



Flexible poly(ethylene carbonate)/garnet composite solid electrolyte reinforced by poly(vinylidene fluoride-hexafluoropropylene) for lithium metal batteries



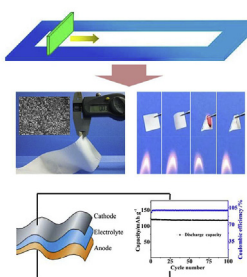
Zijian He, Long Chen, Bochen Zhang, Yongchang Liu, Li-Zhen Fan*

Beijing Advanced Innovation Center for Materials Genome Engineering, Institute of Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China

HIGHLIGHTS

- Nanosized LLZO was synthesized by solution combustion method.
- The flexibility of composite solid electrolytes is enhanced by P(VdF-HFP).
- Composite solid electrolytes have excellent thermal stability.
- Lithium ion transference number is up to 0.82 at 55 °C.
- All-solid-state LiFePO₄|Li cells exhibits stable cyclability at 1C.

GRAPHICAL ABSTRACT



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ABSTRACT

Solid-state electrolytes with high ionic conductivities, great flexibility, and easy processability are needed for high-performance solid-state rechargeable lithium batteries. In this work, we synthesize nanosized cubic Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ (LLZO) by solution combustion method and develop a flexible garnet-based composite solid electrolyte composed of LLZO, poly(ethylene carbonate) (PEC), poly(vinylidene fluoride-hexafluoropropylene) (P(VdF-HFP)) and lithium bis(fluorosulfonyl)imide (LiFSI). In the flexible composite solid electrolytes, LLZO nanoparticles, as ceramic matrix, have a positive effect on ionic conductivities and lithium ion transference number (t_{Li^+}). PEC, as a fast ion-conducting polymer, possesses high t_{Li^+} inherently. P(VdF-HFP), as a binder, can strengthen mechanical properties. Consequently, the as-prepared composite solid electrolyte demonstrates high t_{Li^+} (0.82) and superb thermal stability (remaining LLZO matrix after burning). All-solid-state LiFePO₄|Li cells assembled with the flexible composite solid electrolyte deliver a high initial discharge specific capacity of 121.4 mAh g⁻¹ and good cycling stability at 55 °C.

1. Introduction

Rechargeable lithium ion batteries are one of the advanced technologies for portable electronic devices, electric vehicles and energy storage systems [1,2]. Using lithium metal anode is an attractive way to increase energy density of batteries because of the unprecedentedly

high theoretical capacity of 3860 mAh g⁻¹ and the lowest negative electrochemical potential (-3.040 V vs. the standard hydrogen electrode) [3,4]. Unfortunately, the formation of lithium dendrites together with a low Coulombic efficiency during cycling prevents practical use of lithium metal anode in rechargeable lithium metal battery (LMB). Recently, remarkable progress has been made to address the dendrite

* Corresponding author.

E-mail address: fanlizhen@ustb.edu.cn (L.-Z. Fan).

growth problem in LMB, such as introducing 3D nickel foam host to prestoring lithium [4] and using solid electrolytes to block dendrites [5,6]. Among various strategies, it is important and challenging to develop solid electrolytes for high-voltage, high-energy-density and safe LMB [7–9]. In the past few years, major advances have been achieved in increasing the ionic conductivity of solid state electrolytes [10,11]. For the state-of-the-art solid electrolyte materials, cubic garnet-type $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) has attracted tremendous interest owing to its high ionic conductivity [12] and high stability to lithium metal [13]. After achieving adequate ionic conductivity in the cubic garnet-type LLZO materials, a challenge for LLZO materials is their high interfacial impedance caused by the poor wettability of LLZO against lithium metal [14], resulting in a poor contact between them, an uneven ion flow through interface, and a large polarization. Recently, various interfacial processing techniques have been attempted to reduce the high solid/solid interfacial impedance, such as polymer/ceramic/polymer [15], cosintering [16], and surface coatings [17,18]. Unlike polymer electrolyte [7,19], another challenge facing the ceramic solid electrolyte is lacking of flexibility that leads to poor contact at the electrode/electrolyte interface and high interfacial resistance during cycling. Therefore, the performance of solid-state battery still urgently needs to be improved. Taking advantages of both ion-conducting ceramics and polymers, composite polymer electrolytes have been considered as a potential way to prepare high performance solid electrolyte, which can keep good contact with electrodes during charging and discharging due to the inherent soft features of polymer solid electrolytes [7,19–21]. For example, polymer solid electrolytes loaded with dispersed SiO_2 [22–24], LLZO [25,26] particles or with organic fillers [27], have greatly improved the battery performance. However, one intrinsic obstacle to the conventional polymer-based (such as poly(ethylene oxide)-based) composite solid electrolytes is their relatively low lithium ion transference number (t_{Li^+}), only about 0.2–0.5 [28–30]. Low t_{Li^+} would build up the anion concentration gradients, which may result in salt decomposition and precipitation. Encouragingly, there are more and more research focusing on polycarbonate-based polymer electrolytes recently, such as poly(ethylene carbonate) [31,32], poly(propylene carbonate) [33,34], poly(trimethylene carbonate) [35,36], which have shown high t_{Li^+} . Given the high t_{Li^+} and excellent ability to penetrate into porous electrodes [37] of polycarbonate-based polymer electrolyte, a composite solid electrolyte that combined the advantages of LLZO and polycarbonate polymer is of great interest. In the flexible garnet-based composite solid electrolyte, on one hand the LLZO matrix that interacts with anion can reduce the double-layer electric field between Li metal and electrolyte, and suppress the electrochemical decomposition of polymer solid electrolyte; on the other hand, the polymers allow uniform distribution of Li^+ flux dominated by LLZO nanoparticles and good wetting ability toward porous electrodes. So these are beneficial for the suppression of lithium dendrite growth and the improvement of battery cycling performance.

