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The PVDF-HFP gel polymer electrolyte for Li-O_2 battery

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ABSTRACT

Rechargeable lithium-oxygen (Li-O_2) batteries which deliver a remarkable theoretically specific energy, have been considered as one of the most promising energy storage systems. Replacing the volatile, flammable, leaked liquid electrolytes with the gel polymer electrolytes (GPEs) is generally accepted as an effective approach to solving the issues. As one of the most important matrices for polymer electrolyte, polyvinylidenefluoride-hexafluoropropylene (PVDF-HFP) has been successfully applied to Li-O_2 battery, benefited from its high solubility, lower crystallinity, good electrochemical and mechanical properties. Here we review the recent progress of Li-O_2 batteries with PVDF-HFP electrolytes, and discuss the challenges and solutions of PVDF-HFP electrolytes for Li-O_2 batteries.

1. Introduction

The global impact of carbonaceous emissions from the accelerated depletion of fossil fuels, has created a huge incentive to harvest and store electrical energy from clean and renewable energy, such as wind, hydropower and nearly unlimited solar energy [1–4]. To realize affordable electric vehicles competitive with cars powered by the internal combustion engine and store electrical energy generated by clean and renewable power, new battery strategies are imperatively required. To this end, rechargeable lithium-air batteries (frequently referred to as Li-O_2 batteries since O_2 is reactant) which deliver a remarkable theoretically specific energy of 5–10 times as high as that of the state-of-the-art lithium-ion batteries, have emerged as new generation of energy storage devices for electric vehicles, portable electronic devices, smart grids, and other stationary applications [5–9].

A typical rechargeable non-aqueous Li-O_2 battery is composed of a lithium metal anode, a non-aqueous Li^+ conducting electrolyte, and a cathode with porous structure to ensure accommodation of a large amount of discharge products and to facilitate rapid mass (oxygen and lithium ions) transportation, as shown in Fig. 1 [10–13]. Theoretically, the electrochemical reaction pathway is $2Li + O_2 \leftrightarrow Li_2O_2$, with the forward direction describing the discharge of the cell and the reverse direction describing the charge [14–16]. Since it was initially proposed, the system has presented scientific and technological challenges including the limited energy density, poor round-trip efficiency, poor rate capability, parasitic reactions, low cycle stability [17–20]. Although many great progresses have been achieved by optimizing the sophisticated cathode, catalyst activity, or electrolytes and binder stability to improve the performance, the safety issues of Li-O_2 batteries is largely neglected [10,12].

The issues at least include the volatility, flammability and leakage properties of common organic electrolyte, and the corrosion of lithium by crossover H_2O and CO_2 in the case of its operation in ambient atmosphere [21–23]. And many research results indicated that most electrolytes are not stable enough toward these reactive species, leading to the decomposition of electrolytes and formation of side-products, which will diminish the cycle performances at last [24–26]. Therefore a stable electrolyte is urgently needed for long-life Li-O_2 battery.

Replacing the liquid electrolyte with the gel-polymer electrolytes (GPEs) or solid-state electrolytes is generally accepted as an effective approach to solving the above-mentioned issues. Unlike the liquid electrolytes, solid-state electrolytes have greater electrochemical stability voltage window, enhanced thermal stability, high modulus, high t_{Li+} and diminished flammability [27–29]. The enhanced stability and safety of solid-state electrolytes provides opportunities to simplify and redesign safety measures currently used in the battery cell [30,31]. However, the solid electrolytes have intrinsic drawbacks for practical applications. Except the high interphase resistance between the electrode/electrolyte contact, insufficient ionic conductivities at room temperature for solid polymer electrolytes and difficult fabrication and handling processes for solid ceramic electrolytes are challenges for solid-state Li-O_2 battery [32].

Compared with solid-state electrolyte, GPE serves as a better candidate for the replacement of liquid electrolyte due to excellent ionic

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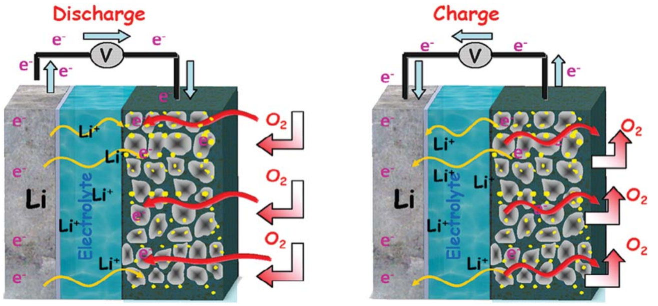

