Interfacial Barrier Free Organic-Inorganic Hybrid Electrolytes for All Solid-State Batteries

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Abstract

Organic-inorganic hybrid solid electrolytes (HSEs) are expected to overcome the inherent limitations of rigid fragile inorganic electrolytes for solid state batteries. Li-ion conductive filler such as garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is proposed for the high performance of HSEs, unfortunately, which suffers from native surface layer resistance to Li-ion transport. Here we present highly conductive polyvinylidene fluoride (PVDF)-based HSEs incorporating LLZO fillers, whose resistive barriers are eliminated by dry etching. Our optimal composition of etched LLZO fillers (30 wt%) leads to ionic conductivity of $4.05 \times 10^{-4} \text{ S cm}^{-1}$, about two-fold improvement from non-etched counterpart. Li symmetric cells with etched fillers exhibit low interfacial resistance of $110 \Omega \text{ cm}^2$ and minimal overpotential of 46 mV. Moreover, high capacity of 79 mA h g^{-1} is highlighted at 4C, comparable or superior to liquid electrolyte or sulfide-based electrolyte devices. Interfacial environment in HSEs ideally modified for Li-ion transport is identified by ^7Li NMR measurements.

Introduction

Since the first commercialization in 1991, Li-ion battery (LIB) has ushered in a new era of mobile devices, including mobile phones and electric vehicles (EVs).^{1,2} Unfortunately, continued accidents relevant to the ignition or explosion of LIBs have raised safety concerns for more reliable LIB systems.^{3,4} Despite the accumulated research efforts for device design and material advancement, however, potential danger still remains, particularly involved with the flammable organic liquid electrolytes (LEs). Solid state batteries (SSBs) have been introduced in this regard, as well as to exploit pure Li metal anode with higher capacity. SSBs also offer a wide range of operational voltages, excellent thermal stability and high voltage design by stacking bipolar electrodes.^{5–8} The ultimate performance of SSB is strongly governed by solid electrolytes (SEs). In the early days of SE research, high ionic conductivity was the top priority, exploiting the inorganic oxides to sulfides.^{9–18} Recently, long-term stability under harsh electrochemical environments have re-emerged as the next critical issue for a practical utilization.

Li-stuffed garnet oxides with the nominal composition of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) are promising SEs, first introduced by Murugan et al. in 2007.¹⁹ Garnet LLZO not only shows genuine high ionic conductivity ($10^{-4} \sim 10^{-3} \text{ S cm}^{-1}$) relying on the 3D connected Li-ion network²⁰ but also mechanical robustness to suppress surface dendrite formation and thermal stability for a wide operating temperature window.^{21,22} Along with chemical modification and processing methodologies for the further improvement of Li-ion conductivity,^{23–27} moreover, garnet LLZO is found to possess the lowest reduction potential against Li metal among all previously reported SEs.²⁸ Presently, several challenges are remaining for the practical utilization of LLZO in SSBs. First, direct device integration of rigid and fragile ceramic LLZO is difficult.^{29,30}

Surface defects in the LLZO may cause the internal short circuit through Li metal penetration.³¹ Second, scale up of large-size LLZO membrane for practical cells demands formidable cost and sophisticated handling process. Current studies mostly rely on pellet-type LLZO, which is inadequate for eventual

scaling up.^{24,29,30} Finally, LLZO frequently suffers from instability under an ambient atmosphere, due to the formation of highly resistive surface layers consisting of Li_2CO_3 .^{32–35}

Motivated from the synergistic potential from organic and inorganic components, hybrid polymer electrolytes (HSEs) has emerged as an ideal composition for SSB. While a polymer matrix offers safe, lightweight and soft intimate contact/strong interfacial adhesion, highly ionic conductive inorganic SE fillers can be effectively integrated without burden for brittle ceramic processing. So far, there have been a few reports for the successful utilization of HSEs with LLZO fillers, particularly exploiting poly(vinylidene fluoride) (PVDF) matrix with a high dielectric constant.^{36–38} Nevertheless, little attention has been paid to the resistive surface layer formation on LLZO fillers. In this work, we introduce a straightforward approach for highly conductive PVDF-LLZO HSEs by eliminating the resistive surface layers of garnet LLZO fillers. To the best of our knowledge, this is the first demonstration for the effective removal of inactive surface layers at powder-type LLZO fillers by reliable dry etching process. Along with the integration of PVDF-based HSEs filled with etched LLZO as the electrolytes, SSBs based on $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}/\text{LLZO}$ -PVDF HSEs/Li noticeably improved the rate capability and cycling performance. Systematic monitoring of Li-ion pathway verifies the augmented Li-ion movements along the activated local environment around LLZO fillers.

