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## Lithium Salt Dissociation Promoted by 18-Crown-6 Ether Additive toward Dilute Electrolytes for High Performance Lithium Oxygen **Batteries**

Fengling Zhang, Jingning Lai,\* Zhengqiang Hu, Anbin Zhou, Huirong Wang, Xin Hu, Lijuan Hou, Bohua Li, Wen Sun, Nan Chen, Li Li, Feng Wu, and Renjie Chen\*

Abstract: Lithium-oxygen batteries (LOBs) are well known for their high energy density. However, their reversibility and rate performance are challenged due to the sluggish oxygen reduction/evolution reactions (ORR/OER) kinetics, serious side reactions and uncontrollable Li dendrite growth. The electrolyte plays a key role in transport of Li<sup>+</sup> and reactive oxygen species in LOBs. Here, we tailored a dilute electrolyte by screening suitable crown ether additives to promote lithium salt dissociation and Li<sup>+</sup> solvation through electrostatic interaction. The electrolyte containing 100 mM 18crown-6 ether (100-18C6) exhibits enhanced electrochemical stability and triggers a solution-mediated Li<sub>2</sub>O<sub>2</sub> growth pathway in LOBs, showing high discharge capacity of 10828.8 mAh  $g_{carbon}^{-1}$ . Moreover, optimized electrode/electrolyte interfaces promote ORR/OER kinetics on cathode and achieve dendrite-free Li anode, which enhances the cycle life. This work casts new lights on the design of low-cost dilute electrolytes for high performance LOBs.

#### Introduction

Lithium-oxygen batteries (LOBs) demonstrate the promising prospects of long-range electric vehicles and portable power equipment owning to their high theoretical energy density ( $\approx 3500 \text{ Whkg}^{-1}$ ).<sup>[1]</sup> However, multi-step ORR/OER reactions lead to sluggish kinetics of LOBs. The insulating discharge product Li<sub>2</sub>O<sub>2</sub> is easy to block the pores in

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cathodes and cause battery "sudden death". Moreover, severe parasitic reactions occur in LOBs due to the existence of highly reactive oxygen species and reductive lithium metal anode, resulting in electrolyte decomposition, electrodes corrosion and uncontrollable Li dendrite growth. Therefore, current LOBs suffer from high overpotential, limited practical capacity, short cycle life and poor rate performance, which are difficult to meet the requirements of practical applications.<sup>[2]</sup> Electrolytes are the links between the oxygen cathodes and Li anodes. Suitable electrolyte designs are crucial to the construction of electrodes/electrolyte interfaces, which further affect the formation/decomposition of discharge products, suppression of side reactions and Li stripping/plating in LOBs.

To solve the aforementioned challenges, a N,N-dimethvlacetamide-based electrolyte was designed to protect the Li anode and promote the cycle performance of LOBs.<sup>[3]</sup> A halide ester additive was introduced into conventional ether electrolytes to promote the dissolution of Li2O2, thus achieving good rate performance and cycle stability of LOBs.<sup>[4]</sup> However, few works concentrated on electrolyte solvation structure design and related electrode/electrolyte interface construction to meet the demands of both cathodes and anodes in LOBs. Localized high-concentration electrolytes (LHCE) using hydro-fluoroether as diluents show high oxygen solubility, low viscosity and good electrochemical stabilities, which lead to the long cycle life of LOBs.<sup>[5]</sup> Considering the high cost of hydro-fluoroether, we designed a local strong solvation effect electrolyte (LSSE) in our previous work, combining the benefits of high-donor number (DN) solvents and low-DN solvents.[2d] Although dilutes are used, the lithium salt concentrations in LHCE and LSSE are still higher than conventional electrolytes. Therefore, high performance dilute electrolyte candidates need to be further designed.

The interaction force between Li<sup>+</sup> and anion is strong in aprotic solvents, and lithium salt is difficult to be completely dissociated in an aprotic electrolyte even at low concentration. Therefore, anions are inevitably involved in the construction of Li+ solvation sheath, which affects the reaction kinetic and stability of electrode/electrolyte interfaces in LOBs. Promoting dissociation of lithium salt and reducing free solvent molecules can broaden the electrochemical stability of the electrolyte.<sup>[6]</sup> Herein, we propose a dilute electrolyte by screening suitable sized crown ether additives based on 1 M LiClO<sub>4</sub>/dimethyl sulfoxide (DMSO)

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electrolyte. We found that large-sized 18C6 additive promotes the lithium salt dissociation and Li<sup>+</sup> solvation by electrostatic interaction, improves ionic conductivity and broadens the electrochemical stability of electrolyte. Accordingly, the electrolyte solvation structure regulated by 18C6 triggers solution-mediated growth mechanism of toroidal Li<sub>2</sub>O<sub>2</sub> formation, suppresses H-abstraction related side reactions inside the battery and facilitates the formation of anion-derived solid electrolyte interphase (SEI) and dendrite-free Li anode (see Scheme 1). The designed LOBs exhibit high discharge specific capacity а  $(10828.8 \text{ mAh} g_{\text{carbon}}^{-1})$ , enhanced OER/ORR kinetics, an improved cyclic stability (over 128 cycles with a capacity of 1000 mAh  $g_{carbon}^{-1}$  at a current density of 400 mA  $g_{carbon}^{-1}$ ). Furthermore, the gases generation caused by the uncontrollable side reactions is significantly inhibited. This work will spur effective electrolyte design and provide a low-cost strategy in enhancing the electrochemical performance of LOBs.

