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Cross-linkable Polymer Matrix for Enhanced Thermal Stability of Succinonitrile-based Polymer Electrolyte in Lithium Rechargeable Batteries

Myung-Hyun Ryou[a,b,‡], Dong Jin Lee[a,‡], Je-Nam Lee[a], Hong Kyeong Lee[a], Myungwon Seo[c], Hyewon Lee[c], Weon Ho Shin[b], Yong Min Lee[c], Jang Wook Choi[b,†], and Jung-Ki Park[a,b,†]

[a]*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea*

[b]*Graduate School of EEWS (WCU), Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea*

[c]*Department of Applied Chemistry, Hanbat National University, Deokmyoung-dong, Yuseong-gu, Daejeon 305-719, Republic of Korea*

ABSTRUCT :

A polymer electrolyte was prepared by using polyvinylidenefluoride-co-hexafluoropropylene (PVdF-HFP) or poly(ethylene glycol) dimethacrylate (PEGDMA) as polymer matrices, succinonitrile as an additive, and lithium perchlorate as a lithium salt. Compared to the polymer electrolyte employing PVdF-HFP, the PEGDMA-based polymer electrolyte exhibits substantially superior thermal stability when exposed to high temperatures. Nonetheless, the ionic conductivity of the PEGDMA-based polymer electrolyte was preserved in a wide temperature range between −20°C and 80°C.

Keywords: Cross-linking polymer, Lithium ion batteries, Polymer electrolyte, Plastic crystal, Succinonitrile

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1. Introduction

Because of high energy densities and excellent cycle lives, lithium ion batteries (LIBs) have been used in a variety of portable electronic devices such as mobile phones, notebook computers, and digital cameras.[1-3] Beyond these applications, LIBs are expanding their applications requiring novel functionalities such as flexibility, bendability, and stretchability. In order to support these more challenging functions, LIBs require solid but flexible electrolyte matrices, which still facilitate ion transport while preserving their mechanical properties.[1,4] To this end, polymer electrolytes are expected to fit well. Compared to conventional liquid electrolytes, polymer electrolytes hold a number of advantages in the perspective of mechanical property, fabrication, and safety. Unfortunately, however, these advantages, in turn, cause the poor ionic conductivities, typically less than 10^{-4} S cm^{-1}.[1,5,6] In general, the ionic conductivity of polymer electrolytes is limited by chain mobility above their glass transition temperature.[7]

On the other hand, plastic crystals have received considerable attention after the recognition of their potential use as a new class of solid electrolytes. Plastic crystal is a kind of mesophase formed predominantly by quasi-spherical or disk-like molecules possessing rotational and/or orientational disorders while preserving long-range translational orders. Among ionic and molecular plastic

†Corresponding author. Tel.:+82-42-350-3965 (J.-K. Park); +82-42-350-1719 (J.W. Choi)
E-mail address: jungpark@kaist.ac.kr (J.-K. Park); jangwookchoi@kaist.ac.kr (J.W. Choi)
‡These authors contributed equally to this work.

crystals which have shown decent conductivities and good mechanical properties at room temperature, to date, succinonitrile is almost the only molecular plastic crystal material that holds the physical characteristics suitable for lithium battery production. As a result, it has been reported to be a versatile matrix for solid-state ionic conductors.[5,8,9] These properties are mainly due to the formation of a plastic crystal phase in the battery operation temperature range between 233 K and 331 K. Although the elementary transport mechanism in plastic crystals including succinonitrile is still elusive, it is believed that the rotation of the CC bond in both CH_2 moieties of succinonitrile (Fig. 1) allows the molecule to rotate from a *gauche* to a *trans* isomer and thus supports the lithium ion transportation.[1,2,4]

Despite the advantageous properties of succinonitrile as an ionic conductor, the mechanical properties of succinonitrile are often deficient or inconvenient to be used for LIBs. In order to overcome this drawback, various efforts have been made, especially focusing on forming polymer composites in which various polymers based on physical cross-linking[4,5,8] or chemical cross-linking[10] function as hosts. The physical properties of composite electrolytes are largely affected by the type of polymer matrix. In general, chemical cross-linking-based polymer electrolytes are thermally more stable over time. In contrast, physical cross-linking-based ones frequently suffer from swelling, dissolution with heat (ΔH), and solution leaking with time (Δt).[11]

