Article

Lithium−Air Batteries: Air-Electrochemistry and Anode Stabilization

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CONSPECTUS: It is a permanent issue for modern society to develop high-energy-density, low-cost, and safe batteries to promote technological innovation and revolutionize the human lifestyle. However, the current popular Li-ion batteries are approaching their ceiling in energy density, and thus other battery systems with more power need to be proposed and studied to guide this revolution. Lithium−air batteries are among the candidates for next-generation batteries because of their high energy density (3500 Wh/kg). The past 20 years have witnessed rapid developments of lithium−air batteries in electrochemistry and material engineering with scientists' collaboration from all over the world. Despite these advances, the investigation on Li−air batteries is still in its infancy, and many bottleneck problems, including fundamental and application difficulties, are waiting to be resolved. For the electrolyte, it is prone to be attacked by intermediates (LiO_2, O_2^-, $^1O_2$, O_2^{2-}) and decomposed at high voltage, accompanying side reactions that will induce cathode passivation. For the lithium anode, it can be corroded severely by H_2O and the side products, thus protection methods are urgently needed. As an integrated system, the realization of high-performance Li−air batteries requires the three components to be optimized simultaneously.

In this Account, we are going to summarize our progress for optimizing Li−air batteries in the past decade, including air-electrochemistry and anode optimization. Air-electrochemistry involves the interactions among electrolytes, cathodes, and air, which is a complex issue to understand. The search for stable electrolytes is first introduced because at the early age of its development, the use of incompatible Li-ion battery electrolytes leads to some misunderstandings and troubles in the advances of Li−air batteries. After finding suitable electrolytes for Li−air batteries, the fundamental research in the reaction mechanism starts to boom, and the performance has achieved great improvement. Then, air electrode engineering is introduced to give a general design principle. Examples of carbon-based cathodes and all-metal cathodes are discussed. In addition, to understand the influence of air components on Li−air batteries, the electro-activity of N_2 has been tested and the role of CO_2 in Li−O_2/CO_2 has been refreshed. Following this, the strategies for anode optimization, including constructing artificial films, introducing hydrophobic polymer electrolytes, adding electrolyte additives, and designing alloy anodes, have been discussed. Finally, we advocate researchers in this field to conduct cell level optimizations and consider their application scenarios to promote the commercialization of Li−air batteries in the near future.
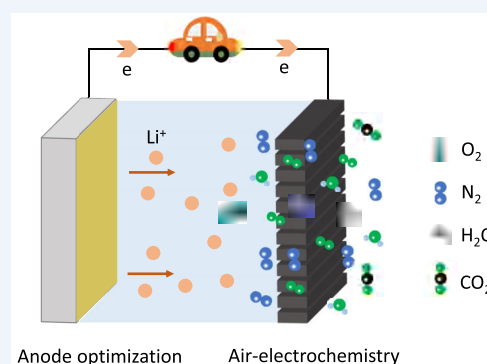
■ KEY REFERENCES

Ma, J. L.; Meng, F. L.; Yu, Y.; Liu, D. P.; Yan, J. M.; Zhang, Y.; Zhang, X. B.; Jiang, Q. Prevention of Dendrite Growth and Volume Expansion to Give High-Performance Aprotic Bimetallic Li−Na Alloy-O_2 Batteries. *Nat. Chem.* **2019**, *11*, 64−70.[1] This paper adopts Li−Na alloy as the anode in metal-O_2 batteries to achieve a stable anode and retain high specific capacity with both Li and Na as active materials on the anode side.

Wang, J.; Huang, G.; Chen, K.; Zhang, X. B. An Adjustable-Porosity Plastic Crystal Electrolyte Enables High-Performance All-Solid-State Lithium−Oxygen Batteries. *Angew. Chem., Int. Ed.* **2020**, *59*, 9382−9387.[2] This reference develops a plastic crystal electrolyte with adjustable porosity for decreasing interfacial resistance and increasing triple phase boundaries in all-solid-state lithium−oxygen batteries. This study achieves the best performance in this field.

Chen, K.; Huang, G.; Ma, J. L.; Wang, J.; Yang, D. Y.; Yang, X. Y.; Yu, Y.; Zhang, X. B. The Stabilization Effect of CO_2 in Lithium−Oxygen/CO_2 Batteries. *Angew. Chem., Int. Ed.* **2020**, *59*, 16661−16667.[3] This work redefines the role of CO_2 in Li−O_2 batteries: CO_2 can help the formation of a protective Li_2CO_3 film on the Li anode and capture O_2^- to reduce side reactions.

1. INTRODUCTION

The rising consumption of fossil fuels has made a great impact on the environment of the earth, including the greenhouse effect,

ozone sphere damage, a sea level rise, and poor air quality. Clean energy sources (solar, wind energy, etc.) have been invested intensely in recent years to relieve the environmental crisis. However, uneven distribution of energy in time and space, leading to the inefficient utilization of these clean energy sources, is really a hard nut to crack. The adoption of rechargeable batteries is an effective tool to alleviate this issue because they can store energy at peaks and release it at troughs to reduce the pressure of power grid. In addition, electrified society also needs batteries to actuate phones, computers, robots, cars, drones, etc. Unfortunately, the current advanced Li-ion batteries cannot satisfy people's growing demand because of limited energy densities. Therefore, developing next-generation and high-energy-density batteries is highly desired. Among various emerging battery technologies, Li−air batteries occupy the top position in energy density, ∼3500 Wh/kg based on Li_2O_2, which is 10 times higher than that of current Li-ion batteries.[4] Consequently, high-performance Li−air batteries are promising to resolve the shortcoming of the low energy densities of current commercial battery systems.

