Recent Progress of Flexible Lithium–Air/O_2 Battery

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Along with the popularity of flexible electronic products, the requirements for flexible energy storage devices are also increasing, including high energy density, long-term stability, and high-grade safety. Among various flexible energy storage devices, flexible lithium–air batteries are expected to be one of the best candidates due to their high energy density and environmental friendliness. In order to realize the broad application of flexible lithium–air batteries with high performance, flexibility, and safety, many efforts are made. Here, the recent achievements in flexible lithium–air batteries are discussed, highlighting the flexible cathodes, polymer electrolytes, flexible anodes, operating in ambient air, and battery structural design. Besides, future research perspectives in flexible lithium–air batteries are presented.

1. Introduction

In recent years, as the progress of science and industrial technology, flexible electronics with the advantages of light weight, portability, and high flexibility, such as Samsung Galaxy Fold, Surface Book, Microsoft Arc Mouse, Beats X, Huawei Mate X, have attracted much attention and brought revolutions to people's lives.[1–7] In order to further realize the popularization of flexible electronics, developing the corresponding flexible energy storage system which can satisfy the portable and flexible standards of flexible electronics and provide an uninterrupted power supply for them is crucial and challenging.[8–13]

In response, many flexible energy storage systems have been successfully developed, for example, flexible solar cells,[14–16] flexible metal-ion batteries,[17–20] and flexible supercapacitors.[21–23] Though various flexible energy storage systems with efficient electrode materials and preferable structural designs have been proposed, their inherent low theoretical energy density makes them hard to satisfy the high energy density demands of flexible electronics.[24,25] The new emerging flexible metal–air batteries are supposed to the ideal candidates for flexible electronics due to their high energy density.[26–35] Different from the metal-ion batteries with the intercalation mechanism, the metal–air batteries operated through the oxygen reduction/evolution reaction (ORR/OER).[36–38] The metal–air battery holds a semiopen structure that the O_2 as the active material does not store in it, reducing the battery mass and volume and improving its energy density.[39–47] Under the proposition of guaranteeing electrochemical performance, the components in the flexible metal–air battery, including active cathodes, metal anodes, separators, current collectors, and packaging materials, should be flexible to endure frequent mechanical strain.[48–54] Moreover, the safety of flexible battery is paramount during repeated deformation conditions.[55–60]

Up to now, there are many flexible metal–air batteries have been proposed, such as flexible lithium (Li)–air battery, flexible Li–CO_2 battery, flexible zinc–air battery, flexible aluminum–air battery, silicon–oxygen battery, and so on.[61–71] Among various metal–air batteries, Li–air batteries have raised much concern and got rapid development as a result of their theoretical energy density up to 5928 Wh kg^{-1}, eco-friendly, good reversibility, and high operating voltage of 2.96 V.[24,25,72–74] Here, we review the latest advances of flexible Li–air battery, focusing on the fabrication of flexible cathodes for improving the electrochemical performance, development of electrolyte for obtaining long durability, design of battery structure for achieving high flexibility. It should be noted that some reported studies on Li–air batteries were tested in the oxygen atmosphere rather than the ambient air, which is described as "Li–O_2 batteries."[27,75]

2. Flexible Cathodes

The typical Li–air battery commonly made of Li metal anode, air cathode and aprotic electrolyte, which worked through the reaction of $2Li + O_2 \rightarrow Li_2O_2$ ($E_{OCV} = 2.96$ V).[76–80] As mentioned above, all components in flexible Li–air batteries should be flexible to accommodate stresses and strains in deformation.[10] However, the cathode and current collector are typically rigid carbon paper or porous metal, which hardly meet the needs of flexible Li–air battery, seriously restricting the development of the battery flexibility.[81–83] Moreover, the cathode should possess high catalytic activity to facilitate the OER and ORR reactions of Li–air battery, and porous structure to store the discharge products.[84–88] Therefore, it is urgently required to develop flexible and high-performance cathode materials with high mechanical stability for flexible Li–air batteries.

Different from carbon paper with a rigid structure, carbon cloth is flexible that woven from multistrands of carbon fiber. Because of its mechanical flexibility and conductivity, carbon cloth was widely used as a flexible substrate material for the cathode in Li–air battery.[89–92] Liu et al. first proposed a flexible Li–O_2 battery with a flexible and recoverable cathode that constructed on the carbon cloth by depositing densely TiO_2

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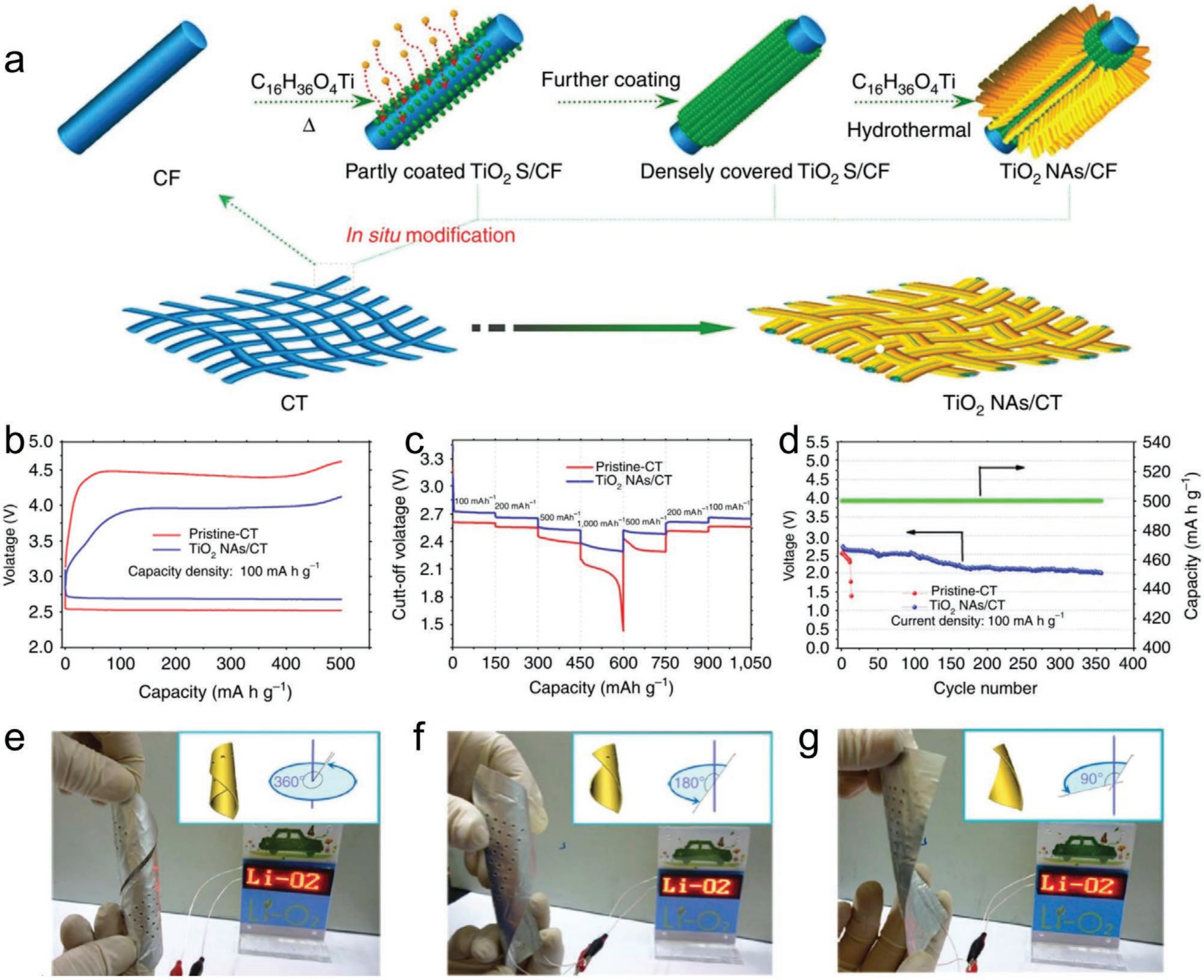

Figure 1. a) Schematic representations for the design and preparation of the TiO_2 nanowire arrays grown onto carbon textiles (TiO_2 NAs/CT). b) First discharge–charge curves of the Li–O_2 cells with a pristine-CT cathode and a TiO_2 NAs/CT cathode at a current density of 100 mA g^{-1}. c) The rate capability of the Li–O_2 cells with the two types of cathodes at different current densities. d) Voltage versus cycle number on the discharge terminal of the Li–O_2 cell with a TiO_2 NAs/CT cathode. e–g) The twisting properties with the device twisted to 90°, 180°, and 360°, respectively. Reproduced with permission.[61] Copyright 2015, Springer Nature.

nanowire arrays (**Figure 1**a).[61] The obtained flexible cathode demonstrated high flexibility and excellent recoverability which can be restored after washing. Significantly, the recoverable feature can extend the cycling life and reduce the cost of flexible Li–O_2 battery. Moreover, based on this cathode with high catalytic activity, the flexible battery displayed improved round-trip efficiency, rate performance and cycling stability (Figure 1b–d). Even under different deformations, the flexible battery with this TiO_2/carbon cloth cathode could steady power a red led display screen (Figure 1e–g). Afterward, they reported another flexible air cathode based on the carbon cloth.[93] First, the Co_3O_4 nanosheet arrays were grown on carbon cloth by electrodeposition. Then, it was decorated by Ru nanoparticles by impregnation and reduction method. The carbon cloth endows this cathode with excellent flexibility; the Co_3O_4 nanosheet arrays remit the problems from carbon oxidation and present sufficient storage space for discharge products; the Ru nanoparticles efficiently decrease the overpotential of battery and improve its cycling life. The 3D hierarchical structure and the uniform distribution of Co_3O_4 nanosheet–Ru on carbon cloth result in the nanosheet-shaped Li_2O_2 growth, and the improved electrochemical performance of the battery. Then, they assembled a flexible Li–O_2 batteries by using this flexible cathode. At the 200 mA g^{-1} and the capacity limited to 1000 mAh g^{-1}, the flexible battery displayed 72 cycles, demonstrating its potential in flexible electronics.

