

Flexible Metal–Air Batteries: Progress, Challenges, and Perspectives

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Flexible metal–air batteries, which are a promising candidate for implantation in wearable or rolling-up electronic devices, have attracted much attention recently due to their relatively high energy density. Various flexible metal–air batteries have been developed recently, including flexible nonaqueous lithium–air batteries, aqueous zinc–air batteries, and aqueous aluminum–air batteries. Although various viable configurations of flexible metal–air batteries have been proposed, challenges regarding electrode design, electrolyte exploitation, and low practical energy density, still exist. Here, a brief introduction is presented as to the recent development of flexible metal–air batteries, regarding the electrodes, electrolyte, and prototype devices. Also, a general perspective on the current challenges and recommended future research directions for the practical use of metal–air batteries is provided.

1. Introduction

Flexible energy-storage devices, which possess aesthetic versatility and facile integration with electronic devices with various shapes, have captured the considerable interest of researchers. They will open a door to propel and accelerate the new development of electronic equipment that is characterized as lightweight, bendable, portable, foldable, and so on.^[1–7] To date, some novel concept and prototype flexible electronics such as such Jawbone, the Philips Fluid flexible smartphone, the Nokia Morph Concept, iPhone ProCare14, and the Samsung Youm flexible display have already been demonstrated.^[8–12] These flexible portable electronic products will be widely used and can influence future lifestyles. Considering the huge attention on flexible electronics, the corresponding flexible energy storage and conversion systems are of interest to sustain an uninterrupted power supply for these flexible electronic products. The concept of flexibility is easy to comprehend, and contrasts to


rigidity and bulk. Consequently, ideal flexible energy storage and conversion systems should be stable when undergoing frequent mechanical strain, such as bending, twisting, and other deformation modes on a long-term basis. In addition to the mechanical properties, security is paramount and cannot be ignored, especially under various deformation conditions.

In response, much progress has been made to develop high-performance flexible energy storage and conversion systems in the past few years, for example, solar cells,^[13–20] flexible chemical batteries,^[21–27] and flexible supercapacitors,^[28–35] to meet the aesthetic demands of flexible electronic. Among the various

types of flexible energy storage and conversion systems, the lithium-ion battery is most widely used and recognized due to its relatively high energy density. Though the battery performance has been greatly improved compared with its first generation introduced by Sony,^[36,37] the energy density still cannot satisfy the energy requirements of advanced electronic devices. Obviously, the development of lightweight, high-energy-density flexible energy storage and conversion systems for future flexible electronics is highly significant. Among the various energy storage and conversion systems, metal–air (metal–oxygen) batteries have been identified as suitable candidates since the exhausted material (oxygen) is stored outside the battery. This endows these systems with high energy density and they could therefore meet the requirements of advanced electronic devices.^[37–40] Different from the intercalation and conversion reactions of commercial lithium-ion batteries, metal–air batteries are based on the oxygen-reduction reaction (ORR) and oxygen-evolution reaction (OER), and usually operate in an open system. Depending on the anode that is used, metal–air batteries can be divided into zinc–air, aluminum–air, lithium–air, potassium–air, sodium–air, and so on. The theoretical specific energies, volumetric energy densities, and nominal theoretical cell voltages of the various metal anodes in metal–air batteries are shown in **Figure 1**.^[41–44] Due to the extreme sensitivity toward water, lithium–air, potassium–air, and sodium–air batteries are often operated nonaqueous systems, and therefore batteries can operate in a high voltage platform. Different from nonaqueous system, the magnesium, aluminum, zinc, and iron anodes are all compatible with aqueous electrolytes and have energy densities comparable to lithium–air batteries, and have also been widely investigated; here, we label them as aqueous systems. In addition, it should be noted that a hydrophobic protecting layer is also needed in the aqueous

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system to prevent electrolyte leakage. Though the polytypes of metal–air batteries have been burgeoning, the most commonly studied ones are the coin-type and Swagelok designs, which are rigid and bulky, and the advantage of energy density cannot be achieved.^[45–49] As a result, the present studied metal–air batteries cannot match practical requirements, to say nothing of use in flexible electronics. Therefore, in addition to improving their inherent electrochemical performance, the design of new prototypes of flexible metal–air batteries with light weight, bendability, portability, and potential foldable character, to effectively improve the practical energy density and promote their practical application in the flexible electronics field, are equally important. Our purpose here is to highlight the pioneering research work on flexible metal–air batteries, which mainly focus on the design of the electrodes, electrolyte exploitation, and assembly of the batteries. We close with a brief discussion of the challenges and perspectives for the development of flexible metal–air batteries.

2. Flexible Electrodes

For the fabrication of flexible metal–air batteries, the development of electrodes with flexible properties is necessary. The anodes that are used for flexible metal–air batteries are usually a metal foil, metal ribbons, or metal rods, or a metallic powder coating on a flexible metal substrate, possessing flexible properties to some extent and able to be used directly in flexible metal–air batteries. Hence, the main focus here is on the fabrication of the air cathode. As is well known, the air cathode is composed of a current collector and active materials; the design and development of flexible current collectors is the key. As a current collector, features such as air permeability, good conductivity, and excellent flexibility should be satisfied.

2.1. Carbon-Based Electrodes

At first glance, due to the excellent conductivity and permeability, commercial carbon textiles, suitable cotton textiles, and a stainless-steel mesh are preferred for use as the current collector.^[50] Active materials such as carbonaceous materials,^[51,52] metal oxides,^[53] noble metals,^[54] etc., have been coated on a flexible current collector to form flexible air cathodes. In view of the excellent conductivity, definite catalytic properties, relative stability, and porous structure, several kinds of carbon have been widely investigated. Among the different kinds of carbon materials, nanotubes and graphene are the most impressive due to their high Young's modulus and tensile strength.^[55,56] what's more, a 3D structure can also be constructed easily, which is beneficial for the battery operation. In order to further improve the catalytic performance of the cathode, some metals or metal oxide/nitride, as catalysts, have been loaded on a carbon substrate.^[40,57–59] For the fabrication of flexible air cathodes, a simple and common method is to spray carbon or carbon-based active materials on carbon textiles.^[52]

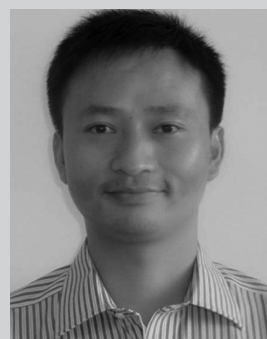
In order to optimize the structure and improve the conductivity of the cathode, active materials have been directly grown on flexible substrates via chemical or electrochemical methods,



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mainly focus on functional inorganic materials for energy storage and conversion with fuel cells and batteries.

finally forming a freestanding cathode.^[48,60] Compared with the common technology for fabricating air cathodes such as spray and printing, the freestanding design has its own advantages, mainly including the following points: (i) the porous architecture, which is easily designed, can promote mass transfer;^[61] (ii) the unemployable polymeric binder can enhance the stability of the cathode;^[62] (iii) direct contact between the active material and the current collector is favorable for electron transport and the kinetics will be improved. Given this, Meng et al. reported a flexible, binder-free air cathode based on Co_4N coupled with a network of carbon fibers, that were directly electrodeposited on carbon cloths ($\text{Co}_4\text{N}/\text{CNW}/\text{CC}$), and the synthesis strategy is illustrated in **Figure 2a**.^[63] Figure 2b–d demonstrates that Co_4N nanoparticles with a size of about 300 nm were inserted into

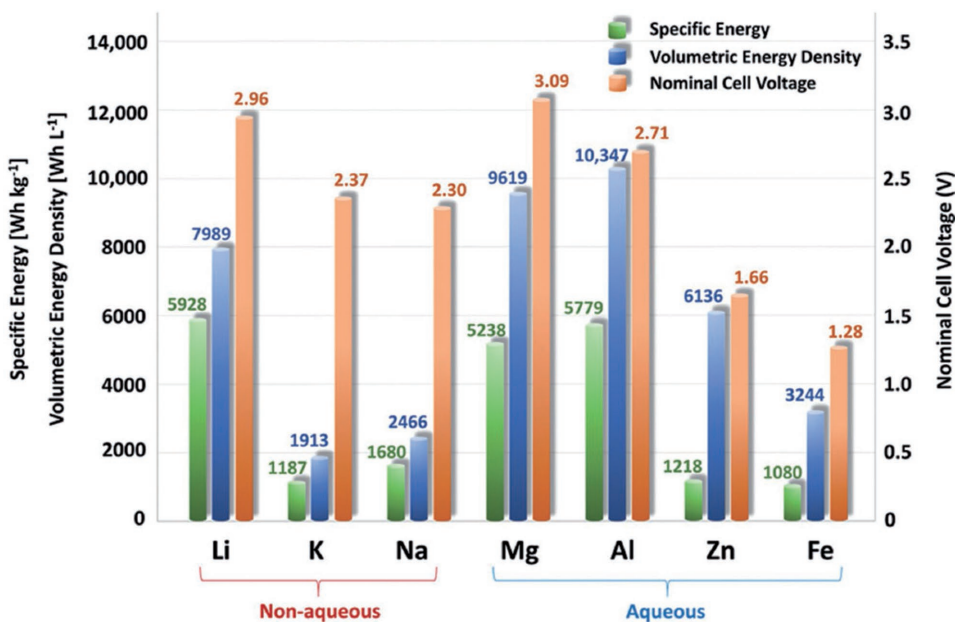


Figure 1. Theoretical specific/volumetric energy densities and nominal cell voltages for various metal–air batteries.^[41] Reproduced with permission.^[63] Copyright 2014, American Chemical Society.

the porous carbon matrices. The porous carbon matrices provide a place for the ORR and OER and the conductive network, while the decorated Co_4N improves the catalytic performance of the air cathode. It is noteworthy that the obtained $\text{Co}_4\text{N}/\text{CNW}/\text{CC}$ cathode inherits the flexibility of the carbon cloths, which provides a guarantee for the assembly of a flexible metal–air battery.

