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A Renaissance of N,N-Dimethylacetamide-Based Electrolyte to Promote the Cycling Stability of Li-O₂ Batteries

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Li-O₂ batteries with ultrahigh theoretical energy density have been regarded as a promising successor to Li-ion batteries for next-generation energy storage. However, their practical application is still facing many critical issues, especially the lack of suitable electrolytes that can tolerate strong oxidizing environment as well as be compatible with Li metal anode. Here, we design a new N,N-dimethylacetamide (DMA)-based electrolyte by regulating the Li⁺ solvation structure under medium concentration to promote the cycling stability of Li-O₂ batteries. And it is also a better lithium metal anode stabilized strategy than high concentration electrolytes. In contrast to high concentration electrolytes with expensive cost, limited protection ability to Li anode, sluggish kinetics and slow mass transfer, this new electrolyte with intrinsic better endurance towards the rigorous oxidative species can simultaneously stabilize the Li anode by facilitating the formation of LiF and LiN_xO_y coexisting solid electrolyte interphase (SEI) film and enable faster kinetics/mass transfer. As a result, both the symmetrical batteries (1800 hours) and the Li-O₂ batteries (180 cycles) achieve the best cycling performances in DMA-based electrolytes. This study breathes new life into electrolyte regulation strategy and paves the way for the development of alkali-O₂ batteries.

Introduction

To meet the high energy density requirements of the rapidly developed electric devices and vehicles, it is urgent and significant to look for a new type of battery with large capacity to replace the current commercial Li-ion batteries.^{1–4} Among all the available energy storage devices, rechargeable

nonaqueous Li-O₂ battery featured with a high theoretical energy density of 3500 Wh kg^{−1} has been regarded as a promising candidate with great development prospect.^{5, 6} As is well known, a stable electrolyte is indispensable for achieving a high-performance Li-O₂ battery. Nevertheless, so far, no electrolyte can be able to withstand the nucleophilic attack from the highly reactive reduced oxygen species (O₂^{•−}, O₂^{2−}, HOO[•] and HO[•]) while still being compatible with Li metal anode, making the long-term cycling and practical application of Li-O₂ batteries full of thorns.^{7–9} Despite polar aprotic N,N-dimethylacetamide (DMA) based electrolytes as an exception are considered stable enough to tolerate the rigorous oxidative environment of Li-O₂ batteries,^{10–14} the serious instability of Li metal anodes in DMA-based electrolytes not only continuously decomposes the electrolyte but also self-degrades to loss active Li, accelerating the failure of the battery.^{10, 15} Moreover, the irregular dendrite growth issue of Li metal anodes also exists, which should be carefully considered to avoid the dendrite induced short-circuit accidents.^{16–19} Therefore, if we could solve the instability issue of Li metal anode in DMA-based electrolytes by electrolyte design, it will fulfill the critical anti-nucleophilic attack ability and Li compatibility requirements of electrolyte for Li-O₂ batteries, and thus achieve high electrochemical performance. How to realize this goal? Since the electrolyte composes of organic solvent and Li salt, and the solvent here is DMA, what we can do is to choose Li salt and electrolyte additive or adjust the concentration of Li salt. In DMA-based electrolytes for Li-O₂ batteries, LiTFSI and LiNO₃ are the most commonly used Li salts. Among them, the use of 0.5 M LiTFSI has only verified the stability of DMA-based electrolyte towards superoxide, while the stability of lithium in this electrolyte is so terrible that the authors have to use LiFePO₄ to replace the Li metal anode to keep the battery running.¹⁰ Although the adoption of 1 M LiNO₃ can help stabilize the Li metal by forming LiNO₃ derived solid electrolyte interphase (SEI), the protection effect is still unsatisfying to prevent the aggravating lithium corrosion.¹⁵ Later, some electrolyte additives, like lithium 2-

