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High-performance $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$/Poly(ethylene oxide)/Succinonitrile composite electrolyte for solid-state lithium batteries

Wenping Zha, Fei Chen*, Dunjie Yang, Qiang Shen, Lianmeng Zhang

State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, 430070, China

HIGHLIGHTS

- LLZTO ceramic electrolyte was combined with PEO polymer electrolyte.
- A solid plasticizer SN was incorporated into LLZTO/PEO composite electrolyte.
- The ionic transport properties and interfacial behaviors were greatly improved.
- The $LiFePO_4$/Li batteries exhibited excellent rate and cycling performance.

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ABSTRACT

In this work, the scalable ceramic-polymer composite electrolytes composed of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$, poly(ethylene oxide), lithium bis(trifluoromethane)sulfonimide, and solid plasticizer succinonitrile are prepared in the form of flexible membranes. The ionic transport properties, electrochemical stability, and interfacial behaviors against lithium electrode of this electrolyte are systematically investigated. Among these electrolytes, the sample containing 60 wt.% $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ and 10 wt.% succinonitrile presents a maximum conductivity of 1.22×10^{-4} S cm^{-1} at 30 °C, and exhibits a broadened electrochemical stability window of 5.5 V vs. Li/Li$^+$. Moreover, the ionic transference number of this electrolyte is improved to 0.41, and the interfacial compatibility against lithium electrode is excellent under both static and dynamic conditions. Excellent cycling and rate performance of the Li/$LiFePO_4$ cells are resulted from the enhanced ionic transport properties and improved interfacial contact between electrolyte and electrodes. The cell run at 0.5C delivers a discharge specific capacity of 151.1 mAh·g^{-1} after 200 cycles under 60 °C, and retains 98% of the maximum specific capacity. Notably, this cell also can be successfully charged and discharged at 45 °C and still delivers a discharge capacity of 124.1 mAh·g^{-1} after 70 cycles at 0.5 C.

1. Introduction

So far, significant attention has been paid to lithium-ion batteries (LIBs) with high output voltage and energy density, because of their widely applications in portable electronic equipment, electric vehicles (EVs) and energy storage systems (ESSs) [1–3]. Unfortunately, the intrinsic safety issue that originates from the volatile and flammable liquid electrolytes is one of the biggest obstacles for the further development of LIBs [4,5]. For this reason, solid-state lithium batteries (SSLBs) fitted with solid electrolytes instead of liquid electrolytes have been developed to improve the safety of conventional lithium-ion batteries and to simplify battery architecture [6].

To develop high-performance SSLBs, an ideal solid electrolyte should simultaneously possess many properties such as high ionic conductivity at room temperature, excellent interfacial contact with electrodes, wide electrochemical stability window, good chemical stability and flexibility [7,8]. However, it is a tough task to integrate all of these properties in one solid-state electrolyte. In the case of ceramic electrolytes, although they usually exhibit relatively high ionic conductivity at room temperature and wide electrochemical window, their brittle property and poor interfacial contact with electrodes prevent their large-scale applications in commercial LIBs [9]. On the other hand, in comparison with ceramic electrolytes, solid polymer electrolytes (SPEs) possess several advantages such as good flexibility, light weight, and relatively intimate adhesion to electrodes [10]. However, most SPEs suffer from low room temperature ionic conductivity, which limits their practical application at ambient temperature [11,12]. Moreover, their poor mechanical properties make them easily pierced

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* Corresponding author.
E-mail address: chenfei027@whut.edu.cn (F. Chen).

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by lithium dendrites, which may cause short circuits between two electrodes [13]. To overcome the intrinsic defects of ceramic electrolytes and SPEs, composite electrolytes incorporating ceramic particles with polymers have been studied to improve ionic transport properties and maintain superior mechanical strength simultaneously [12,14–17].

Despite the chemical sensitivity with moisture [18], the garnet-structured $Li_7La_3Zr_2O_{12}$ (LLZO) and its derivatives have attracted increasing attention as lithium-ion conductors for SSLBs owing to their high ionic conductivity ($10^{-4} \sim 10^{-3}$ S cm^{-1}), wide potential window ($\sim$6V vs. Li/Li$^+$), and chemical stability against lithium metal [19–23]. Among SPEs, poly (ethylene oxide) (PEO)-based electrolytes have numerous advantages such as low cost, ability to solvate a variety of salts, and relatively high chemical and electrochemical stability as compared to other poly-ethers or copolymers [24]. Accordingly, PEO is the most extensively studied and suitable polymer host for free-standing polymer electrolytes. Considering the superiorities of PEO and LLZO, we choose these two kinds of electrolytes as the main materials of composite electrolyte. To further improve the ionic transport properties of electrolyte and the interfacial contact between the electrodes and the electrolyte, the addition of a solid plasticizer, succinonitrile (SN), is considered to be an efficient solution. Unlike liquid plasticizers, SN remains a plastic crystalline phase between −40 °C and the melting point (60 °C) and maintains the mechanical properties and high safety performance of the composite electrolyte [25]. The high polarity of SN molecules enables the dissolution of variety of lithium salts [26], and the interactions between nitrile groups (-C≡N) and Li$^+$ ions contribute to an enhanced ionic conductivity of the electrolyte [10]. Furthermore, the addition of solid plasticizer can improve the plasticity and viscosity of the composite electrolyte, which facilitates the interfacial contact between the electrolytes and the electrodes.

In this study, we prepared a flexible and scalable composite electrolyte composed of tantalum-doped LLZO (LLZTO), PEO-LiTFSI and SN. The ionic transport properties, electrochemical stability, and interfacial behaviors against lithium electrode of this electrolyte were systematically investigated. Further, the feasibility and performance of SSLBs (Li/$LiFePO_4$) fitted with this composite electrolyte were assessed.

