

Improved ionic conductivity of nitrile rubber/ionic liquid composites

Edy Marwanta, Tomonobu Mizumo, Nobuhumi Nakamura, Hiroyuki Ohno*

Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

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Abstract

Polymer electrolytes with high ionic conductivity and good elasticity were prepared by mixing nitrile rubber (poly(acrylonitrile-co-butadiene) rubber; NBR) with ionic liquid, *N*-ethylimidazolium bis(trifluoromethanesulfonyl)imide (EImTFSI). The NBR/EImTFSI composites were obtained as homogeneous and transparent films when the ionic liquid content was less than 60 wt%. Raman spectroscopy suggested the interaction between nitrile group of NBR and TFSI anion. Sample with ionic liquid content of 50 wt% showed the ionic conductivity of $1.2 \times 10^{-5} \text{ S cm}^{-1}$ at 30 °C. Addition of lithium salt to this NBR/EImTFSI composite further enhanced the ionic conductivity to about $10^{-4} \text{ S cm}^{-1}$ without spoiling mechanical properties. DSC studies showed two glass transition temperatures for composites indicating microphase separation.

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1. Introduction

Many solid-state polymer electrolytes have been reported and motivated the development of mobile electrochemical devices such as lithium batteries, fuel cell, electrochromic devices and so on [1]. For the application to these electrochemical devices, polymer electrolytes are requested to have certain level of physical properties such as mechanical strength, elasticity and thermal stability [2]. Many efforts have been conducted to improve the mechanical properties as well as the ionic conductivity. One of attractive ways to provide polymer electrolytes with high tensile strength and elasticity is by giving ion conductive property to common elastomers. Some studies on elastic polymer electrolytes have already been reported [3–6]. In the case of synthetic rubbers, nitrile rubber (NBR)/styrene-butadiene rubber (SBR) latex films were blended with butyrolactone or ethylene carbonate/propylene carbonate mixed solutions of lithium salts to show the ionic conductivity of about $10^{-3} \text{ S cm}^{-1}$ at room temperature [3,4]. Studies of thermoplastic polyurethane containing

hard-soft segments incorporating propylene carbonate/lithium salt solution have also been reported [5,6]. However, the use of organic solvents still has problems such as volatility and high flammability. Thermally stable elastomeric ion conductors have, therefore, been expected.

Previously, we had prepared ion conductive elastomers without organic solvents. Use of natural rubber for polymer electrolytes has been attempted by blending with poly(ethylene oxide) and its derivatives. The obtained blend showed ionic conductivity of $2.7 \times 10^{-5} \text{ S cm}^{-1}$ at 50 °C [7]. We also conducted epoxidation to give polarity onto natural rubber and investigated the conductivity [8,9].

Ionic liquids have been investigated as novel electrolytes because of their high ionic conductivity, good electrochemical stability, non-volatility and so on [10,11]. Some ionic liquids are known to be gelled easily with polymers such as poly(vinylidene fluoride) (PVdF) to give gel electrolytes [12–17]. Combination of elastic polymer and ionic liquids is expected to provide polymer electrolytes with excellent mechanical properties.

In the present study, we employed both NBR and ionic liquid as matrix and ion source for polymer electrolyte, respectively. In our previous study [7], lithium salt played a role to provide ion conductive path in microphase separated structure. It is also essentially important to prepare composite electrolytes showing microphase separation

* Corresponding author. Tel./fax: +81 42 388 7024.

E-mail address: ohnoh@cc.tuat.ac.jp (H. Ohno).

with small amount of ionic liquid to realize highly ion conductive characteristic.