Although carbon cloth has been widely used as the substrate in flexible lithium–air battery due to their flexibility, their poor mechanical strength, inferior conductivity, high cost cannot meet the high demands of practical application of flexible lithium–air battery.[94,95] Lin et al. took a kind of industrial metal wire/cotton fiber yarns with high conductivity as the substrate, and the RuO_2-coated nitrogen doped carbon nanotubes (CNTs) as the catalyst for preparing a freestanding air cathode.[96]

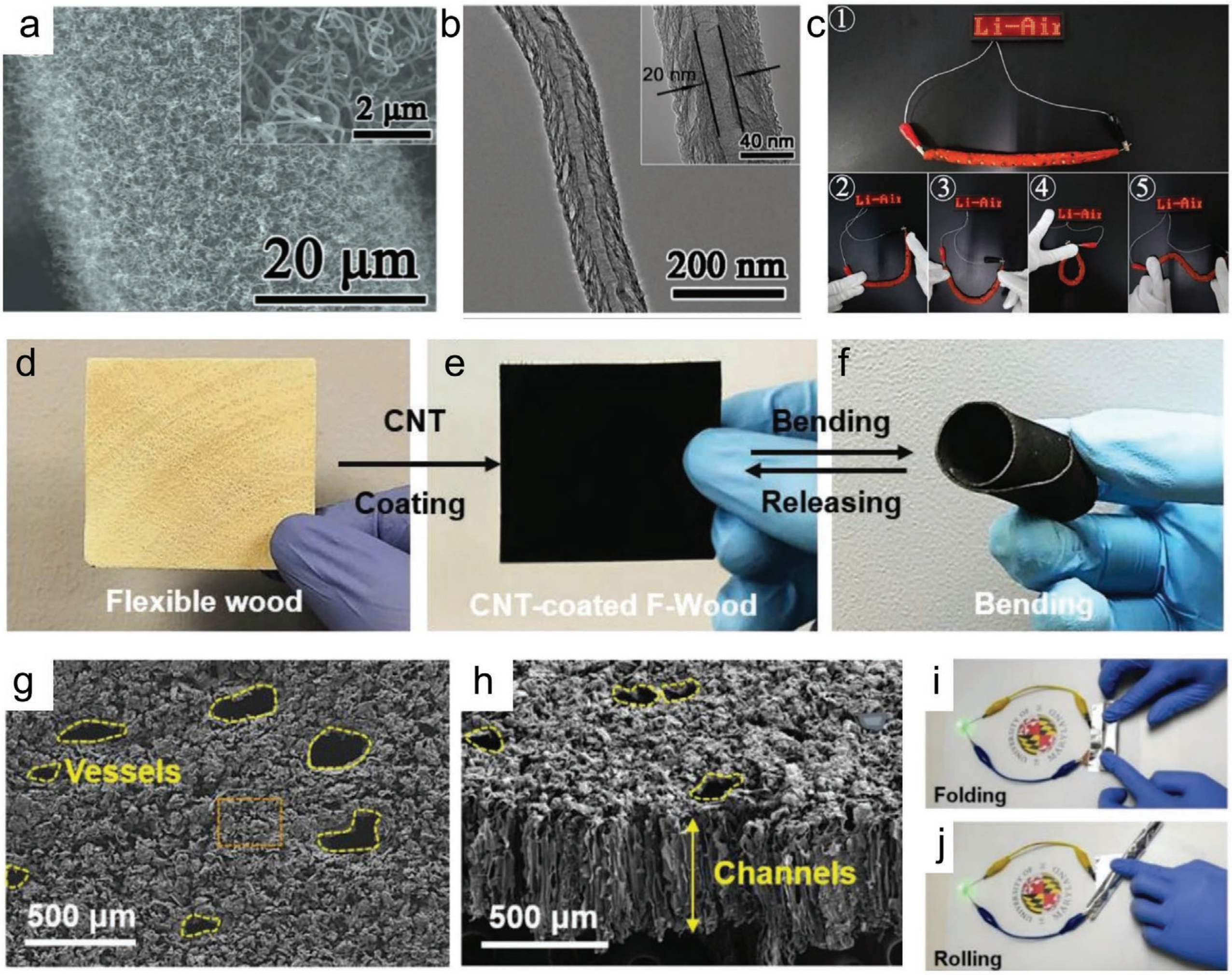

Figure 2. a) SEM images of the N-CNTs@stainless-steel samples. b) TEM image of an N-CNT (inset is an enlarged image of the tube). c) Cable-type flexible Li–air battery powering a commercial red LED display screen under various bent and twisted conditions. Reproduced with permission.[97] Copyright 2018, Wiley-VCH. Photographs of the d) original F-Wood, e) CNT-coated F-Wood, and f) bent CNT-coated F-Wood membranes. SEM images of the CNT/Ru-coated F-Wood membrane: g) top-view image, h) cross-sectional image. Battery stability against various motions: i) folding 1440° and j) rolling. Reproduced with permission.[98] Copyright 2019, Wiley-VCH.

Benefiting from the high absorption property of cotton yarn, the organic electrolyte can be well reserved in the wire electrode and reduce its leakage. The fabricated wire-shaped Li–O_2 batteries showed a long cycling life of 100 cycles without degrading under pristine and bending conditions. There is no doubt that this facile strategy of employ the industrial metal/cotton yarns as a substrate could reduce the cost and expand the employment of flexible Li–O_2 batteries. As a widely used material in the industry, stainless-steel meshes were considered a considerable substrate for flexible Li–air batteries as a result of their excellent mechanical robustness, good conductivity, and low cost. Yang et al. proposed a scalable strategy of directly growing the N-CNTs on stainless-steel mesh as a self-supporting cathode for the flexible Li–O_2 battery.[97] Interconnected hierarchical carbon network can provide sufficient interspace for storing the reaction products and plentiful channels for transporting the reactive mass (**Figure 2**a,b). The good electrical conductivity of stainless-steel mesh can enable the rapid transform of electrons and its high mechanical strength given the cathode with good physical and mechanical properties. Thus, this cathode exhibited excellent flexibility, mechanical strength, high conductivity, hydrophobicity, and long cycle life of 232 cycles. A cable-type flexible Li–air battery constructed by this unique flexible cathode displayed stable mechanical flexibility and electrochemical performances (Figure 2c).

As trees possess the efficient and noncompetitive transport system which the abundant channels can ensure the multiphase transport of mass, Chen et al. inspired from it and developed a flexible wood cathode directly from natural balsa wood (Figure 2d–f) for the fabrication of flexible lithium–air battery.[98] After the delignification treatment and coating CNT/Ru nanoparticles, the wood membrane can convert into the flexible and electroconductive substance. As shown in Figure 2g,h, the wood-based cathode possessed hierarchically channels wherein the coated CNT network ensured continuous electron transport, the cellulose nanofiber with nanopores provided