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bromoethanesulfonate, have been developed to in-situ form protection layers on Li metal anode to improve the performance.^{9, 20} However, these protection layers are liable to be cracked and lose efficacy in the long-term cycling due to the infinite volume change of lithium. Recently, the use of high concentration electrolytes has been demonstrated as an effective strategy to stabilize the Li metal anodes by reducing free solvent molecules and forming steady anion-derived SEI film.^{21, 22} Despite stabilization of the Li anodes, the high concentration electrolytes are also along with many disadvantages, like low ion conductivity and high viscosity, which unavoidably cause slow mass transfer, sluggish electrode kinetics, poor rate performance and high overpotential,^{21, 23} not to mention the large amounts used Li salts induced high cost. Even with these progresses, a DMA-based electrolyte that can permit high-performance cycling of Li-O₂ batteries has not yet developed. Consequently, a new electrolyte design guideline is in crying need for DMA based electrolyte to overcome the disadvantages of the high concentration electrolytes, while maintain their superiorities, thus obtain a DMA based Li-O₂ battery with greatly enhanced electrochemical performances.

In this contribution, we have developed a new electrolyte design guideline to revive the DMA-based electrolyte for enabling long-term cycling of Li-O₂ batteries. This has been realized by the regulation of Li⁺ solvation structure to adjust the SEI film and free solvent molecules under medium concentration of electrolyte, overcoming the disadvantages and even defeating the advantages of the high concentration electrolytes. The *ab initio* molecular dynamics (AIMD) simulations and electrochemical analysis demonstrate that the optimized electrolyte with 2 M LiTFSI 1 M LiNO₃ in DMA successfully endows a satisfying dendrite and corrosion suppression effects toward Li anode, as well as exhibits enhanced kinetic and mass transfer processes. As a result, the cycle life of the Li/Li symmetrical and Li-O₂ batteries has been elongated to 1800 hours and 180 cycles, respectively, which are the best electrochemical performances in the corresponding reported DMA-based batteries.

Results and discussion

As a pilot experiment, we first tested two groups of electrolytes containing different concentrations of LiTFSI or LiNO₃ in DMA solvent. The stability of the Li metal in different electrolytes was prescreened by checking the cycle life of Li/Li symmetrical batteries with a fixed plating/stripping capacity of 1 mAh cm⁻² at a current density of 1 mA cm⁻² (Fig. 1 and Fig. S1-S3). In the group of LiTFSI-DMA electrolytes, the Li/Li symmetrical battery with 4 M LiTFSI shows the longest cycle life of ~78 hours (Fig. 1a, 1d and Fig. S1), which is 38-fold higher than that of 1 M LiTFSI based battery. When LiNO₃ is used as the lithium salt, the electrolyte with 5 M LiNO₃ (the optimal concentration) improves the stability of Li anode

greatly (82 hours, Fig. 1b, 1e and Fig. S2), whereas the cycle life of 1 M LiNO₃ based cell is only 22 hours. These results confirm that the use of high concentration electrolytes can indeed stabilize the Li anodes to some extent, but the improvement is limited and not satisfying. Then, as a proof of concept experiment, a group of electrolytes combining LiTFSI and LiNO₃ salts was prepared to check whether they could further prolong the cycle life of the DMA based Li/Li symmetrical batteries. Here, we selected a medium salt concentration of 3 M as a model system and three kinds of electrolytes (1.5 M LiNO₃ 1.5 M LiTFSI, 1 M LiNO₃ 2 M LiTFSI and 0.5 M LiNO₃ 2.5 M LiTFSI, designated as 3 M mixed electrolyte group) were designed. The electrolyte with 3 M LiNO₃ or 3 M LiTFSI was used as control sample. As can be seen from Fig. 1c, 1f, Fig. S3 and S4, the cells with 3 M mixed electrolyte group are much more stable and deliver longer cycle performance than those of high concentration electrolyte groups. Especially, a more than 400-hour cycle life, ~5 times higher than those of 4 M LiTFSI and 5 M LiNO₃ electrolytes, is achieved in the 2 M LiTFSI 1 M LiNO₃ electrolyte, revealing a much better lithium stabilized effect endowed by this optimized electrolyte. The unexpected findings here imply that our design of this optimized electrolyte with medium concentration can facilitate the formation of a much more stable electrode/electrolyte interface than that of commonly high concentration electrolytes (Fig. 1g-i). The detailed mechanisms and reasons for the wonderful effect of the 2 M LiTFSI 1 M LiNO₃ electrolyte towards Li anode are not clear. In the following parts, a series of experiments have been performed to explore these.

