Increased Ion Conductivity in Composite Solid Electrolytes With Porous Co$_3$O$_4$ Cuboids

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Compared with the fragile ceramic solid electrolyte, Li-ion conducting polymer electrolytes are flexible and have better contact with electrodes. However, the ionic conductivity of the polymer electrolytes is usually limited because of the slow segment motion of the polymer. In this work, we introduce porous Co$_3$O$_4$ cuboids to Poly (Ethylene Oxide)-based electrolyte (PEO) to investigate the influence of these cuboids on the ionic conductivity of the composite electrolyte and the performance of the all-solid-state batteries. The experiment results showed the porous cobid Co$_3$O$_4$ fillers not only break the order motion of segments of the polymer to increase the amorphous phase amount, but also build Li$^+$ continuous migration pathway along the Co$_3$O$_4$ surface by the Lewis acid-base interaction. The Li$^+$ conductivity of the composite polymer electrolyte reaches $1.6 \times 10^{-4}$ S cm$^{-1}$ at 30°C. The good compatibility of the composite polymer electrolyte to Li metal anode and LiFePO$_4$ cathode ensures good rate performance and long cycle life when applying in an all-solid-state LiFePO$_4$ battery. This strategy points out the direction for developing the high-conducting composite polymer electrolytes for all-solid-state batteries.

Keywords: polymer electrolyte, all-solid-state battery, porous cuboid, hydrothermal method, surface interaction

INTRODUCTION

The demand for energy storage in today’s technological society is increasing rapidly (Chen et al., 2009; Luo et al., 2015). With the exhaustion of fossil fuels and the increasingly severe environmental problems, it has become a worldwide trend to seek green, clean, and renewable energy (Abada et al., 2016). Lithium-ion batteries have been widely used in various portable smart devices since commercialized by Sony in 1991 (Thackeray et al., 2012). Lithium-ion batteries have been widely used in various portable smart devices since commercialized by Sony in 1991 (Thackeray et al., 2012). However, the capacity density of the commercial lithium-ion batteries with graphitized carbon anode can no longer meet the demand of electric vehicles (Lu et al., 2013; Cheng et al., 2017). Meanwhile, the flammable characteristic of the liquid electrolyte makes battery safety accidents frequently occur (Doughty and Roth, 2012).

An all-solid-state battery with a lithium metal anode due to its improved energy density and safety characteristic is a strong candidate for higher power and energy density in electrified transport (Lee et al., 2020). In order to ensure the long-term stable cycle of all-solid-state lithium metal batteries, the solid-state electrolyte (SSE) needs to have high Li$^+$ conductivity, good stability with the electrode, and the ability to block lithium dendrites (Goodenough and Singh, 2015). Much progress has been made in the study of inorganic SSEs. The oxide SSEs including garnet (Li et al., 2012; Thangadurai et al.,...
Polymer solid electrolytes have attracted the attention of researchers because of their low cost and easy preparation (Stephan and Nahm, 2006; Wu et al., 2020a). Poly(ethylene oxide) (PEO), which is cheap and flexible, has become one of the most common polymer matrices of polymer solid electrolytes. However, even with the addition of lithium salt, the crystalline PEO phase always exists in PEO/Li-salt polymers, leading to low Li-ion conductivity of about $10^{-6}$ S cm$^{-1}$ (Marzantowicz et al., 2006). Improving the Li$^+$ conductivity of the polymer solid electrolytes is the key point of their practical application. Adding fillers to the polymer is an effective strategy for improving the Li$^+$ conductivity of the electrolytes (Yue et al., 2016). By adding oxide fillers such as Al$_2$O$_3$, SiO$_2$, and TiO$_2$ to the polymer, on the one hand, these oxide particles can interrupt the ordered movement of the polymer chain segments and increase the content of the amorphous phase (Weston and Steele, 1982; Sabrina et al., 2019). On the other hand, the O/OH groups on the surface of the particles can produce Lewis acid-base interaction with lithium salt ions, which further promotes the transport of lithium ions in the composite solid electrolytes (Jayathilaka et al., 2002). Based on this, the main goal of this experiment is to prepare a filler with a large specific surface area that can absorb a large number of O/OH groups and provide a long-term pathway for continuous conduction of lithium ions.

In this study, porous cuboid Co$_3$O$_4$ was prepared by the hydrothermal method with subsequent heat treatment. Adding porous cuboid Co$_3$O$_4$ to PEO/LiTFSI increases the content of the amorphous phase of PEO. Meanwhile, the porous surface of Co$_3$O$_4$ can absorb a large number of O/OH groups so that lithium ions can also be transported along the surface of the Co$_3$O$_4$ cuboid. The Li$^+$ conductivity of the composite polymer electrolyte reaches $1.6 \times 10^{-4}$ S cm$^{-1}$ at 30°C. Moreover, the all-solid-state lithium/LiFePO$_4$ battery employing the electrolyte shows good rate performance and cycle stability at 40°C.