Results

LLZO fillers with cubic phase were obtained by a solid-state synthesis employing double-doping strategy for high ionic conductivity and short reaction time.²⁷ Resistive Li_2CO_3 layers were formed at the LLZO surface upon unavoidable exposure to ambient air. Transmission electron microscopy (TEM) visualizes the Li_2CO_3 layer of ~ 15 nm thickness (Fig. 1a).³⁹ The poorly crystallized Li_2CO_3 layers are hardly detectable by X-ray diffraction (XRD) (Fig. S1). Fig. 1b schematically describes our well-refined dry etching process for the resistive layers. Reactive ion etching (RIE) is a reliable dry etching by means of ion bombardment, widely used in the microfabrication.⁴⁰ Herein, RIE strips off the thin Li_2CO_3 layers at the powder state LLZO fillers, which is difficult with other methods, such as mechanical polishing.^{39,41,42} In a RIE process, the degree of anisotropy for etching rate, generally expressed as $A = 1 - \text{RL}/\text{RV}$ (RL : lateral etch rate, RV : vertical etch rate), is expected to be 1 for an ideal vertical etching.⁴³ Practical RIE cannot feature such an ideal case and sidewall passivation is commonly used to prevent the undercut beneath the etching mask in microelectromechanical system (MEMS) fabrication.⁴⁴ In addition, the typical etching rate with fluorocarbon gases such as CF_4 is significantly higher for the amorphous surface layer rather than crystalline core.⁴⁵ Such a non-ideal directionality of RIE along with high etching selectivity could lead to a conformal etching of Li_2CO_3 layers. Previously, simple thermal treatment has been exploited to remove the Li_2CO_3 layers.⁴⁶ Nonetheless, our etching approach can be generally extended to the unwanted surface layers of other materials even with high thermal vulnerability. We used CF_4 RIE for the selective etching of amorphous surface layers. The crystalline structure of LLZO core was well-maintained after surface etching (Fig. S1).

X-ray photoelectron spectroscopy (XPS) was carried out to confirm the surface chemistry of LLZO fillers. Two distinctive peaks were detected in C 1s scan around 285 and 290 eV for adventitious carbon and carbonate, respectively (Fig. 1c).^{32,41} The carbonate peak diminished with the removal of Li₂CO₃ layers. In O 1s spectra, the carbonate peak at ~532.1 eV decreased with etching, while the peak for crystalline LLZO increased at ~528.5 eV.³⁴ Similarly, Li 1s spectra consist of the two principal peaks at ~55.4 and 54.8 eV for Li₂CO₃ and Li-O, respectively (Fig. 1e). Along with etching time, the intensity of Li₂CO₃ peak decreases and the overall Li 1s peak shifts from ~55.1 to ~54.8 eV, supporting the removal of Li₂CO₃. There is no significant difference in the 15 and 20 min etching, implying that 15 min is sufficient to remove the majority of Li₂CO₃ layers (Fig. S2).

Fig. 1f displays the prominent change of Zr 3d signal at LLZO upon surface etching. A weaker Zr 3d signal was observed at non-etched LLZO, which is quite plausible considering the presence of Li₂CO₃ layer and the detection limit of ~10 nm for XPS. After etching, the intensity of Zr 3d signal strengthened. Quantitative analysis for the etching profile is implemented by plotting the elemental ratios of C/La and C/Zr as a function of etching time (Fig. 1g). Both ratios reduce rapidly within 10 min and saturates around 15 min (Those ratios are higher than zero throughout the etching process due to adventitious carbon).^{39,41} No significant difference in the carbon content was detected between 15 min etched sample and others treated with different conditions (Fig. S3). It is also critical to keep the etched samples in an inert atmosphere to avoid the re-growth of surface layer (Fig. S4). Energy dispersive X-ray spectroscopy (EDS) mapping could directly visualize the surface selective etching of Li₂CO₃ layers (Fig. 1f and Fig S5). While the C signal became blurred after 15 min etching, no significant compositional change was detected in the crystalline LLZO core, as also supported by Raman spectroscopy (Fig. S6).

