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Graphical abstract
High-Areal-Capacity All-Solid-State Lithium Batteries Enabled by Rational Design of Fast Ion Transport Channels in Vertically-Aligned Composite Polymer Electrodes

Xiaofei Yang, Qian Sun, Changtai Zhao, Xuejie Gao, Keegan Adair, Yulong Liu, Jing Luo, Xiaoting Lin, Jianneng Liang, Huan Huang, Jianneng Liang, Rong Yang, Shigang Lu, Ruying Li, and Xueliang Sun

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Keywords
Solid-state electrolyte, Hybrid electrolyte, Lithium batteries, Vertically-aligned structure, Li dendrite

Abstract
All-solid-state lithium batteries (ASSLBs) assembled with solid polymer electrolytes (SPEs) have been regarded as promising next-generation rechargeable batteries with improved safety and high energy densities. However, the Li dendrites and poor Li\(^+\) transport greatly inhibit their practical applications when coupled with relatively high loading cathodes. Herein, we combine a glass fiber (GF)-reinforced composite polymer electrolyte based on poly(ethylene oxide) (labeled as PEO@GF) to suppress Li dendrite growth with a freeze-casted vertically-aligned (VL) electrode to facilitate Li\(^+\) transport in the high loading cathode. Benefiting from the enhanced mechanical

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strength and uniformed Li deposition enabled by the implanted GF, the Li-Li symmetric cells exhibit significantly improved cycling stability up to 2000 h (0.2 mA cm\(^{-2}\), 0.2 mAh cm\(^{-2}\)) and 1000 h (0.42 mA cm\(^{-2}\), 0.4 mAh cm\(^{-2}\)), which are over one order of magnitude longer than those of the pure PEO electrolyte. Furthermore, VL-LFP cathode divides the thick electrode into numerous vertically-aligned “thin electrodes”, which significantly decreases the Li\(^+\) transport distance and enables the 10.5 mg cm\(^{-2}\) LiFePO\(_4\) (LFP)-loaded Li | PEO@GF | VL-LFP cell to deliver a high areal capacity of 1.52 mAh cm\(^{-2}\). The rational structure design of both electrolyte and electrode offers an opportunity for developing high-performance ASSLBs with high active material loadings.

1. Introduction

To meet the increasing demands for higher-energy-density portable electronic devices and electric vehicles, lithium metal batteries have received great attention due to their higher energy density and ability to outperform state-of-the-art liquid lithium-ion batteries.[1-3] During the last few decades, the research of lithium batteries has mostly focused on liquid electrolytes and significant progress has been achieved in terms of energy density and cycling life.[4-6] Despite their high ionic conductivity and excellent wetting properties, liquid electrolyte-based systems still suffer from insufficient electrochemical and thermal stability, low ion selectivity and potential safety risks.[7] To tackle the aforementioned issues, replacing the liquid electrolytes with high ionic conductivity solid-state electrolytes (SSEs) with wide electrochemical stability windows and superior thermal stability is one of the best choices for application in lithium batteries.[8-14] Among the various SSEs, solid polymer electrolytes (SPEs) have been regarded as one of the most promising candidates for practical application in the short term due to their flexibility, easy fabrication, low
cost, low-density, good electrochemical stability, and excellent compatibility with lithium salts.[10, 11, 15-19]

Nevertheless, SPEs still suffer from low mechanical strength at operating temperatures, which limits their ability to prevent Li dendrite penetration, especially when operated at high current densities and high areal capacities.[20-22] Recently, tremendous efforts have been focused on adding multi-architectural and multi-functional inorganic fillers to enhance the mechanical properties as well as improve the ionic conductivity. Among them, SiO$_2$ exhibits strong capabilities in suppressing Li dendrite growth via regulating the Li deposition by the polar functional groups (Si-O, O-H) to realize dendrite-free Li anodes. [23-26] However, it is difficult for the particle fillers to effectively enhance the mechanical strength of the composite electrolytes, which is insufficient for commercial applications. [27] To address this issue, the construction of an integrated 3D scaffold for polymer electrolyte impregnation has been demonstrated that can significantly improve both the mechanical properties as well as ionic conductivity. [27-29] Nevertheless, fabricating such 3D scaffolds via electrospinning, [28] aerogel, [27] hydrogel[29] and template methods [30] need complicated and time-consuming processes, which is not suitable for large-scale electrolyte preparation. In this regard, searching for a low-cost and commercially-viable 3D scaffold is of significance.

