used to measure the ^1H chemical shifts (δ) of TBAQ and DFAQ in the presence of Li $^+$, KO $_2$, Li $^+$ and KO $_2$, respectively (Fig. 2d and f). A theoretical calculation of electron densities at the different carbon atoms of TBAQ and DFAQ was also obtained to evaluate δ (Fig. 2e and g). Compared with a previous report [29], the δ of DFAQ did not change when Li $^+$ was added (red and blue lines, Fig. 2d). The ^1H NMR gave three peaks at δ (ppm) 8.15, 7.92, 7.87, which were assigned to C1/C6, C2/C5, C3/C4, respectively. These were confirmed by theoretical calculation and shown in Fig. 2e (black square). After the addition of KO $_2$ alone, DFAQ was reduced to DFAQ $^-$ by KO $_2$ and six signals appeared at δ (ppm) 6.65, 7.12, 7.65, 7.75, 8.00 and 8.15 (pink line, Fig. 2d). They were confirmed to be C4, C3, C5, C2, C6 and C1, respectively (pink dot, Fig. 2e). After the addition of Li $^+$ and KO $_2$, the number of peaks was unchanged but the corresponding δ moved towards the high field region compared with that of DFAQ $^-$, indicating a decrease of electron density at carbon atoms. The decrease in chemical shift observed for the change from DFAQ $^-$ to DFAQ-LiO $_2$ was due to the introduction of Li $^+$ into situation of DFAQ and KO $_2$. The formation of DFAQ-LiO $_2$ complex was further confirmed by theoretical calculation (blue triangle, Fig. 2e). Similarly, TBAQ was reduced to TBAQ $^-$ when KO $_2$ was added. After adding both Li $^+$ and KO $_2$, the δ of ^1H on C1-C6 were also increased, indicating the transformation of TBAQ $^-$ to TBAQ-LiO $_2$ (Fig. 2f and g). As shown in Fig. 2g, the electron density of C atoms in the case of TBAQ with Li $^+$ and KO $_2$ was different from that of TBAQ with KO $_2$, consistent with the effect of LiO $_2$ on δ of TBAQ. Thus, the stable existence of TBAQ-LiO $_2$ species was demonstrated experimentally and theoretically.

Based on the above evidence, the quinone trapper could capture the LiO $_2$ from solid catalyst surface and transfer it into electrolyte, postponing the passivation of ORR activity sites. Consequently, the bound state of LiO $_2$ on the solid catalyst was also a key parameter requiring investigation. As shown in Fig. 3, taking widely used carbon as a model material, the AEs of LiO $_2$ on pristine graphene layer (Fig. 3a), single vacancy site (Fig. 3b) and hydroxyl

Figure 2 Simulated situation of LiO_2 adsorbed on TBAQ (a), AQ (b) and DFAQ (c). Adsorption energy is also provided for all the molecules. Red spheres represent “O”, green ones represent “Li”, pink ones represent “H”, and brown ones represent “C”. (d) ^1H NMR spectra of DFAQ after adding Li^+ , KO_2 , and both Li^+ and KO_2 . (e) Number of electrons at different carbon positions of DFAQ corresponding to (d). (f) ^1H NMR spectra of TBAQ after adding Li^+ , KO_2 , and both Li^+ and KO_2 . (g) Number of electrons at different carbon positions of TBAQ corresponding to (f). The carbon sites are marked with Arabic numerals in illustrations of DFAQ and TBAQ molecule structure, which are presented as the insets in (e) and (g), respectively.

Figure 3 The adsorption energies of LiO_2 on pristine carbon surface (a), single vacancy site (b) and hydroxyl modified single vacancy (c). The unit of the bond length is Å.

modified single vacancy (Fig. 3c) were calculated and these values were -0.08 , -1.27 , and -0.85 eV, respectively. The latter two results were close to the values of the binding energies of quinones on LiO_2 , which theoretically proved the feasibility of introducing the quinone trapper to prompt the surface-mediated ORR activity.

