Temperature dependence of electrical conduction in PEMA-EMITFSI film

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Abstract. Transparent and flexible film of poly (ethyl methacrylate) incorporated with 1-ethyl-3-methyl imidazolium bis(trifluorosulfonyl) imide (PEMA-EMITFSI) with thickness between 100 and 200 µm was fabricated by using solution casting technique. From the ionic transport measurement, it is confirmed that the electrical conduction in PEMA-EMITFSI film is mainly contributed by ionic transport. Moreover, the temperature-dependence of electrical conductivity measurement for 7 days reveals that the electrical properties of PEMA-EMITFSI film could be able to withstand a number of thermal cycles and be lasting for a period of time for potentially used as thermoelectric material through thermal heating.

1. Introduction
Thermoelectric (TE) devices are able to harvest electricity directly from waste heat and vice versa. The performance of TE devices is determined by a dimensionless figure of merit (ZT)

\[ ZT = \frac{\sigma S^2 T}{\kappa}, \]  \hspace{1cm} (1)

where \( \sigma \) is the electrical conductivity, \( S \) is the thermopower, \( \kappa \) is the thermal conductivity and \( T \) is the absolute temperature of operation. Based on the expression of \( ZT \), it is known that in order to achieve a high \( ZT \), it is necessary to fabricate TE device by using TE material which has high electrical conductivity and thermopower, and low thermal conductivity. Current high \( ZT \) TE materials are mainly inorganic semiconductors like Te based semiconductor material and transition metal oxides [1-5]. However, these materials have facing some issues such as toxicity, highly cost and poor processability, which limit their commercial use. Thus, over the past decade has witnessed remarkable progress in organic TE materials as promising candidates for the development of flexible, cost-effective and scalable TE devices [6-9].
Moreover, the electrical stability of TE material in terms of temperature and time is also important to be considered in practical TE device applications. It is known that the electrical conductivity of organic material such as insulating polymers are mainly governed by ionic transport and strongly depended on the temperature which limits its effectiveness to be applied in wide range temperature TE applications [10]. Moreover, most of the polymer based TE materials are fabricated on a substrate which reduces its flexibility and increases its manufacturing cost [11-13]. In previous study, our group successfully fabricated a free-standing poly (ethyl-methacrylate) incorporated with 1-ethyl-3-methyl imidazolium bis (trifluorosulfonyl) imide ionic (PEMA-EMITFSI) film and found that the film doped with 40 wt.% EMITFSI exhibits the best physicochemical and electrical properties [14]. Therefore, in this study, a same composition of PEMA-EMITFSI film is fabricated and its electrical conductivity is measured. The dependency of electrical conductivity of fabricated PEMA-EMITFSI on temperature and time will be clarified in order to discuss its possibility to be applied as TE material.

2. Experiment
The PEMA-EMITFSI film is fabricated by exactly following the procedure described in our previous report [14]. In the present work, the composition of 40 wt. % 1-ethyl-3-methyl imidazolium bis (trifluorosulfonyl) imide (EMITFSI) was chosen for film fabrication as the film exhibited the highest electrical conductivity at room temperature. 40 wt. % EMITFSI was added into solution containing 1 g PEMA in 20 ml Tetrahydrofuran (THF). The mixture was stirred at 40 °C until it becomes homogeneous. The solution was then casted into teflon petri dish and kept in air to dry. PEMA (Mw ~ 515 000 g mol⁻¹) and EMITFSI were purchased from Aldrich. THF was supplied from R&M Chemicals. All materials were used as received for sample fabrication. The thickness of the samples are between 100 and 200 µm which determined by a digital micrometer (Mitutoyo Corp.).

The electrical conductivity of the film was determined by impedance spectroscopic technique using an impedance analyser (SOLARTRON 1260) over a 100 Hz to 5 MHz frequency range with alternating current (AC) amplitude of 100 mV. The sample was sandwiched vertically between stainless steel blocking electrodes with diameter of 2 cm and placed in a temperature-controlled environmental chamber for measuring temperature-dependence of electrical conductivity from 303 to 373 K. The same procedure was then repeated using the same sample over a period of 7 days. Ionic transport number was measured using direct current (DC) polarization technique in order to confirm the contribution of ionic transport. The sample was sandwiched vertically between stainless steel blocking electrodes with applied potential difference of 1 V. The value of current was monitored until it reached the steady state condition.

