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Improving ionic conductivity of polycrystalline lithium ion conductors by interacting with mesoporous materials

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A B S T R A C T

Mesoporous materials were chosen to interact with polycrystalline $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ to investigate the possibility of improving its conductivity. The chosen mesoporous material, the thermal stability of which was evaluated, was mixed with $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ by ball milling. The mesoporous material maintained a mesoporous structure after annealed at 950 °C and has hindered the grains growth of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ by occupying the surfaces of the grains as evidenced by TEM analysis. Electrochemical impedance spectroscopy showed the participation of mesoporous materials had enhanced the conductivity by one order of magnitude. It was speculated that the thin layer of the mesoporous material, located on the surfaces of the grains, facilitated the migration of lithium ions across the boundaries.

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1. Introduction

Limitations of the flammable organic liquid electrolytes of the Li-ion batteries, such as safety concerns, leakage, corrosion and miniaturization difficulty, have made inorganic solid lithium ion conductors the research hotspot. Polycrystalline lithium ion conductors like Na-superionic conductor (NASICON) type materials have been studied intensively. NASICON materials have a general formula $Li_{1+x}M''_xM'_{2-x}(PO_4)_3$, of which $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) and $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP) exhibit conductivities in the range of $10^{-3} - 10^{-4}$ S/cm [1–4]. Compared to LATP, LAGP has a wide electrochemical window whereas LATP has a narrow one because LATP reacts with Li metal at ~ 2.4 V (vs. Li/Li+) due to the redox reaction of Ti^{4+}. Therefore, intensive studies have been carried out to improve the total conductivity of LAGP. As widely reported [5,6], the total conductivity of polycrystalline lithium ion conductors does not only depend on lithium ion transport in the crystalline grains of higher conductivity, but also through the grain boundaries of lower conductivity. Hence, the total conductivity of granular materials is dictated by the grain boundary conductivity. Therefore, many efforts have been made to increase the grain boundary conductivity through approaches like adding excessive lithium, making glass ceramics and doping Si [7,8]. Blanchard et al. [9] have reported an increase in conductivity of $LiBH_4$ confined in ordered mesoporous silica scaffolds through infiltration. Authors thought a similar effect could be achieved on LAGP if interacting with some mesoporous materials. Since the melting point of $LiBH_4$

is as low as 278 °C, the infiltration approach wouldn't work for LAGP with such a high melting point. Therefore, ball-milling has been chosen in this study to promote the interaction of SBA-15 and LAGP to improve the conductivity of polycrystalline lithium ion conductors. The results show that the interaction between SBA-15 and LAGP is different from $LiBH_4$ confined in ordered mesoporous silica scaffolds reported by Blanchard et al. Instead of filling into the pores of SBA-15, LAGP grains were covered by a thin layer of SBA-15, which is beneficial to the improvement of ion conductions by providing a three-dimensional way for migrations.

2. Experimental

$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ was prepared by solid state reaction method in this study. Start materials used are Li_2CO_3 ($\geq 99\%$), $Al(OH)_3$ ($\geq 99\%$), ZrO_2 ($\geq 99\%$) and $NH_4H_2PO_4$ ($\geq 99\%$). Firstly, stoichiometric raw powders were weighed and mixed thoroughly in a pestle mortar. Then all the mixtures were thermally treated at 700 °C for 0.5 h and then at 900 °C for 2 h to remove any possible volatile components and form LAGP phase. The calcined mixtures were ball milled for 16 h in a speed of 800 rpm with acetone. After drying, some of the milled LAGP mixtures were pressed into pellets in a 15 mm diameter and sintered at 950 °C for 2 h for electrochemical impedance spectra (EIS) measurements. On the other hand, some of the milled LAGP powders were mixed with 10 wt% SBA-15 powders and subjected to a ball milling operation with zironica balls in 300 ml acetone (1: 3 for powders and balls). The ball milling was operated at 600 rpm for 8 h. The milled 10% SBA15-LAGP powders were dried, pressed into pellets and sintered

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at 950 °C for 2 h. SBA-15 powders, which were purchased from Najing JCNANO, were thermally treated at 950 °C and 1150 °C for 2 h respectively for its stability evaluation. The specific surface areas and pore volumes were determined by the Brunauer–Emmett–Teller (BET) method using nitrogen as adsorbate. All the sintered pellets were polished and painted with silver paste on both sides for EIS analysis. The EIS measurements were carried out using a PARSTAT2273 station by applying a stimulus amplitude of 10 mV over the frequency range of $0.1–2 \times 10^6$ Hz at room temperature. The microstructures were examined by using a field emission scanning electron microscope (JSM-7800F). TEM analysis was carried out by using a JEM-3010.

3. Results and discussions

The thermal stability of SBA-15 was evaluated by performing a BET analysis. Fig. 1 is the N_2 adsorption-desorption isotherms of SBA-15 as-received, annealed at 950 °C and 1150 °C. As received SBA-15 presented type IV isotherm patterns, which are characteristic of mesoporous solids. The surface area is ~493 m^2/g and the average pore diameter is ~6 nm. After thermally treated at 950 °C, the isotherms curve of SBA-15 is still shown as a hysteresis loop, but the amount of nitrogen adsorbed decreased, which indicated SBA-15 annealed at 950 °C was still a mesoporous material but the pore volume was lower since the pore channels started to collapse upon annealing. The surface area is ~160 m^2/g and the average pore diameter is ~4 nm. The isotherm curve of SBA-15 annealed at 1150 °C was not a hysteresis loop anymore, indicating all the micropores were collapsed and all the particles were fused together. The material is either non-porous or macroporous. In summary, SBA-15 annealed at 950 °C still maintained a mesoporous structure and can be used to tune the property of polycrystalline conductor in this study.

