

# PEO-LITFSI-SiO<sub>2</sub>-SN System Promotes the Application of Polymer Electrolytes in All-Solid-State Lithium-ion Batteries

Wang Lyu,<sup>[a]</sup> Guoqiang He,<sup>\*[a, b]</sup> and Ting Liu<sup>\*[b]</sup>

All-solid-state polymer lithium-ion batteries are ideal choice for the next generation of rechargeable lithium-ion batteries due to their high energy, safety and flexibility. Among all polymer electrolytes, PEO-based polymer electrolytes have attracted extensive attention because they can dissolve various lithium salts. However, the ionic conductivity of pure PEO-based polymer electrolytes is limited due to high crystallinity and poor segment motion. An inorganic filler SiO<sub>2</sub> nanospheres and a plasticizer Succinonitrile (SN) are introduced into the PEO matrix to improve the crystallization of PEO, promote the formation of amorphous region, and thus improve the movement of PEO chain segment. Herein, a PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN composite solid polymer electrolyte (CSPE) was prepared by solution-casting. The high ionic conductivity of the electrolyte was demonstrated at 60 °C up to  $3.3 \times 10^{-4} \text{ Scm}^{-1}$ . Meanwhile, the electrochemical performance of LiFePO<sub>4</sub>/CSPE/Li all-solid-state battery was tested, with discharge capacity of 157.5 mAhg<sup>-1</sup> at 0.5 C, and capacity retention rate of 99% after 100 cycles at 60 °C. This system provides a feasible strategy for the development of efficient all-solid-state lithium-ion batteries.

## 1. Introduction

In recent decades, rechargeable lithium-ion batteries have attracted extensive attention as an important energy storage technology due to superior performance and high energy density. These systems are widely used in portable electronic devices, electric vehicles and various electronic devices.<sup>[1,2]</sup> In addition, lithium-ion batteries have excellent characteristics such as environmental protection, long cycle life, no memory effect. However, conventional lithium-ion batteries using organic liquid electrolyte may lead to safety problems, leakage of electrolyte in the process of operation, and the electrolyte may heat up due to overcharging,

internal short circuit and other abnormalities, which could potentially result in spontaneous combustion or explosion.

Therefore, all-solid-state lithium-ion batteries with high energy density that can also guarantee safety and long life cycles are becoming the most promising and investigated candidates for energy storage technologies. In all-solid-state lithium-ion batteries, organic liquid electrolytes are replaced by solid electrolytes. This strategy can solve the two key problems of low energy density and short service life of traditional lithium-ion batteries. Meanwhile, it is expected to completely solve the safety problem of battery and adapt to the development direction of new chemical energy storage technology with large capacity in the future.

All-solid-state electrolytes can be classified into three categories: inorganic (ceramic/glass) solid electrolyte,<sup>[3,4]</sup> solid polymer electrolyte(SPE),<sup>[5]</sup> inorganic and polymer composite solid electrolyte.<sup>[6,7]</sup> Among these solid electrolytes, solid polymer electrolytes not only have good electrical conductivity, but also have the characteristic of light weight, softness and easy membrane formation of polymer material, which is considered to be the most promising all-solid-state electrolytes material.<sup>[8]</sup>


Among these polymer electrolytes, PEO-based polymer electrolytes can dissolve various salts through the interaction of ether and oxygen, which are considered to be one of the polymer electrolytes that can be widely used in lithium-ion batteries.<sup>[9]</sup> However, PEO-based polymer electrolytes are highly crystalline at room temperature, thus resulting in ionic conductivities of only  $10^{-6}$ – $10^{-8} \text{ Scm}^{-1}$ , which are difficult to use in lithium-ion batteries.<sup>[10]</sup>

Improving the ionic conductivity of PEO-based polymer electrolytes has become a research field. A common strategy to improve ionic conductivity and electrochemical stability properties of polymer electrolytes is the introduction of organic small molecule plasticizers and inorganic fillers into the polymer matrix. The addition of plasticizers can significantly improve the ionic conductivity by providing thermal stability and reduce crystallinity.<sup>[11,12,13]</sup> The introduction of organic small molecule plasticizer into the polymer matrix improves the ability of dissolving lithium salts and promotes the transfer of lithium-ion based on its chemical properties.<sup>[14,15]</sup> However, the addition of plasticizer will also decrease the mechanical properties of the membrane.