Fig. 1. Schematic operation proposed for the rechargeable aprotic Li-air battery. During discharge, the spontaneous electrochemical reaction 2Li + $O_2 \rightarrow Li_2O_2$ generates a voltage of 2.96 V at equilibrium (but practically somewhat less due to overpotentials). During charge, an applied voltage larger than 2.96 V (~ 4 V is required due to overpotentials) drives the reverse electrochemical reaction $Li_2O_2 \rightarrow$ 2Li + O_2.
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conductivity, low interfacial charge-transfer resistance, high safety, increased shape flexibility, good process ability and mechanical strength [27,33]. Since 1996 Abraham and Jiang firstly reported the Li-O_2 battery with polyacrylonitrile (PAN)-based polymer electrolyte, the polymer electrolytes in Li-O_2 battery have attracted enormous attention [17]. Many polymers and co-polymers were tested as potential electrolytes for polymer electrolyte lithium batteries (the batteries which have lithium as an anode, such as lithium-ion batteries, Li-O_2 batteries), including polyethylene oxide (PEO), polypropyleneoxide (PPO) and their copolymers, or more inert (cage) matrices, for instance polyvinylidene fluoride (PVDF) and its copolymers with hexafluoropropylene [PVDF-HFP], polyacrylonitrile (PAN), polyamide (PA), poly(tetra-fluoroethylene) (PTFE), poly(vinyl alcohol) (PVA) and polymethyl-methacrylate (PMMA) which were selected for their promising performances [28,34]. Among these, PVDF and its copolymers PVDF-HFP used as matrix for polymer electrolyte lithium batteries have been extensively studied because of its high solubility, lower crystallinity, lower glass transition temperature, good electrochemical and mechanical properties, shape and packaging flexibility and improved scalability [35–37].

In the following sections, we provide a succinct introduction to PVDF-HFP electrolytes and discuss their fundamental properties in the context of electrochemical energy storage applications. We then focus on recent progresses in Li-O_2 battery with PVDF-HFP electrolytes and provide some insights to promote the understanding of polymer electrolytes for Li-O_2 battery. Finally, the challenges and future prospects for GPE Li-O_2 battery chemistries and technologies are outlined to expedite the development in this area and thus accelerate Li-air battery application.

2. The PVDF-HFP electrolyte

PVDF based polymer electrolytes are highly electrochemically stable due to the presence of strongly electron-withdrawing functional group (− C-F) and its high dielectric constant ($\varepsilon = 8.4$) which can assist the larger dissolution of lithium salts and subsequent support of a high concentration of charge carriers [31,34]. However, pure PVDF has higher degree of crystallinity because of single monomer throughout the polymer chain providing less free volume to the mobile Li^+ ion, which results in lower conductivity [38].

By comparison, the PVDF-HFP with lower crystallinity, which is available with HFP molar contents in the range 5–25%, is one of the most important matrices [39]. This material was firstly proposed as electrolyte for lithium batteries by Bellcore, which inspired intense researches and developments [40,41], and is currently the most used in the lithium polymer battery market [28].

In these polymers, the crystalline regions which provided sufficient mechanical integrity for the processing of free-standing films and eliminated the need for a cross-linking step (Fig. 2) [31,42]. The CF_3 pendant group in HFP monomers which is randomly mixed with the VDF monomers, would provide steric hindrance and lead to higher amorphicity [38]. The generated amorphous domains in an otherwise predominantly crystalline PVDF structure, could trap large amounts of liquid electrolytes, render the polymer soluble in acetone and lower its melting temperature, resulting in higher ionic conductivity [41].

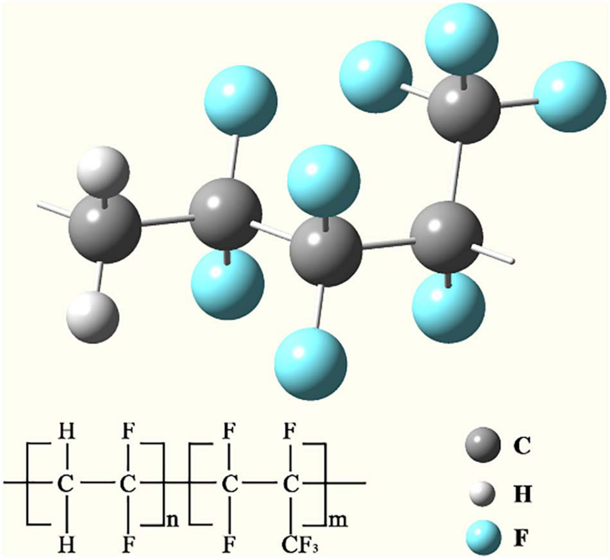

Fig. 2. Schematic representation of the PVDF-HFP.

