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**A ceramic-PVDF composite membrane with modified
interfaces as an ion-conducting electrolyte for solid-state
lithium-ion batteries operating at room temperature**

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Abstract

Solid-state batteries hold great promise because of their safety and high projected energy density. However, the sizeable interfacial resistance between the electrodes and the electrolyte of such batteries is a significant bottleneck in the development of this technology. In this work, we develop a $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO) and polyvinylidene fluoride (PVDF) solid-state composite membrane characterized by high conductivity, tensile strength, and flexibility as well as low impedance if interfacially modified by a minute amount of liquid electrolyte. A solid-state lithium-ion battery using this electrolyte with LiFePO_4 and Li as electrodes delivers excellent rate capability and cycling stability at room temperature. In particular, the battery shows an initial discharge capacity of 155 mAh g^{-1} and, after 100 cycles at 1C, of 145 mAh g^{-1} . Even at 4C, the discharge capacity is 96 mAh g^{-1} . Our study suggests that the interfacially modified LLZTO-PVDF membrane is a promising electrolyte for solid-state lithium-ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) have been widely used commercially because of their higher volumetric and gravimetric energy densities, longer cycle lives, and lower costs, compared to other battery technologies [1, 2]. In addition to being predominantly employed in portable electronic devices, LIBs have shown excellent potential for high-power and energy density applications such as electric vehicles and grid-scale electrochemical energy storage systems [3-5]. However, commercial LIBs often use organic carbonate liquid electrolytes, which have a limited working voltage [6] and high toxicity [7] and are highly flammable and corrosive. These electrolytes also tend to react with active materials causing capacity loss [1, 8, 9] and have a transference number between 0.2 and 0.5 [10]. While various strategies can be used to make the electrolyte composition less flammable [11-13], in many high-power applications the utilization of organic electrolytes requires the implementation of a number of stringent safety measures [14-16].

To address these issues, solid-state electrolytes (SSEs) such as ion-conducting inorganic ceramics [17, 18], organic polymers [4, 19], and ceramic-composites [5, 20, 21] have been investigated as alternatives to liquid electrolytes. Many polymer SSEs, such as poly(ethylene oxide) (PEO), have good mechanical properties [19, 22, 23]. For example, a porous polymer membrane doped with phytic acid showed a critical tensile strength of 20.71 MPa with an elongation-at-break value of 45.7% [24]. However, at room temperature (RT), polymer electrolytes have low ionic conductivities ($<10^{-5}$ S cm⁻¹)

and a low cation transference number (0.3–0.4) [17, 25, 26]. Ceramic SSEs such as garnets [27], perovskites [28], antiperovskites [29], LISICON-like materials [30], and lithium nitrides [31] have several exciting advantages, including thermal stability, nonflammability, and in some cases, most notably for garnets, ionic conductivities exceeding 0.1 mS cm^{-1} at RT [4, 5, 28, 32–34]. However, the grain boundary conductivity of ceramic SSEs is significantly lower than that of the bulk [35, 36]. For example, the RT bulk conductivity of $\text{Li}_{5.68}\text{La}_{3.00}\text{Zr}_{2.03}\text{Al}_{0.26}\text{O}_{11.79}$ was reported to be $\sim 0.25 \text{ mS cm}^{-1}$, while the grain boundary conductivity was determined to be lower than $10^{-8} \text{ S cm}^{-1}$ [37]. Furthermore, electrode/electrolyte interfacial resistances are typically high because of the poor solid-solid contacts at such interfaces [1, 25, 38]. Also, many solid electrolyte materials are unstable at high voltages and may react with the materials of the electrodes [39–43]. Moreover, since ceramic SSEs are brittle, some researchers have questioned their suitability in some applications, most notably in electric vehicles [1, 25]. Composite electrolytes can potentially combine the advantages of both ceramics and polymers by providing a high ionic conductivity with a high cation transference number together with high flexibility and tensile strength. Some researchers have reported such composite electrolytes, including $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ -polyacrylonitrile (PAN) [44], $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ -PEO [45–47], and $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ -PEO [48]. However, due to their low ionic conductivity and the high solid electrode/solid electrolyte interfacial resistance, the electrochemical performance of solid-state LIBs (SSLIBs) with composite electrolytes still lags far behind that of conventional LIBs especially at RT [1, 49].

Recently, Nan et al. reported that dispersing $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ in N,N-dimethylformamide triggered the partial chemical dehydrofluorination of PVDF, thereby increasing the Li conductivity of the composite compared to the individual PVDF membrane [49]. Indeed, PVDF-based electrolytes have shown improved electrochemical, thermal, and mechanical stability compared with PEO-based electrolytes [49-53]. Until now, PVDF-garnet composites have been reported as SSEs for LIBs only by a few research groups [49, 54]. To overcome the high interfacial resistance, tens of μLs of liquid electrolyte have been added to the interface [54]. Alternatively, the electrode may first be infiltrated with a liquid electrolyte-containing solution (i.e. PEO/ lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)/ethylene carbonate/acetonitrile) for interfacial modification and subsequently dried at $60\text{ }^{\circ}\text{C}$ [49]. While previous studies have clearly shown the effectiveness of the membrane, the influence of the liquid electrolyte on the interfacial resistances and cyclic performance of the batteries has not been explicitly studied.