Carbon textiles, as an excellent flexible current collector, have been widely investigated in the field of metal–air batteries; however, the catalytic ability of this collector is inferior. What’s more, with the addition of cathode mass, the energy density of the battery will be reduced. Therefore, it is urgent that the utilization of the air cathode is increased. Recently, the development of self-standing air cathodes has been realized in the field of metal–air batteries, which could

be ready to solve this problem.^[64,65] From the concept of self-standing, it is easy to understand that the current collector is also involved in the active-material participation reaction. For the self-standing air cathode used in flexible metal–air batteries in particular, some features should be satisfied, such as air permeability, good conductivity, catalytic performance, and excellent flexibility. In view of this situation, inspired and motivated by the toad spawning process, as well as the favorable shape and structure of the eggs, Yin et al. reported a strategy to fabricate a self-standing, lightweight, hierarchical macroporous active-carbon fiber cathode via an electrostatic spinning technique.^[66] The nonwoven textiles were interlaced with each other and formed a porous framework that could be directly used as an air cathode in metal–air batteries. The obtained air cathode possessed abundant macroscopic

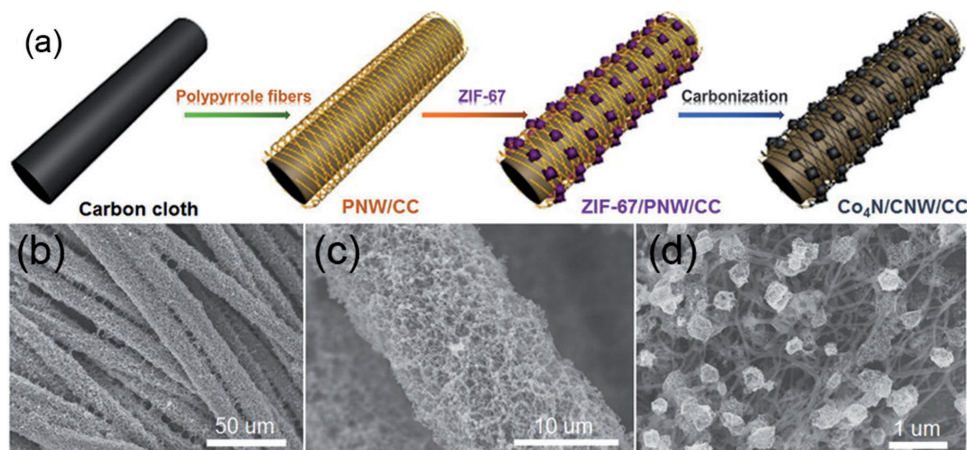


Figure 2. a) Scheme of the synthesis of $\text{Co}_4\text{N}/\text{CNW}/\text{CC}$. b–d) Low- and high-magnification SEM images of $\text{Co}_4\text{N}/\text{CNW}/\text{CC}$. Reproduced with permission.^[63] Copyright 2016, American Chemical Society.

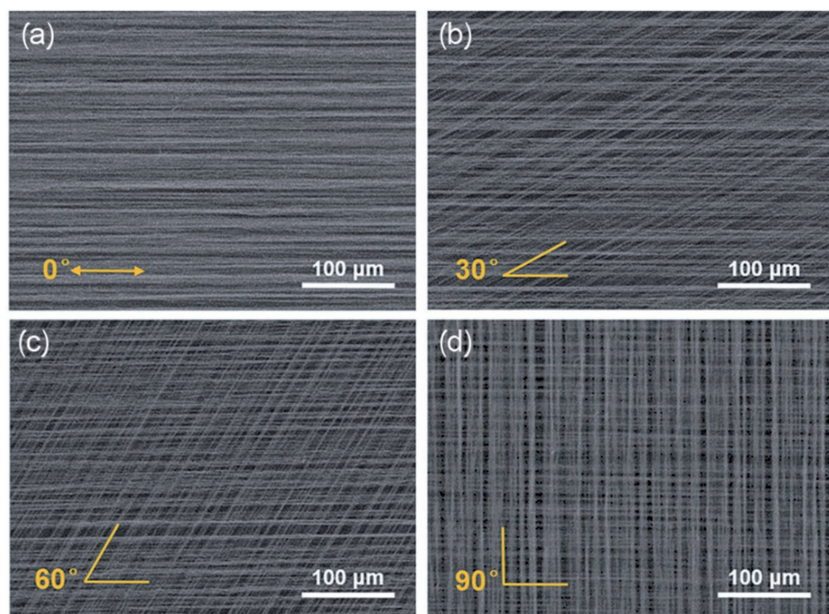


Figure 3. SEM images of CNT sheets with cross-stacking angles of 0°, 30°, 60°, and 90°, respectively. Reproduced with permission.^[72] Copyright 2015, Wiley-VCH.

carbon spheres with plentiful surface openings and interconnected pores, which is favorable for mass transfer. It is noteworthy that the as-synthesized air cathode also possessed excellent flexible properties. Chemical vapor deposition, as an effective technique, has been widely used in the field of carbon-material synthesis.^[67–70] By means of this technique, Peng's group fabricated a free-standing air cathode by cross-stacking the aligned CNTs layer by layer.^[71–73] **Figure 3** displays typical scanning electron microscopy (SEM) images of the obtained air electrodes. It could be found that the cathode remained highly aligned under various conditions. Besides, a porous framework was also formed by aligned CNTs, which is favorable for rapid diffusion of oxygen. The reaction efficiency will also be improved. In addition, thanks to the rational structural organization, the as-fabricated air cathode displays excellent flexibility and a certain stretchability, which provides the possibility for assembling flexible and stretchable metal–air batteries.

2.2. Non-Carbon-Based Electrodes

Though carbonaceous materials have been extensively researched thanks to their excellent conductivity and relative catalytic performance,^[74–77] their stability is poor, especially in non-aqueous-system lithium–air batteries. Carbon decomposes during charging when the charge voltage is above 3.5 V and actively promotes electrolyte decomposition on discharge and charge, leading to cathode passivation and premature cell death.^[78,79] Therefore, identifying an appropriate alternative material to carbon is urgent. Non-carbon-based materials have been widely reported in recent years and the most common materials are metallic oxides,^[80–87] however, the investigation of non-carbon-based cathodes with flexible properties has rarely

been reported. As for the development of flexible metal–air batteries, an air cathode with a flexible character is also necessary. Liu et al. reported a strategy to fabricate a flexible and recoverable air cathode via a facile hydrothermal method.^[77] In their work, hierarchical rutile TiO₂ nanowire arrays (TiO₂ NAs) were uniformly grown on flexible carbon textiles (CTs), forming a binder-free air cathode labeled as a TiO₂ NAs/CT cathode; the fabrication process is shown in **Figure 4a**. SEM images obviously demonstrate that TiO₂ NAs were grown vertically on the CTs with a diameter of about 50 nm (**Figure 4b–d**). Though fully covered with TiO₂ NAs, the obtained TiO₂ NAs/CTs cathode still inherited the flexible characteristic of the CTs, as displayed in **Figure 4e,f**. Compared with the commonly used carbon-based flexible cathode, as discussed above, the active materials used in this work were TiO₂ NAs, which avoided the serious problems caused by carbon decomposition.

In addition, Liu et al. reported a flexible and efficient air cathode based on Ru nanoparticles (Ru NPs) decorated on Co₃O₄ nanosheets (Co₃O₄ NSs) grown on flexible CTs (CTs–Co₃O₄ NSs–Ru cathode),^[88] and this is also classified as a non-carbon-based air cathode since the dominant active material is Co₃O₄ NSs–Ru. The purpose for decorating the Ru NPs on the Co₃O₄ NSs is to further improve the electrochemical performance of the cathode. In the same way as the previous example, the CTs–Co₃O₄ NSs–Ru cathode also inherited the flexibility of the CTs. Although the problem of cathode degradation is well solved compared to carbon, the specific weight of the cathode is increased and the energy density of the associated batteries was prejudiced. Therefore, a compromise must be considered between cathode stability and energy density. What's more, it is also needed that the real reaction mechanism for the non-carbon-based materials is investigated. In addition, the concept of non-carbon-based material is widely investigated in nonaqueous systems, especially in the field of flexible lithium–air batteries; however, whether these noncarbon materials are compatible with the metal–air batteries, which operate in an aqueous system, should also be considered.