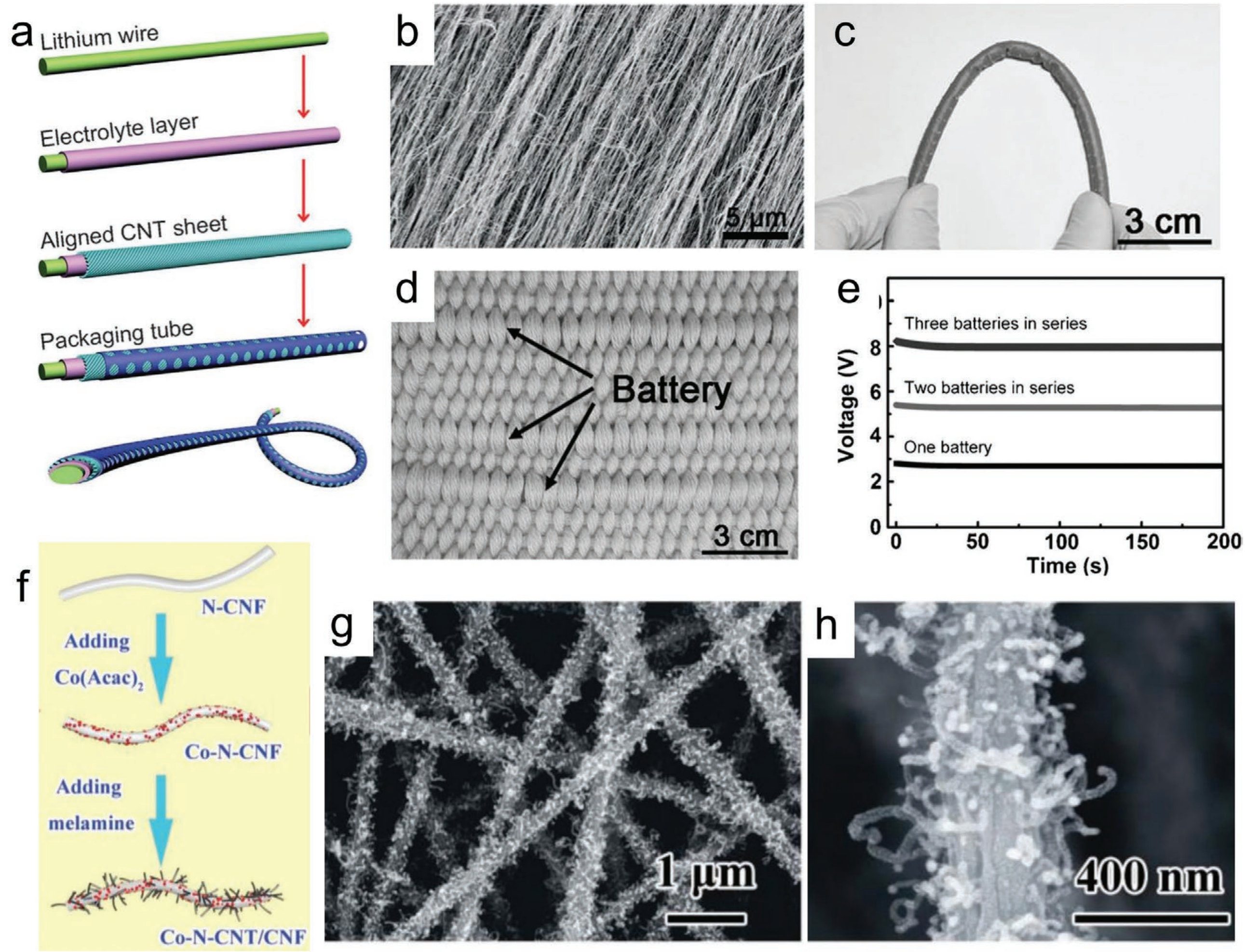

Figure 3. a) Schematic illustration of the fabrication of the fiber-shaped Li–air battery. b) SEM image of aligned CNT sheet wrapped as the outer layer. c) Photograph of the battery under increasing bending angles. d) Photograph and e) discharge curves of a Li–air battery textile. Reproduced with permission.[105] Copyright 2016, Wiley-VCH. f) Schematic illustration of the preparation process for the binder-free and self-standing cobalt–nitrogen-doped carbon nanotube/carbon nanofiber (Co–N-CNT/CNF). g) Low and h) high magnification SEM images of Co–N-CNT/CNF. Reproduced with permission.[106] Copyright 2018, Wiley-VCH.

rapid ion transport, the wood channels offered O_2 gas transport, and the tunable thickness can supply more active material loading and Li_2O_2 product growing. This unusual structure of the flexible wood-based cathode contributed the battery to low overpotential (0.85 V), high discharge capacity (67.2 mAh cm^{-2}), long cycling performance (220 cycles), and endow the obtained flexible $Li–O_2$ cell with high mechanical flexibility (Figure 2i,j).

Whether carbon cloth or metal wire/mesh or flexible wood is used as the substrate to load the cathode catalyst, the high weight of substrates will increase the overall weight and reduce the actual energy density of flexible Li–air batteries. Flexible catalytic carbon materials with the advantages of lighter weight, higher conductivity, larger surface area, and excellent flexibility have been regarded as the favorable cathodes in flexible Li–air batteries.[99–104] As shown in **Figure 3**a, Zhang et al. proposed a fiber-type Li–air battery by employing the flexible CNTs cathode.[105] The binder-free, and lightweight aligned CNTs cathode (Figure 3b) possessed nanosized voids that are favored for the diffusion of air and reactants, high electrical conductivities which can provide continuous electron conduction. Thus, the flexible batteries displayed high discharge capacity (12 470 mAh g^{-1}) and long cycling life (100 cycles). Besides, as shown in Figure 3c–e, the fiber-type battery displayed stable electrochemical properties even during bending conditions or when it is woven into the textile, indicating its wearable applications. Yang et al. prepared another novel flexible cathode for flexible Li–air batteries, in which the carbon nanofiber fabricated by electrostatic spinning was acted as the flexible conductive carbon substrate.[106] The Co–N-doped CNTs were directly grew on carbon nanofibers surface by calcining melamine (Figure 3f). This facile and inexpensive method of the chemical vapor deposition (CVD) prevented the requirement of special equipment, high temperature, and a toxic atmosphere. Benefiting from the porous structure of the carbon nanofiber and the Co–N-CNT with superior catalytic activity (Figure 3g,h), the flexible cathode endowed the $Li–O_2$ batteries with the low overpotentials of 0.67 V, high discharged capacity (11 512.4 mAh g^{-1}) and excellent cycling stability up to 130 cycles.

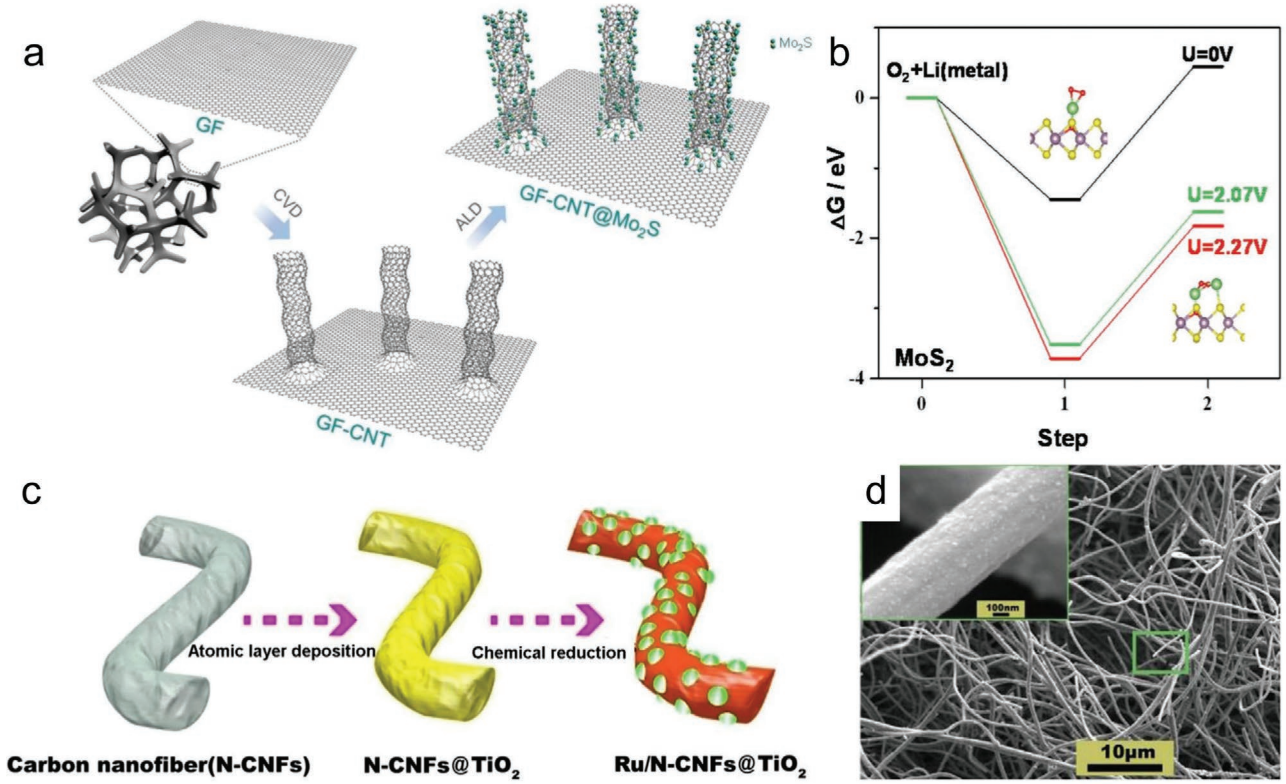

Figure 4. a) Schematics of the fabrication of the amorphous MoS_2 deposited on CNT substrates growing on a 3D graphite foam (GF-CNT@MoS_2). b) Schematic free energy diagrams of oxygen reduction on MoS_2 surface. Reproduced with permission.[108] Copyright 2019, Wiley-VCH. c) Schematic illustration of the synthesis process of Ru/N-CNFs@TiO_2 composite. d) FESEM images of Ru/N-CNFs@TiO_2 composite. Reproduced with permission.[109] Copyright 2017, Elsevier.