2. Experimental

2.1. Materials

NBR in ethyl methyl ketone solution and poly(butadiene) (butadiene rubber) in toluene solution were gifts from Tokai Rubber Industries. NBR and butadiene rubber in solution was coagulated and washed in methanol and then dried in vacuum at 45 °C for 3 days. NBR with nitrile content of 33 mol% was used in this experiment because this is the best composition for their physical properties, compromising the strength and the elasticity. Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI), a gift from Sumitomo 3M, was vigorously dried in vacuo before use. Reagent grade LiBF_4 , purchased from Tokyo Kasei Co. Ltd, was used as received. HTFSI was obtained by ion exchange reaction of LiTFSI using amberlite IR-120B H AG resin. *N*-ethylimidazolium TFSI (EImTFSI), *N*-ethylimidazolium tetrafluoroborate (EImBF₄) and *N*-ethylimidazolium benzenesulfonate (EImBS) were prepared by the previously reported neutralization method [18,19]. *N*-ethylimidazole (Tokyo Kasei Co. Ltd) was dissolved in distilled water and another aqueous solution containing equimolar amount of HTFSI was mixed and stirred at 0 °C for 1 day. The resulting EImTFSI was extracted with dichloromethane. In the case of EImBF₄ and EImBS, these ionic liquids were isolated by precipitating the reacted solution in ether. The ionic liquids were then vacuum dried at 60 °C for 3 days after solvent removal. Structure of the ionic liquids was confirmed by ¹H-NMR spectroscopy.

Just after vacuum drying NBR and ionic liquids were dissolved in various ratios in dry acetone and stirred to obtain homogeneous solutions. Chloroform was used as solvent for butadiene rubber samples. After solvent removal, the samples were vacuum dried at 45 °C for 3 days. Films with thickness of 50 μm were obtained by pressing the composites on teflon plate and dried under vacuum at 45 °C for 1 day. Composites containing lithium salts were prepared by mixing NBR, ionic liquid and lithium salts in a suitable solvent. Then the same procedure was conducted as mentioned above.

2.2. Measurements

Raman spectroscopic study was conducted using NRS-1000 (JASCO) on film samples at room temperature. The wavelength of the laser was 647 nm with output power of 47 mW.

DSC measurement was carried out with DSC-6200 (Seiko instrument) at heating rate of 10 °C/min and temperature range from –140 to 140 °C.

Dynamic mechanical properties of the composites were

determined using IT-DVA 200S (ITK Co., Japan). Rectangular samples with dimensions of 1×5×20 mm³ were prepared through pressing under vacuum at 45 °C. The measurement was run from –120 °C at a heating rate of 5 °C min⁻¹, a frequency of 10 Hz and dynamic tensile strength of 0.1%.

The ionic conductivity was measured by complex-impedance method using impedance analyzer (Solartron model 1260; Schlumberger) under nitrogen gas atmosphere, in the frequency range from 10 Hz to 1.0 MHz and temperature range from 60 to 10 °C. The samples were put between two stainless steel electrodes with 0.50 mm thick teflon spacer.

3. Results and discussion

3.1. NBR/EImTFSI composite

3.1.1. NBR and EImTFSI miscibility

Miscibility between polymer matrix and ionic liquids is quite important factor to control both mechanical properties and ionic conductivity. For the fixed rubber species, since this miscibility is the function of ionic liquid structure, we have analyzed the miscibility using several ionic liquids. NBR/EImTFSI composites were obtained as yellowish transparent films and they were stable for months indicating excellent miscibility. The composites showed good elasticity even when 50 wt% of ionic liquid was added. Composite with ionic liquid content of 75 wt% or more were sticky paste. On the other hand, EImBF₄ and EImBS are not miscible with NBR and completely phase separated indicating the effectiveness of TFSI anions to show miscibility with NBR. It should be mentioned here that the EImTFSI had better miscibility with NBR than the most popular ionic liquid, 1-ethyl-3-methylimidazolium TFSI (EMImTFSI) that was prepared by the quaternization of methylimidazole with ethyl bromide and subsequent anion exchange. EMImTFSI showed poor miscibility with NBR. In the case of butadiene rubber, which has no polar group, no ionic liquid was found to be miscible. These results clearly show that the miscibility of ionic liquid with polymer is the function of their structural characteristic. We here focused on the polar group of rubber and anion of the ionic liquid as factors to govern the miscibility. Raman spectroscopy was performed to investigate the interaction between NBR and the ionic liquid. Fig. 1 shows the Raman spectra of $\nu_s(\text{C}\equiv\text{N})$ mode of NBR. The peak shifted from 2245 to 2248 cm⁻¹ by the addition of EImTFSI, indicating certain interaction between nitrile group and ions.

