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## Solid State Ionics

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# Enhancing Li<sup>+</sup> transport kinetics of PEO-based polymer electrolyte with mesoporous silica-derived fillers for lithium-ion batteries



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#### ABSTRACT

Solid state batteries show great improvement of safety compared to batteries with liquid electrolytes. Polyethylene oxide (PEO) has been the most classic solid polymer electrolyte matrix. However, PEO based polymer electrolyte with lithium salt suffers from high crystallinity, poor Li<sup>+</sup> transport kinetics and low ionic conductivity, especially at room temperature, which hindered its further application. Herein, a mesoporous silica derived active filler has been prepared with Li<sup>+</sup> contained ionic liquid physically immobilized in the nanopore structure. PEO based solid polymer electrolyte with the active filler shows low crystallinity of 30% and a remarkable high ionic conductivity of  $4.3 \times 10^{-4}$  S cm<sup>-1</sup> at 60 °C, at the same time maintaining a good mechanical strength of 1.28 MPa. The assembled lithium symmetric battery shows stable and long cycle performance. And the Li/LiFePO4 also shows stable cycling performance, maintaining 88.4% initial capacity after 80 cycles at 0.1C at 60 °C.

#### 1. Introduction

Lithium-ion batteries (LIBs) have been widely used in 3C electronic products and show great potential in electric vehicles (EVs) and smart power grids [1,2]. However, the traditional LIBs are consisted with liquid electrolyte, which is flammable and leaky, showing potential risk of combustion and explosion [3]. Due to the safety concern, it's important to develop the solid state LIBs [4-6]. Since Wright reported ionic conducting ability of the polyethylene oxide (PEO) and alkali salt in 1973 [7], after which Armand used the PEO and lithium salt as electrolyte for solid state LIBs [8], the PEO-based solid polymer electrolyte has been widely studied and PEO has become the most commonly used polymer electrolyte matrix for solid state LIBs. PEO and lithium salt electrolyte based electromobiles named "Autolib" have been applied by the Bolloré company in the car sharing market in France.

The ion conduction mechanism of PEO is due to its high flexibility of the polymer chain. The oxygen atoms of the ether-oxygen bond on the chain can coordinate with lithium ions and conduct lithium ions by

thermal motion of the chain segment. However, PEO based solid electrolytes still suffers low ionic conductivity ( $\sigma$ ) especially at room temperature. For the PEO-based solid polymer electrolyte, there are various strategies to improve the ionic conductivity [4,6]: (1) adding fillers [9]; (2) plasticizing [10] with ionic liquid (IL) [11], carbonate solvents or low molecular weight oligomer et al.; (3) molecular structure design, such as comb or star structure [12], cross linking [13] and interpenetrating network (IPN) structure [14]; (4) functionalization such as single ion conductor [15–17]. The key factor of these ionic conductivity improving methods is to decrease the crystallinity of PEO and increase the ion motion.

Adding fillers into PEO-based electrolyte could effectively promote the charge carriers' migration by decreasing the crystallinity zone. The common fillers includes: (1) inert inorganic oxide such as  $SiO_2$ ,  $Al_2O_3$ , MgO et al. [18,19]; (2) modified derivatives of inert inorganic oxide, such as silane-modified SiO<sub>2</sub> [20]; (3) ionic conducting ceramics like Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) [21], Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> (LGPS) [22] et al. (4) other sorts of filler such as metal organic framework (MOF) [23,24], molecular sieves, ZSM-5 [25], mesoporous silica SBA-15 [26] et al. and their

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derivates. For example, Cao et al. [27] reported silane-modified SBA-15 as filler for the composite PEO-based electrolyte.

On the basic of various fillers, nano-porous structured fillers absorbing ionic liquid (IL) could further enhance the Li<sup>+</sup> transport kinetics, improve of ionic conductivity and at the same time maintain the mechanical strength while singly adding of IL may cause the weakening of the polymer mechanical strength [28]. Hybrid with ionic liquid, Pan's group reported a Li-IL@MOF based solid like electrolyte with nano wetted interface [29] created by the confined Li-IL. Guo et al. [30] came up with a nonoporous UIO-Li-IL multifunctional filler for PEObased solid state lithium batteries, which greatly enhanced the ionic conductivity and the electrical performance of the LIBs.

