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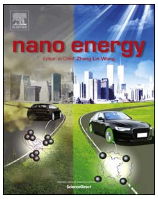

Full paper

PEO/garnet composite electrolytes for solid-state lithium batteries: From "ceramic-in-polymer" to "polymer-in-ceramic"

Long Chen[a], Yutao Li[b], Shuai-Peng Li[a], Li-Zhen Fan[a,b,*], Ce-Wen Nan[c], John B. Goodenough[b,*]

[a] *Beijing Advanced Innovation Center for Materials Genome Engineering, Institute of Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China*
[b] *Materials Science and Engineering Program & Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712, United States*
[c] *School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*

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ABSTRACT

Composite polyethylene-oxide/garnet electrolytes containing LiTFSI as the lithium salt have a Li^+ conductivity $\sigma_{Li} > 10^{-4}$ S cm^{-1} at 55 °C and a low plating/stripping impedance of a dendrite-free Li-metal anode; they have been developed for a safe solid-state Li-metal rechargeable battery. Composites consisting of "ceramic-in-polymer" to "polymer-in-ceramic" that are flexible and mechanically robust are fabricated by hot-pressing. Safe pouch cells with a remarkable flexibility have been fabricated. Solid-state $LiFePO_4|Li$ batteries with electrolytes of "ceramic-in-polymer" and "polymer-in-ceramic" deliver excellent cycling stability with high discharge capacities (139.1 mAh g^{-1} with capacity retention of 93.6% after 100 cycles) and high capacity retention (103.6% with coulombic efficiency of 100% after 50 cycles) at 0.2 C and 55 °C. Both kinds of electrolytes can be applied to solid-state lithium batteries.

1. Introduction

The ability to plate/strip a dendrite-free Li-metal anode from a nonflammable solid electrolyte that is neither reduced on contact with lithium nor oxidized on contact with a high-voltage cathode can offer a safe rechargeable Li-metal battery (LMB) needed for numerous markets requiring stable high-density storage of electric power. In addition to low-cost, the solid electrolyte that provides this ability needs to possess three other essential properties: (a) a Li^+ conductivity $\sigma_{Li} \geq 10^{-4}$ S cm^{-1} at 20 °C, (b) a mechanical flexibility and toughness to allow formation of large-area thin sheets that do not crack either in fabrication or on charge/discharge cycling, and (c) strong chemical bonding to a lithium anode to allow a low-impedance plating/stripping of Li^+ across the anode/electrolyte interface over a long cycle life as well as strong bonding to a plastic electrolyte that accommodates to the changing volume of a host cathode on charge/discharge cycling [1–5].

Solid electrolytes include inorganic-solid electrolytes (ISEs) such as sulfides and oxides and solid polymer electrolytes (SPEs) such as poly (ethylene oxide) (PEO)-based electrolytes that can transfer Li^+ by the segmental motion of polymer [6]. In addition, such SPEs are light weight and easy to form films with good viscoelasticity [3,7]. However, the low ionic conductivities, poor mechanical and electrochemical stability of PEO-based SPEs limit their practical application. Dispersing inorganic fillers in a polymer matrix is an effective strategy [8,9], especially, Li^+-conductive garnet oxide fillers [10].

In this paper, we report the development of a low-cost composite ceramic/polymer solid electrolyte (CPSE) containing the garnet $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) as the ceramic, polyethylene oxide (PEO) as the polymer, and Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as the salt. The composite compositions ranged from "ceramic-in-polymer" [6,10–12] to "polymer-in-ceramic". The bonding of the PEO polymer matrix to the anode permits electrolyte and electrodes to create a large contact area, benefiting the solid/solid interfacial compatibility. The Li^+ transport channel provided by the LLZTO contributes to an enhancement of the Li^+ conduction capability. Rigid LLZTO particles with PEO chain segments provide a mechanically robust and stable framework against the growth of lithium dendrites. The stable chemical and electrochemical performance of LLZTO with Li metal allows the electrolyte/Li interface to achieve a stable state. Except for a $\sigma_{Li} > 10^{-4}$ S cm^{-1} only at temperatures T > 50 °C, these low-cost composite electrolytes fulfill enhanced mechanical properties and a stable electrode/electrolyte interface for an acceptable solid-state LMB.