A typical Li−air battery consists of a Li metal anode, organic electrolyte, and porous cathode, and its working principle is featured in Figure 1. During discharge, Li ions move from the
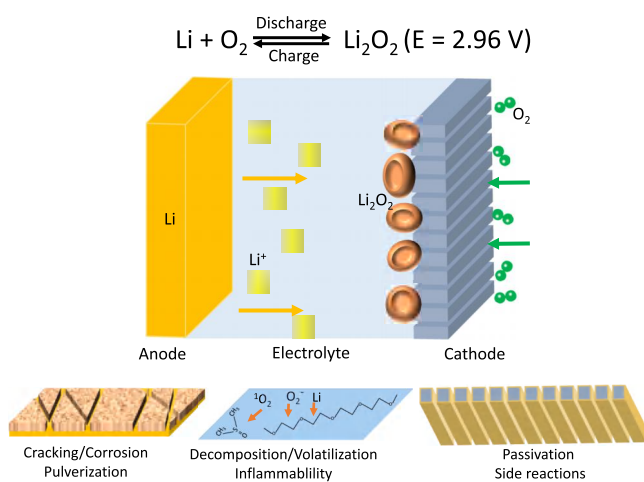

Li + O_2 $\underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}}$ Li_2O_2 (E = 2.96 V)

Figure 1. Working principle and challenges of Li−O_2 batteries.

anode to the cathode to combine reduced O_2 molecule, forming Li_2O_2 and depositing on the cathode surface. During charge, this process proceeds in reverse with Li ions moving back and O_2 released.[5] Even though the Li−air battery holds great application potential, taking full advantage of this system is still very challenging. The problems include anode cracking, corrosion and pulverization, electrolyte decomposition, volatilization and inflammability, cathode passivation, and accompanied side reactions (Figure 1). To solve these problems, the complex air-electrochemistry and the anode degradation mechanism must be fully understood under the premise of stable electrolytes.

Over past decades, many groups have devoted to combating the challenges in Li−O_2 batteries, aiming to realize their promising performance. Our group stepped into this field as early as 2010, and we experienced fast development of Li−air batteries with a deep understanding of the reaction mechanism and a performance leap. Considering that the semiopen Li−air batteries face complex reaction mechanisms and severe side reactions (electrolyte decomposition, cathode passivation, and

anode corrosion), in this Account, we aim to summarize our efforts on how to conquer the issues associated with the electrolyte, cathode, and anode. First, electrolyte engineering, especially the evolution from liquid electrolytes to solid ones, is introduced. Then, cathode design, including carbon-based and all-metal materials, is briefly discussed, followed by identification of the roles of N_2 and CO_2 in Li−O_2 batteries. Subsequently, the anode protection strategies are illustrated. Finally, we share our perspectives on the future directions for Li−air batteries to promote their real-world applications.

2. AIR-ELECTROCHEMISTRY: HUNTING FOR STABLE ELECTROLYTES

2.1. Liquid Electrolytes

The cathode and anode in a battery are bridged by the electrolyte, which transfers the ions for redox reactions. Air-electrochemistry and Li anode stability are highly connected with the characteristics of the electrolyte. Furthermore, from a historic perspective, the advances in the electrolyte have been decisive for promoting the battery performance. Therefore, when talking of the air-electrochemistry and anode protection, the stability of the electrolyte should not be ignored. At the early stage of Li−air batteries, the electrolytes were directly borrowed from Li-ion batteries.[6−8] Later, some researchers found that there were severe side reactions in these batteries due to the electrolyte decomposition induced by the reaction intermediates, like LiO_2, O_2^-, O_2^{2-}, and $^1O_2$.[9,10] As a result, the adoption of the electrolytes that are incompatible in Li−air batteries is a major issue that impedes our study on the reaction mechanism, not to mention how to deliver higher capacities. Therefore, developing highly chemically and electrochemically stable, compatible electrolytes is paramount, and we introduce this section early in the part on air-electrochemistry.

In this regard, we first proposed DMSO (dimethyl sulfoxide) based electrolytes for Li−O_2 batteries in 2012.[11] Compared with TEGDME (tetraethylene glycol dimethyl ether) and PC (propylene carbonate) based electrolytes, the battery with DMSO based electrolytes demonstrated a high discharge plateau (2.8 V vs Li^+/Li) and large capacity (9400 mAh g^{-1}) even using a common carbon cathode (Figure 2a,b). DMSO solvent was also adopted by many other groups to study the reaction mechanisms of Li−air batteries. This further confirmed the success of this solvent. Another solvent, tetramethylene sulfone (TMS), was also proposed in 2012 because it showed high Li salt solubility, low toxicity, superior safety, low volatility, and resistance to high voltage (5.6 V vs Li^+/Li, Figure 2c).[12] As a result, impressive performance has been delivered, 9100 mAh g^{-1} at 0.05 mA cm^{-2} and 1700 mAh g^{-1} at 0.5 mA cm^{-2} (Figure 2d).

Since Yang-kook Sun developed $LiCF_3SO_3$ in TEGDME (1:4) electrolyte,[13] many groups have adopted it in Li−air batteries. However, this electrolyte shows high viscosity, sluggish kinetics, and instability toward superoxide radicals. Despite N,N-dimethylacetamide (DMA) being a solvent that can tolerate aggressive intermediates, like O_2^- and O_2^{2-}, it is not stable with Li metal. Targeting this problem, we tailored the composition and concentration of the Li salts in DMA and found that 2 M LiTFSI combined with 1 M $LiNO_3$ could make the electrolyte become stable with a Li anode.[14] When being applied in Li−air batteries, this medium-concentration electrolyte showed lower polarization (0.9605 V) than those of 4 M LiTFSI/DMA (2.1141 V), 5 M $LiNO_3$/DMA (2.4893 V), and 1
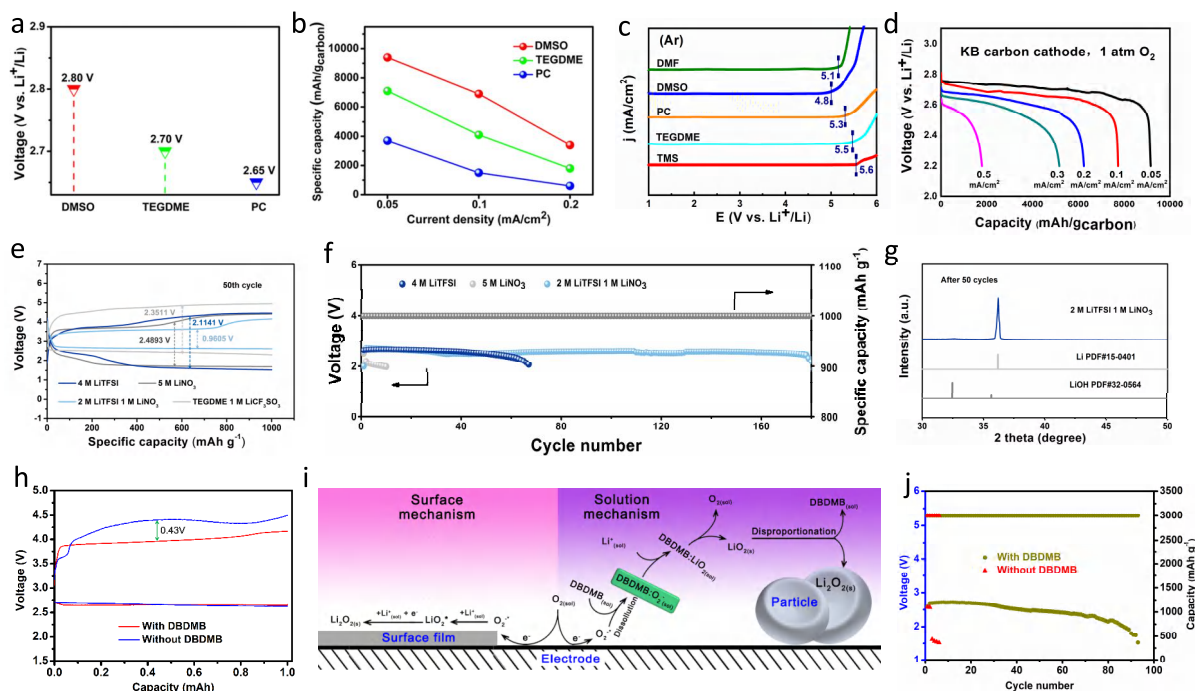
Figure 2. (a) Discharge plateaus of Li−O$_2$ batteries based on DMSO, TEGDME, and PC-based electrolytes and (b) the corresponding capacity at different rates. (c) Electrochemical windows of the solvents. (d) Rate performance of the Li−O$_2$ battery with TMS. (e) Discharge and charge profiles of Li−O$_2$ batteries with different electrolytes. (f) Long-term cycle life of Li−O$_2$ batteries. (g) XRD pattern of lithium metal anode in Li−O$_2$ batteries. (h) Discharge−charge curves of Li−O$_2$ batteries at a current density of 200 mA g^{-1} with a fixed capacity of 1 mAh. (i) Illustration of the different Li$_2$O$_2$ growth pathways. (j) Cycling performance of Li−O$_2$ batteries with/without DBDMB in the electrolyte. Adapted from refs 11, 12, 14, and 15. Copyright 2012, 2012, and 2020 Royal Society of Chemistry and 2020 Wiley-VCH.