### **Results and Discussion**

Molecular dynamics (MD) simulations were carried out to understand the influence of crown ether additives on the solvation structure of LiClO<sub>4</sub>/DMSO mixtures. An NPT simulation (isothermal-isobaric ensemble) was used to equilibrate the mixtures with a pressure of 0.1 GPa and a decay constant of 0.1 ps for 50 ps. The snapshot containing  $20 \text{ Li}^+$  ions,  $20 \text{ ClO}_4^-$  ions and 263 DMSO molecules are shown in Figure 1a to simulate the coordination environment of 1 M LiClO<sub>4</sub>/DMSO electrolyte. On this basis, two 12-crown-4 ether (12C4), 15-crown-5 ether (15C5) or 18C6 molecules were added to verify their effect on the electrolyte solvation structures (Figure S1a, S1b and Figure 1b). The ClO<sub>4</sub><sup>-</sup> inevitably participate in the construction of electrolyte solvation structures, and the electrolyte with 15C5 shows the most concentrated  $Li^+$  and  $ClO_4^-$  distribution. The schematics of the first coordination sheaths around a Li<sup>+</sup> in different electrolytes are extracted from MD simulations (Figure 1c and Figure S2). The electrolyte with 18C6



**Scheme 1.** Schematic illustrations of the reaction path and  $H_2$  release mechanism in LOBs with and without additive electrolyte.

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shows increased free  $\text{ClO}_4^-$  anions and a decreased free DMSO solvent molecules around a Li<sup>+</sup> compared with other electrolytes, indicating that lithium salt dissociation and solvation of Li<sup>+</sup> are promoted.<sup>[7]</sup>

Further information is available from the radical distribution functions (RDF) and corresponding running Li<sup>+</sup> coordination numbers (CN) (Figure 1d and 1e, Figure S1c and 1d). The first  $Li^+$  solvation sheath of 1 M LiClO<sub>4</sub>/ DMSO electrolyte containing 1.83  $ClO_4^-$  and 2.78 DMSO. The electrolyte with 12C4 shows slightly changed results with increased  $ClO_4^-$  (CN=1.87) and decreased DMSO (CN=2.72). The first  $Li^+$  solvation sheath of electrolyte with 15C5 consists the most  $ClO_4^-$  (CN = 2.34) and the least DMSO (2.32), while that of 18C6 shows the opposite trend with 1.44 ClO<sub>4</sub><sup>-</sup> and 2.94 DMSO. The distance between Li<sup>+</sup> and  $O_{ClO_4^-}$  in the first Li<sup>+</sup> solvation sheath of electrolyte with 18C6 increased to 1.87 Å compared with other electrolytes (1.83 Å), further suggesting that 18C6 weakened Li-O CIO<sub>4</sub>- bonds and promoted lithium salts dissociation.<sup>[2d]</sup> 12C4 and 18C6 barely participate in the construction of first Li<sup>+</sup> solvation sheath, while 15C5 shows an obvious Li-O<sub>15C5</sub> peak at 2.83 Å with a CN of 0.25.

The DN values of crown ethers were estimated to explain their different effect on the Li<sup>+</sup> solvation sheath according to the linear trend of the <sup>23</sup>Na nuclear magnetic resonance (NMR) shift (Figure 1f and 1g). The 18C6 shows the lowest chemical shift of -15.691, which indicates the lowest DN value of 2.15 (Table S1, Supporting Information) and the weakest binding ability with Li<sup>+</sup>.<sup>[8]</sup> The larger ring size of the crown ether additive lead to the weaker Li<sup>+</sup> complexation ability.<sup>[9]</sup> The Li<sup>+</sup> complexation ability of 12C4 (DN=27.2) is the strongest among the three crown ethers, but it is still weaker than that of DMSO (DN=29.8). It is difficult for 12C4 to enter the preferentially formed ClO<sub>4</sub>and DMSO-based first Li<sup>+</sup> solvation sheath due to its small ring size. Therefore, the addition of 12C4 has little effect on the solvation structure of DMSO-based electrolyte. 15C5 has medium ring size and moderate complexation ability with Li<sup>+</sup>. It can participate in the construction of the first Li<sup>+</sup> solvation sheath and compete with DMSO solvent molecules to coordinate with Li<sup>+</sup>, but it indirectly enhances the association between Li<sup>+</sup> and ClO<sub>4</sub><sup>-</sup>. 18C6 hardly participates in the construction of the first Li<sup>+</sup> solvation sheath due to its largest ring size and the weakest Li<sup>+</sup> complexation ability. Interestingly, it can promote the coordination of Li<sup>+</sup> with DMSO.

The coordination environments around Li and H atoms in the solvation sheath of different electrolytes were detected by <sup>7</sup>Li and <sup>1</sup>H NMR.<sup>[10]</sup> The detailed shifts are provided in Figure 1h, 1i and Table S2. The <sup>7</sup>Li and <sup>1</sup>H NMR peaks of 100-18C6 electrolyte showed the most negative value, which indicates that the addition of 18C6 increases the solvent-Li<sup>+</sup> interaction in the solvation sheath.<sup>[10b,11]</sup> Fourier transform infrared spectroscopy (FTIR) was performed to assess the organic functional groups in the electrolyte with 18C6. In Figure S3, with increasing of 18C6 concentration, the peaks corresponding to C–H, C–C and C–O–C bonds gradually stronger, which provide more electrophilic/nucleophilic sites to regulate the Li<sup>+</sup> solvation



