Recent advances in lithium-air batteries

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Abstract

Lithium (Li)-ion batteries will play a key role in the electrification of transport, including electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs). However, the present energy storage of Li-ion batteries cannot meet the requirements of transportation in terms of driving range and safety. As a kind of potential alternative energy storage devices, rechargeable Li-air batteries have become one of the most attractive candidates for energy storage and EVs. Li-air batteries can provide several times higher energy density/specific energy of the existing battery systems. In this paper, we mainly focus on the research status, especially some progresses made in our lab, existing challenges and their solutions as well as perspective on the future directions on lithium-air batteries. Copyright © 2018 VBRI Press.

Keywords: Lithium-air battery, air cathode, electrolyte, reaction mechanisms.

Introduction

Energy is the indispernsible component of modern society. The development of novel energy storage and conversion system is highly desired for effective utilization of renewable energy sources in future smart grids and power delivery systems [1-3]. Batteries represent the most popular electrochemical storage devices so far. Among various batteries, Li-ion batteries (LIBs) are promising energy storage devices due to their merits of high energy density, high voltage and excellent cyclability. Li-ion batteries have play a dominant role in the portable electronic market and the electric vehicles (EVs) market. However, LIBs powered EVs are limited to a driving range of 160 km on a single charge and the high cost, as well as more than half of the total cost of cars.

Li-Air batteries are the most promising candidate to power EVs since it can provide 5-10 times greater energy density than the current LIBs [4-14]. The theoretical specific energy density of a Li-air battery is 5200 Wh kg^{-1} if the mass of lithium anode and the oxygen (O_2) gained during discharge are calculated. The practical energy density can reach 1700 Wh kg^{-1} [4]. Figure 1 shows a comparision of the gravimetric energy densities (Wh/kg) of various types of rechargeable batteries with gasoline. Several scientific and technical obstacles remain to be circumvented before commercial applications can be achieved, such as the incomplete decomposition of the discharge products, an inadequate understanding of the catalytic effects, the higher charge over potential compared with the discharge one, the decomposition of carbonate-based electrolytes during discharge and the formation of alkyl carbonates [9].

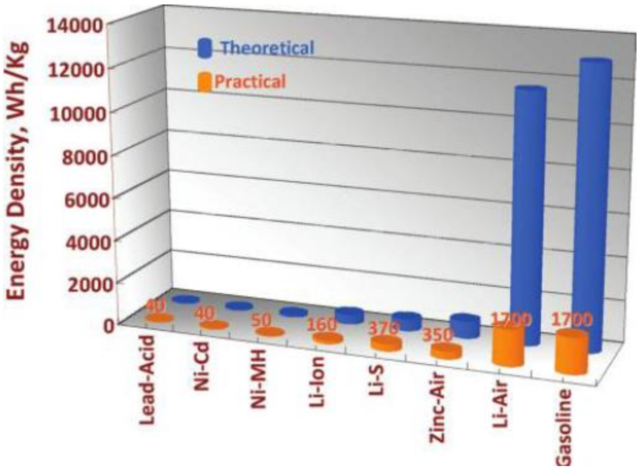

Fig. 1. The gravimetric energy densities (Wh/kg) for various types of rechargeable batteries compared to gasoline. The theoretical density is based strictly on thermodynamics and is shown as the blue bars and numerical values. For Li-air, the practical value is just an estimate. For gasoline, the practical value includes the average tank-to-wheel efficiency of cars [4]. (Reprinted from Ref. 4 with permission from American Chemical Society.)

Configuration and reaction mechanism

The concept of a Li-air battery with an organic electrolyte was introduced in 1996 by Abraham and Jiang [15]. There are four types of Li-air batteries based on the species of electrolyte used: (I) aprotic electrolyte type, (II) aqueous electrolyte type, (III) hybrid electrolytes type, and (IV) Solid-state electrolyte type. Li metal is used in all the four types of Li-air batteries as the anode and O_2 gas is adopted as the cathode. The air electrode in these cells consists of a carbon matrix with a catalyst, serving as the host structure for the reversible formation of Li_2O_2. **Fig. 2** shows schematic cell configurations for the Li-air batteries with aprotic electrolyte and aqueous electrolyte [10].

The involved reaction mechanisms are as follows. At the anode, on discharge, the Li-metal anode is oxidized, releasing Li^+ ions into the electrolyte, while on charge this process is reversed. At the cathode, O_2 from the atmosphere enters the porous cathode, dissolves in the electrolyte within the pores and is reduced at the electrode surface on discharge. When a suitable non-aqueous electrolyte is employed, O_2^{2-} is formed, and reacts with the Li^+ ions from the electrolyte to form Li_2O_2 as the final discharge product. On charge, the peroxide is then decomposed: $2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$. If Li_2O is formed, which would increase the energy stored (twice the Li per O), but may be difficult to reverse on charging [10]. In the case of the cell with anqueous electrolytes, on discharge, the formation of OH^- and then LiOH at the cathode occurs: $2Li^+ + 1/2O_2 + H_2O + e^- = 2LiOH$, while LiOH is oxidized on charge. Since H_2O and O_2 are involved, it is also called a Li-water battery.

