



## Short communication

## All-solid-state polymer electrolyte with plastic crystal materials for rechargeable lithium-ion battery

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## ABSTRACT

In this paper, we report the synthesis and properties of a series of composite polymer electrolytes formed by dispersion of a non-ionic organic plastic material succinonitrile (SN) into poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) complexed with four kinds of lithium salts. The addition of SN greatly enhances ionic conductivities of the electrolytes which is due to the high polarity and diffusivity of SN. The integrity of the plastic-crystalline phase is kept at low temperature range in polymer electrolytes. The high solubility of SN on Li salts is observed by Fourier transform infrared (FTIR) spectra measurement, thus could lead to enhanced lithium-ion transference number. The battery performances of composite polymer electrolytes at different temperatures are tested and the results are comparable to that of the pure plastic crystal electrolytes.

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## 1. Introduction

All-solid-state Li-ion polymer batteries are of great interest due to their high energy density and shape variability [1,2]. Solid polymer electrolyte (SPE) forms a key part of rechargeable polymer batteries. High ionic conductivity at room temperature, and suitable mechanical property along with important technological advantages are related to safety and electrochemical stability makes it attractive compared to liquid electrolyte which is used in commercially Li-ion batteries [3]. In polymer electrolytes, due to faster segmental chain mobility in the amorphous regions, the ionic conductivities are much higher compared to the crystalline regions in the same sample [4]. It has been almost 30 years since the discovery and introduction of polymer electrolytes used in lithium batteries [5,6]. Till now, SPE can be generally divided into two types: dry and gelled system [7]. For dry system, the salt is dissolved in the polymer framework as the case in the familiar polyethylene oxide (PEO) membrane. The ionic conductivities of  $10^{-4} \Omega^{-1} \text{cm}^{-1}$  can be obtained by various modification methods, e.g., by forming copolymer [8], polymer blends [9], and adding inorganic fillers [10–13], to decrease the crystallinity of polymer, typically poly(ethylene oxide) (PEO). This type of SPE has enhanced

conductivities, high mechanical properties and high interface stability with Li anode, but the ionic conductivities are still too low for practical applications at ambient temperature. Gelled system formed by adding large amount of liquid electrolytes into polymer matrix shows higher ionic conductivities than  $10^{-3} \Omega^{-1} \text{cm}^{-1}$  [14–16], but still exhibits all the limits of liquid electrolytes and thus lose the instinct nature of solid electrolytes.

Succinonitrile ( $\text{N}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{N}$ , abbreviated as SN) is a solid organic non-ionic plastic material, where the impurity 'trans' isomer imparts a plastic character in the material before reaching its melting temperature [17]. It shows a phase transition at  $\sim -30^\circ\text{C}$ , above which the material exhibits a stable plastic-crystalline phase until it melts at  $\sim 60^\circ\text{C}$ . The plastic-crystalline phase of SN can be used as a solid solvent for various Li salt (LiX) [18,19]. However, SN is highly plastic and deforms easily without fracture under low stress and snaps easily on little manual stretching [20,21]. Therefore, it cannot be used as a self-standing film as well as polymer electrolytes. Recently we introduced succinonitrile into polymer electrolyte as a versatile additive [22–24]. This kind of material possesses not only high ionic conductivity but also favorable mechanical strength, and thus commercial separators are not required during battery assembling and testing. Here we compare the ionic conductivities of another four kinds of LiX complexes with SN and poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)). The integrity of plastic-crystalline phase is studied by differential scanning calorimetry (DSC) scans and the ionic dissol-

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ability is studied by Fourier transform infrared (FTIR) spectra. The utilization of composite polymer electrolyte in Li-ion batteries is studied by charge/discharge galvanostatic cycling test.