In this study, flexible garnet-based composite solid electrolyte is prepared by incorporating a small amount of PEC with nano-sized LLZO, and further its flexibility is reinforced by poly(vinylidene fluoride-hexafluoropropylene) (P(VdF-HFP)). Optimum t_{Li^+} of 0.82 and stable interface resistance of 124 ohms cm^{-2} at 55 °C were achieved for the flexible composite solid electrolyte. $\text{LiFePO}_4/\text{Li}$ all-solid-state batteries using the optimized composite electrolyte exhibited excellent cycling performance and rate capability. A specific capacity of 121.4 mAh g^{-1} was delivered and the capacity retention is 96.3% at 1 rate (C) after 100 cycles at 55 °C. Remarkable performance can be attributed to the high t_{Li^+} and the excellent ability to penetrate porous electrodes of flexible ceramic-based composite electrolyte.

2. Experimental

LiNO_3 , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and glycine with purity of 99.99% are provided by Aladdin. Lithium bis

(fluorosulfonyl)imide (LiFSI, Sigma), Poly(ethylene carbonate) (PEC, $M_w = \sim 2.38 \times 10^5$, Empower Materials), and poly(vinylidene fluoride-hexafluoropropylene) (P(VdF-HFP), $M_w = \sim 400,000$, Sigma-Aldrich) were dried in a vacuum oven at 80 °C for 24 h.

The nanosized powders of Al-doped cubic $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) were synthesized through solution combustion method followed by ball-milling. Firstly, according to the stoichiometry of $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$, LiNO_3 , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in deionized water. Secondly, glycine was added to the above homogeneous solution at the molar ratio of 1: 4 (glycine to nitrate ion). 10% excess of LiNO_3 was added to compensate for lithium loss during the synthesis. After that, the foam was generated when solution was evaporated gradually in heating process. Subsequently, the foam started to burn with a flame and the obtained combustion products were white powders. The acquired precursor powders were pressed into 2 mm-thick pellets with a diameter of 15 mm. The pellets were calcined in air at 800 °C for 4 h at a heating rate of 5 °C min^{-1} . After cooling down, the pellets were ball milled in Teflon jars in isopropanol for 10 h, followed by drying. The as-prepared LLZO powders were in pure cubic phase, as confirmed by X-ray diffraction (XRD) measurement.

The flexible garnet-based composite solid electrolyte membrane was prepared by solution-casting method. Various stoichiometric mass ratios of PEC, LiFSI, LLZO powder, P(VdF-HFP), and *N,N*-dimethylformamide (DMF) were stirred until forming a highly viscous slurry. After homogenization, the dispersion was cast on Teflon dishes and dried slowly in an Argon filled chamber. Residual solvent was completely removed by heating the electrolyte film in vacuum at 80 °C for 12 h. The weight proportions of nanosized LLZO, PEC, P(VdF-HFP) and LiFSI are 70: 30: 5: *x* in 70LLZO-30PEC-5P(VdF-HFP)-*x*LiFSI composite electrolyte. For example, 7 g LLZO, 3 g PEC, 0.5 g P(VdF-HFP) and 6 g LiFSI denote as 70LLZO-30PEC-5P(VdF-HFP)-60LiFSI composite electrolyte. The thickness of the prepared composite electrolyte membrane can be controlled by optimizing the amount of slurry and the scale of the Teflon mould.

XRD analysis of both the nanosized cubic LLZO powders and 70LLZO-30PEC-5P(VdF-HFP)-60LiFSI composite electrolyte was performed on Rigaku/mac diffractometer equipped with $\text{Cu K}\alpha$ radiation. Particle size distribution of the as-prepared LLZO powders was analyzed with Mastersizer 2000 laser particle size analyzer. Differential scanning calorimetry (DSC) measurements were carried out under nitrogen (N_2) atmosphere with DSC 2000 instrument from –80 °C to 100 °C at a heating rate of 10 °C min^{-1} . Thermo-gravimetric analysis (TGA) was tested with a Discovery TGA instrument under dry N_2 flow at a heating rate of 10 °C min^{-1} over a temperature range of 25–900 °C. Field-emission scanning electron microscopy (FE-SEM) images were obtained with ZEISS SUPRA 55 microscopes.

The ionic conductivities of composite electrolyte membrane were tested by Solartron 1260 + 1287 electrochemical workstation with frequency range from 1 MHz to 1 Hz and amplitude of 10 mV between 25 and 90 °C using stainless steel (SS) as a blocking electrode. The lithium ion transference number of composite electrolytes at 55 °C was measured by alternating current (AC) impedance and direct-current (DC) polarization (with a DC voltage of 10 mV) using a symmetric $\text{Li}|\text{electrolyte}|\text{Li}$ cell. The electrochemical stability of composite solid electrolyte was evaluated using cyclic voltammetry (CV) at a sweep rate of 1 mV s^{-1} between 0 and 5.5 V at 55 °C, with a stainless steel as working electrode and lithium metal as the reference and counter electrode. Galvanostatic cycling of the symmetric $\text{Li}|\text{electrolyte}|\text{Li}$ cell was conducted at a constant current density on a LAND-CT2001A (Wuhan Jinnuo Electronics. Ltd.) battery testing system.

To prepare cathode, the mixture of active material LiFePO_4 (Aleees), Super-P, and poly(vinylidene fluoride) (PVdF) (80:10:10 by weight) was dispersed in *N*-methylpyrrolidone followed by sufficient grounding. The obtained slurry was spread evenly on aluminum foil and dried at 100 °C for 24 h under vacuum. The active material loading of cathode

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