A further investigation of the stability of Li anodes in DMA-based electrolytes is shown in the voltage-time profiles in Fig. 2a at a current density of 0.1 mA cm⁻². It is clear that the battery with 2 M LiTFSI 1 M LiNO₃ electrolyte exhibits a stable and ultra-long cycling performance (1800 hours) with a constantly lower overpotential, which is much superior to those of the cells with 4 M LiTFSI and 5 M LiNO₃. Even increasing the current density to 1 mA cm⁻², the 2 M LiTFSI 1 M LiNO₃ based Li/Li symmetrical battery still exhibits the best electrochemical performance (Fig. 2b), implying that this electrolyte can facilitate the formation of a much more stable electrode/electrolyte interface. What is worth mentioning is that the battery with this 2 M LiTFSI 1 M LiNO₃ in DMA electrolyte shows about 16 times longer cycle life than the battery with traditional 1 M LiCF₃SO₃ in TEGDME electrolyte (Fig. S5), demonstrating that a better performance can be realized by the designed optimized electrolyte than the traditional Li-O₂ battery electrolyte.

The rate performance of the symmetrical batteries with different kinds of electrolytes was then evaluated. As can be seen from Fig. 2c, the batteries with 4 M LiTFSI and 5 M LiNO₃ stop working due to the ultrahigh overpotential over 5 V at current densities of 3 and 5 mA cm⁻², respectively, which can be explained by the unstable electrode/electrolyte interface

and sluggish kinetics/mass transfer process in these high concentration electrolytes. On the contrary, the battery with 2 M LiTFSI 1 M LiNO₃ cycles steadily with a lower overpotential even under a much higher current density of 5 mA cm⁻². Inspiringly, the performances of the symmetrical batteries with 2 M LiTFSI 1 M LiNO₃ electrolyte also surpass those of the previously reported DMA-based symmetrical batteries (Fig. 2d),^{9,20} verifying the effectiveness of the designed electrolyte for protecting Li metal anode.

Fig. 1 Lithium metal anode stability in different kinds of DMA-based electrolytes. Overpotential vs. cycle number curves of Li/Li symmetrical batteries with the electrolyte of 1 M LiTFSI, 3 M LiTFSI, 4 M LiTFSI and 5 M LiTFSI (a), 1 M LiNO₃, 4 M LiNO₃, 5 M LiNO₃ and 6 M LiNO₃ (b), 3 M LiNO₃, 1.5 M LiTFSI 1.5 M LiNO₃, 2 M LiTFSI 1 M LiNO₃ and 2.5 M LiTFSI 0.5 M LiNO₃ (c) cycled at a capacity of 1 mAh cm⁻² and a current density of 1 mA cm⁻². Histograms of the cycle life of Li/Li symmetrical batteries with different concentrations of LiTFSI electrolytes (d), different concentrations of LiNO₃ electrolytes (e), and 3 M electrolytes groups (f). Schematics of the performance of Li/Li symmetrical batteries with 4 M LiTFSI (g), 5 M LiNO₃ (h), and 2 M LiTFSI 1 M LiNO₃ (i).

Electrochemical impedance spectroscopy (EIS) of the symmetrical batteries was employed to further reveal the stability of the electrode/electrolyte interface. It can be seen from Fig. 2e that the bulk, interfacial and charge transfer impedances of the 2 M LiTFSI 1 M LiNO₃ based battery are obviously lower than those of the cells with 4 M LiTFSI and 5 M LiNO₃ electrolytes before cycling. The soaring impedance of the battery with 5 M LiNO₃ after cycling can be attributed to the formation of thick SEI film from the Li plating/stripping induced constant SEI breaking and rebuilding (Fig. 2f). The much reduced impedance of the cycled battery with 4 M LiTFSI can be explained by the dendrite microstructure of the electrode induced micro short circuit.²⁴ For the battery with 2 M LiTFSI 1 M LiNO₃, the impedance only experiences a little

change after cycling (Fig. 2f), indicating the formation of stable electrode/electrolyte interface.