**Figure 1.** MD simulation snapshots of (a) 1 M LiClO<sub>4</sub>/DMSO and (b) 100-18C6+1 M LiClO<sub>4</sub>/DMSO. c) MD simulations of the molecular structures of 100-18C6+1 M LiClO<sub>4</sub>/DMSO. RDF g(r) (broken lines) and n(r) (solid lines) of the Li-O<sub>CIO<sub>4</sub></sub>-, Li-O<sub>DMSO</sub>, and Li-O<sub>12C4/15C5/18C6</sub> pairs calculated from MD simulation trajectories at 303 K in (d) 1 M LiClO<sub>4</sub>/DMSO, (e) 100-18C6+1 M LiClO<sub>4</sub>/DMSO. (f and g) <sup>23</sup>Na NMR of each solvent (DMF: N, N-Dimethylformamide) and DMSO solvent containing different additives. All samples were characterized neat. h) <sup>7</sup>Li NMR and (i) <sup>1</sup>H NMR of different electrolytes. j) The MESP energy surface of DMSO, ClO<sub>4</sub><sup>-</sup> and 18C6 molecules (kcal mol<sup>-1</sup>).

structure.<sup>[6a,12]</sup> The electrophilic/nucleophilic sites of DMSO, ClO<sub>4</sub><sup>-</sup> and 18C6 were predicted via molecular electrostatic potential (MESP) calculation (Figure 1j). In a 18C6 molecule, the C–O–C groups exhibit nucleophilicity, while C–H and C-C groups show electrophilicity, which have electrostatic adsorption effect on negatively charged ClO<sub>4</sub><sup>-</sup> anions to promote lithium salt dissociation.<sup>[13]</sup> Meanwhile, DMSO molecules with strong nucleophilic S=O groups are more involved in the first solvation sheath to bind with Li<sup>+</sup>.<sup>[14]</sup> To optimize the concentration of 18C6 additive, MD simulations of electrolytes containing 50 mM 18C6 (50-18C6) and 200 mM 18C6 (200-18C6) are given in Figure S4, and the CNs of different electrolytes are aggregated in Figure S5. All electrolytes with 18C6 showed decreased CN of Li-O  $_{\text{CIO}_{4}^{-}}$  and increased CN of Li-O\_{DMSO} compared with blank electrolyte, indicating the promoted lithium salt dissociation, enhanced Li+ solvation and decreased free solvent molecules. Among them, 100-18C6 electrolyte showed the lowest CN of Li-O<sub>CIO,-</sub> and the highest CN of Li-O<sub>DMSO</sub>, owing to the appropriate amount of additive and optimized electrolyte solvation structure. This result was confirmed by <sup>7</sup>Li NMR signals of electrolytes containing different concentration of 18C6 (Figure S6). The 100-18C6 electrolyte shifted the most negative value of -0.0477 ppm, indicating the strongest solvent-Li<sup>+</sup> interaction and the maximum electron density around Li<sup>+</sup>.<sup>[10b,11]</sup>

We conducted electrochemical tests by assembling Li-O<sub>2</sub> cells to study the effects of additives on battery performance. The schematic diagram of the battery assembly is shown in Figure 2a, where Li metal is used as the anode and Ketjen black (KB, carbon) as the air cathode. The electrochemical impedance spectra (EIS) of LOBs were tested to contrast the interface impedance between electrolytes and electrodes (Figure 2b). It can be seen that the cell with 100-18C6 additive electrolyte shows the lowest charge transfer impedance  $(R_{ct})$  of 26.67 ohm, followed by 200-18C6 (48.13 ohm), 50-18C6 (66.32 ohm), and 0-18C6 (82.84 ohm) electrolytes. Ionic conductivity of different electrolytes was calculated through EIS measurement of stainless-steel symmetric cells (Figure 2c and Figure S7). The ionic conductivities of 0-18C6, 50-18C6, 100-18C6, 200-18C6 electrolytes are 1.96, 3.03, 3.96,  $3.18 \text{ mS cm}^{-1}$ , respectively. The



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*Figure 2.* a) The schematic of the assembled LOBs. b) The EIS spectra of different electrolytes in LOBs. c) The EIS spectra of different electrolytes in stainless steel pair cells. d) The full discharge performance of LOBs in different electrolytes at a current density of 100 mAg<sub>carbon</sub><sup>-1</sup>. SEM images of the KB cathodes after full discharge in (e) blank electrolyte, (f) 50-18C6, (g) 100-18C6 and (h) 200-18C6 electrolytes. i) CV plots of LOBs with different electrolytes at a scan rate of 0.1 mV s<sup>-1</sup>. j) Cyclic voltammograms measured on a KB working electrode in 100-18C6 electrolyte with O<sub>2</sub> (solid line) and Ar (broken line) atmosphere. k) EIS of first discharged and charged LOBs with 100-18C6 electrolyte and (l) their corresponding analog circuit diagram. m) Cyclic performance of the LOBs with different electrolytes under a capacity limitation of 1000 mAh g<sub>carbon</sub><sup>-1</sup> at 400 mAg<sub>carbon</sub><sup>-1</sup>.