DSC measurements of the NBR/EImTFSI composites were performed. The DSC results showed single glass transition temperature (T_g) which was dropped by increasing ionic liquid content (Fig. 2). The plasticizing effect of ionic liquids on polymer matrix was reported by Scott et al. [20,21]. They employed 1-ethyl-3-methylimidazolium

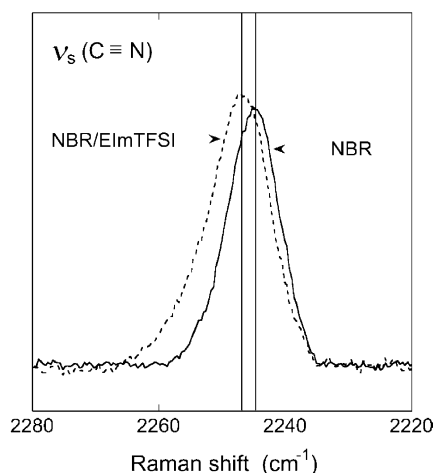


Fig. 1. Raman spectra of the C≡N bond stretching mode in NBR bulk and NBR/EImTFSI composites (EImTFSI content = 50 wt%).

tetrafluoroborate (EMImBF₄) as plasticizers for poly-(methyl methacrylate), resulting excellent compatibility, thermal stability and dynamic properties better than conventional plasticizers. In the present case, NBR and EImTFSI show excellent compatibility through ion-dipole interactions to realize the drop of T_g .

3.1.2. Ionic conductivity of NBR/EImTFSI composites

Fig. 3 shows the temperature dependence of the ionic conductivity of NBR/EImTFSI composites. The conductivity increases as the ionic liquid content increases. This was comprehensible as the results of both the increase of the carrier ion number and the low T_g . NBR/EImTFSI system has unique characteristics different from conventional polymer electrolytes such as PEO/lithium salt complexes, which are difficult to realize high ionic conductivity in higher salt concentration due to T_g elevation and salt aggregation. The composites with ionic liquid content 10, 25 and 50 wt% were obtained as free standing films with good elasticity. Especially, sample with ionic liquid content of 50 wt% showed the ionic conductivity of $1.2 \times 10^{-5} \text{ S cm}^{-1}$

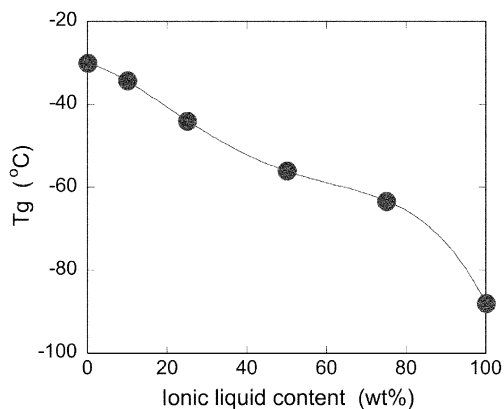


Fig. 2. Glass transition temperature (T_g) of NBR/EImTFSI composites in the function of EImTFSI content.

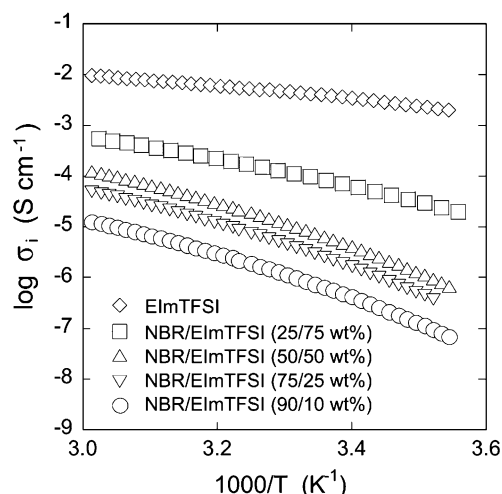


Fig. 3. Temperature dependence of the ionic conductivity for NBR/EImTFSI composites. EImTFSI bulk (\diamond), NBR/EImTFSI with ratio of 25/75 wt% (\square), 50/50 wt% (\triangle), 75/25 wt% (∇) and 90/10 wt% (\circ).

at 30 °C. Sample with ionic liquid content of 75 wt% had the ionic conductivity of $1.5 \times 10^{-4} \text{ S cm}^{-1}$ and showed less temperature dependence of the ionic conductivity, however, this composite was not obtained as films anymore. In any case, these ionic conductivities were considerably lower than that of bulk ionic liquid, $4.6 \times 10^{-3} \text{ S cm}^{-1}$. It should be comprehended to the effect of increased viscosity. In other words, excellent miscibility of NBR and ionic liquid is not so effective to achieve high ionic conductivity. Since excellent miscibility between rubber matrix and ionic liquid always increase the viscosity of the ionic liquid due to sufficient interaction between them. To avoid the elevation of viscosity after mixing, it is essentially important to minimize the interaction between them. Accordingly, design of microphase separated structure is required to provide highly ion mobile pathway in elastomer matrix.