Fig. 2 Electrochemical performance of Li/Li symmetrical batteries. Long-term cycle performance of Li/Li symmetrical batteries with different kinds of electrolytes at current densities of 0.1 mA cm⁻² (a), and 1 mA cm⁻² (b). Insets are the details of the representative voltage vs. time profiles. (c) Rate performance of Li/Li symmetrical batteries under different current densities. (d) Comparison of the cycling performance of Li/Li symmetrical batteries with DMA-based electrolytes. Nyquist plots of Li/Li symmetrical batteries before cycling (e), and after cycling for 80 hours (f) at a stripping/plating capacity of 1 mAh cm⁻² and a current density of 1 mA cm⁻². Inset in Fig. 2f is the Zoom-in view of the Nyquist plots. (g) Arrhenius curves of different kinds of electrolytes. (h) Arrhenius plots and corresponding activation energies from R_{ct} in Li/Li symmetrical batteries. (i) CV curves of Li/Li symmetrical batteries with different kinds of electrolytes.

To reveal the reason of the enhanced electrochemical performance, the mass transfer and electrode kinetics of the above three electrolytes were evaluated. As shown in Fig. 2g and Fig. S6, Arrhenius plots and corresponding activation energy (E_a) are used to reveal the migration barrier for Li⁺ ion in these three electrolytes.²⁵ It is evident that the ionic conductivity of 2 M LiTFSI 1 M LiNO₃ is always much higher than that of 4 M LiTFSI and 5 M LiNO₃ under different temperatures (Fig. 2g). Thus, a much lower activation energy for 2 M LiTFSI 1 M LiNO₃ (0.69 kJ/mol) is calculated than that of

4 M LiTFSI (0.98 kJ/mol) and 5 M LiNO₃ (1.21 kJ/mol) (Fig. S6), indicating the significantly improved Li⁺ migration process. Moreover, the 2 M LiTFSI 1 M LiNO₃ electrolyte has a quite lower viscosity than that of high concentration electrolytes (Fig. S7). The high ion conductivity and low viscosity of 2 M LiTFSI 1 M LiNO₃ make it exhibit a higher ionicity than the high concentration electrolytes (Walden plot in Fig. S8).^{26, 27} Besides, we also evaluate the charge transfer barrier in the three electrolytes, of which the desolvation process of Li⁺ is the rate determining step. The activation energy for the desolvation of Li⁺ in the three electrolytes is shown in Fig. 2h and Fig. S9.^{19, 28} In comparison with the high concentration electrolytes of 4 M LiTFSI (2.50 kJ/mol) and 5 M LiNO₃ (2.0 kJ/mol), the 2 M LiTFSI 1 M LiNO₃ shows the lowest activation energy of 1.85 kJ/mol, implying an easier desolvation process and faster charge transfer kinetics. Finally, cyclic voltammetry (CV) curves of the Li/Li symmetrical batteries with the three electrolytes were measured to estimate the kinetics of the lithium plating and stripping process (Fig. 2i). The battery with 2 M LiTFSI 1 M LiNO₃ electrolyte demonstrates a larger curve slope and higher reduction and oxidation peak current than those with high concentration electrolytes, revealing an easier deposition/dissolution reaction of lithium.^{29, 30} The above results verify the optimized electrolyte with 2 M LiTFSI 1 M LiNO₃ in DMA displays faster mass transfer and electrode kinetics.

Fig. 3 Characterization of the lithium deposition morphology and SEI film components. SEM images of lithium deposition morphology in 5 M LiNO₃ (a), 4 M LiTFSI (b), and 2 M LiTFSI 1 M LiNO₃ (c). In situ optical microscope images of lithium morphology evolution after deposition in 4 M LiTFSI for 0 minute (d) and 30 minutes (e), in 5 M LiNO₃ for 0 minute (f) and 30 minutes (g), and in 2 M LiTFSI 1 M LiNO₃ for 0 minute (h) and 30 minutes (i). (j) Schematic illustrations of lithium deposition evolution in different kinds of electrolytes. Li 1s XPS spectra of lithium after 40 cycles in 4 M LiTFSI (k), 5 M LiNO₃

(l), and 2 M LiTFSI 1 M LiNO₃ (m) before and after etching for 5 minutes.