**EXPERIMENTAL**

**Preparation of the Porous Cuboid Co$_3$O$_4$**

The porous cuboid Co$_3$O$_4$ was prepared via the hydrothermal method with subsequent heat treatment. 1 mmol cobalt acetate tetrahydrate (Co(CH$_3$COO)$_2$$\cdot$4H$_2$O, ACROS Organics) was dissolved in 18 ml ethanol and acetic acid composite solvent. The volume ratio of the ethanol and acetic acid was 3:1. The homogeneous solution was transferred into a 25 ml polytetrafluoroethylene (PTFE) liner and sealed in a stainless steel reaction kettle. After heating at 180°C in an oven for 3 h, the precipitate was washed using ethanol and dried at 80°C. The porous cuboid Co$_3$O$_4$ was obtained by sintering the precursor in a box furnace at 350°C for 1 h.

**Preparation of the Composite Polymer Electrolyte**

Polyethylene oxide (PEO, M.W. ~600,000, ACROS Organics) and Lithium bis (trifluoromethanesulfonyl) imide (LiTFSI, ACROS Organics) were dried at 60°C overnight before use. The dried PEO and LiTFSI were added into anhydrous acetonitrile with the [EO] and [Li$^+$] molar ratio of 10:1. After stirring at 60°C for 12 h, the porous cuboid Co$_3$O$_4$ was added into the solution under vigorous stirring. The composite polymer electrolyte (CPE) was obtained by pouring the homogeneous mixture onto a PTFE plate and drying vacuumed at 60°C for 24 h. According to the weight percentage (5, 10, and 20 wt%) of the porous cuboid Co$_3$O$_4$, the CPEs were named CPE-5, CPE-10, and CPE-20, respectively.

A CPE using purchased Co$_3$O$_4$ (Alfa Aesar) as the filler was prepared using the method mentioned above. The sample was named CPE-purchased Co$_3$O$_4$.

**Characterization**

The phase and the morphology of the porous cuboid Co$_3$O$_4$ and the CPEs are characterized by an X-ray diffractometer (XRD, Rigaku MiniFlex 600), and a scanning electron microscope (SEM, FEI Quanta 650) equipped Bruker energy-dispersive X-ray spectroscopy (EDX) system.

The Li$^+$ conductivity ($\sigma$) of the CPEs is calculated by Eq. 1,

$$\sigma = \frac{l}{RA}$$  \hspace{1cm} (1)

where $l$, $R$, and $A$ correspond to the thickness, impedance, and surface area of the CPEs, respectively. The electrochemical impedance spectroscopy (EIS) of the CPEs is tested by an Autolab workstation using a stainless steel/CPE/stainless steel coin cell, in which the stainless steel is used as the blocking electrode. The frequency is set as 10$^4$ to 0.1 Hz.

The Flourier transform infrared (FTIR) spectra of the CPEs are characterized by an Infinity Gold FTIR spectrometer from 400 to 4,000 cm$^{-1}$.

The differential scanning calorimetry curves (DSC) of the CPEs are recorded at the temperature range −80 to 0°C with a heating rate of 10°C min$^{-1}$.

To calculate the Li$^+$ transference number ($t_{li}^+$) of the CPEs, the Li/CPE/Li battery is applied a dc voltage ($\Delta V$, 10 mV here) until getting a steady current. The $t_{li}^+$ is calculated according to Eq. 2,

$$t_{li}^+ = \frac{I_i R_b (\Delta V - I_b R'_b)}{I_b R_b (\Delta V - I_b R')}$$ \hspace{1cm} (2)

where $I_0$ and $I_i$ are the initial and steady-state current, $R_b$ and $R'_b$ are the bulk resistances before and after applying the $\Delta V$, $R_i$ and $R'_i$ are the interfacial resistances before and after the dc polarization.
The solid-state LiFePO₄ cathode is prepared by mixing the LiFePO₄, PEO, LiTFSI, and carbon black (60:20:10:10 in weight ratio) into anhydrous acetonitrile. After stirring at 60°C for 12 h, the slurry was cast onto a carbon-coated aluminum foil. The LiFePO₄ cathode is obtained by drying in a vacuum at 60°C for 24 h.