The typical properties of HSEs strongly depend on the size, morphology and content of inorganic fillers.⁴⁷ Here, planetary ball milling was used for the size reduction of LLZO fillers, considering its mechanical simplicity and potential large-scale production.⁴⁸ Fig. 2a present SEM images of the as-synthesized (referred to as asLLZO) and ball-milled (referred to as bmLLZO) LLZO, respectively. Compared with asLLZO (12.97 ± 4 μ m), bmLLZO shows a considerably decreased size (1.2 ± 0.5 μ m) (Fig. 2b). XRD patterns of both samples showed identical profiles, implying the well-maintained crystalline structures during the size reduction process (Fig. S7). Next, free-standing films of PVDF-LLZO HSE and the PVDF based solid polymer electrolyte (SPE) were prepared by solution-casting (Fig. S8). XRD patterns of LLZO, pure PVDF, PVDF-SPE and PVDF-LLZO HSEs taken at room temperature are displayed in Fig. 2c and Fig. S9. The diffraction peaks for LiClO₄ salt is absent in the PVDF-SPE, indicating a successful ionic complexation.³⁷ Upon hybridization, the crystalline phase of LLZO does not change. Interestingly, the weak crystallinity of PVDF-SPE becomes slightly less apparent in the HSEs loaded with bmLLZO or etched bmLLZO compared to those with asLLZO. The larger PVDF/LLZO interface area with the smaller-size ball-milled LLZO fillers should contribute to the further broadening of PVDF-SPE peaks, also evidenced by the planar elemental mapping (Fig. S10). The surface etching of Li₂CO₃ layers caused no noticeable difference again in the XRD patterns of HSE-bmLLZO30 (30 wt% bmLLZO in HSE) and HSE-etched bmLLZO30 (Fig. 2c).

While PVDF-SPE film is transparent, HSE films show a dramatic variation in the color, depending on the dimension, composition and surface chemistry of loaded fillers (Fig. 2d and Fig. S11). The interaction between N,N-Dimethylformamide (DMF) solvent and LLZO is known to provide an alkaline-like environment.^{37,49} This can induce the dehydrofluorination of PVDF and thus HSE-bmLLZO30 turns dark brown. By contrast, HSE-etched bmLLZO30 exhibits light brown since a less alkaline-like condition with etched LLZO might alleviate the degradation of PVDF. Furthermore, the good mechanical flexibility is illustrated by the easy deformation of HSE-etched bmLLZO30 film.

For the optimal choice of LLZO fillers, HSE films were prepared with various filler contents of 0–50 wt%. Electrochemical impedance spectroscopy (EIS) of all films presents a similar trend that the ionic conductivity maximizes at 30 wt% content and declines above (Fig. 2e).^{37,47} The HSE-etched bmLLZO30 displays the maximum ionic conductivity of $4.05 \times 10^{-4} \text{ S cm}^{-1}$ approximately two times higher than HSE-bmLLZO30 ($2.12 \times 10^{-4} \text{ S cm}^{-1}$) at room temperature. Temperature-dependent conductivities and activation energies are compared where HSE-etched bmLLZO30 shows the lowest activation energy of 0.31 eV (Fig. 2f and Table S1).

Specific effect from eliminating Li_2CO_3 layers on the electrochemical performance has been investigated in a Li symmetric cell structure and SSBs with the HSEs including 30 wt% LLZO fillers. All the cells were tested at room temperature. Voltage-time profiles of the cells with PVDF-SPE and HSE-asLLZO30 present stable cycling at a low current density of 0.05 mA cm^{-2} (Fig. 3a). However, together with the increase of current density, the overpotential abruptly increased and eventually the cell failure occurred by exceeding a pre-set voltage limit (after 168 h for PVDF-SPE, after 244 h for HSE-asLLZO30), which can be ascribed to the large internal resistance. In HSE-asLLZO30, the relatively small PVDF/asLLZO interfacial area causes a high overall cell resistance, possibly by the dendritic grow of Li metal during cycling. Fig. 3b and c presents the cycling results for HSE-bmLLZO30 and HSE-etched bmLLZO30 cells from 0.05 to 0.15 mA cm^{-2} . Both cells displayed similar trends up to 0.10 mA cm^{-2} in terms of the shape of voltage plateau and cycling stability (Fig. S12). HSE-etched bmLLZO30 maintained the stable cycling with a low overpotential (0.045 mV) and flat voltage plateau at 0.15 mA cm^{-2} , whereas HSE-bmLLZO30 suffered from the increase of overpotential from 0.072 to 0.135 mV along with the irregular shape of the voltage hysteresis. The interfacial resistance of HSE-bmLLZO30 and HSE-etched bmLLZO30 was characterized by EIS upon Li stripping/plating test. (Fig. S13). As summarized in Fig. 3d, the interfacial areal specific resistance (ASR) shows much milder increase in HSE-etched bmLLZO30 (from 72.6 to $110 \text{ } \Omega \text{ cm}^2$) compared to HSE-bmLLZO30 (78 to $232.5 \text{ } \Omega \text{ cm}^2$). This further supports that removal of the Li_2CO_3 layers can boost up Li-ion transport and ultimately suppress the increase of cell resistance.

