



# Article An All-Solid-State Lithium Metal Battery Based on Electrodes-Compatible Plastic Crystal Electrolyte

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**Abstract:** Solid-state plastic crystal electrolytes (SPCEs) have attracted much attention due to their high ionic conductivity at room temperature and polymer-like plasticity. Herein, we made a LiFePO<sub>4</sub> | |Li solid state battery based on SPCEs. A SPCE film is made up of glass fiber, succinonitrile (SN), lithium bis (triflu-romethanesulphonyl) imid (LiTFSI), and LiNO<sub>3</sub>. Glass fiber is introduced to improve the mechanical property, and LiNO<sub>3</sub> served as an additive to stabilize electrolyte/Li interface. The SPCE film delivers a high ionic conductivity of  $7.3 \times 10^{-4}$  S cm<sup>-1</sup> at room temperature and has excellent stability with Li-metal anode. SPCE is also infused into cathode electrode and used as the interface with cathode particles, which can access a large interface contact area and deform reversibly with volume change. The LiFePO<sub>4</sub> | Li solid state battery based on SPCE can work well at ambient temperature, which shows a high initial specific capacity of 121.4 mAh g<sup>-1</sup> and has 86.9% retention after 90 cycles at 0.5 C.

Keywords: plastic crystal; succinonitrile; solid-state batteries; electrode compatible



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 1. Introduction

Li-ion batteries have gained great success for commercial applications [1,2]. Though many efforts have been paid on the development of new cathode and anode materials with high energy and power density [3–6], the energy density of traditional Li-ion batteries cannot meet the practical requirements. So, the ever-increasing demand for higher energy densities has promoted the research using lithium metal as anode electrode [7]. However, the development of Li-metal batteries using traditional liquid electrolyte is plagued by the side reaction between electrolyte and lithium metal and the growth of lithium dendrites [8,9]. In this respect, all-solid-state lithium-metal batteries (ASSLMBs) with solid-state electrolytes (SSEs) are considered next generation battery technology to meet the needs of high energy density and safety [10].

SSEs can mainly be summarized in three types [11–13], inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs), and composite polymer electrolytes (CPEs). Taking into account the brittle nature of ISE thin films, SPEs [14,15], including poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), etc., are considered attractive for their lightweight property, high flexibility, and ease of processing. However, the practical application of SPEs on solid-state batteries (SSBs) is restricted by their low room-temperature conductivity. Taking the most studied system of PEO as an example, they show a low ionic conductivity of around  $10^{-6}$  S cm<sup>-1</sup> at ambient temperature and a low lithium-ion transfer number of about 0.2 [16], which is far from practical needed. To address this drawback, various strategies have been proposed, such as block copolymer crosslinking and addition of fillers or plasticizers to lower the glass transition temperature

and improve ionic conductivity [11]. Even so, the ionic conductivity of SPEs at ambient temperature is still far from the need of practical room-temperature application.

In recent years, succinonitrile (SN) plastic crystals doped with Li salt have become one of the most interesting SSEs. The SN solid-state plastic crystal electrolytes (SPCEs) not only exhibit plastic properties similar to SPEs, but also show a Li-ion conductivity as high as  $10^{-3}$  S cm<sup>-1</sup> at 25 °C due to the high diffusivity and solvating power of SN [17–19]. In solid-state batteries, a common method for a cathode electrode is to add solid electrolyte particles. However, in this strategy, there are only a small fraction of cathode particles contacting with solid electrolyte, which will cause large interface resistance. To address this problem, SPCEs have been studied as cathode/electrolyte interfaces to reduce the interfacial resistance due to its plastic nature [20–22]. On the other hand, due to the high room-temperature ionic conductivity, SPCEs have also been introduced into composite solid-state electrolyte system with improved ionic conductivity. [23–26] The greatest weakness of SPCEs as solid electrolyte is the incompatible of aliphatic nitriles with metallic lithium and solid-state batteries based on SPCEs mainly use Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> as anode [19,27]. In this aspect, additives (e.g., FEC [28], LiDFOB [29], and LiNO<sub>3</sub> [30]) have been introduced to stabilize the interface with Li metal.

In the above research, SN was used as part of solid composite electrolyte or electrode, since SN doped with LiTFSI system was suggested as an effective ambient temperature solid electrolyte, solid-state Li-metal batteries based on SPCE were not reported. In this paper, we proposed a solid-state Li-metal battery with solid SN electrolyte. A glass fiber membrane is used as a host to enhance the mechanical properties of SPCEs. The ionic conductivity of the SPCE film reaches  $7.3 \times 10^{-4}$  S cm<sup>-1</sup> at room temperature. Due to the addition of LiNO<sub>3</sub>, the symmetrical cell shows good stability at room temperature. For the cathode, SPCE was also applied for good solid–solid interface contact. A Li | LiFePO<sub>4</sub> battery was assembled, and it shows excellent cycle performance working at ambient temperature (25 °C).

