Garnet-rich composite solid electrolytes for dendrite-free, high-rate, solid-state lithium-metal batteries

Chaoyi Yan, Pei Zhu, Hao Jia, Zhuang Du, Jiadeng Zhu, Raphael Orenstein, Hui Cheng, Nianqiang Wu, Mahmut Dirican, Xiangwu Zhang

Abstract
Composite solid electrolytes (CSEs), which are composed of inorganic fillers and organic polymers, show improved safety and suppressed lithium dendrite growth in Li-metal batteries, as compared to flammable liquid electrolytes. However, the performance of current CSEs is limited by the agglomeration effect, with low content of inorganic Li\(^{+}\)-conducting fillers and ineffective Li\(^{+}\) transport between the inorganic fillers and the polymer matrix. To address these challenges, a new type of CSE composed of silane-modified Li\(_{6.28}\)La\(_{3}\)Al\(_{0.24}\)Zr\(_{2}\)O\(_{12}\) (s@LLAZO) nanofibers and poly(ethylene glycol) diacrylate (PEGDA) is developed. Employment of the silane coupling agent, 3-(trimethoxysilyl)propyl methacrylate, enables the incorporation of a high content of LLAZO nanofibers (up to 70 wt\%) with the polymer matrix and results in a well-percolated, three-dimensional LLAZO network fully embedded in the PEGDA matrix. Consequently, the silane coupling agent successfully eliminates the agglomeration effect, which ensures higher ionic conductivity, larger lithium transference number, wider electrochemical stability window, and better cycling stability for s@LLAZO-PEGDA CSEs. Excellent cycling stability and extraordinarily high rate capability (up to 10C) are demonstrated in the all-solid-state Li-metal batteries with LiFePO\(_4\) and high-voltage Li[Li\(_{0.33}\)Mn\(_{0.33}\)Co\(_{0.33}\)]O\(_2\) cathodes at ambient temperature. This novel design of CSEs with s@LLAZO nanofibers paves the way for a new generation of improved functioning all-solid-state Li-metal batteries.

1. Introduction

Current Li-ion batteries using an intercalation mechanism exhibit limited energy density which cannot meet the growing demand for energy consumption in large-scale devices, such as electric vehicles and grid energy storage systems. Li metal, owing to its highest energy density (3860 mAh g\(^{-1}\)) and lowest potential (~3.04 V vs. a standard hydrogen electrode), would be the most suitable anode \([1,2]\). Unfortunately, Li metal anode cannot be used directly in liquid electrolyte based Li batteries due to undesirable formation of Li-dendrites \([1-4]\). The replacement of flammable, organic liquid electrolytes with solid-state electrolytes is regarded as the ultimate solution to overcome the problem of dendrite formation and can fundamentally improve battery safety when utilizing Li metal anodes \([5,6]\). Additionally, the relatively wider electrochemical stability window of solid electrolytes allows for use in conjunction with high-voltage cathode materials, which can further improve the overall energy density \([5-7]\).

Polymeric Li\(^{+}\)-conductors as electrolytes were first found in poly(ethylene oxide) with the association of Li salts, and then with other solid polymer electrolytes such as polyacrylonitrile, poly(methyl methacrylate), and poly(vinylidene fluoride) \([5,8,9]\). Although polymer electrolytes demonstrated the feasibility of all-solid-state Li batteries, their low ambient ionic conductivities hindered their practical use \([10,11]\). Reasonable ionic conductivities could only be reached at elevated temperatures near the melting point of the polymer, but operation at this elevated temperature reduced mechanical strength and increased the risk of Li dendrite formation \([5,12,13]\). Therefore, attention was turned to inorganic Li\(^{+}\)-conductors including lithium oxides and lithium sulfides \([6,14]\), which showed high ionic conductivity owing to the relatively low activation energy via ion-hopping mechanisms, leading to a potentially high rate-capability in battery applications \([15]\). Among various inorganic Li\(^{+}\)-conductors, garnet-type (Li\(_{7}\)La\(_{3}\)Zr\(_{2}\)O\(_{12}\), LLZO) ceramics showed...
both high ionic conductivity and excellent stability against Li metal [14, 16,17]. However, the high rigidity of LLZO led to low flexibility and poor interfacial contact with Li metal [17].

In order to take advantage of the properties of both polymers and ceramics while avoiding their limitations, Li\(^+\)-conductive ceramics were incorporated into a polymer matrix to form composite solid electrolytes (CSEs) [18]. In doing so, the ionic conductivity was remarkably improved (~10\(^{-4}\) S cm\(^{-1}\)), and the resultant CSEs showed improved flexibility and good interfacial contact [19,20]. However, severe agglomeration of particles was found at a high level of particulate inorganic fillers. Consequently, only a low volume fraction of fillers could be used in these CSEs, which led to difficulty in forming well-percolated Li\(^+\)-conductive ceramic networks [21–24]. In most cases, the inorganic Li\(^+\)-conductors worked as regular fillers to diminish the crystallinity of the polymers, and the overall electrochemical performance of such CSEs was mainly driven by the polymer properties [19,24]. As a result, the low utilization of inorganic Li\(^+\)-conductors in CSEs greatly restricted the electrochemical stability and cycling stability owing to the dual-ion conducting behavior of polymer electrolytes. More importantly, the high activation energy of Li\(^+\) conduction toward polymer segmental motion extensively hindered the rate performance of solid-state batteries with polymer-rich CSEs.