3.2. NBR/EImTFSI/Li salt composites

Composites consisted of NBR, EImTFSI and lithium salt (LiTFSI and LiBF₄) were prepared. Number of ions per the nitrile group of NBR was changed to clarify the effect of lithium salt concentration. Composites containing lithium salts were prepared by keeping the same number of total ions, i.e. [EImTFSI + lithium salt] was set to be 42.7 mol% to the nitrile group of NBR. NBR/EImTFSI ratio was also kept constant (50/50 wt%).

3.2.1. Physical properties of NBR/EImTFSI/lithium salt composites

Composites consisted of NBR, EImTFSI and lithium salts also gave homogeneous films. Composite containing LiTFSI and LiBF₄ were obtained as yellowish transparent film and opaque one, respectively. Since, EMImBF₄ was not miscible with NBR, salts having BF₄ anions were concluded

to be unsuitable for the preparation of homogeneous NBR composites. We then tried to prepare composite films showing microphase separation with same TFSI salts. NBR/EImTFSI/LiTFSI composites showed better mechanical properties than the composites without lithium salt. Composite with 75 wt% ionic liquid without lithium salt, for example, was sticky paste while the composites containing lithium salts were obtained as free standing films. Furthermore, dynamic mechanical analysis (DMA) were performed for NBR/EImTFSI (ionic liquid 50 wt%) and NBR/EImTFSI/LiTFSI composites (Fig. 4). DMA results showed that composite containing lithium salt has better mechanical strength than the composite without lithium salt. On the other hand, two peaks of loss tangent ($\tan \delta$) for NBR/EImTFSI/LiTFSI composite were observed, suggesting phase separation microscopically.

Raman studies for NBR/EImTFSI/LiTFSI composite films were performed. However, it was difficult to measure the composites containing LiBF_4 because of their opaque nature. Fig. 5 shows the Raman spectra of the nitrile group in NBR/EImTFSI and NBR/EImTFSI/LiTFSI composites. A peak appeared at 2248 cm^{-1} (a) corresponded to the $\nu_s(\text{C}\equiv\text{N})$ mode of NBR in NBR/EImTFSI composite. This peak shifted a little to 2247 cm^{-1} for composites containing LiTFSI. A new shoulder appeared at around 2270 cm^{-1} , which became larger as LiTFSI content increased, while the

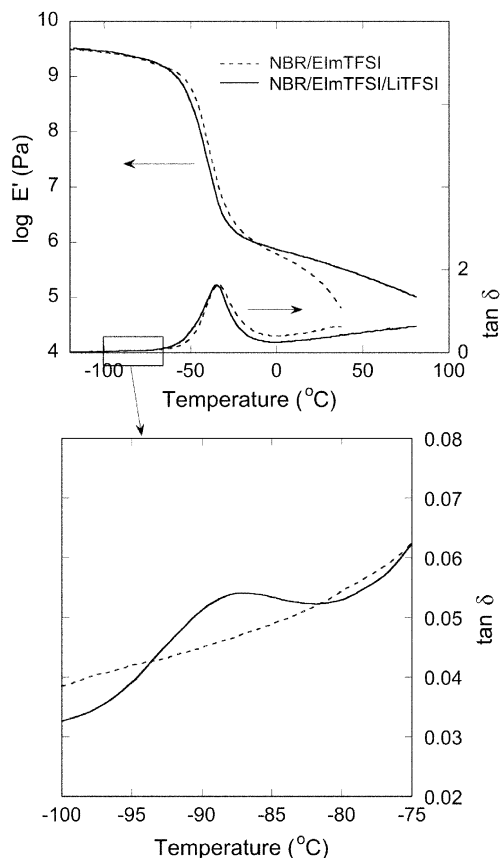


Fig. 4. DMA results for NBR/EImTFSI and NBR/EImTFSI/LiTFSI.