Moreover, the performance of SPEs in most studies are evaluated by coupling the SPEs with thin and low active material-loaded cathodes (LFP loading typically < 3 mg cm$^{-2}$, areal capacity <0.5 mAh cm$^{-2}$), which can’t meet the requirements of high energy density ASSLBs. [31, 32] In such an evaluation system, many potentially fatal issues may be hidden and ignored despite their important roles in affecting the electrochemical performance. For instance, as shown in Scheme 1b, when the SPE
(e.g. a typical PEO-based SPE with an [EO]:[Li⁺] ratio of 16:1) is coupled with a thick and high active materials-loaded electrode (e.g. lithium iron phosphate (LFP)). Li dendrites can easily grow from the surface of the anode and penetrate the PEO electrolyte, resulting in a short-circuit and deteriorated cycling life. Additionally, the poor Li⁺ transport caused by an increase in cathode thickness is another problem that hinders the improvement of capacity output and power density.[33-35]

Herein, the optimization of both electrolyte and cathode structure, aimed at solving the aforementioned lithium dendrite and high areal-loading cathode issues, is investigated to improve the electrochemical performance of ASSLBs assembled with thick and high active material-loaded cathodes. As shown in Scheme 1a, the PEO polymer was impregnated into a glass fiber (GF) scaffold by solution infiltration, labeled as PEO@GF, and serves three functions. Firstly, SiO₂ is the major component of GF, which has been reported to be effective in enhancing the mechanical properties as well as improve the ionic conductivity of PSEs. Furthermore, the large number of functional groups such as Si-O and O-H are beneficial towards the uniform distribution of Li-ion flux, resulting in a dendrite-free Li. [36] Moreover, the GF also acts as a 3D separator to prevent thermal runaway when a short circuit occurs. Meanwhile, a vertically-aligned LFP (VL-LFP) cathode is fabricated by an ice-template freeze-casting method, which transform the thick electrode into numerous vertically-aligned “thin electrodes”, which decrease the Li⁺ transport distance and facilitated the Li⁺ transport. [37] With this in mind, Li-LFP batteries assembled with thick and high LFP loading cathodes are expected to lead to excellent electrochemical performances.

2. Experimental Section

2.1 Synthesis of PEO and PEO@GF electrolytes
The pure PEO electrolyte was prepared by a solution casting method. Firstly, the mixed solution of PEO polymer (M_w: 1000000, 0.60 g) and bis(trifluoromethylsulfonyl) imide (LiTFSI) salt (0.24 g) dissolved in 20 mL acetonitrile and vigorous stirring overnight, where the EO/Li ratio was controlled as 16/1. Then, the solution was cast in a polytetrafluoroethylene (PTFE) dish and dried at 60 °C for 24 h in vacuum. The obtained polymer membrane was labeled as PEO electrolyte. The PEO@GF electrolyte was obtained by infusing 1.0 mL above mixed solution into a GF scaffold with a diameter of 16 mm (around 10 mg). The weight ratio of PEO electrolyte in the PEO@GF is around 80 wt.%.

2.2 Synthesis of LFP and VL-LFP electrodes:
The LFP and VL-LFP electrodes were fabricated by blade casting technique. Typically, the LFP powder, acetylene black and PEO/LITFSI (EO/Li=16/1) was dissolved in the mixture of acetonitrile and water (v/v=1/9) with a weight ratio of 8:1:1 to form a slurry and then coated onto aluminum (Al) foil. After that, the Al foil coated with slurry was divided into two parts, one was directly dried at 60 °C overnight and another was freeze-dried at -50 °C overnight. The obtained cathode were labeled as LFP and VL-LFP electrodes after the surface was modified with another 5 wt.% of PEO/LITFSI electrolyte, respectively.

2.3 Materials Characterization
The morphology, structure, and composition of the hybrid electrolyte and electrode were characterized by SEM (Hitachi S-4800 and Hitachi S-3400).

2.4 Electrochemical measurements
The electrochemical performance of Li-LFP batteries and Li-Li symmetrical cells were tested with CR2032 coin cells, constructed in an Ar-filled glove box. The cathode (LFP and VL-LFP) and Li anode were separated by PEO or PEO@GF
electrolytes. The charge-discharge tests were carried out using a LAND CT-2001A system with voltages arrange from 2.7 V to 4.0 V at temperatures of 60 °C and 80 °C. Constant current densities were applied to the electrodes during repeated Li stripping/plating process.

Electrochemical impedance spectroscopy (EIS) was tested at the open-circuit condition with a frequency range from 5.0x10^5 Hz to 1.0x10^-2 Hz on a versatile multichannel potentiostation 3/Z (VMP3). Cyclic voltammograms (CV) was tested on the same instrument and the data were collected under a scanning rate of 0.1 mV s^-1 between 2.7 V and 4.0 V. The specific capacities mentioned in this work were calculated based on LFP and the voltages were respected to Li^+/Li (vs. Li^+/Li). The ionic conductivity of the electrolytes was determined by EIS measurement utilizing stainless | electrolyte | stainless symmetric cells with controlled temperature. The electrochemical stability window was examined by stainless | electrolyte | Li metal cells.