RESULTS AND DISCUSSION

The XRD pattern of the prepared Co₃O₄ was shown in Figure 1A. All the diffraction peaks correspond well with the Co₃O₄ standard PDF card (#01-073-1701). No impurity phase is observed. As can be seen from Figures 1B,C, the prepared Co₃O₄ shows a porous cuboid structure. The ethanol and acetic acid composite solvent promote the orientation growth of the Co₃O₄. The side length and the height of the cuboid are approximately 100 and 550 μm, respectively. The XRD patterns of the CPEs with different addition of porous cuboid Co₃O₄ were given in Figure 1D. The diffraction peaks of the Co₃O₄ show no change in each CPEs, which means the Co₃O₄ is chemical stable with PEO and LiTFSI. An obvious crystalline peak of PEO exits at 23° in the XRD pattern of the CPE with 5 wt% Co₃O₄. When adding 10 wt% Co₃O₄, the intensity of the PEO crystalline peak becomes weak. And the PEO crystalline peak is invisible in the CPE-20. The amorphous degree of the composite polymer could be increased by adding porous cuboid Co₃O₄ as the fillers, which facilitates the movement of Li⁺ in the CPEs. The CPEs are dense and have a flat surface (Figure 1E). The thickness of the CPEs is controlled at 100 μm (Figure 1F). As can be seen from the top-view and cross-section SEM images (Figures 1E,F), the Co₃O₄ cuboids are uniformly dispersed in the polymer.

The temperature-dependent Li⁺ conductivity of the CPEs with different addition of the porous cuboid Co₃O₄ are shown in Figure 2A. With the increase of the addition amount of the porous cuboid Co₃O₄, the Li⁺ conductivity increases first and then decreases. The CPE with 10 wt% porous cuboid Co₃O₄ shows the highest Li⁺ conductivity among the CPEs, which is 1.6 × 10⁻⁴ S cm⁻¹ at 30°C. When the weight percentage of the porous cuboid Co₃O₄ is 20 wt%, the Li⁺ transport path may be blocked by excess Co₃O₄ in the polymer, leading to a slight decrease of the Li⁺ conductivity (Dissanayake et al., 2003). 10 wt% commercial Co₃O₄ powders were added into the PEO/LiTFSI as the fillers for comparison. Unlike the prepared Co₃O₄, the purchased Co₃O₄ is nearly spherical in morphology (Supplementary Figure S1A). The Li⁺ conductivity of the CPE-purchased Co₃O₄ (2.0 × 10⁻⁵ S cm⁻¹ at 30°C), which is of the same order of magnitude as that of CPEs using other Li-insulator oxide fillers such as Al₂O₃ or TiO₂ (Croce et al., 1998), is much lower than that of CPEs with porous cuboid Co₃O₄. In order to figure out the reason why the Li⁺ conductivity of the CPE-10 is much higher than that of the CPE-purchased Co₃O₄, the FTIR spectra of the two membranes are compared in Figure 2B. Overall, the FTIR spectra of the CPEs with different morphologies show very similar peak positions and relative intensities. After fitting the peaks in the range of
725–755 cm\(^{-1}\), it is worth noting that 90.2% of the lithium salt is dissociated in PEO, forming free Li\(^+\) and TFSI\(^-\) (corresponding to the yellow peak centered at about 739 cm\(^{-1}\)) in the CPE-10. However, in the CPE-purchased Co\(_3\)O\(_4\), there are fewer free cations/anions (82.6%), but 17.4% of ion-paired LiTFSI (corresponding to the blue peak centered at about 744 cm\(^{-1}\)), which has no contribution to the Li\(^+\) transport (Bakker et al., 1995; Wu et al., 2020b). From the DSC curves of the CPE-10 and the CPE-purchased Co\(_3\)O\(_4\) in Figure 2C, the glass transition temperature (\(T_g\)) of the CPE-10 and the CPE-purchased Co\(_3\)O\(_4\) are \(-42.3\) and \(-40.8\)°C, respectively. The lower \(T_g\) of the CPE-10 means that the porous cuboid Co\(_3\)O\(_4\) as fillers have a better impact on inhibiting the crystallization of PEO polymer and promoting the movement of the molecular chains compared to the purchased Co\(_3\)O\(_4\). Moreover, the Li\(^+\) transference number of the CPE-10 is calculated as 0.28 (Figure 2D), which is much higher than that of the CPE-purchased Co\(_3\)O\(_4\) (0.13 as shown in Supplementary Figure S2). The higher Li\(^+\) transference number of the CPE-10 could reduce the concentration polarization during cell cycling and fulfill a long-term cycle life when employing in an all-solid-state battery.