2. Experimental

2.1. Preparation of composite electrolytes

High purity Li_2O (99.99%, Aladdin), La_2O_3 (99.99%, Sinopharm Chemical Reagent Co., Ltd.), ZrO_2 (99.9%, Guangdong Orient Zirconic Ind. Sci. & Tech. Co., Ltd., China), and Ta_2O_5 (99.99%, Aladdin) powders were employed, and the molar ratio among Li, La, Zr and Ta was controlled according to the formula $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO). The mixture was thoroughly dispersed in isopropyl alcohol by ball milling for 24 h and dried at 60 °C for 12 h to evaporate the solvent. LLZTO was fabricated via a one-step sintering method by field assisted sintering technology (FAST) at the temperature of 1100 °C under a constant uniaxial pressure of 10 MPa with a holding time of 3 min [27]. Then the sample was ground into powder and screened with 500-mesh sieves. The ceramic-polymer composite electrolytes (x%LLZTO-PEO$_{18}$-LiTFSI-y %SN) were fabricated via conventional solution-casting technique, wherein x and y represent the mass ratio of LLZTO and SN in the electrolytes, respectively. Taking the sensitivity of the raw materials to water and oxygen into account, all the experiments were carried out in glove boxes (H_2O and O_2 < 0.1 ppm) under argon atmosphere. First, PEO (Mw = 5×10^6, Aladdin) and lithium bis (trifluoromethane) sulfonimide (LiTFSI, 99%, Aladdin) were mixed with molar ratio of 18:1 (EO: Li) and dissolved in acetonitrile (ACN, Aldrich), into which LLZTO powder and SN with different weight ratio were added under vigorous stirring. A homogeneous mixed solution was finally formed after stirring for 24 h at room temperature. Secondly, each slurry was casted onto a Teflon plate using a doctor blade, then the Teflon plate was dried at room temperature for 24 h and followed by vacuum drying at 45 °C for another 24 h to completely evaporate the solvent. Finally, the dried electrolyte membranes were peeled off from the Teflon plate and punched into circles with diameters 18 mm for further measurements. The thickness of the membranes was approximately 100 μm. It should be noted that the content of SN was not increased above 10 wt.%, because the self-standing membranes were difficult to be obtained when the SN content exceeds 10 wt.% [28].

2.2. Characterization of the composite electrolytes

The morphologies of LLZTO particles and composite electrolytes were observed by filed-emission scanning electron microscopy (FESEM, FEI-Quanta-250). The elemental distribution on the cross-sectional area of the composite electrolyte was examined by energy dispersive X-ray spectroscopy (EDX). The particle size distribution of LLZTO powders was obtained from the particle size analyzer (PSA, Mastersizer2000). The phase structures of the LLZTO and composite electrolytes were characterized by X-ray diffraction (XRD, Rigaku Ultima III) measurements with Cu Kα radiation over the range of 10° ~ 60° at the scan rate of 4°/min. The thermal properties of the composite electrolytes were characterized by a low-temperature differential scanning calorimetry (DSC, PYRIS1DSC) instrument with a heating rate of 10 °C·min^{-1} from −60 °C to 90 °C under N_2 atmosphere.

The stainless steel/electrolyte/stainless steel (SS/electrolyte/SS) cells were assembled to investigate ionic conductivities in the range of 20 °C–90 °C. The electrochemical impedance spectroscopy (EIS) measurements were carried out by an electrochemical work station (CHI660E, Shanghai Chenhua instrument Co., Ltd.) with an oscillation voltage of 10 mV over the frequency range from 10 Hz to 10^6 Hz. The ionic conductivity was calculated using following equation

$$\sigma = \frac{L}{R \cdot S} \tag{1}$$

where σ (S·cm^{-1}) is the ionic conductivity, R (Ω) is resistance value of the bulk electrolyte measured by electrochemical impedance spectroscope, and L (cm) is the thickness of electrolyte membrane, and S (cm^2) is the area of stainless steel electrode. To investigate the electrochemical stability window of the composite electrolytes, the linear sweep voltammetry (LSV) experiments were performed by SS/electrolyte/Li cells with a scanning rate of 1.0 mV s^{-1} at 60 °C from 3 V to 6 V (vs. Li$^+$/Li). The lithium ion transference number (t_{Li^+}) was measured by a combination measurement of AC impedance and DC polarization at 60 °C. The symmetric Li/electrolyte/Li cell was polarized under a small polarization potential (ΔV) of 10 mV. The lithium ion transference number was calculated using following equation

$$t_{Li^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{SS} R_{SS})} \tag{2}$$

where I_0 and I_{ss} represent the initial current and steady current flowing through the symmetric cell, and R_0 and R_{ss} represent the initial and steady values of the interfacial resistances between electrolyte and lithium metal. The aging stability between electrolytes and lithium electrode was monitored by measuring the AC impedance of symmetric Li/electrolyte/Li cell for different aging time at 60 °C. The galvanostatic lithium plating and stripping measurements of symmetric Li/electrolyte/Li cells were performed at different current density and 60 °C.

2.3. Preparation and electrochemical performance of SSLBs

The CR2025-type coin cells consisted of $LiFePO_4$ as the positive electrode, the composite electrolyte as the separator, and lithium mental as the negative electrode were assembled. The positive electrode was made up of 70 wt.% $LiFePO_4$ powder, 10 wt.% Super-P, 15 wt.% PEO$_{18}$-LiTFSI, and 5 wt.% SN. The charge and discharge performance of SSLBs was tested on a Land charge/discharge instrument (Wuhan Rambo Testing Equipment Co., Ltd.) at a charge and discharge rate of