We therefore set out to design a CSE toward high-performance, solid-state Li-metal batteries based mainly on inorganic Li-conductors, with supplementary polymer content for improving interfacial contact [23]. Herein, a new type of CSE with enriched inorganic Li-conductors and a well-percolated network was introduced utilizing one dimensional Li\(_{6.28}\)La\(_3\)Al\(_{0.24}\)Zr\(_2\)O\(_{12}\) (LLAZO) nanofibers to provide long-range and fast Li\(^+\) conduction. Additionally, acrylate functional groups (CH\(_2\)=CHCOO\(^-\)) were covalently bonded on the surface of silane-decorated LLAZO nanofibers, which enabled the chemical grafting of functional monomers directly from the nanofiber surfaces. In the resultant composite electrolytes, silane-decorated LLAZO nanofibers (s@LLAZO nanofibers) were cross-linked along with polymerization of monomers. This controlled fabrication of composite structures led to a well-percolated network, forming continuous, 3-dimensional, and fast Li\(^+\) conductive pathways within the CSE. The silane coupling agent significantly prevented the inhomogeneous distribution of inorganic Li\(^+\) conductors and enhanced the interaction between the LLAZO nanofibers and the polymer matrix [23], which improved the mechanical strength of the CSE, favored the amorphization of polymer, and reduced the activation energy of Li\(^+\) conduction between the filler and polymer. Consequently, the introduced CSE exhibited higher ionic conductivity, larger lithium transference number, wider electrochemical stability window, and better cycling stability. The all-solid-state Li||LiFePO\(_4\) cells constructed by this introduced CSE showed excellent cycling stability and remarkable rate-capability at a high current density of 10 C at ambient temperature. More importantly, this design enabled the maximized utilization of garnet LLAZO nanofibers, which exceeded the oxidation limit of the introduced CSE to 5.3 V and further supported it to be applied in high-voltage cathode (Li\([\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]\text{O}_2\), NMC) for higher energy density. Superior cycling performance obtained in all-solid-state Li|NMC cells than that of liquid cells demonstrated the success in this design of CSEs with controlled percolation-network of garnet nanofibers.

![Fig. 1. Schematic of synthesis procedure of s@LLAZO-PEGDA CSE with percolated s@LLAZO network within the composite electrolyte, providing fast and non-tortuous Li\(^+\) conductive pathways.](image-url)
2. Results and discussion

Silane-decorated LLAZO nanofibers (s@LLAZO) were obtained by a hydrolysis reaction with different grafting densities. As illustrated in Fig. 1, owing to the grafted acrylate functional groups on LLAZO nanofibers, a controlled organic-inorganic cross-linked network was obtained via chain-growth polymerization of s@LLAZO nanofibers and poly(ethylene glycol) diacrylate (PEGDA) monomers. The well-controlled composite structure ensured the formation of a percolated network with Li\(^+\) conductors, supporting a highly conductive Li\(^+\) pathway. Conduction of Li\(^+\) occurred both inside and along the surface of percolated LLAZO nanofibers. Moreover, the increased binding force and decreased interfacial resistance between the polymer and inorganic nanofibers enabled the fabrication of CSEs with a high content of inorganic Li\(^+\) conductors. Free-standing films with different silane treatment times and polymer contents were prepared and denoted as s@LLAZO(x)-nPEGDA, where x represents the silane treatment time and n is the weight content of PEGDA polymer.

2.1. Structural and physical properties of silane-coated LLAZO nanofibers

The morphology and crystal structure of calcined LLAZO nanofibers are shown in Figs. S1a and S1b, respectively. The calcined nanofibers maintained a well-defined 3D fibrous network, and the main peaks in XRD diffraction pattern could be clearly indexed with the cubic LLZO crystal structure. As demonstrated with SEM image and EDAX mapping of calcined LLAZO nanofibers (Fig. S2), all elements (La, Zr, O) were uniformly distributed along the 1D fiber direction. The identical features of LLAZO garnet structure and coating conditions were observed by transmission electron microscopy (TEM). As shown in Fig. 2a-e, the silane coating layer was identified as the amorphous layer outside the crystalline structure. For s@LLAZO(6h), s@LLAZO(12h), and s@LLAZO(24h) nanofibers, the coating thicknesses were approximately 2, 5, and 7 nm, respectively. A tiny (<1 nm) amount of silane coating layer was detected for s@LLAZO(3h) nanofibers due to the short treatment time.