Although carbon materials have many advantages, their poor stability will lead to electrolyte decomposition in the cycling progress of Li–O_2 batteries, giving rise to side products.[76,107] Therefore, it is highly required to protect the carbon materials surface for enhancing their stability. Song et al. employed a flexible 3D graphite foam as the substrate for the growth of CNTs by the CVD method, and then deposited amorphous MoS_2 by the atomic layer deposition (ALD) method to protect the carbon surface and improve the catalytic activity (**Figure 4**a).[108] The battery with this integrated cathode displayed improved electrochemical performances (190 cycles, 4844 mAh g^{-1} at 500 mA g^{-1}), benefiting from the high catalytic activity of the 5 nm MoS_2 layer and good ORR activity of the CNTs. The amorphous MoS_2 with the disordered structure could provide adequate catalytic sites, and lower the energy barrier which was proved by the first-principles calculations (Figure 4b). The lightweight carbon materials network which was well protected by the MoS_2 layer has maintained ORR activity during cycling, provided continuous conductivity network, facilitated mass transport. The assembled flexible Li–O_2 battery based on this flexible cathode and a waterproof oxygen-permeable film demonstrated remarkable flexibility, mechanical robustness and water survivability. Yang et al. proposed another flexible cathode which the electrospun N-doped carbon nanofibers were used as substrate (Figure 4c).[109] For improving the stability of carbon nanofibers cathode and preventing electrolyte decomposition caused by the carbon cathode, they deposited an amorphous TiO_2 layer by ALD served as the protection layer. To further improve its catalytic activities, the cathode was decorated with Ru nanoparticles (Figure 4d). The obtained freestanding Ru/NCNFs@TiO_2 cathode displayed good flexibility and was employed to the flake-type Li–O_2 batteries. After compared the adsorption energy of solvent molecular on different substrates, they demonstrated the electrolyte exhibited better stability on the TiO_2 than the carbon.

These flexible binder-free, lightweight, freestanding cathodes with the carbon protection and decoration of highly efficient catalyst might be the promising cathode for flexible Li–air batteries. However, their manufacture is highly dependent on the special equipment and complicated procedures, resulting in the high cost which cannot satisfy the large-scale applications for flexible energy storage systems. Multiple efforts are still needed to develop rational flexible cathodes for batteries to satisfy the high demands of flexible electronics.

3. Polymer Electrolytes

The semiopen structure gives the Li–air battery ultra-high energy density, which also brings many challenges. The commonly organic liquid electrolyte in Li–air batteries exposed to outside the semiopen might lead to the easy volatilization and leakage, and its flammable characteristics can easily cause serious safety issues.[110–113] In addition, the pure lithium metal

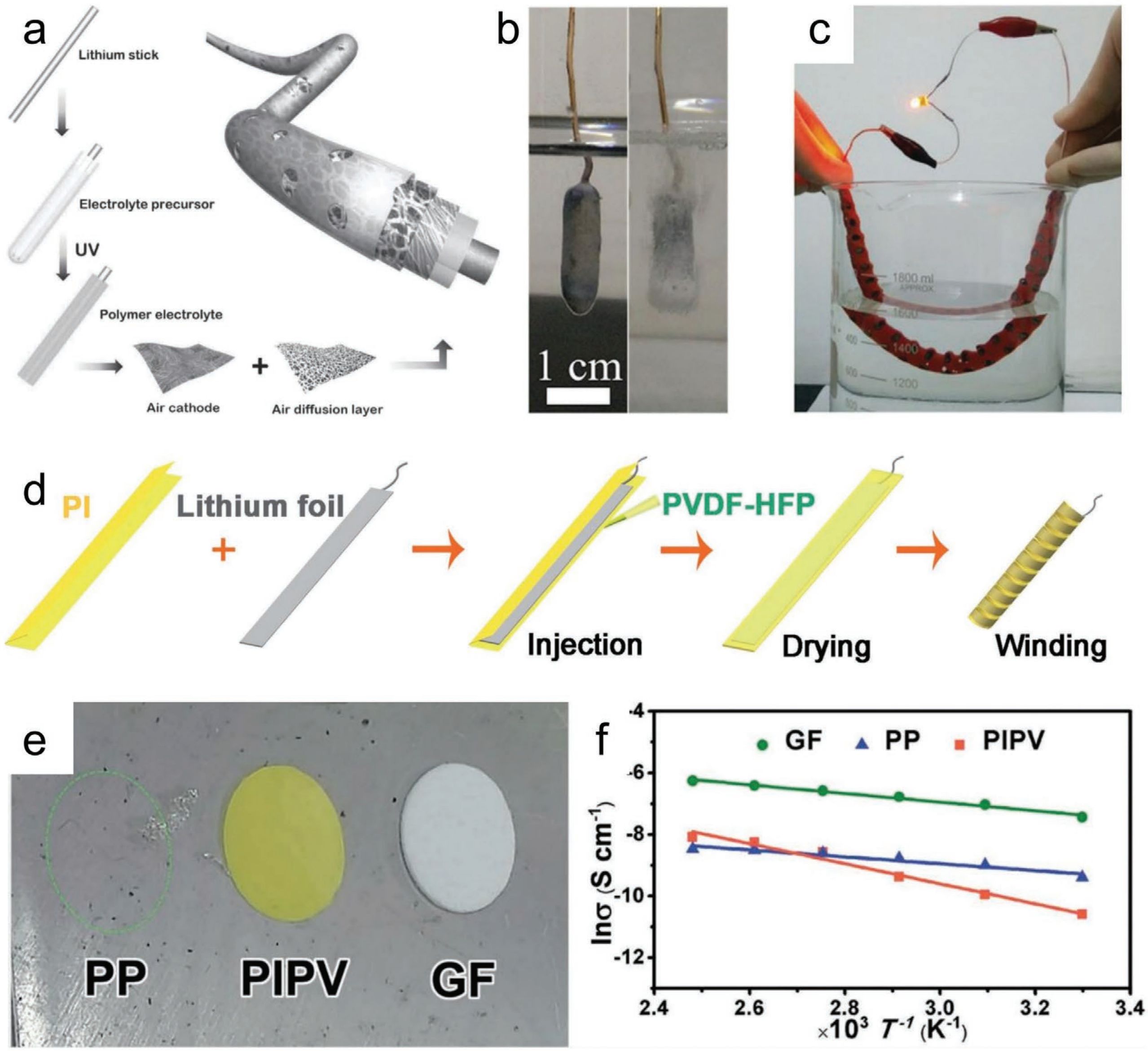

Figure 5. a) Schematic representation for the design and preparation of the cable-type and water-survivable flexible Li–O_2 battery. b) The photographs of Li rod immersed in water with (left) and without (right) the protection of the GPE membrane. c) Cable-type flexible Li–O_2 battery powered a commercial red light-emitting diode immersed in water. Reproduced with permission.[125] Copyright 2016, Wiley-VCH. d) Schematic preparation of composite separator of the safe flexible Li–O_2 battery. e) Heat treatment at 200 °C and f) ionic conductivity for three types of separator. Reproduced with permission.[126] Copyright 2017, Wiley-VCH.

with the high energy density was the chief anode in lithium–air batteries, and they were usually applied without special treatment. However, the reactive lithium metal anode was easily reacted with contamination gas from the air, resulting in the corrosion of anode and poor electrochemical performance of battery.[114–116] The commonly used porous commercial separator in Li–O_2 batteries, such as polypropylene and glass fiber, cannot satisfy the high demand for mechanical stability, let alone the water resistance and thermo stability.[117,118] Therefore, it is urgently needed to protect the Li metal anode for improving battery safety and thus realizing the commercialization of flexible Li–air batteries. Compared to the fragility and poor mechanical flexibility of inorganic solid-state electrolyte, the polymer electrolytes with good flexibility, low interfacial impedance, and high ionic conductivity, are promising alternatives to liquid electrolytes, especially under repeated bending conditions.[46,119–123] In consideration of its intrinsic flexibility and protection for active lithium metal anode, polymer electrolytes are highly compatible to flexible lithium–air batteries.[124] In response, many progress have been made recently to develop polymer electrolytes in flexible Li–air batteries.

Liu et al. in situ prepared the gel polymer electrolyte (GPE) on a lithium metal rod by UV irradiation for the fabrication of cable-type Li–O_2 batteries.[125] The synthesis progress of the battery was shown in **Figure 5**a. The obtained white flexible GPE exhibited uniform porosity which could provide adequate channels for mass transfer between cathode and anode. Its hydrophobicity could effectively prevent the lithium metal anode from the moisture, avoiding the violent reaction when lithium encountered water (Figure 5b). The GPE endowed the flexible Li–O_2 battery with water survivability and enhanced its safety (Figure 5c). The GPE also demonstrated high electrochemical stability and ionic conductivity, resulting in cable-type flexible Li–O_2 batteries delivered high performance, including stable discharge capacity and long cycle life even under constant bending conditions.

Yin et al. proposed another waterproof composite polymer electrolyte separator, and manufactured a high-security flexible Li–air battery based on a unique battery hollow structure.[126] The Figure 5d showed the synthetic strategy of the separator protected winded lithium anode. Besides the water resistance, the separator composed of polyimide and polyvinylidene fluoride-*co*-hexafluoropropylene also exhibited thermal stability and high ionic conductivity (Figure 5e,f). Therefore, the obtained flexible Li–O_2 battery displayed fire resistance and cycling stability (at the current of 1 mA and a capacity of 4 mAh, it can be cycled 218 cycles). This special hollow structure gave the battery high safety, which could pass the nail penetration experiment, and potential for powering underwater flexible electronics.