addition of 18C6 significantly improved the ionic conductivity of 1 M LiClO<sub>4</sub>/DMSO dilute electrolyte, and the 100-18C6 electrolyte showed the best result.<sup>[6b,15]</sup> As shown in Figure 2d, the full discharge capacity of Li-O<sub>2</sub> cells containing different concentrations of 18C6 were tested at a current density of 100 mAg<sub>carbon</sub><sup>-1</sup> with a cutoff voltage of 2.5 V. Among them, the cell with 100-18C6 electrolyte shows the maximum discharge capacity with 10828.8 mAhg<sub>carbon</sub><sup>-1</sup>, followed by cells with 200-18C6 (8879.2 mAhg<sub>carbon</sub><sup>-1</sup>) and 50-18C6 (5928.8 mAhg<sub>carbon</sub><sup>-1</sup>) electrolytes. The discharge capacity of Li-O<sub>2</sub> cell with blank electrolyte is only 1714.0 mAhg<sub>carbon</sub><sup>-1</sup>. It experienced a sudden death owing to serious cathode clogging. In addition, the ORR discharge platforms of cells with 18C6 are significantly higher than that with blank electrolyte, which means 18C6 can reduce the discharge overpotential of LOBs. The Li-O<sub>2</sub> cells with 100-15C5 and 100-12C4 electrolytes deliver low discharge capacity of 2253.0 mAh  $g_{carbon}^{-1}$  and 1247.0 mAh  $g_{carbon}^{-1}$  (Figure S8, Supporting Information), respectively. The results are consistent with MD simulations, which confirmed the enhanced Li<sup>+</sup> solvation in electrolytes containing 18C6. The  $O_2^{-}$  formed during discharging was stabilized in electrolytes containing 18C6 instead of associating with Li<sup>+</sup> to form LiO<sub>2</sub> and fast transforming to Li<sub>2</sub>O<sub>2</sub>. Thus, a solution-mediated Li<sub>2</sub>O<sub>2</sub> growth pathway was triggered, which avoids cathode clogging and increases discharge capacity of LOBs.<sup>[16]</sup> The scanning electronic microscopy (SEM) images of the surfaces of cathodes after full discharge are shown in Figure 2e–h. In the cell without additive, the small granular discharged products completely cover the surface of KB cathode and blocked its pores. In the cell with the 50-18C6

electrolyte, the cathode clogging problem is alleviated but the discharge products are still small particles.

In cells with 100-18C6 and 200-18C6 electrolytes, their discharge products show typical large-sized toroidal structure, and their cathodes remain porous. The results prove that electrolytes with 18C6 can promote the solution-mediated  $\text{Li}_2\text{O}_2$  growth and prevent the pore blockage on the cathode.

Cyclic voltammetry (CV) curve of cells with different concentrations of 18C6 under the O<sub>2</sub> and Ar atmosphere are shown in Figure 2i and 2j. No obvious redox peak was observed in cell with 100-18C6 electrolyte under Ar atmosphere. Under O2 atmosphere, enhanced reduction peaks and oxidation peaks are exhibited corresponding to cells with 18C6, indicating the promoted ORR/OER kinetics. The most obvious promotion effect was observed in cell with the 100-18C6 electrolyte. Moreover, the oxidation peak ascribed to electrolyte or KB cathode decomposition shifted to higher potential of 4.438 V in cell with 100-18C6 electrolyte, compared with 4.371 V in the cell without additive, indicating the broadened electrochemical stability of 100-18C6 electrolyte.<sup>[17]</sup> Figure 2k shows the EIS results of cells with 100-18C6 electrolyte after first discharging and charging. A semicircle and a slope line of EIS contain solution impedance  $(R_s)$ , cathode/electrolyte charge transfer impedance (R<sub>1</sub>), Li anode/electrolyte charge transfer impedance (R<sub>2</sub>) and Warburg diffusion impedance (W), respectively. The change of  $R_1$  is related to the deposition of discharge products. During the discharge process, the surface of the cathode is covered with insulating Li<sub>2</sub>O<sub>2</sub>, resulting in the increase of impedance.<sup>[18]</sup> The corresponding equivalent circuit from the simulation of Nyquist plot are provided (Figure 21). The cell with 100-18C6 electrolyte showed the smallest  $R_1$  of 20.31  $\Omega$  after the first discharging and 16.84  $\Omega$  after the first charging, compared with those cells with other electrolytes (Figure S9, S10, and S11, Supporting Information). The smaller charge transfer resistances represent enhanced solution-mediated reaction mechanism and suppressed side reactions during ORR/OER process. Furthermore, the cycling performance of LOBs with and without additives was studied with a limited capacity of  $1000 \text{ mAh} g_{\text{carbon}}^{-1}$  at a current density of  $400 \text{ mAg}_{\text{carbon}}^{-1}$ .

As can be seen in Figure 2m and in Figure S12, the cell with blank electrolyte only operated 9 stable cycles owning to serious side reactions. The cells with the 50-18C6, 100-18C6 and 200-18C6 electrolytes obtained 20, 128 and 23 stable cycles, respectively. The battery cycle performance with limited capacity is superior to some other reported results (Table S3, Supporting Information). The enhanced cycling performance of cell with 100-18C6 electrolyte is attributed to the promoted ORR/OER kinetics in cathode/ electrolyte interface, suppressed side reactions on carbon cathode or in electrolyte, and stabilized anode/electrolyte interface with increased free ClO<sub>4</sub><sup>-</sup> anions and decreased free DMSO molecules. The SEM images in Figure S13 and Figure S14 are cathode surfaces of cells with different electrolytes after the first discharge/charge process with a limit capacity of 1000 mAh g<sub>carbon</sub><sup>-1</sup> at a current density of  $200 \text{ mAg}_{\text{carbon}}^{-1}$ . In the cell with blank electrolyte, the cathode surface was seriously blocked by the discharge products after discharging and remained partially blocked after charging. The cathodes of the cells with 100-18C6 electrolyte remained porous after discharging, and the discharge product particles completely decomposed after charging.