M LiCF$_3$SO$_3$/TEGDME (2.3511 V; Figure 2e). For the cycling test, this optimized electrolyte sustained a long life of 180 cycles (Figure 2f). After 50 cycles, the anode in the cell with the optimized electrolyte was characterized by XRD, and no LiOH peaks could be observed, indicating that the anode surface was stabilized by the electrolyte (Figure 2g). Systematic investigation on the anode surface proved that the formation of LiF and LiN$_x$O$_y$ in the solid electrolyte interphase was the reason for the stabilization effect.

As mentioned above, most of the electrolytes tend to be attacked by the intermediates to form side products. The continuous accumulation of these side products will subsequently lead to the early death of the batteries; thus reducing the formation and promoting the decomposition of side products are important to boost the performance of Li−air batteries. With this in mind, we introduced a redox mediator, DBDMB (2,5-di-*tert*-butyl-1,4-dimethoxybenzene), into the 1 M LiCF$_3$SO$_3$/TEGDME electrolyte to solve the above problems.[15] This mediator can reduce the charge potential (Figure 2h) and promote the solution discharge route with the generation of toroidal Li$_2$O$_2$ rather than film to enlarge the discharge capacity (Figure 2i). In addition, DBDMB can also capture O$_2^-$ to prevent the disproportionation reaction of O$_2^-$ + O$_2^-$ → O$_2^{2-}$ + ^{1}O$_2$. Further, the relatively high redox potential of DBDMB (4.2 V) can effectively facilitate the decomposition of the main side products of Li$_2$CO$_3$ (3.82 V) and LiOH (3.39 V) to reduce their accumulation. With these benefits, the Li−O$_2$ battery with DBDMB achieved 90 cycles at a high cycling capacity of 3000 mAh g^{-1} and a high rate of 1000 mA g^{-1} (Figure 2j). These achievements have proved that the introduction of a suitable redox mediator is an effective tool to promote the development of high-performance Li−O$_2$ batteries.

2.2. Solid Electrolytes

Recently, solid-state electrolytes have attracted close attention in the battery field because solidifying the electrolyte is promising to resolve safety issues by suppressing Li dendrite growth and retarding the occurrence of combustion. Despite its promise, the construction of high-performance all-solid-state Li−air batteries is full of thorns. On the one hand, the working principle of the Li−air battery requires the cathode to be porous to provide adequate gas−solid−solid interfaces to allow the occurrence of electrochemical reactions. On the other hand, the solid-state electrolyte should touch the cathode closely to ensure ion conductivity, while this is difficult due to the solid−solid contact and the Li$_2$O$_2$ formation and decomposition rendered cathode volume change. In addition, the interface between the solid electrolyte and Li anode should be optimized, otherwise there will be large resistance that even induces battery failure. On the basis of our insight into the Li−air battery system, we have made progress from all liquid batteries to all solid batteries (Figure 3a).