#### 2. Materials and Methods

#### 2.1. Preparation of SPCE

The SN/LiTFSI mixed solution was prepared by heating a mixture of SN (99%, Macklin) and LiTFSI (99%, Aladdin) with a molar ratio of 19:1 at 60 °C, and a clear solution was obtained. In addition, 1 wt.% LiNO<sub>3</sub> was added into the SN/LiTFSI solution to stabilize the lithium metal interface. Glass fiber was soaked into the mixed solution for 12 h at 60 °C, and then cooled down to room temperature to get a SPCE film.

### 2.2. Characterization and Electrochemical Measurements

The morphology of samples was observed by scanning electron microscope (SEM, Phenom Pro X). XRD patterns were recorded using a Bruker D8 diffractometer, with Cu K $\alpha$  radiation. The conductivity of Li ion of the SPCEs was conducted by electrochemical impedance spectroscopy (EIS) performed on biologic electrochemical station SP-500 with a frequency range from 7 MHz to 100 mHz at 60 °C, 50 °C, 40 °C, 30 °C, and room temperature (25 °C), respectively. The electrochemical window of the samples was determined with a stainless steel (SS) | SPCE | Li cell using both electrochemical floating analysis and linear sweep voltammetry (LSV) under a sweep rate of 5 mV s<sup>-1</sup> from 0 to 6 V at room temperature. The lithium-ion transference number ( $\tau_{Li^+}$ ) of SPCE film was evaluated by alternating current impedance combined with direct-current (DC) polarization with a DC voltage of 10 mV with a Li | SPCE | Li cell. The stability of electrolyte with Li metal was carried out by Li plating/stripping experiments with a Li | Li symmetric cell at a current density of 0.1 mA cm<sup>-2</sup> performed on a LAND CT2001A testing system.

#### 2.3. Evaluation of Solid-State Batteries

LiFePO<sub>4</sub> cathode slurry was prepared by grinding LiFePO<sub>4</sub> powder, carbon black, and polyvinylidene difluoride (PVDF) with mass fractions of 80, 10, and 10%, respectively,

followed by the addition of Methylpyrrolidone (NMP) solvent to obtain cathode slurry. The cathode slurry obtained was casted onto aluminum film and dried in a vacuum oven at 120 °C for 12 h. Cathode film was immerged into SPCE solution at 60 °C for 12 h; then, the well-infiltrated cathode and SPCE film were stacked together and cooled down to room temperature for a in situ solidification. Then, 2032-coin cells were assembled with Li foil as anode and SPCE film with 16 mm diameter as separator, and charging/discharging tests of batteries were performed on a LAND CT2001A testing system at room temperature.

## 3. Results

# 3.1. Structural Characterization of SPCE

The preparation process of SPCE is illustrated in Figure 1a. SPCE has a low melting point, and it is infiltrated into glass fiber matrix at 60 °C to obtain a SPCE film (Figure 1b). When doped with Li salt, SN can still maintain solid state at 25 °C (Figure 1c,d); however, the mechanical strength of SN becomes low, and it is almost impossible to prepare a pure SPCE film. Figure S1 shows the picture of pure SPCE, and it is too fragile to obtain electrolyte film. Glass fiber film is adopted in this work for concept, because it is widely used in battery devices, and it has a large pore volume. SEM image of glass fiber is shown in Figure 2a and S2; it has a good microfiber morphology, and the surface of the glass fibers are relatively smooth. Figure 2b shows the morphology of the upper surface of SPCE film. Pores of glass fiber are filled with SN electrolyte, and the surface is very smooth. The SEM images of the cross-sections of SPCE film are shown in Figure 2c and S3. The thickness of SPCE film is about 143  $\mu$ m, and many glass fibers can be seen on the cross-section surface. Thanks to the existence of glass fiber, the SPCE film has very good flexibility (Figure S4). From the cross-section image, we can further confirm that the inner of the glass fiber film was filled with SN electrolyte. The X-ray diffraction (XRD) patterns of pure SN and SPCE are demonstrated in Figure 2d. The diffraction peaks of the two samples all appear at  $19.3^{\circ}$ and 27.5°, and there are no additional diffraction peaks. When doped with Li salt, the diffraction peak intensity of SPCE decreased compared with pure SN plastic crystal, which reflects the solvation effect of high polar SN in dissolving lithium salts. The decrease in crystallization indicates that the defect density increases, which leads to an increase in Li ion mobility.