Figure 3a-h show the X-ray photoelectron spectroscopy (XPS) results of these cathode surfaces in cells with different electrolytes after the first discharge/charge process. The cathode surface in cell with 100-18C6 electrolyte exhibits the strongest Li2O2 peak and the weakest Li2CO3 peak after discharging, and the peaks disappeared after charging, indicating that cell with 100-18C6 electrolyte has the most obvious effect on inhibiting side reactions of reactive oxygen species with electrolyte and carbon cathode.<sup>[19]</sup> In contrast, by-product peaks (Li<sub>2</sub>CO<sub>3</sub> and LiOH) remained on the cathode surface of cells with other electrolytes after charging, inducing large cell impendence, which is consistent with previous EIS results.<sup>[20]</sup> In situ Raman spectra were performed to observe the formation/decomposition process on the cathode/electrolyte interface. As shown in Figure 3i and 3j, the cell with 100-18C6 electrolyte exhibits a low charging plateau at 3.9 V, while the cell with blank electrolyte showed a high charging plateau of 4.4 V. The Li<sub>2</sub>O<sub>2</sub> signal appeared at  $\approx 790 \text{ cm}^{-1}$  during discharging and disappeared during charging in the cell with 100-18C6 electrolyte.<sup>[8a]</sup> In contrast, the cell with blank electrolyte only detected the Li<sub>2</sub>CO<sub>3</sub> peak at  $\approx 1080$  cm<sup>-1</sup> during discharging, Li<sub>2</sub>CO<sub>3</sub> was difficult to decompose during charging. Moreover, new peaks assigned to LiOH (618 cm<sup>-1</sup>) and Li<sub>2</sub>RCO<sub>3</sub> (1008 cm<sup>-1</sup>) appeared during final charging process owing to the irreversible decomposition of electrolyte.<sup>[21]</sup> The  $ClO_4^{-}$  (  $\approx$  935 cm<sup>-1</sup>) and DMSO ( $\approx$  670 cm<sup>-1</sup>) peaks of the two cells decreased during discharging and increased during charging, which reflects the aggregation and decrease of Li<sup>+</sup> on the cathode/electrolyte interface according to electroneutrality principle.<sup>[14,22]</sup> The gas evolution signals of LOBs during charge process were quantitatively investigated by operando differential electrochemical mass spectrometry (DEMS) (Figure S15, Supporting Information). The O<sub>2</sub> generation rate gradually increases as Li<sub>2</sub>O<sub>2</sub> decomposes and then reaches equilibrium, accompanied a CO<sub>2</sub> release signal at the end of charging. The cell with blank electrolyte showed the least  $O_2$  evolution and the maximum  $CO_2$  release, while the cell with 100-18C6 electrolyte showed the opposite results, which verified its inhibition effect on side reactions.

Quantitative DEMS tests combined with CV measurements were used to further explore harmful gases release and electrochemical stability of electrolytes at different potentials under  $O_2$  atmosphere (Figure 3k–n). The red curves are partial CV results, and the complete CV curves are shown in Figure S16. Only a trace amount of CO<sub>2</sub> was generated at 4.33 V in cell with 100-18C6 electrolyte, indicating that side reactions are suppressed during the charging process. The signal of CO<sub>2</sub> appeared at a lower potential of 4.2 V in the cell with blank electrolyte, and its CO<sub>2</sub> release amount was 4 times more than that cell with 100-18C6 electrolyte. Moreover, a small oxidation peak







*Figure 3.* Li 1s XPS fitting of the KB cathodes with (a) blank electrolye, (b) 50-18C6, (c) 100-18C6 and (d) 200-18C6 electrolytes after the first discharging process with a limit capacity of 1000 mAh  $g_{carbon}^{-1}$ . Li 1s XPS fitting of the KB cathodes with (e) blank electrolyte, (f) 50-18C6, (g) 100-18C6 and (h) 200-18C6 electrolytes after the first charging process with a limit capacity of 1000 mAh  $g_{carbon}^{-1}$ . Li 1s XPS fitting of the KB cathodes with (e) blank electrolyte, (f) 50-18C6, (g) 100-18C6 and (h) 200-18C6 electrolytes after the first charging process with a limit capacity of 1000 mAh  $g_{carbon}^{-1}$ . In situ Raman spectra and corresponding discharge/charge curves of LOBs in (i) 100-18C6 electrolyte, (j) blank electrolyte. Operando DEMS test combined with CV measurement of LOBs with CO<sub>2</sub> detection in (k) 100-18C6 electrolyte and (l) blank electrolyte, with H<sub>2</sub> detection in (m) 100-18C6 electrolyte and (n) blank electrolyte.

appears at 4.0 V, which corresponds to the side reaction between C and  $Li_2O_2$  or the decomposition of electrolyte.<sup>[19]</sup>

The  $H_2$  release signals of the two cells are obviously different. As shown in Figure 3m, 3n and Figure S17, no  $H_2$ was released in the cell with 100-18C6 electrolyte during resting or operation time. The  $H_2$  signal in cell with blank electrolyte was began to generated at rest time and steadily increased during operation time, which is attributed to the DMSO degradation under nucleophilic attack of reactive oxygen species.<sup>[1d]</sup> A large amount of  $H_2$  generation would have potential safety hazard for the battery. As can be seen in Figure S18, there are distinct differences in the optical photographs of the surface of the recycled Li anodes in cells with or without additive, serious pulverization was observed on the Li anode without 18C6, while the surface remained smooth on the Li anode with the existence of 18C6. These

(1)