To elucidate the nature of the surface of saline-decorated nanofibers, pristine LLAZO and s@LLAZO nanofibers were analyzed using Fourier-transform Infrared Spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). As shown in Fig. S3, the FTIR spectra of s@LLAZO illustrated the appearance of additional absorption peaks after hydrolysis. The main absorption peaks located at 1650, 1320, 1100, and 940 cm\(^{-1}\) can be attributed to the stretching vibration of C=O, stretch of COO\(^-\), stretching vibration of Si–O, and bending vibration of C–C,
respectively, corresponding to acrylate, siloxane, and vinyl groups as depicted in Fig. S2 [25,26]. Those additional main peaks confirmed the presence of chemically bonded silane coating on the surface of LLAZO nanofibers. The XPS spectra of C 1s, O 1s, Li 1s, and Si 2p showing in Fig. 2f further confirmed the surface configuration of s@LLAZO nanofibers. LLAZO and s@LLAZO nanofibers exhibited the same peaks in Li 1s and C 1s XPS spectra, illustrating the major Li–O (Li 1s at 54.7 eV, and O 1s at 529 eV) bonds in LLAZO structure and possible formation of Li2CO3 (C 1s at 289.2 eV) on the surface due to reaction with moisture in air [27,28]. Additional peaks in O 1s and Si 2p spectra located at 531.5 eV (O 1s) and 102.5 eV (Si 2p) were ascribed to silane molecules on the surface of s@LLAZO nanofibers, which represented Si–O bonds and further demonstrated the success of applied coating layer on the LLAZO nanofibers [29]. Note that, peaks from the signals of Li 4d and Zr 3d failed to be detected due to the penetration limitation of XPS. The weight percentage of silane component in s@LLAZO nanofibers was estimated by thermal gravimetric analysis (TGA). As illustrated in Fig. S4, the approximate silane percentages in s@LLAZO nanofibers were 2.4–5.3 wt% for 3 to 24 h of hydrolysis treatment.

The ionic conductivities of s@LLAZO-PEGDA CSEs were measured using electrochemical impedance spectroscopy (EIS) (Fig. S5) and summarized in Table 1. As calculated with obtained total resistance (intercept of extended semicircles), without the silane coating layer, LLAZO-30PEGDA CSE exhibited the lowest ionic conductivity of 5.2 × 10⁻⁵ S cm⁻¹ at room temperature. The relatively low ionic conductivity was due to the extremely high content of LLAZO nanofibers within the CSE, which led to a severe agglomeration of fillers and destruction of conducting pathways. In contrast, with the presence of silane coating layers, s@LLAZO-30PEGDA CSEs showed significantly higher ionic conductivities. The s@LLAZO(6h)-30PEGDA CSE reached the maximum ionic conductivity of 4.9 × 10⁻⁴ S cm⁻¹ at room temperature, manifesting the improved Li⁺ conduction within the composite structure with use of s@LLAZO nanofibers. A slight decrease in ionic conduction was observed with longer coating time (s@LLAZO(24h)-30PEGDA, 3.9 × 10⁻⁴ S cm⁻¹), possibly due to the suppression of surface Li⁺ conduction with a thicker coating. The distribution of Li⁺ conductors in CSEs was further investigated by scanning electron microscope (SEM). As shown in Figs. S6a and S6b, the distribution of untreated LLAZO nanofibers in LLAZO-30PEGDA CSE was extremely ununiform. At high filler content, the nanofibers preferred to locate on the periphery of the solid electrolyte membrane, resulting in disturbed Li⁺ pathways. With silane modification, the acrylate groups on s@LLAZO nanofibers were activated along with polymerization, leading to the homogeneous assembly of Li⁺ conductors and polymer in the composite structure (Figs. S6c–d). It was the well-percolated, fast conducting pathways provided by interconnected s@LLAZO nanofibers that maximized the ionic conductivities in the introduced CSEs.