In this work, we prepared a composite electrolyte containing LLZTO powder, a PVDF matrix, and LiClO_4 . While the addition of LiClO_4 leads to the decrease of crystallinity of PVDF [55], the presence of the LiClO_4 salt is a key factor to increase the ionic conductivity [56]. Moreover, the formation of LiClO_4 and PVDF complexes enhances the mechanical strength and improves the transport properties [57]. We also investigated the impact of wetting the electrode/electrolyte interfaces on the

electrochemical performance of the SSLIBs. The obtained composite electrolyte had high ionic conductivity and thermal stability. It also featured a wider electrochemical window and a lower electrode/electrolyte resistance after the incorporation of a minute amount of liquid electrolyte. Furthermore, the correspondingly prepared SSLIB exhibited an improved cycling stability performance and rate capability.

2. Results and discussion

2.1 Basic chemical, physical and mechanical properties

As shown in **Fig. S1a**, the XRD pattern of the LLZTO pellet shows a pure cubic phase structure without impurities, matching well with the standard pattern of the cubic garnet phase (JCPDS 80-0457). This cubic phase is preferred because of its higher conductivity compared with the tetragonal phase [58-60]. Based on the EIS result (**Fig. S1b**), the RT total ionic conductivity of the LLZTO pellet is estimated to be $\sim 2 \times 10^{-4} \text{ S cm}^{-1}$, a value comparable to those reported in the literature [58, 59, 61, 62]. **Fig. S1c and d** show the top-view and cross-section of the LLZTO pellet. It is clear that the LLZTO pellet is dense, with an average grain size of $\sim 2 \text{ }\mu\text{m}$.

After successfully obtaining cubic LLZTO, we prepared SSEs by blending the sieved LLZTO powder with PVDF and LiClO_4 . The formed SSEs are denoted as SSE-X (X = 0, 10, 20, and 30), where X indicates the weight percentage of LLZTO. Interestingly, the pH and color changed as a function of X, see **Fig. 1a**. The pH increased from 7.2 to 8.6, 9.2, and 9.7 with X, and the membrane turned from transparent to dark brown. The

change in pH and color is ascribed to the interaction between PVDF and LLZTO and results from the chemical dehydrofluorination of the PVDF skeleton [49]. This interaction may, in turn, have an impact on the ionic conductivity of SSE-X with X = 10, 20, and 30) [49]. We measured the RT ionic conductivities (**Table 1**) of the SSE-X membranes, while the corresponding Nyquist plots are shown in **Fig. 1b**. It should be noted the ionic conductivities of the SSE-10, SSE-20, and SSE-30 membranes are higher than that of SSE-0. In the SSE-X series, SSE-10 has the best conductivity with a tenfold improvement over SSE-0. As suggested by Zhang and coworkers [49], the introduction of LLZTO into the polymer facilitates the formation of LLZTO/polymer interfacial regions characterized by high ionic conductivity. It is important to note that increasing the LLZTO content beyond 10 wt.% leads to a decrease in ionic conductivity, perhaps as a consequence of LLZTO particle aggregation [44]. To analyze the distribution of LLZTO and other compounds in the composite, we acquired several EDX images and we report only representative elements, see **Fig. S2**. The SSE-10 EDX maps, which are reported in **Fig. S2a**, suggest a seemingly uniform distribution of LLZTO (La), PVDF (F) and LiClO₄ (Cl). In contrast, the LLZTO in SSE-20 and SSE-30, see **Fig. S2b and c**, does not appear to be evenly distributed. This suggests that aggregation preferentially takes place at loadings beyond 10 wt.%, consistent with a previous study [42].

Table 1. pH, ionic conductivity, tensile strength, and Young's modulus of SSE-X.

Membrane	pH	Ionic conductivity	Tensile strength	Young's modulus
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		(S cm ⁻¹)	(MPa)	(MPa)
SSE-0	7.2	9.6×10^{-6}	6.8	15.4
SSE-10	8.6	1.1×10^{-4}	12.1	20.6
SSE-20	9.2	5.5×10^{-5}	9.3	19.0
SSE-30	9.7	3.1×10^{-5}	7.0	13.7

Fig. 1. (a) pH and color of SSE-X. (b) EIS of the SS|SSE-X|SS cell. Picture showing shrinkage of a Celgard® polypropylene (PP) separator and the SSE-X at (c) 100 °C and (d) 200 °C. (e) Stress-strain curves of SSE-X.

The thermal stability and mechanical properties are also of critical importance for the development of SSEs. **Panels c and d of Fig. 1** compare the thermal stabilities of the SSE-X and a commercial PP separator (Celgard®) at 100 °C and 200 °C. SSE-X and Celgard® separator were heated in air on a hotplate under identical conditions. The commercial Celgard® separator began to reduce in size at ~100 °C (**Fig. 1c**), whereas the SSE-X showed excellent thermal stability with no noticeable shrinkage at temperatures as high as 200 °C (**Fig. 1d**). Typical stress-strain curves for the SSE-X are presented in **Fig. 1e**. After adding the micron-sized LLZTO powder to PVDF, the SSE-X could withstand significantly increased strain. The tensile strength values and Young's modulus of the SSE-X are listed in **Table 1**. Consistent with previous reports [49], the SSE-10 shows, among the investigated SSE-X, the highest tensile strength (12.1 MPa) and Young's modulus (20.6 MPa), much higher than those of the PEO-based electrolyte [22, 63]. For example, a critical tensile strength of 0.35 MPa was reported for the PEO-LiClO₄ membrane [64].

Fig. 2. XRD patterns of PVDF, SSE-0, SSE-10, and the LLZTO powder.