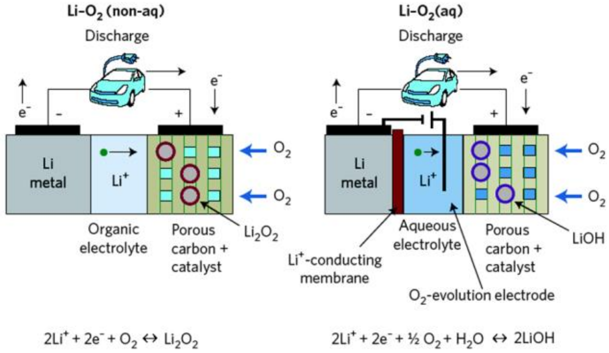

Fig. 2. Schematic cell configurations for the Li-air batteries with aprotic electrolyte and aqueous electrolyte [10]. (Reprinted from Ref. 10 with permission from Nature Publishing Group.)

Challenges of Li-air batteries

The performance of Li-air batteries are influenced by various factors, for example, relative humidity [**16**], oxygen pressure [**17**], catalysts [**18**], electrolyte components [**19**], structures of air electrodes [**20,21**], micro/nanostructure of carbon [**22**], and the design of cells [**16,23**]. We will introduce the challenges of air cathode, electrolyte and metal lithium anode, respectively.

The challenge of air cathode

The performance of Li-air cells is mainly dominant by the air cathode since most of the cell voltage drop is originated from the air cathode [5]. Until now, the performance of non-aqueous Li-air cell is below the theoretical value [5], due to the precipitate blocking the pore in the cathode. Therefore, it is critical to design an optimized air electrode consisting of micrometer-sized open porosity for rapid oxygen diffusion and substantial nanoporosity (2-50 nm) to catalyze $Li-O_2$ reactions while excessive growth of the discharge products is inhibited [**24**]. More challenging is the Li-air batteries require an inexpensive, stable bifunctional catalyst not only for the ORR, but also for the reverse oxygen-evolution reaction (OER). Moreover, the asymmetry of the ORR and OER introduces different discharge and charge voltages, which lower the efficiency of electrical-energy storage in a Li-air cell, and the rates of charge and discharge depend on the catalytic activities of the ORR and OER [42].

The cathode catalysts normally used to catalyze the air reactions are carbon black or carbon loaded with a noble metal. Shao-Horn et al. [**26**] have used Pt-Au nanoparticles as a bifunctional catalyst to reduce the voltage gap between the ORR and OER to less than 0.8 eV at 50 mAh g^{-1} by using Au to enhance the ORR and Pt to lower the OER voltages, as shown in **Fig. 3**. Ishihara et al. [**27**] reported that Pd/mesoporous α-MnO_2 electrode is highly active as an air electrode for Li-air batteries with lower charge potential, improved energy efficiency（~80%）and cycling performance. However, sluggish kinetics of ORR and OER, poor rate performance, and short cyclic life, as well as limited resource of noble metals remain to be circumvented before practical applications can be achieved.

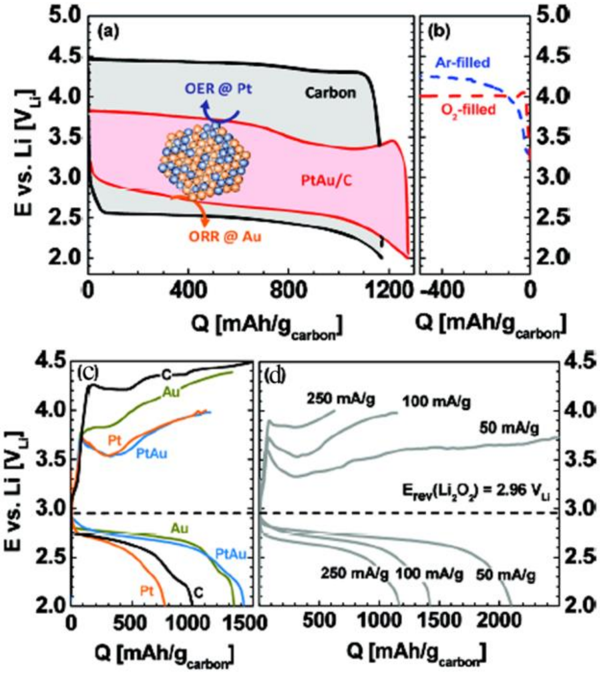

Fig. 3. (a) $Li-O_2$ cell discharge/charge profiles of carbon (black, 85 mA/g_{carbon}) and PtAu/C (red, 100 mA/g_{carbon}), (b) Background measurement during charging at 100 mA/g_{carbon} of Ar- and O_2-filled cells (Charging first) for PtAu/C catalyst, (c) $Li-O_2$ cell discharge/charge profiles of carbon at 85 mA/g_{carbon} and of Au/C, Pt/C, and PtAu/C at 100 mA/g_{carbon}, (d) $Li-O_2$ cell discharge/charge profiles (first cycle) of PtAu/C at 50, 100, and 250 mA/g_{carbon}. (Reprinted from Ref. 26 with permission from American Chemical Society)