SEM photos of LAGP pellets and 10%SBA15-LAGP pellets are shown in Fig. 2. Both samples presented a dense morphology with small and big faceted grains co-existed. 10%SBA15-LAGP pellets seemed to have smaller grains (the smallest is ~0.4 μm) compared to LAGP pellet (the smallest is ~1 μm) in general, which showed mesoporous SBA-15 hindered the grains to grow during the process of sintering. Therefore, it was speculated that SBA-15 powders covered the surfaces of LAGP particles during ball milling and thereby hindered the grains growth in the following step of sintering.

TEM images of LAGP and 10%SBA15-LAGP are shown in Fig. 3 (a) and (b). The insets are the lower magnification images which exhibit several grains of LAGP and 10%SBA15-LAGP. Most of the grains in LAGP are larger than 1 μm, while the grains of 10% SBA115-LAGP are much smaller, less than 0.6 μm in general. Compared to Fig. 3(a), a thin layer of SBA-15 was observed on the surface of 10%SBA15-LAGP sample in Fig. 3(b), the thickness is around 20 nm. While the edge of LAGP grains are clear and sharp.

XRD examinations have been done on both LAGP and 10% SBA15-LAGP and the patterns with references are shown in Fig. 4. The XRD patterns have shown that the phases in LAGP and 10% SBA15-LAGP are all pure $LiGe_2(PO_4)_3$ with no other phases detected. Only the peaks in 10%SBA15-LAGP are not as sharp as those in LAGP. The absence of SBA-15 peak in XRD patterns is due to the amorphous nature of SBA-15.

A grain boundary is the interface between two grains in a polycrystalline material. When the grains became smaller in the case of interacting with SBA-15 as shown in Figs. 2 and 3, the amount of grains boundaries were increased correspondingly. It seems that a lower total conductivity is expected for 10%SBA15-LAGP as in Refs. [5–9]. Therefore 10%SBA15-LAGP pellets sintered at 950 °C were carried out EIS measurements at room temperature to investigate the effect of SBA-15 on the total conductivity and the Nyquist plot is shown in Fig. 5. Both plots presented a single semicircle followed by a tail, which indicated an ionic conductor. The grain and grain boundary responses were indistinguishable in Nyquist plot for both samples, but the impedance of LAGP was much larger than that of 10%SBA15-LAGP. The smaller impedance of 10%SBA15-LAGP has revealed the participation of mesorous SBA-15 was beneficial to lithium ion conductions in polycrystalline LAGP in this case. The total conductivity was calculated as 1.2×10^{-6} S cm^{-1} for LAGP which is comparable to the value of 3.6×10^{-6} S cm^{-1} reported by Feng et al. for LAGP prepared at same conditions [4] and the total conductivity of 10%SBA15-LAGP was 1.0×10^{-5} S cm^{-1}. It is obvious that the total conductivity was enhanced by nearly one order of magnitude after interacting with mesoporous SBA-15. This appears to contradict with the effect of smaller grains on the total conductivity. The contradiction originates the other role of SBA-15, which was thought to facilitate the migration of lithium ions across grain boundaries by occupying the surfaces of grains as indicated by TEM images. Similar to the role of an amorphous boundary layer reported by Mei et al. [7], this thin layer of SBA-15 could have also provided a three-dimensional way for the migration of lithium ions and helped the ions access to other grains through boundaries easily. The role of SBA-15 to help the migration of lithium ions outweighs the effect of smaller grains.

4. Conclusions

Mesoporous materials, SBA-15, were chosen to interact with polycrystalline $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ to investigate the possibility of improving its conductivity. SBA-15 still maintained the mesoporous structure even after annealed at 950 °C for 2 h, although the pore volume was decreased. Both the microstructures of LAGP and 10%SBA15-LAGP exhibited a dense morphology with a mixture of small and large grains, but the grains of 10%SBA15-LAGP was smaller in general, which indicated the presence of mesoporous SBA-15 has hindered the growth of LAGP grains. It was thought that SBA-15 covered the surfaces of LAGP particles during ball milling and then prevented the growth of grains subsequently during annealing. The total conductivity of 10%SBA15-LAGP pellets was enhanced by one order of magnitude compared to LAGP, which could be possibly attributed to the existence of SBA-15 on the surface of LAGP grains. SBA-15 has helped lithium ions to migrate across the boundaries. Further investigations are needed to reveal the interacting mechanism.
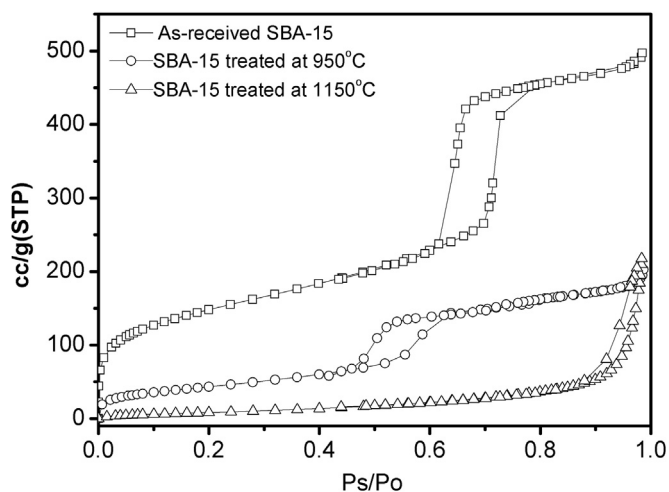

Fig. 1. N_2 adsorption-desorption isotherms plot of SBA-15.