In 2018, we reported a sandwich-structure electrolyte (organic/ceramic/organic electrolyte, OCOE) by placing a solid ceramic LLZO (Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$) pallet between liquid organic electrolytes (OE, 1 M LiCF$_3$SO$_3$/TEGDME).[16] This ceramic electrolyte can suppress the crossover of oxygen and protect the anode from corrosion. As seen in Figure 3b, the discharge capacity of the cell using OCOE is 3 times higher than that of the cell with OE at 200 mA g^{-1}. After charge, the anodes were characterized by SEM (Figure 3c). The Li anode with OE was severely corroded with cracks and pulverization on the surface, while the Li anode with OCOE maintained a smooth surface, indicating the inspiring role of LLZO in protecting the Li anode. For the cycling performance, the battery with OCOE
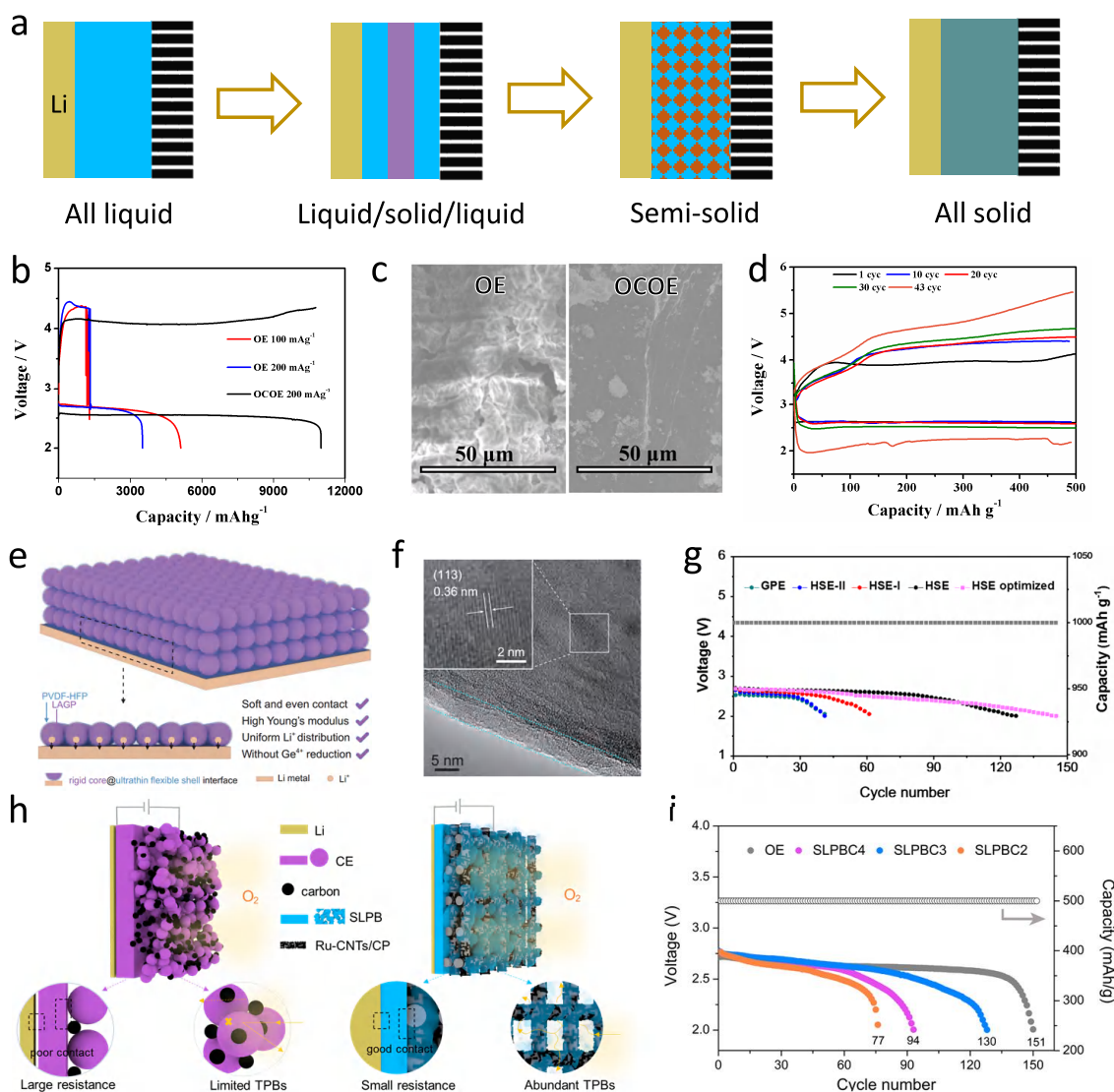
Figure 3. (a) From all liquid to all solid Li−O_2 batteries. (b) Discharge and charge performance of Li−O_2 batteries with OE and OCOE. (c) SEM pictures of Li anodes with OE or OCOE. (d) Cycling performance of the Li−O_2 battery with OCOE. (e) Schematic representation of dendrite-free lithium deposition enabled by hybrid solid electrolyte (HSE). (f) TEM picture of the core−shell structure of HSE. (g) Cycling performance of the Li−O_2 batteries with different electrolytes. (h) Schematic illustration of the conventional and porosity-adjustable electrolyte based all solid-state batteries. (i) Cycling performance of batteries with different electrolytes. Reproduced with permission from refs 16, 17, and 2. Copyright 2018 Springer Nature, 2020 Oxford University Press, and 2020 Wiley-VCH.

demonstrated 43 stable cycles, much longer than the 14 cycles of the OE based battery (Figure 3d).

To suppress Li dendrite growth, the solid electrolyte should possess a high modulus and flexible contact with the Li anode. These requirements cannot be met by the inorganic ceramic electrolytes. Therefore, we designed a hybrid solid electrolyte (HSE) that consists of a rigid $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) core and soft poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) shell (Figure 3e).[17] In this HSE, the stiff LAGP core acts as a bracket to maintain the structure integrity and ensure a high Young's modulus, and the soft and flexible PVDF-HFP shell enables close contact with the Li anode to achieve stable interface and homogenize the Li+ flux (Figure 3e). The thickness of the flexible polymer shell is ∼5 nm (Figure 3f). Thanks to the combined advantages of polymer and ceramic electrolytes as well as the unique core@shell structure, a Li−O_2 battery with an optimized HSE could achieve 146 cycles at 300 mA g^{-1} and 1000 mAh g^{-1} (Figure 3g).