3. Result and Discussion
The morphology and structure of the as-prepared PEO@GF and pure PEO electrolytes are firstly investigated by scanning electron microscopy (SEM). As shown in Figure S1, the pure PEO electrolyte exhibits a flat surface with a thickness of 370 µm, while the thickness of PEO@GF is 350 µm (Figure 1d). Compared with PEO electrolyte, the surface of PEO@GF is relatively rough because of the capillary force of GF during the infiltration process (Figure 1a~c). From the cross-sectional SEM images in Figure 1d~f, it can be noted that the pores among the GF are completely filled by the polymer electrolyte, which is beneficial for Li^+ transport. As less volume percentage of PEO electrolyte is used, the PEO@GF electrolyte exhibits a lower but comparable ionic conductivity of 1.9x10^-4 S cm^-1 to that of PEO
electrolyte (3.0×10^{-4} S cm^{-1}) at a working temperature of 60 °C (Figure S2a). Moreover, benefitting from the interactions between the functional groups on GF and the Li salt/PEO electrolyte, the PEO@GF electrolyte presents a wider electrochemical stability window compared with PEO electrolyte (4.9 V vs. 4.3 V, Figure S2b). The thermal stability test of the PEO and PEO@GF electrolytes is performed by heating the two electrolytes in a oven with controlled temperatures (Figure S3). When the temperature rises to 60 °C, the melting point of the polymer, the color of the PEO electrolyte changed due to partial melting of the polymer. Further increasing of the temperature to 120 °C leads to complete melting of the PEO electrolyte into a liquid state. In contrast, the GF@PEO electrolyte maintains its scaffold even at a high temperature of 120 °C. In other words, if a thermal run-away occurs, the polymer electrolyte inevitably melts and shrinks due to the increased temperature, which may cause direct contact between cathode and anode, resulting in significant safety concerns. The PEO@GF electrolyte is helpful in addressing this issue because the GF acts as a physical barrier to inhibit the cathode and anode contact, even after melting of the polymer.

To evaluate the electrochemical stability of the PEO@GF electrolyte, Li-Li symmetrical cells are assembled using two Li foils with a diameter of 1.0 cm. Figure 2a~b shows the cycling stability of the cells with PEO@GF and PEO electrolytes at a current density of 0.2 mA cm^{-2} with a capacity of 0.2 mAh cm^{-2}. Similar to the liquid electrolyte, the voltage hysteresis is attributed to the mass-transfer resistant throughout the whole plating-stripping process.[5, 38] For the PEO electrolyte, an initial over-potential of 125 mV (versus Li^+/Li) is observed, which is slightly smaller than PEO-GF electrolyte (140 mV) due to the higher ionic conductivity of PEO. However, the PEO electrolyte can only operate for 116 h before a short circuit occurs due to the poor mechanical properties and non-uniform Li deposition. In contrast,
PEO@GF electrolyte exhibits very stable performance in Li-Li symmetrical cells, where the overpotential only slightly increases to 170 mV after 2000 h of stripping and plating. After further increasing the capacity to 0.8 mAh cm\(^{-2}\), the overpotential of the Li-Li symmetrical cell with PEO electrolyte increases to around 300 mV and shows the fluctuating voltage profiles after the first cycle (Figure 2c~d). The appearance of fluctuating voltage profiles can be attributed to detrimental Li dendrite growth and rapid formation of dead Li, resulting in a soft short circuit [39]. After 162 h, the overpotential is instantly reduced to around 0 V and a short circuit is observed. Promisingly, PEO@GF electrolyte achieves stable plating/stripping performance at this elevated capacity for 1000 h with an overpotential of around 420 mV. Meanwhile, the cycling performance is also investigated at a current of 0.42 mA cm\(^{-2}\) with a capacity of 0.4 mAh cm\(^{-2}\). The results demonstrate that the PEO@GF electrolyte shows very stable performance up to 1000 h of continuous stripping/plating with minimum changes to the voltage hysteresis (Figure 2e~f). In contrast, due to the more serious Li dendrite growth at high current densities, the intermittent short-circuit performance is observed for PEO electrolyte after 10 h. After 66 h, complete short-circuiting is presented. The obvious difference in cycling performance of Li-Li symmetrical cells can be attributed to the strong capability of PEO@GF in suppressing Li dendrite growth. The excellent plating/stripping performance of Li-Li symmetric cells assembled with GF@PEO electrolyte are superior to recent publications based on SPEs, as shown in Figure 2g~i and Table S1. [26, 31, 40-47]