Transition-metal oxides have less cost as alternative catalysts. The oxoperovskite cobaltates have been extensively studied as cathodes in solid oxide fuel cells operating in the temperature range 500-800°C [**28**]. Shao-Horn et al. [**29,30**] have shown that transition-metal oxoperovskites containing surface cations with an

e_g^1 electron configuration and good bulk electronic conductivity give a fast ORR and OER in alkaline solution. Sun et al. found that perovskite $Sr_{0.95}Ce_{0.05}CoO_{3-\delta}$ (SSCO) loaded with Cu nanoparticles are shown to be excellent, low-cost and stable bifunctional catalysts for the oxygen-reduction and oxygen-evolution reactions in aqueous solution. The performance of the SSCO-based catalysts is better at higher current rates (>0.1 mA cm^{-2}) than that of Vulcan XC-72 and even close to that of the 50wt%Pt/C catalyst, as shown in **Fig. 4** [**31**].

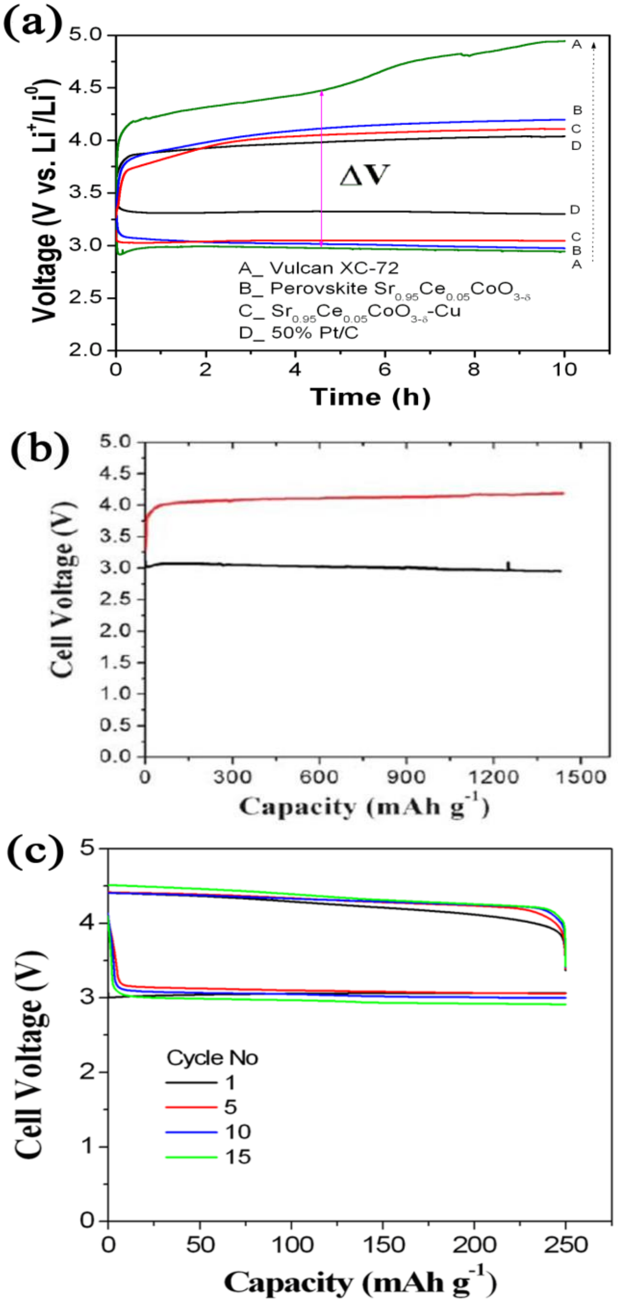

Fig. 4. (a) The first discharge-charge curves of the prepared lithium-air batteries with different catalysts, (b) Voltage versus discharge-charge capacity for the lithium-air, (c) The discharge-charge curves of the prepared lithium-air batteries with the SCCO-Cu catalyst at a current density of 0.2 mA cm^{-2} at different cycles [31]. (Reprinted from Ref. 31 with permission from Royal Society of Chemistry).

Considering the high conductivity, excellent mechanical properties as well as good anti-corrosion properties of graphene, highly active and stable graphene (G)-Co_3O_4 nanocomposite electrocatalysts were synthesized via a facile hydrothermal route and subsequent thermal treatment process by Sun *et al*. [**32**]. Low-magnification SEM and TEM images show that Co_3O_4 and Co nanoparticles are well dispersed on the surface of the graphene sheets. **Fig. 5b** and **5c** show annular dark-field (ADF) scanning transmission electron microscopy (STEM) images of the as-prepared graphene-Co_3O_4 prepared under Ar and H_2-Ar atmosphere, respectively. The Co_3O_4 particles have a diameter of about 200 nm and consist of many smaller NPs, forming a porous structure as shown in **Fig. 5c**. The ORR and OER properties of G-Co_3O_4 nanocomposite are systematically studied. The G-Co_3O_4 nanocomposite catalyst shows an excellent catalytic activity toward ORR including a much more positive half-wave potential (-0.23V) than the pristine graphene (-0.39V) as well as higher cathodic currents. Importantly, this catalyst shows a better long-term durability than the commercial Pt/C catalyst in an alkaline solution. These results indicate that the graphene-Co_3O_4 nanocomposite is an efficient and stable bifunctional catalyst for a Li-air battery, as shown in **Fig. 5e-g.**