It is clear that cathode engineering to simultaneously realize good ion and electron conductivity is the prerequisite for advancing the development of high-performance all-solid Li−O_2 batteries. However, the simultaneous realization of high ion and electron conductivity seems impossible by conventional methods due to the poor solid−solid contact between them. To conquer this, we fabricated a plastic crystal electrolyte (PCE) with adjustable porosity through the thermally induced phase separation (TIPS) technique using succinonitrile, lithium bis(trifluoromethanesulphonyl)imide (LiTFSI), poly-(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (denoted as SLPB).[2] By in situ introduction of the porous PCE on the surface of the Ru-CNTs cathode, a solid-state cathode (SLPBC) with good Li+/e− conductivity and an ample O_2 transfer pathway was realized (Figure 3h). When pairing the solid-state cathode with a compact PCE, a close interface contact was achieved, and thus the resistance was largely reduced. The use of this porosity
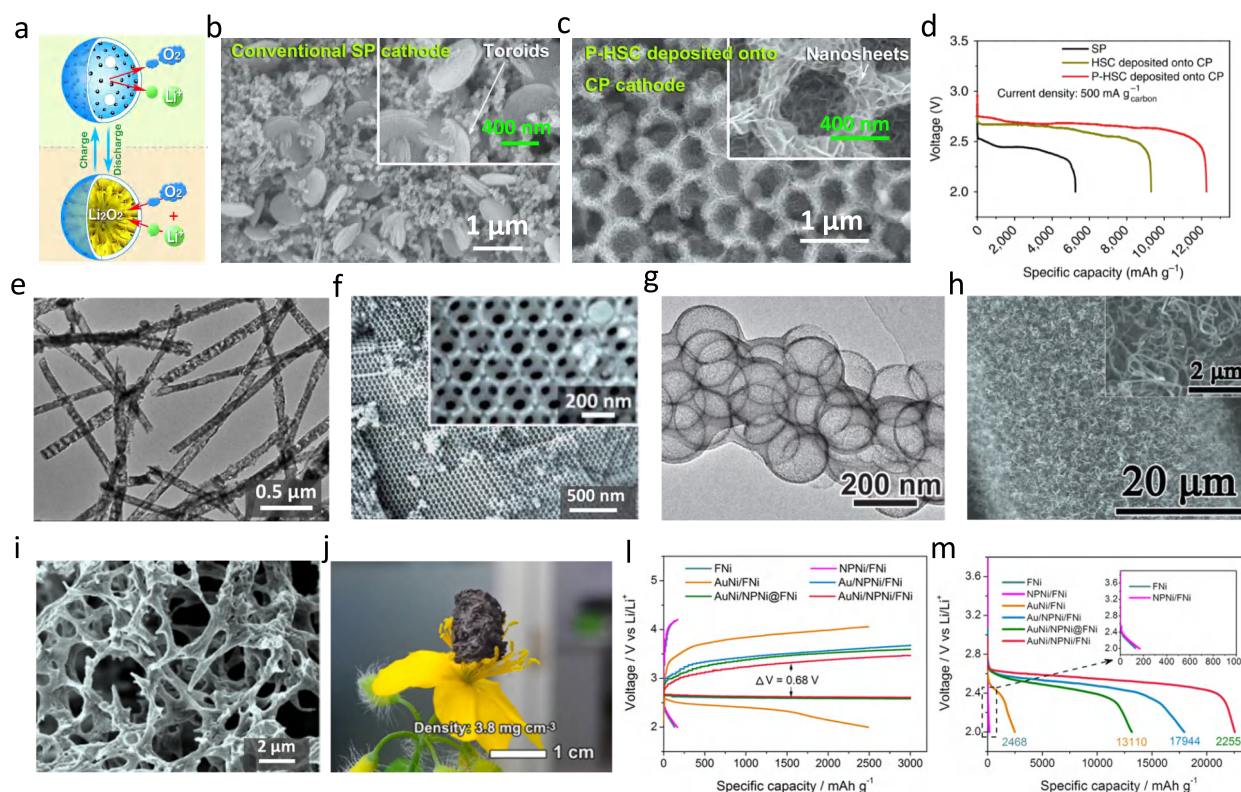
Figure 4. (a) Schematic of Li_2O_2 growth in the Pd-decorated carbon sphere. The morphology of discharge products on (b) SP and (c) P-HSC cathodes. (d) Full discharge performance of the batteries with different cathodes. Structure of (e) tubular $La_{0.75}Sr_{0.25}MnO_3$, (f) honeycomb $LaFeO_3$, (g) interconnected carbon nanofiber, and (h) CNT grown on SSM. (i) SEM image of the synthesized all-metal AuNi/NPNi/FNi cathode and its picture on a stamen (j). (l) First charge–discharge curves and (m) full discharge performance of Li–O_2 cells with different cathodes. Adapted with permission from refs 25−29 and 33. Copyright 2013 Nature Publishing Group, 2013 Wiley-VCH, 2014 Royal Society of Chemistry, 2016 Wiley-VCH, 2018 Wiley-VCH, and 2017 American Chemical Society.

adjustable PCE not only provides abundant triple-phase boundaries but also enables fast reaction kinetics, making the battery realize a high specific discharge capacity of 5963 mAh g^{-1} and a long life of 130 cycles with a current density of 200 mA g^{-1} and a capacity of 500 mAh g^{-1} at 32 °C (Figure 3i). Though the life of the PCE based all-solid cell is shorter than the 151 cycles of the battery with an organic electrolyte (OE), this work indeed represents a leap from the semisolid to the all-solid Li–O_2 battery. Future works must take the cathode engineering as a priority so as to achieve stable structure, good Li$^+$/e$^-$ conductivity, and a high active reaction area, while the strategies for anode stabilization can be borrowed from the solid Li-ion batteries.

3. AIR-ELECTROCHEMISTRY: CATHODE ENGINEERING AND AIR COMPONENTS INFLUENCE

Air-electrochemistry involves the electrochemical reactions happened at the cathode and the electrolyte. Both the composition and structure of the cathode material and the air components (N_2, CO_2, H_2O, etc.) will affect the air-electrochemistry. This makes the depth of our research in air-electrochemistry determine whether we can realize true Li–air batteries. It has been reported that there are many different Li_2O_2 morphologies on varied cathodes,[18−22] revealing the critical role of the cathode in tailoring the air-electrochemistry. When replacing O_2 with air, N_2 and CO_2 will participate in the (electro)chemical reactions during the discharge and charge processes, thus changing the reaction mechanisms. Therefore, it is important to investigate how the reaction mechanisms evolve

and what kind of interactions of N_2/CO_2 with Li_2O_2, O_2^-, LiO_2, etc there are.