3. Recent progress of PVDF-HFP in Li-air/O_2 battery

As one of the most important GPEs which combine the cohesive features typical of solid systems with liquid-like transport properties, PVDF-HFP has attracted widely attentions. There are several papers related to the PVDF-HFP polymer electrolyte for Li-air/O_2 batteries are provided recently.

In 2010, Yu et al. reported hydrophobic ionic liquid-silica-PVDF-HFP polymer composite electrolyte is synthesized and employed in Li-air batteries for the first time (Fig. 3). The fabricated polymer composite electrolyte delivers a high ionic conductivity of 1.83×10^{-3} S cm^{-1} at room temperature which is in the same order of ionic liquid electrolyte. When it was used for Li-air batteries, the batteries show a higher capacity of 2800 mAh g^{-1} of carbon in the absence of O_2 catalyst than pure ionic liquid as electrolyte. The flat discharge plateau and large discharge capacity indicate that the hydrophobic ionic liquid-silica-PVDF-HFP polymer composite electrolyte membrane can effectively protect lithium from moisture invasion [21].

In addition, a quasi-solid-state Li-O_2 battery was constructed by Lee et al. using a gel polymer electrolyte with an ionic liquid (designated as IL-GPE). The composite electrolyte, which combined advantages of PVDF-HFP and pyrrolidinium-based IL (*N*-methyl-*N*-butyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide, PYR14TFSI), provided a more effective barrier to water transport toward the Li anode, and showed a discharge capacity of 72 mAh at the current density of 0.25 mA cm^{-2}. Compared to the conventional liquid electrolyte, the IL-GPE not only resulting in the formation of a more conductive and stable solid electrolyte interface (SEI) on the lithium metal anode, but also provides a more effective barrier to water crossover toward the lithium anode. Their study also verified that IL-GPEs provide a promising strategy for designing and fabricating large-scale Li-O_2 batteries with high capacity [43]

However, ionic liquid-based electrolytes do have some serious drawbacks, such as high cost, low Li ion transference number in the

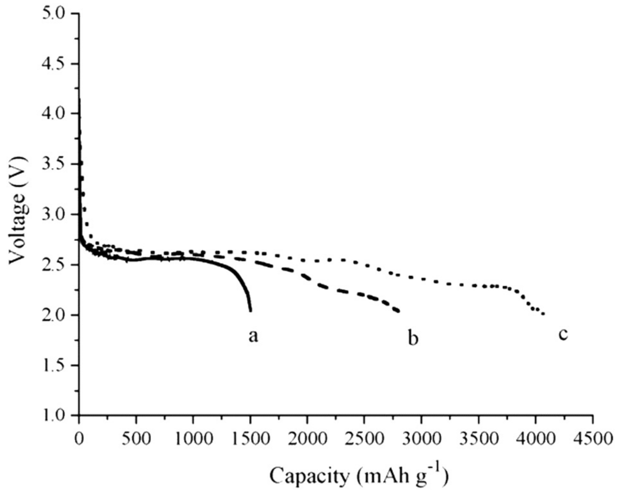

Fig. 3. Discharge curves of Li-air batteries with different electrolytes. (a) LiTFSI-PMMITFSI based non-catalyzed Li-air battery (solid), (b) LiTFSI-PMMITFSI-silica-PVDF-HFP polymer composite electrolyte based non-catalyzed Li-air battery (dash) and (c) LiTFSI-PMMITFSI-silica-PVDF-HFP polymer composite electrolyte based α-MnO_2 catalyzed Li-air battery (dot) in ambient atmosphere at the discharge current density of 0.02 mA cm^{-2}.
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case of most ILs (< 0.12), low Li salt solubility, and, for many ILs, low conductivity [22,44].

Liao et al. prepared a Polymer gel electrolyte by blending PVDF-HFP and cellulose acetate (CA), wherein CA plays as an additive to improve the wettability and ionic conductivity of the blending membranes. A Li-O_2 battery with the fabricated membrane which has good electrolyte uptake and high ionic conductivity as well as excellent thermal and electrochemical stability, exhibits good rate capability and enhanced cycling capacity retention. Compared to the conventional system using polyethylene separator and liquid electrolyte, this enhanced performance is attributed to PGE, which may prevent the diffusion of oxygen from the air cathode to the Li metal anode [22].