In this work, a mesoporous silica SBA-15 derived filler with the physically immobilization of non-flammable Li-ion containing ionic liquid (LiIL) in the nanopore is prepared (denoted as SBA-15-LiIL) and added into the PEO-based polymer electrolyte. The mesoporous SBA-15 acts as a host and the Li-IL as a guest which turned the inert filler into an active ion conductor. Composite electrolyte with this filler shows great enhancement both in ionic conductivity and mechanical strength, which result in a stable cycle performance for the lithium symmetric batteries and lithium iron phosphate (LiFePO<sub>4</sub>) batteries.

#### 2. Experimental details

#### 2.1. Materials

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI), lithium bis(trifluoro methanesulfonyl)imide (LiTFSI) and PEO (Mw = 600,000), *N*-methyl-2-pyrrolidone (NMP) were purchased from Aladdin. The anhydrous acetonitrile (AN) was from AlfaAesar. Tetraethyl orthosilicate (TEOS) was bought from Xilong Scientific Co., Ltd. The polyethylene oxide-polypropylene oxide-polyethylene oxide (P123) is from BASF.

#### 2.2. Synthesis and preparation

#### 2.2.1. Preparation of the mesoporous SBA-15 and SBA-15-LilL filler

The SBA-15 was prepared by hydrothermal method. Dissolved 1.5 g P123 in 30 ml deionized water, and then added 30 ml 4 M HCl as well as 1 g NaCl as ion directing agent. After 4 h of stirring, added 3.21 g TEOS slowly and then put the solution in 40 °C water bath under vigorous stirring for 12 h. Then transferred the white solution into reaction kettle and then crystalized for 24 h under 100 °C. Then filtrated the white crystallization sediment by filtration with water and ethyl alcohol (1: 1, in volume ratio). Dried the white powder in the drying oven at 80 °C and then calcined it under 550 °C for 2 h at the heating rate of 2 °C/min in the tube furnace. Then obtained the mesoporous structured silica SBA-15.

For the active filler SBA-15-LiIL, prepared 0.2 M LiIL solution by dissolving LiTFSI into the EMIMTFSI ionic liquid. Mixed the SBA-15 and the LiIL by mass ratio of 1:1, added 40 ml acetonitrile (AN) solvent and then mixed them adequately by condensation reflux at 80 °C for 1 h. Then removed the solvent by the rotary evaporator. Treated the product in vacuum at 120 °C for 4 h. Then the active powder filler SBA-15-LiIL was obtained.

## 2.2.2. Preparation the PEO-based electrolytes

The three PEO-based electrolytes without filler, with SBA-15 filler and SBA-15-LIIL active filler are remarked as PEOLi, PEOLi/SBA and PEOLi/SBA-LIIL, respectively. To prepare the PEOLi/SBA-LIIL electrolyte, the active filler SBA-15-LIIL was synthesized at first as it is mentioned above. Mixed the PEO, LITFSI and the active filler with AN solvent, stirred the solution for 24 h and then casted it in the Teflon plate. After a vacuum drying process at 60 °C for 48 h, the final electrolyte was obtained. The PEOLi and PEOLi/SBA electrolytes as contrast samples were also prepared by casting method. The component ratio of the three electrolytes has been listed in Table S1. The mass ratio of the ionic liquid in the PEOLi/SBA-LiIL electrolyte is 8.85%.

#### 2.2.3. Assemble of the batteries

The lithium symmetric battery was assembled by sandwiching the solid electrolyte between two lithium plates. The LiFePO<sub>4</sub> battery was assembled by sandwiching the electrolyte membrane between LiFePO<sub>4</sub> cathode and Li metal anode. Uniformly mixed LiFePO<sub>4</sub>, acetylene black (AB), and the binder with a mass ratio of 0.65: 0.2: 0.15 by AN and NMP solvent as the cathode slurry. The composition of binder for different batteries is the same with the electrolyte.