3.1. Cathode Engineering

The cathode development has been summarized in detail in our previous review.[23] Here, we only introduce several examples to elucidate the design principles of the air cathode. An ideal cathode should possess high electron conductivity, porous structure for discharge product accommodation, good electrolyte wettability, and high catalytic activity and stability.[24] In 2013, we reported a free-standing palladium (Pd)-decorated hollow spherical carbon (P-HSC) as a cathode (Figure 4a), which was deposited on the carbon paper by electrophoresis.[25] This cathode with a hollow structure and catalyst inside could induce nanosheet-like Li_2O_2 growth (Figure 4c), being different from the toroidal-plate Li_2O_2 on a Super P (SP) cathode (Figure 4b). Moreover, these dense Li_2O_2 plates on SP exposed limited surface areas to the electrolyte, leading to poor charge kinetics and thus inferior cycling performance. In contrast, the Li_2O_2 nanosheets on P-HSC grew uniformly and loosely on the carbon sphere, providing sufficient Li_2O_2/electrolyte interfaces, thus a high-performance Li–O_2 battery was achieved. As indicated in Figure 4d, the battery with a P-HSC cathode delivers a long life of 205 cycles and a capacity of 12254 mAh g^{-1}, much higher than the HSC's 9280 mAh g^{-1} and SP's 5250 mAh g^{-1}. In addition, we have also developed other kinds of cathodes, like tubular perovskite oxides ($La_{0.75}Sr_{0.25}MnO_3$, Figure 4e),[26] honeycomb 3D ordered macroporous $LaFeO_3$ (Figure 4f),[27] macroporous interconnected hollow carbon nanofibers (Figure 4g),[28] and
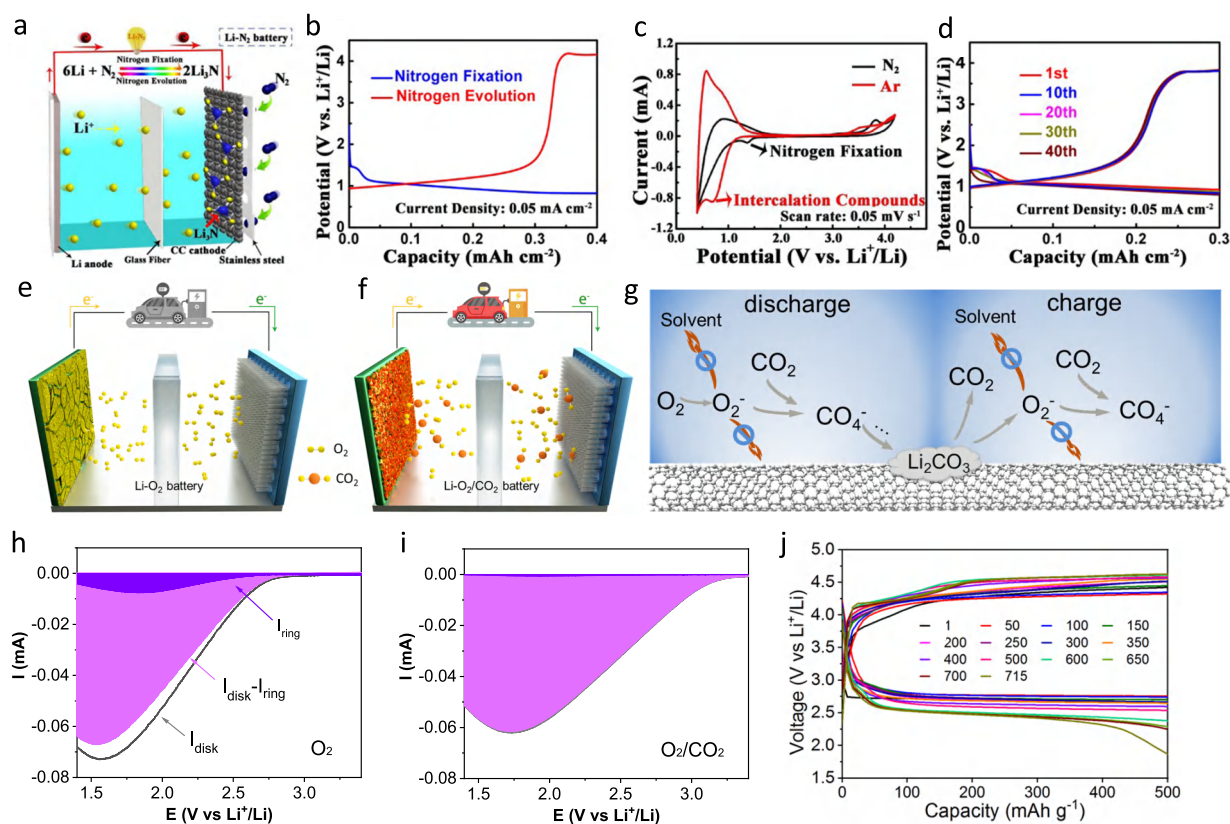
Figure 5. (a) Schematic illustration of the Li−N₂ battery. (b) Discharge−charge curves and (c) cyclic voltammetry of the Li−N₂ battery. (d) Cycling performance of the Li−N₂ battery. (e,f) Schematic representation of the Li−O₂ and Li−O₂/CO₂ battery. (g) The discharge and charge reaction mechanisms of the Li−O₂/CO₂ battery. (h,i) RRDE test to confirm the capture of O₂⁻ by CO₂. (j) Cycling performance of the Li−O₂/CO₂ battery. Reproduced with permission from refs 34 and 3. Copyright 2017 Elsevier and 2020 Wiley-VCH.

CNT forests on stainless steel mesh (SSM; Figure 4h).[29] When applying these cathodes in Li−O₂ batteries, all of them exhibit improved discharge capacity, rate capability, and cycling stability due to their unique structures for fast kinetics and tailoring product deposition.

The above cathodes are carbon-based materials, either as catalysts or as substrates. However, carbon materials have been confirmed unstable toward the intermediates (LiO_2, O_2^-) and Li_2O_2, thus developing carbon-free cathodes while retaining the advantages of carbon is vital to avert carbon associated side reactions.[30−32] In 2017, we developed an ultralight, porous, all-metal cathode for Li−O₂ batteries (Figure 4i,j).[33] Nickel foam was selected as the substrate, and Au was deposited to promote the catalytic effect, and finally followed by conducting an alloying process. This nickel foam-based, Au-integrated, nanoporous cathode (AuNi/NPNi/FNi) enables the Li−O₂ battery to achieve a low overpotential of 0.68 V (Figure 4l) and a high specific capacity of 22551 mAh g⁻¹ (Figure 4m). Unexpectedly, the battery with this all-metal cathode can sustain a long life of 286 cycles at 1.0 A g⁻¹ and 3000 mAh g⁻¹. Furthermore, due to the enhanced stability of the metal cathode, side reactions involving the formation of Li_2CO_3 and Li carboxylates have been greatly suppressed.

3.2. Influences from Air Components

As to Li−air batteries, N₂ must be considered because it is the main component (∼78%) in air. Then, the question is whether N₂ will participate in the electrochemical reactions of Li−O₂ battery. We constructed a Li−N₂ battery by adopting N₂ to replace O₂ as the active gas.[34] Beyond our expectation, Li_3N was

verified to be the discharge product, and it could be decomposed during the charge process, thus a rechargeable Li−N₂ battery was realized (Figure 5a). The discharge plateau of the Li−N₂ battery is around 1 V (Figure 5b). The cyclic voltammetry curves in Figure 5c reveal that the Li−N₂ battery allows reversible N₂ fixation and release, which has been further confirmed by FTIR, XRD, XPS, and colorimetric analysis. When carbon cloth was used as the cathode, the Li−N₂ battery achieved 40 stable cycles. This proof-of-concept experiment proves that N₂ can be electroactive, which has long been neglected in Li−air batteries.