It is necessary to find a filler that can improve the mechanical properties of polymer electrolytes. Generally, inorganic fillers are introduced into the PEO-based polymer matrix to change crystallization kinetics by creating local

[a] W. Lyu, Prof. G. He  
School of Resources, Environment and Materials  
Guangxi University  
Nanning, Guangxi, 530004 (China)

[b] Prof. G. He, Dr. T. Liu  
Foshan (Southern China) Institute of New Materials  
17 Shenhai Road, Foshan, Guangdong 528200 (China)  
E-mail: gqhe@gxu.edu.cn  
liuting@fscinm.com

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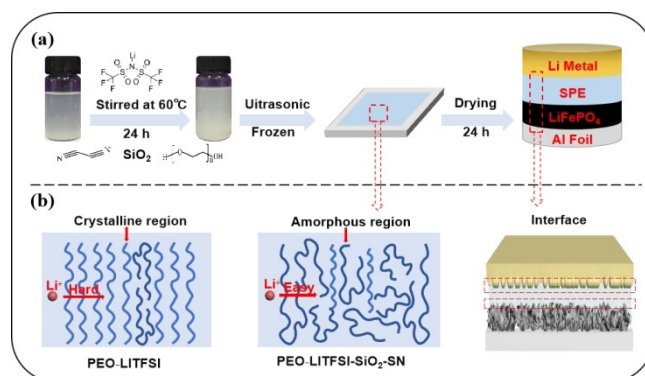
amorphous regions at the filler-polymer interface.<sup>[16,17,18]</sup> The density of entanglement in the amorphous region is increased through the construction of network nodes in the interface of filler-polymer, thereby has the effect of increasing mechanical properties of the materials.<sup>[18,19,20]</sup> The migration efficiency of  $\text{Li}^+$  is increased, which effectively increases  $\text{Li}^+$  conduction.<sup>[21,22,23]</sup> The composite inorganic solid polymer electrolyte constructed by the addition of inorganic filler, can significantly improve the ionic conductivity and material mechanical properties, and effectively inhibit the penetration of lithium dendrites into the electrolyte membrane.<sup>[24]</sup> It has previously been reported that by adding  $\text{SiO}_2$  and LLZTO to the PEO-based polymer electrolyte has achieved satisfactory results.<sup>[25,26,27,28]</sup> Meanwhile, it is necessary to consider whether the all-solid-state electrolyte can have excellent compatibility with the electrode material, form a good interface contact with the electrode material. Excellent interface will contribute low interfacial contact resistance and build a stable charge-discharge interface.

Herein, we report the preparation of a composite solid polymer electrolyte with excellent properties from high content PEO matrix, low content SN and  $\text{SiO}_2$  nanospheres.  $\text{SiO}_2$  has a good affinity with organic solvents in the composite polymer electrolyte,  $\text{SiO}_2$  nanospheres cannot provide and conduct the role of lithium ions, so it is used as an "inert filler" to be added into the PEO matrix to reduce the crystallinity of PEO and obtain good ionic conductivity. Solid plasticizer SN and inorganic filler  $\text{SiO}_2$  nanospheres were added to increase the amorphous regions of the PEO matrix and obtain higher ionic conductivity and build an excellent compatibility with the electrode material. Meanwhile, we optimized the preparation process of the film, adopted ultrasound and freezing to eliminate the bubbles in the film, and obtained a more uniform film. The conductivity and electrochemical properties of the composite solid polymer electrolyte were studied systematically. The application of composite electrolyte in all-solid-state lithium-ion batteries is analyzed.