In addition to the thermodynamic binding energy results, the kinetic diffusion ability of these AQ-derivatives was another important parameter to enhance the surface-mediated ORR activity. The diffusion coefficient (DC) of AQ derivatives was then calculated by analyzing the CV curves with different scan rates. DFAQ and AQ both gave the comparable DCs (1.53×10^{-6} vs. $1.54 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), which were higher than those of TBAQ ($1.07 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and DBBQ ($6.28 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) (Fig. S1). The different DC values can be ascribed to the steric hindrance of functional groups, because one and two *tert*-butyl groups were present in TBAQ and DBBQ molecules, respectively. The above results indicated that DFAQ and AQ had high capabilities of transferring LiO_2 from the electrode to electrolyte. Additionally, the stability of these molecules was also investigated to confirm whether they were suitable to be used in Li-O₂ batteries. Fig. S2 shows that the CV curves of AQ and DFAQ were overlapped perfectly over 200 cycles. In contrast, a small

oxidation peak appeared in the profiles of DBBQ and TBAQ in the potential range of 3–4 V vs. Li^+/Li , which may be related to the oxidation of *tert*-butyl groups. We further confirmed the chemical stability of AQ derivatives and DBBQ after storage in KO_2 -saturated TEGDME solvent. This confirmed the high chemical stability of AQ and TBAQ toward O_2^- species (Fig. S3).

Influence of trapper- LiO_2 complex on surface-mediated ORR activity

Based on above results, the relationship between the AE of trapper- LiO_2 and the surface-mediated ORR activity was then investigated. As shown in Fig. 4a–c, the onset ORR potentials at the graphite carbon electrode were higher than the redox potentials of the three AQ derivatives (black line vs. red line), suggesting that the first step of ORR was O_2 accepting an electron from the electrode surface and combining with Li^+ to form LiO_2 [31]. In addition, all the AQ derivatives exhibited the new cathodic peaks (2.21 V for TBAQ, 2.40 V for AQ and 2.46 V for DFAQ) and the new cathodic peaks of the CV curves under O_2 could be assigned to the trapper- LiO_2 complex (blue line). These greatly enhanced ORR currents can be attributed to the improved surface-mediated ORR rate with the aid of quinone trappers. It should be

Figure 4 4 CV curves of AQ (a), TBAQ (b), DFAQ (c) under Ar (red), O_2 (blue) and the CV profiles of direct O_2 reduction (black). (d) Comparison of CV curves of AQ (black), TBAQ (red) and DFAQ (blue) under Ar. (e) Comparison of CV curves of these molecules under O_2 . (f) The relationship between ORR activity and adsorption energy of the trapper to LiO_2 . The electrolyte is 1 mol L^{-1} LiTFSI/TEGDME; a piece of CP is used as the working electrode; metallic lithium foils are used as the counter and the reference electrodes; the concentration of all additives is 10 mmol L^{-1} . The applied scan rate is 10 mV s^{-1} .

noted that the peak current densities of TBAQ- and DFAQ-assisted ORR were higher than that obtained with AQ (~ 0.8 vs. ~ 0.6 mA cm $^{-2}$). This may be due to the limited solubility of AQ molecule in LiTFSI/TEGDME electrolyte (<10 mmol L $^{-1}$, the solubility of TBAQ and DFAQ is much higher than 10 mmol L $^{-1}$). Owing to the electron-donating *tert*-butyl group of TBAQ and electron-withdrawing fluoro group of DFAQ, their redox potentials locate on the left and right of the original AQ, respectively (Fig. 4d). This trend is followed by the CV profiles under O $_2$ atmosphere (Fig. 4e), indicating that the surface-mediated ORR potentials are related to the stability of trapper-LiO $_2$ complex. At a current density of -0.3 mA cm $^{-2}$, the corresponding ORR potentials with the addition of TBAQ, AQ and DFAQ were 2.45, 2.52 and 2.60 V vs. Li/Li $^+$, respectively. At a constant ORR potential of 2.5 V vs. Li/Li $^+$, the current densities with the addition of TBAQ, AQ and DFAQ were -0.22 , -0.39 and -0.64 mA cm $^{-2}$, respectively (Fig. 4f). These results showed that AQ derivatives with different electron-donating/electron-withdrawing groups could regulate their redox potentials and the stability of trapper-LiO $_2$ species in a role that was a key to accelerate the surface-mediated ORR. The same situation was also found in polar DMSO solvent (Fig. S4), although higher redox potentials were obtained for AQ derivatives compared with those in TEGDME. This phenomenon could be attributed to the different polarities of the two solvents, and a similar result was observed in previous reports [32,33]. In this study, DBBQ, one of the best soluble ORR catalysts reported so far, was also chosen as the reference. The comparison of ORR current densities of these AQ derivatives and DBBQ in Fig. S5 showed that DFAQ- and TBAQ-assisted ORR currents were as high as the DBBQ-assisted value at the flat carbon electrode.