Subsequently, flame retardancy, as an important parameter for evaluating the safety performance of flexible lithium–air batteries, has gradually attracted people's attention. Guo et al. developed a flame-resistant GPE for the belt-shaped Li–air battery. The GPE containing poly(vinylidene fluoride-*co*-hexafluoropropylene), LiI and 4 wt% SiO_2 was prepared using UV curing technology.[127] In the GPE, the LiI additive was used to promote the products decomposed at a low overpotential, while SiO_2 additive was applied to improve its resistance to flame and the melting point. In addition, the GPE exhibited a high ionic conductivity, good protective effect for Li metal anode and no leakage of electrolytes. As a result, a high flexible belt-shaped Li–air battery has been achieved, which displayed low overpotential in the air, long cycle life, and unchanged discharge curves under the bending conditions. Afterward, Shu et al. proposed another flame-retardant quasi-solid-state polymer electrolyte composed of the poly(vinylidene fluoride-*co*-hexafluoropropylene) and superhydrophobic nanofumed silica for the Li–O_2 battery.[128] The developed polymer electrolyte delivered good performances, such as high ionic conductivity, strong thermal tolerance (up to 120 °C), superhydrophobicity, suppression the growth of dendritic Li, and the prevention of species transfer such as O_2 and H_2O to the Li anode. Thus, the anodic reversibility in symmetric lithium metal cells was increased to 850 h and the cycle life of Li–O_2 battery was improved to 89 cycles. Profiting from the desirable features of the polymer electrolyte, the assembled pouch-type Li–O_2 battery can light the LED array at various bending conditions, after puncturing and even during the tailoring process, indicating its outstanding safety.

4. Flexible Anodes

In the current research of flexible Li–air batteries, lithium metal anodes are widely used due to the advantages of a large capacity of 3860 mAh g^{-1} and a low potential of -3.05 V.[129,130] Because of the semiopen structure of the Li–air battery, the lithium metal anode is likely to react with water, O_2, and electrolyte in the cycling process. After continuous desorption and deposition, the surface of lithium metal anode is prone to powdering to form an uneven surface, which seriously affects the performance of the anode. Besides, as the Li metal is highly active, there are some safety issues when it used in the flexible Li–air battery with the half-open system. Many research efforts are also devoted to improving the performance and safety of metal lithium anodes in Li–air batteries through various means, such as applying artificial SEI layer, gel polymer electrolyte, adding additives, and so on.[131] In addition to these problems, pure lithium metal anodes are easily generated cracks and thus be destroyed during repeated bending, resulting in poor battery safety. In order to solve this problem, Liu et al. proposed to divide the complete metal lithium sheet into several small lithium sheets, and then connect them through copper wires, and then assemble into the flexible battery.[132] The results prove that this strategy can effectively solve the problem of cracking caused by the bending of metallic lithium. To highly improve the strength of the flexible lithium metal anode to replay with multiple bendings, Yang et al. combined the lithium metal sheet and the stainless-steel meshes by the rolling progress.[133]

At present, there are few kinds of researches on flexible lithium metal anodes. In the future, researches on anodes of flexible Li–air batteries might focus more on safety, electrochemical performance, mechanical strength, and even the prevention of lithium dendrite growth.

5. Operating in Ambient Air

As mentioned above, because the Li–air batteries still in its initial stages, most reported batteries were operated in the pure O_2, which was attributed to the contamination including H_2O, CO_2, and N_2 in the air poisoned the battery, accelerating the battery failure. Furthermore, the extra O_2 gas storage equipment inevitably decreased the overall energy density of Li–air batteries, cannot satisfy the portability demands of flexible electronic products. Therefore, it is important and challenging to make efforts to fulfill the flexible Li–air battery operating in ambient air.

Wang et al. designed a linear flexible Li–air battery by combining the low-density polyethylene film, the gel electrolyte, and the redox mediator LiI (**Figure 6**a).[134] The film can block water erosion and suppress the side reactions of lithium peroxide to form lithium carbonate. The LiI, as the redox mediator, can promote the decomposition of discharge products lithium peroxide in the charging progress and thus improve the battery performance, including the low overcharge potential, high rate capability and long cycling life (610 cycles in the air). Besides, the obtained linear Li–air battery integrated into textiles can charge for the phone (Figure 6b). In consideration of the individually prepared gel electrolytes with the poor interfacial contact and the low ionic conductivity, Lei et al. presented a novel way for the development of gel electrolytes to realize a stable cycling performance of flexible Li–air batteries in ambient air.[135] As shown in Figure 6c, lithium ethylenediamine first generated on Li metal surface, then it reacted with the liquid TEGDME and obtained the gel polymer electrolytes. They have

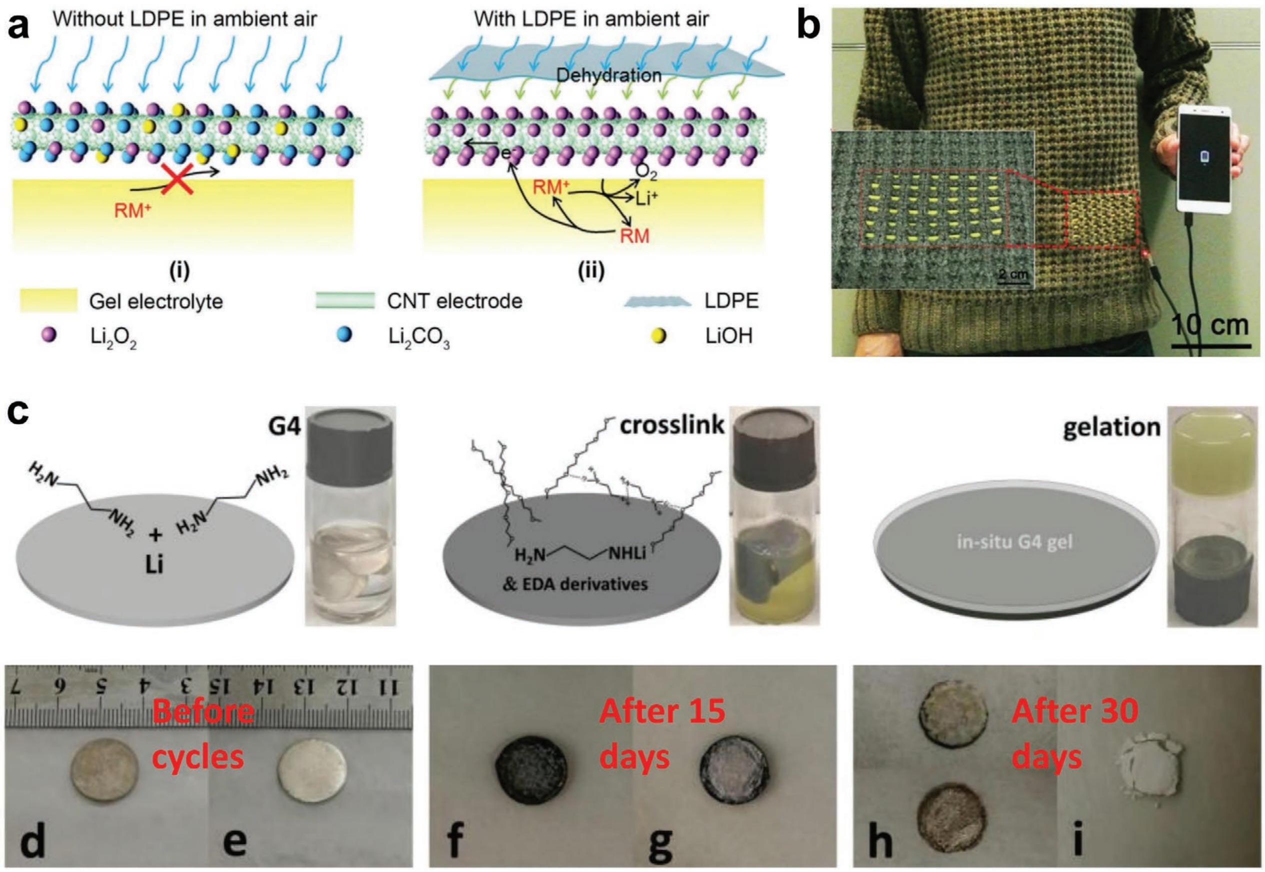

Figure 6. a) Schematic illustration to the working mechanism of the redox mediator (RM) i) with and ii) without the low-density polyethylene film in our Li–air battery operated in ambient air. b) Photographs of flexible fiber-shaped Li–air batteries being woven into clothes to charge a smartphone. Red dashed boxes indicate the Li–air batteries. Reproduced with permission.[134] Copyright 2017, Wiley-VCH. c) Schematic and photographic illustration of the G4 gel formation process. Digital photos of Li metal anodes disassembled from coin type Li–air batteries after exposing to ambient air for different periods by using d,f,h) G4 gel and e,g,i) liquid electrolyte. Reproduced with permission.[135] Copyright 2018, Wiley-VCH.

proved this gel can enhance the interfacial contact, and reduce their detachment during battery bending, giving the flexible battery with high mechanical robustness. Profiting from the favorable protection on the Li metal anode from the gel electrolyte, there is less corrosion on the anode (Figure 6d–i), leading to the fabricated flexible Li–air battery exhibited an improved cycling performance of 235 cycles.

Shao's group has developed a GPE in which nonwoven fabric supported the aerogel SiO_2-filled thermoplastic polyurethane matrix.[136] This GPE demonstrated advantageous features, including good flexibility, high ionic conductivity, fire resistance and inhibition of dendrite growth. A planar Li–air battery was constructed and examined in the air to prove the applicability of this GPE in the flexible battery. As shown in **Figure 7**a, during various bending angles, the discharging–charging curves of the flexible battery were almost unchanged in the static air, indicating its high flexibility and stability. The authors attributed the improved performance to the rapid O_2 gas spreading, massive Li conducting COOLi groups, strong crosslinked structures, and excellent dendrite impermeability. Soon afterward, to meet the strict demands of operating the battery in the air, the Shao's group made another attempt with an O_2-permeable external membrane (Figure 7b) which was fabricated based on the hydrogen-bond cross-linking between the silica aerogel and the polydimethylsiloxane components (OPSP).[137] The high-performance OPSP with waterproof could solve the problems of Li metal anodes corrosion caused by moisture, and the organic liquid electrolytes evaporation in the air. The obtained Li–air batteries with the OPSP delivered a much-improved cycling life of 660 h compared to that without OPSP (220 h). It is worth noticing that even at different current densities, the discharge polarization of the battery with OPSP was almost unchanged, further showing the high O_2 permeability of OPSP. As shown in Figure 7c, the OPSP endowed the flexible Li–air batteries long cycle life in a humid atmosphere, and the stable performance when immersed in liquid water. The development of this O_2-permeable membrane would be the key technology for the future commercialization of flexible Li–air batteries.