3. Electrolyte

The electrolyte is a medium for metal-ion and oxygen transportation during the process of battery operation. An electrolyte used in metal–air batteries should have the following features:^[89,90] (i) high stability in oxygen-rich electrochemical conditions; (ii) low viscosity, supporting fast lithium ion transport; (iii) high solubility of lithium salt; (iv) high accommodation against other cell components; (v) nontoxicity and economic use. In addition, for flexible lithium–air batteries, the electrolyte must be able to endure various deformation modes. Otherwise, it may cause safety issues. With the development of

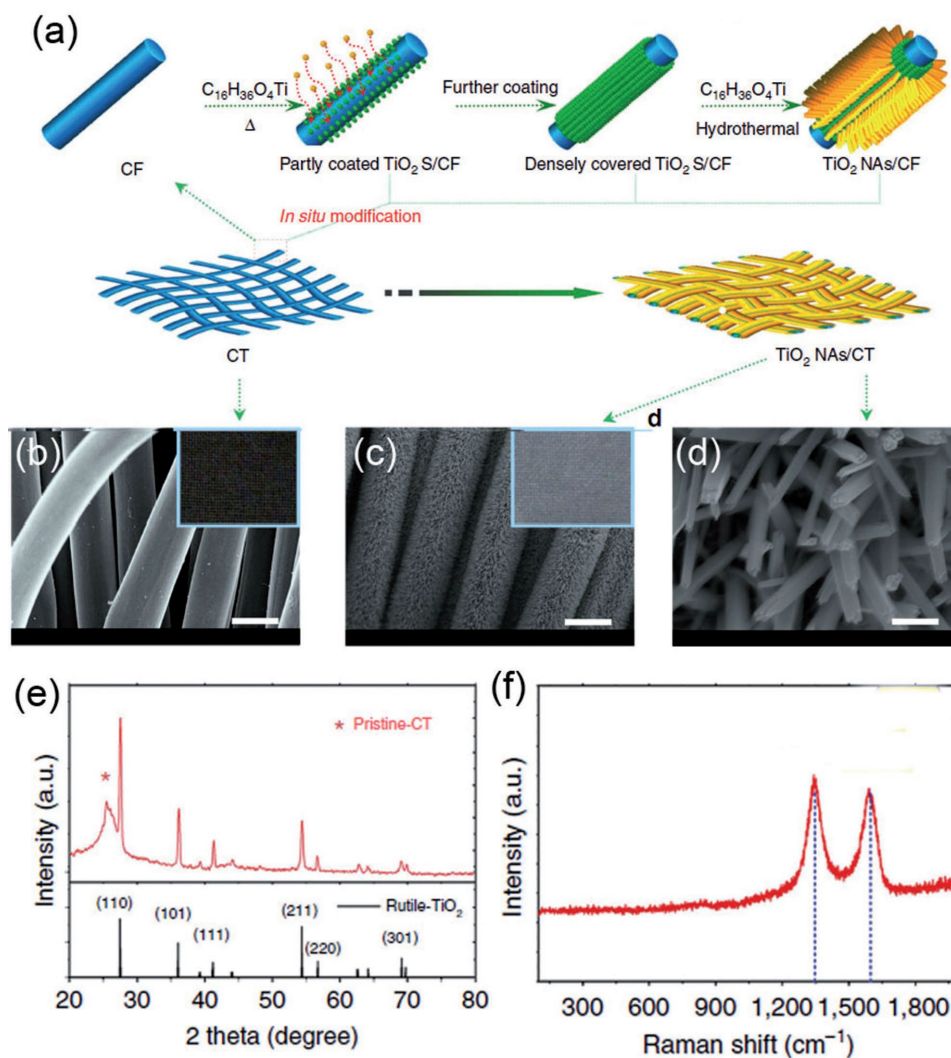


Figure 4. a) Schematic representations for the design and preparation of the TiO₂ NAs/CT. b,c) SEM image and photograph (inset) of pristine-CT (b) and TiO₂ NAs/CT cathode (c). d) Enlarged image of (c). e) X-ray diffraction patterns of the obtained TiO₂ NAs/CT cathode. f) Raman spectra of the TiO₂ NAs/CT cathode. Adapted with permission.^[96] Copyright 2015, Nature Publishing Group.

metal–air batteries, a series of electrolytes has been exploited. In general, electrolyte can be categorized into two types according to their appearance: liquid electrolytes and solid electrolytes.

3.1. Liquid Electrolyte

According to different operation systems, liquid electrolytes are generally divided into aqueous- and non-aqueous-based electrolytes. Aqueous alkaline solutions, such as KOH, NaOH, and LiOH, have been used as the electrolyte in metal–air batteries due to their superior ionic conductivity. Among these alkaline solutions, KOH-based electrolytes are more commonly used for fabricated flexible metal–air batteries due to their relative stability compared to NaOH- and LiOH-based electrolytes. Meng et al. successfully applied a KOH-based electrolyte to a flexible zinc–air battery and obtained an excellent cycle life

(up to 408 cycles), demonstrating the stability of this system.^[63] Although aqueous alkaline solutions have been widely studied on metal–air batteries, the working potential window for these aqueous solutions is very low and cannot satisfy the need for high energy density.

Recent developments of nonaqueous metal–air batteries such as lithium–air batteries, potassium–air batteries, and sodium–air batteries have attracted the attention of researchers. The commonly operated nonaqueous liquid systems for metal–air batteries are electrolytes based on sulfones, ethers, and amides, which can bear a wider electrochemical window compared to aqueous systems;^[46,91–93] hence, the energy density of energy-storage devices has significantly improved, as shown in Figure 1. Among the various electrolyte systems, lithium triflate in tetraethylene glycol dimethyl ether (TEGDME) exhibits preferable electrochemical performance and relative stability due to its relative stability and low volatility, which is favorable for fabricating flexible metal–air batteries.^[91,94,95] Because of the

Table 1. Some typical liquid electrolytes for application in metal–air batteries.

Composition	System	Performances of the battery	Advantage	Limit	Ref.
KOH–H ₂ O	Aqueous	408 cycles with overpotential of 1.09 V	High ion conductivity	Narrow electrochemical window	[63]
LiClO ₄ –DMSO	Nonaqueous	100 cycles with voltage limited from 2.3 to 4.0 V			[46]
LiClO ₄ –DMF	Nonaqueous	Discharge capacity of about 1500 mA h g ⁻¹ with voltage limited to 2.2 V			[91]
LiCF ₃ SO ₃ –TEGDME	Nonaqueous	100 cycles with capacity limited to 1000 mA h g ⁻¹			[92]
LiNO ₃ –DMA	Nonaqueous	80 cycles with capacity limited to 1 mA h cm ⁻¹			[93]
LiTFSI–PYR ₁₄ TFSI	Ionic-liquid-based	30 cycles with capacity limited to 1 mA h cm ⁻²	Low ion conductivity	Wide electrochemical window	[99]

difficulty of molding techniques in processing potassium and sodium, the research into nonaqueous metal–air batteries has mainly been focused on flexible lithium–air batteries. Aiming at this opportunity, Zhang and co-workers applied this electrolyte and fabricated a series of flexible lithium–air batteries, which all exhibited excellent electrochemical stability.^[96] Though electrolytes based on sulfones/ethers/amides possess a wider electrochemical window compared to aqueous systems, the stability of these electrolyte is also suspicious when the battery operates at high potential.^[91] Ionic liquids are low-temperature molten salts and are also used as new electrolytes for metal–air batteries due to their nonflammability, good thermal stability, high oxidation potential, and wide working potential window.^[97–99] However, the kinetics for metal are depleted; in addition, the cost is another issue that limits its wide application in metal–air batteries. In summary, some typical liquid electrolytes for metal–air application are summarized in **Table 1**.

Though nonaqueous liquid electrolytes have exhibited certain advantages for fabricating flexible metal–air batteries, the leakage problem should be considered, since batteries operate in an open system; what's more, the leakage problem will be even worse when batteries are subjected to frequent bending, twisting, and other deformation modes over a long period. Therefore, nonaqueous liquid electrolytes are not a preeminent candidate in developing the fabrication of flexible metal–air batteries.

3.2. Solid-State Electrolytes

Solid-state electrolytes have been investigated for many years, and represent a good solution for electrolyte leakage. In addition, the pursuit solid-state electrolytes is also intended to broaden the working potential window, improve battery safety, and develop all-solid-state batteries.^[100–103] Based on their composition, solid-state electrolytes are classified into solid inorganic electrolytes and solid organic electrolytes. Solid inorganic electrolyte, with types of perovskite,^[104,105] NASICON,^[106,107] LISICON,^[108] LiPON,^[109–111] Li₃PO₄–Li₄SiO₄,^[112,113] GARNET,^[114,115] etc., are widely investigated in lithium-ion batteries. Abraham and co-workers and Zhou's group studied a series of highly Li-ion conductive solid-electrolyte membranes and successfully applied them to metal–air batteries.^[116–119] However, the above-discussed inorganic solid electrolytes are rigid and are not appropriate for assembling

flexible metal–air batteries; what's worse, the ionic conductivity of this inorganic solid electrolyte is also pitiful. As for assembling flexible metal–air batteries, solid electrolytes with flexible properties must be considered, and the recent development of solid organic electrolytes represents a good solution to this problem.