Xiao and co-works adopted colloidal microemulsion to fabricate hierarchically porous 3D graphene cathode with interconnected pore channels at both the micro and nanometer scales [24]. The SEM images indicate the presence of porous architectures (**Fig. 6a and b**). It suggests that lattice defects on functionalized graphene play a critical role through hosting the small, nanometer-sized discharge products (Li_2O_2) (**Fig. 7c and d**), which is also observed by DFT modeling (**Fig. 6e and f**). The combination of hierarchical pore structure and graphene surface defects produces an exceptionally high capacity of ≈15 000 mAh g^{-1} at the first discharge cycle (**Fig. 6g**). The challenge is to obtain a high density porous graphene material for an improved volumetric capacity and also to make the system rechargeable.

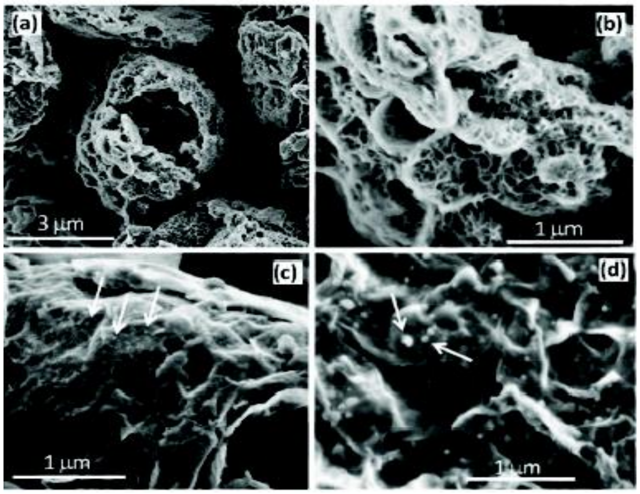

Fig. 6. (a) SEM image of egg shell structured FGS with large pores, (b) SEM image of the nanopores in FGS, (c) Small Li_2O_2 nanoparticles produced on FGS with C/O=14. (d) Large Li_2O_2 nanoparticles of FGS with C/O=100.

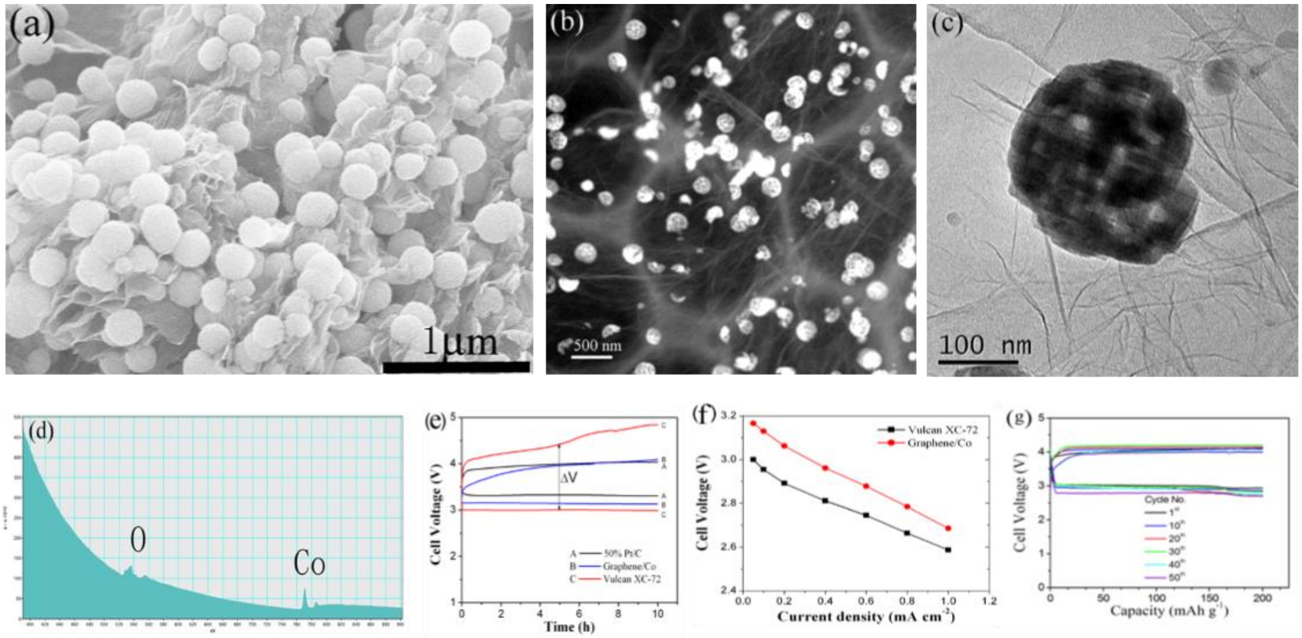

Fig. 5. (a) SEM, (b) ADF-STEM, and (c) TEM images of the as-prepared graphene-Co_3O_4 prepared under Ar atmosphere, (d) The corresponding EELS analysis taken at the nanoparticle, (e) Comparison of the first charge and discharge curves of the prepared Li-air batteries with various catalysts at a current density of 80 mA g^{-1}, (f) comparison of discharge voltage as a function of current densities at different current densities between Vulcan XC-72 and the graphene-Co_3O_4 catalyst, (g) the discharge-charge curves of the prepared Li-air batteries with the graphene-Co_3O_4 catalyst at a current density of 160 mA g^{-1} at different cycles. Catalyst loading was 1.25 mg [32]. (Reprinted from Ref. 32 with permission from Royal Society of Chemistry)

