Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries

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Beyond state-of-the-art lithium-ion battery (LIB) technology with metallic lithium anodes to replace conventional intercalation anode materials is highly desirable because of lithium’s highest specific capacity (3,860 mA\textperiodcentered g) and lowest negative electrochemical potential (~3.040 V vs. the standard hydrogen electrode). In this work, we report for the first time, to our knowledge, a 3D lithium-ion-conducting ceramic network based on garnet-type Li\textsubscript{6.4}La\textsubscript{3}Zr\textsubscript{2}Al\textsubscript{0.2}O\textsubscript{12} (LLZO) lithium-ion conductor to provide continuous Li\textsuperscript{+} transfer channels in a polyethylene oxide (PEO)-based composite. This composite structure further provides structural reinforcement to enhance the mechanical properties of the polymer matrix. The flexible solid-state electrolyte composite membrane exhibited an ionic conductivity of 2.5 × 10\textsuperscript{-4} S/cm at room temperature. The membrane can effectively block dendrites in a symmetric Li | electrolyte | Li cell during repeated lithium stripping/plating at room temperature, with a current density of 0.2 mA/cm\textsuperscript{2} for over 500 h and a current density of 0.5 mA/cm\textsuperscript{2} for over 300 h. These results provide an all-solid-ion-conducting membrane that can be applied to flexible LIBs and other electrochemical energy storage systems, such as lithium–sulfur batteries.

Significance

This work describes a flexible, solid-state, lithium-ion-conducting membrane based on a 3D ion-conducting network and polymer electrolyte for lithium batteries. The 3D ion-conducting network is based on percolative garnet-type Li\textsubscript{6.4}La\textsubscript{3}Zr\textsubscript{2}Al\textsubscript{0.2}O\textsubscript{12} solid-state electrolyte nanofibers, which enhance the ionic conductivity of the solid-state electrolyte membrane at room temperature and improve the mechanical strength of the polymer electrolyte. The membrane has shown superior electrochemical stability to high voltage and high mechanical stability to effectively block lithium dendrites. This work represents a significant breakthrough to enable high performance of lithium batteries.


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ceramic as the inorganic component because of several desired conductivity approaching $10^{-5}$ S/cm at 30 °C, which needs additional improvement to achieve a higher ionic conductivity at room temperature. Based on our understanding, therefore, creating a continuous nanosized network with interconnected long-range ion transport and controlling a minimum/nonfiller agglomeration are the main directions to design high ionic-conductive polymer composite electrolytes.

In this work, we have successfully developed a 3D ceramic network based on garnet-type Li$_{x}$La$_{y}$Zr$_{z}$Al$_{n}$O$_{12}$ (LLZO) nanofibers to provide continuous Li$^+$ transfer channels in PEO-based composite electrolytes as all solid ion-conducting membranes for lithium batteries. Here, we select garnet-type lithium-ion-conducting ceramic as the inorganic component because of several desired physical and chemical properties, including (i) high ionic conductivity approaching $10^{-3}$ S/cm at room temperature with optimized element substitution, (ii) good chemical stability against lithium metal, and (iii) good chemical stability against air and moisture (11, 30, 31). Fig. 1 shows the schematic structure consisting of interconnected small crystallites to form a preformed 3D ceramic structure into Li salt–polymer electrolyte membrane. The Li salt–PEO polymer is then filled into the porous 3D ceramic networks, forming the 3D garnet–polymer composite membrane. Different from conventional methods to prepare polymer electrolytes, the 3D garnet–polymer composite membrane does not need to mechanically mix fillers with polymers; instead, we can directly soak nanofibers into polymer electrolyte membrane. As shown in Fig. 1, the electrolyte membrane maintains the framework of 3D garnet nanofiber networks and is believed to have a better mechanical property because of the continuous nanofiber structure that enhances the integrity of polymer electrolyte.