To understand the behavior of Li stripping and plating within different electrolytes, the Li-Li symmetrical cells operated at a current density of 0.2 mA cm\(^{-2}\) with a capacity of 0.2 mAh cm\(^{-2}\) after cycling are disassembled and the morphology of electrolyte and Li anode are examined by SEM. As shown in Figure 3a~b, after 200 h
of operation, large amounts of dendritic Li with diameters of around 1~3 µm are observed on the surface of Li anode. Additionally, some large broken Li dendrites with diameters of 10~20 µm, shown in Figure 3c–d and Figure S4d–f, are detected on the surface of PEO polymer. In order to confirm the white point is Li, the electron beam is focused on the area with a white point for 10 min. As exhibited in Figure S4a–c, the morphology of the white point changes due to the melting of Li under the high-energy electron beam. These large Li dendrites not only lead to safety risks but also cause poor efficiency of lithium batteries.[2, 48, 49] However, it is noteworthy that on the Li anode coupled with the PEO@GF electrolyte (Figure 3e–f), no dendritic Li is detected, suggesting the strong capability of PEO@GF in suppressing Li dendrites. Moreover, the PEO@GF electrolyte maintains its original morphology and also no Li dendrites can be observed (Figure 3g–h). The strong capability of PEO@GF in inhibiting dendrite growth can be attributed to two merits: 1) The functional groups such as Si-O, O-H on the GF can facilitate the Li\(^{+}\) uniform distribution during plating/stripping process, resulting in uniform deposition of Li and a Li dendrite-free deposition process. 2) The GF can significantly improve the mechanical strength, especially at a high operating temperature of 60 °C, which is helpful for suppressing Li dendrite growth.

Apart from the Li dendrite suppression, the Li\(^{+}\) transport in thick electrodes has a huge impact on the electrochemical performance. The large Li\(^{+}\) transport resistance in high areal-loading electrodes already observed in liquid electrolyte-based systems can be more serious in solid-state battery systems because of the poor wetting properties and lower ionic conductivity of the polymer SSEs. Hence, the enhancement of Li\(^{+}\) transport in SSLBs is of significant importance. For the cathode prepared by a traditional blade casting method and oven/vaccum drying at a high temperature, the morphology is shown in Figure
S5, which exhibits a dense structure and the top-down Li\(^+\) transport mode (Figure S6b) with long Li\(^+\) transport distance of 60 µm if ignored the tortuosity (Figure S5c). This dense structure significantly limits the Li\(^+\) transport in the cathode side and results in poor performance, especially under high C-rates. To tackle the potential issues, a VL-LFP cathode with vertically-aligned structure is fabricated for facilitating Li\(^+\) transport ASSLBs. According to the ice growth kinetics, as shown in Figure 4a, the ice is preferably grown along the a axis, while the rate of ice growth along b axis is limited, resulting in lamellar ice morphology. [50] During this process, the electrode materials are pressed into lamellar structure among the ice. After the ice is removed via a freeze-drying method, a VL-LFP cathode with vertically-aligned structure is obtained. The morphology and relative elemental mappings are shown in Figure 4b~i. The VL-LFP cathode divide the thick electrode into numerous “thin electrodes” with a thickness of around 20 µm, giving rise to bi-directional Li\(^+\) transport pathways in the VL-LFP (Figure S6a) which can significantly decreases the Li\(^+\) transport distance (around 10 µm, 1/6 of the LFP electrode) and Li\(^+\) transport resistance. With this in mind, coupling the PEO@GF electrolyte with the VL-LFP cathode is a good strategy to solve the issues of Li dendrite and Li\(^+\) transport in thick cathodes, thus excellent electrochemical performance can be expected.