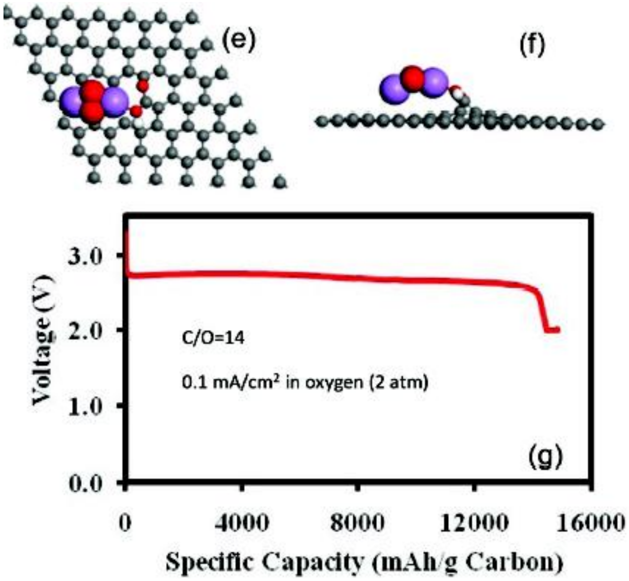

Fig. 6. (e,f) Top and side views of optimized Li_2O_2 on the 5-8-5 defect graphene with COOH functional groups. (g) Discharge curve for Li-air battery using FGS (C/O=14). (Reprinted from Ref. 24 with permission from American Chemical Society)

Recently, Zhang et al. [**33**] prepared perovskite $La_{0.75}Sr_{0.25}MnO_3$ nanotubes（PNT-LSM）by an electrospinning technique combined with a wet impregnation method. As a catalyst for Li-O_2 batteries, it significantly suppresses the ORR and especially OER overpotentials and thus improves the round-trip efficiency with a high specific capacity, superior rate capability, and good cyclability.

The challenge of electrolytes

The commonly used aprotic electrolytes include organic carbonates (ethylene carbonate, propylene carbonate, dimethyl carbonate), ethers (tetrahydrofuran (THF), dioxolane), and esters (γ-butyrolactone), which solvate lithium salts, such as $LiPF_6$, $LiAsF_6$, $LiN(SO_2CF_3)_2$, and $LiSO_3CF_3$ [**4,34**].

Read *et al.* [**35,36**] studied oxygen solubility in common electrolytes and the relationship between the oxygen transport properties and the performance of Li-O_2 batteries. Kuboki *et al.*[**37**]studied the performance of Li-O_2 batteries with ionic liquid electrolyte in ambient environment. Xu *et al.* [**38**] investigated the effect of various properties of organic electrolyte on the performance of Li-O_2 batteries and found that the polarity of electrolyte is the most important factor. One of important challenge for Li-air batteries is enhancing the reaction kinetics, especially for the charging process. Differential electrochemical mass spectrometry (DEMS) was also used by Barile *et al.* to characterize the Li-O_2 battery in an electrolyte containing tetraethylene glycol dimethyl ether (TEGDME) and lithium triflate (LiOTf) [**39**]. Au nanoparticles increase the amount of O_2 evolved during charge and improve the cycleability of the cell while Pt, Pd, and Cu (II) oxide catalysts are detrimental to cell performance because they can catalyze solvent or carbon cathode decomposition as evidenced by CO_2 evolution. Regardless of the catalyst employed, the amount of O_2 measured upon charge is much less than that expected for complete Li_2O_2 formation and decomposition, which is consistent with the rapidly fading capacity observed during battery cycling. Thus, TEGDME is not a suitable solvent for a reversible Li-O_2 battery.

As for a hybrid electrolyute Li-air battery system, or called Li-water battery, a solid-state electrolyte pellet is needed. The power density of the batteries is normally limited by the relatively poor conductivity of the solid electrolyte, 1.0×10^{-4} S cm^{-1}. In recent years, many efforts have been devoted to improve the lithium ionic conductivity of the solid electrolytes. Aono *et al.* [**40**] reported that the maximum ionic conductivity of the $Li_{1.3}M_{0.3}Ti_{1.7}(PO_4)_3$ (M=Al or Sc) is 7.0×10^{-4} S cm^{-1}at room temperature. Thokchom *et al.* reported that the highest total conductivity of the LAGP glass-ceramic material reaches 5.0×10^{-3} S cm^{-1} at 27 ^{o}C [**41**]. Moreover, the stable electrolyte materials both in acidic and in alkaline solutions are also highly disired [**42**].

