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# Flexible interfaces between Si anodes and composite electrolytes consisting of poly(propylene carbonates) and garnets for solid-state batteries

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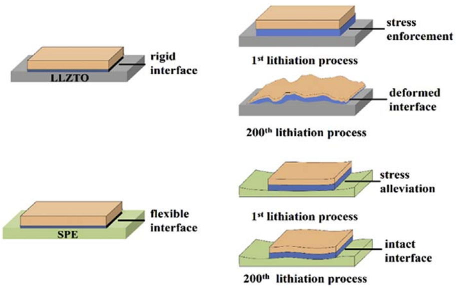
## HIGHLIGHTS

- Flexible interfaces between Si anodes and composite electrolytes are constructed.
- The SPEs show the conductivity of $4.2 \times 10^{-4}\,S\,cm^{-1}$ at room temperature.
- The SPEs greatly alleviate the stress resulting from volume change of Si.
- The Si/SPE/Li cells exhibit good cycle and rate performance.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Flexible interfaces between Si anodes and composite electrolytes consisting of poly(propylene carbonates) (PPCs) and garnets have been fabricated. The solid polymer electrolytes (SPEs) of PPC/garnet/LiTFSI show the conductivity of $4.2 \times 10^{-4}\,S\,cm^{-1}$ at room temperature. Their combination with the Si layer anodes allows great alleviation of internal stress resulting from the large volume variation during lithiation and delithiation process of Si anodes. As a result, the Si/SPE/Li cells exhibit 2520 mAh $g^{-1}$, 2260 mAh $g^{-1}$, 1902 mAh $g^{-1}$, 1342 mAh $g^{-1}$ at 0.1 C, 0.2 C, 0.5 C, and 1 C, respectively. Furthermore, with such compatible and stable interfaces of Si/SPE and the $LiFePO_4$ cathodes in solid-state batteries, the specific capacity of 2296 mAh $g^{-1}$ in terms of Si is obtained, which remains 82.6% after 100 cycles at room temperature and 0.1 C. The results here indicate that constructing of flexible interfaces between Si anodes and SPEs is a promising strategy to develop high performance solid-state batteries.

## 1. Introduction

Recently, rechargeable lithium batteries are requested to achieve the increased energy density and the improved safety property in order to satisfy the rapid development of electric vehicles, portable electronic devices, and grid energy storage [1,2]. Under such circumstances, the solid-state lithium batteries (SSLBs), with great potential in enhancement of energy density as well as improvement of safety, have attracted intensive interests [3–5].

One of the key materials for developing SSLBs is the solid polymer

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electrolytes (SPEs), which have been paid attention since Wright et al. discovered ionic transport of Polyoxyethylene (PEO) complex with alkali metal salts [6]. A great deal of studies have been carried out on improvement of the ionic conductivity, electrochemical window, and high thermal stability for SPEs, including polymer blending [7–10], cross-linking polymer matrices [11,12], incorporation of plasticizers [13], impregnation with ionic liquids [9,14], and doping inorganic fillers [15–19]. Though much progress has been made previously, the problem of lithium dendrite growth though the SPEs is still the challenge for their application in the batteries with the Li metal anodes [20,21]. In contrast, the Si anodes show the high theoretical capacity of 4200 mAh $g^{-1}$ through alloying $Li_{4.4}Si$ [22]. Little problem of dendrite growth is expected in case of using Si anode. However, very few reports could be found for the combination of Si anodes with the SPEs. Recently, Takada et al. used the amorphous Si anodes in combination with the $Li_2S$-$P_2S_5$ based sulphide solid electrolytes, observing the superior rate and cycle performance of the solid-state batteries [23,24]. This implies that the Si anodes in combination with the garnet could also help improve the relevant cell performance, which nevertheless has not ever been reported.

Herein, the interfaces between Si and solid polymer electrolytes (SPEs) based on poly(propylene carbonates) (PPCs) and $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) have been fabricated by deposition of the Si layer on the SPEs at 25 °C. The SPEs show the flat surface as well as high ionic conductivity. Introduction of LLZTO powders into the SPEs promotes complete dissociation of lithium salt as well as enhances the migration of $Li^+$, achieving the conductivity of $4.2 \times 10^{-4}$ S $cm^{-1}$ at room temperature [25]. Taking advantages of flexible Si/SPE interfaces, the Li/SPE/Si cells exhibit excellent cycle stability and low charge-transfer resistance after 200 cycles. The reason can be attributed to the effective alleviation of internal stress from volume variation during repeatedly lithiation and delithiation progress. It is indicated that the flexible interfaces are more favorable to reduce the effect of the large volume change, in comparison with rigid interfaces. With the sustainable interfaces between the Si anodes and SPEs, the SSLBs with $LiFePO_4$ cathodes exhibit good cycle performance and high capacity retention at room temperature.

## 2. Experimental section

### 2.1. Materials preparation

The PPCs (Mv = $5 \times 10^4$ g $mol^{-1}$, sigma-Aldrich) were dried at 60 °C overnight under vacuum prior to the sample preparation. The $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) ceramic powders were prepared by conventional solid-state reaction as described in our previous paper [26]. Crushed by planetary ball-milling and high-energy ball-milling, the initial LLZTO particles of approximately 5 μm were reduced to 200 nm. LiTFSI (99.95%, sigma-Aldrich), acetone (Sigma-Aldrich), PVDF (Aladdin), super-p conductive additives (SP, Timcal), $LiFePO_4$ (LFP) were used as received.