**Results and Discussion**

Fig. 2 schematically shows the procedure to synthesize flexible solid-state garnet LLZO nanofiber-reinforced polymer composite electrolytes. As shown in Fig. 2A, garnet LLZO nanofibers were prepared by electrospinning of polyvinylpyrrolidone (PVP) polymer mixed with relevant garnet LLZO salts followed by the calcination of the as-prepared nanofibers at 800 °C in air for 2 h. On the drum collector of the electrospinning setup, a thin nonwoven fabric was covered to collect the nanofibers. The schematic fabrication of fiber-reinforced polymer composite (FRPC) lithium-ion–conducting membrane using the 3D porous garnet nanofiber network is shown in Fig. 2B. A PEO polymer mixture with Li salt, such as bis(trifluoromethane)sulfonimide lithium salt (LiTFSI), is prepared. Then, the Li salt–PEO polymer is reinforced by the 3D nanofibers to form a composite electrolyte, which can be called FRPC electrolyte membrane. Compared with filler-containing polymer electrolyte, the FRPC electrolyte membrane maintains the framework of 3D garnet nanofiber networks and is believed to have a better mechanical property because of the continuous nanofiber structure that enhances the integrity of polymer electrolyte.

Fig. 3 shows the morphological characterization of the garnet nanofibers and resulting FRPC electrolyte. As shown in Fig. 3A, garnet nanofibers were bonded together at their intersection points, forming a cross-linked network. These interconnected garnet nanofibers offer a continuous ion-conducting pathway because of the extended long-range lithium transport channels, which should be superior to the isolated particle fillers that are distributed in typical polymer matrices (22). Fig. 3B and C shows the transmission electron microscopy (TEM) images of the garnet nanofibers. The garnet nanofiber has a polycrystalline structure consisting of interconnected small crystallites to form
the long, continuous nanofiber (Fig. 3B). Fig. S1 shows the magnified TEM image of a garnet nanofiber with an average grain size of 20 nm in diameter. Fig. 3C indicates the highly crystallized structure of the garnet grain.

The morphologies of FRPC electrolyte were examined by SEM (Fig. 3 D–F). The FRPC electrolyte exhibited a smooth surface, which came from the PEO–LiTFSI polymer (Fig. 3D). Inside of the FRPC electrolyte, we can see that the 3D porous garnet nanofiber network supported the main structure of the composite and that the PEO–LiTFSI polymer was infiltrated into the porous garnet network and filled the interspace between garnet nanofibers. The cross-section image of the FRPC electrolyte showed a thickness of 40–50 μm (Fig. 3E). To increase interphase contact between garnet nanofibers and PEO–LiTFSI polymer, the FRPC electrolyte was thermally treated at 60 °C, which is slightly above the polymer melting temperature ($T_m$), to enable the melted PEO–LiTFSI polymer to fully infiltrate the 3D porous garnet nanofiber network. As shown in Fig. 3F, after thermal treatment, PEO–LiTFSI polymer was fully embedded with garnet nanofibers. We can see that garnet nanofibers increased to an average diameter of 500 nm because of the PEO–LiTFSI polymer coating. The interconnected pores were filled with polymer to maintain good lithium-ion transfer. The FRPC electrolyte membrane is proposed to have three ion-conducting pathways: the first one is the interwelded ceramic garnet nanofiber network, the second one is the continuous garnet fiber–polymer interface, and the third one is the Li salt-containing polymer matrix. Because of the higher ionic conductivity of garnet-type electrolytes than that of Li salt-containing polymer electrolyte, we believe that the former two ion-conducting pathways are the dominant factors to provide improved ionic conductivity to the electrolyte membrane.
The FRPC electrolyte is able to address this concern, because the polymer electrolyte becomes flammable after loss of the polymer. Even after loss of the polymer, the FRPC electrolyte provides a ceramic barrier to physically block cathode and anode contact, even after loss of the polymer.