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[*] Corresponding authors.
E-mail addresses: fanlizhen@ustb.edu.cn (L.-Z. Fan), jgoodenough@mail.utexas.edu (J.B. Goodenough).

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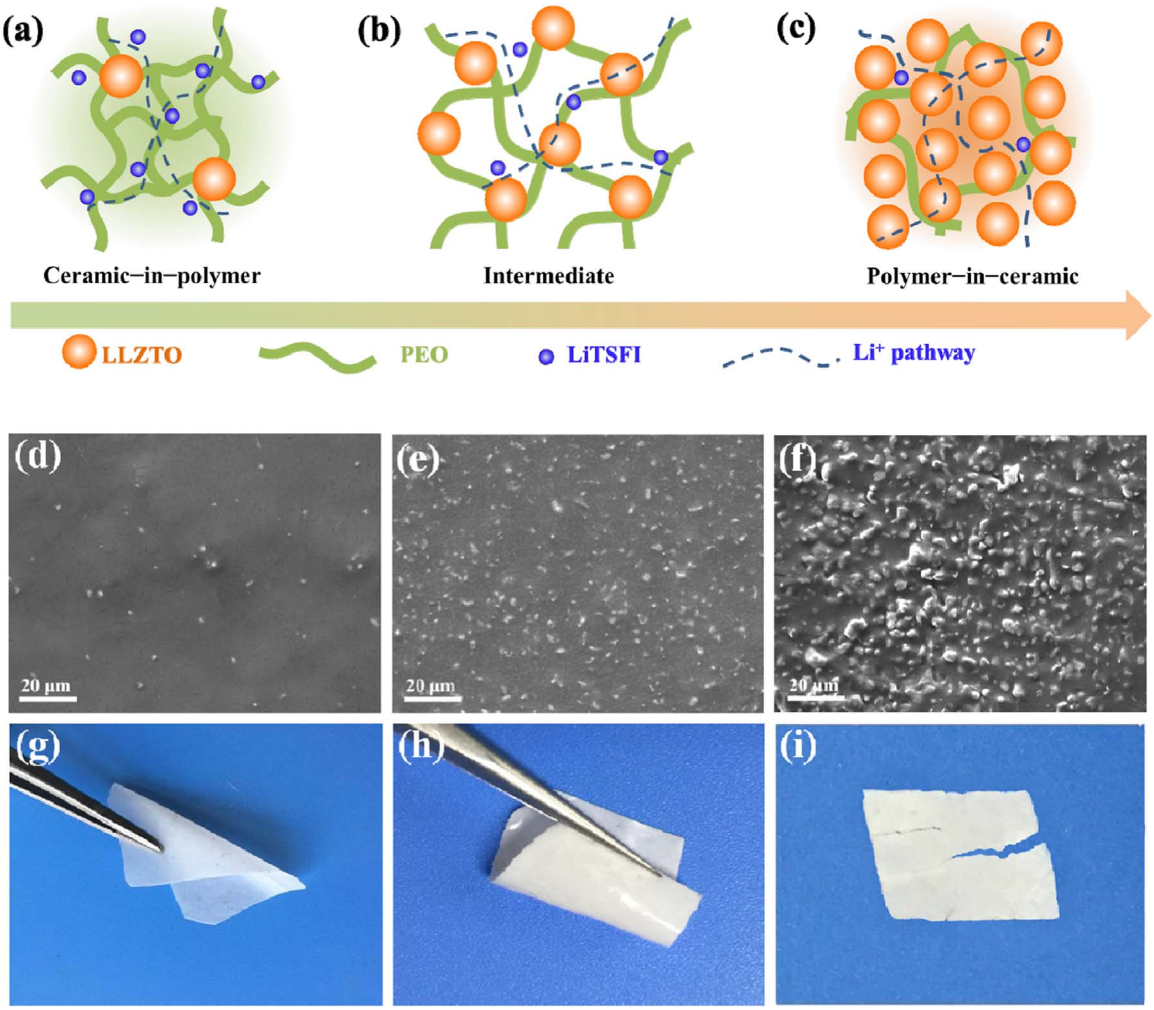