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results confirmed the severe decomposition of DMSO-based electrolyte in LOBs, and verified the enhanced electrochemical stability of electrolytes with 18C6 additive. The specific DMSO degradation and H<sub>2</sub> release mechanism during redox reaction as follows:<sup>[23]</sup>

$$CH_3 = \overset{O}{\underset{}} \overset{H}{\underset{}} \overset{H}{\underset{}} \overset{O}{\underset{}} \overset{O}{\underset{}} \overset{O}{\underset{}} \overset{H}{\underset{}} \overset{O}{\underset{}} \overset{O}{\underset{}} \overset{O}{\underset{}} \overset{O}{\underset{}} \overset{H}{\underset{}} \overset{O}{\underset{}} \overset{O}{\underset{}} \overset{O}{\underset{}} \overset{O}{\underset{}} \overset{H}{\underset{}} \overset{O}{\underset{}} \overset{O}{\overset{}} \overset{O}{\underset{}} \overset{O}{\overset{}} \overset{O}{\overset{$$

$$\begin{array}{c|c} & \mathsf{CH} & \mathsf{H} \\ & \mathsf{CH}_3 & \underbrace{\mathsf{S}}^{\mathsf{O}} & \mathsf{CH}_2 \end{array} \xrightarrow{\mathsf{CH}_2} \mathsf{Hoo}^{\mathsf{I}} + \mathsf{Li}^{\mathsf{I}} & \underbrace{\mathsf{H-abstraction}}_{\mathsf{CH}_3} & \underbrace{\mathsf{O}}_{\mathsf{CH}_3} & \underbrace{\mathsf{H}}_{\mathsf{I}} + \mathsf{LiOH} \end{array}$$
(2)

$$CH_{3} = \underbrace{CH_{2}}_{CH_{2}} CH_{2} + \underbrace{LiQH}_{LiQ} H-abstraction} CH_{3} = \underbrace{O}_{O} CH_{2} Li^{\oplus} + LiOH$$
(3)  
$$CH_{3} = \underbrace{CH_{2}}_{CH_{2}} CH_{2} + \underbrace{LiOH}_{CH_{3}} H-abstraction} CH_{3} = \underbrace{O}_{O} Li^{\oplus} + H_{2}O$$
(4)

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$
(5)

To further investigate the stability and safety of anode/ electrolyte interfaces in the Li-O<sub>2</sub> cells, the morphology of the Li anode after the first cycle was observed. The cells were discharged/charged with a current density of 200 mA g<sub>carbon</sub><sup>-1</sup> and a limited capacity of 1000 mAh g<sub>carbon</sub><sup>-1</sup>. As shown in Figure 4a, a rough Li anode surface with severe dendrites was observed in the cell with the blank electrolyte, implying poor interfacial stability. The anode with 50-18C6 (Figure S19a) and 200-18C6 (Figure S19b) additives appeared more uniform Li deposition than the blank electrolyte, but the dendrites were still observed. In contrast, the Li anode with 100-18C6 electrolyte showed a relatively flat and clean surface (Figure 4b). The atomic force microscope (AFM) images also reveal the uneven surface of cycled Li anode in blank electrolyte (Figure 4c) and a continuous film with a smooth morphology of cycled Li anode in 100-18C6 electrolyte (Figure 4d). Moreover, Young's modulus analysis was obtained to describe the mechanical properties of anode/electrolyte interface. The cycled Li anode in blank electrolyte shows a non-normal distributed Young's modulus (mean: 1.638 Gpa, Figure 4e), confirming the non-preferred orientation of Li deposit. The cycled Li anode in 100-18C6 electrolyte exhibits an average Young's modulus of 8.498 GPa (Figure 4f), indicating that the formed SEI layer can effectively prevent lithium dendrites growth and withstand high stress from large volume changes.<sup>[24]</sup>

Furthermore, XPS analysis was performed to study the components of SEI films. In Figure 4g-h and Figure S19c-d, the C 1s spectra signals at 284.8, 286.0, 287.5 and 289.2 eV correspond to C-H, C-O, CH<sub>3</sub>CO<sub>2</sub>Li and Li<sub>2</sub>CO<sub>3</sub>, respectively.<sup>[2d,25]</sup> Owing to the severe side reactions on the anode/electrolyte interface, the SEI film of the cell without additive showed the highest contents of Li<sub>2</sub>CO<sub>3</sub> compared with cells with 18C6 electrolytes. However, almost no Li<sub>2</sub>CO<sub>3</sub> peak was observed on the Li anode surface of cell with 100-18C6 electrolyte. The O 1s spectra signals were also detected and showed in Figure 4i-j and Figure S19e-f, and the peaks at 528.6, 531.6, and 533.0 eV are attributed to Li<sub>2</sub>O, CH<sub>3</sub>CO<sub>2</sub>Li, and Li<sub>2</sub>SO<sub>4</sub>, respectively.<sup>[25,26]</sup> The Li<sub>2</sub>SO<sub>4</sub> signals are originated from the solvent DMSO degradation, and the Li<sub>2</sub>O belong to the inorganic reduced products on the surface of Li anodes, which originates from reactions of Li anode with O2 dissolved in electrolyte or the decomposition of ClO<sub>4</sub><sup>-.[14]</sup> The higher proportion of Li<sub>2</sub>O signal



*Figure 4.* SEM images, AFM image reconstruction and Young's modulus distribution histogram of the Li anodes disassembled from (a, c and e) blank electrolyte, (b, d and f) 100-18C6 electrolytes after the first charging process with a limit capacity of 1000 mAh  $g_{carbon}^{-1}$ . C 1s and O 1s spectra of the Li anodes disassembled from the LOBs using (g and i) blank electrolyte and (h and j) 100-18C6 electrolytes.