In light of the above results, the following part of this article will primarily study SSE-10. **Fig. 2** shows XRD patterns of the PVDF powder, SSE-0, SSE-10, and the LLZTO powder. PVDF has three characteristic peaks at 18.3° , 20.0° , and 26.1° , which can be assigned to the (020), (110), and (021) planes of its α -phase [65, 66]. For the SSE-0 and SSE-10, the peaks at 18.3° and 26.1° disappear, and the dominant peak is located at 20.2° , suggesting the formation of the polar β - and γ - phase of PVDF [66]. The XRD pattern of SSE-10 indicates that the bulk crystals of LLZTO are preserved even in the membrane. The evolution of phase structure of PVDF suggests that the PVDF chains interact with LLZTO [67]. As outlined above, this interaction is also evidenced by the change of the pH, color, and conductivity of SSE-X after the introduction of the LLZTO powder.

The SEM images of the ball-milled LLZTO powder, SSE-0, and SSE-10 are shown in **Fig. 3**, where the sieved particles of the ball-milled LLZTO are generally below 2 μm in diameter (**Fig. 3a**). The SSE-0 membrane has a high porosity with a pore diameter below 3 μm (**Fig. 3b**). After blending the LLZTO powder with PVDF, the morphology changes and SSE-10 shows a well-connected and relatively dense microstructure, and the size of the PVDF pores decreases dramatically, see **Fig. 3c**. Moreover, the cross-sectional view of the SSE-10 membrane (**Fig. 3d**) indicates the absence of interconnected pores across the membrane. Therefore, it is plausible that, when wetted, the membrane's surface is primarily affected especially if a minute amount of liquid electrolyte is introduced. The actual densification is likely linked to the strong interaction between PVDF and LLZTO and is, as shown above, beneficial to the transportation of lithium ions [68]. In order to make fully dense membranes with no pores on the surface or across the membrane, nano-sized LLZTO will be prepared in the future.

Fig. 3. SEM images of (a) the ball-milled LLZTO powder, (b) SSE-0 top view, (c) top and (d) cross-sectional views of SSE-10.

We also evaluated the thermal characteristics of SSE-X by TG (**Fig. S3a**). The decomposition of PVDF alone occurs at ~ 460 °C. SSE-0 experiences a sharp weight loss at lower temperatures compared to PVDF alone. This phenomenon, likely following from the inclusion of LiClO_4 in SSE-0, indicates that there is an interaction between the lithium ions from the salt and the PVDF matrix [49]. It should be noted that the temperature, at which the weight loss of SSE-10 initiates, is even lower than that of SSE-0. Further, a full degradation occurs at ~ 328 °C, a temperature higher than the one observed for commonly used liquid organic electrolytes, such as LiPF_6 in ethylene carbonate (EC) : dimethyl carbonate (DMC) and LiTFSI in EC : DMC [1, 3,

69]. The DSC curves of the PVDF, SSE-0, and SSE-10 membranes were also recorded (**Fig. S3b**). All samples display endothermic peaks at temperatures higher than 140 °C. Concomitantly, the glass transition temperature (T_g) decreases from 153.7 °C (PVDF) to 142.8 °C (SSE-0) and 134.8 °C (SSE-10), suggesting that the introduction of LiClO₄ and LLZTO reduces the crystallinity of PVDF [70-72]. The relatively low glass transition temperature of SSE-10 compared to that of PVDF and SSE-0 indicates the low crystallization of PVDF in the SSE-10 electrolyte membrane. This property is beneficial to the ionic conduction.

2.2 SSE-X with wet interfaces

To investigate the impact of wetting the electrode/electrolyte interfaces, we constructed a cell with 2 μ L of the liquid electrolyte at each such interface (we estimated the volume liquid to solid ratio to be $\sim 8.5\%$, see Note **S1**), see **Fig. 4**. In contrast, 20 μ L (estimated volume ratio $\sim 32.5\%$) were used in another study [54]. As shown in **Fig. 5a**, the ohmic resistance of SS|SSE-10|SS is much higher than that of a similar cell with wet SSE-10 (WSSE-10), and the corresponding ionic conductivities of SSE-10 and WSSE-10 are 1.1×10^{-4} and 9.6×10^{-4} S cm⁻¹. The greater ionic conductivity of WSSE-10 may be ascribed to the gelation of the membrane itself. However, it should be mentioned that such process is expected to take place primarily on the surface since only a minute amount (2 μ L) of liquid electrolyte was added to the relatively dense surface. Li/Li symmetric cells and SSLIBs were assembled using both SSE-10 and wet SSE-10. The corresponding EIS spectra are shown in **Fig. 5b & c**. It is worth noting that applying 2

μL of the liquid electrolyte at the electrode and electrolyte interface dramatically reduces the total resistance. The interfacial resistances of the $\text{Li}|\text{SSE-10}|\text{Li}$ symmetric cell and the $\text{Li}|\text{SSE-10}|\text{LFP}$ cell were $\sim 450\ \Omega$ and $\sim 603\ \Omega$, respectively. In contrast, the interfacial resistances of cells with WSSE-10 decreased to $\sim 140\ \Omega$ and $\sim 14\ \Omega$, respectively. These results successfully demonstrate that a minute amount of liquid electrolyte at the electrode and electrolyte interface enhances the interfacial contacts, thereby reducing the interfacial resistance of SSE-10. This synergy is also beneficial to the battery performance as we will discuss in the next section.

Fig. 4. Schematic illustration of the assembly of a coin-type cell with SSE-X.