The mechanism of surface-mediated ORR in the presence and absence of trapper

In the absence of AQ derivatives, the LiO $_2$ produced *via* surface-mediated ORR are prone to self-disproportionation, resulting in the generation of film-like Li $_2$ O $_2$ products ($\text{Li}^+ + \text{O}_2 + \text{e}^- \rightarrow \text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2$) and deactivation of catalytic sites on the cathode surface [34,35]. In the presence of AQ derivatives, LiO $_2$ can be captured, stabilized and transferred from the cathode surface through the formation of stable complex with these additives. In this way, the surface LiO $_2$ disproportionation reaction was inhibited, and solution-growth of Li $_2$ O $_2$ was achieved. As a result, the catalytic active sites on the cathode surface can be regenerated, thus enhancing the catalytic ORR

current densities. Although the bond strength of DFAQ-LiO $_2$ (1.06 eV) was only 0.05 and 0.08 eV higher than those of AQ-LiO $_2$ (1.01 eV) and TBAQ-LiO $_2$ (0.98 eV), respectively, the surface-mediated ORR activities were greatly promoted (Fig. 4f). For example, at a potential of 2.5 V vs. Li/Li $^+$, the current density with the addition of DFAQ (-0.64 mA cm $^{-2}$) was about 2.9 and 1.6 times those of TBAQ and AQ, respectively. It indicates that a small increase of bond strength between the trapper and LiO $_2$ can greatly accelerate the capture and transfer of LiO $_2$ from the electrode surface. Thus, DFAQ can rapidly regenerate the catalytic active sites and promote the surface-mediated ORR activities.

The performance of Li-O $_2$ battery in the presence of trapper-LiO $_2$ complex

The above results showed that DFAQ trapper had the advantages of promoting surface-mediated ORR and high electrochemical stability. Therefore, it was introduced as additives in the LiTFSI/TEGDME electrolyte to improve the performance of Li-O $_2$ batteries. The self-supporting CP@CNTs (the preparation method of CP@CNT electrode and its morphology is shown in Fig. S6) and metallic lithium were used as the O $_2$ cathode and anode, respectively. A PSS-Li/GO-Li/GF membrane separator was used to alleviate the diffusion of redox chemicals from cathode to anode (the surface morphology of PSS-Li/GO-Li/GF separator is shown in Fig. S7, and the inhibited diffusion of redox chemicals by PSS-Li/GO-Li/GF separator can be found in Fig. S8). Fig. 5a–d and Fig. S9 show that batteries without additive and with 10 mol L $^{-1}$ AQ, TBAQ, DFAQ, DBBQ molecules could deliver 5.2, 7.0, 7.5, 13.5 and 6.5 mA h cm $^{-2}$, respectively, at a current density of 100 μ A cm $^{-2}$. When the current density was increased to 500 μ A cm $^{-2}$, the corresponding capacities decreased to 2.3, 4.5, 5.5, 10.6, and 2.7 mA h cm $^{-2}$, respectively. The results clearly showed that DFAQ could provide the maximum improvements of battery capacities from 5.2 to 13.5 mA h cm $^{-2}$ and 2.3 to 10.6 mA h cm $^{-2}$, respectively, at different current densities compared with those of the blank references. Fig. 5a also shows that the batteries with DFAQ had the lowest capacity fade rate of 22%, indicating its excellent rate capability. Compared with previously reported AQ, the capacities of the battery with DFAQ increased to about 2.0 times at 100 μ A cm $^{-2}$ ($7.0 \rightarrow 13.5$ mA h cm $^{-2}$) and 2.4 times at 500 μ A cm $^{-2}$ ($4.5 \rightarrow 10.6$ mA h cm $^{-2}$). The enhanced capacity could be attributed to the higher surface-mediated ORR activity in the presence of DFAQ than that of AQ. To confirm the role of these additives on the cell capacities, the mor-

Figure 5 (a) Cell discharge capacities with the additives at different current densities. SEM images of the discharged products with (b) AQ, (c) TBAQ, (d) DFAQ and (e) DBBQ at a capacity of 2 mA h cm^{-2} . (f) Schematic diagram for the role of LiO_2 adsorption energy on battery capacity.

phology of discharge products was observed by SEM (Fig. 5b–e). The discharge products without AQ derivatives exhibited a typical toroid structure with a diameter of about 500 nm (Fig. S10). For DFAQ (Fig. 5d), the diameter and thickness of the discharge products increased when compared with those without additives, like the condition of AQ and TBAQ (Fig. 5b and c). The discharge products in the presence of DBBQ were of a larger size compared with those obtained using AQ derivatives. The different morphologies of the discharge products with different quinones can be attributed to different ORR mechanisms, of which the enhanced surface-mediated and solution-mediated ORR activities evolved in the presence of AQ derivatives and DBBQ, respectively.