Another game-changer in the air is CO₂. Many papers have investigated the influences of CO₂ on Li−O₂ batteries and revealed that CO₂ can change the discharge product from Li_2O_2 to Li_2CO_3.[35−37] Since Li_2CO_3 has poorer electron conductivity than Li_2O_2, it is more difficult to decompose during the charge process, leading to high overpotential and low energy efficiency. As a result, it is supposed that CO₂ should be avoided. However, these results only focused on the CO₂-induced impact on the cathode side, and few studies have paid attention to the anode and electrolyte parts. To systematically investigate the role of CO₂ in a Li−O₂ battery, we constructed a Li−O₂/CO₂ (1:1) battery with Pd/CNT as a cathode.[3] Typically, the Li anode in the Li−O₂ battery is severely corroded after 20 cycles, just like the cracks shown in Figure 5e. In contrast, even after 500 cycles, the Li plate in the Li−O₂/CO₂ battery is still smooth. After detailed characterization, we found that nanosheet-like Li_2CO_3 formed on the anode surface through the reaction between LiOH and CO₂, and this Li_2CO_3 layer could behave as a
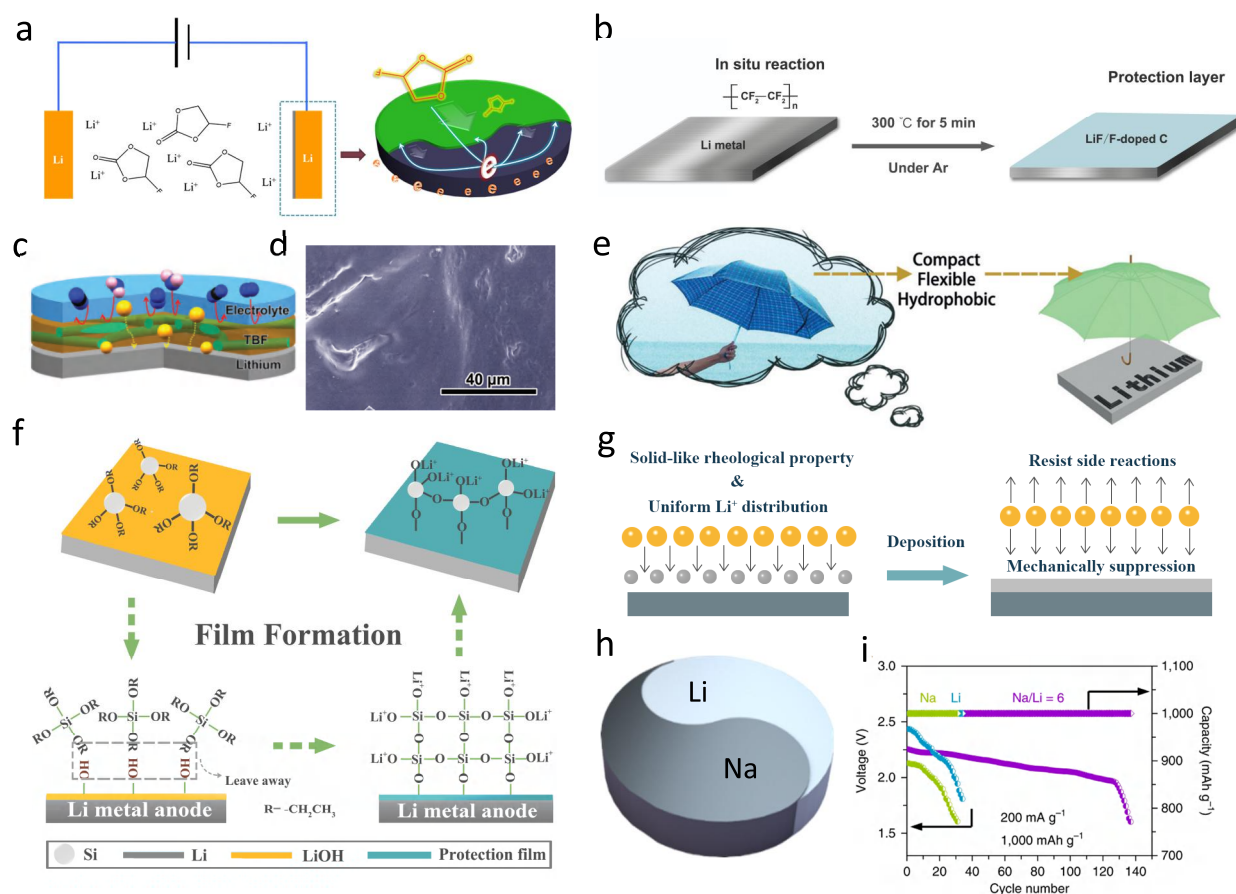
Figure 6. (a) Illustration of the formation of anode-protective film using electrochemical method. (b) In situ formation of a gradient protection layer on the Li anode surface. (c) Tissue-directed/reinforced bifunctional protection film (TBF). (d) SEM image of the TBF after 40 cycles. (e) Li protection by a stable hydrophobic composite polymer electrolyte. (f) Schematic illustration of the formation of a self-healing protective film on Li anode. (g) Solid-like electrolyte to block Li dendrite growth and regulate Li^+ flux. (h) Li−Na alloy and (i) cycling performance of alloy−O_2 battery. Reproduced with permission from refs 48−53 and 1. Copyright 2015, 2020, 2017, 2019 Wiley-VCH; 2019, 2019 Elsevier; and 2019 Nature Publishing Group.

protection film to repel the attack from aggressive intermediates and H_2O (Figure 5f). The reaction mechanism of the Li−O_2/CO_2 (1:1) battery is illustrated in Figure 5g. It can be observed that CO_2 can capture O_2^- with the formation of CO_4^-. This has been validated by the rotating ring-disk electrode (RRDE) test. Being different from the existence of both disk and ring current in the O_2 atmosphere (Figure 5h), only disk current can be detected in the O_2/CO_2 atmosphere (Figure 5i), indicating that the reduced O_2^- can be immediately captured by CO_2 without diffusing to the ring. As O_2^- is captured, the singlet oxygen ($^1O_2$) generated from the disproportionation of O_2^- can be inhibited.[38] The suppression of these active intermediates alleviates the parasitic reactions involving the cathode and electrolyte. Therefore, the introduction of CO_2 can simultaneously protect the whole battery system, endowing a very stable Li−O_2/CO_2 (1:1) battery with an ultra long life of 715 cycles at 500 mA g^{-1} and 500 mAh g^{-1} (Figure 5j).

The above discussion just considers the influences of N_2 and CO_2; however, the air components are far more complex. When moisture, SO_x, and NO_x are involved, the air-electrochemistry becomes more elusive. Despite the concentrations of these components being very low, they will display accumulative effects as cycling goes on, making the air-electrochemistry time-dependent. Considering this, in-depth investigation on these impacts should be performed. In one word, there still remain many problems and challenges waiting to be resolved for truly understanding the complicated air-electrochemistry.