The difference in Li dendrite suppression for PEO and PEO@GF electrolytes and Li\(^+\) transport in LFP and VL-LFP electrodes are investigated by electrochemical cycling and C-rate performance testing. The cycling performance of Li-LFP cells with PEO/PEO@GF as electrolytes and LFP/VL-LFP as cathodes (LFP loading: 3 mg cm\(^{-2}\)) are studied at a C-rate of 0.2 C (1C =170 mA g\(^{-1}\)) between 2.7 V and 4.0 V. As shown in Figure 5a, in the first few cycles, the capacity of all cells increased gradually and exhibit an activation process due to the wetting of the electrode interface by the
electrolyte. Afterwards, reversible capacities of around 155 mAh g\(^{-1}\) for all cells are obtained. It should be noted that both PEO@GF/LFP and PEO@GF/VL-LFP cells present a high and stable Coulombic efficiency of 100% within 100 cycles, while the Coulombic efficiency of PEO/LFP cell dramatically dropped to 83.5% at the 18th cycle from 100% at 15th cycle. Considering the same anode and cathode used in PEO@GF/LFP and PEO/LFP cells, such significant difference in Coulombic efficiency can be attributed to the different electrolytes in the two cells. Due to a high capacity of 155 mAh g\(^{-1}\) with a relatively high loading of 3 mg cm\(^{-2}\) delivered by PEO/LFP cell, corresponding to an areal capacity of 0.47 mAh cm\(^{-2}\), the PEO electrolyte can’t meet the demand according to the Li-Li symmetrical cells in Figure 2c and 2e. In this case, a soft short-circuit occurs, which is confirmed by the charge/discharge profiles of the PEO/LFP cell. As shown in Figure S7c, a fluctuating charge profile followed by a sudden voltage drop when charging to 100 mAh g\(^{-1}\) at the 18th cycle suggests the occurrence of a soft short-circuit and results in low Coulombic efficiencies. In contrast, the same phenomenon hasn’t been observed for both PEO@GF/LFP and PEO@GF/VL-LFP cells during the whole charge/discharge process, further demonstrating the strong capability of PEO@GF in suppressing Li dendrite. Even after 100 cycles, PEO@GF/LFP and PEO@GF/VL-LFP cells still retain capacities of 142 and 132 mAh g\(^{-1}\), respectively, corresponding to capacity retentions of 91.6% and 85.2% The slight capacity decay is mainly attributed to the dead Li deposited on the surface of the anode and increases of the overpotential by around 40 mV (Figure S7a~b). The long-term cycling stability of the PEO@GF/VL-LFP cell is also tested at a high C-rate of 0.5C. As shown in Figure 5e, after the activation process in the first few cycles, a reversible capacity of over 120 mAh g\(^{-1}\) is achieved. Even after 200 cycles, a high capacity of 100 mAh g\(^{-1}\) is retained with a low
The C-rate performance of PEO/LFP, PEO@GF/LFP, and PEO@GF/VL-LFP cells are investigated from 0.1C to 2C. As shown in Figure 5b, a short circuit occurs in the PEO/LFP cell when the C-rate increases to 0.3C, and the Coulombic efficiency significantly drop to 61.2%, which is further confirmed by the charge/discharge profiles in Figure S8. These results suggest that the PEO can’t meet the demand of high loading LFP cells in suppressing Li dendrite formation at a relatively high C-rate. There is no short circuit phenomenon observed for PEO@GF/LFP and PEO@GF/VL-LFP cells and both cells deliver capacities of 161, 155 and 148 mAh g\(^{-1}\) at 0.1, 0.2 and 0.3C. The differences become apparent when the C-rate increases to 0.5C, where the PEO@GF/VL-LFP cell can deliver a capacity of 136 mAh g\(^{-1}\), while the capacity of PEO@GF/LFP cell drops to 106 mAh g\(^{-1}\). When the C-rate is further increased to 1C, PEO@GF/VL-LFP cell delivers a capacity of 100 mAh g\(^{-1}\), which is almost 2 times of the PEO@GF/LFP cell. Moreover, a high capacity of around 50 mAh g\(^{-1}\) is retained for the PEO@GF/VL-LFP cell at 2C, while the capacity delivered by the PEO@GF/LFP cell is almost 0 mAh g\(^{-1}\). Such huge differences in C-rate performance can be mainly attributed to the lower overpotential of the PEO@GF/VL-LFP cell. For instance, as shown in Figure S9 and Figure 5c~d, the PEO@GF/LFP cell exhibits an overpotential of 143 mV at 0.1C, which is only 2 mV larger than that of the PEO@GF/VL-LFP cell. When the C-rate increased to 0.5C and 2C, the overpotential difference is 40 mV and 228 mV, respectively. Considering the same anode and electrolyte are used in both PEO@GF/LFP and PEO@GF/VL-LFP cells, the different C-rate performance and electrochemical kinetics can be attributed to the different structures of cathodes. [51, 52]
The large difference in electrochemical kinetics between LFP and VL-LPF cathodes is further investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The CV curves of PEO@GF/LFP and PEO@GF/VL-LFP cells obtained at a scan rate of 0.1 mV s\(^{-1}\) are shown in Figure S10. Between 2.7 V and 4.0 V, both electrodes exhibited one oxidation peak and one reduction peaks located at 3.7 V and 3.1 V, corresponding to Li\(^+\) deintercalation and intercalation processes. The smaller potential difference between the oxidation peak the reduction peak for PEO@GF/VL-LFP reflects fast electrochemical kinetics. [53] The differences in electrochemical kinetics between PEO@GF/LFP and PEO@GF/VL-LFP cells are further quantitatively analyzed by EIS and their equivalent circuits (Figure S11). According to the fitted semi-circle values in EIS (fitted by the equivalent circuit inset of Figure S11a) and Li\(^+\) diffusion coefficient (D)-Warburg coefficient (\(\sigma\))-angle frequency (\(\omega\)) relationship in our previous report, [33, 54] charge transfer resistance (\(R_{ct}\)) and Li\(^+\) diffusion coefficients are given in Table S2 to investigate the the electrochemical activity and Li\(^+\) diffusion. PEO@GF/VL-LFP cell possesses smaller \(R_{ct}\) of 93.6 Ω cm\(^{-2}\) and a larger D of \(6.63 \times 10^{-12}\) cm\(^2\) s\(^{-1}\), which is 0.1 and 4.4 times greater than that of the PEO@GF/LFP (912.4 Ω cm\(^{-2}\), \(1.49 \times 10^{-12}\) cm\(^2\) s\(^{-1}\)), respectively, suggesting higher electrochemical activity and faster Li\(^+\) diffusion. [33, 34] Due to the use of the same anode and electrolyte, such differences in electrochemical kinetics can be mainly attributed to the different structures of the cathodes. In the VL-LFP cathode, the vertically-aligned structure enables Li\(^+\) transport along the 3D electrode and transport into the LFP particles via a bi-directional transport pathway, which significantly decreased the Li\(^+\) transport distance and Li\(^+\) transport resistance. [37] On the contrary, for the LFP cathode, the dense
structure and top-down Li$^+$ transport mode forces longer Li$^+$ transport distances and larger resistance, resulting in poor C-rate performance and electrochemical kinetics.