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indicates the more stable anode/electrolyte interface. As shown in Figure 4j, no Li<sub>2</sub>SO<sub>4</sub> signal and strong Li<sub>2</sub>O signal were detected on the Li anode of cell with 100-18C6 electrolyte, indicating the stabilized anode/electrolyte interface. In the S 2p spectra signals (Figure S20, Supporting Information), the Li anode of the cell with blank electrolyte showed the largest proportion of peaks related to the solvent DMSO decomposition (DMSO<sub>2</sub>, CH<sub>3</sub>SCH<sub>3</sub> and Li<sub>2</sub>SO<sub>4</sub> signals). In Figure S21, the Li 1s spectra of cell with 100-18C6 showed the largest proportion of Li<sub>2</sub>O among the four cells, the results are consistent with above O 1s spectra signals. The stabilized anode/electrolyte interface is attributed to the increased free ClO<sub>4</sub><sup>-</sup> and decreased free DMSO in the 100-18C6 electrolyte, which improved the electrochemical stability of DMSO-based electrolytes and constructed stable anion-derived SEI on the Li surface to protect the Li metal from reacting with reactive oxygen species, significantly enhancing cycling stabilities of LOBs.

#### Conclusion

In this work, we proposed an electrolyte tailoring strategy to develop dilute electrolytes for LOBs. Optimized crown ether additive promotes the lithium salt dissociation through electrostatic interaction, changes the solvation structure of electrolyte with more DMSO and fewer ClO<sub>4</sub><sup>-</sup> in the first Li<sup>+</sup> solvation sheath, resulting in enhanced electrode/ electrolyte interfaces in LOBs. Specifically, the enhanced cathode/electrolyte interface stabilizes O<sub>2</sub><sup>-</sup> in electrolyte, triggers the solvation-mediated toroidal Li2O2 formation, and promotes ORR/OER kinetics. Side reactions are inhibited due to the broaden of electrolyte electrochemical stability, leading to fewer by-product formation and fewer harmful gases release. Additionally, the formation of stable anion-derived SEI on anode/electrolyte interface protects Li anode from attacking of reactive oxygen species and free DMSO, results in dendrite-free Li anode. Finally, the optimized 100-18C6 electrolyte was applied to LOBs and showed large specific capacity of  $10828 \text{ mAh} g_{carbon}^{-1}$  and long-term cycle stability of 128 cycles with a capacity of  $1000 \text{ mAh} g_{\text{carbon}}^{-1}$ . The electrolyte tailoring strategy proposed in this work provides a research basis for the exploitation of high-performance LOBs, and is expected to promote the further development of disruptive energy storage technologies.

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#### **Conflict of Interest**

The authors declare no conflict of interest.

#### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Crown Ether • Dilute Electrolyte • Lithium Salt Dissociation • Lithium-Oxygen Battery

- a) J. Zhang, Y. Zhao, B. Sun, Y. Xie, A. Tkacheva, F. Qiu, P. He, H. Zhou, K. Yan, X. Guo, S. Wang, A. M. McDonagh, Z. Peng, J. Lu, G. Wang, *Sci. Adv.* **2022**, *8*, eabm1899; b) X. Chi, M. Li, J. Di, P. Bai, L. Song, X. Wang, F. Li, S. Liang, J. Xu, J. Yu, *Nature* **2021**, *592*, 551; c) H. Yang, Y. Qiao, Z. Chang, H. Deng, P. He, H. Zhou, *Adv. Mater.* **2021**, *33*, 2100827; d) H. D. Lim, B. Lee, Y. Bae, H. Park, Y. Ko, H. Kim, J. Kim, K. Kang, *Chem. Soc. Rev.* **2017**, *46*, 2873.
- [2] a) J. Yi, S. Guo, P. He, H. Zhou, *Energy Environ. Sci.* 2017, 10, 860; b) H. Wang, X. Wang, M. Li, L. Zheng, D. Guan, X. Huang, J. Xu, J. Yu, *Adv. Mater.* 2020, 32, 2002559; c) D. Zhao, P. Wang, H. Di, P. Zhang, X. Hui, L. Yin, *Adv. Funct. Mater.* 2021, 31, 2010544; d) J. Lai, H. Liu, Y. Xing, L. Zhao, Y. Shang, Y. Huang, N. Chen, L. Li, F. Wu, R. Chen, *Adv. Funct. Mater.* 2021, 31, 2101831.
- [3] Y. Yu, G. Huang, J.-Y. Du, J.-Z. Wang, Y. Wang, Z.-J. Wu, X.-B. Zhang, *Energy Environ. Sci.* **2020**, *13*, 3075.
- [4] D. Wang, F. Zhang, P. He, H. Zhou, Angew. Chem. Int. Ed. 2019, 58, 2355; Angew. Chem. 2019, 131, 2377.
- [5] W.-J. Kwak, S. Chae, R. Feng, P. Gao, J. Read, M. H. Engelhard, L. Zhong, W. Xu, J.-G. Zhang, ACS Energy Lett. 2020, 5, 2182.
- [6] a) X. Fan, C. Wang, *Chem. Soc. Rev.* 2021, *50*, 10486; b) Y.-F. Huang, T. Gu, G. Rui, P. Shi, W. Fu, L. Chen, X. Liu, J. Zeng, B. Kang, Z. Yan, F. J. Stadler, L. Zhu, F. Kang, Y.-B. He, *Energy Environ. Sci.* 2021, *14*, 6021.
- [7] a) S. Xu, R. Xu, T. Yu, K. Chen, C. Sun, G. Hu, S. Bai, H.-M. Cheng, Z. Sun, F. Li, *Energy Environ. Sci.* 2022, *15*, 3379;
  b) G. B. Appetecchi, D. Zane, B. Scrosati, *J. Electrochem. Soc.* 2004, *151*, A1369.
- [8] a) L. Johnson, C. Li, Z. Liu, Y. Chen, S. A. Freunberger, P. C. Ashok, B. B. Praveen, K. Dholakia, J. M. Tarascon, P. G. Bruce, *Nat. Chem.* 2014, 6, 1091; b) C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed., Wiley-VCH, Weinheim, 2003.
- [9] Z. Lu, Y. Guo, S. Zhang, S. Wu, R. Meng, S. Hong, J. Li, H. Xue, B. Zhang, D. Fan, Y. Zhang, C. Zhang, W. Lv, Q. H. Yang, *Adv. Mater.* 2021, *33*, 2101745.
- [10] a) C. V. Amanchukwu, X. Kong, J. Qin, Y. Cui, Z. Bao, Adv. Energy Mater. 2019, 9, 1902116; b) C. V. Amanchukwu, Z. Yu, X. Kong, J. Qin, Y. Cui, Z. Bao, J. Am. Chem. Soc. 2020, 142, 7393.
- [11] Y. Chen, Z. Yu, P. Rudnicki, H. Gong, Z. Huang, S. C. Kim, J.-C. Lai, X. Kong, J. Qin, Y. Cui, Z. Bao, J. Am. Chem. Soc. 2021, 143, 18703.
- [12] A. Narayanan Kirshnamoorthy, K. Oldiges, M. Winter, A. Heuer, I. Cekic-Laskovic, C. Holm, J. Smiatek, *Phys. Chem. Chem. Phys.* 2018, 20, 25701.
- [13] L. Yang, Y. Huang, M. K. Tufail, X. Wang, W. Yang, Small 2022, 18, 2202060.

