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Composite electrolytes of polyethylene oxides/garnets interfacially wetted by ionic liquid for room-temperature solid-state lithium battery

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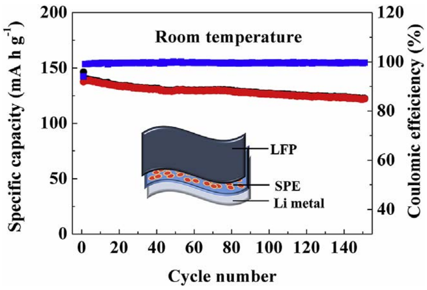
HIGHLIGHTS

- The ionic liquid was used to wet the interfaces between PEO and LLZTO.
- The ionic liquid of 1.8 μL cm^{-2} remained the solid state of membrane electrolytes.
- The improved conductive paths along the interfaces were studied.
- $LiFePO_4$/Li and $LiFe_{0.15}Mn_{0.85}PO_4$/Li batteries were tested at room temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Paramount attention has been paid on solid polymer electrolytes due to their potential in enhancement of energy density as well as improvement of safety. Herein, the composite electrolytes consisting of Li-salt-free polyethylene oxides and 200 nm-sized $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ particles interfacially wetted by $[BMIM]TF_2N$ of 1.8 μL cm^{-2} have been prepared. Such wetted ionic liquid remains the solid state of membrane electrolytes and decreases the interface impedance between the electrodes and the electrolytes. There is no release of the liquid phase from the PEO matrix when the pressure of 5.0×10^4 Pa being applied for 24 h. The interfacially wetted membrane electrolytes show the conductivity of 2.2×10^{-4} S cm^{-1} at 20 °C, which is one order of magnitude greater than that of the membranes without the wetted ionic liquids. The conduction mechanism is related to a large number of lithium ions releasing from $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ particles and the improved conductive paths along the ion-liquid-wetted interfaces between the polymer matrix and ceramic grains. When the membranes being used in the solid-state $LiFePO_4$/Li and $LiFe_{0.15}Mn_{0.85}PO_4$/Li cells at 25 °C, the excellent rate capability and superior cycle stability has been shown. The results provide a new prospect for solid polymer electrolytes used for room-temperature solid-state lithium batteries.

1. Introduction

Recently, a great deal of research has been carried out on the solid-state lithium batteries (SSLBs) with high energy densities and long cycle life, due to demand of electric vehicles and electrical energy storage systems [1–4]. As one of the most important components, the solid-state electrolytes should have superior ionic conductivity, high safety characteristics, electrochemical stability and long cycle life [5,6]. Compared to both inorganic solid electrolytes and liquid ones, solid polymer electrolytes (SPEs), in general, show the better flexibility in

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combination with the higher safety [7–9].

Polymers of polyethylene oxide (PEO) have been studied as hosts of SPEs for several decades since Wright et al. discovered ionic transport of PEO complex with alkali metal salts [10]. PEO-based SPEs exhibit many advantages, such as high capacity in salt complexation, high ionic conductivity in amorphous state, acceptable commercial cost, mechanical flexibility and good corrosion resistance [11,12]. Moreover, PEO-based membranes can be used in SSLBs in a free standing form without modifying current battery fabrication. However, the low conductivity of approximately 10^{-7} S cm^{-1} at ambient temperature attributed to the low effective carrier mobility in the crystalline region below melting temperature (~60 °C) limits its technical application [13,14]. To overcome such shortcoming, a variety of methods were applied to improve the Li-ion conductivity in the PEO matrix including reduction of crystallization and weaken of the interaction between the Li-ion and the PEO chains. A conventional approach was introduction of liquid plasticizers such as propylene carbonate (PC) and ethylene carbonate (EC) into the PEO-LiX matrix in order to maintain the amorphous state of the polymer [15]. In addition, the polymer blending by introducing another polymer like polymethyl methacrylate (PMMA) could also enhance the ionic conduction of PEO-based systems [16]. However, these composite membranes with plasticizers or another polymer show poor mechanical strength and high reactivity with electrodes. Inorganic nanomaterial fillers such as Al_2O_3, TiO_2, and SiO_2 were also used to decrease polymeric crystallinity, which could improve the ionic conductivity [17,18].

In our previous work, the SPEs consisting of Li-salt-free PEO and $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) particles in different size were prepared and their properties were investigated [19]. The membranes with 40 nm-sized LLZTO exhibit the excellent conductivity of 2.1×10^{-4} S cm^{-1} at 30 °C beneficial by the percolation effect. Compared to the PEO doped with the lithium salt, the membranes with pure PEO showed the improved ability to suppress the lithium dendrite growth. This was attributed to the fact that the accumulation of lithium was hampered in the Li-salt-free polymer. With these membranes, the $LiFePO_4$/Li and $LiFe_{0.15}Mn_{0.85}PO_4$/Li cells showed good cycle performance. Nevertheless, these cells had to operate at 60 °C due to high interfacial resistance between the electrodes and the electrolytes at room temperature. In fact, the operation temperature above 60 °C raises problems concerning the stability of electrolyte membranes. In addition, 40 nm-sized LLZTO particles which are important for the high conductivity are difficult with the ball-milling process, and the agglomeration tend makes the reproducibility poor. Recently, the incorporation of ionic liquids (ILs) into the polymer electrolytes becomes a very promising approach to enhance conductivity [20,21]. Their desirable properties such as non-volatility, non-flammability, high conductivity and high thermal stability attract intensive interest [22,23].