Fig. 2g illustrates the temperature dependence of ionic conductivities by Arrhenius plots. All curves obeyed linear behavior with respect to temperature because the cross-linked polymer matrix was fully amorphous and had no phase change with increasing temperature. It was noted that all s@LLAZO-30PEGDA CSEs exhibited lower activation energy (E_a (~0.30 eV)) than LLAZO-30PEGDA (0.41 eV). This difference in E_a indicated the different Li⁺ conduction preferences in CSEs with and without silane modification. Interconnected fibrous garnet phase played the dominant role in Li⁺ conduction in s@LLAZO-30PEGDA CSEs. While in LLAZO-30PEGDA CSE with untreated LLAZO nanofibers, Li⁺ was mostly conducted by the segmental motion of polymer chains due to the highly aggregated LLAZO phase that blocked Li⁺ conduction [21,30]. To better illustrate the percolated structure formed with s@LLAZO nanofibers, ionic conductivities were measured for s@LLAZO-PEGDA and LLAZO-PEGDA CSEs with different nanofiber weights. As shown in Figs. S7 and S8, the ionic conductivities of s@LLAZO(6h)-PEGDA CSEs increased continually with increasing weight content of nanofibers. The trendline of the curve up to 70 wt% of filler content fitted well with the percolation models derived by Yu [21,22]. This indicated the well-established Li⁺ percolation network within the CSE. Remarkably, the silane coating layer totally eliminated the agglomeration of fillers and enhanced the conductivity with a higher degree of percolated framework. Due to the limitation of the created interphase in the composite structure, the ionic conductivities remained similar from 50 wt% (4.7 × 10⁻⁴ S cm⁻¹) to 70 wt% (4.9 × 10⁻⁴ S cm⁻¹) @ s@LLAZO nanofibers. In contrast, the CSEs with non-coated LLAZO nanofibers (LLAZO-PEGDA) demonstrated maximum ionic conductivity of 2.2 × 10⁻⁴ S cm⁻¹ at 15 wt% of filler content (Fig. S8) [50,51]. After that, the ionic conductivity decreased with the increasing filler content from 15 to 50 wt% (5.3 × 10⁻⁴ S cm⁻¹ at 50 wt% LLAZO filler content), which was attributed to the severe aggregation of inorganic filler within the polymer matrix. Fig. S9 shows the schematic drawing of Li⁺ conduction mechanisms in these two different CSEs. With s@LLAZO filler, the distribution of garnet fibers was uniform, leading to the formation of a well-percolated garnet network. As known, the polymer/garnet interfaces created by the addition of Li⁺-conductive filler were highly conductive due to Lewis acid-base interactions [18,21,22]. With a percolated garnet network, the volume ratio of polymer/garnet interfaces was maximized. Because the garnet filler was well-distributed, this highly conductive polymer/garnet interface was overlapped and connected through the system, favoring the continuously transport of Li⁺ within the CSE. On the other hand, the volume ratio of polymer/garnet interfaces significantly decreased if the garnet fibers were severely aggregated. The Li⁺ conduction of CSEs with non-coated LLAZO filler was discontinuous because the aggregated garnet fibers were located far apart from each other, resulting in separated polymer/garnet interfaces. Therefore, in LLAZO-PEGDA CSEs, Li⁺ tended to be conducted by polymer chains directly without the help of LLAZO filler, and the ionic conductivity of LLAZO-PEGDA CSEs is comparable to that of bare PEGDA solid polymer electrolyte when the filler content increased to the range of 20–50 wt%. To further demonstrate the achieved huge improvement in ionic conductivities of s@LLAZO-PEGDA CSEs was not solely caused by the amorphization of polymer chains, non-Li⁺-conductors (SiO₂, TiO₂ nanoparticles) were prepared with the same experimental conditions to investigate the filler effect on the resultant conductivities (Fig. 2h). After increasing filler content beyond 15 wt%, the ionic conductivities of s@SiO₂(6h)-PEGDA and s@TiO₂(6h)-PEGDA CSEs dramatically decreased. In contrast, a high content of Li⁺-conductors (s@LLAZO(6h)-50PEGDA) with a well-percolated network provided a fast and continuous Li⁺ pathway, leading to the further improvement in ionic conductivity with increasing filler content. Although the morphology of the inert fillers (nanoparticles) was different from that of the active s@LLAZO nanofibers, the significant difference (~10⁻³) in ionic conductive Li⁺ (4.9 × 10⁻⁴ S cm⁻¹) and non-Li⁺-conductive fillers (9.5 × 10⁻⁴ S cm⁻¹) confirmed that the enhanced ionic conductivity in s@LLAZO-PEGDA CSEs was highly related to the significant contribution of active (s@LLAZO) nanofibers to the Li⁺ conduction in the composite electrolytes.

In addition to conductivity, high mechanical strength is desirable to control the growth of Li dendrites in solid-state Li-metal batteries [4,31]. Since the ionic conductivities remained the same after filler content of

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Time (h)</th>
<th>Ionic Conductivity (S/cm) (at 25 °C)</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLAZO-30PEGDA</td>
<td>0</td>
<td>5.2 × 10⁻⁵</td>
<td>0.41</td>
</tr>
<tr>
<td>s@LLAZO(24h)-30PEGDA</td>
<td>3</td>
<td>9.4 × 10⁻⁵</td>
<td>0.31</td>
</tr>
<tr>
<td>s@LLAZO(6h)-30PEGDA</td>
<td>6</td>
<td>4.9 × 10⁻⁴</td>
<td>0.29</td>
</tr>
<tr>
<td>s@LLAZO(12h)-30PEGDA</td>
<td>12</td>
<td>4.6 × 10⁻⁴</td>
<td>0.30</td>
</tr>
<tr>
<td>s@LLAZO(24h)-30PEGDA</td>
<td>24</td>
<td>3.9 × 10⁻⁴</td>
<td>0.30</td>
</tr>
</tbody>
</table>
s@LLAZO nanofibers increased beyond 50 wt%, the optimum filler concentration was assumed at 50 wt% based on the criteria of flexibility and Li wettability of the solid electrolyte. Fig. 2i characterizes Young’s modulus, tensile strength, and elongation of s@LLAZO-PEGDA CSEs with 50 wt% filler content, and the corresponding values are summarized in Table 2. The pristine PEGDA polymer electrolyte showed a Young’s modulus of 18.1 MPa, tensile strength of 1.36 MPa, and maximum elongation of 7.9%. With the addition of LLAZO nanofibers, LLAZO-50PEGDA showed increased elongation (21%) and tensile strength (1.74 MPa) but reduced Young’s modulus (10.4 MPa) due to the plasticized effect. When the polymer was directly grafted on s@LLAZO nanofibers through the silane coupling agent, the tensile strength and Young’s modulus increased dramatically to 24.8 MPa and 3.7 MPa for s@LLAZO-50PEGDA CSE, respectively.