## 2. Experimental

P(VDF-HFP) containing 10% HFP unit, PEO (Mw 600,000), LiCl, LiClO<sub>4</sub>, LiPF<sub>6</sub>, SN from Aldrich and Lithium bisperfluoroethylsulfonilimide (abbreviated as LiBETI, Li(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N) from UBE industries LTD in Japan are used as received. Anhydrous acetonitrile and acetone from Merck are used as organic solvents for PEO and P(VDF-HFP), respectively. The composite polymer electrolytes are prepared via the traditional solution casting technique. The polymers used are 1 g for P(VDF-HFP) and 0.032 mol for PEO respectively. SN and LiX are 0.02 and 0.002 mol, respectively. The composites are prepared firstly by dissolving predetermined amounts of PEO/P(VDF-HFP) and LiX, followed by the addition of SN. This solution is stirred at room temperature until the mixture appeared to be homogeneous. The mixture is cast on a Teflon plate followed by evaporating the solvent in a dry box for 2 days. Finally, the samples are dried under vacuum at 30 °C for 2 days. SN/LiX composites without polymer are prepared by directly adding LiX into melted SN.

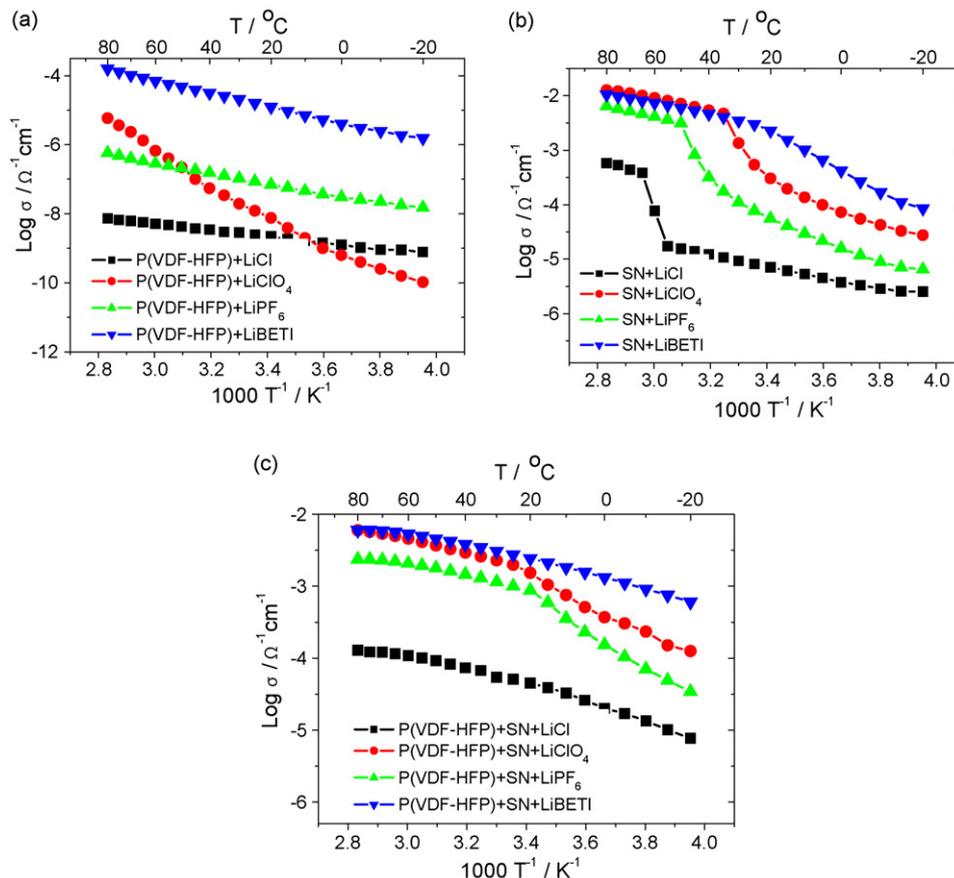
The ionic conductivity is measured by ac impedance spectroscopy using a HP 4192A LF impedance analyzer in the frequency range from 5 Hz to 2 MHz at temperatures between –20 and 80 °C. The samples are kept at each temperature for 1 h during impedance measurement. DSC measurements are carried out under nitrogen atmosphere with Dupont TA 2910 modulated DSC. The samples are

loaded in hermetically sealed aluminum pans and measurements are taken at a heating rate of 10 °C min<sup>-1</sup>. FTIR spectra are recorded on a PerkinElmer Spectrum GX instrument.