Elemental substitution is usually used to increase conductivity of electrolyte materials [**43**]. By incorporating phosphorus and germanium into Li_3PS_4 crystal, Kanno *et al.* prepared a $Li_{3.25}P_{0.75}Ge_{0.25}S_4$ crystal with a high conductivity of 2.2×10^{-3} S cm^{-1} at room temperature. $Li_{10}GeP_2S_{12}$ with a new three-dimensional framework structure shows an extremely high lithium ionic conductivity of 12 mS cm^{-1} at room temperature [**44**]. **Fig. 7** shows the thermal evolution of the ionic conductivity of the new $Li_{10}GeP_2S_{12}$ phase compared with other electrolytes used in practical batteries. This solid-state electrolyte have many advantages in term of fabrication, safety and electrochemical properties.

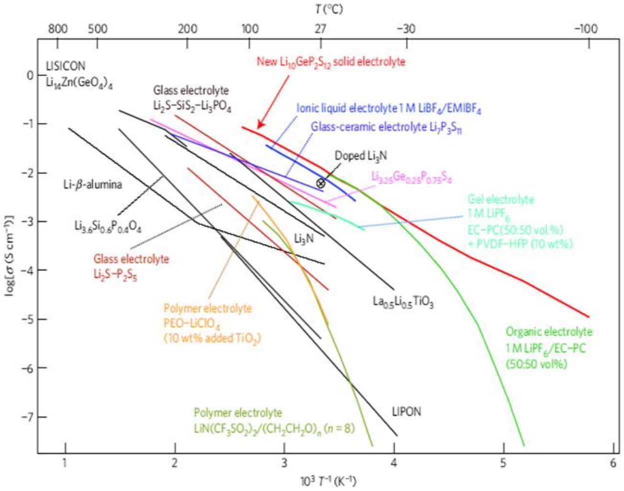

Fig. 7. Ionic conductivity of $Li_{10}GeP_2S_{12}$ phase in comparison with other kinds of electrolytes. (Reprinted from ref. 44 with permission from Nature Publishing Group)

Fig. 8 shows the crystal structure of $Li_{10}GeP_2S_{12}$. The framework is composed of $(Ge_{0.5}P_{0.5})S_4$ terahedra and LiS_6 octahedra, which are connected to LiS_6 octahedra by a common corner **(Fig. 8b).** LiS_4 tetrahedra at the 16*h* and 8*f* sites share a common edge, forming a 1D conducting pathway along the *c* axis.

