



Full paper

A durable and safe solid-state lithium battery with a hybrid electrolyte membrane

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ABSTRACT

Polymer–ceramic composite electrolytes are emerging as a promising solution to achieving high ionic conductivity, optimal mechanical properties, and good safety for developing high-performance all-solid-state rechargeable batteries. In this work, we report a garnet ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$)-based hybrid solid electrolyte (HSE) membrane designed for high performance solid-state lithium batteries for the first time. The composite HSE membrane is composed of LLZO particles and PVDF–HFP polymer matrix. The solid-state lithium battery with this HSE membrane, Li metal anode and LiFePO_4 cathode exhibits an initial reversible discharge capacity of 120 mA h g^{-1} at a charge/discharge current density of 0.5 C at room temperature. This solid-state battery is used to store the energy harvested by a TENG at different rotation rates. The solid state battery can efficiently store the pulsed energy, especially for output at high frequencies.

1. Introduction

The ever-increasing energy crisis and environment pollution demands the development of clean and efficient energy storage devices. Among various energy storage devices, Li-ion batteries are the most popular type because of their high volume and gravimetric energy densities [1–3]. However, the present energy densities of Li-ion batteries based on intercalation materials cannot meet the requirement of long-distance transport (i.e., > 300 km). Moreover, the use of flammable liquid electrolytes in Li-ion batteries raises potential safety concerns, especially for large batteries in electric vehicles (EVs) and grid applications. Therefore, solid-state lithium batteries (SSLBs) with solid state electrolytes are highly desired due to several advantages, including higher energy density, longer cycle life, and better safety, and so on, compared with the traditional Li-ion batteries [4–7]. For the solid electrolytes, lithium-stuffed garnet-type oxide with the formula of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) has been widely studied because of its high conductivity above $10^{-4} \text{ S cm}^{-1}$ at room temperature, excellent thermal performance, and stability against Li metal anode [8–11]. However, the electrochemical performances of solid-state batteries are poor because of the high interfacial resistance between solid electrolytes and solid electrodes [12,13]. Moreover, the ceramic materials are too hard and brittle for flexible battery applications [14].

As one of the most favorable solid state electrolytes, solid polymer electrolytes (SPE) have caused the extensive concern because of their flexibility, a wide range of operation temperature, and excellent cycle life. Meanwhile, the SPE can effectively suppress the growth of Li dendrites and thus avoid short-circuit of batteries [15–17]. Although various polymers have been widely studied as solid state electrolytes, including poly(ethylene oxide) (PEO) [18,19], poly(vinylidene fluoride)(PVDF) [20,21], poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) [22,23], polyacrylonitrile (PAN) [24], poly(methyl methacrylate) (PMMA) [25], there still are many intrinsic challenges for SPEs. For example, PEO-based solid polymer electrolytes have good mechanical properties like high flexibility and lightweight, but they tend to exhibit low ionic conductivity ($< 10^{-5} \text{ S cm}^{-1}$ at room temperature) with a low cation transference number ($t = 0.2\text{--}0.4$) and poor oxidation resistance [26]. Therefore, it is very urgent to develop an electrolyte simultaneously with high ionic conductivity, good interfacial and mechanical properties, fine thermal and electrochemical stabilities, as well as safety. As a possible candidate, PVDF-HFP is widely used as a host for SPEs because of its high dielectric constant and high ionic conductivity at room temperature arising from low crystalline and some functional groups with strong electron withdrawing effect [27,28]. However, the mechanical strength and the ionic conductivity of pure SPE membranes are not satisfactory. To solve this

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problem, some ceramic particles such as passive materials TiO₂ [29], SiO₂ [30], ZrO₂ [31], or active materials Li_{1.5}Al_{0.5}Ti_{1.5}(PO₄)₃ (LATP) [32], Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂ (LLZTO) [33] were dispersed or embedded into the polymer matrix to reinforce the mechanical stability. Moreover, the interaction of inorganic particles with polymer electrolyte not only can increase the mechanical strength, but also can decrease the crystallization of the polymer and as a result enhance the ion migration [33,34]. Because addition of the ceramic fillers are favorable for the formation of low-crystalline composite hybrid solid electrolyte (HSE) [35].

Herein, we report a garnet-based hybrid solid electrolyte (HSE) designed for a high safety solid-state lithium battery for the first time. The composite HSE design has several advantages, including high ionic conductivity, a wide electrochemical window, low solid/solid interface resistance and high thermal stability. The solid-state lithium battery with this HSE, a Li metal anode and a LiFePO₄ cathode exhibits an initial discharge capacity of 120 mA h g⁻¹ at a charge and discharge current density of 0.5 C at room temperature. It is also used to store the electrical energy harvested by TENG.

2. Experimental

2.1. Synthesis of the LLZO powders

LLZO was prepared via a facile sol-gel method. In a typical process, firstly, 0.0248 mol C₆H₈O₇·H₂O, 0.01224 mol C₁₀H₁₆N₂O₈, 0.007 mol LiNO₃, 0.003 mol La(NO₃)₃·6H₂O, 0.00175 mol ZrO (NO₃)₂·xH₂O, 0.00024 mol Al(NO₃)₃·9H₂O and 0.00025 mol C₂NbO₄ were dissolved in 40 ml deionized water under stirring. Then a certain amount of concentrated nitric acid and NH₃·H₂O was added to the above solution until the pH ≈ 8. Finally, a homogeneous solution was obtained and it was heated at 80 °C to vaporize solvent under magnetic stirring. The obtained sol was dried at 250 °C for 3 h and then eventually became gel. The obtained product was grounded and calcined at 850 °C in air atmosphere for 2 h in a muffle furnace.