Thermogravimetry analysis (TGA) was used to study the garnet nanofiber formation during the calcination process. The TGA was carried out under airflow with a rapid heating rate of 10 °C/min. Fig. 4A shows the TGA profile of the as-spun nanofibers containing PEO polymer and garnet precursor. The result shows that, above 750 °C, the weight become stable, indicating that stable garnet nanofibers were formed. Fig. 4B compares the TGA profiles of the PEO–LiTFSI and the FRPC electrolyte. Both electrolytes were thermally stable to around 200 °C. In the rapid heating process, polymers began to decompose above 200 °C and showed a significant weight loss at around 400 °C because of the almost complete decomposition of the polymer. The slope at 400 °C was the decomposition of LiTFSI. For the FRPC electrolyte, the weight was stable at 500 °C, and the remaining was the garnet nanofiber membrane caused by the superior stability of garnet material in air. For the polymer electrolyte, the weight was stable at 650 °C, leaving with decomposed LiTFSI salt.

Thermal stability is an important consideration for using solid-state electrolytes, especially polymer electrolyte. Traditional liquid electrolytes, such as carbonate electrolytes, tend to cause thermal runaway when batteries are under extreme conditions of short circuits, overcharge, and high temperature (19). Because of its relatively high thermal stability, polymer electrolyte becomes a safer choice compared with liquid electrolyte. Because traditional polymer electrolytes are built on their own polymer structure and fillers cannot offer sufficient mechanical support for the electrolyte, the polymer electrolyte inevitably melts and shrinks at high temperature, especially above the polymer thermal decomposition temperature, which may cause direct contact between cathode and anode and is a significant safety concern. The FRPC electrolyte is able to address this concern, because the garnet nanofiber membrane within the polymer electrolyte provides a ceramic barrier to physically block cathode and anode contact, even after loss of the polymer.

Fig. 4C and D compares the combustion tests of a traditional polymer electrolyte and the FRPC electrolyte developed in this work. The traditional polymer electrolyte was prepared using the same recipe used to prepare the PEO–LiTFSI polymer but using garnet nanopowders (vs. the 3D garnet network) as fillers. The mass ratio of polymer and filler was controlled at 4:1. In Fig. 4C, the polymer electrolyte caught fire instantly when it came close to the ignited lighter and was quickly burned off into ashes. This high flammability indicates poor thermal stability of the polymer electrolyte. In comparison, the FRPC electrolyte exhibited an outstanding thermal stability; although the polymer component was gone, the garnet nanofiber membrane still retained its structure (Fig. 4D). This low-flammability FRPC electrolyte can provide enhanced safety for all lithium metal and LIBs.

Powder X-ray diffraction (XRD) patterns of LLZO garnet nanofibers that were calcined at 800 °C for 2 h are shown in Fig. 5A. Almost all of the diffraction peaks match very well with those of cubic-phase garnet Li5La3Nb2O12 (Joint Committee on Powder Diffraction Standards card 80-0457). Li5La3M2O12 (M = Nb, Ta) is the first example, to our knowledge, of a fast lithium-ion–conductive processing garnet-like structure, which is the typical structure that has been widely used as a model to study the garnet structure of LLZO material. Here, we use the standard Li5La3Nb2O12 XRD profile to identify the synthesized garnet nanofiber structure. A small amount of La2Zr2O7 was identified, but other impurities were below detection limit. According to the thermogravimetric results, decomposition of precursors to oxide was completed at ~750 °C. Additional heating at 800 °C resulted in reaction of the oxides and formation of cubic-phase LLZO garnet structure. However, the small amount of La2Zr2O7 phase could also be formed by lithium loss at elevated temperature.

The total lithium-ion conductivity of FRPC electrolyte was characterized by electrochemical impedance spectroscopy (EIS). Fig. 5B shows the typical Nyquist plots of FRPC electrolyte sandwiched between stainless steel blocking electrodes in the frequency range from 1 Hz to 1 MHz. Each impedance profile shows a real axis intercept at high frequency, a semicircle at intermediate frequency, and an inclined straight tail at low frequency. The intercept of the extended semicircle on the real axis and the semicircle in the high- and intermediate-frequency range represent the bulk relaxation of FRPC electrolyte. The low-frequency

Fig. 4. Thermal properties and flammability tests of the solid-state FRPC electrolyte. (A) TGA curve of the as-spun nanofibers. (B) TGA curves of Li salt–PEO polymer and FRPC electrolyte membrane. (C) Flammability test of Li salt–PEO polymer mixed with garnet nanoparticles. (D) Flammability test of FRPC electrolyte membrane.