Considering the strong capability of PEO@GF electrolyte in suppressing Li dendrite growth and fast Li$^+$ transport capability in VL-LFP cathode, PEO@GF/VL-LFP cells with higher LFP loadings are explored. As shown in Figure 5f, similar to 3mg cm$^{-2}$ LFP loaded cells, both PEO@GF/VL-LFP and PEO@GF/LFP cells with a LFP of 6 mg cm$^{-2}$ present an activation process in the first 20 cycles and then stabilize with reversible capacities of 128 mAh g$^{-1}$ and 117 mAh g$^{-1}$, respectively. The lower capacity output and more obvious activation process of PEO@GF/LFP cell are because of the poor electrochemical kinetics. After 100 cycles, capacities of 120 mAh g$^{-1}$ and 91 mAh g$^{-1}$ are maintained, equaling to capacity retentions of 94.5% and 77.8%, respectively. The faster capacity drop of PEO@GF/LFP can be attributed to the dead Li deposited on the anode site, which further worsens the Li$^+$ transport and limits the capacity output. Additionally, in order to achieve improved energy density, a PEO@GF/VL-LFP cell assembled with a 10.5 mg cm$^{-2}$ LFP-loaded VL-LFP electrode is investigated at an operating temperature of 80 °C. As shown in Figure 5g, the PEO@GF/VL-LFP cell delivers a capacity of 145 mAh g$^{-1}$ at the 9$^{th}$ cycle, corresponding to areal capacities of 1.52 mAh cm$^{-2}$. The LFP loading and areal capacity are much higher than recent publications, shown in Figure 5h and Table S3. [26, 31, 32, 41, 43-46, 55-60] After 50 cycles, a high capacity of 127 mAh g$^{-1}$ is retained, showing potential for application in high-performance ASSLBs.

4. Conclusions

In summary, we have successfully developed a high-areal capacity ASSLB by combining glass fiber-reinforced composite polymer electrolyte with a vertically-
aligned electrode, which are beneficial for Li dendrite suppression and fast Li$^+$ transport, respectively. The synergistic effect of uniform Li deposition promoted by the functional groups on GF and enhanced mechanical strength significantly suppress the Li dendrite growth. Excellent cycling performances of over 2000 h (0.2 mA cm$^{-2}$, 0.2 mAh cm$^{-2}$) and 1000 h (0.42, 0.4 mAh cm$^{-2}$) are achieved by the Li-Li symmetric cells, which are over one order of magnitude longer than pure PEO electrolyte. Moreover, the shorter Li$^+$ transport distance in the VL-LFP electrode is realized by converting the thick electrode into numerous vertically-aligned “thin electrodes” with a thickness of 20 µm, which greatly enhanced the electrochemical kinetics. The PEO@GF/VL-LFP cell assembled with 10.5 mg cm$^{-2}$ LFP-loaded VL-LFP electrode achieves a high areal capacity of 1.52 mAh cm$^{-2}$. Additionally, the 3 mg cm$^{-2}$ LFP-loaded PEO@GF/VL-LFP cell maintains a high capacity over 100 mAh g$^{-1}$ at 0.5C within 200 cycles.

**Author contributions**

X. Yang conceived and designed the experimental work and prepared the manuscript; C. Zhao helped with SEM characterization; X. Gao helped with VL-LFP electrode preparation; Q. Sun, K. Adair, J. Luo, Y. Liu, X. Lin, J. Liang, H. Huang, L. Zhang, R. Yang, S. Lu, and R. Li participated in the discussion of the data; X. Sun supervised the overall project. All authors have given approval to the final version of the manuscript.

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**Scheme 1** Schematic illustration of the Li deposition process and Li$^+$ transport process in (a) PEO@GF/VL-LFP cell and (b) PEO/LFP cell.