The used solid organic electrolytes mainly include polymers and metal salts, which play the roles of framework supports and ionic conductors, respectively. As for alkaline polymer electrolytes, poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), poly(vinylpyrrolidone) (PVP), poly(acrylic acid) (PAA), and their hybrids, as excellent organic frameworks have been extensively investigated.^[120–124] Simultaneously, accommodative cross-linkers are often added to improve the mechanical properties of solid organic electrolytes.^[125] Typically, these fabricated solid organic electrolytes often present a relatively lower ionic conductivity than their liquid counterparts. To obtain flexibility, the content of the polymer or cross-linker should be increased and the ionic conductivity of the electrolyte should be further reduced. Therefore, there is a trade-off between flexibility and ionic conductivity. The goal for the fabrication of flexible solid organic electrolytes is to develop all-solid-state flexible metal–air batteries. Among the various polymers, the hybrid system of PVA and PEO is mostly reported as a flexible electrolyte used in fabricating flexible metal–air batteries due to their good solubility in water and compatibility with a wide range of compounds, respectively. It has been reported that the ionic conductivity can reach as high as 10⁻² S cm⁻¹ at room temperature by optimizing the proportions of PVA, PEO, and KOH.^[121]

Besides the preceding polymers, some biomass materials have been reported as a rational precursor for fabricating flexible solid electrolytes. Park et al. synthesized a freestanding gel polymer electrolyte via dissolving gelatin powder in KOH solution, as shown in **Figure 5a**.^[126] The fabricated gel polymer electrolyte exhibited excellent flexibility (**Figure 5b**). The ionic conductivity of this electrolyte was determined by AC impedance spectroscopy via using two pieces of stainless steel (**Figure 5c**), showing 3.1 × 10⁻³ S cm⁻¹. Very recently, Fu et al. developed a facile strategy for fabricating a nanoporous electrolyte membrane via using natural cellulose nanofibers. In this system, micrometer-sized cellulose fibers and fine fibrils were interlaced with each other (**Figure 5d**).^[127] The micrometer-sized cellulose fibers acted as a strong scaffold to maintain the integrity of this solid electrolyte while the fine fibrils played a main role for alkaline-exchange (**Figure 5e**). Due to the smaller size

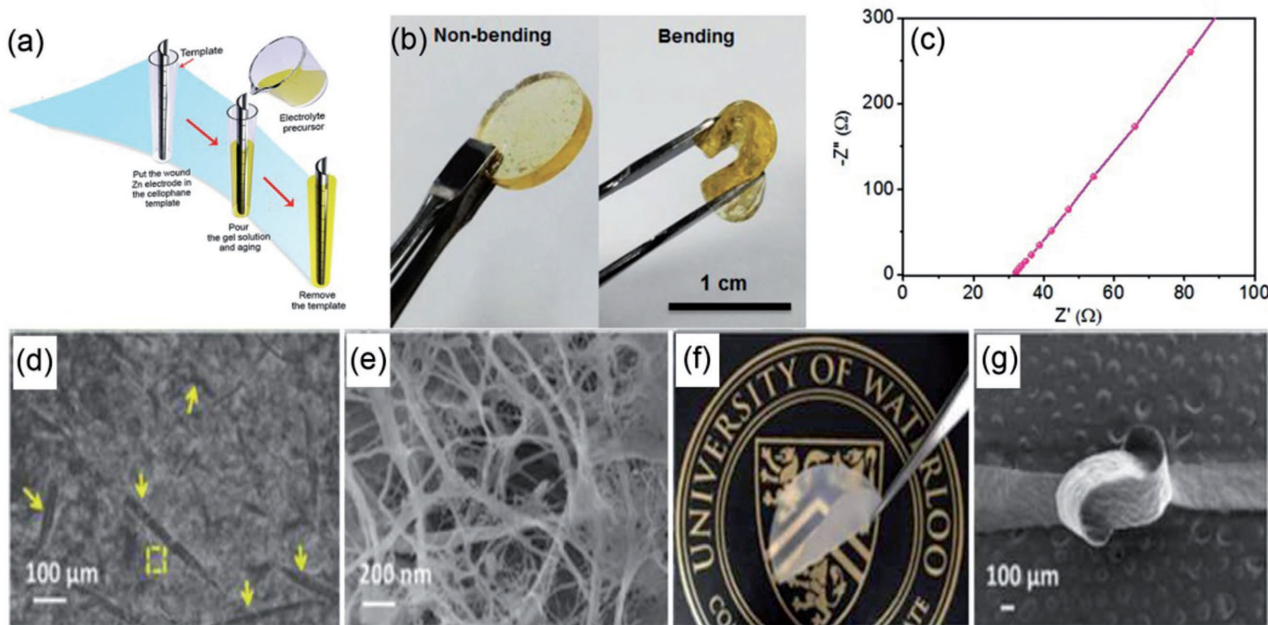


Figure 5. a) Schematic representations for the preparation of GGPE on the surrounding spiral zinc anode. b) Digital photograph of the obtained GGPE. c) AC impedance spectra of the GGPE. d,e) SEM images of the nanoporous electrolyte membrane. f) A photograph of the obtained membrane having a translucent appearance. g) SEM image of a knotted nanoporous electrolyte membrane showing excellent flexibility. a–c) Reproduced with permission.^[126] Copyright 2015, Wiley-VCH. d–g) Reproduced with permission.^[127] Copyright 2016, The Royal Society of Chemistry.

of pores and nanofibers compared to visible light, the obtained membrane was translucent as shown in Figure 5f. In addition, the fabricated membrane also exhibited excellent mechanical properties, which is appropriate for assembling flexible metal–air batteries (Figure 5g). In addition, the ionic conductivity of this membrane was as high as 21.2 mS cm^{-1} .

The discussed alkaline polymer electrolyte successfully solved the problem of electrolyte leakage and realized flexible properties. However, the polymers summarized above are hydrosoluble, which means they cannot be used in lithium/sodium/potassium–air batteries. For the synthesis of polymer electrolytes used in lithium/sodium/potassium–air batteries, two aspects must be considered: (i) high accommodation against other components; (ii) the polymer electrolyte must be stable when the cell is operated in an elevated potential window in the presence of oxygen. Recently, some studies on all-solid-state flexible lithium–air batteries have been propelled by imitating the studies on lithium-ion batteries. The commonly used solid electrolyte is a 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP)-based polymer.^[100] Typically, the photoinitiator and HMPP were added to an electrolyte containing lithium triflate dissolved in TEGDME, along with the poly[(vinylidene fluoride)-*co*-(hexafluoropropylene)] (PVDF-HFP) dissolved in *N*-methyl-2-pyrrolidinone (NMP) and formed a homogeneous mixture solution; then, this polymer electrolyte precursor was cast onto an anode (lithium rod or lithium strip) and exposed to UV-irradiation for a certain period of time. Through the above process, a freestanding gel polymer electrolyte (GPE) was obtained. Liu et al. fabricated a free-standing GPE that was successfully used in assembling a flexible lithium–air battery. The synthetic process is shown in Figure 6a.^[128] The fabricated GPE

also had excellent bendability and mechanical stability as presented in Figure 6b, which are beneficial for its electrochemical performance when the assembled flexible lithium–air battery undergoes various deformation modes. The SEM images show that GPE is porous, which provides adequate channels for ion transmission and inevitably improves the reaction dynamics (Figure 6c). It is worth noting that this GPE possesses exhibited hydrophobicity and can protect Li from reacting with H_2O , thus guaranteeing the safety of the assembled battery to some extent (Figure 6d). The ionic conductivity of this GPE was determined by AC impedance spectroscopy using two pieces of a stainless-steel mesh (Figure 6e). Unexpectedly, the GPE showed 2.843 mS cm^{-1} at 30°C compared to organic liquid electrolyte ($15.925 \text{ mS cm}^{-1}$ at 30°C). Although GPE has been applied in flexible lithium–air batteries and exhibits excellent mechanical properties and electrochemical performance, the stability of this electrolyte is suspect, since the mechanism for this system has not been systematically studied so far. Finally, some recent developments on solid-state electrolytes are also listed in Table 2.