4. ANODE STABILIZATION

In Li−air batteries, the Li anode will experience cracking, corrosion, and pulverization due to its reactions with H_2O, O_2, and the intermediates generated during the cycling process.[39,40] To suppress these parasitic reactions, many strategies have been adopted, like construction of an artificial protection film on the Li surface to repel the active species,[41−43] modification of the separator/electrolyte to prevent the diffusion of these species,[44−46] and design of the alloy anode to enhance the corrosion resistance ability.[47] In our group, we have developed a series of protection strategies to alleviate the anode degradation and thus prolong the battery life.

In 2015, we reported a facial way to construct a protection layer on the Li surface by electrochemically treating Li metals with the fluoroethylene carbonate (FEC) electrolyte in a symmetrical cell (Figure 6a).[48] The decomposition of the FEC during cycling formed a film that composes of Li_2CO_3, LiF, polyene, and C−F species on the surface of the Li metal. With this protected Li anode, the Li−O_2 battery demonstrated a long life of more than 100 cycles. However, this artificial protection film is too thin and fragile and cannot bear long-term cycling, thus a robust film should be constructed for a longer battery life.

To design such a film, a LiF/F-doped carbon protection layer was built by in situ reaction of molten Li with PTFE (poly tetrafluoroethylene) at high temperature (Figure 6b).[49] The thickness of this layer is ~20 μm, so that the protection effect is more obvious. This layer can not only repel the offensive species but also act as Li$^+$ regulator to make uniform the Li$^+$ flux to inhibit dendrite formation. As a result, the Li anode stability was much improved with Li/Li symmetrical batteries displaying a cycling life of 1000 h at 0.1 mA cm^{-2} and with a capacity of 0.1 mAh cm^{-2}, and the Li−O$_2$ battery demonstrated 180 stable cycles at 300 mA g^{-1} and 1000 mAh g^{-1}.

In addition to the construction of artificial films on the Li surface, modifying the separator and electrolyte, can be another option to protect the Li anode. The pores of conventional glass fibers are so large that the Li$^+$ flux cannot be tailored and the diffusion of offensive species from the cathode side to the anode side is unobstructed. Therefore, designing functional separators that are compatible with Li−O$_2$ batteries is indispensable to realize a highly stable Li anode. With this in mind, we designed a tissue-based bifunctional separator (TBF), which could also act as a Li anode protection film in 2017.[50] This TBF with dense structure and high stability (Figure 6c) can play a role to defend the anode from attack by water, O$_2$, and O$_2^-$. Consequently, the Li−O$_2$ battery with the TBF separator could cycle up to 300 times at 200 mA g^{-1} and 500 mAh g^{-1}. Later, inspired by the umbrella, we fabricated a stable and hydrophobic composite polymer electrolyte (SHCPE) that was composed of thermo-plastic polyurethane (TPU) and hydrophobic SiO$_2$ nano-particles (Figure 6e).[51] This hydrophobic electrolyte can effectively resist moisture from the air, thus enabling the Li−air battery to run 95 cycles in the ambient air, much higher than the 24 cycles of the battery with a glass fiber separator. In addition, this hydrophobic electrolyte could also increase the safety of the Li−air battery, which can even bear the water-immersing and nail-penetration tests.

The main corrosion product on the Li surface has been proved to be porous LiOH, thus reactive species can easily and continuously penetrate inside through the pores until all Li is used up. So we considered whether we could consume the resultant LiOH through chemical reactions to heal the corroded surface. We selected tetraethyl orthosilicate (TEOS) as an example to conduct this proof-of-concept experiment.[52] As expected, TEOS can spontaneously and efficiently react with LiOH to form a self-healing protective film to prevent further Li corrosion (Figure 6f). Thanks to the optimized Li surface, the life of the Li−O$_2$ battery was extended from 70 cycles to 144 cycles. Another strategy to prevent Li corrosion is based on the fact that the corrosive species come from the cathode part, including air permeation and intermediates formed during the OER and ORR. It is promising to block the diffusion of these species by increasing the viscosity of the electrolyte. Therefore, we combined CF$_3$SO$_3^-$ and hydrophobic silica colloidal nanoparticles through an electrostatic interaction to form an electrolyte with solid-like rheological properties.[53] Adding 10 wt % silica to the electrolyte can enable the diffusion rate of the corrosive species to be much slower with a 980-fold increase of the anticorrosion effect when compared to the electrolyte without silica. In addition, this electrolyte with a unique structure can also tailor the deposition behavior of Li$^+$ to form a dendrite-free anode (Figure 6g). Consequently, the symmetrical Li/Li battery can run more than 700 h at 0.1 mA cm^{-2} and 0.1 mAh cm^{-2}, and the Li anode can survive 550 cycles in the Li−O$_2$ battery.

Anode alloying has been widely used in Li-ion batteries;[54] however, the metals (Sn, Ge) that are normally alloyed with Li are not active to deliver capacity, thus the mass specific capacity of the alloy anode is compromised. To this end, we prepared a Li−Na alloy anode in which Li and Na were both active to contribute capacity, improving the anode stability without sacrificing the electrode capacity (Figure 6h).[1] The discharge products of the Li−Na alloy−O$_2$ battery were Na$_2$O$_2$ and Li$_2$O$_2$, confirming that the two metals were both active in discharge. Moreover, the electrostatic shield effect of Li$^+$ could enable uniform deposition of Li and Na, and the addition of DOL (1,3-dioxolane) to the electrolyte facilitated the formation of an elastic SEI. They together contributed to a long symmetrical alloy/alloy battery (~870 h, 0.5 mA cm^{-2} and 0.5 mAh cm^{-2}) and a long-life (137 cycles) alloy-O$_2$ battery (Figure 6i).

5. CONCLUSIONS AND OUTLOOK

In this Account, we have reviewed our works in developing stable and high-performance Li−air (O$_2$) batteries, including the selection of electrolytes, elaboration of air-electrochemistry, and optimization of a Li anode. Despite the academic field having witnessed great progress in the fundamental understanding of Li−air batteries, their practical application is still not on the horizon. There are still many problems needed to be resolved to maintain such sound momentum of development, which requires collaborations from material scientists, in the battery field and beyond. The performance should be constantly optimized by rational cathode structure design, looking for new stable electrolytes or optimizing current electrolytes, and developing highly stable Li anode to sustain more than 1000 cycles. In the future, optimizations must be further made at the cell level or even package level, rather than just focus on one of the battery components. More importantly, the application scenarios of the Li−air batteries should be identified, and applicable Li−air batteries need to be explored or even manufactured as soon as possible to promote this technology into the market.

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