For realizing flexible Li–air batteries operating in the air with high safety, it is critical to solving the problems of lithium metal anode including corrosion, dendrite growth, and the poor performance of separators. As shown in **Figure 8**a, inspired by the umbrella which with compact, flexible, hydrophobic features could protect people from rainwater, solar heat and wind, Liu et al. in situ prepared a polymer electrolyte protective film

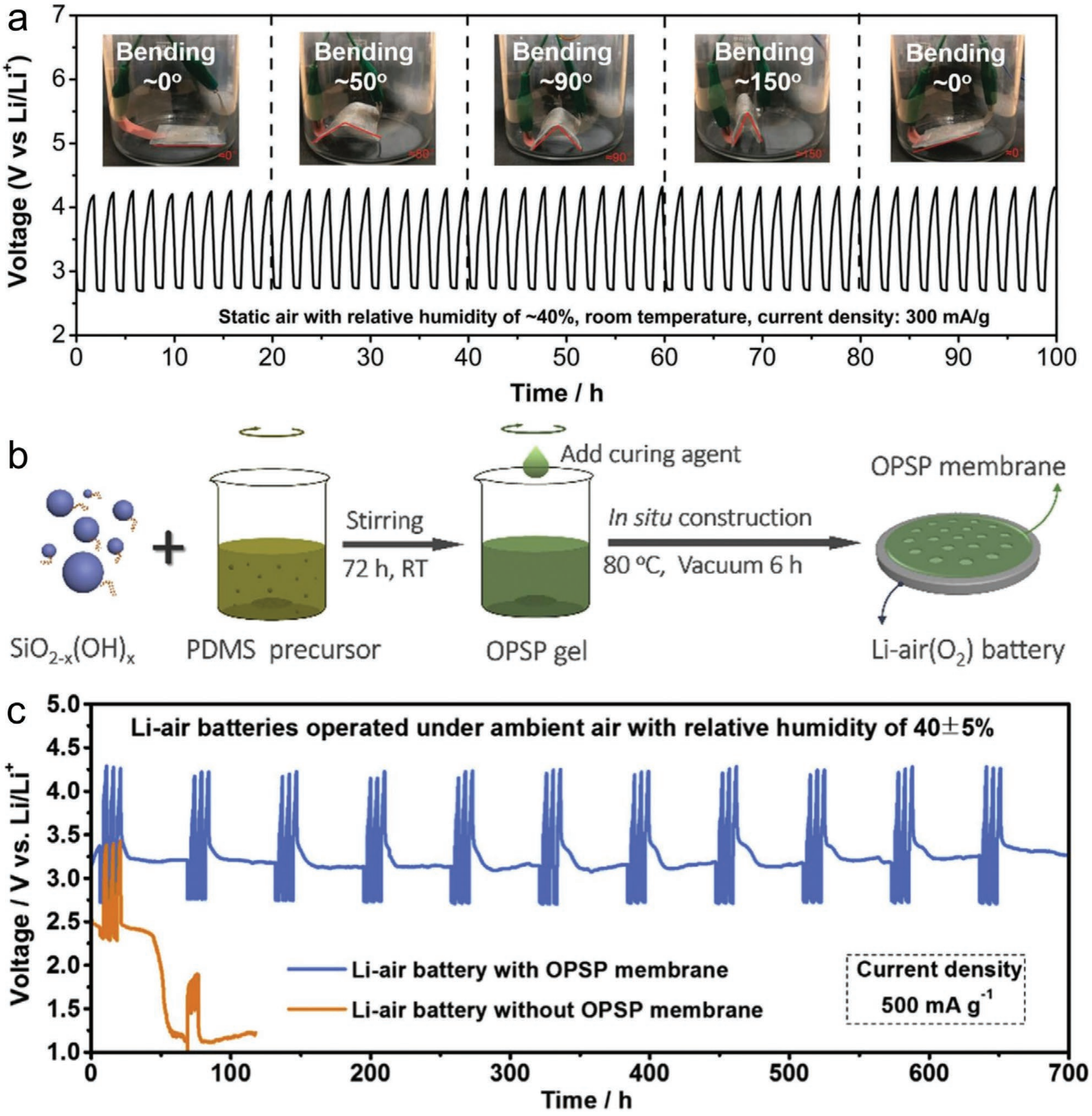

Figure 7. a) The voltage–time profiles of the Li–air battery assembled with fabric supported aerogel SiO_2-filled thermoplastic polyurethane matrix with tetraglyme liquid component (FST-GPE), and the inset figures correspond to the bending state during test. Reproduced with permission.[136] Copyright 2018, Wiley-VCH. b) Schematic showing the main fabrication processes of the OPSP. c) Comparison of the batteries with and without OPSP being cycled in humid air (relative humidity, 40 ± 5%) at current density 500 mA g^{-1}. Reproduced with permission.[137] Copyright 2020, Elsevier.

on lithium metal surface to protect it from destructive substances.[138] The fabricated protective film exhibited good hydrophobicity, heat stability, flexibility, anode protection, and lithium dendrite resistance, thereby improving the overall battery performance in the air. Furthermore, the prepared pouch-type flexible Li–air battery with this film has demonstrated excellent safety and stable performances even under harsh conditions, such as different deformations, immersed in water, nail puncture and high temperature (Figure 8b–d). This facile strategy would facilitate the investigations of alkali metal anodes protection for the realization of flexible Li–air batteries.

6. Battery Structural Design

At present, most of the structures of flexible Li–air batteries are winding-type 1D linear structure and stacked-type 2D planar structure, these designs have been proven to successfully meet

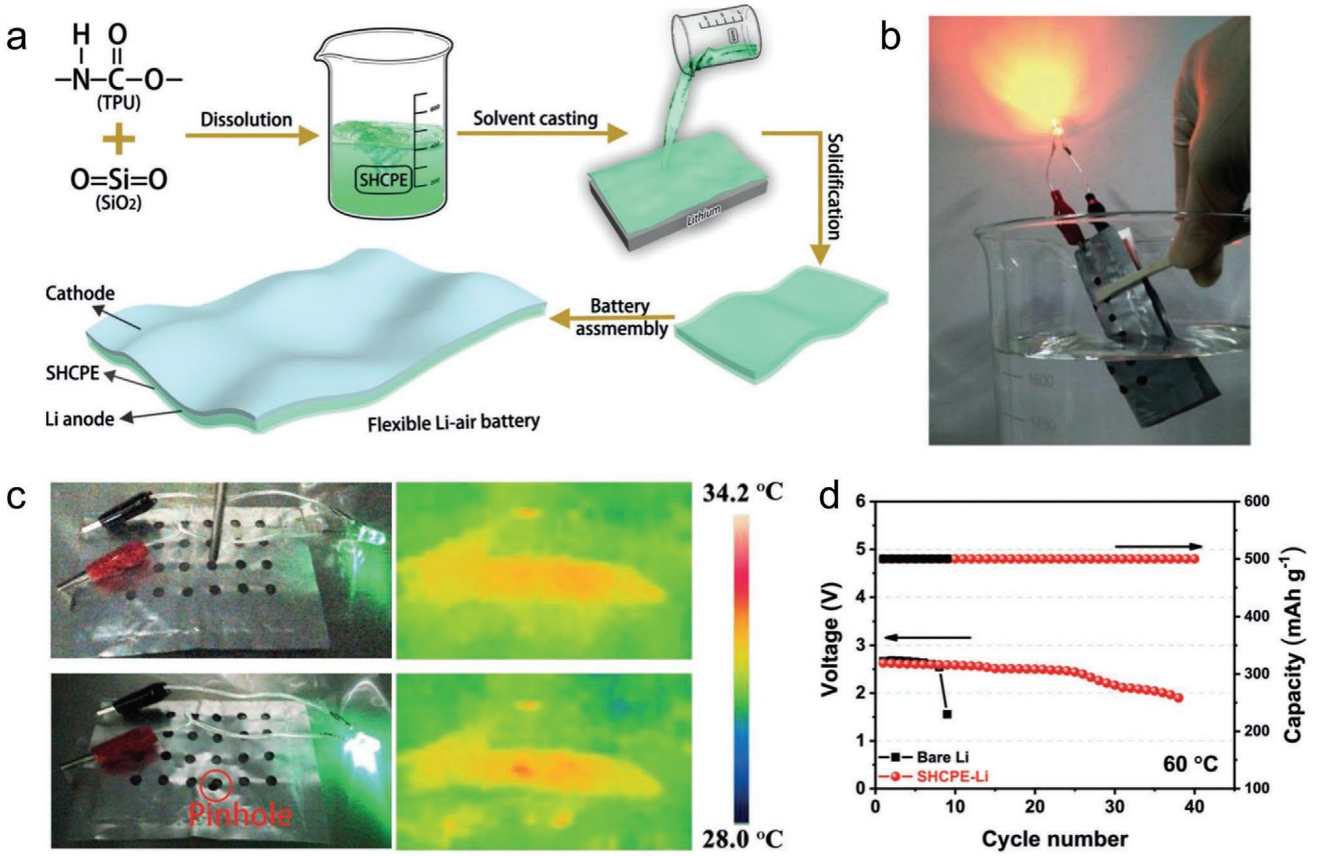

Figure 8. a) Schematic fabrication process of the flexible Li–air battery. b) Photograph of the pouch-type flexible Li–air battery which partially immersed in water and powered a red LED. c) Photographs and corresponding infrared thermal imaging results of the pouch-type flexible Li–air battery before and after nail penetration test; the nail hole is marked with a red circle. d) Cycling performances of the battery with bare Li and protective-Li at 60 °C. Reproduced with permission.[138] Copyright 2018, Wiley-VCH.

mechanical deformation. In addition, there are some flexible Li–air batteries with special structural design that can meet different needs.