In this study, as an endeavor to improve the thermal stability of succinonitrile-based polymer electrolytes by implementing different types of polymer matrices, we develop a self-standing polymer electrolyte based on an UV-curable polymer network, namely poly(ethylene glycol) dimethacrylate (PEGDMA). We also compare this polymer electrolyte with a conventional polymer electrolyte consisting of typical linear polymer, polyvinylidenefluoride-co-hexafluoropropylene (PVdF-HFP). The thermal stability of both polymer electrolyte systems at high temperatures up to 60°C was analyzed.

2. Experimental

2.1. Materials and preparation of the polymer electrolytes

Succinonitrile (SN, 99%, Aldrich), poly(ethylene glycol) dimethacrylate (PEGDMA, $M_w = 400$, PolyScience), polyvinylidenefluoride-co-hexafluoropropylene (PVdF-HFP, Kynar2801, Elf Atochem), methyl benzoylformate (photoinitiator, 98%, Aldrich) and lithium perchlorate ($LiClO_4$, Ukseung Chemical Co., Ltd.) were used without further purification. The chemical structure of succinonitrile is shown in Fig. 1.

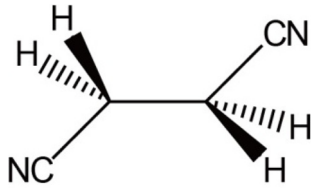

Fig. 1. Chemical structure of succinonitrile.

To obtain the polymer electrolytes, the equivalent amount of succinonitrile (5.0 g) and polymer materials (5.0 g), PEGDMA or PVdF-HFP, were mixed with a proper amount of $LiClO_4$ (0.6642 g, 10/1 = SN/$LiClO_4$ by molar ratio) and vigorously stirred for a day at 60°C in an argon-filled glove box. For the solution employing PEGDMA, 0.05 wt.% of methyl benzoylformate was additionally mixed prior to the casting that is performed for UV-curing. Then, both solutions were cast on glass substrates using the doctor blade technique with a 250 μm gap. The polymer electrolytes employing PVdF-HFP were easily obtained from the cast polymer solution in the course of time. For this polymer, however, the cast solution should be exposed to UV irradiation (8 mW cm^{-2}, 365 nm) for 10 min. The thickness of the resulting polymer electrolytes varies from 150 μm to 200 μm.

2.2. Characterization of polymer electrolytes

Differential scanning calorimetry (DSC, TA instruments Q20 DSC) studies were performed to determine the transition temperature from normal crystal to plastic crystal phase (T_{cp}) and melting peak temperature (T_m).

Fourier transform infrared (FT-IR) spectroscopy in attenuated total reflectance (ATR) mode was performed using a Bruker Alpha instrument with a spectral resolution of 4 cm^{-1}.

2.3. Ionic conductivities of the polymer electrolytes

Ionic conductivities of polymer electrolytes were measured by preparing cells in which the polymer electrolytes were sandwiched between stainless steel blocking electrodes (diameter: 1.6 cm). The ionic conductivities (σ) were determined from bulk resistances (R), which were measured by AC complex impedance analyses using a Solartron 1255 frequency response analyzer

(FRA) in combination with a Solartron 1287 electrochemical interface over a frequency range from 1 mHz to 1 MHz. The ionic conductivities were calculated according to the following equation, $\sigma = l/RS$, where l is the thickness of the polymer electrolyte, and S is the contact area between the separator and stainless steel blocking electrodes.[1)]

3. Results and Discussion

The effect of UV exposure upon succinonitrile was monitored by using FT-IR spectrum. Succinonitrile was exposed to UV on equal terms with the preparation condition (8 mW cm^{-2}, 365 nm, 10 min) of the polymer electrolytes based on succinonitrile. As shown in Fig. 2(a), a band at 2252 cm^{-1} corresponding to cyano functional group (C ≡ N) was well maintained even after UV exposure, which implies that the cyano functional group of succinonitrile was not largely affected upon UV treatment. In addition, we also investigated the thermal treatment influences upon acrylate functional groups of PEGDMA. PEGDMA was excessively heated (80°C, 24 h) and then monitored by using FT-IR. As described in Fig. 2(b), a band at 1729 cm^{-1} corresponding to the C = C double bond was well preserved even after excessive heat treatment. This implies that the acrylate functional groups did not participate in crosslinking reaction after heat exposure and thus it can be concluded that the heat treatment does not significantly influence on properties of PEGDMA.