Herein, we use 200 nm-sized LLZTO particles and $[BMIM]TF_2N$ of 1.8 μL cm^{-2} to wet the interface of PEO/LLZTO, leading to the conductivity comparable with that of PEO combined with 40 nm-sized LLZTO. $[BMIM]TF_2N$ as imidazolium-based ILs shows low viscosity, which is good at mobility increase of ionic carriers. In addition, $[BMIM]TF_2N$ exhibits large electrochemical window of 5 V and it is stable against PEO matrix and Li anodes [24]. The composite electrolytes of PEO/LLZTO interfacially wetted by IL (abbreviated PEO/LLZTO@IL) are homogeneous solid electrolytes rather than the gel electrolytes. Compared with a large amount of IL adding in the system, there is no liquid-phase release from the PEO matrix when the pressure of 5.0×10^4 Pa being applied for 24 h. The PEO/LLZTO@IL shows high conductivity, large electrochemical window and low activated energy at 20 °C. In addition, the composite membranes are sticky, which can firmly adhere with electrodes to decrease the interface impedance. As a result, the good cycle stability and high capacity retention are achieved in $LiFePO_4$/Li and $LiFe_{0.15}Mn_{0.85}PO_4$/Li batteries at 25 °C.

2. Experimental section

2.1. Materials preparation

PEO (Mv = 2×10^6 g mol^{-1}, sigma-Aldrich) was dried at 60 °C overnight under vacuum prior to the sample preparation. $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) ceramic powders were prepared by conventional solid-state reaction as described in our previous paper [25]. Crushed by planetary ball-milling and high-energy ball-milling, the initial LLZTO particles of approximately 5 μm were reduced to 200 nm. LiTFSI (99.95%, sigma-Aldrich), anhydrous acetonitrile (ACN, Sigma-Aldrich), PVDF (Aladdin), super-p conductive additives (SP, Timcal), $LiFePO_4$ (LFP), $LiFe_{0.15}Mn_{0.85}PO_4$ (LFMP), $[BMIM]TF_2N$ (sigma-Aldrich) were used as received.

2.2. The fabrication process of the composite electrolytes of PEO/LLZTO@IL

The fabrication process of PEO/LLZTO@IL was illustrated as follows: a certain volume of LLZTO particles with $[BMIM]TF_2N$ (0.2 mL) were added into ACN (25 mL) and dispersed by sonication to improve the dispersion. After that, PEO (1 g) were added into the solution and stirred continuously for 8 h. Then, homogenized colloidal solution was cast onto a glass plate. Consequently, the ACN of the slurry was evaporated in a vacuum oven at 60 °C for 12 h. All the procedures sensitive to moisture or oxygen were carried out in an Ar-filled glovebox (M-Braun, Germany) with H_2O and O_2 contents below 0.1 ppm. The PEO/LLZTO@IL was successfully prepared and the typical thickness of the membranes was approximately 20 μm. PEO/LLZTO solid polymer electrolyte (abbreviated PEO/LLZTO) and PEO-only membranes were also fabricated by the same methods.

2.3. Sample characterization

The X-ray diffraction (XRD) was performed on the Bruker D2 Phaser with Cu K_α radiation (λ = 1.5406 Å) with 2θ in range of 10°-80° and collected with a step-width of 0.02° at 20 °C to characterize the crystalline structure of ingredients and synthesized membranes. The particle size distribution was tested by Zeta Plus (Brookhaven) laser particle size analyzer, using ethanol as solvent and triethanolamine (TEA) as dispersant. The field emission scanning electron microscope (FESEM, Magellan 400) was employed to determine the morphologies of surface and cross-section of the samples. The cross-section was obtained by liquid nitrogen quenching and all the samples for FESEM were coated with a thin gold layer via sputter coating. The content of Li^+ releasing from LLZTO particles was measured by inductively coupled plasma mass spectrometry (ICP-MS).

2.4. Electrochemical measurement and cells assembly

The ionic conductivity of the SPEs was measured by the NOVOCONTROL spectrometer fitted with a temperature control system at varied temperatures from 20 °C to 60 °C, which was carried out in the frequency range from 0.01 Hz to 40 MHz. The block/SPE/block cells were used stainless steel (SS) electrodes as the block. The lithium ion transference number was tested in a Li/SPE/Li cell (Autolab PGSTAT 302N system). The symmetric battery was polarized with a DC voltage of 10 mV. The AC impedance spectroscopy before and after polarization were obtained. Linear sweep voltammetry (LSV) was conducted on each composite electrolyte from 3 V to 6 V at a scan rate of 10 mV s^{-1} by Arbin BT-2000. The LFP, PVDF, LiTFSI and SP with the optimum weight ratio of LFP or LFMP: LiTFSI: SP: PVDF = 5: 3.5: 1: 0.5 were coated on Al foils to form the composite cathode [26]. The lithium metals in thickness of approximately 50 μm pressed on Cu foils were used as the anodes. LFP or LFMP/SPE/Li 2025 type cion cells with SPE films of 19 mm diameter were charged and discharged between 2.8 V and