Fig. 1. Schematic illustration for PEO-LLZTO CSE: (a) “ceramic-in-polymer”; (b) “intermediate”; (c) “polymer-in-ceramic”; the typical surface morphologies and flexibility of composite electrolyte (1-x) wt%[PEO_8-LiTFSI]-x wt% LLZTO: (d, g) 10 wt%; (e, h) 50 wt%; (f, i) 80 wt%.

2. Experimental section

2.1. Materials preparation

PEO (M_w: 600,000) and polyethylene glycol (PEG, M_w: 400) was purchased from Sigma-Aldrich and dried under vacuum at 50 °C for 24 h before use. LiTFSI was purchased from Sigma-Aldrich and dried under vacuum at 100 °C for 12 h and kept in a glove box filled with Ar atmosphere. The cathode material $LiFePO_4$ was obtained from Aleees. The garnet LLZTO LLZTO was synthesized by solid-state reaction according to reference [13–15].

The composite solid electrolyte membranes were prepared by hot pressing without any organic solvent. Predetermined amounts of LLZTO powder, PEO, and LiTFSI were ground in a mortar to obtain a rough-sheet film. The EO to Li molar ratio was around 8:1 and the content of LLZTO powders varied from 0 to 80 wt%; the sheet film was sealed and transferred to a vacuum oven for 12 h at 70 °C. Subsequently, by pressing for 3 min at 70 °C under 10 MPa, a uniform “ceramic-in-polymer” composite membrane with a thickness of ~ 70 μm could be achieved. For the “polymer-in-ceramic” electrolyte, the preparation procedure is the same, but a small amount of PEG was added in the mortar to enhance the flexibility of the membrane. The thickness of “polymer-in-ceramic” electrolyte is ~ 100 μm. All the samples were prepared in an Ar filled glove box.

2.2. Sample characterization

X-ray diffraction (XRD) was used to observe the crystalline structure of LLZTO with Cu K_α radiation in the 2θ range of 10 ~ 60°. The average particle size of LLZTO was calculated with a Laser particle-size analyzer (Mastor 2000). The morphology of LLZTO and composite electrolyte were characterized by field-emission scanning electron microscopy (FE-SEM, JSM 6330). Differential scanning calorimetry (DSC) measurements were carried out on a TA Instrument (Q5000IR) with a heating rate of 10 °C min^{-1} from 15 to 85 °C under N_2 atmosphere.

2.3. Electrochemical characterization of the PEO-LLZTO membrane

The ionic conductivities of the composite electrolytes were measured by electrochemical impedance spectroscopy with an AC amplitude of 5 mV in the frequency range of 10^5–0.1 Hz at temperatures from 20 to 80 °C on a Solartron electrochemical station 1260 + 1287. The composite electrolyte was sandwiched between two stainless-steel blocking electrodes to form the test cells; the cells were kept at each test temperature for 30 min to reach thermal equilibrium. The electrochemical stability window of the composite electrolyte was evaluated via linear sweep voltammetry in the potential range from 2.5 to 6.0 V at a scanning rate of 1 mV s^{-1} with a stainless steel plate as working electrode and Li metal as a reference and counter electrode. The interface stabilities of the composite electrolytes against a Li-metal electrode were examined by recording the values of interfacial resistance