The physical appearances of the polymer electrolytes employing PVdF-HFP and PEGDMA are presented in Fig. 3. Both polymer electrolytes appear to be solidified gel-like and the mechanical strength of both polymer electrolytes was sufficient enough to form free-standing films.

To investigate thermal properties of polymer electrolytes, DSC tests were conducted. Fig. 4 shows the DSC curves of the pure succinonitrile, succinonitrile containing lithium salt (SN/$LiClO_4$ = 10/1 by molar ratio), and polymer electrolytes based on PVdF-HFP and PEGDMA. As previously reported, the pure succinonitrile revealed two characteristic endothermic peaks: one at −32°C assigned to the solid state transition from nor-

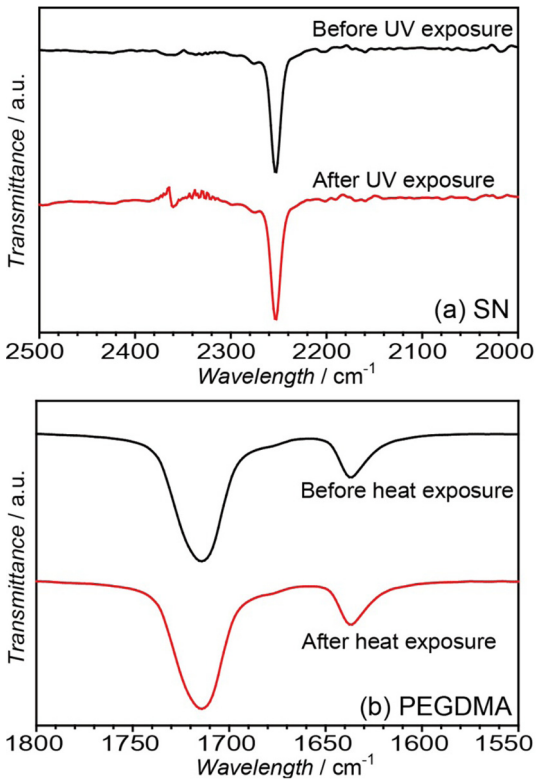

Fig. 2. FT-IR spectrum of (a) succinonitrile and (b) PEGDMA before and after UV exposure (8 mW cm^{-2}, 365 nm, 10 min) and heat treatment (80°C, 24 h), respectively.

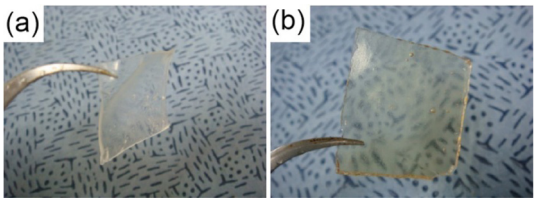

Fig. 3. Digital camera images of polymer electrolytes based on (a) PVdF-HFP and (b) PEGDMA.

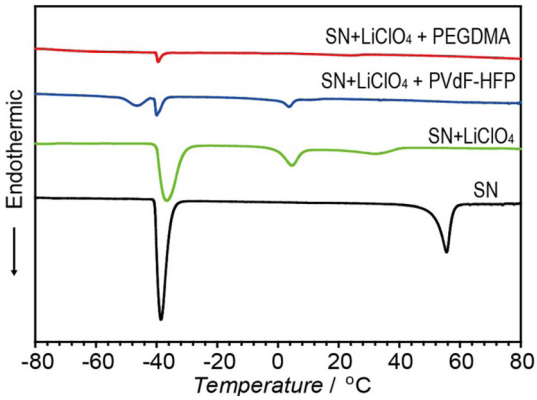

Fig. 4. DSC profiles of pristine SN, SN with lithium salt ($LiClO_4$), the polymer electrolytes based on PVdF-HFP and PEGDMA.