Field emission scanning electron microscopy (FESEM) was employed to check the morphology of the deposited Li in the three electrolytes. As indicated in Fig. 3a-c and Fig. S10, the deposited Li in 5 M LiNO₃ and 4 M LiTFSI presents different extents of uncontrollable dendrite growth. The alleviative dendrite growth in 5 M LiNO₃ than 4 M LiTFSI can be explained by the reason that LiNO₃ is a well-known salt to assist stable SEI film formation.^{15, 31} By contrast, the Li in 2 M LiTFSI 1 M LiNO₃ exhibits relative smooth surface without observed Li dendrites, demonstrating the uniform deposition behavior of lithium. In addition, in-situ optical microscopy was also employed to visually observe the morphology evolution of the deposited lithium. As depicted in Fig. 3d-j, irregular dendrite deposition and large volume expansion can be seen in 4 M LiTFSI and 5 M LiNO₃ electrolytes, while the deposition of lithium in 2 M LiTFSI 1 M LiNO₃ electrolyte is homogeneous with smooth and compact morphology, enabling a powerful and satisfying dendrite suppression effect.

The enhanced cycling stability and dendrite-free behavior of the 2 M LiTFSI 1 M LiNO₃ based Li/Li symmetrical batteries can be attributed to the formation of stable electrode/electrolyte interface, thus, in-depth X-ray photoelectron spectroscopy (XPS) spectra were collected to probe the composition of the SEI film on the lithium after long-time cycling (Fig. 3k-m and Fig. S11-S13). As is well known, LiF-rich and LiN_xO_y-rich films are beneficial to stabilize the lithium/electrolyte interface.^{31, 32} The existence of LiN_xO_y in the SEI film can be observed in all the three electrolytes and LiN_xO_y is one of the main components of the SEI film (Fig. 3k-m). Even after etching for 5 minutes, the LiN_xO_y still exists, indicating its relative homogeneous distribution. Despite with fluorine-containing anion of TFSI⁻ in 4 M LiTFSI, nearly no LiF can be observed before and after etching (Fig. 3k and Fig. S11), revealing that TFSI⁻ does not participate in the formation of SEI film. For the SEI film in 2 M LiTFSI 1 M LiNO₃, it is surprisingly found that both LiF and LiN_xO_y exist and the content of LiF even increases after etching for 5 minutes (Fig. 3m and Fig. S13). Compared with the SEI film formed in 4 M LiTFSI, the existence of LiF in the SEI film in 2 M LiTFSI 1 M LiNO₃ can be explained by the introduction of LiNO₃, which enables the TFSI⁻ to take part in the formation of SEI film, thus generation of LiF.³¹ Consequently, combining LiNO₃ and LiTFSI salts together in DMA can facilitate to build a more stable SEI film for an improved electrode/electrolyte interface.

AIMD simulations were then used to confirm the solvation sheath structure of Li⁺ in the selected electrolytes. The snapshots shown in Fig. 4a-d and Fig. S14 simulate the coordination environment of Li⁺ in 3 M LiTFSI, 2 M LiTFSI 1 M LiNO₃, 4 M LiTFSI and 5 M LiNO₃ electrolytes, respectively. In 3 M LiTFSI electrolyte, lots of the solvation structures of Li⁺ are contact ion pairs (CIPs), like Fig. 4e. With the introduction of LiNO₃ to prepare 2 M LiTFSI 1 M LiNO₃ electrolyte, some aggregates (AGGs) form and the solvation effect enhances (Fig. 4f). This can be confirmed by the chemical shift of peaks in ⁷Li

nuclear magnetic resonance (NMR) and ^{19}F NMR spectra for 2 M LiTFSI 1 M LiNO_3 compared to that of 3 M LiTFSI (Fig. S15). For high concentration electrolytes (4 M LiTFSI and 5 M LiNO_3), more AGGs emerge and the interactions between Li^+ and solvents/anions further increase (Fig. S16 and S17). The large amount of AGGs in the high concentration electrolytes will unavoidably impede the fast mass transfer and electrode kinetics. Therefore, strong solvation effect is not always conducive to better electrochemical performance and thus medium concentration electrolyte should be considerable. Similar conclusion can also be obtained from radical distribution functions (RDF) results in Fig. 4g,h. The electrolyte with 2 M LiTFSI 1 M LiNO_3 shows a strong solvent effect like high concentration electrolytes, but a quite different solvation environment compared to that of 3 M LiTFSI based electrolyte. The appearance of a new peak of Li-N at around 2.7 Å and the decrease of the peak intensity at around 4.1 Å in the 2 M LiTFSI 1 M LiNO_3 electrolyte confirm that an easier tendency involvement of NO_3^- than TFSI $^-$ in the first coordination shell. These changes of the solvation structure may influence the lowest unoccupied molecular orbital (LUMO) of the electrolyte and finally lead to an anion-derived SEI film.²¹ In Fig. 4i, the mean square displacement (MSD) reveals the diffusion property of the 2 M LiTFSI 1 M LiNO_3 , 4 M LiTFSI and 5 M LiNO_3 electrolytes. Compared with the high concentration electrolytes, the 2 M LiTFSI 1 M LiNO_3 electrolyte shows enhanced ion movement, which is consistent with the above experimental result.^{33, 34}

