A novel composite solid polymer electrolyte based on copolymer P(LA-co-TMC) for all-solid-state lithium ionic batteries

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\textbf{ABSTRACT}

The safety issue of lithium ion battery is still a big challenge especially at high temperature. To solve the problem, the biodegradable copolymer P(LA-co-TMC) (Poly Lactide-Trimethylene Carbonate), as a brand new polymer electrolyte host, is firstly applied in lithium ionic battery. A novel composite solid polymer electrolyte (CSPE) was prepared by dip-coating P(LA-co-TMC)/succinonitrile/LiTFSI (P(LA-co-TMC)-SPE) into Celgard 2325 membrane. The results of IR, XRD and SEM demonstrated that the Celgard 2325 membrane was completely coated and permeated by P(LA-co-TMC)-SPE. And the DSC results revealed that the thermostability of CSPE was improved. This CSPE showed high ionic conductance, high lithium ion transference number (tLi\textsuperscript{+} = 0.563) and wide electrochemical window (> 5.2 V). The all-solid-state lithium ion battery with the CSPE based on P(LA-co-TMC) exhibited outstanding cycling performance and > 98% coulombic efficiency at 55 °C. Furthermore, it also presented high capacity retention (nearly 100% when returning to 0.1 C) and attractive capacities of 130.4, 122.3, 93.6 and 46 mAh g\textsuperscript{-1} at C-rates of 0.1, 0.2, 0.5 and 1 C, respectively. From all the results above, the novel CSPE, with high electrochemical performance and safety at elevated temperature, is a good candidate for the application of all-solid-state lithium battery.

1. Introduction

Since Sony opened the market of commercial lithium-ion batteries in 1991, a large number of inventions and patents of lithium ionic batteries (LIBs) have been achieved constantly. Although the capacity of LIBs has been improved greatly, it still cannot meet the high growth commercial requirements of energy storage [1–3]. At the same time, wearable and flexible electronic terminals are attracting more and more attentions of producers and consumers [4,5]. It can be undoubtedly predicted that high performance flexible LIBs will take center stage in the near future. However, the safety issue of traditional LIBs is also hindered by thermodynamically unstable liquid organic electrolyte, especially at elevated temperature [6–11].

Numerous researchers devote themselves to solve the problem. Lots of encouraging progresses have been achieved. Solid polymer electrolyte (SPE) is one of the effective solutions that attract much attention of the scientists [12]. A variety of polymers have been applied to SPEs, such as polyethylene oxide (PEO) [13–17], polyacrylonitrile (PAN) [18,19], polymethyl methacrylate (PMMA) [20], poly(3,4-ethylene-dioxythiophene) (PEDOT) [21], polyvinylidene fluoride (PVDF) [22] and polytrimethylene carbonate (PTMC) [23]. Nevertheless, low ionic conductivity, narrow electrochemical stability window and poor mechanical strength hinder the applications of SPEs in high-energy solid-state Li batteries [24–27]. As time goes by, rigid lithium dendrites still have chance to impale SPEs, which can make cell short circuit happen. In order to overcome the barriers of SPEs, composite solid polymer electrolytes (CSPEs), which combine the stronger membrane and SPE, are expected to play a vital role in LIBs. Especially for all-solid-state LIBs, CSPEs can apply lithium metal as anodes to enhance the energy storage [26,28,29]. Recently, it has been reported that, as a promising candidate, the CSPE based poly(propylene carbonate) can be applied to fabricate thinner, safer and more flexible LIBs [30].