2.2. Preparation of hybrid solid electrolyte (HSE) membranes

First, 1.5 g PVDF-HFP (Aldrich reagent Mw = 400000) was dissolved in 9 ml of mixed solvent of N, N-dimethylacetamide (DMAc) and acetone by a volume ration of 1:2. Then, 1.5 g LLZO powders were dispersed in the above PVDF-HFP solution, and the mixed LLZO and PVDF-HFP suspension was magnetically stirred with 2000 rpm to obtain homogeneous solution. Then, the resultant viscous homogeneous solution was spread on a clean Teflon plate by a doctor blade apparatus with a gap of 120 μm and the solvent was slowly evaporated to get the membrane. The collected solid membrane was oven dried at 60 °C for 5 h and then vacuum dried for 12 h. The uniform membrane was punched into circles with diameters of 16 mm and 14 mm respectively and then pressed at 8 MPa for further measurements.

2.3. Structure characterization of hybrid membranes

The morphologies of LLZO particles and hybrid electrolyte membranes were analyzed by a field emission scanning electron microscope (Hatchi SU8020). The crystal structure of LLZO particles and hybrid electrolyte membrane were examined by X-ray diffraction (XRD) measurements (Panalytical instrument X'Pert 3 Powder) with Cu Kα radiation in the range of 10–80°. The thermal stability of the pure PVDF-HFP electrolyte and PVDF-HFP/LLZO hybrid solid electrolyte were measured with a Seiko 6300 thermo-gravimetric (TG) analyzer under 200 ml min⁻¹ air flow with a heating rate of 10 °C min⁻¹. Tensile strength was conducted by using a universal mechanical tester (Instron4465, Instron Corp., USA) at room temperature. Six dumbbell shape specimens of dimension of 75 × 4 × 1 mm³ were tested at 100 mm min⁻¹.

2.4. Electrochemical measurements and cells assembly

The stainless steel (SS)/hybrid electrolyte membrane/SS cells were assembled to determine ionic conductivities. The electrochemical impedance spectroscopy (EIS) were measured in the temperature range from 25 °C to 100 °C using a ZENNIUME electrochemical workstation (Zahner, Germany) in the frequency range from 10⁶ Hz to 10⁻² Hz with a perturbation of 10 mV. The electrolyte membrane was sandwiched between a pair of stainless steel blocking electrodes with a diameter of 16 mm. And the ionic conductivity (σ) was calculated from the Eq. (1), where R is the resistance value of the bulk electrolyte measured by EIS with AC amplitude of 10 mV from 10⁶ Hz to 10⁻² Hz, and L is the thickness of electrolyte membrane, and S is the area of electrode.

$$\sigma = \frac{L}{RS} \quad (1)$$

The electrochemical stability window of the membranes were determined by linear sweep voltammograms (LSV) of the Li|HSE|SS cell with a working electrode of stainless steel and a counter electrode of lithium metal performed on CHI604E at a scan rate of 1 mV s⁻¹ over the potential range of 2–6 V at 25 °C.

Lithium ion transference number (t_{Li^+}) of the HSE was measured by a combination measurement of AC impedance and DC polarization using a symmetrical cell of Li/SPE/Li and was calculated using Eq. (2) as proposed by Vincent and co-workers [36]. The Li/SPE/Li cell was polarized by a DC voltage of 10 mV, and initial (I_0) and steady (I_{ss}) current flowing through the cell were measured. R_0 and R_{ss} , representing the resistance values before and after the perturbation of the system respectively, were obtained by impedance spectra of the cell in the frequency range from 1 MHz to 0.01 Hz with an oscillation voltage of 10 mV.

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

The electrochemical properties of the solid-state batteries were tested with a standard coin cell (CR2032) assembled in an argon-filled glove box. The lithium foil was used as anode in the cells and the HSE membrane was used as both electrolyte and separator. The cathode electrode slurry was mixed by LFP/carbon black/LLZO-PEO-LiClO₄ with a weight ratio of 7:1:2. In detail, the PEO ($M_w = 10^6$) = 0.13 g, LiClO₄ = 0.04 g, LLZO = 0.03 g, the prepared composite cathode has higher ionic conductivity. Then, the mixture of the components with acetonitrile was stirred for 24 h and cast onto aluminum current collectors. After vacuum drying at 60 °C for 5 h, the composite cathode electrode was obtained. The mass loading for LFP in the cathode pellets is in the range from 2.1 mg to 2.3 mg. For improving the interface contact of the HSE and metallic lithium foil, 20 μl liquid electrolyte of 1 M LiTFSI in TEGDME was introduced on the surface of the HSE membrane.

3. Result and discussion

3.1. Characterization of the PVDF-HFP: LLZO membrane

Cubic LLZO is one of the most promising solid state electrolytes for solid-state batteries because of its high ionic conductivity with a high cation transference number, chemical and electrochemical stability, as well as high mechanical strength. However, the cubic LLZO is usually prepared by a high temperature solid-state reaction. In this work, we synthesized the LLZO powder by a low temperature sol-gel method.

The Li ion conducting HSE, prepared via a simple tape casting method, is composed of LLZO powder, a poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) polymer matrix, and 1 M LiTFSI in TEGDME. In detail, we add 20 μL liquid electrolyte to the interface of HSE/electrode to reduce the interface resistance. The diameter of the

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