We also studied the electrochemical stability window of the SSE-10 and WSSE-10 by CV from $-1\ \text{V}$ to $5\ \text{V}$ at a scan rate of $20\ \text{mV s}^{-1}$. The current-voltage curves of $\text{SS}|\text{SSE-10}|\text{Li}$ and $\text{SS}|\text{WSSE-10}|\text{Li}$ cells are shown in **Fig. 5d**, where no oxidation peaks of the $\text{SS}|\text{WSSE-10}|\text{Li}$ cell are observed at potentials higher than $4.5\ \text{V}$ (versus Li/Li^+). In contrast, the oxidation peak of the $\text{SS}|\text{SSE-10}|\text{Li}$ cell occurs at a potential below $4.0\ \text{V}$

(versus Li/Li^+). These results demonstrate that WSSE-10 has a wider working potential window and better electrochemical stability than SSE-10. As the commercial liquid electrolyte (LiPF_6 in EC, DMC and ethylmethyl carbonate (EMC)) has a relatively low oxidation stability [73], these results also suggest that the electrochemical stability of wetted polymer electrolytes is not merely related to the lithium salt, but also to the solvents and polymers present.

Fig. 5. EIS of (a) the SS|WSSE-10|SS and SS|SSE-10|SS cells, (b) symmetric Li|WSSE-10|Li and Li|SSE-10|Li cells, and (c) asymmetric Li|WSSE-10|LFP and

Li|SSE-10|LFP cells (Ohmic resistances are subtracted in Fig. b and c to allow a direct comparison of the interfacial resistances). (d) Cyclic voltammetry response of the SS|WSSE-10|Li, and SS|SSE-10|Li cells.

We carried out Li plating and stripping experiments to assess the compatibility between Li and SSE-10. **Fig. 6a** shows a 65 h cycling test of a Li|WSSE-10|Li symmetric cell at current densities of ± 0.1 , ± 0.2 , and ± 0.5 mA cm⁻², whose response voltages stabilize at ~ 24 mV, ~ 74 mV, and ~ 175 mV, respectively. The cell short circuits when the current density reaches 1.0 mA cm⁻². In contrast, the Li|SSE-10|Li symmetric cell shows an unstable and large voltage response after 8 cycles at a current density of 0.1 mA cm⁻² (**Fig. 6b**). To investigate the impact of the LLZTO powder in the composites, we galvanostatically cycled the symmetric Li/Li cells with WSSE-0 and WSSE-10 at a current density of 0.5 mA cm⁻², see **Fig. 6c**. It is worth noting that the total resistance of a Li|SSE-0|Li symmetric cell is as high as ~ 275 Ω . Also, the voltage of this cell exceeds 3 V after only 25 cycles. In contrast, the total resistance of Li|WSSE-10|Li cell drops to ~ 160 Ω , a value that is consistent with the interfacial resistance obtained from EIS (**Fig. 5b**). Furthermore, Li|WSSE-10|Li has a relatively stable voltage response even after 2100 min of operation. We can conclude that the addition of a small amount of liquid electrolyte decreases the contact resistance and improves the compatibility between the SSE-10 and Li electrode.

Fig. 6. Plating and stripping cycling test of (a) a Li|WSSE-10|Li cell, and (b) a Li|SSE-10|Li cell. (c) Galvanostatic cycling of a Li|WSSE-10|Li and a Li|WSSE-0|Li cell under a current density of 0.5 mA cm^{-2} .

2.3 Battery performance

The cycle capability of the Li|SSE-10|LFP cell was further investigated in the voltage range from 2.5 to 4.2 V. **Fig. 7a** shows the first charge-discharge capacity curve of the Li|SSE-10|LFP cell cycled at 0.05C. The first charge capacity reached 163 mAh g^{-1} , while the discharge capacity was only 42 mAh g^{-1} . Furthermore, the discharge capacity decreased rapidly to 0 mAh g^{-1} after 10 cycles. Concurrently, both the ohmic and

polarization resistances increased significantly during cycling (**Fig. S4**), suggesting a worsening interfacial contact. In contrast, as shown in **Fig. 7b**, the Li|WSSE-10|LFP cell delivered a discharge capacity of 155 mAh g⁻¹ in the first cycle with an initial coulombic efficiency of 91% at 1C. Furthermore, the battery maintained a discharge capacity of 145 mAh g⁻¹ with a coulombic efficiency >99% for the ensuing 100 cycles, see **Fig. 7c**. Both ohmic and polarization resistances (inset of **Fig. 7c**) grew slightly as a consequence of cycling. This increase can be linked to a decreased discharge capacity and suggests that optimizing the interface further may lead to improved batteries. The rate performance of the Li|WSSE-10|LFP cell is shown in **Fig. 7d**. Even at 4C, we were able to obtain a stable capacity of 96 mAh g⁻¹. When the current density returned to 1C, 99.6% of the initial capacity was recovered. It should be noted that the thickness of the electrolyte membrane used in this work is ~150 μm, while the thickness of commercial separators is usually ~25 μm. It is therefore expected that the energy and power density, as well as the rate capability of our batteries, can be further improved by optimizing the thickness of the electrolyte membrane [74] using advanced fabrication techniques and architectures [75-77].