For the demonstration of practical cell performance, SSBs based on the configuration of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}/\text{LLZO-PVDF}$ HSEs/Li were assembled and cycled at room temperature. The rate performances of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}/\text{HSE-bmLLZO30}/\text{Li}$ and $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}/\text{HSE-etched bmLLZO30}/\text{Li}$ are compared in Fig. 3e. There is a similar level of discharge capacity for both samples at low current density ($\leq 0.5 \text{ C}$, $1 \text{ C} = 170 \text{ mA g}^{-1}$). However, a higher current density reveals the superior cycling profile of the SSB with HSE-etched bmLLZO30. Noticeably, SSB with HSE-etched bmLLZO30

exhibits a high discharge capacity of $\sim 79 \text{ mA h g}^{-1}$ at 4 C, which is three times higher than the one with HSE-bmLLZO30 ($\sim 26 \text{ mA h g}^{-1}$) as well as comparable to or even higher than the previous conventional batteries based on $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}$ cathode with liquid electrolyte⁵⁰ or sulfide-based electrolyte.⁵¹ This outstanding rate performance is the highest value among HSE-based SSBs employing the high capacity cathode materials such as $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}$ or LiFePO_4 reported to date (Fig. 3f and Table S2). The selected charge/discharge curves for each rate step are compared for clarification (Fig. S14). The voltage-capacity profiles during the long cycling are displayed in the inset in Fig. 3e. SSB with HSE-etched bmLLZO30 exhibits a more stable cycling stability than HSE-bmLLZO30. In addition, cycling test was also conducted at a low temperature of 10 °C (Fig. S15). The SSB with HSE-etched bmLLZO30 still exhibited the high capacity of 167 and 163 mA h g^{-1} at 0.1 and 0.2 C, respectively, while the SSB with non-etched LLZO delivered relatively inferior capacity (155 and 133 mA h g^{-1} at 0.1 and 0.2 C).

Underlying mechanism for the promoted performance of the HSEs with etched LLZO fillers could be characterized with solid-state magic angle spinning (MAS) ^7Li nuclear magnetic resonance (NMR). The plausible route for Li-ion migration within HSE volume consists of PVDF polymer matrix, LLZO fillers and/or the interface between them. From ^7Li NMR profiles, the resonance peaks for LLZO fillers and PVDF-SPE were observed at 0.36 and -0.63 ppm , respectively (Fig. 4a). The bmLLZO shows a slightly broad and weak profile compared to the etched counterpart, indicating the influence from surface barrier layer, resistant to mobile Li-ion.⁵² Narrow and intense peak for PVDF-SPE originates from LiClO_4 salt, homogeneously dissolved and complexed within the polymeric matrix. Non-blocking Li symmetric cells of 6Li/HSE-bmLLZO30 or HSE-etched bmLLZO30/6Li were assembled and cycled repeatedly at $10 \mu\text{A cm}^{-2}$ for every 5 min. 6Li from an electrode passes through HSE and reaches the opposite electrode while partly replacing ^7Li in the preferable pathway. Monitoring of the residual ^7Li in HSE can trace the possible Li-ion pathways. Noticeably, dissimilar NMR signals were detected in those samples after cycling, suggesting distinct Li-ion migration behaviors. (Fig. S16) Further, the NMR spectra can be deconvoluted to reveal a new peak at -0.28 ppm in addition to the two main signals, which is attributed to locally modified environment at LLZO and PVDF-SPE interface (Fig. 4b and Fig. S17).^{53,54}