**Figure 1.** (a) Schematic diagram of the preparation of SPCE film. (b) Photo image of SPCE film. Photo images of the state of SPCE solution at (c)  $60 \degree C$  and (d) room temperature.



**Figure 2.** SEM images of (**a**) glass fiber film, the upper (**b**) and the cross-section (**c**) of SPCE film. (**d**) XRD patterns of SN and SPCE.

## 3.2. Electrochemical Properties of SPCE Film

SN plastic crystal displays a disorder structure, but molecules are ordered into a crystalline lattice. So, SN molecules have high local rotatory motions leading to high molecular mobility (illustrated in Figure S5); combined with the not too strong attraction with Li metal ions of nitrile groups, they can promote charge separation of Li salt and give a high ionic conductivity of Li<sup>+</sup>.

Figure 3a shows the electrochemical impedance spectra (EIS) of SPCE film at room temperature of 25 °C, and the ionic conductivity of SPCE film is as high as  $7.3 \times 10^{-4}$  S/cm, which is mainly due to the high dielectric constant (ε-55), good solubility, and high molecular diffusivity of SN. EIS of SPCE film at various temperatures were also collected and shown in Figure 3b, and the impedance of SPCE film decreases with the increase in temperature, which can be fitted to Arrhenius equation  $\sigma = \sigma_0 exp(-\frac{E_a}{kT})$ , where  $\sigma$  is ionic conductivity,  $\sigma_0$  is a pre-exponential factor,  $E_a$  is the activation energy, and k is Boltmann's constant. Arrhenius plot of SPCE film (Figure 3c) can clearly show the trend of impedance change with temperature, and the calculated activation energy  $E_a$  for SPCE is 0.23 eV. The electrochemical window is also a critical parameter of a solid electrolyte; the electrochemical window of the SPCE is measured with electrochemical floating analysis [31] and linear sweep voltammetry (LSV) method. Electrochemical floating analysis provides a stringent test of the oxidative stability of SPCE film and the curve is shown in Figure 4a. The results show that at voltages below 4.7 V (vs. Li/Li<sup>+</sup>), the leakage current measured in the SPCE is small, and the oxidation process can be observed at 4.7 V. The results of LSV reported in Figure S6 show the same result, that the electrochemical window of the SPCE is 4.6 V.  $\tau_{Li^+}$  of SPCE is measured with DC polarization and alternating current impedance technology, and it is calculated from the results shown in Figure 4b by the Bruce–Vincent–Evans equation, giving 0.458, which is higher than that of pure PEO electrolyte (~0.2).



**Figure 3.** EIS test with SS | |SS cells. (**a**) Nyquist plot of SPCE at room temperature. (**b**) Nyquist and (**c**) Arrhenius plots of SPCE at different temperatures (25, 30, 40, 50, and 60 °C).



**Figure 4.** (a) Electrochemical floating analysis of SPCE with SS | |Li cell. (b) Current–time curve and EIS plots before and after polarization of SPCE with Li | |Li symmetric cell.

Generally, aliphatic nitrile of SN is incompatible with Li metal anode. To improve the interfacial compatibility of SN and Li metal, LiNO<sub>3</sub> was introduced into the SPCE. Figure 5a compares the Li ions plating/stripping behaviors of SPCE with LiNO<sub>3</sub> addition and SPCE without LiNO<sub>3</sub> addition with Li | Li symmetric batteries at 0.1 mA cm<sup>-2</sup>. The overpotential of Li | Li cells using SPCE without LiNO<sub>3</sub> increases with the increase in the cycle number, and a short-circuit occurred after 150 h of cycling. In contrast, the initial voltage of Li | Li cells using SPCE with LiNO<sub>3</sub> is only 18 mV and the battery can maintain a stable voltage cycle more than 500 h. The results confirm that SPCE with LiNO<sub>3</sub> and Li metal have good interface stability. Figure 5b shows that Li | SPCE | Li has good cycle stability at different current densities, even at 0.5 mA cm<sup>-2</sup>. By comparison of the nyquist plots before and after cycling at different rates (Figure 5c), we can see that the interface contact between electrolyte and Li metal (represented from the first arc of EIS curve) is not very good at beginning but becomes better after cycling. It further proves the excellent compatibility of SPCE with Li metal.



**Figure 5.** Electrochemical performance of Li | SPCE | Li cell. (a) Cycling curves of SPCE with and without LiNO<sub>3</sub> additive. (b) Cycling curves of SPCE film at different rate and (c) EIS test before and after the cycle test in (b).