#### 2.3. Characterizations

Field emission transmission electron microscopy (TE-TEM, F30) has been used for the investigation of the filler morphology, and the TEM element mapping has also been used to check the active filler. The X-ray diffraction (XRD, Ultima-IV) was applied to characterize the structure of the filler. Brunner-Emmet-Teller (BET) was used to test the surface area as well as the distribution of the pore diameter before and after the physical immobilization of the LiIL of the SBA-15 filler. The high magnification surface morphology was obtained by field electron scanning electron microscopes (FE-SEM, Hitachi, S-4800) system with energy dispersive X-ray spectrometer (EDS). And the EDS was used for the element distribution in the electrolyte. Fourier transform infrared spectroscopy (FT-IR, Nicolet IS5) measurement was taken with the wavenumber in the range of 4000–400  $\text{cm}^{-1}$ . The differential scanning calorimetry (DSC) curves was measured by DSC 214 polyma (NETZSCH) apparatus with a heating rate of 10 °C/min with N<sub>2</sub> as protector gas. The mechanical stability of three electrolytes has been measured by the Universal Material Testing Machine (UTM-4000, SUNS).

The ionic conductivity of the electrolyte was tested by block battery sandwiching electrolyte membrane between two stainless steels (SS) in the CR 2016 coin cell by electrochemical impedance spectroscopy (EIS) method using Solartron electrochemical workstation (SI-1260) within  $0.1-10^5$  Hz and calculated by the following equation (Eq. (1)):

$$\sigma = d/(R \times A) \tag{1}$$

in which d stands for the thickness of the solid electrolyte, R refers to the impedance of the electrolyte, A is the area of the SS electrode.

The cycle performance of the three electrolytes assembled Li symmetric batteries and Li/LiFePO<sub>4</sub> batteries was measured by the NEWARE (BTS-610, Neware Technology Co., Ltd) measurement equipment. The batteries were all stored in the constant temperature oven at 60 °C during the whole cycle process.

## 3. Results and discussion

The fillers were characterized and confirmed by TEM and BET specific surface area tester and XRD. TEM image shows obvious mesoporous structure of SBA-15 (Fig. 1a) which agrees well with the XRD result SBA-15 (Fig. S1) with character peaks of (100), (110), (200) of the mesoporous silica. After the physically immobilization of LiIL (Fig. 1b), the TEM image shows the substance immobilized on the surface and incorporated in the porous of the SBA-15. Further TEM elemental mapping of the active SBA-15-LiIL filler shows the C, N, S element of the LiIL, proving the existence of LiIL composited with SBA-15 (Fig. 1c). BET results show a sharp decrease of the surface area from 480 m<sup>2</sup> to 18.8 m<sup>2</sup> after the physically immobilization and modification of LiIL on the SBA-15 (Fig. 1d). And the Barrett-Joyner-Halenda (BJH) plot (Fig. 1e) also shows the decrease of pore volume due to the successful composition of the LiIL and the SBA-15, corresponding to the BET results. Besides, the most pore diameter also decreased from 7.5 nm to 6 nm. The pore diameter's shift to smaller value and the pore volume's sharp decrease both reveal the filling up of the pores by LiIL.



Fig. 1. TEM images of (a) pristine SBA-15 and (b) SBA-15-LiIL active filler; (c) The TEM element mapping of the SBA-15-LiIL; (d) BET curve and (e) BJH curve of the SBA-15 and SBA-15-LiIL.

The TEM, XRD and BET characterization confirmed the success of the composition of the guest LiIL and the host SBA-15 of the active filler. The tight composition may due to the capillary effect of the mesoporous pore to the LiIL during the preparing process by co-solvent rotation evaporation method.

The optical image shows that the PEOLi/SBA-LiIL electrolyte is semitransparent, flat and self-supporting in solid state (Fig. 2a). Seeing from the SEM images, SBA-15-LiIL active filler shows similar oval particle morphology with the pristine SBA-15 filler (Fig. 2b, c). The PEOLi solid polymer electrolyte shows distinct spherulites (Fig. 2d), while that of the PEOLi/SBA is smaller (Fig. 2e) because SBA-15 fillers broke the PEO's crystal zone. Furthermore, the PEOLi/SBA-LiIL electrolyte membrane with the active filler is relatively smooth (Fig. 2f). This suggests less crystallization zone in the PEOLi/SBA-LiIL electrolyte. In the PEO polymer, the Li-ion conduction is mainly in the amorphous phase by segment thermal motion and less crystallization is good for enhancing the ionic conductivity. Further element mapping shows uniform distribution of Si, F and S element in the PEOLi/SBA-LiIL electrolyte (Fig. 2g–i), revealing the homogeneous distribution of the SBA-LiIL fillers in the composite PEO-based polymer electrolyte.