In this study, the CSPE is composed of the random copolymer of lactide and trimethylene carbonate (P(LA-co-TMC)), succinonitrile (SN), lithium bis(trifluoromethane)-sulfonimide (LiTFSI) and Celgard 2325 membrane. The first three components act as the SPE, and the last...
one serves as the mechanical framework. The CSPE is fabricated by dip-coating method. Put Celgard 2325 membrane in the anhydrous acetonitrile solution of P(LA-co-TMC)/SN/LiTFSI for a moment, then pull out the membrane and dry it in oven. P(LA-co-TMC) has always been applied as a kind of drug carrier or medical apparatus because of its significant biocompatibility, biodegradability and film-forming property [31–34]. Considering that P(LA-co-TMC) contains plenty of oxygen atoms in its molecular structure which can act as lithium ionic transport channel, it is firstly applied as the host polymer candidates in CSPE. SN is employed as a plasticizer, since SN can suppress the crystallinity of the polymer to enhance the ionic conductivity [35]. In this study, XRD, IR and SEM were performed to reveal the chemical and morphology of the novel CSPE. The tests above demonstrated the homogeneous distribution of P(LA-co-TMC)-SPE in the Celgard 2325 framework. We also deeply investigated the ionic conductivity and electrochemical performance of the CSPE. Its ionic conductivity, lithium ion transference number and electrochemical window were enlarged greatly. The result of DSC scan showed the thermostability of the CSPE. The novel CSPE displayed greatly improvement in mechanical and electrochemical properties. In addition, the all-solid-state lithium batteries (LiFePO4/CSPE/Li) can operate stably at 55 °C. Consequently, the Celgard 2325 membranes were immersed into the P(LA-co-TMC)-SPE solution for 0.5 h. Finally, the membranes were put into the oven to remove acetonitrile completely at 60 °C for 24 h. The thickness of the products was 35 ± 2 μm after dried. All the experimental operations were carried out in Ar glove box, and the samples were stored in an Ar atmosphere box for use.

2. Experimental

2.1. Materials

Celgard 2325 separators were employed as the upholder substrates with a thickness of 25 μm. The random copolymer of P(LA-co-TMC) was purchased from Jinan Daigang Biomaterial Company (mole ratio between LA and TMC = 1: 1), with a number average molecular weight 100,000. SN and LiTFSI were provided by Aldrich. Anhydrous acetonitrile was bought from J&K Scientific Ltd. All the materials mentioned above were stored at a glove box with dry Ar.

![Fig. 1. Schematic illustration for the preparation route of P(LA-co-TMC) based CSPE.](image)

2.2. Preparation of CSPE based P(LA-co-TMC)

Fig. 1 displays the preparation process of the novel CSPE. P(LA-co-TMC) (20 wt%) was added in anhydrous acetonitrile. After stirring at room temperature for 2 h, P(LA-co-TMC) could be completely dissolved in acetonitrile. Then LiTFSI (6.7 wt%) and SN (6.7 wt%) were put into the P(LA-co-TMC) solution and stirred at room temperature for 12 h. Subsequently, the Celgard 2325 membranes were immersed into the P(LA-co-TMC)-SPE solution for 0.5 h. Finally, the membranes were put into the oven to remove acetonitrile completely at 60 °C for 24 h. The thickness of the products was 35 ± 2 μm after dried. All the experimental operations were carried out in Ar glove box, and the samples were stored in an Ar atmosphere box for use.

2.3. Characterization

Fourier transformed infrared attenuated total reflection (ATR/FT-IR) (Thermo Nicolet 670FT-IR) was used to record the ATR/FT-IR spectra of samples from 1000 to 4000 cm⁻¹. Surface and cross-section morphologies of samples were observed with a JSM-6700F field emission scanning electron microscope (FESEM). In order to measure the thermostability of the samples, differential scanning calorimeter (DSC) was performed at the range from −70 °C to 150 °C with 5 °C min⁻¹ heating rate in flowing N₂ atmosphere. The mechanical properties of the samples (1 × 5 cm) were tested by AL-700S-G tensile testing machine (Gotech Ltd) with the tensile rate 50 mm min⁻¹.

Linear sweep voltammetry (LSV) of CSPE was performed by electrochemical work station (CHI760B, Shanghai, China) between 0 and 6 V at the rate of 1 mV s⁻¹ to investigate the electrochemical window. The samples were sandwiched between two stainless electrodes, and the AC impedances were measured by CHI760B at different temperature with the frequency from 0.1 to 10⁵ Hz. After AC impedance tests, the ionic conductivities of samples were calculated by the equation: 

$$\sigma = \frac{d}{RA}$$

where A was the effective area, d was the thickness.