Preferable Li-ion pathway was evaluated from the integral area of deconvoluted NMR spectra, as plotted in Fig. 4c. Significant reductions in ^7Li were observed in the PVDF-SPE (from 30.6 to $\sim 16.5 \%$) and interface (from 24.5 to 7.9 %) particularly for HSE-etched bmLLZO30. These results suggest the preferable Li-ion pathways through the polymer matrix and interface. Obviously, the interface seems more dominant as follows. First, LLZO fillers are known to modify the local surrounding environment by increasing mobile Li-ions.^{55–57} Second, uniform dispersion of LLZO fillers increases the total interfacial area in HSE, establishing abundant routes for ion transport, hardly achieved with a lower ($< 20 \text{ wt}\%$) or higher ($> 40 \text{ wt}\%$) filler loading (see Fig. 2e). Noteworthy that severe agglomeration of LLZO fillers could occur at the higher loading and result in a less generation of active interfaces.^{37,47}

Fig. 4d displays the imaginary part of impedance plotted against frequency, known as a Debye plot together with a fitting of a Lorentzian function, where the relaxation time is related to ion hopping within a

conductive medium. The characteristic frequency at the Debye peak maxima can be determined by the reciprocal of conductivity relaxation time (τ) or conductivity (σ) according to the following equation.^{58,59}

$$2\pi f_{max} = \omega = (\tau)^{-1} = \sigma(e_0\varepsilon')^{-1} \quad (1)$$

Where e_0 is the permittivity of free space ($8.854 \times 10^{-14} \text{ F cm}^{-1}$) and ε' (real component in complex permittivity) is the permittivity independent of frequency. Interestingly, no significant difference in the peak maxima signifies the similar level of ionic mobility for both HSEs.

Consequently, the promoted Li-ion conductivity in HSE-etched bmLLZO30 should be attributed to the higher population of mobile Li-ions particularly around the modified interface. The dielectric constant (relative permittivity) of doped cubic phase LLZO is known to be 40- 60, sufficiently high enough to promote Li-ion dissociation from salt.⁵⁵ In addition, surface defects or vacancies at etched LLZO surface may complex with Li-ions through Lewis acid- base reaction to further increase the concentration of free Li-ions in HSE.⁵⁶ Here, the surface Li_2CO_3 layers with much lower dielectric constant of 4.9 may weaken the dissociation of ions around LLZO.⁵⁷ Taken together, a proposed scheme is depicted for the ionic conductivity enhancement in Fig. 4e. While Li-ion transport can be facilitated with the enriched Li-ions around LLZO fillers, effective removal of the resistive surface layers can boost up the population of mobile ions and ultimately lead to the improved ionic conductivity and rate performance.

Discussion

We have demonstrated a straightforward yet highly effective interfacial design of HSEs, consisting of PVDF, Li salt and the garnet LLZO, without resistive interfacial barrier. For the first time, our study shows that the resistive surface layers can be removed in the powder state of inorganic SE fillers by reliable dry etching process, which in turn promotes the Li-ion conductive pathways along the modified interfaces. Moreover, dry etching approach, which is generically compatible with pre-existing industrial infrastructure, can be utilized in a large- scale production of novel SEs with cost-effectiveness. Mechanically flexible and solution- processable HSE films were readily attained and utilized for SSBs with the record-high rate performance.

Significantly, our MAS ^7Li NMR analysis clarifies the locally modified polymer-inorganic interfaces and neighboring environments as the principal pathways for Li-ion transport. As supported by EIS measurements, effective increase of mobile ions in the major pathways is the enhancement mechanism of ionic conductivity in the heterogeneous system. This unprecedented clear picture among the previous controversial mechanisms for HSE enables a novel design concept and principle for the optimal interface, widely useful for the materials and devices relying on the ionic transport through practical heterogeneous structures. Our systematic research unveils a rarely explored opportunity for the high performance interface engineered HSE, generally demanded for the safe and efficient energy storage systems in deformable electronics, microbatteries, electrochemical sensors and so on.