4. Encapsulating Materials

In order to achieve all-solid-state flexible metal–air batteries, the package model should be considered and the main task is how to select appropriate encapsulating materials. The development of encapsulating materials used in flexible metal–air batteries should follow these guidelines: (i) excellent flexibility and intensity, which is a premise for fabricated flexible metal–air batteries; (ii) high compatibility against other components; (iii) low

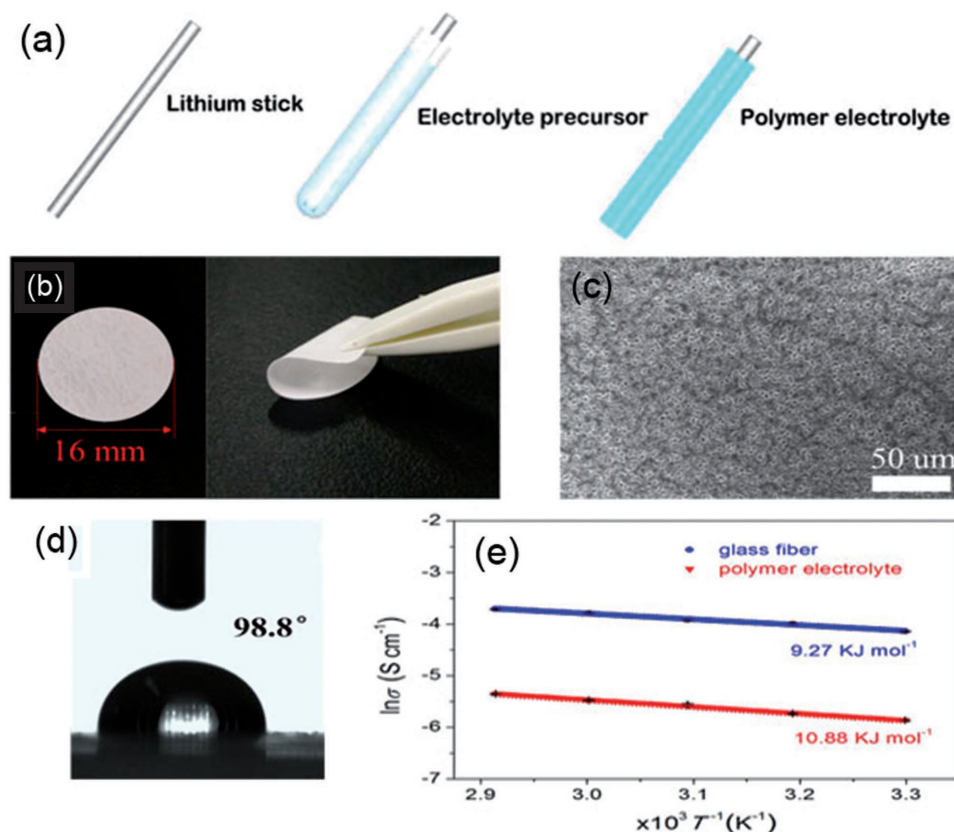


Figure 6. a) Schematic representation for the design and preparation of GPE-coated lithium anode. b) Optical photographs of the fabricated GPE at flat and bent conditions, with the c) corresponding SEM image and d) water contact angle. e) Ionic conductivity of the lithium–air batteries with GPE or glass fiber. Reproduced with permission.^[128] Copyright 2016, Wiley-VCH.

density to improve the energy density of the cell; (iv) easy availability and economy. Up to now, aluminum–plastic films,^[96,129] thermoplastic materials,^[126,130–132] poly(ethylene terephthalate)

(PET),^[133] poly(dimethylsiloxane) (PDMS),^[134] etc., have been applied in the flexible-energy-storage field and some have been used in the flexible lithium–air battery field (Figure 7).

Table 2. Composition and conductivity of solid-state electrolytes for application in metal–air batteries.

Type	Composition	Conductivity [S cm ⁻¹]	Advantage	Limit	Ref.
Inorganic electrolyte	Perovskite	2×10^{-5}	Wide electrochemical window	Rigid and low ion conductivity	[104]
	NASICON	5×10^{-3}			[107]
	LISICON	6.4×10^{-4}			[108]
	LIPON	3.3×10^{-6}			[110]
	Li ₃ PO ₄ –Li ₄ SiO ₄	2.8×10^{-6}			[112]
	GARNET	4×10^{-5}			[114]
Organic electrolytes	P(ECH-co-EO)–KOH	10^{-3}	Flexible	Relatively narrow electrochemical window	[120]
	PEO–PVA	10^{-2}			[121]
	PVA–PVP	1.5×10^{-4}			[122]
	PVA, PAA,	2.6×10^{-1}			[123]
	LiCF ₃ SO ₃ –ETPTA–PvDF–HFP	1.6×10^{-3}			[128]

5. Prototype Flexible Metal–Air Batteries

As mentioned above, the fabrication of flexible metal–air batteries is mainly based on two purposes: (i) expanding their application to daily life, especially with regard to flexible energy-storage devices; and (ii) increasing the actually used energy density of metal–air batteries. For these goals, several prototypes of flexible metal–air batteries have been proposed to date, which can be divided into four categories according to the assembly scheme: planar batteries, cable-type batteries, woven-type battery packs, and battery array packs.

5.1. Planar Batteries

Recent reports on planar flexible metal–air batteries have imitated the commonly

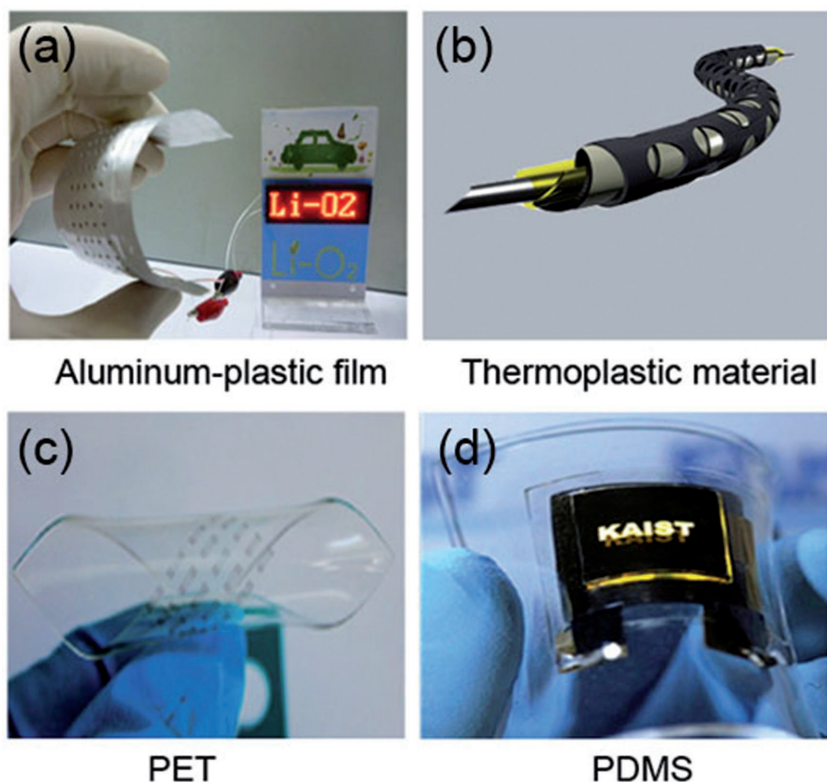


Figure 7. a–d) Flexible energy-storage devices packed with aluminum–plastic film, thermoplastic material, PET, and PDMS. a) Reproduced with permission.^[96] Copyright 2015, Nature Publishing Group. b) Reproduced with permission.^[126] Copyright 2015, Wiley-VCH. c) Reproduced with permission.^[133] Copyright 2013, Wiley-VCH. d) Reproduced with permission.^[134] Copyright 2011, Wiley-VCH.

researched lithium-ion batteries. The only difference is the permeability of the packaging, and all of them have a sandwich design. Fu et al. fabricated a flexible rechargeable zinc–air battery comprising a PVA-based polymer electrolyte sandwiched between a carbon-cloth air cathode loaded with $\text{LaNiO}_3/\text{N-CNT}$ catalyst and a Zn-film anode.^[135] The electrochemical performance of the fabricated cell at various bending angles was tested, showing a stable cycling performance at the current density of 50 A kg^{-1} ; in addition, the charge-transfer resistance is barely changed. The volumetric energy density and gravimetric energy density were also tested in this work: they were as high as 2905 W h L^{-1} and 581 W h kg^{-1} respectively, suggesting its promising application for high-energy-storage flexible devices. Besides for zinc–air batteries, the sandwich design was also used in flexible lithium–air batteries, Liu et al. first fabricated a flexible rechargeable lithium–air battery containing a flexible pristine TiO_2 NAs/CT air cathode, a glass-fiber membrane, and a lithium-foil anode, and the assembly mode is shown in **Figure 8a**.^[96] Finally, the cell was obtained by coupling with aluminum–plastic. The fabricated cell exhibited excellent electrochemical performance such as low overpotential, high capacity rate performance, etc. Notably, the cell could sustain a stable cycling life for more than 350 cycles with capacity limit of 500 mA h g^{-1} at current density of 100 mA h g^{-1} (**Figure 8b**). To demonstrate its potential application in flexible electronics, severely bent and

twisted cells at various angles were used to power a commercial red light-emitting diode (LED) display screen (**Figure 8c–e**). Simultaneously, the stability of the cycling performance was tested and it was found that the terminal discharge voltage plateaus were barely influenced. Inspired by this work, some studies for fabricating flexible lithium–air batteries have also been carried out.^[88,136] However, liquid electrolyte (lithium triflate–TEGDME) was used in these studies and electrolyte leakage is inevitable, especially when batteries undergo various bending and twisting conditions. Therefore, the development of all-solid-state flexible lithium–air systems is urgent.