To relieve the problem of electrolytes decomposition during charge process, as shown in Fig. 4, Wang et al. prepared a promising free-standing GPE with PVDF-HFP matrix and which was then plasticized with tetraethylene glycol dimethyl ether (TEGDME) through a solvent-casting method. The as-prepared gel polymer electrolyte exhibited a large operating window (up to 4.6 V) and acceptable ionic conductivity (1.0 mS cm^{-1}), and it showed high initial discharge capacity and excellent cycling performances (50 cycles) when applied in Li-O_2 batteries [24].

Benefiting from the good mechanical flexibility, high safety and no liquid electrolyte leakage of polymer electrolyte, flexible/stretchable Li-air/O_2 batteries, holding great promise to be used in the emerging field of flexible/wearable electronic devices, were successfully developed recently.

To achieve both high ionic conductivity and good protection for Li from oxidization over long-term cycling, a hybrid gel-solid-state polymer electrolyte which combine both solid electrolytes and gel electrolytes together was also developed for Li-O_2 battery by Chou et al. Benefiting from its high ionic conductivity and low activation energy, excellent cycling performance is attained, in which the terminal voltage is higher than 2.2 V after 140 cycles at 0.4 mA cm^{-2} with a limited capacity of 1000 mAh $g_{(composite)}^{-1}$. In addition, a flexible battery was fabricated with the hybrid gel-solid-state polymer electrolyte and it demonstrates good cycling performance even was bent [45].

A cable-type water-survivable flexible Li-O_2 battery was investigated by our group, wherein a free standing gel polymer electrolyte and a flexible cathode play key roles (Fig. 5). The GPE composed