The rate performance of a Li|WSSE-0|LFP cell was also evaluated to demonstrate the positive role of adding the LLZTO powder. Although the coulombic efficiency was as high as that of the WSSE-10 cell, the discharge capacity of the Li|WSSE-0|LFP cell was substantially lower, i.e., 102 mAh g⁻¹, 80 mAh g⁻¹, and 48 mAh g⁻¹ at 1C, 2C, and 4C, respectively. As shown in **Fig. S5a**, when the current density goes back to 1C, the

capacity of 100 mAh g^{-1} was still achieved, showing the good operating stability of the membrane. We have shown that the enhanced performance is due to the synergy between the SSE-10 and the wetting of the interfaces. To verify that a working battery cannot be prepared using only the liquid electrolyte we used, we assembled a Li/LFP cell using a commercial Celgard® PP separator with $2 \mu\text{L}$ of liquid electrolyte at the interface of electrode and electrolyte. In contrast to the Li|WSSE-10|LFP, this battery could not complete the charging process to 4.2 V at 1C , see **Fig. S5b**.

Fig. 7. (a) The 1st charge/discharge curve of a Li|SSE-10|LFP cell at 0.05C. (b) The 1st charge/discharge curve of a Li|WSSE-10|LFP cell at 1C. (c) Cycling performance and coulombic efficiency of a Li|WSSE-10|LFP cell at 1C. (d) Rate performance of a Li|WSSE-10|LFP cell at 1C, 2C, and 4C.

3. Conclusions

In this article, we fabricated SSEs with LLZTO, lithium salt, and a PVDF polymer matrix as an ion-conducting electrolyte. The SSE-10 exhibited the best RT ionic conductivity in the series of membranes studied and displayed high tensile strength and flexibility. The interfacial resistances dramatically dropped after adding only 2 μL of liquid electrolyte to the membrane. The correspondingly modified WSSE-10 displayed remarkable electrochemical stability up to ~ 4.5 V (versus Li/Li^+). More importantly, the fabricated $\text{Li}|\text{WSSE-10}|\text{LFP}$ cell showed a good rate capability and cycling stability. The battery had an initial discharge capacity of 155 mAh g^{-1} , and held to 145 mAh g^{-1} after 100 cycles at 1C. Even at 4C, a discharge capacity of 96 mAh g^{-1} was still achieved. Our study suggests that the liquid modified LLZTO-PVDF membrane is a promising electrolyte for SSLIBs.

Experimental Section

Materials synthesis

The LLZTO powder was prepared with a conventional solid-state reaction method [78]. We mixed and ball milled stoichiometric amounts of $\text{LiOH}\cdot\text{H}_2\text{O}$ ($\geq 99.0\%$, Sigma-Aldrich), La_2O_3 (99%, $<100 \text{ nm}$, Sigma-Aldrich), ZrO_2 ($<100 \text{ nm}$, Sigma-Aldrich), and Ta_2O_5 ($\geq 99.99\%$, Ourchem) in isopropanol for 90 min at 500 rpm with zirconia balls in a zirconia jar. The La_2O_3 powder was pre-dried at 900°C for 12 h before preparation. Then, we dried the mixed powders at 200°C for 2 h and heated them at 900°C for 12

h in air inside a MgO crucible. We added an extra 10 wt.% of $\text{LiOH} \cdot \text{H}_2\text{O}$ to compensate for the loss of Li during heating as well as adding 0.3 wt.% Al_2O_3 as a sintering aid [61]. We ground the mixed powders for a second time and pressed them into pellets. We covered the obtained pellets with the mother powder and annealed them at 1140 °C for 16 h. Finally, the LLZTO pellets were ground with isopropanol by ball-milling for 90 min at 500 rpm, and the resulting powder was sieved.

The free-standing SSEs were prepared by film casting. We dried LiClO_4 (99.99%, Sigma-Aldrich), LiNO_3 (99.99%, Aldrich), and PVDF (Kynar HSV900, Arkema) in a vacuum at 80 °C for 24 h to remove moisture. We first mixed 0.3 g of PVDF and 0.1 g of LiClO_4 with 4 mL of N,N-dimethylformamide (DMF, 99.9%, Prolabo), and then stirred the mixture at 50 °C for 4 h on a hot plate to form a transparent solution. To form a smooth and dense protective film on the Li anode [79], we added 5 wt.% of LiNO_3 . The LLZTO powder was subsequently added to the solution and stirred for another 6 h at 60 °C. The LLZTO content was set at 0, 10, 20, and 30 wt.%. Finally, the homogeneous mixture was cast onto a glass dish and dried in a vacuum oven at 60 °C for 30 h to remove the DMF solvent. The thickness of the electrolyte membrane was consistently measured to be $\sim 150 \mu\text{m}$.

Materials characterizations

The pH values were measured with a pH meter (AZ8651 pH & ORP Meter, AZ Instrument). X-ray diffraction (XRD, PANalytical Empyrean) was performed using Cu

K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range from 10° to 90° (step size of 0.033°) at an operating voltage of 40 kV and a current of 40 mA. Scanning electron microscopy (SEM, JEM 6700F) and energy-dispersive X-ray spectroscopy (EDX) were carried out to obtain the morphologies and compositions of the electrolyte membranes, respectively. Thermo-gravimetry (TG, Q5000-TA) was carried out from RT to 600°C , and differential scanning calorimetry (DSC, STA 449 F3) was performed from RT to 170°C at a heating rate of $10^\circ\text{C min}^{-1}$ in Ar. Inspired by the work of Kim and co-workers [25], we examined the shrinkage of the membranes by placing them on a hot plate for 15 min at either 100°C or 200°C . The stress-strain curves of the electrolyte membranes ($\sim 16 \text{ mm} \times 40 \text{ mm} \times 0.15 \text{ mm}$) were obtained at RT with a stretching rate of 10 mm min^{-1} using an Alliance RT/05 machine.