Fig. 4 AIMD simulations of electrolyte solvent structure in different kinds of electrolytes. Snapshots of the AIMD simulation box for 3 M LiTFSI (a), 2 M LiTFSI 1 M LiNO_3 (b), 4 M LiTFSI (c), and 5 M LiNO_3 (d) electrolytes. Schematics of the solvation structures in 3 M LiTFSI (e), and 2 M LiTFSI 1 M LiNO_3 (f) electrolytes. Radical distribution functions of Li-O (g) and Li-N (h) in different kinds of electrolytes. (i) MSD of different kinds of electrolytes as a function of the simulation time.

Fig. 5 Electrochemical characterization of Li-O₂ batteries. (a) Schematic of Li-O₂ battery with 2 M LiTFSI 1 M LiNO_3 DMA-based electrolyte. Discharge and charge profiles of Li-O₂ batteries with different kinds of electrolytes at the 1st cycle (b), 50th cycle (c), and the corresponding histogram of the overpotential comparison (d). (e) Rate performance of Li-O₂ batteries with different kinds of electrolytes. (f) Long-term cycle life of Li-O₂ batteries with different kinds of electrolytes. (g) Summarization of the cycle performances of DMA-based Li-O₂ batteries reported here and in previous literatures. SEM image (h) and XRD patterns (i) of lithium metal anode in Li-O₂ batteries after 50 cycles. (j) Comparisons of the performances and properties of the three kinds of electrolytes based Li-O₂ batteries.

To explore the practical application ability of the prepared DMA-based electrolyte, Li-O₂ batteries with different kinds of electrolytes were assembled (Fig. 5a). CV test was first conducted to evaluate the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics of the Li-O₂ batteries (Fig. S18). The CV curve of the battery with 2 M LiTFSI and 1 M LiNO_3 displays a typical Li-O₂ battery behavior and shows the strongest anodic and cathodic peak intensities, indicating an improved ORR and OER kinetics.^{35, 36} The discharge and charge performance of the Li-O₂ batteries without any cathode catalysts at a fixed specific capacity of 1000 mAh g^{-1} and a current density of 300 mA g^{-1} is then evaluated in Fig. 5b-d. We can see that the charge plateaus of the 2 M LiTFSI 1 M LiNO_3 and 5 M LiNO_3 based batteries are much lower than that of the battery with 4 M LiTFSI due to the redox catalytic activity of LiNO_3 on the air cathode (Fig. 5b).³⁷⁻³⁹ The low charge potential not only means the easy decomposition of the discharge products, but also assists to reduce the electrolyte and carbon cathode decomposition. Despite the 5 M LiNO_3 based battery with a relative low charge plateau, the high concentration induced sluggish mass transfer and kinetics as well as less O_2 solubility makes it exhibit a large discharge overpotential (Fig. 5b). For the battery with 4 M LiTFSI, the situation is even worse with both large discharge and charge overpotentials (Fig. 5b). As a result, at the 1st cycle,