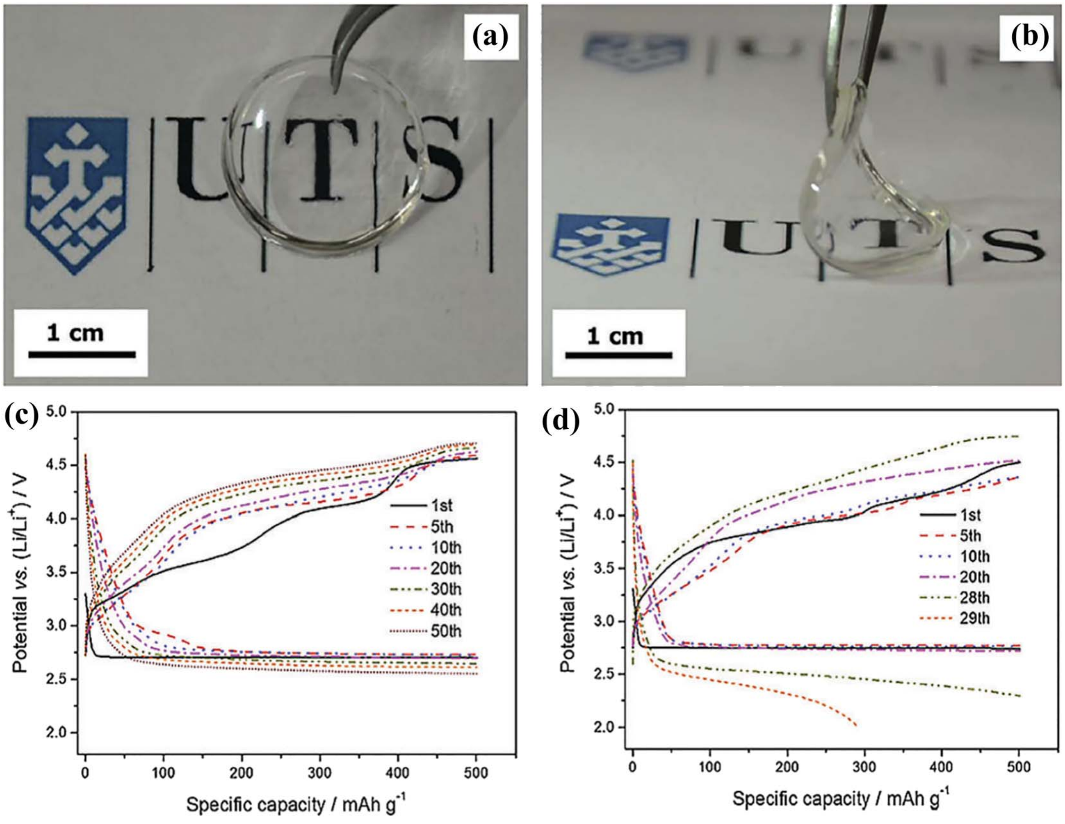

Fig. 4. (a, b) A transparent, homogeneous, and free-standing membrane based on TEGDME and PVDF-HFP polymer matrix. The discharge and charge profiles of Li-O_2 batteries with a fix capacity of 500 mAh g^{-1} when using (c) TEGDME gel polymer electrolyte, and (d) liquid TEGDME electrolyte. The current density was 50 mAh g^{-1}.
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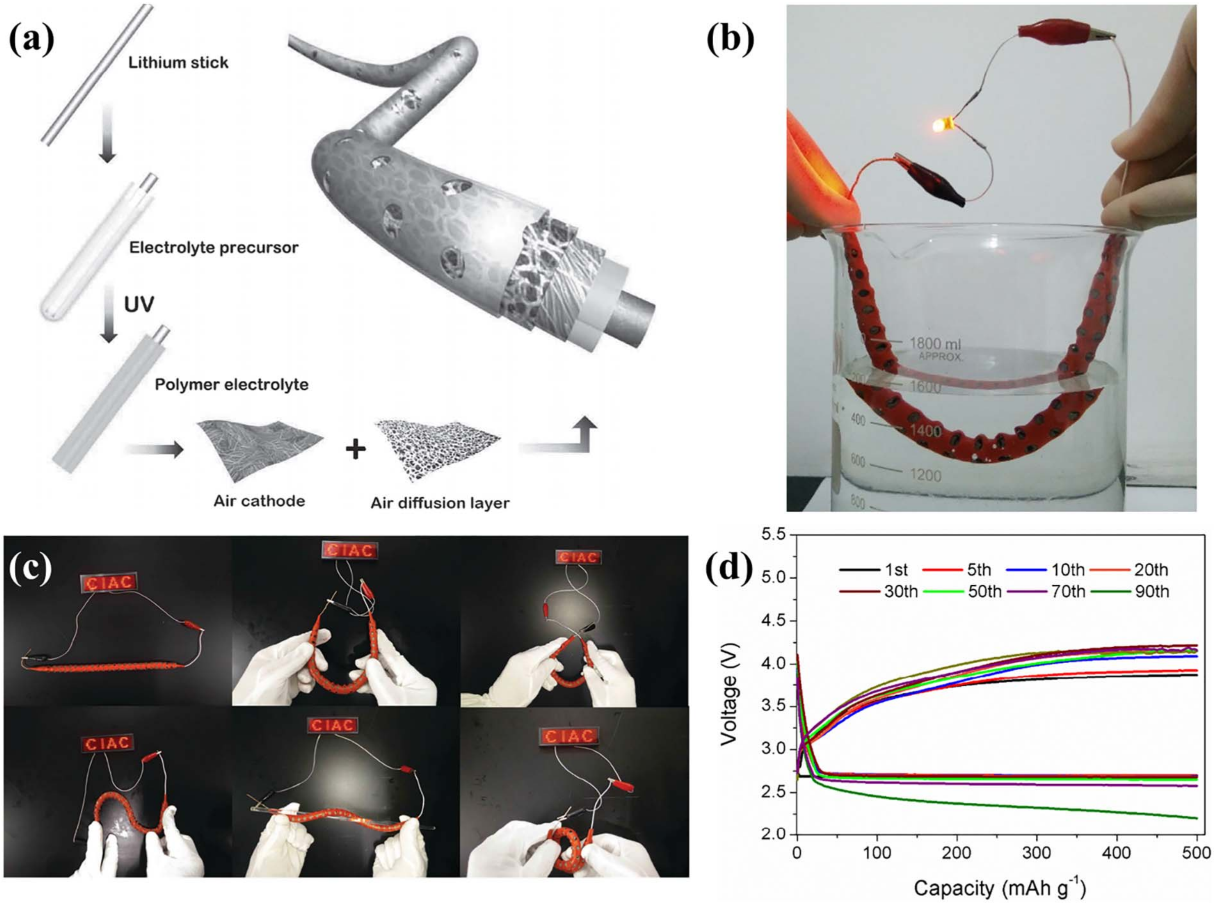

Fig. 5. (a) Schematic representation of a cable-type, water-survivable flexible Li-O_2 battery. (b) The flexible Li-O_2 battery powers a commercial red light-emitting diode immersed in water and under various bending and twisting conditions (c), and (d) charge-discharge curves of flexible Li-O_2 battery.
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ethoxylated trimethylolpropanetriacrylate (ETPTA) and PVDF-HFP, holds high mechanical flexibility, electrochemical stability and high ionic conductivity as well as superior hydrophobicity which provide the possibility of protecting lithium from the corrosion of moisture. The obtained novel cable-type flexible Li-O_2 battery exhibits superior electrochemical performances including high specific capacity, good rate capability, and cycling stability under stringently bended condition and even immersed in water [46].