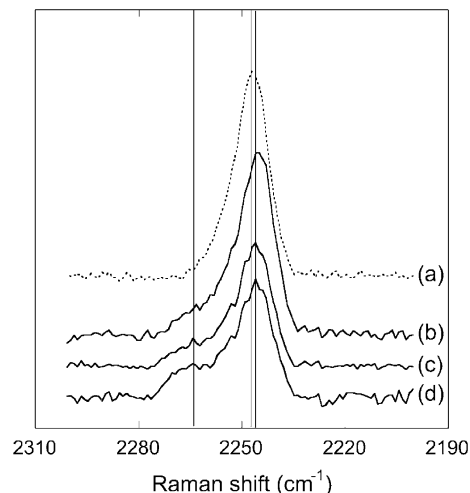


Fig. 5. Raman spectra of the $\text{C}\equiv\text{N}$ bond stretching mode of NBR in (a) NBR/EImTFSI, NBR/EImTFSI/LiTFSI with lithium salt content of (b) 20 mol%, (c) 40 mol% and (d) 80 mol% to EImTFSI. The new shoulder appeared at around 2270 cm^{-1} indicating the interaction between $\text{C}\equiv\text{N}$ group and Li^+ ion.

intensity of peak at 2247 cm^{-1} decreased as the intensity of the shoulder peak increased. This shoulder reflects the interaction between $\text{C}\equiv\text{N}$ group of NBR and Li^+ ion. This result agreed well with some reports about interaction between nitrile group and metal [22,23]. Ferry et al. reported the Raman study of poly(acrylonitrile) (PAN)/ LiCF_3SO_3 composite and detected the interaction between Li^+ ion and the $\text{C}\equiv\text{N}$ group [22]. Wang et al. reported that this interaction was also confirmed in PAN/propylene carbonate/LiTFSI gel polymer electrolyte system [23]. Considering chemical properties of the nitrile group, this interaction can be attributed to the electron donating nature of the nitrile group.

Fig. 6 shows the DSC thermograms of NBR/EImTFSI composites with or without lithium salts. Two T_g s based on NBR/ionic liquid (T_{g1}) and bulk ionic liquid (T_{g2}) were seen in the DSC chart for both composites containing LiTFSI and LiBF_4 . These results agree well with the dynamic

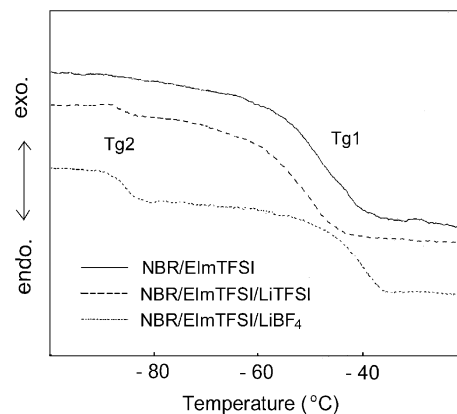


Fig. 6. DSC thermograms of NBR/EImTFSI, NBR/EImTFSI/LiTFSI and NBR/EImTFSI/ LiBF_4 composites.

mechanical analysis results as mentioned above. It indicated that the presence of lithium salts induced microphase separation. The presence of LiBF_4 led the elevation of T_{g1} from -57.5 to -45.9 °C while LiTFSI caused no significant change of T_{g1} .

From the Raman spectroscopic study for NBR/EImTFSI composite, the ionic liquid was strongly suggested to have certain interaction with NBR. Considering that many ionic liquids are known to dissolve lithium salts, a part of ionic liquid was separated from NBR composite in the presence of lithium salts. However, since Li^+ ion can interact with both nitrile group of NBR and TFSI anion of ionic liquid, these phases were not separated macroscopically but kept microscopic phase separation. Li^+ ion is assumed to play a role as ‘binder’ between these two phases. Microphase separation was also considered as the factor to improve the mechanical properties.

3.2.2. Ionic conductivity of NBR/EImTFSI/lithium salt composites

Fig. 7 shows the ionic conductivity of NBR/EImTFSI/LiTFSI films as the function of LiTFSI concentration ($[\text{EImTFSI} + \text{Li salt}] = 42.7$ mol% to the nitrile group). The presence of lithium salts significantly enhanced the conductivity. The ionic conductivity increased as the lithium salt increased until LiTFSI/EImTFSI was 20 mol%. Further addition of LiTFSI caused the decrease of ionic conductivity, which was attributable to the elevated viscosity and glass transition temperature.