Fig. 5. Phase structure of garnet fiber and electrical properties of solid-state FRPC electrolyte. (A) XRD pattern of the garnet nanofibers and the powder diffraction file (PDF) of Li5La3Nb2O12. (B) EIS profiles of the FRPC electrolyte membrane at different temperatures (25 °C, 40 °C, and 90 °C). (C) Arrhenius plot of the FRPC electrolyte membrane at elevated temperatures (from 20 °C to 90 °C and record every 10 °C increase). (D) LSV curve of the FRPC electrolyte membrane to show the electrochemical stability window in the range of 0–6 V. OCV, open-circuit voltage.
metal electrode to mimic the operation of charging and discharging lithium metal batteries. Fig. 6A represents the schematic of the symmetric cell setup. The FRPC electrolyte membrane was sandwiched between two lithium metal foils and sealed in a coin cell. Fig. 6B shows the time-dependent voltage profile of the cell with FRPC electrolyte membrane cycled over 230 h at a constant current density of 0.2 mA/cm² and a temperature of 15 °C. The symmetric cell was periodically charged and discharged for 0.5 h. The positive voltage is the Li stripping, and the negative voltage value refers to the Li plating process. In the first 70 h, the cell’s voltage slightly increased from 0.3 to 0.4 V and then, stabilized at 0.4 V.

When the testing temperature increased to 25 °C, the voltage dropped to 0.3 V because of the improved ionic conductivity at elevated temperature as shown in Fig. 6C. In the following long-time cycles, the voltage kept decreasing to 0.2 V with increasing cycle time to 700 h (Fig. S2). The fluctuation of voltage was caused by the surrounding environmental temperature change. Two voltage profiles of the symmetric cell at two different stripping/plating process times were compared as shown in Fig. S3. The voltage hysteresis apparently decreased with increase of cycle time. This decrease in voltage is quite different from the liquid electrolyte system, in which the voltage normally increases with the increase of time and is mainly ascribed to the non-uniform Li deposition and severe electrolyte decomposition that cause impedance increase (32). Similar voltage decrease has been observed in recent polymer electrolyte studies, but the reason why voltage keeps decreasing with the increasing cycle time has not yet been explained (23, 33). Based on our understanding, the decrease in voltage might be because of the improved interface between the electrolyte membrane and lithium metal during the repeated Li electrodeposition, which is confirmed by the EIS spectra of the symmetric cell measured at 300, 500, and 700 h (Fig. 6D). The depressed semicircles at lower frequency indicate decreased interfacial impedance between electrolyte membrane and lithium metal during cycling. At high frequency (Fig. 6E), the semicircle also decreased with the increased cycle time, indicating the decreased bulk impedance of the electrolyte membrane. When the current density increased to 0.5 mA/cm², the voltage increased to 0.3 V, and the cell also exhibited slight decrease in voltage with increasing time to 1,000 h (Fig. 6F), showing good cycling stability with long cycle life.

**Conclusion**

In conclusion, all solid ion-conducting membranes of 3D garnet–polymer composite were synthesized for lithium batteries. 3D garnet nanofiber networks were prepared by electrospinning and high-temperature annealing. The garnet nanofibers constructed an interwelded 3D structure that provides long-range lithium-ion transfer pathways and further provides structural reinforcement to enhance the polymer matrix. This flexible solid-state electrolyte composite membrane exhibited an ionic conductivity of 2.5 × 10⁻⁴ S/cm at room temperature. The membrane can effectively block dendrites in a symmetric Li | electrolyte | Li cell during repeated lithium stripping/plating at room temperature, with a current density of 0.2 mA/cm² around 500 h and a current density of 0.5 mA/cm² over 300 h. The decrease of voltage with increasing cycle time is observed for the symmetric cell, which is possibly because of the improved interfaces during repeated lithium electrodeposition. Our work is the first report, to our knowledge, of the development of 3D lithium-ion-conducting ceramic materials in solid-state electrolytes, which can be potentially applied to flexible LIBs and other electrochemical energy storage systems, such as lithium–sulfur batteries.

