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Integrated solid electrolyte with porous cathode by facilely one-step sintering for an all-solid-state Li–O₂ battery

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Abstract

All-solid-state Li–O₂ batteries are receiving intense interest because of the substitution of solid electrolytes for toxic and flammable liquid electrolytes. However, new issues are arising in the aspect of the electrolyte cathode interface. On the one hand, in a traditional sandwiched battery structure, the reaction sites of the cathode are restricted to the finite planar electrode–electrolyte interface, resulting in limited performance of all-solid-state Li–O₂ batteries. On the other hand, integrating the electrolyte with the cathode to achieve good interfacial contact often requires complex sintering processes. Herein, this work reports a solid electrolyte cathode assembly (SECA) which consists of a dense Li_{1.5}Al_{0.5}Ge_{1.5}P₃O₁₂ (LAGP) layer and a carbon coated porous LAGP layer fabricated by facilely one-step sintering. As a result, Li–O₂ batteries adopting the SECA showed a relatively high discharge capacity of 0.48 mAh cm⁻² at $5 \,\mu\text{A cm}^{-2}$. It was found that the high capacity can be attributed to the high surface area of porous cathode structure.

Keywords: solid electrolyte cathode assembly, solid-state electrolyte, $Li-O_2$ battery, cathode catalyst, Li metal anode, porous cathode

(Some figures may appear in colour only in the online journal)

Introduction

Li– O_2 batteries have received widespread interest due to the high theoretical specific energy [1]. However, traditional Li– O_2 batteries are operated with liquid electrolytes that are toxic, flammable, and chemically and electrochemically unstable [2]. Moreover, the Li metal anode suffers from corrosion caused by humidity transporting through the electrolytes from the air cathode [3]. A promising approach to overcome these problems is the substitution of solid-state electrolytes for liquid electrolytes and developing all-solidstate Li–O₂ batteries (ASSLBs) [4]. Solid-state electrolytes can not only operate in a wide thermal and electrochemical range but also possess excellent densification to block O₂, H₂O or CO₂. State-of-the-art solid electrolytes include polymer electrolytes [5] and inorganic electrolytes [6]. Typical polymer electrolytes are composed of Li salt and polymer backbone, such as poly-(ethylene oxide) [7], poly-acrylonitrile [8], poly(vinylidene fluoride-*co*-hexafluoropropylene) [9], etc. These electrolytes are flexible and show relatively

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low Li⁺ conductivity $(10^{-7} \sim 10^{-6} \text{ S cm}^{-1})$ without plasticizers. Comparatively, inorganic electrolytes are rigid and can be divided to various types, including Na⁺ superionic conductor (NASICON), sulfide, garnet, perovskite and lithium phosphorous oxynitride (LiPON) [10]. Among these electrolytes, NASICON, sulfide and garnet electrolytes have applicable ionic conductivity for large-scale ASSLBs. Besides, NASICON-type electrolytes are highly stable in ambient air compared with sulfide and garnet-type electrolytes [10], indicating that they can be more easily synthesized and are more suitable for Li-air batteries. One of the typical NASICON-type electrolytes, Li_{1.5}Al_{0.5}Ge_{1.5}P₃O₁₂ (LAGP), has a moderate ionic conductivity exceeding 10⁻⁴ S cm⁻¹ and electrochemical stability up to 6 V, enabling its application in Li-air batteries [11–13].

Despite outstanding intrinsic properties of LAGP, issues remaining in the cathode-electrolyte interface still need to be addressed. For the cathode of an ASSLB, the electrochemical reaction takes place at a triple-phase boundary of O2, electronic conductor and ionic conductor. LAGP combined with carbon materials forms a 3D conducting network of ions, electrons and O₂ molecules. However, the rigid contact between LAGP and carbon particles introduces a large interfacial impedance. Many efforts have been devoted to address the challenges above. Zhou and co-workers [4, 12] sintered the mixture of active materials and LAGP onto one side of the LAGP electrolyte as a cathode and achieved improved interfacial contact. Zhang et al [13] mixed ionic liquid with carbon nanotubes (CNTs), instead of LAGP, and printed the mixture onto a LAGP pellet, leading to improved interfacial contact and ionic conductivity without high-temperature sintering. Nevertheless, unlike liquid electrolytes that can emerge into the cathode, there will be less passageways for continuous Li⁺ transportation among LAGP particles in the case of a LAGP-contained cathode sintered onto a LAGP pellet. Additionally, low porosity of the air cathode after high-temperature sintering is unfavorable for O₂ diffusion and products accumulation, which can be optimized by adopting 3D porous cathode with interconnected pores [14–16]. Moreover, the 3D porous cathode with a high surface area can conduct both electrons and ions, which facilitates high capacity [17, 18]. So, it is necessary to design a solid electrolyte cathode assembly (denoted as SECA) with integrated 3D porous cathode and solid electrolyte.