FT-IR spectroscopy was applied for the characterization of the composition of different electrolytes (Fig. 3). Compared with pure PEO membrane, PEOLi and PEOLi/SBA solid electrolyte, the PEOLi/SBA-LiIL electrolyte membrane shows new absorption peaks at  $1575 \text{ cm}^{-1}$  (C=C stretching vibration) [31] and at  $3125 \text{ cm}^{-1}$ ,  $3159 \text{ cm}^{-1}$  (C-H stretching vibration) [32], deriving from the imidazole cation of the EMIMTFSI ionic liquid in the LiIL, indicating the composition of the active filler with the PEO (Fig. 3a). In the finger print region (1300–400 cm<sup>-1</sup>), the peak at 460 cm<sup>-1</sup> is attributed to the Si-O-Si bond of the SBA-15 [33,34] in the PEOLi/SBA and PEOLi/SBA-15 electrolyte, suggesting the composite of the SBA-15 and SBA-15-LiIL filler with the PEO-based solid polymer electrolyte, respectively

(Fig. 3b). The peaks at 1241 cm<sup>-1</sup> and 1280 cm<sup>-1</sup> are the specific spectrum of asymmetric CH<sub>2</sub> twisting vibration in the crystallization phase of PEO [35,36], which decreased after the adding of SBA-15 and further reduced with the SBA-15-LiIL active filler. This demonstrates a reduction in crystallinity of the PEO. And this was further verified by the DSC characterization.

Fig. 3c and d shows melting temperature (Tm) and glass transition temperature (Tg) of the three electrolytes: PEOLi, PEOLi/SBA and the PEOLi/SBA-LiIL by DSC method. The PEOLi/SBA-LiIL shows the lowest Tm of 48.2 °C compared with PEOLi (56.1 °C) and PEOLi/SBA (54.4 °C). And the corresponding crystallinity of PEO ( $\chi_c$ ) could be calculated by the following equation (Eq. (2)):

$$\chi_{\rm c} = \frac{\Delta H_{\rm exp}}{\Delta H} \times \frac{1}{\rm w_f} \times 100\%$$
<sup>(2)</sup>

where  $\Delta H_{exp}$  refers to the melting enthalpy of the electrolytes, in which PEO is the only crystallizable polymer,  $\Delta H$  represents the constant of the melting enthalpy of 100% crystallized PEO (213.7 J/g) [37] and w<sub>f</sub> represents the PEO mass ratio in three electrolytes. The PEOLi/SBA-LiIL shows the smallest crystallinity of 30% compared with pure PEO matrix (63.5%), pure PEOLi electrolyte without filler (40.2%) and PEOLi/SBA (38.3%). Besides, the PEOLi/SBA-LiIL also shows the lowest Tg of -48.5 °C and the lower Tg is more benefit for the ionic transport by thermal motion of the polymer chain.

The mechanical strength of the PEOLi, PEOLi/SBA and PEOLi/SBA-LiIL electrolyte membrane was measured (Fig. 4). Results show that the PEOLi/SBA-LiIL shows moderate mechanical strength of 1.28 MPa and PEOLi/SBA shows the highest value of 2.3 MPa, higher than pure PEOLi electrolyte (0.45 MPa). The reinforcement mechanism of the PEOLi/ SBA electrolyte is the SBA-15 inorganic filler's adhesion to the PEO polymer chain [20]. With the immobilization of the LiIL on the SBA-15, the PEOLi/SBA-LiIL electrolyte shows smaller mechanical strength than



Fig. 2. (a) Optical image of the PEOLi/SBA-LiIL electrolyte; SEM morphology of (b) pristine SBA-15, (c) SBA-15-LiIL active filler, (d) pure PEOLi electrolyte, (e) PEOLi/SBA electrolyte and (f) PEOLi/SBA-LiIL electrolyte; EDS element mapping of (g) Si, (h) F and (i) S element of the PEOLi/SBA-LiIL electrolyte.

PEOLi/SBA with bare SBA-15 filler. Nevertheless, the maximum breaking elongation ratio of PEOLi/SBA-LiIL shows an increasing of the flexibility and a good tenacity.

