

Preparation and performance of a non-ionic plastic crystal electrolyte with the addition of polymer for lithium ion batteries



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ABSTRACT

A soft matter solid electrolyte was prepared by polymerizing a monomer trimethylolpropane trimethylacrylate (TMPTMA) using in situ thermal polymerization into a non-ionic plastic crystal electrolyte, which is consisted of 5 mol% lithium bis-trifluoromethanesulfonimide dissolved in succinonitrile (SN). X-ray diffraction, differential scanning calorimetry and conductivity measurements are used to investigate the structural and electrochemical performance of the polymer electrolyte films. It exhibits high ionic conductivities, wide electrochemical window and excellent mechanical strength. The solid electrolyte with 7.5 wt% TMPTMA displays a high initial discharge capacity of 160.3 mA h g⁻¹ at 0.1 C when combined with a LiFePO₄ cathode and excellent capacity retention. With their beneficial properties, the polymer electrolytes are considered to have significant potential applications for lithium ion batteries.

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1. Introduction

The electrolytes used in rechargeable lithium ion batteries is generally a lithium salt (widely used is LiPF₆, which easily forms corrosive HF on exposure to moisture) dissolved in organic solvents (usually carbonates such as dimethyl carbonate and ethyl carbonate), which is flammable as excessive heat can be generated if a short circuit occurs [1]. Consequently, polymer electrolytes are expected to be the alternative electrolytes to satisfy the needs for power storage device as well as electric vehicles with high efficiency, high energy density and long life [2–4]. Polymer electrolytes can be divided into two types: all-solid-state electrolyte and gel electrolyte. For dry system, the solid electrolytes have commonly been prepared by dissolving the salt into the polymer framework as the case in the familiar polyethylene oxide (PEO) membrane. The ambient temperature ionic conductivities of polymer electrolytes are still found to be low owing to their slower segmental chain mobility in the crystalline regions compared to the amorphous regions, although various modification methods have been adopted, e.g., by adding inorganic fillers [5], forming copolymer [6], decreasing the crystallinity of polymer. Gel polymer electrolytes [7] formed by immersing large amount of liquid organic electrolytes into polymer framework have very high ambient temperature ionic conductivities, but they still suffer from several disadvantages,

such as worsening of mechanical properties, increased reactivity towards the metal electrode and release of volatiles.

Finding the ideal electrolyte maintaining the good transport properties appears to be a difficult task, and as expected, most solid electrolyte systems do not perform as well as liquids at room temperature. Materials known as “plastic crystal electrolyte” have interesting properties that may help achieve these apparently contradictory requirements [8–11]. Plastic crystals are effectively the inverse of liquid crystals, which have positional order but orientational disorder, perform a number of desirable properties, such as high plasticity and diffusivity. Succinonitrile (N≡C–CH₂–CH₂–C≡N, abbreviated as SN) has been identified as the potential base for an electrolyte and it is a highly polar and non-ionic solid organic molecular plastic material, which forms a promising matrix for generation of solid ionic conductors. High conductivities of 1 × 10⁻³ S cm⁻¹ (at 25 °C) in the case of SN complexed with lithium bis-trifluoromethanesulfonimide (LiTFSI) can be achieved [9]. It has been reported to be a versatile matrix for solid-state ionic conductors due to its suitable temperature range of plastic crystal stability from approximately –32 °C to melting at 57 °C which enables dissolution of various types of salts [12,13]. There have been a few reports on doping pure ionic plastic crystals (*N,N*-methyl propylpyr-rolidinium tetrafluoroborate, P₁₃BF₄) with small amounts of polymers in order to improve the mechanical properties of the electrolytes [14]. For SN-based plastic crystal electrolytes, it could not form freestanding films because of their poor mechanical properties. By adding other high mechanical-strength polymers, such as polyacrylonitrile (PAN) [15–17], polyethylene oxide (PEO) [10,16,18], poly(vinylidene

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fluoride-co-hexafluoropropylene) (P(VDF-HFP) [13], polyethylene glycol (PEG) [16] to SN-based electrolytes, the mechanical properties of plastic crystal electrolytes could be remarkably enhanced. However, the high crystallinity of the polymers and the low solubility of the polymers may make the drastic decrease of the ionic conductivities.

In this work, an innovative preparation is demonstrated by adding trimethylolpropane trimethylacrylate (TMPTMA) with three vinyl bonds at the end of the chain into SN based plastic crystal electrolyte, followed by in-situ thermal polymerization. The Addition of polymerized TMPTMA into non-ionic plastic crystal electrolyte could not only improve its mechanical strength, but also have no obviously detrimental effect in terms of loss of ionic conductivities. Furthermore, the composite electrolytes are used to fabricate cell using LiFePO_4 as cathode and they exhibit excellent capacity retention.

2. Experimental

LiTFSI ($\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$) and SN were obtained from Sigma Aldrich. All the reagents were of battery grade and used without further purification. The plastic crystal electrolytes (SN-LiTFSI) were prepared by mixing LiTFSI with succinonitrile at a weight ratio of 5:95, and then heated at 70°C under dry Ar atmosphere until a homogeneous mixture was obtained. The precursor solution composed of a monomer TMPTMA ($\text{C}_{18}\text{H}_{26}\text{O}_6$) and a thermal initiator 2,2'-Azobis-(2,4-dimethylvaleronitrile) (ABVN, $\text{C}_{14}\text{H}_{24}\text{O}_4$) was prepared. The content of the initiator was 0.5 wt% of the monomer [19], and the monomer concentration was ranged from 0 to 10 wt% of the total weight of SN-LiTFSI. After that, the precursor solution was added to the SN-LiTFSI molten solution, and then cast in a Teflon plate. Finally, the plastic crystal electrolyte films with polymer inside were formed by heating the above mixture at 70°C for 10 min. The polymer can be dispersed with LiTFSI-SN uniformly by this process. The SN-based plastic crystal electrolyte without TMPTMA was stored in 5 ml vials under vacuum at 25°C until further use, which was impossible to cast in Teflon plate owing to its wretched mechanical strength. All procedures for preparing the electrolytes were handled in an Ar-filled glove box due to the moisture sensitivity of the lithium salt.