Herein, an ASSLB composed of a Li metal anode and a SECA was fabricated (figure 1(a)). The SECA pellet consisting of a porous LAGP layer and a dense LAGP layer was synthesized from a facile one-step sintering process. The pores of the porous LAGP layer have a diameter of several micrometers. The channels in the porous LAGP layer interconnect with each other. This assembly contributed to a low interfacial resistance and reversible discharge–charge of ASSLBs in pure oxygen. Furthermore, the solid and gaseous products were characterized by Raman spectrum and mass spectrum, respectively.

Experimental section

Synthesis of LAGP powder

LAGP powder was synthesized through a traditional solidstate reaction. The stoichiometric raw materials Li_2CO_3 (10% excess) (99%, Alfa Aesar), Al_2O_3 (AR, Nanjing Chemical Reagent Co., P. R. China), $NH_4H_2PO_4$ (99%, Aladdin), and GeO₂ (99.999%, Sinopharm Chemical Reagent Beijing Co., P. R. China) were ball-milled (Pulverisette 6, Fritsch) with a ball-to-powder weight ratio of 4/1 at a speed rate of 400 rpm. And then the well-mixed powder was calcined at 600 °C for 1 hour and then 900 °C for 6 hours with a heating rate of 2 °C min⁻¹. Ball milling was repeated after every calcination.

Facilely-sintered SECA pellet

LAGP powder and starch were grounded in an agate mortar with a weight ratio of 1/1, and then the mixed powder (porous layer) and LAGP powder (dense layer) were spread out in a die of a 19 mm diameter layer by layer with a weight ratio of 3/2, followed by pressing under a pressure of 30 MPa for 5 min. Lastly, the pressed pellet was sintered to 900 °C with a heating rate of $2 \,^{\circ}C \,^{-1}$ and kept for 1 hour in ambient air. The same pressing procedure was performed for LAGP powder to obtain dense LAGP pellets with a heat preservation time of 6 hours.

Carbon coating on porous LAGP layer

10 wt% aqueous solution of sucrose was dropwise injected into the porous side of the SECA, firstly 80 μ l in total and then 70 μ l, with heating at 80 °C to evaporate water during the whole process. At last, the dried pellets were transferred into a tube furnace and heated up to 650 °C with a heating rate of 5 °C min⁻¹ under argon atmosphere and kept for 3 hours.

Cell assembly

Au was sputtered (Gatan 682) onto both sides of the ceramic pellets (SECA pellets and LAGP pellets) to assemble symmetric cells for ionic conductivity tests. The ASSLBs were assembled into a commercial ventilation battery (Kejing company, Hefei, P. R. China) with lithium metal as the anode attached on the dense side of SECA pellet. Stainless steel was used as current collector for anode and Al mesh for the carbon coated porous side of SECA pellet. The ASSLBs were assembled in glovebox with Ar atmosphere, and then were ventilated with pure O_2 for 30 min before electrochemical tests.

Characterization

X-ray diffraction test was performed on a Bruker D8 Advanced x-ray diffractometer. Raman spectra were obtained using an instrument (Renishaw PLC, Wotton-under-Edge, Gloucestershire, GL12 8JR). SEM characterization was conducted on a Hitachi SU8010 scanning electron microscope. GC-MS was conducted with a commercial ventilation battery



Figure 1. (a) Schematic diagram of a Li– O_2 battery based on a SECA pellet; (b) cross-section of SECA pellet; (c) to (d) morphology of porous LAGP layer of different scale; (e) XRD pattern of SECA pellet.

test device (Kejing company, Hefei, P R China) connected to Clarus 680 and SQ 8S equipment, the data points were collected every 10 min. Thermogravimetric analysis (TGA) was conducted on a thermogravimetric analyzer (Netzsch STA-449F3) under oxygen atmosphere to determine the content of carbon coated onto the porous LAGP layer. The carbon coated SECA was firstly ground into a homogenous powder in an agate mortar. Then about several milligrams of powder was used for the TGA test from room temperature to 900 °C with heating rate of 15 °C min^{-1} .