Methods

Preparation of LLZO solid electrolyte

Multi-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) solid electrolytes were prepared by using a solid-state method. A stoichiometric mixture of Li_2CO_3 (99.998 %, Alfa Aesar), La_2O_3 (99.99 %, Alfa Aesar), ZrO_2 (99 %, Sigma Aldrich) with both Al_2O_3 (Sigma Aldrich) and Ta_2O_5 (99.99 %, Sigma Aldrich) as dopants (0.2 mol for Al_2O_3 , 0.2 mol for Ta_2O_5) was ball-milled (Fritsch, Pulverisette 5) at 250 rpm for 12 h in isopropyl alcohol. The resulting slurry was calcined at 1000 °C for 4 h, followed by annealing at 1200 °C for 12 h to obtain high crystalline LLZO with cubic phase. As-synthesized LLZO was further ball-milled at 300 rpm for 7.5 h with isopropyl alcohol (Fritsch, Pulverisette 7). The ball-milled LLZO was dried thoroughly at 60 °C for 1 day. The resistive layers at LLZO surface was eliminated through reactive ion etching (RIE) (100 W, 50 sccm CF_4). LLZO powders were evenly spread onto Si wafer and then RIE was conducted for a given etching time.

Fabrication of solid polymer electrolyte and hybrid solid electrolyte

Poly(vinylidene fluoride) (PVdF, Arkema, Solef ^R 5130, MW : 1,000,000–1,200,000) solid polymer electrolyte (SPE) was prepared by solution casting method. PVDF-SPE solution was obtained by dissolving LiClO_4 (99.99 %, Sigma Aldrich) and PVDF (10 wt% in solution) at a 1:2 wt ratio in N,N-Dimethylformamide followed by mixing homogeneously. After that, PVDF-SPE solution was cast onto a Teflon mold (4 x 4 cm²) and then dried at 50 °C for 12 h in a vacuum oven to gain a free-standing film with a thickness of 100 ~ 150 µm. A series of PVDF-LLZO hybrid solid electrolytes (HSEs) were prepared by adding LLZO fillers at various compositions (10, 20, 30, 40, 50 wt % versus PVDF) to the PVDF-SPE solution. LLZO fillers were uniformly distributed in the PVDF-SPE solution through a high-speed mixing at 2000 rpm for 10 min. The resulting solution was cast and dried in the same procedure for the fabrication of PVDF-SPE. All the procedures were performed in a dry room with nearly moisture-free condition.

Material Characterization

Morphology of LLZO, PVDF-SPE and PVDF-LLZO HSEs was examined by FESEM (Hitachi, S-4800) and TEM (Talos F200X). EDS-mapping images were obtained using EX-250 (Horiba). XRD patterns were obtained by a X-ray diffractometer (X'pert Pro, Philips, $\text{Cu K}\alpha$: 1.54056 Å). XPS measurements (Thermo VG Scientific, K-alpha) provided high-resolution core scans of C 1s, O 1s, Li 1s, Zr 3d and La 3d before and after dry etching process. Raman spectra (Horiba, LabRAM HR Evolution) were measured to confirm the presence of Li_2CO_3 layers on the LLZO surface. The ionic conductivities and activation energies were characterized by impedance analyzer using a frequency response (Solartron HF 1225, 10–1~105 Hz) in the temperature range of 0 to 100 °C. Solid state MAS ^7Li NMR spectra were obtained using a Bruker

AVANCE III 400 spectrometer with 1.9 mm HX-MAS probe at the spinning rate of 25 kHz. As a reference for ^7Li chemical shift, solid LiCl at 0 ppm was used.

Electrochemical Characterization

All the cells for electrochemical characterization were assembled into a CR2032 coin-type cell in dry room. EIS measurements were performed by constructing the sandwich-type cell of stainless steel (SS)/SPE or HSEs/SS over the frequency range of 10–1 to 105 Hz at room temperature. To obtain the activation energy, the impedance spectra were examined in the temperature range of 0 to 100 °C. Symmetric cells of Li/SPE or HSEs/Li were prepared to measure the resistance change of samples and the overpotential during Li plating/stripping tests. The Li symmetric cells were cycled at diverse current rates from 0.05 to 0.15 mA cm^{-2} and the direction of current was switched every 60 min with 10 min rest. EIS test was conducted at each current step to investigate the resistance change. For a battery test, the NCM electrode was prepared by mixing $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622, L&F Co), carbon black as a conducting agent and PVDF-SPE as a binder with a weight ratio of 92:4:4. Then, the resulting slurry was coated on Al foil and dried at 60 °C for 24 h in a vacuum oven. The loading level of active material was controlled to be $\sim 3.0 \text{ mg cm}^{-2}$. Liquid electrolyte of $\sim 3 \text{ uL}$ was used as a buffer layer between cathode and HSE. The charge/discharge curves and rate performances of SSBs based on the cell configuration of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}/\text{LLZO-PVDF HSEs/Li}$ were evaluated under galvanostatic cycling condition from 3.0 to 4.2 V at room temperature (Toyo System, Toscat–3000). For the tracing of Li-ion pathway in PVDF-LLZO HSEs, 6Li – ^7Li replacement strategy was used. The 6Li symmetric cells of $6\text{Li/PVDF-LLZO HSEs}/6\text{Li}$ were prepared. 6Li foils made by compressing 6Li chunk (95%, Sigma Aldrich) were attached at both sides of PVDF-LLZO HSE films. A constant current density of 10 uA cm^{-2} was applied.