Their ionic conductivities' behavior basically fits the Arrhenius law (Fig. 5a). Besides, there is an obvious inflection point for the bare PEOLi electrolyte around the melting point of PEO. This is due to the different ion conduction barrier in the crystallization phase below Tm and the

The ionic conductivity of different electrolytes are shown in Fig. 5.



Fig. 3. The FT-IR spectra of pure PEO membrane, EMIMTFSI ionic liquid, PEOLi, PEOLi/SBA, PEOLi/SBA-LiIL PEO-based polymer electrolyte: (a) Full spectra; (b) Enlarged view of the finger print region. (c) Tm and (d) Tg of the DSC curves of PEOLi, PEOLi/SBA and PEOLi/SBA-LiIL electrolyte.



Fig. 4. Strain-stress mechanical strength tests of PEOLi, PEOLi/SBA and PEOLi/SBA-LiIL electrolyte membrane, respectively.

amorphous phase above Tm of PEO. The plot flattened after the addition of SBA-15 and SBA-15-LiIL fillers. This is due to the decreased melting point and crystallinity [33], coincidence with the DSC results. The PEOLi/SBA-LiIL electrolyte has the highest ionic conductivity compared with pure PEOLi and PEOLi/SBA, showing ionic conductivity of  $7.5 \times 10^{-6}$  S cm<sup>-1</sup> at 25 °C. With the increase of the temperature, the AC Impedance value decrease and the ionic conductivity reach  $4.3 \times 10^{-4}$  S cm<sup>-1</sup> at 60 °C (Fig. 5b). And this is due to that the ionic liquid immobilized mesoporous silica filler provides fast lithium ion transportation kinetics [38] at the wetted interface between the active filler and the polymer matrix where Li-ion transport velocity is improved. So the PEOLi/SBA-LiIL shows a good ionic conductivity while maintaining a good mechanical strength.

In order to investigate the inhibitory effect of different electrolytes on lithium dendrites, lithium symmetrical batteries were assembled for charging and discharging cycles. The results show that the polarization voltage of PEOLi/SBA-LiIL is the smallest (33 mV) when the current density is 0.02 mA cm<sup>-2</sup> with the capacity of 0.02 mA cm<sup>-2</sup> for 500 cycles (Fig. 6a). The pure PEOLi without filler shows shortest cycle life and the highest voltage above 100 mV. What's more, the PEOLi/ SBA-LIIL electrolyte shows the flat and smallest voltage platform seeing from the first two cycles (Fig. 6b). Moreover, it can be seen from the voltage capacity curve (Fig. 6c–e) of three kind of PEO-based electrolyte that the charging and discharging curves of PEOLi/SBA-LiIL are relatively flat and the voltage platform is almost the same at the 1st, 2nd and 100th cycle, compared with PEOLi and PEOLi/SBA electrolyte. The longer cycling life and the smallest polarization voltage of the PEOLi/SBA-LIIL is because of its high ionic conductivity and mechanical strength which could present a physical force to the dendrite growth [39].

When the current rise to 0.1 mA cm<sup>-2</sup> with capacity of 0.1 mAh cm<sup>-2</sup> (Fig. 7a), the electrolyte PEOLi/SBA-LiIL also shows the smallest polarization voltage of around 73 mV, which was corresponding to its higher ionic conductivity. The lithium electrodes after cycling at 0.1C were further investigated by SEM. As shown in Fig. 7b–d, the PEOLi/SBA and PEOLi/SBA-LiIL shows flatter lithium surface than PEOLi due to the higher mechanical strength which could suppress the growth of the lithium dendrite. The relatively smooth lithium surface with PEOLi/SBA-LiIL after cycling is attributed to the good compatibility of the electrolyte and lithium electrodes in addition to the good mechanical strength of the PEOLi/SBA-LiIL. Rate performance up to 0.3 mA cm<sup>-2</sup> of the PEOLi/SBA-LiIL was further studied (Fig. 7e). As the increase of the current rate, the polarization voltage increase slightly, showing values of 43 mV, 68 mV, 108 mV and 158 mV at 0.05, 0.1, 0.2, 0.3 mA cm<sup>-2</sup>, respectively.