2.2. Advanced electrochemical performance of s@LLAZO-PEGDA composite solid electrolytes

The structural and chemical advantages of the silane coating make s@LLAZO nanofibers ideal for reinforcing the mechanical and electrochemical properties of CSEs. Fig. 3a shows a digital image of the as-prepared s@LLAZO(6h)-50PEGDA solid electrolyte membrane. The entire flexible membrane was able to be twisted, bent, and rolled up without cracking (Fig. S11), suggesting that s@LLAZO(6h)-50PEGDA had sufficient mechanical flexibility to be applied in solid-state Li metal batteries. In previous work on conventional CSEs, to maximize the ionic conductivity, the content of inorganic fillers was controlled below 15 wt% to avoid the particulate agglomeration. Therefore, conventional CSEs often exhibited low lithium transference number (tLi+) and poor electrochemical stability, which in turn led to insufficient cycling stability in solid-state Li metal batteries. In addition, the oxidation of PEO-based polymer occurred at low voltage (~4.2 V), preventing the development of high-power Li-metal batteries [32]. As illustrated in Fig. 3b, the anodic current onset is linked to electrochemically oxidized decomposition. The bare PEGDA and LLAZO-50PEGDA solid electrolytes exhibited similar anodic stability because of the high content of PEO cross-linked polymer. Nevertheless, owing to the excellent electrochemical stability of the inorganic Li+ conductor and low polymer content in @LLAZO-50PEGDA CSE, the oxidized decomposition onset started at 5.3 V, which greatly extended the overall stability window (Fig. S12). Cyclic voltammetry (CV) was conducted to further study the electrochemical stability windows of the as-prepared s@LLAZO(6h)-50PEGDA CSEs (Fig. S13). Except for the redox peaks at 0 V versus Li/Li+ that corresponded to the Li+/Li+ plating and stripping process, there was no other large current peak over the whole scan range from 0V to 5.5 V [33,34]. Therefore, it could be concluded that s@LLAZO(6h)-50PEGDA has a wide electrochemical window and a good compatibility with lithium metal. Moreover, the lithium transference number (tLi+) was calculated by Bruce’s equation with the obtained initial current (I0), steady-state current (I0), and the corresponding impedances at two states [35]. As shown in Fig. 3c and Fig. S14, given the typical DC polarization curve of Li symmetric cells, the s@LLAZO(6h)-50PEGDA CSE exhibited a tLi+ as high as 0.61 due to the improved utilization of inorganic Li+ conductors. In contrast, tLi+ was 0.2, 0.26, and 0.41 for bare PEGDA, LLAZO-90PEGDA, and LLAZO-50PEGDA solid electrolytes, respectively. Significant improvement in tLi+ of s@LLAZO(6h)-50PEGDA CSE was attributed to the strong Lewis acid-base interaction between s@LLAZO nanofibers and Li salts, which restricted the delocalized anions and promoted free Li+ mobility. Benefiting from the silane modification, the introduced CSE exhibited well-percolated LLAZO network within the composite structure. Extremely high content of inorganic Li+ conductors was utilized in s@LLAZO(6h)-50PEGDA CSE, leading to the higher tLi+ compared to bare PEGDA, LLAZO-90PEGDA solid electrolytes. On the other hand, even with the same filler content, LLAZO-50PEGDA CSE demonstrated much lower tLi+. This was attributed to the limited polymer/garnet interfaces created within LLAZO-50PEGDA CSE because of the agglomeration effect with non-coated LLAZO nanofibers. Therefore, this controlled formation of organic-inorganic framework greatly enhanced electrochemical stability and tLi+, which greatly influenced the safety and stability in all-solid-state Li batteries.

Long-term, lithium transference number and compatibility of s@LLAZO(6h)-50PEGDA was evaluated by galvanostatic stripping (0.5 h) and plating (0.5 h) measurement. As shown in Fig. 3d, stable DC cycling as a function of current density was achieved over the entire test period. At initial cycling stage with current density of 0.05 mA cm\(^{-2}\), the overpotential of symmetric cell decreased gradually with increasing cycle time and finally stabilized at 39 mV, which was attributed to the improved interface between the solid electrolyte membrane and Li metal during the repeated Li electrodeposition. Afterward, the symmetric cell remained low overpotentials of 69, 159, and 518 mV at current densities of 0.1, 0.2, and 0.5 mA cm\(^{-2}\), respectively, demonstrating the high ionic conductivity of introduced s@LLAZO(6h)-50PEGDA CSE. Additionally, a smooth Li stripping/plating process was achieved for over 600 h, indicating the stable interfacial properties of s@LLAZO(6h)-50PEGDA CSE and excellent electrochemical stability against Li metal [30,36].