**Figure 1.** (a)–(c) Surface and (d)–(f) cross-sectional morphology of PEO@GF electrolyte at different magnifications.
Figure 2. Comparison of the cycling stability of the Li-Li symmetrical cells assembled with PEO@GF and PEO electrolyte at (a-b) a current density of 0.2 mA cm$^{-2}$ with a capacity of 0.2 mAh cm$^{-2}$, (c-d) a current density of 0.2 mA cm$^{-2}$ with a capacity of 0.8 mAh cm$^{-2}$, (e-f) a current density of 0.42 mA cm$^{-2}$ with a capacity of 0.4 mAh cm$^{-2}$. Comparison of the recently reported plating/stripping performances of SPEs-based Li-Li symmetric cells with respect to (g) current density and areal capacity, (h) current density and cycling life, (i) areal capacity and cycling life.
Figure 3. SEM images of (a)~(b) PEO electrolyte-based Li and (c)~(d) PEO electrolyte after 200 h; SEM images of (e)~(f) PEO@GF electrolyte-based Li and (g)~(h) PEO@GF electrolyte after 200 h.

Figure 4. (a) The mechanism growth of lamellar ice inside the VL-LFP electrode; (b)~(d) SEM images of VL-LFP electrode and corresponding elemental mappings of (f) C, (g) O, (h) P and (i) Fe.
Figure 5. (a) Cycling performance at 0.2C and (b) C-rate performance at various C-rate from 0.1C to 2C of the PEO/LFP, PEO@GF/LFP and PEO@GF/VL-LFP cells with a LFP loading of 3 mg cm$^{-2}$. Charge-discharge profiles of (c) PEO@GF/VL-LFP and (d) PEO@GF/LFP cells at various C-rate with a LFP loading of 3 mg cm$^{-2}$. (e) Long-term cycling performance of PEO@GF/VL-LFP cell at 0.5C. (f) Cycling performance of the PEO@GF/LFP and PEO@GF/VL-LFP cells at 0.1C with a LFP loading of 6 mg cm$^{-2}$. (g) Cycling performance of the PEO@GF/VL-LFP cell at 0.1C with a LFP loading of 10.5 mg cm$^{-2}$. (h) Comparison of LFP loading and areal capacity of this work with recent publications. (The operating temperatures in Figure a-f is 60 °C and Figure g is 80 °C.)
References


Vitae

Dr. Xiaofei Yang is currently a postdoctoral associate in Prof. Xueliang (Andy) Sun's Nanomaterials and Energy Group. He received his B.E. degree in Chemical Engineering from Anhui University, China, in 2013 and Ph.D degree in Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China, in 2018 under the supervision of Prof. Huamin Zhang. His research interests focus on Li-S batteries, all-solid-state Li-ion and Li-S batteries and battery interface studies via synchrotron X-ray characterizations.
Dr. Qian Sun is a postdoctoral associate in Prof. Xueliang (Andy) Sun’s Group at the University of Western Ontario (Western University), Canada. He received his B.S. degree in Chemistry in 2006, M.S. degree in Physical Chemistry in 2009, and Ph.D. degree in Applied Chemistry in 2013 under the supervision of Prof. Dr. Zheng-Wen Fu on the study of Li-/Na-ion batteries and Na-air batteries, all at Fudan University, China. He joined Prof. Sun’s group in 2013 and his current research interests focus on Na-air, Na-ion, and room temperature Na-S batteries as well as solid-state Li/Na batteries.

Dr. Changtai Zhao is currently a postdoctoral associate in Prof. Xueliang (Andy) Sun's Nanomaterials and Energy Group. He gained his Bachelor’s degree from Department of Chemical Engineering, Qingdao University, China in 2012 and Ph.D degree in Dalian University of Technology, China, in 2017 under the supervision of Prof. Jieshan Qiu. His research interests focus on nanocarbon and advanced functional
materials as well as their applications in energy conversion and storage, especially for Na/Li-ion batteries, Li-S batteries, Li-O_2 batteries and solid-state Li-O_2 batteries.

Xuejie Gao is currently a Ph.D. candidate in Prof. Xueliang (Andy) Sun's group at the University of Western Ontario, Canada. She received her B.S. degree in chemistry in 2014 from Ludong University and obtained her M.S. degree in Chemistry in 2017 from Soochow University. Currently, her research interests focus on the development of 3D printing applied for lithium batteries. She is also co-supervised by Prof. T. K. Sham from Chemistry Department in the University of Western Ontario. Part of her work is related to the study of energy materials via synchrotron radiation.

Keegan Adair received his B.Sc. in chemistry from the University of British Columbia in 2016. He is currently a Ph.D. candidate in Prof. Xueliang (Andy) Sun's Nanomaterials and Energy Group at the University of Western Ontario, Canada. Keegan has previously worked on battery technology at companies such as E-One Moli Energy and General Motors. His research interests include the design of
nanomaterials for lithium metal batteries and nanoscale interfacial coatings for battery applications.

Yulong Liu is currently a postdoctoral fellow in Prof. Xueliang (Andy) Sun’s Nanomaterials and Energy Group at the University of Western Ontario, Canada. He received his Bachelor degree from Central South University, China, in 2010, and Master degree in 2013. In 2017, he obtained his Ph.D. degree in Materials Science and Engineering from University of Western Ontario. His research interests include nanomaterials for lithium-ion batteries, especially LiFePO$_4$ (in collaboration with Johnson Matthey Inc., previous Phostech), and the development of the solid state batteries.