As shown in Fig. 6, inspired by the unique structure of Chinese bamboo slips, we further developed a flexible/wearable Li-O_2 battery based on hydrophobic GPE (ETPTA/PVDF-HFP/liquid electrolyte). In contrast to the stack-type assembly manner, the cathodes and anodes were crisscross-woven (Fig. 6a), enabling them to press against each other and eliminate the need for other components to provide pressure to ensure the normal operation of the battery, inevitably improving the energy density (over 523 Wh kg^{-1}). Besides, the electrochemical performance characteristics of the flexible/wearable Li-O_2 battery were not influenced even in various bending and twisting conditions. The hydrophobic GPE also endows battery with water-survival properties, makes the battery could operate in a moist atmosphere (Fig. 6b) [47].

At the same time, Peng et al. developed all-solid-state Li-air batteries with a flexible fiber shape and high electrochemical performances by designing a PVDF-HFP-based GPE and an aligned carbon nanotube (CNT) sheet air electrode (Fig. 7). The gel polymer electrolyte prevented air diffusion to the lithium metal anode and alleviate its corrosion, and it endowed the battery exhibited a discharge capacity of 12,470 mAh g^{-1} and could stably work for 100 cycles in air. The fiber shape makes the Li-air battery flexible and weaveable, and the electrochemical properties were maintained under and after bending [48].

Moreover, for the first time, they have also designed a new flexible and stretchable Li-air battery by designing a rippled air electrode, a lithium array electrode and a GPE (PEO/PVDF-HFP). The developed battery exhibited high electrochemical properties and it was able to sustain thousands of repeated deformations without obvious decay in performance [49].

The above studies demonstrate that PVDF-HFP GPE can provide an alternative avenue for Li-air/O_2 batteries, and highlight the potential application of flexible Li-air batteries in flexible electronic devices.

4. The challenges of PVDF-HFP electrolyte

4.1. Interfacial stability

The interfacial stability toward lithium metal PVDF-based polymer electrolyte may be the most critical issue. In fact, owing to an interfacial reaction between lithium and fluorine which leads to the formation of LiF, the fluorinated polymers are not chemically stable toward lithium and PVDF-based electrolytes are unsuitable for batteries using lithium metal anodes [31]. However, some reports declared that the generated LiF containing film on Li anode could prevent the Li anode from corroding by electrolyte or/and dissolved O_2 [3,50].

4.2. Chemical stability

Differentiating from the lithium-ion battery charge and discharge mechanism, Li-O_2 battery in the cycle will generate a series of reactive discharge/charge products (Li_2O_2, LiO_2, LiOH, Li_2CO_3, O_2, etc.). Thus, the chemical stability of polymer electrolytes of course including PVDF-