2.3. High performance of all-solid-state Li-metal batteries

All-solid-state batteries were assembled with the s@LLAZO(6h)-PEGDA CSEs as the electrolyte, pure Li metal as the anode and LiFePO\(_4\) as the cathode. Three CSEs with different s@LLAZO nanofiber contents were studied to establish the relationship between cycling performance and filler content. To control the thickness of solid electrolyte membranes, the precursor solution was cast and polymerized between two quartz plates. As shown in Fig. S15, the thickness of the as-prepared s@LLAZO(6h)-50PEGDA CSE was 52 μm. The same polymerization process was followed for s@LLAZO(6h)-30PEGDA and s@LLAZO(6h)-70PEGDA CSEs, and the thicknesses of all prepared solid electrolyte membranes were controlled in range of 50–80 μm. Fig. 4a shows the EIS profiles of Li/LiFePO\(_4\) cells with three different CSEs, where the partial semicircle at the high-frequency range was attributed to the bulk impedance (Rb) of solid electrolyte and the large semicircle in the medium-frequency range was attributed to a the charge transfer (Rct) and diffusion processes at the electrolyte/electrode interface [37]. All three cells demonstrated similar Rb in the range of 70–100 Ω, which indicated similar ionic conductivities of the three solid electrolytes. However, compared to s@LLAZO(6h)-70PEGDA and s@LLAZO(6h)-50PEGDA solid electrolytes, s@LLAZO(6h)-30PEGDA showed much higher Rct (~800 Ω), indicating that it had higher interfacial resistance and poorer contact with the electrode. The corresponding cycling performance with the three CSEs is illustrated in Fig. 4b. At a current density of 0.5C, the cell with s@LLAZO(6h)-30PEGDA delivered the lowest initial capacity of 93 mA h g\(^{-1}\) due to high internal resistance attributed to poor contact with the Li metal. Retained capacities of 153 and 147 mA h g\(^{-1}\) were obtained for the cells with s@LLAZO(6h)-70PEGDA and s@LLAZO(6h)-50PEGDA, respectively. Fig. S16 shows the charge and discharge profiles at the first cycle for solid-state cells with these three

<table>
<thead>
<tr>
<th>Samples</th>
<th>PEGDA Content (%)</th>
<th>Young’s Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLAZO-50PEGDA</td>
<td>50</td>
<td>18.1</td>
<td>1.4</td>
<td>7.9</td>
</tr>
<tr>
<td>s@LLAZO(6h)-50PEGDA</td>
<td>50</td>
<td>10.4</td>
<td>1.7</td>
<td>21.0</td>
</tr>
<tr>
<td>s@LLAZO(12h)-50PEGDA</td>
<td>50</td>
<td>27.6</td>
<td>4.1</td>
<td>20.9</td>
</tr>
<tr>
<td>s@LLAZO(24h)-50PEGDA</td>
<td>50</td>
<td>29.5</td>
<td>4.2</td>
<td>19.1</td>
</tr>
</tbody>
</table>

**Table 2** Mechanical properties of s@LLAZO-PEGDA CSEs.
CSEs. The cell with s@LLAZO(6h)-30PEGDA exhibited higher polarization potential, indicating larger reaction barriers due to unsatisfied contact against electrodes [38]. The Coulombic efficiency of the first cycle was 96.5%, 98.7%, and 99.4% for cells with s@LLAZO(6h)-70PEGDA, s@LLAZO(6h)-50PEGDA, and s@LLAZO(6h)-30PEGDA CSEs, respectively, which indicated more stable redox reactions processed with higher content of inorganic filler. Therefore, s@LLAZO(6h)-30PEGDA demonstrated the best cycling stability with a high capacity retention of 98% after 100 cycles. Clearly, the increasing content of s@LLAZO nanofibers provided more stable cycling due to enhanced electrochemical stability and increased $t_{Li^+}$, resulting in decreased mobility of TFSI$^-$ anions and alleviation of the internal concentration gradient of accumulated anions. In overall consideration, the cell assembled with s@LLAZO(6h)-50PEGDA showed optimum cycling performance with relatively high capacity retention of 98% after 100 cycles. We anticipate that the cells with s@LLAZO(6h)-30PEGDA would deliver even better cycling performance with appropriate interfacial modification between Li metal and solid electrolyte.