Jing Luo received her B.S. degree in Chemical Engineering from the University of Illinois—Urbana Champaign (U.S.A.) in 2013 and M.S. degree under the supervision of Prof. Nae-Lih Wu from National Taiwan University (Taiwan) in 2016. She is now pursuing her Ph.D. degree in Prof. Xueliang (Andy) Sun's group at University of
Western Ontario, Canada. Her current research interests focus on atomic layer deposition in the application of Li-ion batteries and polymer based solid-state batteries.

**Xiaoting Lin** is currently a Ph.D. candidate in Prof. Xueliang (Andy) Sun’s group at the University of Western Ontario, Canada. She received her B.S. degree in Applied chemistry in 2012 from Liaocheng University and obtained her M.S. degree in Physical Chemistry in 2016 from Ningbo University. Currently, her research interests focus on the development of advanced nanomaterials for Na-O$_2$ batteries as well as solid-state Na-O$_2$ batteries.

**Jianneng Liang** is currently a Ph.D. candidate in the department of Mechanical and Materials Engineering at the University of Western Ontario, Canada. He got his B.S. in metallurgical engineering in 2015 from Central South University, China. Currently,
his research interests include solid-state polymer electrolytes, hybrid electrolyte, all solid-state LIBs and Li-S batteries, and the interfacial study in all-solid-state batteries.

Dr. Huan (Henry) Huang received his Ph.D. from University of Waterloo in 2002. He is currently a General Manager for the company. He has extensive experience in lithium ion cylindrical cells and serves as a Research Scientist at E-One Moli Energy Corp., before managing GLABAT. His research interests focus on the development and commercialization of solid-state batteries with robust and consistent performance.

Dr. Li Zhang is currently a senior scientist of China Automotive Battery Research Institute Co., Ltd., Beijing, China. He received his Ph.D. degree in Electrochemistry from University of Science & Technology Beijing, China in 2009. He has more than 10 years of power sources experience with expertise in battery materials as well as electrode design. Currently, his research interests include solid-state electrolytes, all-solid-state Li-air, and lithium batteries.
**Dr. Rong Yang** received his Ph.D. degree in inorganic chemistry from Peking University in 2011. He is currently a senior engineer in China Automotive Battery Research Institute. His research interests are focused on cathode materials for lithium-ion batteries, solid-state lithium ionconductors, and solid-state lithium-ion batteries.

**Dr. Shigang Lu** is Vice president of China Automotive Battery Research Institute Co., Ltd. He has the responsibility for technology innovations in the area of automotive battery application. He has extensive experience in many energy research areas including fuel cells, and lithium-ion batteries. Dr. Lu received his Ph.D. degree in Chemistry from Moscow State University in 1993. He has extensive experience in novel material processing techniques for automotive battery applications. His current research interests include new energy electrochemistry, lithium-ion battery and related materials, solid-state battery and related materials.
**Ruying Li** is a research engineer at Prof. Xueliang (Andy) Sun's Nanomaterial and Energy Group at the University of Western Ontario, Canada. She received her master in Material Chemistry under the direction of Prof. George Thompson in 1999 at University of Manchester, UK, followed by work as a research assistant under the direction of Prof. Keith Mitchell at the University of British Columbia and under the direction of Prof. Jean-Pol Dodelet at Institut national de la recherche Scientifique (INRS), Canada. Her current research interests are associated with synthesis and characterization of nanomaterials for electrochemical energy storage and conversion.

**Prof. Xueliang (Andy) Sun** is a Canada Research Chair in Development of Nanomaterials for Clean Energy, Fellow of the Royal Society of Canada and Canadian Academy of Engineering and Full Professor at the University of Western Ontario, Canada. Dr. Sun received his Ph.D. in materials chemistry in 1999 from the University of Manchester, UK, which he followed up by working as a postdoctoral fellow at the University of British Columbia, Canada and as a Research Associate at
L’ Institut National de la Recherche Scientifique (INRS), Canada. His current research interests are focused on advanced materials for electrochemical energy storage and conversion.
Highlights

1. The Li-Li symmetric cells with PEO@GF electrolyte exhibit significantly improved cycling stability up to 2000 h (0.2 mA cm\(^{-2}\), 0.2 mAh cm\(^{-2}\)) and 1000 h (0.42, 0.4 mAh cm\(^{-2}\)).

2. The VL-LFP electrode divides the thick electrode with numerous “thin electrodes, which significantly decreases the ion transport distance and improves the capability of Li\(^+\) transport.

3. 10.5 mg cm\(^{-2}\) LFP loaded Li | PEO@GF | VL-LFP battery delivers a high areal capacity of 1.52 mAh cm\(^{-2}\).