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Broader context

Among the numerous successors for Li-ion batteries, $Li-O_2$ cells have become promising candidates owing to their higher theoretical energy density. However, the serious electrolyte decomposition resulting from the strong oxidizing environment in $Li-O_2$ batteries impedes their practical applications. Although there are some electrolytes that can tolerant the fatal nucleophilic attack, they are out of use due to the instability towards the lithium metal anode. So the protection of a lithium metal anode to make it compatible with these electrolytes is of vital importance. Recently, high concentration electrolytes have been demonstrated to be effective in stabilizing the lithium metal anode, but many accompanying disadvantages including sluggish kinetics, slow mass transfer and high cost seriously restrict their real-world implementation. In this work, we design a new electrolyte regulation strategy by adjusting the Li^* solvation structure under a medium concentration of an *N*_i*N*-dimethylacetamide based electrolyte to protect the Li metal anode from dendrite growth and corrosion. The optimized electrolyte not only inherits the advantages but also gets rid of the disadvantages of the concentrated electrolytes, as a result, significantly promoting the performance of $Li-O_2$ batteries. This electrolyte design strategy can effectively alleviate the dependent application of concentrated electrolytes and be extended to enhance other battery performance aspects.

Introduction

To meet the high energy density requirements of the rapidly developing 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 batteries featuring a high theoretical energy density of 3500 W h kg⁻¹ have been regarded as a promising candidate with great development prospects.^{5,6} As is well known, a stable electrolyte is indispensable for achieving high-performance Li–O₂ batteries. Nevertheless, so far, no electrolyte has been able to withstand the nucleophilic attack from the highly reactive reduced oxygen species (O₂⁻⁷, O₂²⁻⁷, HOO⁻ and HO⁻) while still being compatible with a Li metal anode, making the long-term cycling and practical application of Li–O₂ batteries full of thorns.^{7–9}

A renaissance of *N*,*N*-dimethylacetamide-based electrolytes to promote the cycling stability of Li–O₂ batteries†

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Li– O_2 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 a strong oxidizing environment as well as being compatible with a 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– O_2 batteries. And it is also a better lithium metal anode stabilization strategy than using high concentration electrolytes. In contrast to high concentration electrolytes with expensive cost, limited protection ability toward the 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 a 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– O_2 batteries (180 cycles) achieve the best cycling performances in DMA-based electrolytes to our knowledge. This study breathes new life into the electrolyte regulation strategy and paves the way for the development of alkali– O_2 batteries.



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Paper

Although 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 leading to loss of 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 dendrite induced short-circuit accidents.^{16–19} Therefore, if we could solve the instability issue of a Li metal anode in DMA-based electrolytes by electrolyte design, it would fulfill the critical anti-nucleophilic attack ability and Li compatibility requirements of an electrolyte for Li–O₂ batteries, and thus achieve high electrochemical performance.

How can we realize this goal? Since the electrolyte is composed of an organic solvent and Li salt, and the solvent here is DMA, what we can do is to choose the 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-bromoethanesulfonate, have been developed to in situ form protection layers on a Li metal anode to improve the performance.9,20 However, these protection layers are liable to be cracked and lose efficacy in 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 a steady anion-derived SEI film.^{21,22} Despite stabilization of the Li anodes, the high concentration electrolytes also exhibit 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 of Li salts used inducing high cost. Even with this progress, a DMAbased electrolyte that can permit high-performance cycling of Li-O₂ batteries has not yet been developed. Consequently, a new electrolyte design guideline is in need for a DMA based electrolyte to overcome the disadvantages of the high concentration electrolytes, while maintain their superiorities, thus obtaining a DMA based Li-O₂ battery with greatly enhanced electrochemical performance.

In this contribution, we have developed a new electrolyte design guideline to revive the DMA-based electrolyte for enabling long-term cycling of $\text{Li}-O_2$ batteries. This has been realized by the regulation of a 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 satisfactory dendrite and corrosion suppression effects toward the 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 to our knowledge.