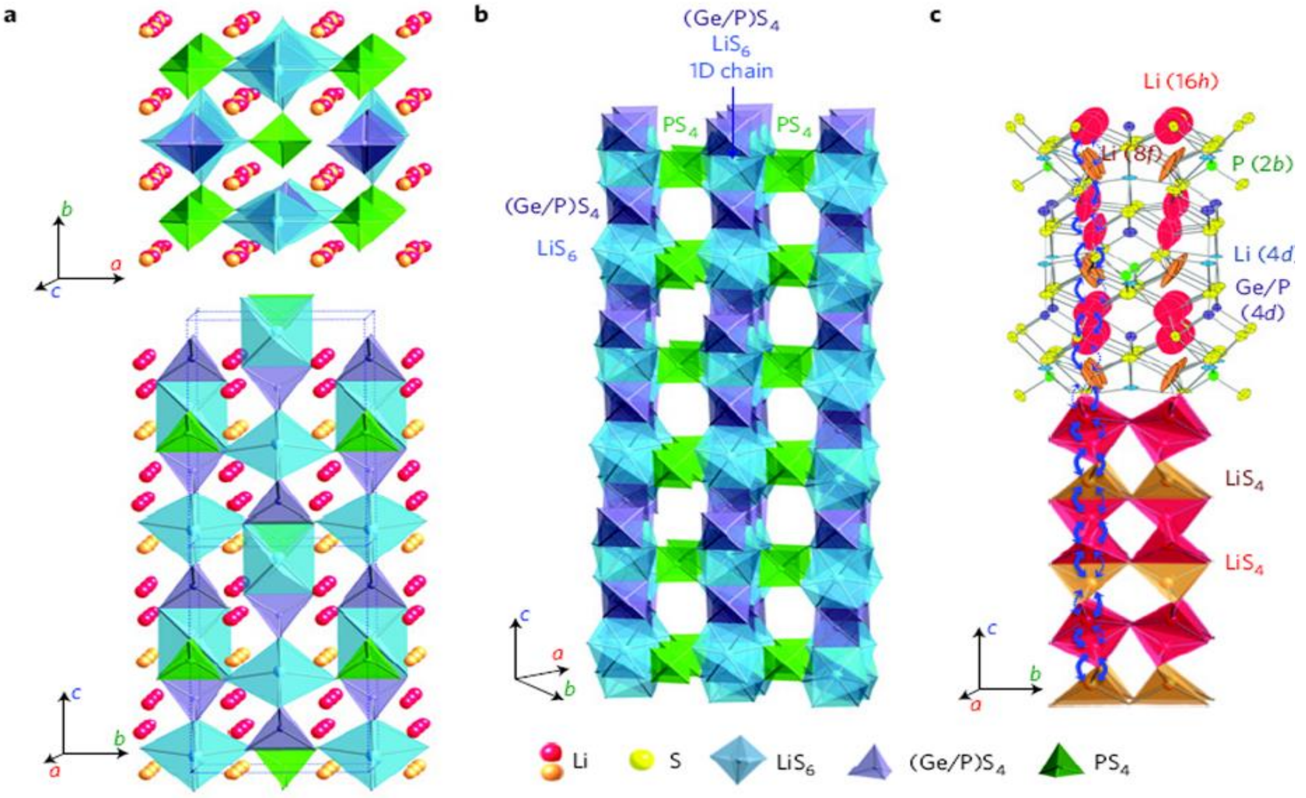

Fig. 8. Crystal structure of $Li_{10}GeP_2S_{12}$. (a) Framework structure and lithium ions that participate in ionic conduction; (b) Framework structure of $Li_{10}GeP_2S_{12}$; (c) Conduction pathways of lithium ions. (Reprinted from ref. 44 with permission from Nature Publishing Group).

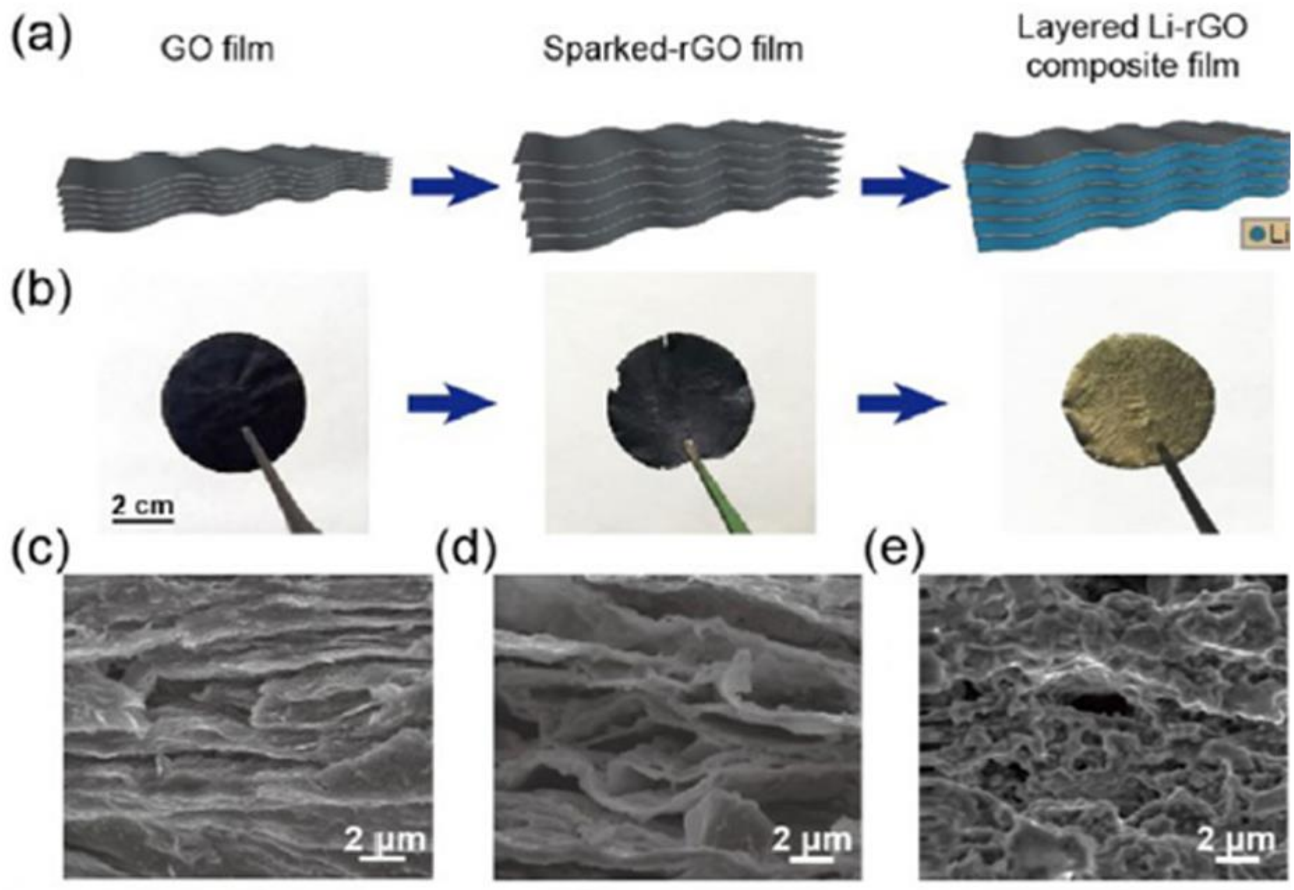

Fig. 9. (a) Schematic of the fabrication process for the layered Li-rGO composite electrode, (b) Corresponding digital camera images, and (c-e) Cross-sectional SEM images of the layered Li-rGO electrode (c) before and (d) after Li stripping, and (e) after one stripping/plating cycle [47]. (Reproduced with the permission from the Copyright Nature Publishing Group 2016).