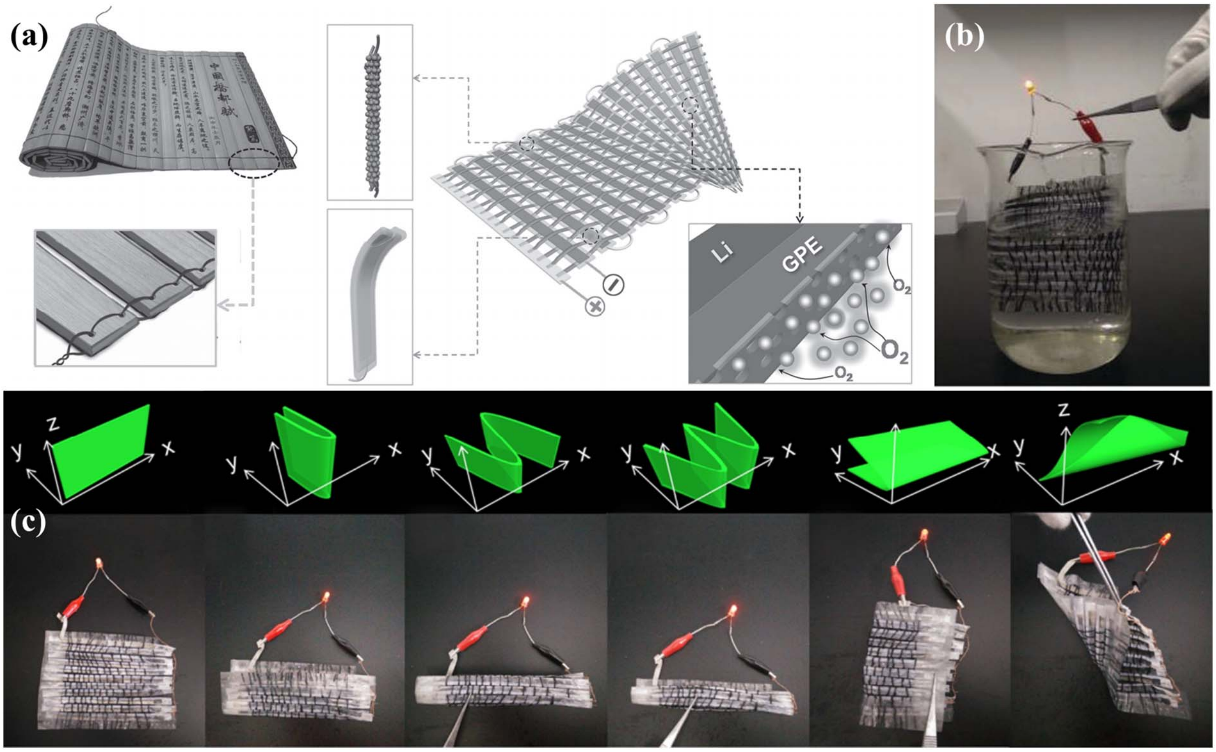

Fig. 6. (a) Inspired by the ancient bamboo slips, a flexible and wearable Li-O_2 battery was fabricated. (b) The flexible and wearable Li-O_2 battery powered a commercial red-light-emitting diode immersed in water. (c) Optical images of the fabricated flexible and wearable Li-O_2 battery powering a commercial red-light-emitting diode under various bending and twisting conditions.
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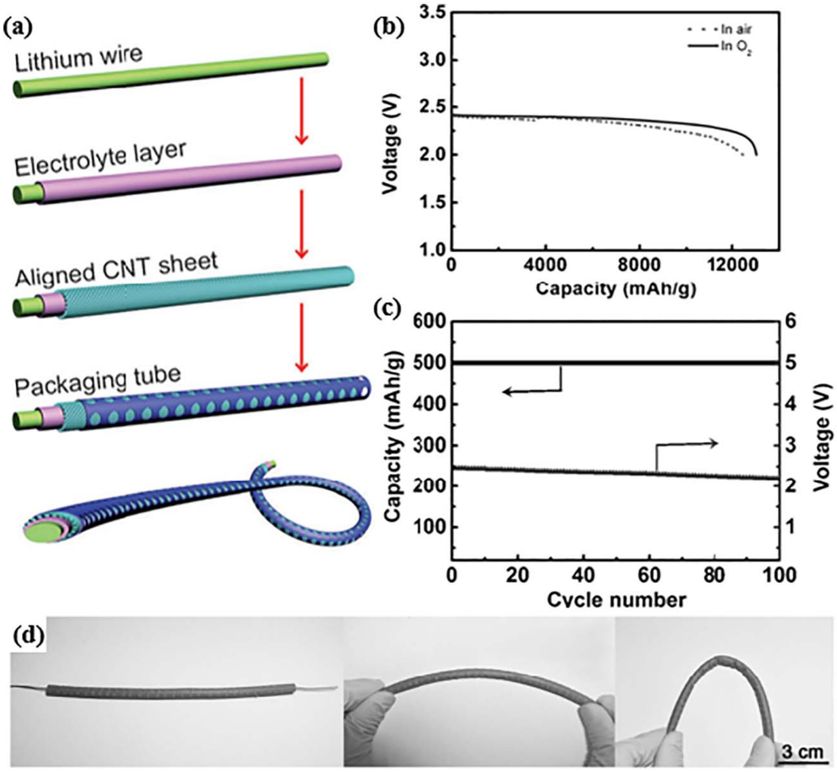

Fig. 7. (a) Schematic illustration of the fabrication of the fiber-shaped Li-air battery. (b) Galvanstatic discharge curves at current density of 1400 mAg^{-1}. (c) Cycling performance at current density of 1400 mAg^{-1} in air. (d) Photographs of fiber-shaped Li-air batteries under increasing bending angles. Reprinted with permission from Ref. [48]. Copyright 2016 Wiley.

HFP against the attack by above products is still questionable. For PVDF-HFP, the reactive component of it is presumed to be PVDF but not HFP, as HFP is fully fluorinated with no protons on the polymer backbone. The presence of the electron-withdrawing halogens and adjacent α and β hydrogen atoms that become electron-deficient due to hyperconjugation makes PVDF-HFP undergo dehydrohalogenation reactions with Li_2O_2 [51–53].