5.2. Cable-Type Batteries

Compared to the sandwich structure of flexible metal–air batteries, the development of the cable-type design also attracts great attention in the field of flexible electronics due to its improved omnidirectionality, flexibility, and twistability, and such devices can be woven into many shapes and applied in many areas. Typically, cable-type metal–air batteries, from the inside out, are made up of a metal foil or metal rod as the anode, a gel polymer electrolyte, and a flexible air cathode (including air diffusion layer), and these components are finally wrapped with a perforated packing insulator: thus, cable-type metal–air batteries are obtained. Park et al. first fabricated a flexible cable-type zinc–air battery containing a spiral zinc-foil anode, a gelatin-based gel polymer electrolyte, and an Fe/N/C-composite-based air cathode. Finally, these components were encapsulated with a punched heat-contraction rubber cable.^[126] **Figure 9a,b** shows a photograph and a cross-sectional image of the prototype cable-type zinc–air battery. The discharge voltage plateaus and the duration time of the batteries with and without electrocatalyst were tested. These electrochemical performances of the cable-type system were found to be not as far behind the stack type, as shown in **Figure 9c**. In addition, a bending test was also carried out, showing no differences in the discharge voltage plateaus with the battery bent in various conditions. The result indicates that the cable-type flexible zinc–air battery can be successfully operated in various deformation modes (**Figure 9d**). Followed by this work, Xu et al. fabricated a flexible, stretchable, and rechargeable cable-type zinc–air battery containing a zinc spring anode, a PVA/PEO-based solid-state electrolyte, and an air cathode made from aligned carbon nanotubes decorated with RuO_2 .^[72] The main attraction in this work is the battery’s rechargeability and stretchability, as evidenced by the discharge/charge voltage plateaus. Significantly, this fabricated cable-type zinc–air battery could maintain 30 cycles with a current density of 1000 mA g^{-1} . Owing to the unique structure of the aligned carbon nanotubes and zinc spring, the

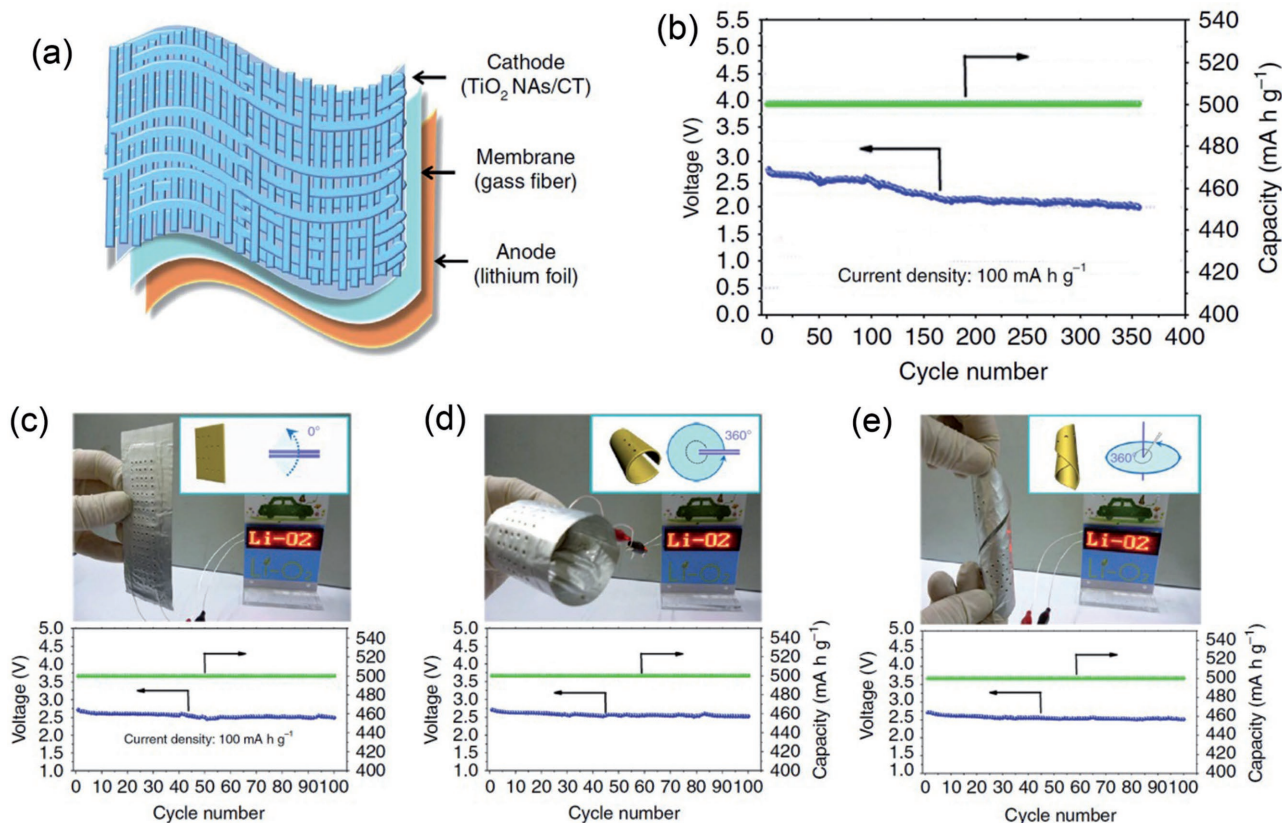


Figure 8. a) Schematic of the battery internal structure. b) Cycling performance of a battery with a TiO₂ NAs/CT cathode. c–e) The bending and twisting properties of the fabricated flexible lithium–air battery. Adapted with permission.^[96] Copyright 2015, Nature Publishing Group.

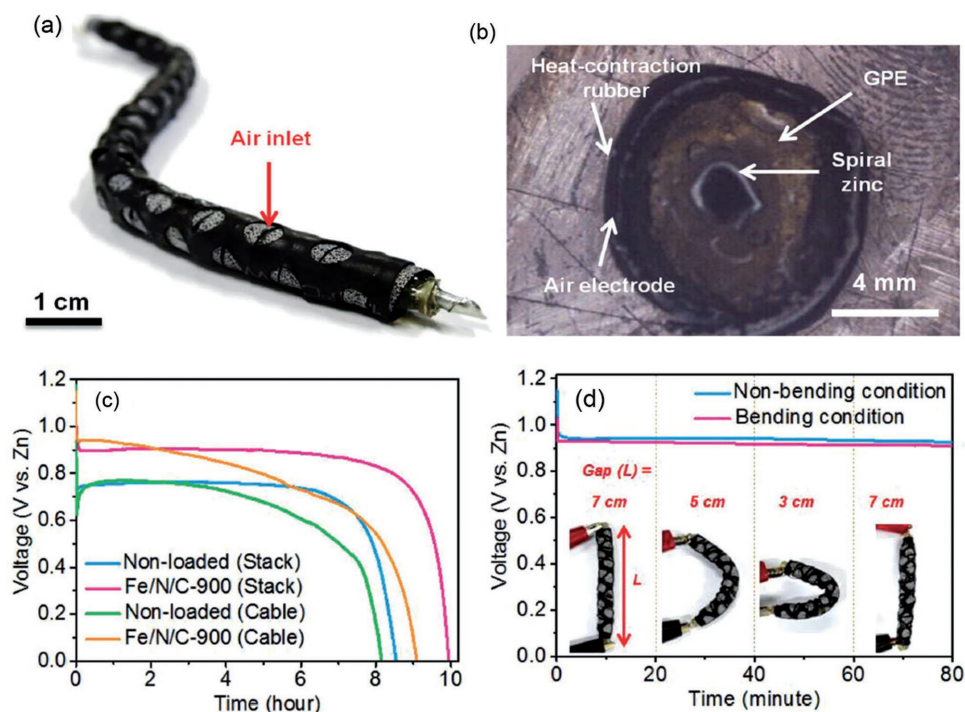


Figure 9. Photograph of a) the prototype cable-type flexible zinc–air battery and b) its cross section by optical microscopy. c) Discharge curves of stack-type and cable-type flexible zinc–air batteries with and without Fe/N/C electrocatalysts, respectively. d) Discharge curves of a cable-type flexible zinc–air battery by applying bending strain every 20 min. Adapted with permission.^[126] Copyright 2015, Wiley-VCH.