Figure 2. Nyquist plots of (a) dense LAGP pellet and (b) SECA pellet at 25 °C, the battery structure is Au/pellet/Au. Insets are equivalent circuits and graphs of amplified axis ranges.

Electrochemical tests

For the ionic conductivity test, alternating-current impedance was performed on an impedance analyzer (Solartron 1287 coupled with Solartron 1260) applying an alternating signal with an amplitude of 5 mV in the frequency range of 1 MHz to 0.1 Hz. A galvanostatic discharge–charge test was performed on a HJ1001SD8 (Hokuto Denko Coroparation) within the voltage range of 2 to 5 V. All the tests were conducted at 25 °C.

Results and discussion

The SECA pellet was about 1.75 cm in diameter and 0.6 cm thick (figure 1(b)). The size distribution of the LAGP particles is from hundreds nanometers to about $2 \,\mu$ m. The thicknesses of the dense LAGP layer and porous LAGP layer were about 200 and 400 μ m, respectively. The cross-section of the SECA (figures 1(b), (c)) showed interconnected channels consisting of pores with diameter of several micrometers (figure 1(d)), which formed after burning up starch in air [15]. The interface between the dense LAGP layer and porous LAGP layer is continuous, indicating fast transportation of Li⁺ across these two layers. According to the XRD patterns as shown in figure 1(e), it is suggested that the crystallinity of LAGP has no change even after sintering with starch. The structure of co-sintered LAGP is consistent with previous literature [19] which reported the phase of $LiGe_2(PO_4)_3$ with a minute amount of AlPO₄ impurities.

The Nyquist plots of the dense LAGP pellet and SECA pellet at 25 °C are shown in figure 2, both consisting of a depressed semi-circle at high-frequency and a tail at low frequency. Equivalent circuits were established in figure 2. R1 is the intercept of the Nyquist plot with horizontal axis, referring to the resistance of grains. R2 parallel with CPE1 refers to the resistance of the grain boundary. W1 is the Warburg element associated with the diffusion of ions at low

frequency. The ionic conductivity was calculated using the equation:

$$\sigma = \frac{L}{S \times (R_1 + R_2)}$$

where *L* is the thickness of the pellet, *S* is the area, R_1 and R_2 are obtained from the fitting results of Nyquist plots according to the equivalent circuit. The conductivity of the dense LAGP pellet was 1.6×10^{-4} S cm⁻¹ and the ISE pellet was 2×10^{-5} S cm⁻¹ at 25 °C. The decreased conductivity of the SECA pellet could be ascribed to the decreased area and densification compared with dense LAGP, but it was acceptable for battery tests after coating cathode materials.

As seen in the photograph of figure 3(a), the SECA pellet after sintering was white. Grains of the LAGP phase and pore in the porous layer can be clearly observed in the SEM image. After carbonization of sucrose in Ar, the porous LAGP layer turned black. It is also confirmed by Raman spectra in figure 3(c), showing the D band at 1355 cm⁻¹ and G band at 1575 cm⁻¹ of graphite [20]. According to TGA results in figure 3(d), the mass loading of carbon was about 1.67 mg cm⁻² (0.969% of the SECA pellet) for the 150 μ l solution of sucrose. It is expected that the coated carbon may be used as catalyst for Li–O₂ batteries.

To evaluate the performance of this elegant structure, the SECA and Li metal anode were assembled into a commercial ventilation device. As seen in figure 4(a), the discharging voltage plateau was from 2.5 V to 2 V and did not drop vertically near 2 V. It is speculated that the decreased cut-off voltage of discharge would result in a further increased discharging capacity and increase of charge voltage plateaus can be observed at a higher current of 10 μ A cm⁻² compared to the one at 5 μ A cm⁻². As a result, the batteries adopting SECA showed a relatively high discharging capacity of 0.48 mAh cm⁻² for 5 μ A cm⁻² current and 0.38 mAh cm⁻² for 10 μ A cm⁻², respectively. Meanwhile, an ASSLB adopting RuO₂@CNTs as a catalyst was also assembled according to the literature [12] and a similar result was obtained as



Figure 3. SEM images of (a) pristine porous LAGP layer shows pore of 10 μ m and (b) carbon coated surface of pore, insets are photographs of pellets; (c) Raman spectra for the porous LAGP layer before and after carbon coating; (d) TGA results of the carbon coated SECA.

shown in figure 4(b). Even though the specific capacity is as high as 1000 mAh g⁻¹, this battery can only achieve an areal capacity less than 50 μ Ah cm⁻², which was only one tenth of the ASSLB adopting SECA. The high specific capacity was owing to the high electronic conductivity and catalytic activity of RuO₂@CNTs and the low areal capacity resulted from the low mass loading of catalysts compared to the porous cathode.