To further demonstrate the cycling stability at higher current densities, the cell with s@LLAZO(6h)-30PEGDA CSE was galvanostatically cycled at a current density of 1C. As shown in Fig. 4c, the cell retained a capacity of over 115 mA h g$^{-1}$ up to 250 cycles, resulting in 89% capacity retention. The Coulombic efficiency remained high at 99%, which indicated good reversibility of the redox reactions processed in the battery system. EIS profiles were investigated during cycling at current density of 1C. As illustrated in Fig. S17, the overall impedance decreased from 486 Ω (fresh) to 215 Ω after 20 cycles, which was attributed to the reduced interfacial resistance of CSEs against the electrodes after cycling [38,39]. The interfacial conditions improved continuously after 50 cycles, which resulted in continuously increased capacity shown in Fig. 4c. Afterward, the overall impedance remained stable for 100 cycles. A slight decrease in capacity and fluctuation in Coulombic efficiency was observed after 200 cycles, which may be due to the diminished interfacial contact and detachment of active materials in the cathode after long cycle time at high current density [39–42]. More impressively, along with the excellent cycling stability, solid-state Li|s@LLAZO(6h)-50PEGDA|LiFePO$_4$ cells also showed remarkable rate capability (Fig. 4d). Discharge capacities of 158, 147, 135, 113, and 78 mA h g$^{-1}$ were obtained at varied rates of 0.2, 0.5, 1, 2, and 5 C, respectively (Fig. S18). Even at a high current density of 10 C, the cell could still deliver a capacity of 44 mA h g$^{-1}$. After applying cycles at higher current densities, the discharge capacity increased again to as high as 158 mA h g$^{-1}$ when the current density was reduced to 0.2 C. Such high C-rate performance is remarkable for all-solid-state batteries operated at room temperature. This was mainly attributed to the well-established percolated LLAZO network that

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Fig. 3. (a) Digital image of s@LLAZO(6h)-50PEGDA CSE, (b) Linear sweep voltammetry curves of PEGDA, LLAZO-90PEGDA, and s@LLAZO(6h)-50PEGDA CSEs, (c) DC polarization curves, and (d) lithium plating/striping cycles of symmetric Li|s@LLAZO(6h)-50PEGDA|Li cell.
provided fast and non-tortuous Li\textsuperscript{+} conduction in the composite structure. Fig. 4f shows typical charge-discharge curves at different C rates. Distinct plateaus at 3.49 and 3.36 V were shown in the charging and discharging curves at low current density (0.2, 0.5, and 1 C), which were equivalent to the Li\textsuperscript{+} extraction and insertion to LiFePO\textsubscript{4} at the voltage region for the Fe\textsuperscript{3+}/Fe\textsuperscript{2+}, respectively [43,44]. The excellent rate performance in all-solid-state Li-ion batteries again validated the superior electrochemical properties of s@LLAZO(6h)-50PEGDA CSEs and critical influence of the silane coating layer. Li dendrite formation was evaluated after cycling as shown in Fig. S19. The majority of Li electrode surface was flat without observable dendrite formation. Therefore, our introduced s@LLAZO(6h)-50PEGDA CSE showed great suppression of lithium dendrites after long cycles due to the superior mechanical rigidity.

To ultimately prove the utility of our newly-designed garnet-rich solid electrolyte, the successful application along with a high-voltage cathode (Li\{Ni\textsubscript{1/3}Mn\textsubscript{1/3}Co\textsubscript{1/3}\}O\textsubscript{2}, NMC) is critical. As a promising cathode, NMC has a higher discharge potential (~3.9 V vs. Li\textsuperscript{+}/Li), while most Li|NMC cells reported in literature exhibited poor cycle life due to the materials degradation and gas evolution because of the poor stability of carbonate electrolyte at high voltages [45–47]. As shown in Fig. 4e, rapid capacity fading was observed for NMC cathodes in liquid cells, which was attributed to chemical oxidation of the electrolyte caused by release of reactive oxygen from the delithiated NMC surface at high-voltage cut-off [46,48]. In contrast, the cells with garnet-rich CSEs displayed superior cycling stability owing to an enlarged oxidation limit (>5.3 V) with a high content of inorganic Li\textsuperscript{+} conductors. Increasing capacity was observed at initial cycles because of the improved surface contact of CSEs with electrodes. In later cycles, the cell stabilized at 110 mA h g\textsuperscript{-1} for over 250 cycles (capacity retention 97%) at 0.5 C at room temperature. Much higher Coulombic efficiency (~99.2%), compared to liquid electrolyte cells (~95.5%), indicated stable redox reactions and effectively controlled electrode degradation [49]. Similarly,
all-solid-state Li/NMC cell demonstrated high rate capability at room temperature as illustrated in Fig. 4f. Comparable capacities were observed in solid-state and liquid Li@LLAZO(6h)-50PEGDA/NMC cells at all tested C rates (0.2–5 C). The stable plateaus and low over-potentials at all C rates (Fig. S20) again indicated the high Li⁺ conductivity and excellent electrochemical stability of the introduced garnet-rich CSEs. The success of the s@LLAZO-PEGDA CSEs along with NMC cathode was another step forward in underpinning its impact. With such superior electrochemical properties, we anticipate the same remarkable performance in conversion cathodes with s@LLAZO-PEGDA CSEs.