3. Results and Discussion
Figure 1 shows the photograph of fabricated PEMA-EMITFSI film with a diameter of ~8 cm. From this figure, the sample which is fabricated without a substrate is seen to be transparent and flexible. This result shows a possibility to obtain TE material based on transparent and flexible material. The time evolution of normalized-measured polarization current of fabricated sample which was cut into 2 cm in diameter is shown in Figure 2. From Figure 2, it is found that the normalized current abruptly decreases with time which is usually observed in characteristic of ionic conducting material [15-16]. Considering the DC polarization technique [17-18], the ionic transport number, $T_{\text{ion}}$ of fabricated PEMA-EMITFSI film was determined to be 0.96 by using following equations:

$$T_e = \frac{\sigma_e}{\sigma_i + \sigma_e} = \frac{i_e}{i_T}, \quad (2)$$

$$T_{\text{ion}} = 1 - \frac{i_e}{i_T} = 1 - T_e, \quad (3)$$
Figure 1. Photograph of free-standing PEMA-EMITFSI film

Figure 2. Time evolution of normalized-measured polarization current of PEMA-EMITFSI film at room temperature.

where $\sigma_i$ is the ionic conductivity, $\sigma_e$ is the electronic conductivity, $i_r$ is the residual current and $i_T$ is the total current. Therefore, these results indicate that the fabricated free-standing transparent film is an ionic conducting material since the calculated value of $T_{ion}$ is close to 1.

Figure 3 shows the measured electrical conductivity of the fabricated sample in logarithm as a function of inverse temperature for day 1 and 5. The broken lines show the linear regression line. The
result of day 1 is in good agreement with our previous report which shows a good reproducibility of fabricated sample [14]. Moreover, the electrical conductivity of PEMA-EMITFSI is found to be $\sim 10^{-7}\, \text{S cm}^{-1}$ which is four orders of magnitude higher compared with reported value of PEMA film which is $\sim 10^{-11}\, \text{S cm}^{-1}$ [14]. From Figure 3, it is found that the logarithmic electrical conductivity linearly increases with increasing the temperature for both cases of day 1 and 5. This strong temperature dependent behavior is consistent with usually observed dependency in polymer materials which can be explained by free-volume model [10]. When temperature is increased as well as the thermal energy, the polymer chain can expand easily and gains higher free volume. This free volume promotes segmental motion of the polymer chains and leads to an increase in ionic mobility. That is, increasing the ionic mobility will increase the electrical conductivity in the polymer network system. Therefore, these results show that the fabricated film is more suitable for higher temperature TE application with low temperature fluctuation.

Moreover, from Figure 3, it is observed that there are differences of electrical conductivity values between day 1 and 5, especially near room temperature region. In order to clarify the influence of time on the electrical conductivity, the logarithmic measured electrical conductivity is replotted in Figure 4 as a function of day for measurement temperature at 303 and 343 K. From Figure 4, it is found that the electrical conductivity decreases with increasing the day for measurement at 303 K. This changes in electrical conductivity of fabricated film is likely due to the physical aging effect which is observed in amorphous polymers [19]. The physical aging effect describes the time-dependent molecular and structural changes which significantly effects on mechanical, structural and electrical properties of the material [19]. However, by heating again the sample around 343 K, the value of electrical conductivity of day 3, 5 and 7 are again identical with the value of day 1, as shown in Figure 4. Thus, it is considered that through physical aging effect the separation of polymeric chains will be reduced and then by thermal heating, a better separation will be obtained again which results pronounced movements of ion through higher free volume. Consequently, since the electrical conductivity is likely can be reset by thermal heating, the PEMA-EMITFSI film is expected can be applied as TE material at higher temperature.
4. Conclusion
We have measured the electrical conductivity of PEMA-EMITFSI film doped with 40 wt. % EMITFSI, with thickness between 100 and 200 µm. It is found that the electrical conductivity of PEMA-EMITFSI film increases with increasing the temperature. The increase of electrical conductivity is likely due to the expanding of polymer chain which increases the ionic mobility. In addition, by considering the calculated ionic transport number, it is also confirmed that the electrical conduction in PEMA-EMITFSI film is mainly governed by ionic transport. Moreover, the electrical conductivity decreases with increasing the time which is likely due to the physical aging effect. The electrical conductivity is considered can be increased again by thermal heating. Consequently, PEMA-EMITFSI film may be considered as a good potential for transparent and flexible TE device applications.

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