4.3. Electrochemical stability

Due to the main discharge product Li_2O_2 with intrinsic poor electronic conductivity, the large over-potentials often cause a charge potential higher than 4 V and the circumstantial decomposition of the electrolyte is a very large obstacle for the development of high efficiency Li-O_2 battery [24]. Hence, the electrochemical stability of the polymer electrolyte is one important area of concern in the long-life polymer electrolyte Li-O_2 battery. Typically, electrochemical stability is evaluated by several parameters, including the Li/polymer electrolyte interfacial resistance, the electrochemical window and the polymer electrolyte behaviour during cycling [33]. It is critical for electrolytes used in rechargeable lithium batteries to have a wide operating potential window to ensure minimal side reactions, especially for Li-O_2 battery. According to Wang et al., the TEGDME/PVDF-HFP electrolyte was found stable in the voltage range up to 4.6 V vs. Li/Li^+ while the liquid TEGDME electrolyte suffered from severe decomposition at a lower voltage. The as-prepared TEGDME/PVDF-HFP electrolyte showed better stability than the liquid TEGDME plasticizer electrolyte, demonstrating the potential qualification to be used as electrolytes in Li-O_2 battery [24].

4.4. Ionic conductivity

For GPE in Li-O_2 battery, high ionic conductivity is one of the most important prerequisites for maintaining a smooth transport of Li^+. The ionic conductivity of gel electrolytes can be increased by improving the pore structure to facilitate transport of lithium ion in the solvent. This can be accomplished by adding plasticizers, nanofillers, polymer blends, and so on [54–60]. An increase in ionic conductivity (4.2×10^{-4} S cm^{-1}) was observed after adding the polysiloxanecomb-propyl(triethylene oxide) (PSx-PEO_3) relative to compared with the corresponding pure PVDF-HFP system (7.1×10^{-5} S cm^{-1}) [61].

4.5. Mechanical strength

To realize practical use of a polymer electrolyte, the electrolyte must remain structurally stable during manufacturing, cell assembly, storage, usage, and be capable of preparation in an easy and repeatable manner. Wu et al. prepared electrospun TPU/PVDF blending membrane with 3% in situ TiO_2, and 9% solution of TPU/PVDF in DMF/acetone. It generally observed that electrochemical stability, ionic conductivity and mechanical properties are improved after the addition of ceramic fillers [62].

In a word, although PVDF-HFP still has some deficiencies at present, we quite believe it will be one of the most promising polymer electrolytes for Li-air batteries. And more research efforts are eager to satisfy following requirements for the further development of polymer electrolytes in Li-air batteries: (1) excellent chemical/electrochemical stability, the necessary prerequisite for the polymer electrolyte, avoiding the reaction of lithium metal anode, high reactive discharge intermediates (superoxide radical anion O_2^- and peroxide radical anion O_2^{2-}), CO_2 and H_2O, both of which derived from the electrolyte decomposition; (2) good interfacial contact, ensuring the transfer of Li^+ ion through the interface between polymer electrolytes and electrodes; (3) high ionic conductivity, maintaining a fast transport of Li^+ in the polymer electrolytes; (4) excellent mechanical strength, facilitating processing and avoiding damage from the battery assembly and cyclic process; (5) other functional properties, such as hydrophobicity, heat resistance, enlarging the applicable area of Li-O_2 battery.

5. Conclusions

The organic liquid electrolytes are the main hindrance for the practical application of Li-O_2 batteries, thus developing Li-O_2 batteries with polymer electrolyte might be a promising solution. As one of the most important matrices for polymer electrolyte, PVDF-HFP has been extensively studied in lithium batteries due to its high solubility, lower crystallinity, good electrochemical and mechanical properties, and it has been successfully applied to Li-O_2 battery. Due to the exclusive open system and the special discharge/charge products of Li-O_2 batteries which are different from the lithium-ion battery, PVDF-HFP used in Li-O_2 battery confronts a more sophisticated challenge. Practical applications of Li-O_2 battery with PVDF-HFP are currently limited by the interfacial stability, chemical stability, electrochemical stability, ionic conductivity, mechanical strength and so on. Although some progress has been obtained, there are still some fundamental issues on PVDF-HFP and other polymer electrolyte needed to be addressed. And some optimization of PVDF-HFP polymer electrolyte may be procured by incorporation with different lithium salt, blend/crosslink with other polymer, combination with ionic liquids, adding plasticizers/ceramic/functional nanofillers, and so on [33]. More research efforts are still required to promote the understanding and expedite development of polymer electrolytes for Li-O_2 batteries and thus accelerate Li-O_2 battery applications.

Acknowledgments

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