mal crystal to plastic crystal phase (T_{cp}) and the other at around 57°C assigned to the melting (T_m).[12,13] Upon the addition of $LiClO_4$ into the pure succinonitrile, however, the magnitude of the melting endotherm (ΔH_m) decreased and T_m was shifted to lower temperature (5°C), while there was little effect on T_{cp}, indicating the presence of unreacted succinonitrile.[5,12] The change of melting properties is ascribed to the hindrance of the crystal phase of succinonitrile resulted from the solvation effect due to the highly polar nature of succinonitrile, which acts as a solvent for lithium salt.[5,9,13] On the other hand, the enthalpy for both thermodynamic transitions, T_m as well as T_{cp}, is known to decrease largely with employing polymer matrices, which is well consistent with those of previous reports.[5,8] Little detectable peaks over the whole heating range indicate that a large portion of plastic crystal phase of succinonitrile for those samples disappeared.

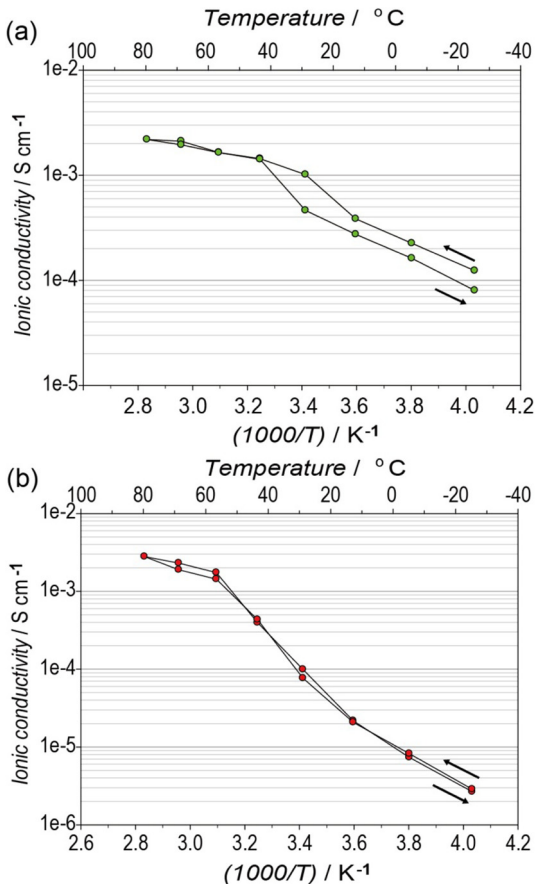

Fig. 5. Temperature dependence of ionic conductivities of the polymer electrolytes based on (a) PVdF-HFP and (b) PEGDMA.

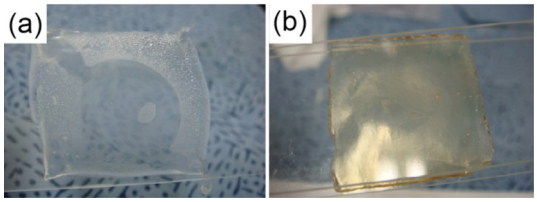

Fig. 6. Digital camera images illustrating the polymer electrolytes based on (a) PVdF-HFP and (b) PEGDMA after exposure at 80°C for 30 min.

The temperature-dependence of the ionic conductivities of the polymer electrolytes was illustrated in Fig. 5. The measurements were first conducted in the direction of from −25 to 80°C and then from 80 to −25°C with 15°C intervals.[1] In order to guarantee steady-state temperature conditions, the polymer electrolytes were stored for 1 h at each temperature before the measurements. Contrary to the polymer electrolyte employing PVdF-HFP, the ionic conductivity of the polymer electrolyte employing PEGDMA was well maintained during round trip temperature scanning (no hysteresis) in the given temperature range. In addition, Fig. 6 shows digital camera images of the polymer electrolytes based on PVdF-HFP and PEGDMA, which were sandwiched between two glass plates and stored at 80°C for 30 min. It can be clearly noticed that a larger amount of plasticized succinonitrile were smeared out from polymer electrolyte containing PVdF-HFP during high temperature storage compared to that of PEGDMA-based system. Again, considering these aspects, it seems that the plasticized succinonitrile is strongly entrapped in the polymer electrolyte matrix containing PEGDMA without leakage, which is also well consistent with previous report.[1,14]