In order to investigate the electrical performance of different electrolytes, the Li/LiFePO<sub>4</sub> batteries were assembled and tested at 0.1C at 60 °C (Fig. 8) after two cycles of small current activation. In Fig. 8a, three electrolytes assembled cells all shows high coulombic efficiency above 99% during the cycle process. The PEOLi/SBA-LiIL electrolyte assembled battery shows the highest discharge capacity retention ratio of 88.4% after 80 cycles, higher than that the PEOLi/SBA electrolyte of 85.7%, as well as the PEOLi electrolyte of 41.7% with which the battery decayed quickly after 55 cycles. And the stable cycle performance is due to the higher ionic conductivity and the reasonable mechanical stability. As shown in Fig. 8b, the PEOLi/SBA-LiIL shows higher discharge capacity of 150.3 mAh g<sup>-1</sup> at 0.07C, and the discharge capacity maintained 90.4% after 90 charge-discharge cycles.

#### 4. Conclusion

A high performance PEO-based solid polymer electrolyte PEOLi/SBA-LiIL has been prepared by adding SBA-15-LiIL active filler. The filler is made by physically immobilizing the LiIL into the mesoporous silica SBA-15. The active filler could create solid-liquid hybrid interface without sharp decrease of the mechanical stability, providing fast Li<sup>+</sup> transportation kinetics. The PEOLi/SBA-LiIL electrolyte with the active filler shows greatly enhancement of the ionic conductivity with  $4.3 \times 10^{-4}$  S cm<sup>-1</sup> at 60 °C as well as an increase of the mechanical modulus. The LiFePO<sub>4</sub> battery with PEOLi/SBA-LiIL electrolyte shows stable cycle performance at 0.1C at 60 °C. Besides, the Li symmetric cell with PEOLi/SBA-LiIL also shows smaller polarization voltage and longer life for the lithium dendrite suppression of the PEOLi/SBA15-LiIL electrolyte with high ionic conductivity and high mechanical strength. This composite PEO-based electrolyte shows great potential in



Fig. 5. (a) The ionic conductivity change behavior with temperature of different electrolytes; (b) the AC impedance resistance of PEOLi/SBA-LiIL at different temperature.



**Fig. 6.** (a) The lithium deposition and striping experiment of PEOLi, PEOLi/SBA, and PEOLi/SBA-LiIL electrolyte by lithium symmetrical battery at 0.02 mA cm<sup>-2</sup> with the capacity of 0.02 mAh cm<sup>-2</sup> at 60 °C; (b) voltage-time plot of the first two discharge-charge (deposition-striping) cycles; the voltage-capacity plot of (c) PEOLi, (d) PEOLi/SBA and (e) PEOLi/SBA-LiIL electrolyte, respectively.



**Fig. 7.** (a) The lithium symmetric battery deposition-stripping test with PEOLi, PEOLi/SBA, and PEOLi/SBALIIL electrolyte at 60 °C at the current density of 0.1 mA cm<sup>-2</sup> with capacity of 0.1 mAh cm<sup>-2</sup> and (b–d) the corresponding SEM images after cycling. (e) The rate performance of lithium symmetric battery with PEOLi/SBALIIL electrolyte at current rate of 0.05, 0.1, 0.2, 0.3 mA cm<sup>-2</sup> and capacity of 0.05, 0.1, 0.2, 0.3 mAh cm<sup>-2</sup>, respectively.

the electromobile application for the city in the future.

#### Credit author statement

Xiu Shen: Conceptualization, Methodology, Writing-original draft

preparation. Ruiyang Li: Data curation. Haoshen Ma: Data curation. Zhipeng Wen: Visualization. Longqing Peng: Investigation. Boyang Huang: Validation. Peng Zhang: Supervision, Writing-review & editing. Jinbao Zhao: Project administration, Funding acquisition.



Fig. 8. (a) The Li/LiFePO<sub>4</sub> cycle performance with PEOLi, PEOLi/SBA, and PEOLi/SBA-LiIL electrolyte at 0.1C at 60 °C; (b) the Li/LiFePO<sub>4</sub> battery's cycle performance with PEOLi/SBA-LiIL electrolyte at 0.07C at 60 °C. The LiFePO<sub>4</sub> loading is 1.0 mg cm<sup>-2</sup> for the 0.1C cycle and 3.0 mg cm<sup>-2</sup> for the 0.07C cycle.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

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