In order to calculate the lithium ion transference number (tLi⁺) of the CSPE, the symmetric Li/CSPE/Li battery was assembled. The potentiostatic polarization method was performed by CHI760B electrochemical working station at 55 °C. The tLi⁺ of the CSPE was calculated.
by the Bruce-Vincent-Evans equation: \( t_{\text{Li}} = \frac{t_0 (\Delta V - t_0 \Delta f)}{t_0 \Delta V - t_0^2 \Delta f} \) where \( \Delta V \), \( t_0 \), \( I_{\text{SO}} \) and \( I_{\text{SS}} \) were the applied voltage (10 mV), initial current, steady-state current, initial impedance and steady-state impedance correspondingly [36].

The cathode was made up of 70% LiFePO\(_4\), 20% P(LA-co-TMC) and 10% super P. The LiFePO\(_4\) cathode and Li anode were used to sandwich the CSPE to assemble coin cells in Ar glove box. The cells were charged and discharged on a land cycle system (CT2001A, Wuhan, China) between 2.0 and 3.8 V at 55 °C.

3. Results and discussions

3.1. IR spectra, XRD patterns and SEM analyses

FTIR scans were performed as an effective method to characterize the structure of P(LA-co-TMC), Celgard 2325, SN, LiTFSI, P(LA-co-TMC)-SPE and CSPE. As shown in Fig. 2a, the strong characteristic absorbance peak of P(LA-co-TMC) at 1739 cm\(^{-1}\) corresponds to the stretching vibration of ester groups. And peaks at 1186 and 1080 cm\(^{-1}\) are the stretching vibration absorbance of C=O. As we can see from Fig. 2a, there is no melting/crystalline peak at the DSC curves of P(LA-co-TMC)-SPE, P(LA-co-TMC)-SPE without SN and CSPE. But the clear platform at 20.5 °C reveals the glass transition temperature of P(LA-co-TMC), which indicates that P(LA-co-TMC) can become softer rubbery state above 20.5 °C.

3.2. Stress-strain behavior and DSC analyses

Mechanical property is an important parameter for all-solid-state electrolytes. The CSPE membrane needs to overcome big stress during cell assembling and cycling. As shown in Fig. 4a, the tensile strength of P(LA-co-TMC)-SPE is only 0.29 MPa with an elongation at 30%. Compared to the bare routine separator, the tensile strength of P(LA-co-TMC)-SPE is only 0.29 MPa with an elongation at 30%. With P(LA-co-TMC)-SPE, the membrane can withstand big stress. The curve of P(LA-co-TMC)-SPE without SN, which demonstrates they are largely amorphous. In the curve of Celgard 2325, the characteristic peaks at 14.2, 17.1, 18.6, 21.8 and 24.2 are all stemmed from the alpha crystal form of PP in Celgard 2325 [42]. After dip-coating Celgard 2325 with P(LA-co-TMC)-SPE, the peak position of CSPE is just the same as that of Celgard 2325, but the peak intensity of CSPE is much weaker than that of Celgard 2325, because Celgard 2325 is covered by amorphous P(LA-co-TMC)-SPE. Herein, the degree of crystallization of CSPE is decreased by filling with P(LA-co-TMC)-SPE.

Fig. 3a and b show the surface morphology of Celgard 2325. As we can see from Fig. 3a and b all the pores are well distributed, and the diameter of the pore is about 100 nm. The porosity of bare Celgard 2325 is also very high, which can be a favorable frame for being filled with P(LA-co-TMC)-SPE. Compared to the bare routine separator, the average thickness of CSPE is only 0.29 MPa with an elongation at 30%. With P(LA-co-TMC)-SPE, the tensile strength of P(LA-co-TMC)-SPE is only 0.29 MPa with an elongation at 30%. Compared to the bare routine separator, the tensile strength of CSPE is 10 μm thicker than bare Celgard 2325. The smooth surface and cross-section of CSPE demonstrate that the CSPE with continuous homogenous structure has been obtained successfully, which is in accordance with the results of XRD and IR.