## Experimental Section

### Materials

Since the experimental materials are sensitive to oxygen and water during the experiment, all the materials are vacuum dried and then transferred to vacuum glove box ( $\text{H}_2\text{O}$  and  $\text{O}_2 < 0.1$  ppm) under argon atmosphere. PEO (Aladdin,  $M_v = 600,000$ ) was dried at  $60^\circ\text{C}$  under vacuum for 12 hours. Succinonitrile (SN 99%, Aladdin), LiTFSI (99%, Aladdin) and  $\text{LiFePO}_4$  (Carbon coating, Aladdin) were dried at  $120^\circ\text{C}$  under vacuum for 12 hours.  $\text{SiO}_2$  nanospheres is synthesized in our laboratory according to relevant literature reports.<sup>[29]</sup>



**Figure 1.** a) The preparation process of  $\text{PEO}_{18}$ -LiTFSI-5% $\text{SiO}_2$ -5%SN composite electrolyte membrane and  $\text{LiFePO}_4$ -Li system; b) The schematic diagrams of the microstructure, interface between electrolyte and electrode material and  $\text{Li}^+$  transfer.

### Preparation of Composite Solid Polymer Electrolyte Membrane and Cathode

Composite solid polymer electrolyte ( $\text{PEO}_{18}$ -LiTFSI-5% $\text{SiO}_2$ -5%SN) was synthesized by traditional solution-casting technique. In order to ensure the mechanical properties and ionic conductivity of polymer electrolyte, the proportion of plasticizer and inorganic filler should not be too large. Therefore, the amount of  $\text{SiO}_2$  nanospheres and SN added in this experiment is 5% relative to the mass ratio of PEO. First, LiTFSI,  $\text{SiO}_2$  nanospheres and SN were added to acetonitrile (ACN) and stirred magnetically at  $60^\circ\text{C}$  for 2 hours after 30 minutes of ultrasonic treatment. Then, PEO was added to continue magnetic stirring at  $60^\circ\text{C}$  for 24 hours to obtain a uniform solution. Secondly, the obtained homogeneous solution was ultrasonic for 2 hours and then frozen for 20 minutes in order to remove bubbles from the solution. The solution was then transferred to a vacuum glove box, and the prepared solution was poured into a teflon mold evaporated for 24 hours. After obtaining the membrane, it was dried in vacuum at  $60^\circ\text{C}$  for 12 hours to remove the residual solvent. Finally, the membrane was cut into wafer with diameter of 16 mm and 14 mm for further measurements. The thickness of the membrane was measured, and the surface morphology of the membrane was studied by SEM, mainly to observe whether  $\text{SiO}_2$  nanospheres could be completely embedded in the PEO matrix, and whether pores and other defects would occur on the surface of the membrane. Crystallization degree of electrolyte obtained by analyzing XRD. The EDS of composite electrolyte to illustrate the dispersion of  $\text{SiO}_2$  nanospheres and SN in the PEO matrix. The membrane preparation process and schematic diagrams of the microstructure are shown in Figure 1.

All-solid-state batteries were prepared by  $\text{LiFePO}_4$ -Li system. The cathode was mixed in the proportion of  $\text{LiFePO}_4$ :PEO:super P = 8:1:1, stirred in NMP solution for 6 hours, and then evenly applied on the carbonized aluminum foil. Drying at  $80^\circ\text{C}$  for 2 hours and then transfer to the vacuum-dryer at  $120^\circ\text{C}$  for 12 hours. Finally, cut into wafer with diameter of 14 mm and put in the glove box for later use.

### Battery Preparation and Electrochemical Performance Test.

Symmetrical blocking cells (SS/CSPE/SS) were prepared for AC impedance testing at different temperatures. The ionic conductivity of polymer electrolyte can be obtained by the analysis and calculation of alternating current impedance (AC impedance).<sup>[30]</sup> The scanning frequency range is 0.1 Hz~1MHz, the scanning rate is 10 mV, and the test temperature range is 30–80 °C, all tests were conducted after 2 hours of insulation. The measurement of ionic conductivity ( $\sigma$ , S cm<sup>-1</sup>) is calculated according to Equation:

$$\sigma = \frac{L}{R \times S}$$

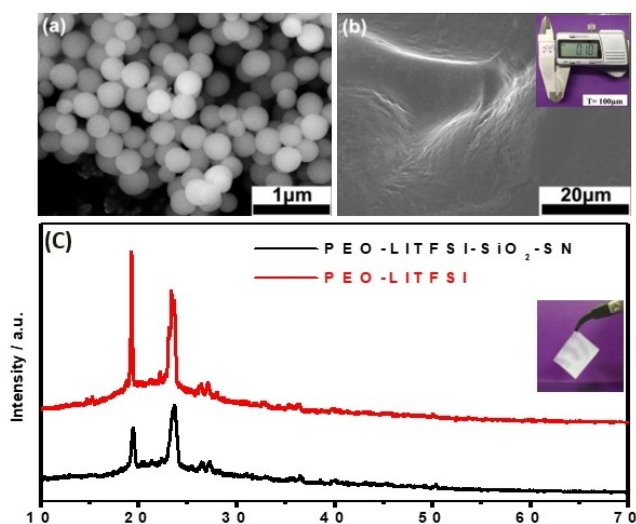
R ( $\Omega$ ) is resistance value of the bulk electrolyte, L (cm) is the thickness of electrolyte membrane, and S (cm<sup>2</sup>) is the surface area of the polymer electrolyte.

Meanwhile, LiFePO<sub>4</sub>/CSPE/Li battery was prepared for charge-discharge performance test at 60 °C. The electrochemical performance data of battery charge-discharge platform, specific capacity, cycle performance, multiplication performance and battery polarization degree could be obtained through analysis of battery charge-discharge curve.

## 2. Results and discussion

### 2.1. Characterization of PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN Composite Polymer Electrolyte Membrane.

As shown in Figure 2(a, b), the diameter of SiO<sub>2</sub> nanospheres ranges from 200 nm to 300 nm. the thickness of the membrane is ~100  $\mu$ m, which can be controlled by the amount of pouring solution. By observing the SEM figure of the membrane, the surface of the membrane presents wavy



**Figure 2.** a) SEM images of SiO<sub>2</sub> nanospheres (200–300 nm); b) SEM images of PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN solid polymer electrolyte membrane and photograph of membrane; c) XRD patterns of PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN and PEO<sub>18</sub>-LiTFSI.

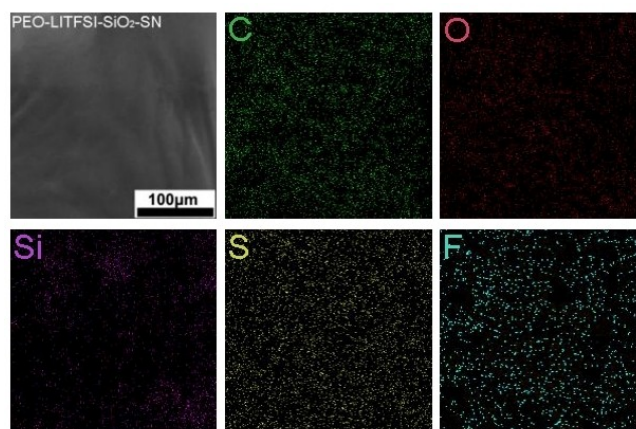
folds, and no pore structure, indicating the excellent densification of the membrane. Meanwhile, no exposed SiO<sub>2</sub> particles were observed on the surface of the membrane, indicating that SiO<sub>2</sub> nanospheres was well embedded in the PEO matrix through the action of stirring mechanism.

Figure 2(c) shows the XRD pattern of PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN composite solid polymer electrolyte. we can observe two characteristic diffraction peaks corresponding to the PEO chains at 2 $\theta$  = 19° and 23°. By comparing the intensity of the diffraction peaks, diffraction peak intensity of PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN solid polymer electrolyte is lower, indicating that the crystallinity of PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN is lower than PEO<sub>18</sub>-LiTFSI. It means that the addition of SiO<sub>2</sub> nanospheres and SN can effectively reduce the crystallinity of PEO.