Electrochemical characterizations

We measured the ionic conductivity of the LLZTO pellets and the electrolyte membranes by electrochemical impedance spectroscopy (EIS) using an electrochemical workstation (VSP-300, Bio-Logic). For the measurement of the ionic conductivity of the LLZTO pellets and SSE-X, we prepared an Au|LLZTO|Au cell and a CR2032 coin cell, respectively. For the latter, we sandwiched the electrolyte membrane between stainless steel (SS) disks (SS|SSE-X|SS). The ionic conductivity, σ , was calculated using $\sigma = \frac{l}{R \times A}$, where l is the thickness of the electrolyte membrane, R is the measured total resistance, and A is the surface area of the electrolyte. To evaluate the electrochemical stability window of the electrolyte by cyclic voltammetry (CV), we

assembled a cell, where the electrolyte membrane was sandwiched between a SS disk and a foil of Li. The CV test of the cell was conducted from -1 V to 5 V vs. Li/Li⁺ at a scan rate of 20 mV s⁻¹. All preparation procedures were conducted inside a glovebox (Mikrouna, [O₂] < 0.1 ppm, [H₂O] < 0.1 ppm) filled with ultrapure Ar (≥ 99.999%, Air products).

To prepare the LiFePO₄ (LFP) electrodes, a viscous slurry containing LFP (Aleees, Taiwan), Super-P carbon black (MTI, TIMICAL SUPER C65), PVDF, and LiClO₄ at 8 : 1 : 0.75 : 0.25 weight ratio was mixed in 2 mL of N-methyl-2-pyrrolidone (NMP, MTI, 99.9%). The slurry was coated on an aluminum foil and dried at 80 °C in a vacuum oven for 18 h. After drying, the aluminum foil was cut into the disks with a diameter of 12.0 mm with an active material loading of ~1.5 mg cm⁻². Then, the LFP cathode layer and Li foil anode layer were assembled into a battery in the glovebox. To lower the interfacial resistance, a minute amount (2 μL) of liquid electrolyte (1.0 M LiPF₆ with 1.0 % vinylene carbonate in EC : DMC : EMC = 1 : 1 : 1, v/v) was homogeneously dropped onto each side of the electrolyte membrane. The charge-discharge curves and cycling rates of the batteries were measured in the range from 2.5 to 4.2 V using a battery test system (CT2001A, LANHE, China).

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Keywords: lithium-ion battery, solid-state electrolyte, polyvinylidene fluoride, $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$, interfacial resistance

References

- [1] H.W. Kim, P. Manikandan, Y.J. Lim, J.H. Kim, S.-C. Nam, Y. Kim, *J. Mater. Chem. A* **2016**, *4*, 17025-17032.
- [2] J.-M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359-367.
- [3] J.B. Goodenough, Y. Kim, *Chem. Mater.* **2009**, *22*, 587-603.
- [4] K. Xu, *Chem. Rev.* **2014**, *114*, 11503-11618.
- [5] J.W. Fergus, *J. Power Sources* **2010**, *195*, 4554-4569.
- [6] L. Hu, S.S. Zhang, Z. Zhang, Electrolytes for lithium and lithium-ion batteries, in: *Rechargeable Batteries*, Springer, 2015, pp. 231-261.
- [7] M.S. Whittingham, *Chem. Rev.* **2004**, *104*, 4271-4302.
- [8] J.C. Bachman, S. Muy, A. Grimaud, H.-H. Chang, N. Pour, S.F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, *Chem. Rev.* **2015**, *116*, 140-162.
- [9] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* **2011**, *4*, 3243-3262.
- [10] K. Xu, *Chem. Rev.* **2004**, *104*, 4303-4418.
- [11] R.S. Kühnel, N. Böckenfeld, S. Passerini, M. Winter, A. Balducci, *Electrochim. Acta* **2011**, *56*, 4092-4099.
- [12] A. Guerfi, M. Dontigny, P. Charest, M. Petitclerc, M. Lagacé, A. Vijh, K. Zaghib, *J. Power Sources* **2010**, *195*, 845-852.
- [13] J. Wang, Y. Yamada, K. Sodeyama, E. Watanabe, K. Takada, Y. Tateyama, A. Yamada, *Nat. Energy* **2018**, *3*, 22-29.
- [14] P.G. Balakrishnan, R. Ramesh, T. Prem Kumar, *J. Power Sources* **2006**, *155*, 401-414.
- [15] S. Abada, G. Marlair, A. Lecocq, M. Petit, V. Sauvant-Moynot, F. Huet, *J. Power Sources* **2016**, *306*, 178-192.
- [16] J. Zhu, T. Wierzbicki, W. Li, *J. Power Sources* **2018**, *378*, 153-168.
- [17] E. Quartarone, P. Mustarelli, *Chem. Soc. Rev.* **2011**, *40*, 2525-2540.