As shown in Fig. 5f, the higher AE of LiO_2 can assist the transfer of LiO_2 from the electrode surface into the electrolyte more efficiently, avoiding the formation of film-like Li_2O_2 and further ensuring the availability of surface-active sites. Under these conditions, surface-mediated ORR can occur efficiently on the cathode surface. As discussed above, the high AE of LiO_2 can efficiently regenerate surface-active sites to maintain the duration of high ORR rates. Shortly after, the high cell capacity and rate capability are realized. It is interesting to note that the capacity of the battery with DBBQ reduced by 59% when the current was increased from 100 to $500 \mu\text{A cm}^{-2}$ (Fig. 5a). There were two reasons that could explain this result. Firstly, solution-mediated ORR with DBBQ had a different discharge mechanism compared with surface-mediated ORR with the AQ derivative [22,36–38]. DBBQ was initially reduced to DBBQ^-Li^+ in the electrolyte and then oxidized by O_2 to form DBBQ-LiO_2 , which further transferred back to DBBQ after disproportionation ($2\text{DBBQ-LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + 2\text{DBBQ} + \text{O}_2$) or reduction ($\text{DBBQ-LiO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{DBBQ} + \text{Li}_2\text{O}_2$). The rate

of solution-mediated ORR based on an indirect electron transfer pathway was much lower than the surface-mediated ORR pathway based on a direct electron transfer pathway. Secondly, DFAQ possessed a higher DC than DBBQ (1.53×10^{-6} vs. $6.28 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$). The solution growth of Li_2O_2 via the assistance of DFAQ was much faster than that via DBBQ. The acceleration of surface-mediated ORR by LiO_2 trapper is of great significance to solve the problems of electron transfer constraints and deactivation of active sites caused by the film-like and insulating Li_2O_2 . This finding will help to overcome the low capacity and rate capability limitations of Li– O_2 batteries.

The increased stability of LiO_2 intermediate without and with trappers not only affects the capacity and rate capability of Li– O_2 batteries, but also influences their cycle stability due to the reduced oxidation activity of LiO_2 in the bound state (anthraquinones– LiO_2). To confirm this point, the cyclic tests of assembled Li– O_2 batteries were conducted at a fixed capacity of 0.5 mA h cm^{-2} at $100 \mu\text{A cm}^{-2}$. As shown in Fig. S11, the batteries without additive and with DBBQ, AQ, TBAQ, DFAQ were maintained over 20, 29, 32, 28 and 53 cycles, respectively.

As previously reported, the cathode surface was usually passivated during battery cycling. This was due to the accumulation of byproducts caused by the electro-oxidation of electrolyte/electrode at high charging potentials, and the chemical reaction between electrolyte/electrode and radical species, such as MO_2 and the singlet O_2 ($^1\text{O}_2$) which was also detected during battery operation, especially at high charging potentials [39–43]. To evaluate the critical role of quinones during battery operation more accurately, the side reaction originating from high charging potentials and $^1\text{O}_2$ species should be reduced as much as possible. Consequently, the introduction of oxygen evolution reaction (OER) redox mediators was

considered as an efficient method to reduce charging potentials, and 2,2,6,6-tetramethylpiperidine-*N*-oxyl [44,45] was simultaneously added into the electrolyte. As expected, and DFAQ-assisted Li-O₂ battery also performed the best (Fig. 6b). The battery cycle life with DFAQ was 2.6 times compared with those with AQ (105 vs. 40 cycles) and 4.0 times compared with those without additives (105 vs. 26 cycles) (Fig. 6a).