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Declarations

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Author contributions

D.O.S. conceived the idea for this study. D.O.S. and M.J.L. synthesized LLZO. M.J.L. conducted etching experiment and characterized the samples under the guidance of D.O.S.

M.J.L. conducted electrochemical characterization with help from J.Y.K., J.O., J.K. and S.H.K.

D.O.S. performed NMR analyses. D.O.S. organized the results and drew relevant figures.

D.O.S., M.J.L., Y.G.L., K.M.K. and S.O.K. analysed and interpreted the results. D.O.S., S.O.K. and Y.G.L. supervised the project and wrote the manuscript. All authors commented on the data and the manuscript.

Competing interests

The authors declare no competing interests.

Figures

Figure 1

(a) High-resolution TEM image of LLZO surface covered with poorly crystallized Li_2CO_3 layers. (b) Schematic illustration for dry etching (CF_4 RIE) of surface Li_2CO_3 layers. Deconvoluted XPS core scans of (c) C 1s, (d) O 1s and (e) Li 1s collected from LLZO fillers at various etching times. (f) XPS for Zr 3d before and after surface etching. (g) Atomic ratios (C/La and C/Zr) at LLZO filler surface vs. etching time. (f) EDS-mapping images for La and C elements from as-synthesized and 15 min etched LLZO. Si substrate was used for etching process for a clear signal of carbon.

Figure 2

(a) SEM images of as-synthesized (asLLZO) and ball-milled LLZO (bmLLZO). (b) Statistical size distribution of asLLZO ($12.97 \pm 4 \mu\text{m}$) and bmLLZO ($1.2 \pm 0.5 \mu\text{m}$). (c) Comparative XRD patterns of asLLZO, PVDF-SPE and the HSEs with the same content (30 wt%) of asLLZO, bmLLZO and etched bmLLZO. (d) Photographic images of prepared films for PVDF-SPE, HSE-asLLZO30, HSE-bmLLZO30 and

HSE-etched bmLLZO30. (e) Ionic conductivities vs. LLZO content at room temperature. (f) Temperature-dependent conductivities and activation energies.

Figure 3

Voltage vs. time profiles of Li symmetric cells with (a) PVDF-SPE, HSE-asLLZO30, (b) HSE-bmLLZO30 and (c) HSE-etched bmLLZO30 upon cycling with stepwise current density increase (0.05 and 0.01 mA cm-2 for 100 h, 0.15 mA cm-2 for 120 h). Current direction was switched at every 1 h. Enlarged cycling profiles from 290 to 310 h are shown as insets. (d) Comparison for ASR changes of HSE-bmLLZO30 and HSE-etched bmLLZO30 before and after cycling (300 h). (e) Rate capabilities of LiNi0.6Mn0.2Co0.2/Li cells with HSE- bmLLZO30/Li and HSE-etched bmLLZO30/Li. The cyclabilities at 0.2 C are shown in the inset. (f) Comparison of rate capabilities between HSE-etched bmLLZO30 and previously reported HSEs based SSBs.

Figure 4

(a) MAS ^7Li NMR spectra of bmLLZO, etched bmLLZO and PVDF-SPE. (b) Deconvoluted MAS ^7Li NMR profiles for HSE-bmLLZO30 and HSE-etched bmLLZO30 after cycling in 6Li symmetric cells. (c) Quantitative comparison of deconvoluted NMR peak areas before and after cycling. Relative percentage of integral area is calculated. (d) Imaginary part of impedance plotted vs. logarithmic frequency (Debye plots) with fitting for HSE-bmLLZO30 and HSE-etched bmLLZO30. The Debye maxima are indicated by

vertical line. (e) Schematics for preferred Li-ion transport pathways in (i) HSE-bmLLZO30 and (ii) HSE-etched bmLLZO30. Modified interface depicted (greenish halo around LLZO fillers) is more apparent in HSE-etched bmLLZO30, implying a higher population of mobile Li-ions.

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