As shown in figure 4(c), ASSLB was cycled with both capacity and cut-off voltage limitation. The ASSLB can achieve six cycles with a capacity of 0.08 mAh cm⁻² between 2-5 V. The discharge plateau fading can be ascribed to increased internal resistance during cycling. This degradation of the battery was related to the reaction of LAGP and Li metal because Ge⁴⁺ in LAGP can be reduced by Li metal [21]. As shown in figure 4(d), after cycling the dense side of the SECA pellet turned black, indicating the reaction between Li metal and dense side of LAGP. These black by-products may increase the interfacial impedance.

To understand mechanism of discharging–charging reactions in prepared ASSLB, Raman spectra and mass spectra were performed to investigate the solid and gaseous products, respectively. Firstly, the prepared battery was discharged to 2 V at a current of 5 μ A cm⁻², then Raman spectra test for a porous LAGP layer of the cathode was conducted with the wavenumber from 870 cm⁻¹ to 200 cm⁻¹. For comparison, the Raman spectra data for the bare porous LAGP layer and carbon coated porous LAGP layer before discharging are shown in figure 5(a1 and a2). The porous

LAGP layer and carbon coated porous LAGP layer showed nearly the same spectrogram and the highest intensity occurred at 460 cm⁻¹. These peaks can be classified to the characteristic peaks of the electrolyte pellet. For the porous LAGP layer after discharging to 2 V, a new peak at around 796 cm⁻¹ appeared as shown in figure 5(a3), which is the characteristic peak of Li₂O₂ [22]. In order to obtain a sufficient amount of evolved O₂ for *in situ* GC-MS analysis, a higher current of 20 μ A cm⁻² was adopted. After charging for 10 min, O₂ was evolving out from the cathode (figure 5(b)) and increasing continuously during charging. The amount of O₂ decreased gradually after the charge ending. Combining the Raman spectra data and GC-MS results, reversibility of formation and decomposition of Li₂O₂ were confirmed.

Conclusions

In conclusion, a solid electrolyte cathode assembly consisting of porous LAGP layer and dense LAGP layer was successfully synthesized through one-step sintering. The SECA pellet has an ionic conductivity of 2×10^{-5} S cm⁻¹ at 25 °C. The porous LAGP layer was coated with carbon of about 1.67 mg cm⁻² and the coated carbon was used as a catalyst for Li–O₂ batteries. The ASSLBs showed capacity of 0.48 mAh cm⁻² at 5 μ A cm⁻² and 0.33 mAh cm⁻² at 10 μ A cm⁻² discharging to 2 V, respectively. And the ASSLB can achieve six cycles with a capacity of 0.08 mAh cm⁻² between 2–5 V. Furthermore, Raman spectra



Figure 4. Galvanostatic discharging and charging curves of ASSLBs, (a) porous cathode, current of 5 μ A cm⁻² and 10 μ A cm⁻² between 2–5 V; (b) cathode containing CNTs, RuO₂ and LAGP, current of 5.13 μ A cm⁻² (100 mAh g⁻¹) [12]; (c) porous cathode, cycling curves at 10 μ A cm⁻² and restrict the capacity to 0.08 mAh cm⁻²; (d) photograph of the dense side of SECA pellet before (left) and after (right) cycling.



Figure 5. Raman spectra of (a1) pristine porous LAGP layer, (a2) carbon coated porous LAGP layer before discharging and (a3) carbon coated porous LAGP layer after discharging to 2 V; (b) *in suit* GC-MS results.

and *in situ* mass spectra observed the formation and decomposition of Li_2O_2 , consistent with the typical reaction in $Li-O_2$ batteries. Lastly, our future work may focus on homogeneously depositing catalysts particles into the pores to improve the voltage hysteresis of cycles and cycling stability.

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