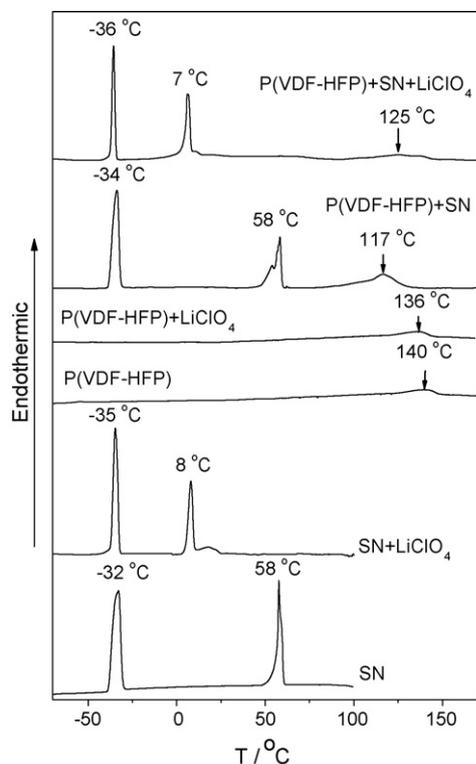
Batteries test were performed by using two-electrode Swagelok-type cells. The cells were composed of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> as anodes and LiCoO<sub>2</sub> (Nippon Chemical Cooperation) as cathodes. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> [25], was prepared by heating a mixture of anatase TiO<sub>2</sub> and LiOH·H<sub>2</sub>O in a 5:4.2 molar ratio (5% Li excess) for 8 s at 800 °C. For preparing electrode, 85% LiCoO<sub>2</sub>/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> active material, 5% carbon black, and 10% poly(vinylidene fluoride) solution were mixed and pasted on pure Al or Cu foil (Goodfellow, 99.6%) and dried under vacuum. A P(VDF-HFP) + SN + LiBETI polymer electrolyte film was used as both electrolyte and separator between the LiCoO<sub>2</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> electrodes. The cell was assembled in an argon-filled glove box. The cells were cycled from 1.7 to 2.8 V (vs. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) on a Wuhan Land battery test system at 25 and –10 °C.

## 3. Results and discussion

Fig. 1 presents the temperature dependence of ionic conductivities of P(VDF-HFP) + LiX, SN + LiX, and P(VDF-HFP) + SN + LiX. For pure P(VDF-HFP) + LiX films, the ionic conductivities increase with the temperature linearly and no obvious transition is observed because the melting temperatures (*T<sub>m</sub>*) of P(VDF-HFP) + LiX are more than 110 °C, which are higher than the measured temperature range here. The ionic conductivities of P(VDF-HFP) + LiX at ambient temperature are all below 10<sup>-4</sup> Ω<sup>-1</sup> cm<sup>-1</sup>. The difference of ionic conductivities for P(VDF-HFP) + LiX lies in the behavior of LiX. The ionic conductivities of P(VDF-HFP) + LiBETI are much higher than