In recent years, Zhang's group has committed to designing flexible Li–air batteries with different structures and has made some progress. Inspired from Chinese brush painting and writing, Liu et al. prepared a foldable Li–O_2 battery with a flexible cathode which fabricated by dipping the ink on commonly used paper (**Figure 9**a).[139] The flexible paper cathode made by this facile and scalable fabrication strategy showed lightweight and low cost. Besides, the successfully assembled foldable Li–O_2 battery composed of several paralleled cells demonstrated their feasibility in the flexible energy storage field (Figure 9b,c). The foldable design could effectively improve the mass/volume energy density of the battery (Figure 9d). Later, inspired from the Chinese bamboo slips, they presented a flexible/wearable Li–O_2 batteries with a novel interlaced structure (Figure 9e).[140] The anode of the battery is Li metal whose surface is covered with the GPE and PP film to avoid the Li corrosion caused by the water. The cathode of the battery is a flexible carbon wire loaded with Super P as the active catalyst. The flexible/wearable battery with the interlaced structure in which the cathodes and anodes can press against each other, resulting in the high structural stability that it can operate stably under various deformation conditions. This unique design of the battery avoided the employment of package materials that supply external force to guarantee its normal work. Therefore, the battery displayed the energy density up to 523 Wh kg^{-1} (Figure 9f), far beyond that of Li-ion battery, exhibiting the possibility of powering next-generation flexible electronics. As the commonly used anode in flexible Li–air batteries, metallic lithium is problematic due to the easily formed cracks after repeated deformations, inevitably leading to lower robustness and premature failure of the battery. In response, Liu et al. built an array type flexible Li–O_2 battery which was assembled by many small cathodes and anodes discs.[132] The unique structure dispersed the force that the battery suffered in the process of deformation very well, thereby achieving good structural stability and electrochemical performance.

The flexible self-powered energy system which could accumulate energy from ambient sources and supply for flexible energy storage devices is a promising technology for flexible electronics. Yang et al. constructed a flexible self-powered system via a scalable encapsulate method, in which the flexible solar cell could charge the flexible Li–O_2 battery (**Figure 10**a).[141] The bifunctional cathode that grown porous TiN/TiO_2 composite nanowires on carbon cloth exhibited good electrochemical and photocatalytic activity, enable the flexible battery with excellent electrochemical performance (Figure 10b–e). They also proved this cathode in the battery could be recharged by the solar cell, demonstrating its good reversibility. As shown in

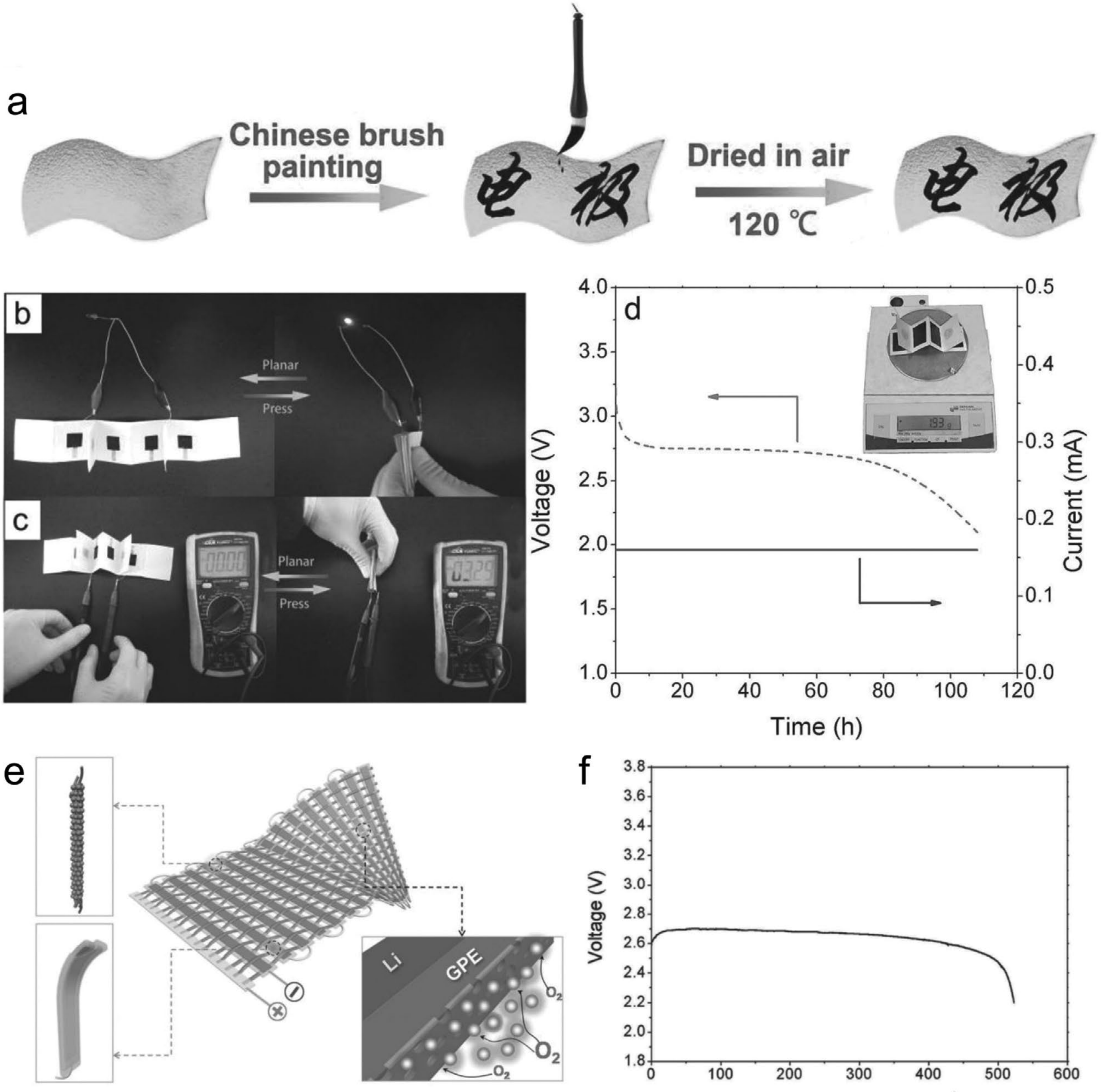

Figure 9. a) Schematic representations for the design and preparation of the PI cathode. b) Photograph of a foldable Li–O_2 battery pack turning on a red LED. c) Open-circuit voltage of this battery packs. d) Discharge voltage versus time and discharge current versus time, inset is the mass of the assembled foldable Li–O_2 battery pack. Reproduced with permission.[139] Copyright 2015, Wiley-VCH. e) Inspired by the ancient bamboo slips, a flexible and wearable Li–O_2 battery was fabricated. f) Discharge voltage versus energy density curve of the Li–O_2 battery. Reproduced with permission.[140] Copyright 2016, Wiley-VCH.

Figure 10f–h, this flexible solar cell/Li–O_2 battery hybrid device could power the LED screen with and without the illumination and even during different deformations, demonstrating its feasibility in application to flexible electronics.