the overpotential of the batteries follows the sequence of 2 M LiTFSI 1 M LiNO₃ (0.7873 V) < 5 M LiNO₃ (1.0957 V) < 4 M LiTFSI (1.6403 V) (Fig. 5b,d). Even after 50 cycles, the overpotential of the 2 M LiTFSI 1 M LiNO₃ is still only 0.9605 V, much lower than that of the 5 M LiNO₃ (2.4893 V) and 4 M LiTFSI (2.1141 V) (Fig. 5c,d). It is worth mentioning that the overpotential of the 2 M LiTFSI 1 M LiNO₃ is also quite lower than that of the commonly used 1 M LiCF₃SO₃ TEGDME electrolyte for Li-O₂ batteries at both the 1st cycle and the 50th cycle. Fig. S19 and S20 show the full discharge performance of Li-O₂ batteries with a cut-off voltage of 2 V under different current densities. The batteries with 2 M LiTFSI 1 M LiNO₃ display much larger discharge capacities than the batteries with 5 M LiNO₃ and 4 M LiTFSI at high rates of 1000 mA g⁻¹ and 2000 mA g⁻¹. Moreover, the battery with 2 M LiTFSI 1 M LiNO₃ also behaves much better rate performance with stable voltage plateau and lower overpotential than the batteries with 5 M LiNO₃ and 4 M LiTFSI (Fig. 5e). The long-time cycling tests have been also presented in Fig. 5f and Fig. S21-S23. The cycle life of the Li-O₂ batteries with the electrolytes of 4 M LiTFSI, 5 M LiNO₃ and 2 M LiTFSI 1 M LiNO₃ is 67 cycles, 8 cycles and 180 cycles, respectively. The 2 M LiTFSI 1 M LiNO₃ enabled lifetime of 180 cycles here is the longest cycle life among the DMA-based Li-O₂ batteries (Fig. 5g).^{15, 20, 40, 41}

The O₂ cathode evolution during cycling in 2 M LiTFSI 1 M LiNO₃ was tested by FESEM and XRD. It is clear that the typical crystalline toroid Li₂O₂ forms and decomposes in the discharge and subsequent recharge processes (Fig. S24 and S25), verifying that the 2 M LiTFSI 1 M LiNO₃ based Li-O₂ battery follows the typical Li-O₂ electrochemistry of 2Li + O₂ ⇌ Li₂O₂ and behaves a good reversibility.⁴² To demonstrate the 2 M LiTFSI 1 M LiNO₃ electrolyte rendered anti-corrosion effect on Li anode, the battery after 50 cycles was disassembled to investigate the status of the lithium metal anode. As exhibited in Fig. 5h,i, the cycled Li anode in 2 M LiTFSI 1 M LiNO₃ still has a relative smooth and flat surface without any detected Li dendrite formation and obvious LiOH peaks, indicating that there is indeed a protection effect on the Li anode from the designed electrolyte.⁴³ While for the Li anode in 4 M LiTFSI, it exhibits uneven surface morphology with serious corrosion and obvious LiOH formation (Fig. S26), reveal that the 4 M LiTFSI electrolyte cannot protect Li from corroding. Because the Li-O₂ battery with 5 M LiNO₃ cannot run for 50 cycles before reaching the cut-off discharge voltage of 2.0 V, we do not provide the SEM images and XRD curves of the cycled lithium in 5 M LiNO₃ electrolyte for comparison. These results verify that the optimized electrolyte with 2 M LiTFSI 1 M LiNO₃ in DMA can alleviate the side reactions between DMA, O₂, H₂O and active lithium, thus making the Li metal anode can be directly used in this DMA based Li-O₂ battery and achieve superior electrochemical performances. As a result, the electrolyte regulation strategy developed here successfully revives the DMA-based Li-O₂ batteries via the advantages of faster mass transfer and electrode kinetics, stabilized Li metal anode, lower overpotential, better rate performance and longer cycle life (Fig. 5j).

Conclusions

In conclusion, the renaissance of DMA-based electrolytes for promoting the cycling lifetime of Li-O₂ batteries has been realized by stabilizing the Li metal anode via our new electrolyte design principle of regulating the solvation structure of Li⁺ under medium concentration. The experiment results and AIMD simulations demonstrate that the optimized electrolyte with 2 M LiTFSI 1 M LiNO₃ in DMA can facilitate the formation of LiF and LiN_xO_y-rich SEI film to protect the Li anode from dendrite growth and corrosion, and enable faster mass transfer and electrode kinetics, defeating both the advantages and disadvantages of the high concentration electrolytes. The unique superiorities of the optimized electrolyte make the Li/Li symmetrical batteries (1800 hours) and Li-O₂ batteries (180 cycles) deliver the best electrochemical performances among the batteries with DMA-based electrolytes. This work provides a novel electrolyte design guideline to solve the incompatibility between electrolyte and Li metal anode and brings new insights in the development of practical alkali-O₂ batteries.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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