As we concerned, the high temperature safety and stability of electrolytes are of great importance for LIBs, since the gas-producing and flammable liquid electrolytes have great potential risk of fire or explosion under the conditions such as overcharge, short circuits and heat circumstance. As shown in Fig. 4b, there is no melting/crystalline peak at the DSC curves of P(LA-co-TMC)-SPE, P(LA-co-TMC)-SPE without SN and CSPE. But the clear platform at 20.5 °C reveals the glass transition temperature of P(LA-co-TMC), which indicates that P(LA-co-TMC) can become softer rubbery state above 20.5 °C.
The glass transition temperature of P(LA-co-TMC)-SPE is −34.5 °C, because of the effect of plasticizer SN. Compared with P(LA-co-TMC), the rubbery state range of P(LA-co-TMC)-SPE is wider. However, the use of LIBs with P(LA-co-TMC)-SPE still has the risk of short circuit owing to the poor mechanical property of P(LA-co-TMC)-SPE in a rubbery state at high temperature. The Celgard 2325 membrane with high mechanical strength is chosen to support the P(LA-co-TMC)-SPE, because the P(LA-co-TMC)-SPE is largely amorphous and shows insufficient mechanical stability. In order to investigate the thermal stability of bare supporting membrane and CSPE, DSC tests were also performed. For Celgard 2325 and CSPE, there are two sharp peaks at 133.5 °C and 132 °C respectively, both of which show the melting points temperature of PE in Celgard 2325 membranes. It can be deduced that CSPE is exceedingly thermal stable below 130 °C, which may have a favorable effect on the integral safety of LIBs.

### 3.3. Electrochemical analyses

Fig. 5a shows the ionic conductivity of P(LA-co-TMC)-SPE and CSPE at different temperatures ranging from 25 to 100 °C. The conductivities of the P(LA-co-TMC)-SPE and the CSPE are higher than the conductivity of P(LA-co-TMC)-SPE without SN, owing to the adding of SN. Because SN can improve the dissociation of Li salt and reduce the activation energy of ionic transport effectively, SN is used as a versatile additive for solid state ionic conductors to promote ion transport [43,44]. AppARENTLY, ionic conductivity of P(LA-co-TMC)-SPE is 4.72 × 10⁻⁴ S cm⁻¹ at room temperature, which is higher than that of CSPE (3.64 × 10⁻⁴ S cm⁻¹). Although Celgard 2325 membrane has higher porosity, it can inhibit lithium ion delivery at the part without pores. Therefore, it's reasonable that the conductivity of CSPE is a little lower than that of P(LA-co-TMC)-SPE. As the results of DSC, the glass transition temperature of solid P(LA-co-TMC) is around 20 °C. The existence of crystalline part of P(LA-co-TMC) prevents the transport of lithium ion, which also leads to the lower ionic conductivity of P(LA-co-TMC)-SPE and CSPE at ambient temperature. In spite of this, the conductivity of CSPE is still five orders of magnitude higher than that of SPE based on PTMC (10⁻⁹ S cm⁻¹) [23], due to its much higher amorphous area proportion and softer polymer chains. This is caused by the introduction of PLA. In comparison with PTMC, the oxygen content of the copolymer P(LA-co-TMC) greatly increases, as is shown in Fig. 1. Since lithium ions can be preferential transported through the local coordination effect of ester carbonyl oxygen atoms in the P(LA-co-
TMCO-SPE [45]. The higher oxygen content has a positive effect on the integral ionic conductivity. As can be seen, with the temperature increasing, both of the conductivities of P(LA-co-TMC)-SPE and the CSPE are improved significantly. The ionic conductivity of CSPE increases to 5.21 × 10^{-4} S cm^{-1}, while the P(LA-co-TMC)-SPE increases to 6.5 × 10^{-4} S cm^{-1} at 55 °C. The measuring results show that the increase of lithium ionic conductance of the CSPE may be owing to the weakening of the interactions between lithium ions and bulk anion groups (TFSI−) by plasticizer SN at elevated temperature. The enhanced amorphous area favors higher lithium ionic transportation. This evidence is in terrific agreement with the IR and SEM results. Herein, it can be properly deduced that the increase of amorphous structure of CSPE improves the mobility of the polymer chains, lowers the activation energy for lithium ionic transportation and favorably enhances ionic conductivity of CSPE. With the increase of temperature, the ion conductivity of CSPE increases to 7.94 × 10^{-4} S cm^{-1} at 100 °C, which is very close to the conductivity of P(LA-co-TMC)-SPE (9.09 × 10^{-4} S cm^{-1} at 100 °C). Comprehensively considering the superior safety and high ion conductivity of CSPE based on P(LA-co-TMC), the CSPE is an appropriate choice as a kind of novel solid electrolyte at elevated temperature.