Compared to flexibility, stretchability is a more attractive and challenging property for the Li–air batteries, in which the devices must accommodate substantial strain deformations and dynamic motions. By a feasible strategy to build the battery on a stretchable elastic substrate, Wang et al. reported the first stretchable Li–air battery which was made by the rippled CNT sheets, gel electrolyte, lithium array electrode, Cu springs current collectors, and elastic polymer substrates (**Figure 11**a).[142] Figure 11b–d showed the stretchable Li–air battery delivered a stable discharge voltage plateau even after stretching to 100% or under twisting deformations. In addition, the stretchable battery also presented the potential for wearable applications,

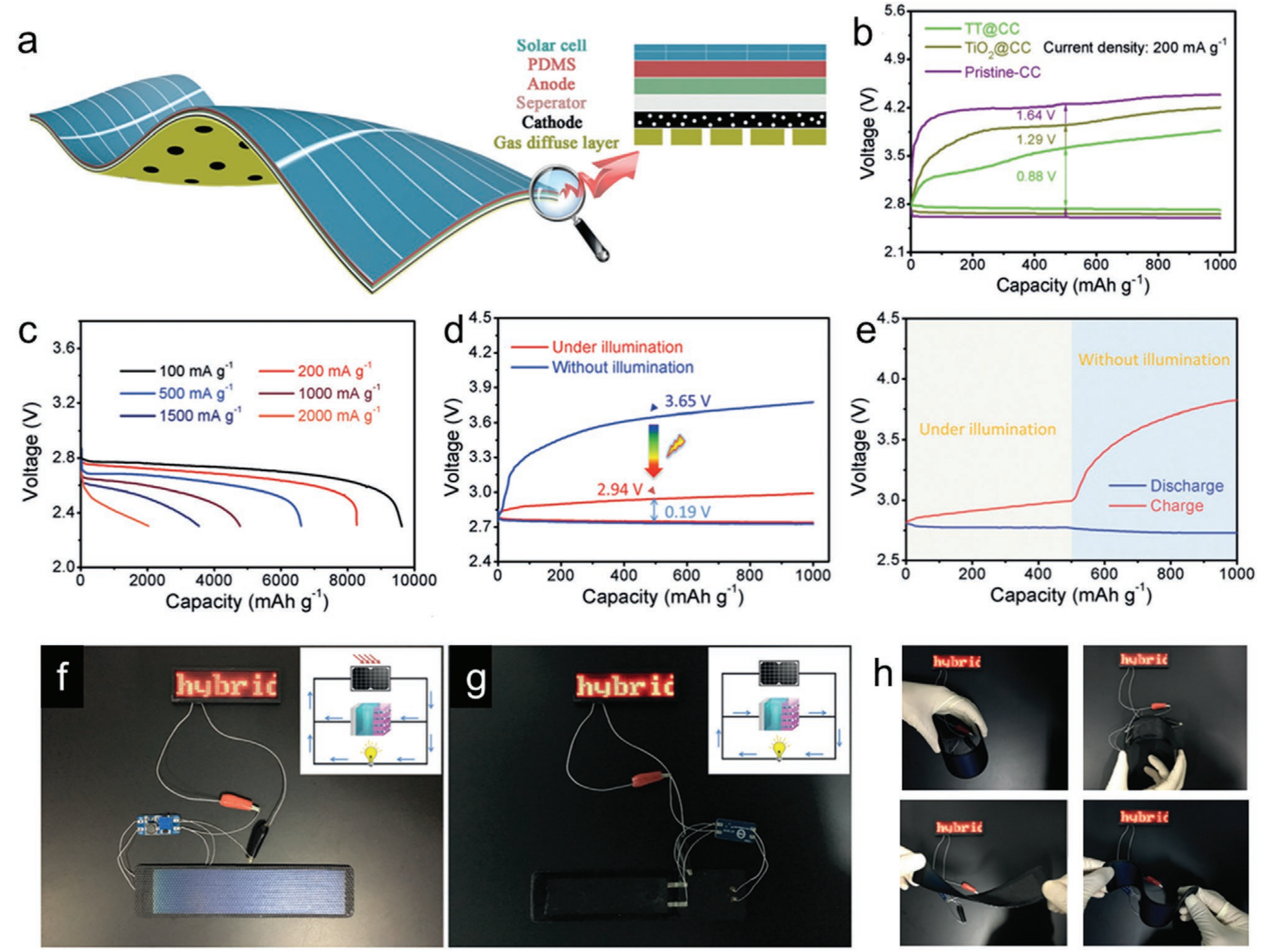

Figure 10. a) Illustration of the structure of the self-powered energy system. b) The first discharge–charge curves of the Li–O_2 batteries with three different cathodes. c) Discharge curves of the Li–O_2 battery with the cathode at different current densities with the voltage restricted to 2.3 V. d) The discharge–charge curves of the Li–O_2 batteries with or without illumination. e) Dynamic light-response discharge–charge voltage of the Li–O_2 battery. Digital photograph of the assembled self-powered energy system working f) with or g) without the light: inset shows the working circuit connection. h) The self-powered energy system powering a commercial red LED display screen at various bent and twisted conditions. Reproduced with permission.[141] Copyright 2019, Wiley-VCH.

such as it can be integrated in a wearable physiological monitoring system and be woven into a cloth (Figure 11e,f).

7. Conclusion

Flexible Li–air batteries have made rapid development and great progress in the past few years. Many models of flexible Li–air batteries were successfully demonstrated, exhibiting their potential in flexible/wearable electronics. Because flexible Li–air batteries are in the initial stage, they still far away from commercialization due to their low safety, poor performance, complex preparation process and high cost. Before their practical application, efforts are still needed in the following areas. First, develop efficient and stable flexible air cathodes with freestanding structures or constructed them on flexible substrates to increase the overall performance of the battery. Second, explore polymer electrolytes with multifunctional characteristics, such as good interfacial contact, high ionic conductivity, waterproof, fire resistance, suppression dendrite growth, lithium metal protection, to improve battery performance and safety. Third, exploit the flexible Li–air batteries operating in the air based on multiple strategies working together, avoiding the use of oxygen storage equipment and improving its practical energy density. Fourth, design various flexible Li–air batteries with different configurations for meeting the needs of different application scenarios, such as stretching and folding. With the deepening of the research on the mechanism, considerable improvement in performance, and upgrade in the assembly technology, we believe flexible Li–air batteries will get more progress before long. In the future, the flexible Li–air battery might be applied to smart bracelets, portable power banks, smart cards, electronic textiles, flexible sensors, medical monitoring, and so on. Besides, integrating the flexible Li–air batteries with other flexible energy harvest devices, such as flexible solar batteries and flexible nanogenerators, would broaden the application of flexible electronics and revolutionize human life.

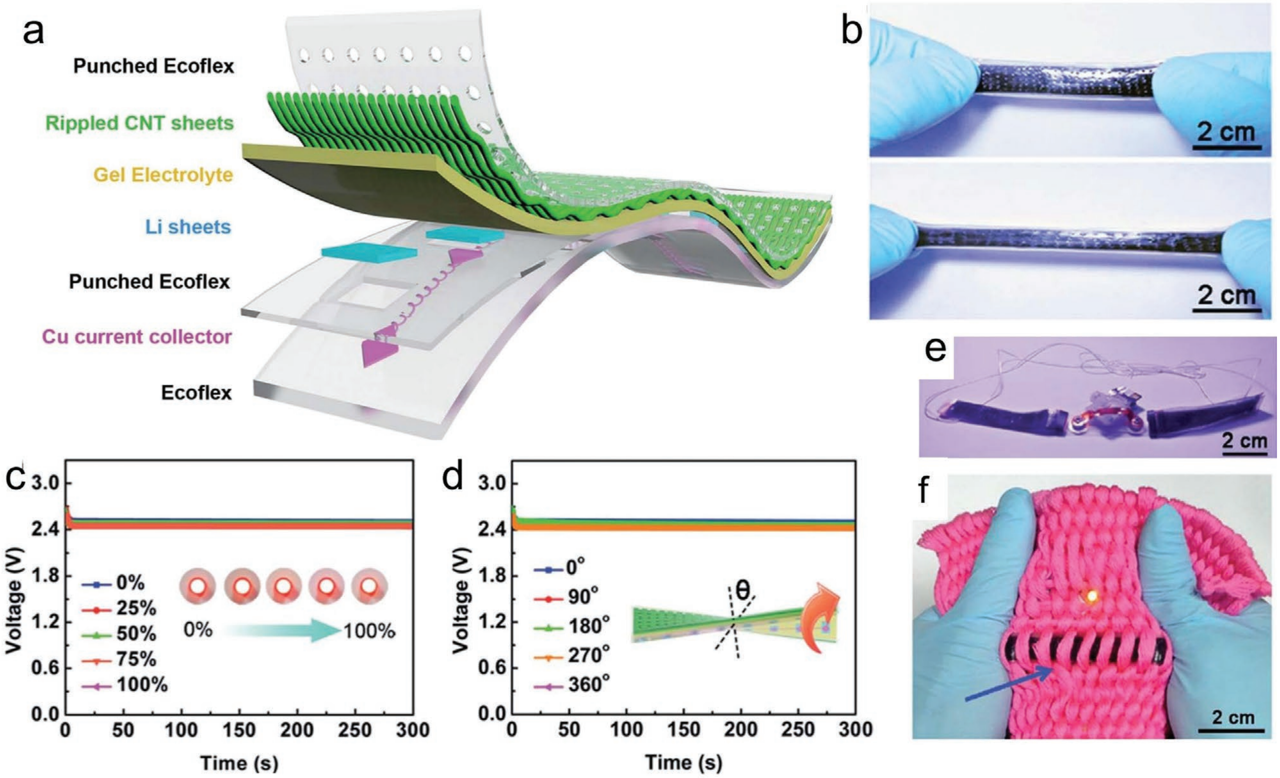

Figure 11. a) Multilayered structure of the stretchable Li–air battery. b) Photographs of the stretchable Li–air battery before and after stretching, respectively. c) Discharge curves of the stretchable Li–air battery under increasing strains. The inserted photographs display a red LED lit up by the Li–air battery under increasing strains. d) Discharge curves of the stretchable Li–air battery under twisting with increasing angles. e) Photograph of a wearable physiological monitoring system. f) Photograph of a stretchable Li–air battery woven into textile to power a yellow LED under deformations. Blue arrows indicate the stretchable Li–air battery. Reproduced with permission.[142] Copyright 2016, the Royal Society of Chemistry.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

battery design, flexible cathodes, flexible Li–air/O_2 batteries, polymer electrolytes

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