- [18] B. Zhang, R. Tan, L. Yang, J. Zheng, K. Zhang, S. Mo, Z. Lin, F. Pan, *Energy Storage Mater.* **2018**, *10*, 139-159.
- [19] L. Yue, J. Ma, J. Zhang, J. Zhao, S. Dong, Z. Liu, G. Cui, L. Chen, *Energy Storage Mater.* **2016**, *5*, 139-164.
- [20] Y. Tian, F. Ding, H. Zhong, C. Liu, Y.-B. He, J. Liu, X. Liu, Q. Xu, *Energy Storage Mater.* **2018**, *14*, 49-57.
- [21] P. Ramakrishnan, H. Kwak, Y.H. Cho, J.H. Kim, *ChemElectroChem* **2018**, *5*, 1265-1271.
- [22] J. Zhang, X. Zang, H. Wen, T. Dong, J. Chai, Y. Li, B. Chen, J. Zhao, S. Dong, J. Ma, *J. Mater. Chem. A* **2017**, *5*, 4940-4948.
- [23] Z. Xue, D. He, X. Xie, *J. Mater. Chem. A* **2015**, *3*, 19218-19253.
- [24] B. Liang, Q. Jiang, S. Tang, S. Li, X. Chen, *J. Power Sources* **2016**, *307*, 320-328.
- [25] J.-K. Kim, Y.J. Lim, H. Kim, G.-B. Cho, Y. Kim, *Energy Environ. Sci.* **2015**, *8*, 3589-3596.
- [26] K.M. Diederichsen, E.J. McShane, B.D. McCloskey, *ACS Energy Letters* **2017**, *2*, 2563-2575.
- [27] H. El Shinawi, J. Janek, *J. Power Sources* **2013**, *225*, 13-19.
- [28] S. Stramare, V. Thangadurai, W. Weppner, *Chem. Mater.* **2003**, *15*, 3974-3990.
- [29] Z. Lu, C. Chen, Z.M. Baiyee, X. Chen, C. Niu, F. Ciucci, *Physical Chemistry Chemical Physics* **2015**, *17*, 32547-32555.
- [30] Y. Deng, C. Eames, B. Fleutot, R.n. David, J.-N.I. Chotard, E. Suard, C. Masquelier, M.S. Islam, *ACS Appl. Mater. Interfaces* **2017**, *9*, 7050-7058.
- [31] B.D. Adams, E.V. Carino, J.G. Connell, K.S. Han, R. Cao, J. Chen, J. Zheng, Q. Li, K.T. Mueller, W.A. Henderson, J.-G. Zhang, *Nano Energy* **2017**, *40*, 607-617.
- [32] G.Y. Adachi, N. Imanaka, S. Tamura, *Chem. Rev.* **2002**, *102*, 2405-2430.
- [33] V. Thangadurai, S. Narayanan, D. Pinzaru, *Chem. Soc. Rev.* **2014**, *43*, 4714-4727.
- [34] C. Chen, Z. Lu, F. Ciucci, *Scientific Reports* **2017**, *7*, 40769.
- [35] J.A. Dawson, P. Canepa, T. Famprikis, C. Masquelier, M.S. Islam, *J. Am. Chem. Soc.* **2018**, *140*, 362-368.
- [36] S. Yu, D.J. Siegel, *Chem. Mater.* **2017**, *29*, 9639-9647.
- [37] X. Zhan, S. Lai, M.P. Gobet, S.G. Greenbaum, M. Shirpour, *PCCP* **2018**, *20*, 1447-1459.
- [38] D. Santhanagopalan, D. Qian, T. McGilvray, Z. Wang, F. Wang, F. Camino, J. Graetz, N. Dudney, Y.S. Meng, *J. Phys. Chem. Lett.* **2013**, *5*, 298-303.
- [39] X. Han, Y. Gong, K.K. Fu, X. He, G.T. Hitz, J. Dai, A. Pearse, B. Liu, H. Wang, G. Rubloff, *Nat. Mater.* **2017**, *16*, 572-579.
- [40] R. Koerver, I. Aygün, T. Leichtweiß, C. Dietrich, W. Zhang, J.O. Binder, P. Hartmann, W.G. Zeier, J. Janek, *Chem. Mater.* **2017**, *29*, 5574-5582.
- [41] Y. Zhu, X. He, Y. Mo, *J. Mater. Chem. A* **2016**, *4*, 3253-3266.
- [42] L. Wang, Z. Zhou, X. Yan, F. Hou, L. Wen, W. Luo, J. Liang, S.X. Dou, *Energy Storage Mater.* **2018**, *14*, 22-48.
- [43] A. La Monaca, F. De Giorgio, F. Soavi, G. Tarquini, M. Di Carli, P. Paolo Prosini, C. Arbizzani, *ChemElectroChem* **2018**, *5*, 1271-1278.
- [44] W. Liu, N. Liu, J. Sun, P.-C. Hsu, Y. Li, H.-W. Lee, Y. Cui, *Nano Lett.* **2015**, *15*,

2740-2745.