As we known, low lithium ion transference number is a major shortcoming for solid electrolytes used in LIBs. So it’s crucial to enhance lithium ion transference number to improve the performance of all-solid-state LIBs. Fig. 5b shows the potentiostatic polarization curve of the symmetric Li/CSPE/Li cell at 55 °C. As shown in the inset of Fig. 5b, R0 and Rs are 303 Ω and 325 Ω, respectively. After computation, the tLi+ of CSPE is 0.563, which indicates the CSPE based on P(LA-co-TMC) is beneficial for lithium ion-dominant conduction behavior. Beside of thermal stability and ion conductivity, wide electrochemical window of CSPE is also essential to its practical application in all-solid-state lithium batteries, because the electrochemical window can be used to estimate the range of safe operating voltage. The electrochemical stability of CSPE was performed by LSV in the Li/CSPE/stainless steel cell at ambient temperature. The LSV curve of CSPE is exhibited in Fig. 5c. The curve is nearly a straight line without obvious fluctuation till 5.2 V, suggesting that there is no decomposition reaction of the CSPE till 5.2 V. It also demonstrates CSPE based on P(LA-co-TMC) can be applied in batteries with high-voltage electrode materials.

3.4. Battery performance

In order to elucidate the cycle performance of the novel CSPE based on P(LA-co-TMC), all-solid-state batteries (LiFePO4/CSPE/Li) were assembled and cycled between 2 V and 3.8 V at 55 °C. The 1st and 50th typical charge/discharge voltage profiles of the cell are presented in Fig. 6a. There are two voltage plateaus at around 3.5 and 3.4 V, which can be attributed to the two characteristic behavior of two-phase reaction of LiFePO4 [46,47]. In contrast to the 1st cycle discharge capacity (123 mA h g^{-1}), the 50th discharge capacity increases to 140.2 mA h g^{-1}. The enhancement of the capacity during the battery cycling may be ascribed to the activation effect of P(LA-co-TMC)-SPE, which can improve interfacial contact with the electrodes. This phenomenon is common to the LiFePO4 all-solid-state batteries with SPE membranes [48]. Because of the gradual permeation of P(LA-co-TMC)-SPE at the very beginning, the capacity is relatively lower. The stable interface between the electrolyte and electrode forms after a few cycles, resulting in the stable electrical performance. Since the CSPE becomes soft and smooth at elevated temperature, P(LA-co-TMC)-SPE can penetrate into the composite cathode. Interfacial stability between electrodes and electrolyte in all-solid-state lithium cell is greatly improved during the cycling life.

In Fig. 6b, the typical discharge capacity and coulomb efficiency using CSPE is shown at the rate of 0.1 C (17 mA h g^{-1}). The initial discharge capacity is 123 mA h g^{-1}, while the average capacity of the all-solid-state battery is above 135 mA h g^{-1}. With the increased cycle number, the discharge capacity gradually enhances in the beginning, and then the capacity tends to be stable. The gradual enhancement of the capacity at the start cycling may be owing to the improved interface contact between cathode and CSPE. More importantly, the coulomb efficiency maintains above 98% during the cycling life, showing a significant improvement in cycle stability. The stable discharge capacity and high coulomb efficiency of all-solid-state batteries demonstrate the improved ionic conductivity and low resistance of the CSPE, which may be attributed to the more favorable dissociation of Li+-polymer and the softening of the electrolyte with the help of SN. The results show that the P(LA-co-TMC)-SPE can be integrated into supporting membrane (Celgard 2325), and the CSPE plays a significant role as an electrolyte in all-solid-state cells.