# 3.3. LiFePO<sub>4</sub> | | Li Solid-State Cell Performance

For solid state batteries, interface between solid cathode particles and solid electrolyte is also a big challenge due to the solid-solid contact. SN has a low melting point, and it can be injected into cathode directly without solvent. Additionally, SN-based SPCEs have a plasticity nature, resulting in a good interface between cathode particles and solid electrolyte. So, it is an effective strategy to assemble solid state batteries all based on SPCEs, and the structure is illustrated in Figure 6a. Figure 6b shows the charge and discharge curves of LiFePO<sub>4</sub> | SPCE | Li after the 1st, 20th, 50th, and 80th cycles at 0.5 C. As the number of cycling times increase, tiny polarization can be found for the LiFePO<sub>4</sub> | SPCE | Li cell, which proves good interface characteristics. The cycling performance of LiFePO<sub>4</sub> | Li battery is shown in Figure 6c; the electrochemical reaction of charge process can be described as:  $LiFePO_4 - xLi^+ - xe^- \rightarrow xFePO_4 + (1-x)LiFePO_4$ . The initial charge capacity of the battery with the SPCE is as high as 121.4 mAh  $g^{-1}$  at 0.5 C, and the capacity is 105.5 mAh  $g^{-1}$  after 90 cycles; the first-cycle coulombic efficiency is 93.74% and is always maintained at over 97% after the 6th cycle, which shows that LiFePO<sub>4</sub> has good contact with SPCE and good cycle stability. The relatively low first-cycle coulombic efficiency is mainly due to the unstable initial interface of SPCE with Li anode, which is consist with Li | Li cycling data in Figure 5. The wettability of SN based SPCE electrolyte is not so good, as we have mentioned in the experiment section, cathode electrode needs to be dipped into solution at 60 °C for 12 h to let electrolyte solution infused into the electrode. So, the slow degradation of the capacity may be caused by the interface fading between electrode material and solid electrolyte during cycling. Figure 6d shows that the capacity of LiFePO<sub>4</sub> | SPCE | Li at 0.2 C, 0.5 C, and 1 C is 147.1 mAh  $g^{-1}$ , 137.8 mAh  $g^{-1}$ , and 102.3 mAh  $g^{-1}$ , respectively. When the solid-state battery returns from 1 C to 0.2 C, the charge capacity can still be maintained at 141.4 mAh  $g^{-1}$ . These results demonstrate that the LiFePO<sub>4</sub> | SPCE | Li cell possesses excellent rate performance, which is attributed to the good interfacial stability between electrolyte and both cathode and Li anode. Figure 6d shows the charge–discharge voltage curves of LFP | SPCE | Li battery at different rates. The small voltage polarization of the battery can provide good electrochemical reversibility for the battery reaction.



**Figure 6.** (a) Schematic diagram of the structure of  $\text{LiFePO}_4 \mid |\text{Li solid-state battery.}$  (b) Voltage profile at different cycles. (c) Long-term cycling performance at 0.5 C. (d) Voltage profiles at different cycling rate. (e) Rate performance of the cell. All results are collected at room temperature.

## 4. Summary

In summary, SPCE is proved to be an effective ambient-temperature solid electrolyte for all solid-state Li-metal batteries. For the SPCE film, commercial glass fiber film is introduced as the framework to improve mechanical properties. The ionic conductivity of the SPCE film is as high as  $7.3 \times 10^{-4}$  S cm<sup>-1</sup> at room temperature. Furthermore, with LiNO<sub>3</sub> additive, the SPCE have a good contact surface with lithium metal and excellent mechanical properties, which can enable the symmetrical Li | Li cell to stably cycle more than 500 h at 0.1 mA cm<sup>-2</sup>. More importantly, SPCE shows excellent cycle stability and superior rate performance in LiFePO<sub>4</sub> | Li solid-state battery, where SPCE also serves as an interface between cathode and SPCE film. Thus, based on our research, the design of all solid-state batteries based on SPCEs is feasible. For a more practical application, more optimizations may need to be studied, such as searching for a more effective 3D framework to obtain an ultrathin SPCE film or finding other additives to substitute LiNO<sub>3</sub>, etc. **Supplementary Materials:** The following are available online at https://www.mdpi.com/article/ 10.3390/en14216946/s1, Figure S1: Photograph of pure SPCE, Figure S2: SEM image of glass fiber film, Figure S3: SEM image of cross section of SPCE film, Figure S4: Photographs of SPCE film, Figure S5: Schematic diagram of the structure of SN doped with LiTFSI salt, Figure S6: LSV curve with SS | SPCE | Li cell.

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