The challenge of metal lithium anode

Lithium metal anodes are considered as the best choice for Li-air cells due to their extremely high energy density compared to the common lithium-intercalated carbon anodes but high capacity may be disaccounted if heavy intercalation anodes are used. The disadvantage of lithium metal anodes is dendrite formation and the resultant shorts between the anode and cathode, which may influence the cycle life and safety of rechargeable batteries with Li-metal anodes. Brandt [45] had well reviewed these issues. Other strategy is fabricating interfacial or protective layers coated on the metallic lithium to separate a lithium anode from the liquid electrolyte, which are comprised of polymers, ceramics, or glasses conducting lithium ions. Other strategy is applying solid polymer electrolyte or solid ceramic electrolyte materials being inert to lithium metal instead of liquid electrolyte [**43**], which are Li-ion conductors and can prevent dendrites formation.

The challenges associated with Li metal anodes are the high reactivity and the large volume change during cycling. Although various approaches have been suggested to stabilize the Li-electrolyte interface, the importance of keep stable Li anode dimensions has not been paied attention. Large volume change leads to mechanical instability in fragile SEI layers, resulting in continuous side reactions and uneven Li deposition. Moreover, changed electrode-separator interfaces can damage cells, creating potential safety hazards and tremendous engineering challenge for implementing batteries in confined spaces [**46**].

Recently, Cui *et al* used stable nanoscale scaffolds host materials to pre-storing Li via molten Li infusion to decrease anodic volume change during cycling. Reduced graphene oxide (rGO) has a unique molten Li wettability, or lithiophilicity [**46,47**]. When contacting molten Li, densely stacked GO film can be rapidly reduced via a "spark reaction", simultaneously creating nanogaps between the rGO layers. Fast and uniform Li infusion can be accomplished in the subsequent step by placing the edge of the rGO film in molten Li, due to the synergetic effects of the lithiophilic nature of sparked rGO and the capillary force of the nano-gaps, as shown in **Fig. 9a** and **b**.

To prevent the reactivity of LISICON toward metal lithium, a common approach is utilizing an interlayer between the LISICON membrane and the anode. The interlayer material should be stable and have an adequate high Li^+-bulk conductivity without any barrier for Li-ion transport. Several steps of materials were proposed to mediate a contact between LISICON and lithium metal, such as common Li-compatible non-aqueous battery electrolytes [**48,49**] and SPE [50-54]. Materials such as lithium phosphorous nitride (LiPON), Li_3N, Li_3P, LiI, LiBr, LiCl and LiF were also used to mediate interlayer interface as well [**55**].

It is noted that IBM has been carried out a "Battery 500" project [**56**], which is aming at developing a lithium-air battery with a 500-Mile Range for Electric Cars. The huge jump in energy density could effectively multiply electric vehicle's range from 100 miles to 500 miles. It is expected that a commercial battery can be achieved by 2020. In China, several National Key R&D Programs on Li-air batteries have also been initiated.

Conclusions and perspective

Li-air batteries with ultrahigh energy density can be used in various applications from portable electronics to electric vehicles. Currently, Li-air batteries are still in their early development stage. Critical factors that influence the performance of Li-air batteries include electrolytes, air cathodes (electrode architecture and electrocatalysts) and lithium metal anodes, as well as oxygen-selective penetrating membranes. Although important progress has been made by many authors, great challenges remain as follows.

(1) Understanding of the electrochemical reactions and their correlation to the discharge/charge currents is beneficial to improve the chemical reversibility and Coulombic efficiency of the battery during cycling. It is critical to develop stable catalysts operating at high potential and in O_2 atmosphere to make it feasible to reversibley oxidize lithium. Undernsting elementary reactions and optimizing the design of air catalysts can be achieved by means of density functional theory (DFT) calculations [57,58].

(2) Air cathodes with hierarchical structures may allow transport of adequate oxygen and Li-ion to the active and electron-conducting surfaces, and provide enough room to accommondate solid reaction products. Moreover, the porosity of the air cathode can affect its electrochemical performance. Thus, increasing the cathode porosity is benifical for oxygen transport, thus leading to improved ORR kinetics.

(3) The polarity, viscosity, oxygen solubility and tolerance to oxidation are important factors that can affect the electrochemical performance. Electrolyte systems with high oxygen transport ability and low volatility are highly needed. Adequate barrier layers consisting of several layers for oxygen, moisture and CO_2 diffusion toward the battery anode are required as well.

(4) The dendrite and the low cycling efficiency of lithium metal anodes are the two main obstacles for the practical applications. Approaches to forming stable SEI film on the metal lithium are highly desired, e.g., some electrolyte additives. Development of a robust lithium metal or lithium composite electrode is important for repeated cycling at higher current densities.

(5) Oxygen selective membranes for oxygen supply are important for rechargeable Li-air. Impurities in ambient air such as moisture and CO_2 are detrimental to Li metal anodes. It is urgent to develop a protective layer that limits the deleterious effects of environmental contamination on the lithium and inhibits dendrite growth.

(6) Development of flow-type Li-air batteries may be feasible for storing lithium oxide products outside the battery. This configuration can greatly increase the energy density of the Li-air batteries.

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