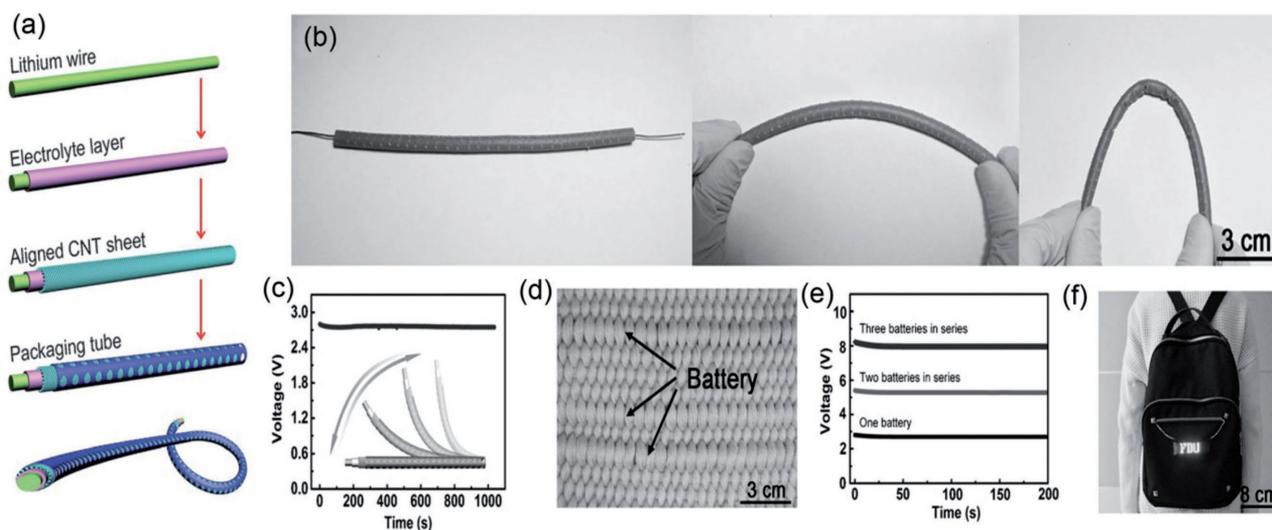


Figure 10. a) Schematic illustration of the fabrication of the cable-type lithium–air battery. b) Photographs of the cable-type lithium–air battery under different bending angles. c) Discharge curve under a dynamic bending and release process. d) Photograph and discharge curves of cable-type lithium–air batteries. f) A battery woven into a knapsack to power a commercial LED. Adapted with permission.^[71] Copyright 2016, Wiley-VCH.

fabricated cable-type zinc–air battery could endure stretching to some extent without damage and the electrochemical stability was barely influenced.

Apart from zinc–air batteries, the cable-type design has also been applied in the lithium–air battery field recently. Zhang et al. first fabricated a cable-type lithium–air battery containing a lithium wire anode, an HMPP-based gel polymer electrolyte, and an aligned-carbon-nanotube cathode. The fabrication process of the cable-type lithium–air battery is schematically illustrated in **Figure 10a**.^[71] Different from the cable-type zinc–air battery, the hydrosoluble alkaline polymer electrolyte was not applied due to its incompatibility toward lithium metal. Similar to cable-type zinc–air battery, the cable-type lithium–air battery also exhibited a high flexibility, and could be deformed into various shapes without damage (**Figure 10b**). In addition, the electrochemical and mechanical stability was investigated, and the discharge voltage plateaus were almost unchanged under a dynamic bending process at a speed of $10^{\circ} \text{ s}^{-1}$ (**Figure 10c**). In order to demonstrate the practicability of this fabricated cable-type lithium–air battery, three batteries were connected in parallel and woven into a flexible powering textile (**Figure 10d**): this battery pack could deliver a discharge voltage up to 8 V (**Figure 10e**). In order to further demonstrate its application in a daily routine, this fabricated cable-type lithium–air battery was integrated into a knapsack and could power commercial LED equipment successfully, as shown in **Figure 10f**. By adopting the same approach, Liu et al. fabricated a cable-type lithium–air battery containing a lithium-rod anode, an HMPP-based gel polymer electrolyte, and an active-carbon (Super P) air cathode.^[128] The mechanical properties and electrochemical stability of this fabricated battery were estimated. It was found that the electrochemical performance, such as the discharge capacity, round-trip efficiency, etc., was not deeply affected, regardless of the deformation mode of this battery. In addition, the safety of the fabricated battery was further investigated. Thanks to the hydrophobic polymer electrolyte,

which can well isolate lithium and water, this endowed the battery excellent security. A submerging test was carried out and it was found that the cable-type lithium–air battery could effectively power a commercial LED in water. Inspired by this design, a cable-type aluminum–air battery was also proposed in recent studies.^[65,137] Compared with the sandwich structure, the cable-type design possesses high tensile strength in the twisted state and has extreme omnidirectional flexibility, which ensures their potential use in flexible electronic devices.

5.3. Woven-Type Batteries

The sandwich design and cable-type design of metal–air batteries all fall into the “stack-type” category, which is the same as the traditional coin cell and columnar type. However, some components used in a battery occupy a large portion of the weight, although they are not key components contributing to the energy, and this inevitably reduces the energy density. For metal–air batteries, the influence of the energy density caused by their components is more severe, since an additional air-diffusion layer is required in this system compared to other energy-storage systems. Unfortunately, the integral practical energy density of the commonly investigated metal–air batteries, especially the lithium–air battery, is very low, and this is mainly caused by the low current density and irrational assembly structures. The increasing current involves material exploitation and air-cathode design; here, we have mainly discussed the assembly structures. For improving the actual energy density of metal–air batteries, somewhat different ideologies toward fabrication of metal–air batteries are urgently needed. Though the integral practical energy density of metal–air batteries with flexible design has been greatly improved, a big gap between the theoretical energy density and that observed in practice still exists. Inspired by the structure of Chinese bamboo slips, Liu et al. reported a new strategy to fabricate a woven-type battery

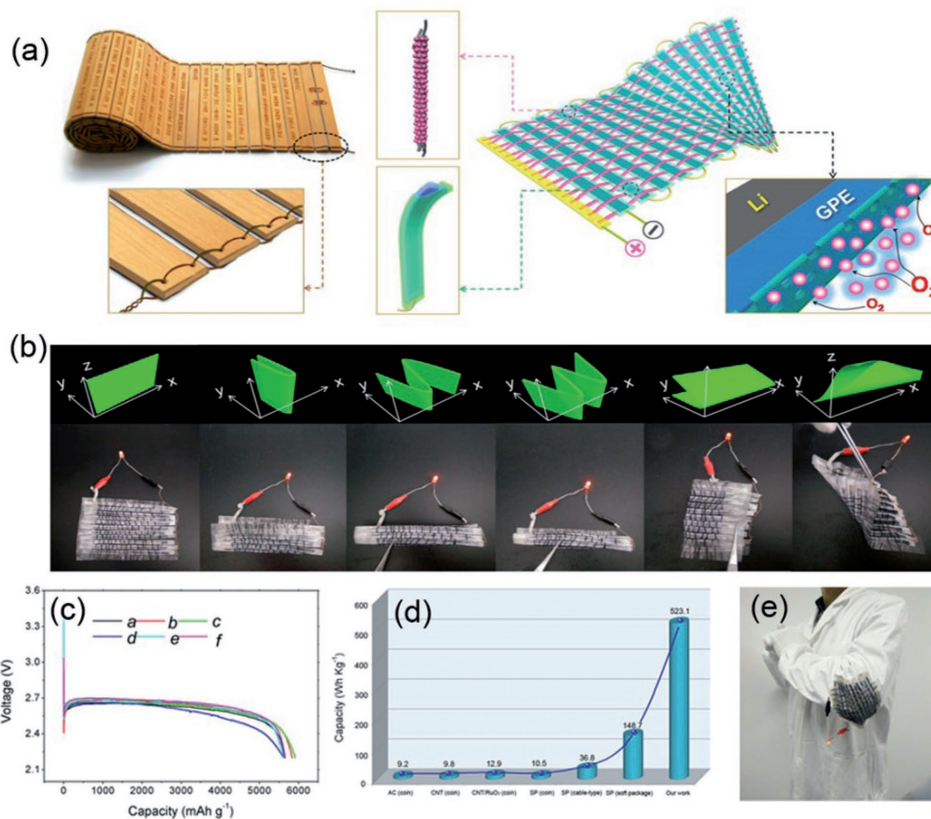


Figure 11. a) Schematic illustration of the fabrication of a flexible and wearable lithium-air battery. b) Optical images of the fabricated lithium-air battery powering a commercial LED under various bending and twisting conditions. c) First discharge curves of flexible and wearable lithium-air batteries under various bending and twisting conditions. d) A rough comparison of the energy densities of various types of lithium-air batteries. e) Photograph of a fabricated flexible and wearable lithium-air battery integrated within clothes. Adapted with permission.^[138] Copyright 2016, Wiley-VCH.

pack with an interlaced manner, as shown in **Figure 11a**.^[138] In this system, the battery consisted of a lithium-foil anode, a polymer electrolyte, and an air cathode. An air-diffusion layer and packing material were avoided: these are the main contributors to the weight in commonly assembled metal-air batteries. In addition, this manner of assembly possesses many advantages in comparison with other reported flexible metal-air batteries as described: (i) avoiding an air-diffusion layer and packaging materials enhanced the battery's energy density; and (ii) the kinetics of the battery were improved, since gas could easily access the reaction sites via both of the two sides. To demonstrate the electrochemical and mechanical stability of this woven-type battery, the as-obtained battery was used to power a commercial red LED in various bending and twisting conditions, as shown in **Figure 11b**, indicating the excellent mechanical suppleness of the fabricated woven-type battery pack. In addition, the electrochemical stability of this battery pack was evaluated simultaneously, as well. About $5800\ mA\ h\ g^{-1}$ capacity was obtained from their fabricated batteries and the mean voltage remained almost unchanged (**Figure 11c**). The highlight of the work is the boosted integral energy density, which is as high as $523\ W\ h\ kg^{-1}$, far greater than other types of batteries (coin type, cable type, and soft package), as listed in **Figure 11d**. To demonstrate wearable applications, the fabricated lithium-air battery was integrated

on clothes, as shown in **Figure 11e** and it was found that the as-obtained lithium-air battery can operate normally even on an elbow joint that was under continual movement. In summary, this fabrication strategy can also be extended to other metal-air batteries to improve their integral energy density, giving us new ideas for fabricating new types of metal-air batteries.