Figure 3 shows the EDS spectrum of composite solid polymer electrolyte. S and F are evenly distributed, indicating that LiTFSI was evenly dispersed in the peo matrix. The addition of SN to promote the dissociation of lithium has been better demonstrated. The uniform distribution of Si indicates that SiO<sub>2</sub> nanospheres were evenly dispersed in the PEO matrix by mechanical stirring, ultrasonic and solution casting methods. The C and O (mainly come from PEO and SN) maintained uniform distribution, indicating that the composite solid electrolyte obtained by adding SN and SiO<sub>2</sub> nanospheres into the PEO matrix maintained uniform dispersion.

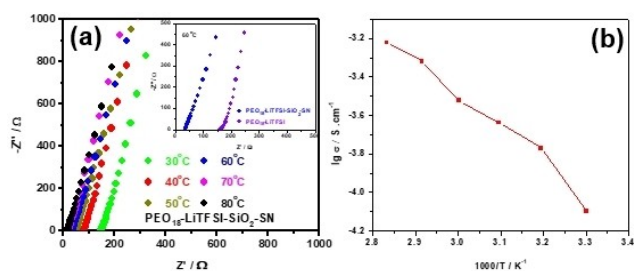
### 2.2. Ionic Conductivity Analysis of Composite Solid Polymer Electrolyte

Figure 4 (a, b) is the EIS curve of polymer electrolyte obtained by AC impedance test at different temperature, and the Arrhenius curve of ionic conductivity changing with temperature. The ionic conductivity of polymer electrolyte reached 0.8 × 10<sup>-4</sup> S cm<sup>-1</sup>, 3.3 × 10<sup>-4</sup> S cm<sup>-1</sup>, 6.0 × 10<sup>-4</sup> S cm<sup>-1</sup>, at room temperature, 60 °C and 80 °C, respectively.



**Figure 3.** SEM and EDS mapping of PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN.





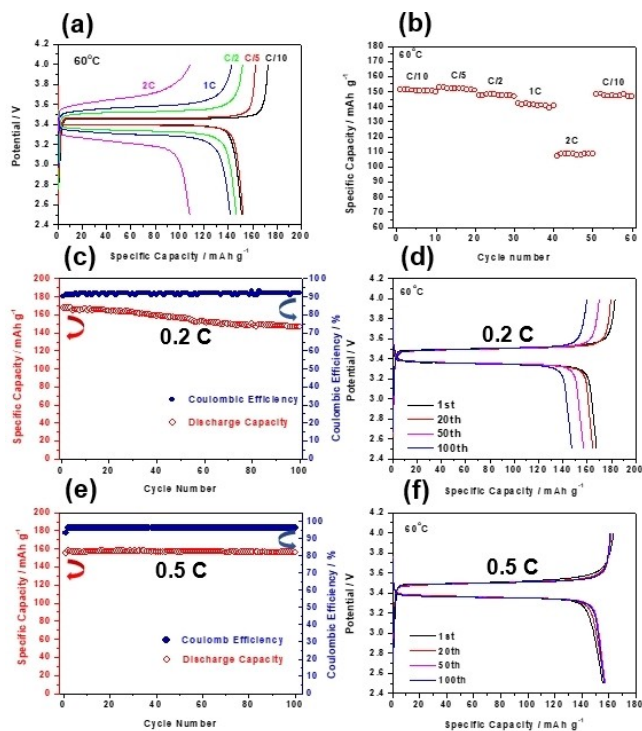
**Figure 4.** a) Impedance curves of  $\text{PEO}_{18}\text{-LiTFSI-5\%SiO}_2\text{-5\%SN}$  solid polymer electrolyte membrane at 30–80 °C. Inset: Impedance curves of  $\text{PEO}_{18}\text{-LiTFSI-5\%SiO}_2\text{-5\%SN}$  and  $\text{PEO}_{18}\text{-LiTFSI}$  at 60 °C; b) Arrhenius plots for the ionic conductivities of CSPE and the thickness of the membrane.