3. Conclusion

In conclusion, a novel composite solid electrolyte (CSE) was developed with enriched LLAZO garnet nanofibers. The s@LLAZO nanofibers enabled direct monomer grafting, resulting in a controlled formation of an organic-inorganic network that successfully eliminated the agglomeration effects typically encountered in conventional CSEs with high inorganic filler contents. Benefiting from strong coupling, high concentration and uniform distribution of s@LLAZO nanofibers in composite structure, the resultant CSEs (s@LLAZO(6h)-50PEGDA) exhibited high room-temperature ionic conductivity, large lithium transference number, and wide electrochemical stability. Remarkably, all-solid-state Li-metal batteries assembled with the developed CSEs demonstrated stable cycling performance for 250 cycles and extraordinary high rate capability (up to 10 C) at room temperature owing to the maximized utilization of fast Li⁺ conductors (LLAZO) in the composite structure. Moreover, the enlarged electrochemical window of introduced CSEs enabled the stable redox reactions in solid-state Li/NMC cells at high upper cut-off voltage, resulting in much longer cycle life. In short, this novel structural design of CSEs has significant potential in the development of improved functioning all-solid-state Li-metal batteries.

4. Methods

4.1. Fabrication of Li₀.₂₈La₀.₃₆Al₀.₂₄Zr₂O₁₂ (LLAZO) nanofibers

The electropinning precursor solution was first prepared by dissolving stoichiometric amounts of 9.42 mmol of LiNO₃, 4.5 mmol of La(NO₃)₃⋅6H₂O, 0.36 mmol of Al(NO₃)₃⋅9H₂O, and 3 mmol of Zr(OCH₂CH₂CH₂CH₃)₄ in 20 ml of DMF with 15 vol% acetic acid. Excess LiNO₃ (15 wt%) was added to compensate for lithium loss during the subsequent calcination procedure. After stirring for 30 min, 2 g of PVP i-thiolae ligands at room temperature and to activate alkoxy groups to silanols (Si–OCH₃). After being slightly grounded, the as-spun fibers were later calcined at 850 °C for 2 h to obtain LLAZO nanofibers.

4.2. Fabrication of silane-modified Li₀.₂₈La₀.₃₆Al₀.₂₄Zr₂O₁₂ (s@LLAZO) nanofibers

For a typical synthesis of s@LLAZO nanofibers, the silane precursor solution was first prepared, which consisted of 2.5 vol% 3-(trimethoxysilyl)propyl methacrylate, 2.5 vol% acetic acid, 5 vol% water, and 90 vol% ethanol. The precursor solution was left for 1 h to stabilize the pH value and to activate alkoxy groups to silanols (Si–OH). 600 mg of LLAZO nanofibers were then added into 40 ml of precursor solution and kept stirring for 3 h, 6 h, 12 h, and 24 h at 70 °C. After silanization, s@LLAZO nanofibers were collected by centrifugation and washed three times with ethanol.

4.3. Fabrication of s@LLAZO-PEGDA composite solid electrolytes

The composite solid electrolytes were fabricated by first dispersing the s@LLAZO nanofibers in N-Methyl-2-pyrrolidone (NMP), followed by sonication for 5 min to get uniform dispersion. The initiators (AIBN), monomers (PEGDA, Mw=575), and lithium salts (LiTFSI) were then added into the solution. For cross-linked polymer, the amount of initiator was controlled 0.1 wt% based on the total weight of monomers, and the amount of lithium salts was controlled at [EO]/[Li⁺]=12. The prepolymer solution was then casted on the quartz plate and cross-linked into thin films at 80 °C for 30 min in argon-filled glove box. During polymerization, another quartz plate was placed on the top to control the thickness of solid electrolyte membrane in the range of 50–80 μm. After polymerization, the solid electrolyte membrane was allowed to be dried at 80 °C under vacuum overnight to eliminate the residual NMP solvent. The resultant composite solid electrolytes were denoted as s@LLAZO(x)-nPEGDA, where x represented the silane treatment time and n the weight content of PEGDA polymer.

4.4. Synthesis of Li[Ni₁/₃Mn₁/₃Co₁/₃]O₂ (NMC) nanoparticles

A simple sol-gel method, followed by high-temperature calcination process, was used to prepare NMC nanoparticles. An aqueous solution was made by dissolving 10 mmol LiCH₃COO⋅2H₂O, 3.3 mmol Ni(CH₃COO)₂⋅4H₂O, and 3.3 mmol Co(CH₃COO)₂⋅4H₂O in 18 ml deionized water. Citric acid solution (1 M) was added to form chemical bonds with metal ions and a sol-gel precursor according to the metal ions to citric acid ratio of 1:1.6. The reactant solution was heated to 90 °C for 4 h with magnetic stirring and then kept at 80 °C overnight to evaporate the solvent, followed by calcinated at 450 °C for 1 h to remove the acetate groups. After being slightlygrounded, the intermediate powder was further calcinated at 900 °C for 12 h to obtain the NMC nanoparticles.

Declaration of competing interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ensm.2019.11.018.

References