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 mA h cm⁻² at a current density of 1 mA cm⁻² (Fig. 1 and Fig. S1–S3, ESI†). 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, d and Fig. S1, ESI†), which is 38-fold higher than that of the 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 the Li anode greatly (82 hours, Fig. 1b and e and Fig. S2, ESI†), whereas the cycle life of the 1 M LiNO₃ based cell



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), and 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 mA h 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 electrolyte 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).

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 satisfactory. 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 a control sample. As it can be seen from Fig. 1c and f and Fig. S3 and S4 (ESI[†]), the cells with a 3 M mixed electrolyte group are much more stable and deliver longer cycle performance than those of high concentration electrolyte groups. In particular, a more than 400 hour cycle life, \sim 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 the 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 DMAbased 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, ESI⁺), 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. In contrast, 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 a 2 M LiTFSI 1 M LiNO₃ electrolyte also surpass those of the previously



Fig. 2 Electrochemical performance of Li/Li symmetrical batteries. Longterm cycling 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 mA h cm⁻² and a current density of 1 mA cm⁻². Inset in (f) is the zoomed-in view of the Nyquist plots. (g) Arrhenius curves of different kinds of electrolytes. (h) Arrhenius plots from R_{ct} in Li/Li symmetrical batteries. (i) CV curves of Li/Li symmetrical batteries with different kinds of electrolytes.

reported DMA-based symmetrical batteries (Fig. 2d),^{9,20} verifying the effectiveness of the designed electrolyte for protecting the Li metal anode.

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 a 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.

To reveal the reason for 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 (ESI⁺), Arrhenius plots and corresponding activation energy (E_a) are used to reveal the migration barrier for Li⁺ ions in these three electrolytes.²⁵ It is evident that the ionic conductivity of 2 M LiTFSI 1 M LiNO₃ is always much higher than those 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 $LiNO_3$ (0.69 kJ mol⁻¹) is calculated than that of 4 M LiTFSI $(0.98 \text{ kJ mol}^{-1})$ and 5 M LiNO₃ $(1.21 \text{ kJ mol}^{-1})$ (Fig. S6, ESI[†]), 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, ESI[†]). 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, ESI⁺).^{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 (ESI[†]).^{19,28} In comparison with the high concentration electrolytes of 4 M LiTFSI (2.50 kJ mol⁻¹) and 5 M LiNO₃ (2.0 kJ mol⁻¹), the 2 M LiTFSI 1 M LiNO3 shows the lowest activation energy of 1.85 kJ mol⁻¹, 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 that the optimized electrolyte with 2 M LiTFSI 1 M LiNO3 in DMA displays faster mass transfer and electrode kinetics.

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 (ESI⁺), 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 a relatively 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.



Fig. 3 Characterization of the lithium deposition morphology and SEI film components. SEM images of the 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.

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, and 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, ESI^{\dagger}). As is well known, LiF-rich and LiN_xO_v-rich films are beneficial for stabilizing the lithium/electrolyte interface.^{31,32} The existence of $\text{LiN}_x O_y$ in the SEI film can be observed in all 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 relatively homogeneous distribution. Despite the fluorine-containing anion of TFSI⁻ in 4 M LiTFSI, nearly no LiF can be observed before and after etching (Fig. 3k and Fig. S11, ESI[†]), 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 LiNxOv exist and the content of LiF even increases after etching for 5 minutes (Fig. 3m and Fig. S13, ESI[†]). 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, and thus generation of LiF.³¹ Consequently, combining LiNO₃ and LiTFSI salts together in DMA can help 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 (ESI⁺) 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 ¹⁹F NMR spectra for 2 M LiTFSI 1 M LiNO3 compared to that of 3 M LiTFSI (Fig. S15, ESI⁺). For high concentration electrolytes (4 M LiTFSI and 5 M LiNO₃), more AGGs emerge and the interactions between Li⁺ and solvents/anions further increase (Fig. S16 and S17, ESI⁺). The large amount of AGGs in the high concentration electrolytes will unavoidably impede the mass transfer and electrode kinetics. Therefore, a strong solvation effect is not always conducive to better electrochemical performance and thus medium concentration electrolyte should be considerable. A similar conclusion can also be obtained from radical distribution function (RDF) results in Fig. 4g and h. The electrolyte with 2 M LiTFSI 1 M LiNO₃ shows a strong solvent effect like high concentration electrolytes, but a quite different solvation environment compared to that of the 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 LiNO₃ electrolyte confirms an easier tendency involvement of NO₃⁻ than TFSI⁻ in the first coordination shell. These changes of the solvation structure may influence the lowest unoccupied