The ionic conductivity increases with the increase of test temperature, due to the increase of temperature, the mobility of lithium-ions increases. With the temperature approaching the glass transition temperature ( $T_g$ ) of PEO substrate, the electrolyte softened and the interface contact with the electrode became better and reduce the interfacial impedance improve the ionic conductivity. The ionic conductivity of the solid composite polymer electrolyte at room temperature is much higher than that of the pure PEO-based polymer electrolyte ( $\sim 10^{-7} \text{ S cm}^{-1}$ ). For PEO-based electrolyte, if the whole electrolyte system consists only of PEO matrix and lithium source, the ionic conductivity of this pure solid electrolyte system will be very low.<sup>[31]</sup>

By compared the impedance of  $\text{PEO}_{18}\text{-LiTFSI-5\%SiO}_2\text{-5\%SN}$  and  $\text{PEO}_{18}\text{-LiTFSI}$  at 60 °C, the impedance of  $\text{PEO}_{18}\text{-LiTFSI-5\%SiO}_2\text{-5\%SN}$  is significantly lower than  $\text{PEO}_{18}\text{-LiTFSI}$ . As the addition of  $\text{SiO}_2$  nanospheres and SN effectively promoted the dissociation of lithium salts, more free lithium-ions were released.  $\text{SiO}_2$  nanospheres and SN effectively reduce the crystallinity of the PEO matrix, so that the PEO chain segment can better bind and release  $\text{Li}^+$ . Therefore,  $\text{PEO}_{18}\text{-LiTFSI-5\%SiO}_2\text{-5\%SN}$  system can effectively improve the ionic conductivity.

### 2.3. Cycle and Rate Performance of $\text{LiFePO}_4/\text{CSPE}/\text{Li}$ .

$\text{PEO}_{18}\text{-LiTFSI-5\%SiO}_2\text{-5\%SN}$  composite polymer electrolyte is applied in all-solid-state lithium-ion battery with lithium as negative electrode and  $\text{LiFePO}_4$  as positive electrode. Figure 5(a) shows the initial charge-discharge curves at different rate at 60 °C. The results show that the specific capacities of  $\text{LiFePO}_4/\text{CSPE}/\text{Li}$  battery' first discharge are 151.5, 153.2, 147.3, 141.6 and 108.7  $\text{mAh g}^{-1}$  at rates of 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C, respectively. Under the rates of 0.1 C and 0.2 C, the flat charge-discharge voltage platform of the battery was 3.4 V and 3.46 V, respectively, corresponding to the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  REDOX couple reaction on the cathode during charge-discharge. According to the related literature, the low polarization of charge-discharge voltage can reflect the low impedance of polymer electrolyte body and the low interface impedance of CSPE/Li anode



**Figure 5.** The cycling and rate performance under 60 °C for all-solid-state battery  $\text{LiFePO}_4/\text{CSPE}/\text{Li}$ ; a) The initial charge-discharge curves under different rates (0.1 C, 0.2 C, 0.5 C, 1 C, 2 C); b) The rate cycling performance of the all-solid-state battery; c) Cycling performance at 0.2 C; d) The charge-discharge curves at 0.2 C; e) Cycling performance at 0.5 C; f) The charge-discharge curves at 0.5 C.

and cathode.<sup>[32]</sup> The battery charge-discharge voltage polarization of this system is very low, only 0.06 V. It shows that  $\text{PEO}_{18}\text{-LiTFSI-5\%SiO}_2\text{-5\%SN}$  composite solid polymer electrolyte has the characteristics of low impedance, and effectively reduces interface impedance, so that it can be well used in all-solid-state lithium-ion battery. At the same time, the discharge capacity of 0.2 C is higher than 0.1 C, according to the study of charge-discharge process of electrode materials, when the battery is charged-discharged at high rate, the active substance reacts quickly, and lithium-ions are quickly released and embedded.<sup>[33,34]</sup> From the interface properties of electrode material and solid electrolyte, which may be because the activation process of charge-discharge at a small rate improves the interface between electrolyte and electrode material, lithium-ions transmission channel can be better formed.<sup>[35,36]</sup> It indicates that  $\text{PEO}_{18}\text{-LiTFSI-5\%SiO}_2\text{-5\%SN}$  polymer electrolyte can establish stable interface structure both with anode and cathode.