5.4. Battery-Array Packs

Commonly used batteries will be destroyed when they are in constant deformation modes. This can cause serious security issues. Aiming at addressing this problem, Xu et al. proposed battery arrays implanted in a flexible substrate: the unit cells were connected by conducting frameworks, and a battery array pack was finally obtained.^[25] This "break up the whole into parts" strategy endows this battery with robust mechanical properties, since the damage to the small unit cells is limited when the flexible substrate is subjected to serious deformation modes. Inspired by this design, Liu et al. built a novel lithium-air battery-array pack that consisted of arrays of small-scale air cathodes and lithium anodes interconnected by carbon ropes and copper wires.^[139] The air cathodes and anodes were isolated by polymer electrolyte, as shown in **Figure 12a**. Compared with other strategies for fabrication of flexible metal-air batteries,

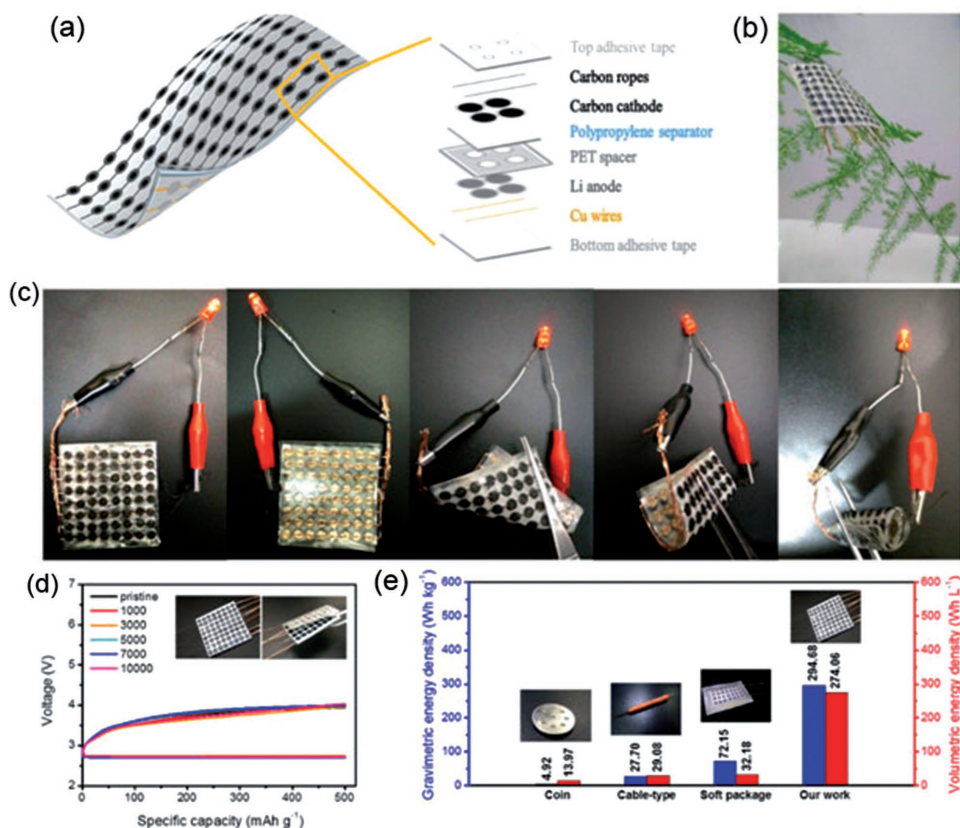


Figure 12. a,b) Schematic illustrations of an ultrathin, lightweight, and wearable lithium–air battery. c) The obtained lithium–air battery powering a commercial LED at various bending and twisting conditions. d) Charge–discharge curves after bending thousands of times. e) A rough comparison of the energy densities of various types of lithium–air batteries. Adapted with permission.^[139] Copyright 2017, Wiley-VCH.

the obtained battery-array pack holds many advantages: (i) the used materials in this work are very lightweight and thin (Figure 12b); this endows the battery with high gravimetric/volumetric energy density; (ii) the battery was broken up into many tiny units and, remit the stress of battery, the mechanical properties were greatly enhanced. To investigate the flexibility, the as-obtained battery powered a commercial LED; when it was intentionally deformed in various modes, the LED remained constantly powered under all the testing conditions and still ran normally (Figure 12c), indicating the excellent mechanical suppleness of this battery-array pack. To clarify the influence caused by the repetitive external force, the battery was folded, and then its electrochemical performance was evaluated. Surprisingly, discharge–charge plateaus were barely changed even after 10 000 cycles of folding/stretching, showing excellent mechanical stability (Figure 12d). In addition to the mechanical properties, the gravimetric energy density and volumetric energy density are two important indicators that should be taken into account. The weight of a fabricated battery-array pack is about 0.6 g, which is lighter than other conventional coin batteries. The as-obtained battery-array pack possesses high gravimetric energy density and volumetric energy density as high as 294.68 Wh kg⁻¹ and 274.06 Wh L⁻¹, respectively (Figure 12e). We are confident that the value will be enhanced if the battery structure is further optimized.

6. Challenges and Perspectives on Flexible Metal–Air Batteries

Flexible metal–air batteries exhibit much higher theoretical energy density than other conventional flexible energy-storage systems such as lithium-ion, lead–acid, Ni–HM batteries, etc. They are a promising candidate for implantation in wearable or rolled-up electronic devices. However, the development of flexible metal–air batteries is still in its infancy. Significant challenges still exist, though fantastic progress has been achieved in recent years, and some advanced battery models have been fabricated in the laboratory. The most important criteria for flexible metal–air batteries are the practical energy density (Wh kg⁻¹ or Wh L⁻¹). Before their practical application, the following essential challenges also need to be overcome:

- i) The electrochemical performances (capacity, rate capability, cycle life, efficiency, etc.) of the battery need further development, which involves developing and designing rational cathodes, exploring accommodative electrolytes, and protecting the lithium anode.
- ii) As they operate in an open system, parasitic reactions caused by contamination (H₂O, N₂, CO₂, etc.) that occur in particular on the anode put sand in the wheels of the development of metal–air batteries. Some approaches, such as using a special electrolyte and additives, coating a protective layer, and

soaking with organic solvent, have been carried out. In addition, the application of a flexible solid-state electrolyte may alleviate these problems to a large extent; however, low ionic conductivity is another serious problem. In addition, there have been very few investigations toward the detailed characterization of the reaction dynamics for the solid-based system. Therefore, the development of flexible solid-state electrolytes with high ionic conductivity, and accommodation for all battery components is critical.

iii) The energy density of the recently investigated metal–air batteries is very low and far below their theoretical value, due to the mass proportion of the active material being relatively high. The development of flexible metal–air batteries avoids the use of bulky and rigid stainless-steel packing so that the energy density is improved to some extent. However, it is far from a satisfactory value. Increasing the proportion of active material and reducing the mass of other components may be appropriate ways to improve the practical energy density.

In addition, the safety of flexible metal–air batteries also needs to be considered, especially when lithium/sodium/potassium metal is used as the anode. Batteries may short circuit and cause serious accidents when subjected to frequent bending.

Besides the challenges stated above, insightful understanding of the reaction mechanisms of metal–air batteries during cycling is also of paramount importance. In order to deepen the understanding of the electrochemical mechanisms, both experimental and theoretical models are needed. In addition to basic research, technical research is equally important for the development of flexible metal–air batteries, since the assembly method will affect the energy density of the battery to a large extent. In this view, among the various gases in our world, only oxygen is used in these metal–air batteries, and other gases in air such as H₂O, N₂, CO₂, etc., are identified as contaminants. However, recent reports have demonstrated that N₂ and CO₂ could be used as active materials in metal–air batteries,^[140–147] thus, chances are great that these gases can be used in flexible metal–air batteries. In addition, by integrating with other energy systems, such as solar cells, to construct self-powered systems, the application of flexible metal–air batteries will also be broadened, and this strategy has already been applied in other flexible chemical batteries.^[148]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

batteries, challenges, flexible, perspectives, progress

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