Angew. Chem. Int. Ed. 2023, e202301772 (8 of 9)

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- [14] J. Lai, N. Chen, F. Zhang, B. Li, Y. Shang, L. Zhao, L. Li, F. Wu, R. Chen, *Energy Storage Mater.* **2022**, 49, 401.
- [15] Z. Hu, F. Zhang, Y. Zhao, H. Wang, Y. Huang, F. Wu, R. Chen, L. Li, Adv. Mater. 2022, 34, 2203104.
- [16] Q. Xiong, G. Huang, Y. Yu, C. L. Li, J. C. Li, J. M. Yan, X. B. Zhang, *Angew. Chem. Int. Ed.* **2022**, *61*, e202116635; *Angew. Chem.* **2022**, *134*, e202116635.
- [17] Q. Zhang, S. Rao, S. V. C. Vummaleti, E. T. Poh, W. Dai, X. Cui, J. Wu, J. Zhang, W. Chen, *Adv. Energy Mater.* **2022**, *12*, 2200580.
- [18] Q. Xia, L. Zhao, Z. Zhang, J. Wang, D. Li, X. Han, Z. Zhou, Y. Long, F. Dang, Y. Zhang, S. Chou, *Adv. Sci.* **2021**, *8*, 2103302.
- [19] S. H. Oh, R. Black, E. Pomerantseva, J.-H. Lee, L. F. Nazar, *Nat. Chem.* 2012, 4, 1004.
- [20] a) Z. Sun, X. Cao, M. Tian, K. Zeng, Y. Jiang, M. H. Rummeli,
  P. Strasser, R. Yang, *Adv. Energy Mater.* 2021, *11*, 2100110;
  b) C.-L. Li, G. Huang, Y. Yu, Q. Xiong, J.-M. Yan, X.-b. Zhang, *J. Am. Chem. Soc.* 2022, *144*, 5827.
- [21] Y. Qiao, S. Wu, Y. Sun, S. Guo, J. Yi, P. He, H. Zhou, ACS Energy Lett. 2017, 2, 1869.
- [22] C. Wang, H. Zhang, S. Dong, Z. Hu, R. Hu, Z. Guo, T. Wang, G. Cui, L. Chen, *Chem. Mater.* **2020**, *32*, 9167.

- [23] a) M. A. Schroeder, N. Kumar, A. J. Pearse, C. Liu, S. B. Lee, G. W. Rubloff, K. Leung, M. Noked, ACS Appl. Mater. Interfaces 2015, 7, 11402; b) D. G. Kwabi, T. P. Batcho, C. V. Amanchukwu, N. Ortiz-Vitoriano, P. Hammond, C. V. Thompson, Y. Shao-Horn, J. Phys. Chem. Lett. 2014, 5, 2850; c) D. Sharon, M. Afri, M. Noked, A. Garsuch, A. A. Frimer, D. Aurbach, J. Phys. Chem. Lett. 2013, 4, 3115; d) N. Mozhzhukhina, L. P. Méndez De Leo, E. J. Calvo, J. Phys. Chem. C 2013, 117, 18375.
- [24] a) C. Chen, Q. Liang, G. Wang, D. Liu, X. Xiong, Adv. Funct. Mater. 2021, 31, 2107249; b) D. Luo, L. Zheng, Z. Zhang, M. Li, Z. Chen, R. Cui, Y. Shen, G. Li, R. Feng, S. Zhang, G. Jiang, L. Chen, A. Yu, X. Wang, Nat. Commun. 2021, 12, 186.
- [25] X.-P. Zhang, Y.-Y. Sun, Z. Sun, C.-S. Yang, T. Zhang, Nat. Commun. 2019, 10, 3543.
- [26] Z. Huang, J. Ren, W. Zhang, M. Xie, Y. Li, D. Sun, Y. Shen, Y. Huang, Adv. Mater. 2018, 30, 1803270.

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# **Research Articles**



# **Research Articles**

### Li-O<sub>2</sub> Batteries

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Lithium Salt Dissociation Promoted by 18-Crown-6 Ether Additive toward Dilute Electrolytes for High Performance Lithium Oxygen Batteries



The introduction of 18-crown-6 ether additive regulates the solvation structure of electrolyte, avoids nucleophilic attack of reactive oxygen species on the solvent, and reduces harmful gases release. The solution-mediated mechanism is triggered to enhance the discharge capacity, and the anion-derived SEI protects Li anode to improve the cycling stability of lithium-oxygen batteries.