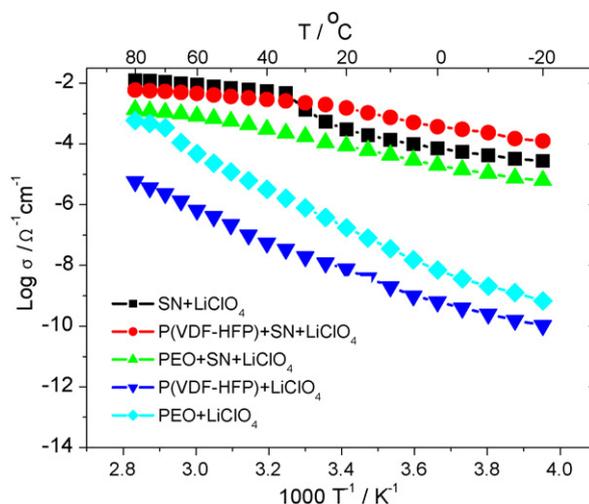
**Fig. 1.** Temperature dependence of ionic conductivities of (a) P(VDF-HFP) + LiX, (b) SN + LiX, and (c) P(VDF-HFP) + SN + LiX, where LiX are LiCl, LiClO<sub>4</sub>, LiPF<sub>6</sub>, and LiBETI, respectively. The amount of P(VDF-HFP), SN and LiX are 1 g, 0.02 and 0.002 mol, respectively.



**Fig. 2.** DSC curves of SN, SN+LiClO<sub>4</sub>, P(VDF-HFP), P(VDF-HFP)+LiClO<sub>4</sub>, P(VDF-HFP)+SN, and P(VDF-HFP)+SN+LiClO<sub>4</sub>, respectively. The amount of P(VDF-HFP), SN and LiClO<sub>4</sub> are 1 g, 0.02 and 0.002 mol, respectively.

that of P(VDF-HFP)+LiCl because LiBETI is much more dissociable and has larger ionic radius (0.447 nm) than that of LiCl (0.181 nm). For SN+LiX composites, the ionic conductivities are much higher than their polymer counterparts because of the solvent role of SN [18,19]. There are transitions in the curves corresponding to the  $T_m$  of the SN+LiX. By adding SN into P(VDF-HFP)+LiX, the ionic conductivities enhance over the whole temperature ranges. The effect of SN on P(VDF-HFP)+LiX can also be clearly observed. The ionic conductivities of P(VDF-HFP)+SN+LiX at low temperature (for example, from  $-20$  to  $60$  °C for LiCl) are surprisingly higher than pure SN+LiX composite. The ionic conductivity can reach at  $1 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$  at  $10$  °C for P(VDF-HFP)+SN+LiClO<sub>4</sub> composite, at  $20$  °C for P(VDF-HFP)+SN+LiPF<sub>6</sub> composite and at  $-10$  °C for P(VDF-HFP)+SN+LiBETI composite, respectively. The conductivity of the P(VDF-HFP)+SN+LiClO<sub>4</sub> is found to be  $\sim 1 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$  at  $-20$  °C, approximately  $1.2 \times 10^6$  times of the magnitude of P(VDF-HFP)+LiClO<sub>4</sub> film at the same temperature ( $\sim 1 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$ ). At  $20$  °C, the ionic conductivity of P(VDF-HFP)+SN+LiClO<sub>4</sub> is still more than  $2 \times 10^5$  times higher compared to pure P(VDF-HFP)+LiClO<sub>4</sub> composite. The ionic conductivity enhancement can be attributed to the decrease in crystallinity of P(VDF-HFP) as observed in DSC (Fig. 2) as well as the high polarity and diffusivity of SN, i.e., its capability to act as a solvent for Li salts [22–24].

The DSC scans (Fig. 2) of the pure SN, SN+LiClO<sub>4</sub> and P(VDF-HFP)+SN, P(VDF-HFP)+SN+LiClO<sub>4</sub> were performed in order to check the integrity of the plastic-crystalline phase of SN. For pure SN, it exhibits a plastic-crystalline phase between  $-32$  °C (the transition from normal crystal to plastic-crystalline phase,  $T_{pc}$ ) and  $58$  °C ( $T_m$ ). Upon the addition of LiClO<sub>4</sub>, the melting point was depressed to  $8$  °C which is due to the solvating ability of SN, while  $T_{pc}$  remained unaffected. The addition of P(VDF-HFP) into SN and SN+LiClO<sub>4</sub> did not obviously affect the  $T_m$  and  $T_{pc}$  of SN. So the



**Fig. 3.** Comparisons of ionic conductivities of P(VDF-HFP)+LiClO<sub>4</sub>, SN+LiClO<sub>4</sub>, P(VDF-HFP)+SN+LiClO<sub>4</sub>, PEO+LiClO<sub>4</sub> and PEO+SN+LiClO<sub>4</sub>. The amount of P(VDF-HFP), PEO, SN and LiClO<sub>4</sub> are 1 g, 0.032, 0.02 and 0.002 mol, respectively.

polymer films P(VDF-HFP)+SN+LiClO<sub>4</sub> could keep inside ingredient totally solid below  $7$  °C, at which its ionic conductivity is still as high as  $\sim 0.8 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ .

We further compare the ionic conductivities (Fig. 3) of P(VDF-HFP)+SN+LiClO<sub>4</sub> and PEO+SN+LiClO<sub>4</sub>. SN has more effect on the ionic conductivities of P(VDF-HFP)-based polymer electrolyte than PEO-based films. The activation energies estimated from Arrhenius fitting from  $-20$  to  $20$  °C are summarized in Table 1. The activation energies of P(VDF-HFP)/PEO+SN+LiClO<sub>4</sub> comprise between P(VDF-HFP)/PEO+LiClO<sub>4</sub> and SN+LiClO<sub>4</sub>, which indicate both P(VDF-HFP)/PEO and SN have effect on LiClO<sub>4</sub> dissociation and ionic transfer. In addition to high ionic conductivities, all the films are self-standing and very flexible, and they can be used in Li-ion polymer batteries without introducing commercial separators.

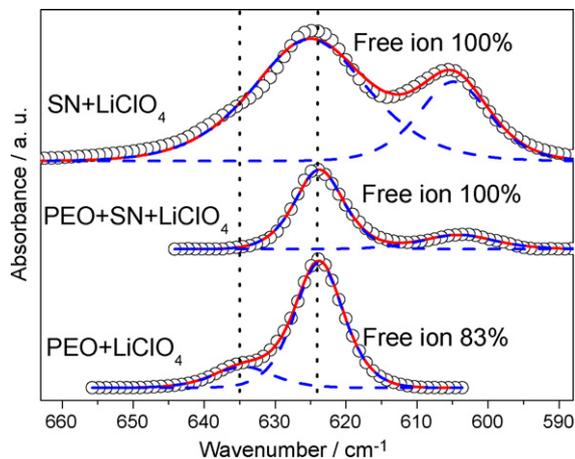
The effect of SN addition on LiClO<sub>4</sub> dissolution in the PEO-based polymer electrolytes is studied by fitting the  $\nu_4(\text{ClO}_4^-)$  envelope in FTIR spectra (Fig. 4) to Gaussian–Lorentzian product function [26]. The  $\nu_4(\text{ClO}_4^-)$  envelope could be split into two separate bands: the peak at  $\sim 624 \text{ cm}^{-1}$  is assigned to the “free”  $\text{ClO}_4^-$  anion vibrations (including free and solvent-separated anion), while the peak at  $\sim 635 \text{ cm}^{-1}$  represents  $[\text{Li}^+\text{ClO}_4^-]$  contact ion pairs [27–29]. By comparing the area under the “free”  $\text{ClO}_4^-$  band to the total  $\nu_4(\text{ClO}_4^-)$  envelope, the fraction of free anions can be calculated. For the SN-free sample PEO+LiClO<sub>4</sub>, about 84% anion is free and 16% of anion exists as  $[\text{Li}^+\text{ClO}_4^-]$  ion pairs. As SN is added, the ratio of free anions increases to 100% as it is in SN+LiClO<sub>4</sub> composite. From this, we speculate that the addition of SN could enhance the  $\text{Li}^+$  ion transference number of polymer electrolytes. This solubility also leads to the enhanced ionic conductivity for composite polymer electrolytes.