Figure 5(b) shows the cycle performance of  $\text{LiFePO}_4/\text{CSPE}/\text{Li}$  all-solid-state battery at different rates (0.1 C – 2 C – 0.1 C). It can be excellently charged and discharged at a corresponding rate and shows high specific capacity. At the rate of 0.1 C, the discharge capacity of the battery was basically stable at 151  $\text{mAh g}^{-1}$ . When the charge-discharge rate gradually increased to 0.2 C, 0.5 C, 1 C and 2 C, the

discharge capacity was still remain: 155, 150, 147, 142 and 109 mAhg<sup>-1</sup>, respectively. The rate is returns to 0.1 C, the specific discharge capacity can still reach 150 mAhg<sup>-1</sup>, almost fully recovered. The performance of rate cycle indicates that PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN solid polymer electrolyte has high stability and reversibility in electrochemical process.

The cycle performance of LiFePO<sub>4</sub>/CSPE/Li battery at rate of 0.2 C and 0.5 C is shown in Figure 5(c, d, e, f), stable cycle performance can be observed. The initial specific discharge capacity of 0.2 C reached 167 mAhg<sup>-1</sup>, the specific discharge capacity remained at 150 mAhg<sup>-1</sup> after 100 cycles, the capacity decay rate was only 11.3%, and the capacity retention rate was still 89.7%. The coulombic efficiency remained above 92% throughout the process. After a long time of charge-discharge, the battery still has high discharge capacity, which indicates that the electrolyte has excellent mechanical properties, and the generation of lithium dendrites is successfully inhibited during charge-discharge, the short circuit in the battery is prevented because the electrolyte has not been penetrated. The initial specific discharge capacity at 0.5 C reached 157.5 mAhg<sup>-1</sup>, the specific discharge capacity remained at 156 mAhg<sup>-1</sup> after 100 cycles, and capacity retention 99%, the coulombic efficiency remained above 96% throughout the process. The capacity retention rate at 0.5 C is better than the cycle performance at 0.2 C. Because the time spent in 100 cycles of 0.2 C is more than 0.5 C, and the electrolyte may decompose over time, affecting the cycle performance of the battery. The stability and life of electrolyte need to be further improved and optimized. Meanwhile, the increase of the rate caused the temperature of the battery to rise, resulting in the cycle temperature at 0.5 C higher than 0.2 C, which increases the ionic conductivity of the electrolyte and reduces the impedance. The relatively stable cycling supports the PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN composite solid polymer electrolyte has good electrochemical stability.

### 3. Conclusions

The composite solid polymer electrolyte of PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN system was successfully constructed by introducing inorganic filler SiO<sub>2</sub> nanospheres and plasticizer SN into a PEO matrix. This new CSPE system can increase the ionic conductivity to 10<sup>-4</sup> Scm<sup>-1</sup>, higher than pure PEO-based polymer electrolyte, ionic conductivity at 60 °C up to 3.3 × 10<sup>-4</sup> Scm<sup>-1</sup>. Meanwhile, AC impedance shows that the CSPE builds a stable interface that provides good contact both with anode and cathode.

LiFePO<sub>4</sub>/CSPE/Li all-solid-state lithium-ion battery exhibits satisfactory electrochemical performance at 60 °C. The specific capacity at 0.2 C the first discharge capacity is 167 mAhg<sup>-1</sup>, and the specific capacity of the 2 C first discharge remains 108.7 mAhg<sup>-1</sup>, the battery charge-discharge voltage polarization of this system is very low, only 0.06 V. Furthermore, the capacity at 0.5 C after 100 cycles

was kept at 156 mAhg<sup>-1</sup>, and the capacity retention rate was 99%, the coulombic efficiency remained above 96%. The discharge capacity was almost completely recovered in the rate cycle (0.1 C – 2 C – 0.1 C). Therefore, PEO<sub>18</sub>-LiTFSI-5%SiO<sub>2</sub>-5%SN composite solid polymer electrolyte system has excellent performance, and it will be of great significance to apply it in all-solid-state lithium-ion battery.

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### Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** all-solid-state · composite electrolytes · PEO-based polymers · lithium-ion batteries · energy storage

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