Fig. 6c shows that the charge-transfer resistance after the initial cycle is 500  Ω. The resistance value reduces to 350  Ω after 50 cycles, demonstrating the improvement of the interfacial property. The improved interfacial property is mainly owing to the permeability and flexibility of the copolymer electrolyte, resulting in high capacity retention during cycling at elevated temperature.

In order to investigate the rate capabilities of CSPE, the batteries were charged and discharged at different C-rate (0.1 C, 0.2 C, 0.5 C and 1 C) under 55 °C. As shown in Fig. 6d, the reversible capacities of all-solid-state LIB are obtained: 130.4, 122.3, 93.6 and 46 mA h g^{-1} for discharge rates of 0.1, 0.2, 0.5 and 1 C correspondingly. It is only a tiny capacity fading that happens at the rate of 0.2 C, in comparison with the discharge capacity at the rate of 0.1 C. The good C-rate cycling performance is mainly due to the unique structure of P(LA-co-TMC), which creates a continuous conductive net between the electrodes. SN and the cathode with P(LA-co-TMC) are also favorable for reversible capacity. They serve to form lithium ions conducting bridges between cathode

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Fig. 5. (a) Temperature dependency comparison of ionic conductivity of P(LA-co-TMC)-SPE, P(LA-co-TMC)-SPE without SN and CSPE. (b) Potentiostatic polarization of the symmetric Li/CSPE/Li cell under a dc bias of 10 mV at 55 °C. The inset is the Nyquist plots of the cell under open circuit and polarized conditions at 55 °C. (c) The LSV curve for CSPE. The inset is the magnification of the LSV curve in the voltage range of 1-5 V.
and CSPE based P(LA-co-TMC). When the rate returns to 0.1 C, the average discharge capacity of the cell is still as high as 131.3 mAh g$^{-1}$. Therefore, the high capacity retention is demonstrated to be brilliant with no noticeable fading in capacity. The excellent capacity retention value of the cell may be related to the amorphous form of P(LA-co-TMC)-SPE at high temperature. In addition, coulombic efficiencies are close to 100%, much in agreement with the previous discoveries on analogous CSPE systems based upon polyesters or polycarbonates \[48,49\]. The results of rate performance of the cell also indicates its lower resistance, due to the better ionic transport capability of the CSPE, demonstrating that the CSPE based on P(LA-co-TMC) has great potential in all-solid-state LIBs at elevated temperature.

4. Conclusions

In this study, a novel CSPE based on copolymer P(LA-co-TMC) was successfully prepared by dip-coating method. P(LA-co-TMC)-SPE was fully embedded into the pores of the framework membrane. When the ratio of P(LA-co-TMC): SN: LiTFSI was 3: 1: 1, the conductivities of the CSPE reached to $3.64 \times 10^{-4}$ Sc m$^{-1}$ at 25 °C and $5.21 \times 10^{-4}$ Sc m$^{-1}$ at 55 °C, respectively. The lithium ion transference numbers of the CSPE was as high as 0.563. The LSV curve demonstrated that the electrochemical stability of the CSPE was greatly improved (electrochemical window > 5.2 V). Finally, LiFePO$_4$/CSPE/Li batteries were assembled, and they showed outstanding electrochemical performance for high capacity retention (almost 100% after 50 cycles at 55 °C) and superior C-rate performance. The prepared CSPE exhibited thermal stability, safety, flexibility, remarkable mechanical property and high ionic conductivity, resulting in the high performance of all solid battery. The dip-coating method enhanced the efficiency of the assembly process of all-solid-state LIBs. The results demonstrate that the novel CSPE has great application potential for high-performance flexible all-solid-state lithium battery at elevated temperature.

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