In order to clarify the reason for the effect of the LiO₂ bound state on cell cyclic stability, the composition of product on the cathode was characterized with different techniques. XRD patterns showed two peaks at about 33° and 35° assigned to crystalline Li₂O₂ (Fig. 6c) [46,47]. The Raman spectra showed the peaks at 250 and 790 cm⁻¹ corresponding to Li₂O₂. When AQ, TBAQ and DBBQ were added, peaks corresponding to C-O bond appeared at ~1100 cm⁻¹, indicating the existence of Li₂CO₃ in these cases (Fig. 6d) [46,48,49]. The peak at 1100 cm⁻¹ was not observed for DFAQ, consistent with the effect of DFAQ-LiO₂ complex on the stability of the electrolyte and batteries. Specifically, DFAQ could effectively bind and stabilize the LiO₂ intermediate, avoiding the formation of byproducts caused by LiO₂ (Fig. 6e). Infrared (IR) spectra further confirmed that Li₂O₂ was the primary discharge product (Fig. S12).

Based on the above findings, we investigated the influence of trapper concentration on ORR activity and the performance of Li-O₂ batteries (Figs S13–S15). The cell capacities and cyclic stability of the Li-O₂ batteries reach

the maximum value of 16.8 mA h cm⁻², and 170 cycles with 30 mmol L⁻¹ DFAQ at a fixed capacity of 0.5 mA h cm⁻² at 100 μA cm⁻². The SEM, XRD, Raman and IR results confirmed that Li₂O₂ was the only product (Figs S16 and S17). These results demonstrated the most improved cooperative ORR catalysis in M-O₂ batteries reported so far.

CONCLUSIONS

To date, the attainment of high activity and stability in ORR involving 1e⁻ and 2e⁻ pathways in aprotic media has been impeded by the low stability of MO₂ intermediate, which severely limits the discharge capacity, rate performance and cycle life of M-O₂ batteries. In this study, an aprotic Li-O₂ system, representing a 2e⁻ ORR model, was used to modulate the stability of MO₂ by introducing AQ derivatives as the cocatalyst. Among the studied molecules, DFAQ with electron-withdrawing substituents had the highest LiO₂ AE and formed the most stable complex with LiO₂, i.e., DFAQ-LiO₂. This greatly improved the surface-mediated ORR rate and reduced the side reactions related to LiO₂. Compared with the batteries without LiO₂ trapper, the capacity, cycle life and rate performance of Li-O₂ batteries with DFAQ were increased by 4, 5 and 3 times, respectively. These findings surpassed the reported performance of DBBQ catalyst and AQ trapper, which had, so far, exhibited the highest capability in enhancing cathodic ORR. This study provides an important understanding of the mechanism of

Figure 6 (a) Comparison of cell cyclic stability of the battery without quinone (black), with DBBQ (red), with AQ (blue), with TBAQ (pink), and with DFAQ (green) in the presence of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO). (b) Charge/discharge profiles of battery with DFAQ and TEMPO. (c) XRD and (d) Raman spectra of the discharged electrodes with additives. The dashed rectangle in (d) indicated the byproducts. (e) Schematic diagram for the influence of LiO₂ adsorption energy on side reaction induced by LiO₂.

surface-mediated ORR and its application in M-O₂ batteries. It should also provide a valuable guide for improving the performance of other energy storage devices and the catalytic reactions with similar mechanisms.

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金属-氧气电池中调控超氧化物稳定性实现大幅增强的固体催化剂氧还原反应活性

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摘要 单电子或双电子氧还原反应(ORR)是非质子型金属-氧气电池的关键过程, 其中超氧化物中间体或产物(O₂^{•−}, LiO₂, NaO₂等)的稳定性决定了催化剂的ORR活性/稳定性和电池的整体性能。然而, 超氧化物具有高反应活性的特点导致其稳定性难以调控。本文将蒽醌衍生物作为助催化剂, 成功实现了超氧化物稳定性的调控。在ORR过程中, 该助催化剂首先吸附固体催化剂表面生成的超氧化物, 并将其转移至电解液中。研究发现, 含吸电子基团的1,4-二氟蒽醌(DFAQ)对超氧化物的吸附强度最高, 能最大程度地将LiO₂稳定在电解液中, 从而大幅提高了表面ORR的反应速率和稳定性。这一结果证明助催化剂对LiO₂吸附能的强弱对ORR的活性/稳定性具有重要影响。以锂氧电池作为金属-氧气电池的模型器件, 发现DFAQ分子的引入能够显著提高电池的容量、倍率性能和循环稳定性。本工作有助于深入理解ORR反应机制和提高金属-氧气电池的电化学性能。