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Supporting Information

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**SI Text**

**Fabrication of Garnet Nanofibers.** An LLZO composition was selected for study. This Al concentration was chosen, because it was in the range where highly ion-conductive cubic phase would be formed (34). Stoichiometric amounts of LiNO$_3$ (99%; Alfa Aesar), La(NO$_3$)$_3$·6H$_2$O (99.9%; Alfa Aesar), ZrO(NO$_3$)$_2$·6H$_2$O (99.9%; Alfa Aesar), and Al(NO$_3$)$_3$·9H$_2$O (99.9%; Alfa Aesar) were dissolved in dimethylformamide with 15 vol % acetic acid. PVP (molecular weight, ~1,300,000) was dissolved in dimethylformamide with a concentration of 10 wt%. The salt solution and PVP solution were mixed at a 1:1 ratio in volume to prepare the precursor solution for electrospinning. During electrospinning, a high voltage of 20 kV was applied between the needle and the drum collector. The drum collector was connected to the ground. The distance between the needle and the drum collector was 10 cm. The drum collector was covered with a thin nonwoven fabric to collect the as-spun nanofibers. The rotation speed was controlled, and the humidity of the electrospinning chamber was no more than 20%. After electrospinning, the as-spun nanofibers were peeled off the nonwoven fabric and kept in a vacuum oven for 24 h to dry completely. The free-standing nanofiber mat was then calcinated at 800 °C for 2 h in air at a heating rate of 10 °C/min. After thermal annealing, a garnet nanofiber mat was obtained.

**Preparation of Electrolyte Membrane.** The Li salt–polymer composite solution was prepared by dissolving LiTFSI (Sigma) and PEO (molecular weight, ~600,000) in acetonitrile. Then, the solution was dropped onto the garnet nanofiber membrane that was fixed by tweezers. The wetted garnet nanofiber membrane was first dried in a flow of dry air environment for 1 h and then, dried in a vacuum oven for an additional 2 h to further remove the solvent. This wetting and drying process was repeated several times until the garnet nanofiber membrane was fully embedded in the PEO polymer matrix. The solid-state membrane was kept in the vacuum oven before assembling batteries in a glovebox.

**Structural Characterization.** The morphology of the samples was examined by a field emission scanning electron microscope (JEOL 2100F). The crystallographic and chemical structures were studied by wide-angle X-ray diffraction (Bruker C2 Discover X-Ray Powder Diffraction System). A transmission electron microscope (JEOL 2100F) was used to examine the crystal structure of garnet nanofibers. TGA (STAR System) was conducted to determine the thermal properties of samples.

**Electrochemical Characterization.** The symmetric Li | solid-state electrolyte | Li full cell was assembled in a glovebox. The electrolyte membrane was sandwiched between two surface polished lithium metal foils and sealed in 2,032 coin cells. The ionic conductivity was tested by sandwiching the electrolyte membrane in the between of two stainless steel plates for the EIS measurement at elevated temperatures. The EIS was performed in a frequency range of 1 MHz to 100 MHz. The electrochemical stability of the electrolyte membrane was measured using LSV mode at a sweep rate of 1 mV/s in the range of 0–6 V. In the LSV test, the electrolyte membrane was sandwiched between stainless steel as a working electrode and lithium metal foil as a counter and reference electrode.
Fig. S1. Magnified TEM of garnet fiber to show the polycrystalline structure.

Fig. S2. Voltage profile of the continued lithium plating/stripping cycling to 700 h at a current density of 0.2 mA/cm$^2$ at 25 °C.

Fig. S3. Voltage profiles of the symmetric cells at two different stripping/plating process times. (A) The voltage plateau of the cell is stabilized at 0.3 V after 300 h of cycling. (B) The voltage plateau of the cell is decreased to 0.2 V after around 700 h of cycling.