- [45] J. Zhang, N. Zhao, M. Zhang, Y. Li, P.K. Chu, X. Guo, Z. Di, X. Wang, H. Li, *Nano Energy* **2016**, *28*, 447-454.
- [46] R.-J. Chen, Y.-B. Zhang, T. Liu, B.-Q. Xu, Y.-H. Lin, C.-W. Nan, Y. Shen, *ACS Appl. Mater. Interfaces* **2017**, *9*, 9654-9661.
- [47] K.K. Fu, Y. Gong, J. Dai, A. Gong, X. Han, Y. Yao, C. Wang, Y. Wang, Y. Chen, C. Yan, *Proc. Natl. Acad. Sci.* **2016**, *113*, 7094-7099.
- [48] Y.-J. Wang, Y. Pan, D. Kim, *J. Power Sources* **2006**, *159*, 690-701.
- [49] X. Zhang, T. Liu, S.F. Zhang, X. Huang, B.Q. Xu, Y.H. Lin, B. Xu, L.L. Li, C.W. Nan, Y. Shen, *J. Am. Chem. Soc.* **2017**, *139*, 13779-13785.
- [50] J. Nunes-Pereira, C. Costa, S. Lanceros-Méndez, *J. Power Sources* **2015**, *281*, 378-398.
- [51] F. Liu, N.A. Hashim, Y. Liu, M.M. Abed, K. Li, *J. Membr. Sci.* **2011**, *375*, 1-27.
- [52] Y. Zhu, F. Wang, L. Liu, S. Xiao, Z. Chang, Y. Wu, *Energy Environ. Sci.* **2013**, *6*, 618-624.
- [53] C.-Y. Hsu, R.-J. Liu, C.-H. Hsu, P.-L. Kuo, *RSC Adv.* **2016**, *6*, 18082-18088.
- [54] W. Zhang, J. Nie, F. Li, Z.L. Wang, C. Sun, *Nano Energy* **2018**, *45*, 413-419.
- [55] L.Y. Tian, X.B. Huang, X.Z. Tang, *J. Appl. Polym. Sci.* **2004**, *92*, 3839-3842.
- [56] Z. Xue, D. He, X. Xie, *J. Mater. Chem. A* **2015**, *3*, 19218-19253.
- [57] M.L. Yeow, Y. Liu, K. Li, *J. Membr. Sci.* **2005**, *258*, 16-22.
- [58] E. Rangasamy, J. Wolfenstine, J. Sakamoto, *Solid State Ionics* **2012**, *206*, 28-32.
- [59] R. Murugan, V. Thangadurai, W. Weppner, *Angew. Chem. Int. Ed.* **2007**, *46*, 7778-7781.
- [60] X. Tao, Y. Liu, W. Liu, G. Zhou, J. Zhao, D. Lin, C. Zu, O. Sheng, W. Zhang, H.-W. Lee, *Nano Lett.* **2017**, *17*, 2967-2972.
- [61] Y. Wang, P. Yan, J. Xiao, X. Lu, J.-G. Zhang, V.L. Sprenkle, *Solid State Ionics* **2016**, *294*, 108-115.
- [62] J.L. Allen, J. Wolfenstine, E. Rangasamy, J. Sakamoto, *J. Power Sources* **2012**, *206*, 315-319.
- [63] Q. Wang, W.-L. Song, L.-Z. Fan, Y. Song, *J. Membr. Sci.* **2015**, *492*, 490-496.
- [64] L. Fan, C.-W. Nan, M. Li, *Chem. Phys. Lett.* **2003**, *369*, 698-702.
- [65] B. Jaleh, S. Sodagar, A. Momeni, A. Jabbari, *Mater. Res. Express* **2016**, *3*, 085028.
- [66] S.K. Karan, R. Bera, S. Paria, A.K. Das, S. Maiti, A. Maitra, B.B. Khatua, *Adva. Energy Mater.* **2016**, *6*, 1601016.
- [67] C.-Y. Chiang, Y. Shen, M.J. Reddy, P.P. Chu, *J. Power Sources* **2003**, *123*, 222-229.
- [68] J. Zheng, M. Tang, Y.Y. Hu, *Angew. Chem. Int. Ed.* **2016**, *128*, 12726-12730.
- [69] N. Pylahan, M. Kerner, D.-H. Lim, A. Matic, P. Johansson, *Electrochim. Acta* **2016**, *216*, 24-34.
- [70] N. Angulakshmi, S. Thomas, K.S. Nahm, A.M. Stephan, R.N. Elizabeth, *Ionics* **2011**, *17*, 407-414.
- [71] B.-E. El Mohajir, N. Heymans, *Polymer* **2001**, *42*, 5661-5667.
- [72] A. Manuel Stephan, K.S. Nahm, *Polymer* **2006**, *47*, 5952-5964.
- [73] B. Qin, Z. Liu, J. Zheng, P. Hu, G. Ding, C. Zhang, J. Zhao, D. Kong, G. Cui, *J.*

Mater. Chem. A **2015**, *3*, 7773-7779.

[74] H. Lee, M. Yanilmaz, O. Toprakci, K. Fu, X. Zhang, *Energy Environ. Sci.* **2014**, *7*, 3857-3886.

[75] S.E. Burns, P. Cain, J. Mills, J. Wang, H. Sirringhaus, *MRS Bull.* **2003**, *28*, 829-834.

[76] M. Ulbricht, *Polymer* **2006**, *47*, 2217-2262.

[77] S. Karan, Z. Jiang, A.G. Livingston, *Science* **2015**, *348*, 1347-1351.

[78] M. Saccoccio, J. Yu, Z. Lu, S.C. Kwok, J. Wang, K.K. Yeung, M.M. Yuen, F. Ciucci, *J. Power Sources* **2017**, *365*, 43-52.

[79] X. Liang, Z. Wen, Y. Liu, M. Wu, J. Jin, H. Zhang, X. Wu, *J. Power Sources* **2011**, *196*, 9839-9843.

Interface engineering: A highly conductive solid-state membrane comprising LLZTO and PVDF was developed. The membrane is characterized by a high tensile strength, good flexibility, and low impedance when it is interfacially modified with 2 μL of liquid electrolyte. A solid-state lithium-ion battery with LiFePO_4 and Li as electrodes delivers an excellent rate capability and cycling stability at room temperature. This work suggests that the interfacial modified LLZTO-PVDF membrane is a promising electrolyte for solid-state lithium-ion batteries.