The ionic conductivities of the plastic crystal electrolyte films were measured by electrochemical impedance spectroscopy (EIS) method. The test cell was a small piece of plastic crystal electrolyte film sandwiched between two stainless steel blocking electrodes (12 mm diameter) in Swagelok-type cells assembled in an Ar-filled glove box, then kept at each test temperature for at least half an hour before electrochemical impedance measurements in order to reach thermal equilibrium. The electrochemical impedance spectroscopy measurements were carried out by applying the frequency range from 100 kHz to 0.1 Hz at temperatures between -20 and 80°C with oscillation amplitude of 5 mV on a CHI660C Electrochemical Workstation (Shanghai Chenhua). The electrochemical stabilities of the electrolytes were studied with cyclic voltammetry (CV) at a scan rate of 1 mV s^{-1} in the voltage range of -0.5 to 5 V in a three-electrode system. A stainless steel blocking electrode was used as the working electrode, while a lithium metal was used as the reference and the counter electrode in this system.

The electrolytes for differential scanning calorimetry (DSC) measurements were loaded in hermetically sealed aluminum pans under nitrogen atmosphere and cooled down to -100°C in approximately 10 min before heated to 200°C at a rate of $10^\circ\text{C min}^{-1}$ using a TA 2920 modulated instrument. Crystalline phases of the films were identified by X-ray diffraction measurements (XRD, Rigaku/mac 250) using $\text{Cu K}\alpha$ radiation in the 2θ range of 10 – 50° . The fourier transform infrared (FTIR) spectra was recorded on

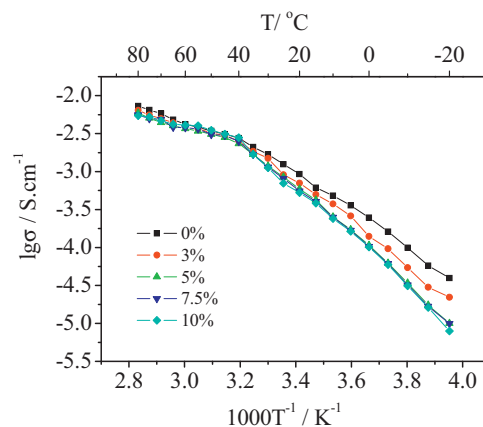


Fig. 1. Temperature dependence ionic conductivities of $(100-x)\%[\text{LiTFSI-SN}]-x\%\text{TMPTMA}$ ($x=3-10$) and SN-LiTFSI.

a PerkinElmer Spectrum GX instrument at ambient temperature. Mechanical stress versus strain measurements of electrolytes were performed by applying stress with a compression speed of 0.5 mm min^{-1} using circular plastic crystal/polymer electrolyte plates with the diameter of 20 cm and the thickness of 1 mm on a WDS-5 electronic universal testing machine (Changchun Chaoyang test instrument co., LTD) at 25°C .

The electrochemical characterization was carried out by galvanostatic charge/discharge method in two-electrode CR2032 coin-type cells. The working electrodes were consisted of active materials (80 wt% LiFePO_4), carbon black (15 wt%), and polyvinylidene fluoride (5 wt%) spread on an Al foil current collector. Lithium foil was used as the counter electrode. Film was used as the electrolyte. The plastic crystal electrolyte solution, with 7.5 wt% polymer and 0.5 wt% initiator (the mass of monomer), was filled into the cells. The assembled cells were polymerized at 70°C for half an hour in an oven after 2-h standing which could ensure the precursor solution well wetted into the electrodes. Test cells using 1 M LiPF_6 /ethylene carbonate (EC)/ethylmethyl carbonate (EMC)/dimethyl carbonate (DMC) (1:1:1 in volume) as electrolyte and a polypropylene microporous film (Celgard 2400) as separator were assembled for comparison purpose. The cells were galvanostatic charged/discharged under different rates between 2.0 and 4.2 V using a battery test system (LAND CT2001A, Wuhan Jinnuo Electronics, Ltd.).

3. Results and discussion

In the preparation process, LiTFSI-SN acts as the matrix for solvating TMPTMA. Primarily, the precursor solution of TMPTMA (as monomer) and ABVN (as thermal initiator) was prepared. The as-prepared precursor solution was then added into the SN-LiTFSI molten solution. The homogeneous LiTFSI-SN-TMPTMA was finally obtained after magnetic stirring. Subsequently, The polymer prepared by in situ polymerization can be dispersed with LiTFSI-SN uniformly. The related mechanism is similar to the results in the recent literature [20].

Fig. 1 presents temperature dependence ionic conductivities of SN-LiTFSI and $(100-x)\%[\text{LiTFSI-SN}]-x\%\text{TMPTMA}$ ($x=3-10\%$). For SN-LiTFSI, the conductivity was found to be $1.3 \times 10^{-3}\text{ S cm}^{-1}$ at 25°C . The high ionic conductivity mainly attribute to the existence of highly conductive SN-LiTFSI phase, in which succinonitrile act as a solid solvent for the Li salt [8,9]. With the addition of TMPTMA-based polymer, a slightly decrease in ionic conductivities at low temperature was observed because polymerized TMPTMA is not a good lithium ion conductor, but a framework for hosting SN-LiTFSI

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