The Li\(^+\) conductivity of a CPE could be improved by adding Li-insulator oxide fillers into PEO/LiTFSI for two reasons. Firstly, oxides dispersed in the PEO/LiTFSI matrix could break the ordered arrangement of PEO chain segments, thus decrease the crystalline amount and inhibit the re-crystallization. Secondly, the Lewis acid-base type O/OH groups on the filler surface could interact with cations and anions to create high
FIGURE 4 | The voltage profile of a Li/CPE-10/Li battery cycled at 40°C under different current densities.

FIGURE 5 | (A) Rate performance, (B) voltage-capacity curves, (C) cycle stability and Coulombic efficiency of the Li/CPE-10/LiFePO₄ batteries at 40°C.
conducting Li⁺ pathways\textsuperscript{[24, 25]}. The transport paths of Li⁺ in the CPE-10 and the CPE-purchased Co₃O₄ are shown in Figure 3. The Co₃O₄ particles are easy to agglomerate (Supplementary Figure S1B), resulting in uneven distribution when adding into the PEO/LiTFSI matrix. Li⁺ cannot pass through agglomerate particles. Li⁺ transfer will slow down in the crystalline area due to a lack of fillers. On the contrary, in the homogeneous CPE-10, Li⁺ moves fast through the PEO segments and the Co₃O₄ porous cuboids. What’s more, lots of O/OH groups are absorbed on the Co₃O₄ porous surfaces (Yan and Sautet, 2019; Chen et al., 2020). The Li⁺ cation in the LiTFSI is quite a strong Lewis acid (the TFSI-anion is a Lewis base). The surface O/OH groups will absorb cations and anions, respectively, by Lewis acid-base interaction, promoting the dissociation of the lithium and the movement of the ions (Wieczorek et al., 1996). The Lewis acid-base interaction between O/OH groups and ions could create continuous, long-term Li⁺ transport paths along the Co₃O₄ porous cuboid surface, leading to an increase in Li⁺ conductivity.

To determine the electrochemical properties of the CPE-10, all-solid-state Li/Li and Li/LiFePO₄ batteries were assembled using the CPE-10 as the electrolyte. The profile of the Li/CPE-10/Li battery cycled at 40°C under different current densities is shown in Figure 4. The battery exhibits excellent cycle stability under 50–200 μA cm⁻² for 500 h. The polarization is 0.018, 0.034, 0.048, and 0.057 V when current density is 50, 100, 150, and 200 μA cm⁻², respectively. After current density decreasing back to 100 μA cm⁻², the voltage recovers to 0.039 V. No sudden increase or drop in voltage polarization was observed, indicating a stable interface between the Li metal and the CPE-10.

All-solid-state Li/CPE-10/LiFePO₄ batteries were cycled at 40°C to evaluate the practical possibilities of the CPE-10. As can be seen from Figure 5A, the discharge capacity of the battery is about 155, 140, 132, and 126 mAh g⁻¹ when current density increases from 50 to 200 μA cm⁻², and the discharge capacity recovers to 132, 139, and 150 mAh g⁻¹ when the current density is 150, 100, and 50 μA cm⁻², respectively. The outstanding rate performance and tiny voltage polarization (Figure 5B) demonstrates that the electrodes and electrolyte have good compatibility. Based on it, a Li/CPE-10/LiFePO₄ battery was cycled under 50 μA cm⁻² at 40°C to estimate the cycle life of the battery (Figure 5C). After 150 cycles, the discharge capacity is 132 mAh g⁻¹. The capacity retention is high as 83%. The Coulombic efficiency keeps over 98% during the long cycle life. The good rate performance and long cycle life prove that the low-cost electrolyte has a promising application in all-solid-state lithium metal batteries.

CONCLUSION

The porous cuboid Co₃O₄ fillers, which are synthesized via the hydrothermal method, is added into the PEO/LiTFSI to prepare a composite polymer electrolyte. The porous cuboid Co₃O₄ fillers not only break the order motion of segments of the polymer to increase the amorphous phase amount, but also build Li⁺ continuous migration pathway along the Co₃O₄ surface by the Lewis acid-base interaction. The Li⁺ conductivity of the composite polymer electrolyte reaches 1.6 × 10⁻⁴ S cm⁻¹ at 30°C. The good compatibility of the composite polymer electrolyte to Li metal anode and LiFePO₄ cathode ensures good rate performance and long cycle life when applying in an all-solid-state LiFePO₄ battery.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

QZ: experimental design, data analysis and discussion, and manuscript writing. SL and L-HG: experimental design and data analysis and manuscript writing. SZ and YC: electrochemical performance test. All authors contributed to the article and approved the submitted version.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmats.2021.697257/full#supplementary-material

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