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 LiNO₃ (b), 4 M LiTFSI (c), and 5 M LiNO₃ (d) electrolytes. Schematics of the solvation structures in 3 M LiTFSI (e), and 2 M LiTFSI 1 M LiNO₃ (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.

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 LiNO₃, 4 M LiTFSI and 5 M LiNO₃ electrolytes. Compared with the high concentration electrolytes, the 2 M LiTFSI 1 M LiNO₃ electrolyte shows enhanced ion movement, which is consistent with the above experimental result.^{33,34}

To explore the practical application ability of the prepared DMA-based electrolyte, Li-O2 batteries with different kinds of electrolytes were assembled (Fig. 5a). A 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, ESI[†]). The CV curve of the battery with 2 M LiTFSI 1 M LiNO₃ displays a typical Li-O₂ battery behavior and shows the strongest anodic and cathodic peak intensities, indicating 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 mA h 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 LiNO3 and 5 M LiNO3 based batteries are much lower than that of the battery with 4 M LiTFSI due to the redox catalytic activity of LiNO3 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 LiNO₃ based battery with a relative low charge plateau, the high concentration induced sluggish mass transfer and



Fig. 5 Electrochemical characterization of Li–O₂ batteries. (a) Schematic of the Li–O₂ battery with a 2 M LiTFSI 1 M LiNO₃ DMA-based electrolyte. Discharge and charge profiles of Li–O₂ batteries with different kinds of electrolytes at the 1st cycle (b), and 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 literature reports. SEM image (h) and XRD patterns (i) of the lithium metal anode in Li–O₂ battery with 2 M LiTFSI 1 M LiNO₃ DMA-based electrolyte after 50 cycles. (j) Comparisons of the performances and properties of the three kinds of electrolyte based Li–O₂ batteries.

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kinetics as well as less O2 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 $(0.7873 \text{ V}) < 5 \text{ M LiNO}_3 (1.0957 \text{ V}) < 4 \text{ M}$ LiTFSI (1.6403 V) (Fig. 5b and 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 and d). It is worth mentioning that the overpotential of the 2 M LiTFSI 1 M LiNO₃ is also quite a bit 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 (ESI⁺) 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 exhibits 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 (ESI⁺). The cycle life of the Li-O₂ batteries with the electrolytes of 4 M LiTFSI, 5 M LiNO3 and 2 M LiTFSI 1M LiNO3 is 68 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 to our knowledge (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, ESI⁺), verifying that the 2 M LiTFSI 1 M LiNO3 based Li-O2 battery follows the typical Li–O₂ electrochemistry of $2\text{Li} + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2$ and exhibits a good reversibility.⁴² To demonstrate the 2 M LiTFSI 1 M LiNO3 electrolyte rendered anti-corrosion effect on the Li anode, the battery after 50 cycles was disassembled to investigate the status of the lithium metal anode. As exhibited in Fig. 5h and 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, ESI[†]), revealing that the 4 M LiTFSI electrolyte cannot protect Li from corrosion. 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 meaning that 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– O_2 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_v -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 to our knowledge. This work provides a novel electrolyte design guideline to solve the incompatibility between the electrolyte and Li metal anode and brings new insights into the development of practical alkali-O2 batteries.

Conflicts of interest

There are no conflicts to declare.

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