To investigate the ion transport mechanism in polymer electrolytes, the temperature-dependence of the ionic conductivity of polymer electrolytes was fitted with the following Arrhenius equation:[1,15,16]

$$\sigma = \sigma_0 \exp(-E_a/RT)$$

Here, R, σ, σ_0 and T are the gas constant, the conductivity of polymer electrolyte, the pre-exponential index, and the testing absolute temperature, respectively. The ionic conductivity values of polymer electrolytes measured at increasing temperatures shown in Fig. 5 were used for the fitting.

Contrary to other conventional polymer electrolytes which are fitted as a straight line for over the entire tem-

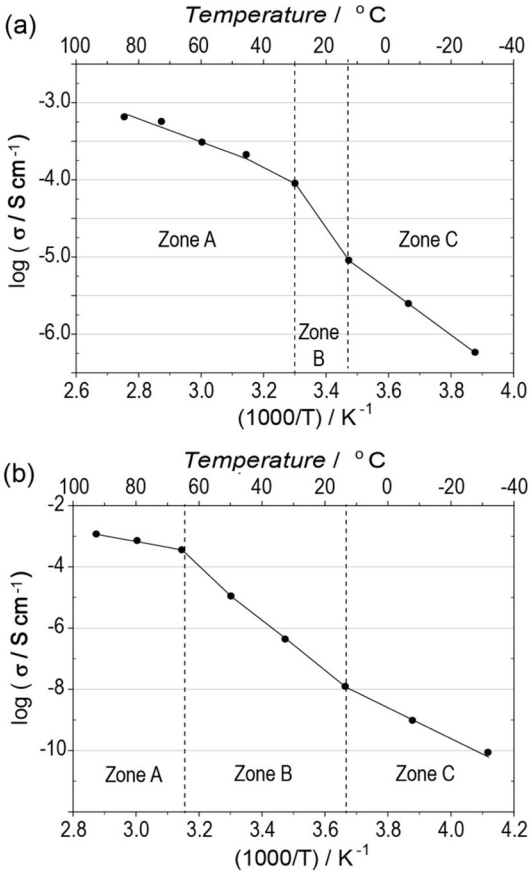

Fig. 7. Arrhenius plots of the polymer electrolytes based on (a) PVdF-HFP and (b) PEGDMA.

perature range,[1,15] both plots of PVdF-HFP and PEGDMA were separated into three distinctive zones as displayed in Fig. 7. Although these results are not very common, the results were reproducible over multiple trials. Obviously, the ionic conduction mechanism is largely influenced by the physical state of polymer electrolytes, and thus we tried to anticipate the physical states of polymer electrolytes from the DSC results. As already described in Fig. 5, the physical properties of the polymer electrolytes based on succinonitrile are rapidly changed depending on the temperature range. Considering these aspects, the unique ionic conduction mechanism of the polymer electrolytes based on succinonitrile can be speculated as follows:[17] 1) Zone A: This region is resulted from the liquid-like ionic conduction. The ionic conduction is linearly dependent on temperature with low activation energy, which can be correlated with the smaller slant of the plots compared to that of other zones. 2) Zone B: This region corresponds to the plastic crystal properties of the materials. It is suggested that the ionic conduction can be derived from the existence of long dislocated defects, which result in interconnected channels that provide ionic pathways. 3) Zone C: This region corresponds to the conventional crystal properties of materials showing low ionic conductivities.

4. Conclusions

We developed free-standing polymer electrolytes based on succinonitrile by using linear polymer matrix and cross-linked polymer matrix represented by PVdF-HFP and PEGDMA. The Polymer electrolyte based on PEGDMA remarkably improved thermal stability compared to that of the polymer electrolyte based on PVdF-HFP due to the substantially reduced leakage of succinonitrile during exposure to high temperatures.

Acknowledgement

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