### 2.2. The fabrication process of the SPE/Si interfaces

Firstly, the SPEs consisting of PPC and LLZTO (PPCL-SPEs) were fabricated by a mechanochemical route. 1.0 g PPC, 0.2 g LLZTO, and 0.5 g LiTFSI were stirred in 10 mL acetone for 1 h, using high-energy ball-milling (FRITSCH Pulverisette 7 Planetary Mciro Mill). The uniform slurry was cast on a Polytetrafluoroethylene (PTFE) plate, and evaporated in a vacuum oven at 60 °C for 8 h. The PPC/LiTFSI composite electrolytes (PPC(LiTFSI)) were prepared via the same method as those without LLZTO. The typical thickness of the membranes was approximately 70 μm.

The Si anodes were deposited on the PPCL-SPE by DC magnetron sputtering at 25 °C. The base pressure in the sputtering chamber was below $2 \times 10^{-4}$ Pa. And high-purity Ar was introduced into the chamber before plasma ignition with the pressure of 0.55 Pa. The PPC-based substrates were at 15 cm distance from the silicon target (N-type, $1.25 \times 10^2$ S $cm^{-1}$) and the sputtering was carried out using DC power of 30 W with deposition rate of approximately 9 nm $min^{-1}$. Thin film of Cu used as current collector was coated on the Si films by the same method. Subsequently, the samples were transported into an Ar-filled glovebox with oxygen and moisture contents below 0.1 ppm. For comparison, the LLZTO ceramic plates in thickness of 1 mm were also used as sputtering supports to construct LLZTO/Si interfaces [27].

### 2.3. Sample characterization

The field emission scanning electron microscope (FESEM, Magellan 400) was employed to determine the morphologies of surface and cross-section of the samples. All the samples for FESEM were coated with a thin gold layer via sputter coating. Raman spectra were obtained on a Bruker RFS100/S. Wavenumbers were calibrated by reference to the emission lines of neon. Differential Scanning calorimeter (DSC) was tested from −20 to 60 °C at a heating rate of 10 °C $min^{-1}$ under nitrogen atmosphere. The modulus tests were conducted with a model 5948 MicroTester Instron instrument.

### 2.4. Electrochemical measurement and cells assembly

Ionic conductivities of the SPEs were measured by the NOVOCONTROL spectrometer fitted with a temperature control system, which was carried out in the frequency range from 0.01 Hz to 40 MHz. Stainless steel plates were used as the block electrodes for block/SPE/block cells. The cyclic voltammetry (CV) of Si/Li was performed from 0.05 V to 1.5 V at a scan rate of 10 mV $s^{-1}$ by Arbin BT-2000. The LFP, PVDF, LiTFSI and SP with the optimum weight ratio of LFP: LiTFSI: KP: PVDF = 5: 3.5: 1: 0.5 were coated on PPCL-SPE to form the composite cathode [28]. The LFP/PPCL-SPE/Si cells were charged and discharged between 2.0 V and 3.4 V at varied current densities.

## 3. Results and discussion

The PPCL-SPEs were fabricated by a mechanochemical method, which was widely used to synthesize inorganic and organic compounds [29]. Toxic acetonitrile in conventional solution casting route is replaced by acetone. And the strong ball-milling force accelerates the dissolving speed of PPC, thus the process time being greatly shortened [30].

The cross section SEM of PPCL-SPE in Fig. 1a shows the thickness of the membranes is approximately 70 μm. In our previous work, the PEO/LLZTO composite electrolytes with the thickness of 20 μm were successfully fabricated [31]. When substituting PPC for PEO, the PPC/LLZTO membranes of 20 μm are too sticky to be separated from the PTFE plates. The reason is attributed to the fact that the molecular weight of PPC is much smaller than that of PEO. The 70 μm is an appropriate thickness to keep the initial homogenous shape of membranes as separated them from the substrates. As shown in Fig. S1a, the diameter of LLZTO particles in terms of $D_{50}$ is 192 nm. SEM measurements presented in Fig. S1b further demonstrate the particle size of LLZTO concentrates at approximately 200 nm. The 200 nm-sized LLZTO particles disperse homogenously in the PPC matrix, which is critically helpful to prevent possible micro-scaled short circuit [32,33]. Depicted in Fig. S2, the surfaces of PPCL-SPE are smooth and homogenous, which is able to decrease the interfacial impedance of SPE/Si.

Fig. 1b shows the conductivity of PPCL-SPE is $4.2 \times 10^{-4}$ S $cm^{-1}$ at 25 °C, which is 2.5 times larger than that of PPC(LiTFSI). The enhanced conductivity of PPCL-SPE is attributed to the critical effect of LLZTO particles. Firstly, the highly improved conductive paths along the interfaces between PPC and LLZTO due to the percolation effect play a significant role in the conductivity increment of PPCL-SPE [25,31]. In addition, the LLZTO has the ability to promote the complete