Fig. 8 shows the temperature dependence of the ionic conductivity for NBR/EImTFSI and NBR/EImTFSI/Li salt composite ($\text{Li/EImTFSI} = 20$ mol%). The ionic conductivity of $1.0 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C was obtained for the composite containing LiTFSI, that was about 100 times higher than that of composite without lithium salts. This tendency was different from a mixture of ionic liquid and lithium salt, in which the ionic conductivity of bulk

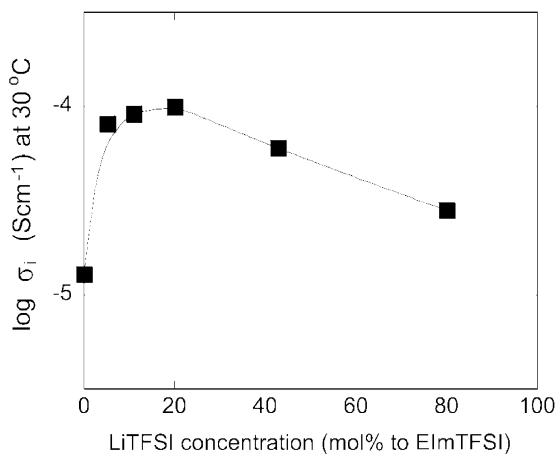


Fig. 7. The ionic conductivity of NBR/EImTFSI/LiTFSI as the function of LiTFSI concentration.

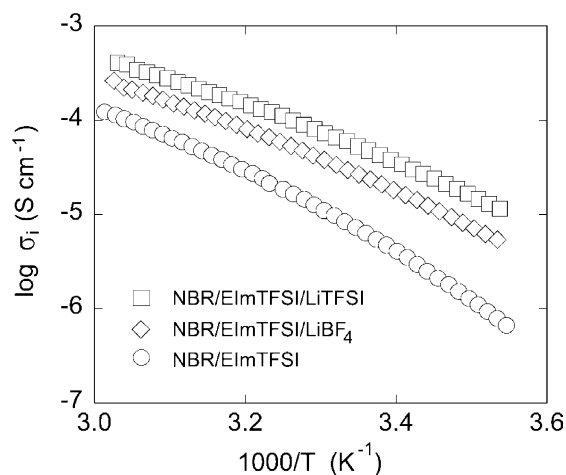


Fig. 8. Temperature dependence of the ionic conductivity for NBR/EImTFSI, NBR/EImTFSI/LiBF₄ and NBR/EImTFSI/LiTFSI.

EImTFSI dropped by the addition of lithium salts due to the elevated T_g and increased viscosity.

Ionic conductivity is the product of carrier ion number and ion mobility. Carrier ion number depends on the degree of salt dissociation, while ion mobility depends on T_g and viscosity. Therefore, low T_g and low viscosity generally lead high ionic conductivity. In this case, the number of ions was the same (42.7 mol% to nitrile group). DSC studies showed that there was no significant change in the T_g for composite containing LiTFSI. Moreover, elevated T_g was seen in the composite containing LiBF_4 . We concluded that the microphase separation into NBR/EImTFSI phase and ionic liquid phase contributed in the improvement of the ionic conductivity.

Finally, the compatibility of NBR/EImTFSI/LiTFSI film with lithium metal was investigated. According to the method reported by Fauteux [24], the electrolyte film was sandwiched between lithium metal electrodes and the interfacial resistance (R_i) at 29 °C was measured by impedance spectroscopy. The sample thickness was 100 μm and the surface area was 0.28 cm^2 . The interfacial resistance, R_i simply increased from $5.5 \times 10^3 \Omega$ (0 h) to $1.8 \times 10^5 \Omega$ (4 h) indicating the formation of passivating layer.

4. Conclusion

Composites consisted of NBR and ionic liquids were prepared as elastic and thermally stable polymer electrolytes. EImTFSI showed good miscibility with NBR. The presence of lithium salts in NBR/EImTFSI composites enhanced the ionic conductivity about 100 times to $1.0 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C. Raman spectroscopic studies suggested certain interaction between nitrile group of NBR and ions. Thermal analysis studies indicated microphase separation in NBR/EImTFSI/Li salt composites that was considered to play an important role to improve the ionic conductivity.

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