Galvanostatic charge/discharge behavior of the cell LiCoO<sub>2</sub>|P(VDF-HFP)+SN+LiBETI|Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> was investigated at different temperature. The cells exhibit a charge/discharge plateau at  $\sim 2.35 \text{ V}$  as reported in [23]. Fig. 5 shows the results for the cycle life tests

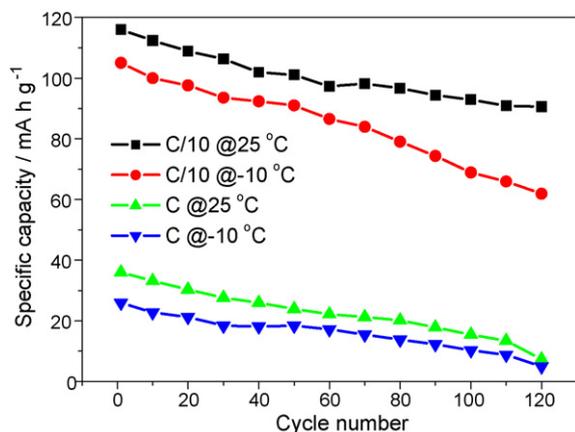
**Table 1**

Activation energies estimated from Arrhenius fitting (from  $-20$  to  $20$  °C) for polymer+LiClO<sub>4</sub>, polymer+SN+LiClO<sub>4</sub>, and SN+LiClO<sub>4</sub>

Polymer film	PEO (eV)	P(VDF-HFP) (eV)
Polymer+LiClO <sub>4</sub>	0.89	0.69
Polymer+SN+LiClO <sub>4</sub>	0.45	0.40
SN+LiClO <sub>4</sub>	0.37	



**Fig. 4.** FTIR results of PEO + LiClO<sub>4</sub>, SN + LiClO<sub>4</sub> and PEO + LiClO<sub>4</sub> + SN, where the sphere points, solid line and dashed lines represent experimental data, fitted envelope and fitted peaks, respectively. The amount of PEO, SN and LiClO<sub>4</sub> are 0.032, 0.02 and 0.002 mol, respectively.



**Fig. 5.** Variation of discharge capacity of LiCoO<sub>2</sub> with cycle numbers for LiCoO<sub>2</sub> |P(VDF-HFP) + SN + LiBETI| Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> at different discharge rates and temperatures. The amount of P(VDF-HFP), SN and LiBETI are 1 g, 0.02 and 0.002 mol, respectively.

by using above cell at a rate of  $C/10$  and  $C$  at 25 and  $-10^\circ\text{C}$ . The cell gave an initial discharge capacity of  $116\text{ mA h g}^{-1}$  ( $25^\circ\text{C}$ ) and  $105\text{ mA h g}^{-1}$  ( $-10^\circ\text{C}$ ) at  $C/10$ , after 120 cycles, the cell retained 78% ( $25^\circ\text{C}$ ) and 60% ( $-10^\circ\text{C}$ ) of the initial capacity. Li intercalation capacity decreases with increasing current density. At currents of  $C$ , the capacity is still as high as  $36\text{ mA h g}^{-1}$  ( $25^\circ\text{C}$ ) and  $26\text{ mA h g}^{-1}$  ( $-10^\circ\text{C}$ ). This results are comparable to that obtained with a cell using the pure plastic crystal SN + LiTFSI as electrolyte [30], but the beneficial mechanical properties of polymer electrolyte allowed us to assemble the cell without using a typical commercial separator. Further investigations on cycle stability in composite polymer electrolytes are in progress.

## 4. Conclusions

All-solid-state P(VDF-HFP) and PEO based composite polymer electrolytes has been obtained by complexing a non-ionic plastic material SN. The highly enhanced ionic conductivities using four different kinds of Li salt exhibit the versatility of SN as a solid solvent. Thermal analysis results show that SN can keep the integrity of plastic-crystalline phase at low temperature range in composite polymer electrolytes. The high solubility of SN on Li salts is found in polymer + SN + LiX composites by FTIR spectra measurement indicating the high Li-ion transference number. The battery tests indicate that polymer electrolytes with succinonitrile are promising electrolytes for future Li-ion batteries at low temperature range.

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