

## Synthesis and characterization of new solid polymer electrolyte (PEG + CH<sub>3</sub>COONa) for solid-state sodium batteries

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Using the solution-cast approach, new solid polymer electrolyte films containing sodium acetate (CH<sub>3</sub>COONa) in poly (ethylene glycol) were prepared. These polymer electrolyte systems have been characterized using a variety of experimental approaches, including temperature-dependent conductivity and DSC. The endothermic peak at 59.42°C, which corresponds to the melting temperature of pure PEG, is revealed by DSC measurements. Due to the addition of salt to the polymer, a minor movement in the melting point,  $T_m$ , towards lower temperatures has been detected. At 30°C, the 80PEG+20CH<sub>3</sub>COONa electrolyte system had a maximum conductivity of  $7.9 \times 10^{-6}$  S/cm. When compared to pure PEG, the conductivity enhanced by two orders of magnitude. The magnitude of conductivity increased as the temperature raised.

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### 1. Introduction

Due to its technological importance and effect in the realm of solid-state ionic device applications, ion conducting electrolytes have attracted a lot of attention. Polymer systems with high ionic conductivity at ambient temperatures are gaining attention these days, since they may have unique uses in rechargeable batteries, fuel cells, solar cells, and supercapacitors [1–4]. Polymer electrolytes have several advantages over their glassy and inorganic crystalline equivalents, including ease of manufacture, mechanical flexibility, and corrosion resistance. In these polymer electrolytes, ionic transport is linked to metal salt dissolution and the coupling of ions with polymer chain segmental movements [5]. Most commercial rechargeable batteries containing liquid electrolytes frequently suffered from potential safety risks due to leakage, limited temperature range of operation, spontaneous combustion of the electrolyte and volatility [6]. Solid polymer electrolytes have thus been widely used in solvent-free rechargeable batteries to address the safety concern with batteries.

In 1973, the first metal ion conducting solid polymer electrolyte was reported [7], and in 1979, the first solid polymer electrolyte (SPE) based battery was practically constructed [8]. Since then, a great variety of solid-state ion conducting materials have been reported, involving various kinds of mobile ionic species as charge carriers, such as H<sup>+</sup>, Ag<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and so on. In terms of complexation behaviour with different metal salts, large molecular weight polymers (~10<sup>6</sup>), such as poly (ethylene oxide) (PEO), were the most extensively described among the polymer systems [9]. Low molecular weight polymers, such as poly (ethylene glycol) (PEG), have a few reports [10]. Due to the similar structures of PEO and PEG, as well as the presence of identical repeating units, it is expected that the metal salt complexes of the latter will have high ionic conductivities equivalent to those of the former. Because Na<sup>+</sup> is a fast ion conducting in a

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variety of crystalline and amorphous materials, it is possible that adding it to a polymeric system will increase its electrical and electrochemical performance [11].

With this in mind, we used the solution casting technique to prepare solid polymer electrolytes based on PEG with a molecular weight of 4,000 and  $\text{CH}_3\text{COONa}$  salt. The resultant electrolyte materials have been characterized by differential scanning calorimetry (DSC) for investigating thermal properties. In the temperature range of 303–333 K, the conductivity of the polymer electrolytes was determined using the ac impedance approach.

## **2. Experimental**

### **2.1. Materials**

A molecular weight of 4,000 poly (ethylene glycol) (PEG) from CDH, India, was dried at 45 °C under vacuum for 24 hours. Sodium acetate ( $\text{CH}_3\text{COONa}$ ; 98 %, CDH, India) was vacuum dried at 45 °C for 24 hours. We used distilled water as the solvent for preparing the PEG-induced Sodium acetate solution.

### **2.2. Polymer electrolyte preparation**

Using the solution casting process, pure and doped PEG – Sodium acetate solid polymer electrolyte films were made in weight percent ratios of 100:0, 90:10, 80:20, and 70:30. Constant stirring for 15 hours at room temperature was used to achieve system homogeneity. The solution was then put onto glass petri dishes and allowed to slowly evaporate under vacuum at room temperature. In a control situation, the films peeled off by evaporating the solvent. After that, the solid polymer electrolyte samples were placed in desiccators to dry out further before being characterized.

### **2.3. Characterization**

The thermal response of these solid polymer electrolyte materials was investigated using differential scanning calorimetry (TA Instruments model 2920 calorimeter) in a static nitrogen environment at a heating rate of 5 °C / min in a temperature range of 0 to 100 °C to learn more about their nature. The HIOKI 3532–50 LCR Hitester was used to measure conductivity throughout a frequency range of 100 Hz to 1 MHz in the temperature range 303–333 K.

## **3. Results and discussion**

### **3.1. Differential scanning calorimetry (DSC)**

Thermal characteristics are significant in solid polymer electrolytes for improving melting point, glass transition temperature, and rubbery phase. Figure 1 shows DSC thermograms of pure PEG and its controlled composites with  $\text{CH}_3\text{COONa}$ . With increasing  $\text{CH}_3\text{COONa}$  concentrations, the melting temperatures ( $T_m$ ) of PEG-based polymer electrolytes dropped.

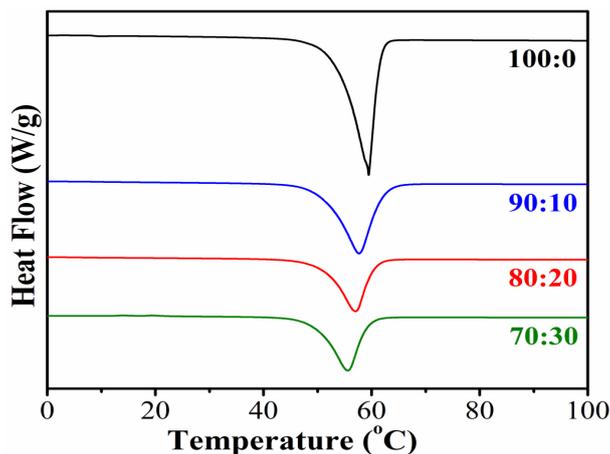


Fig. 1. DSC curves of different concentrations of PEG – CH<sub>3</sub>COONa polymer electrolytes.

The melting point of 70PEG–30 CH<sub>3</sub>COONa was found to be low. In comparison to pure PEG, the SPEs have a lower enthalpy of fusion ( $H_m$ ). The relative percentage of crystallinity ( $X_c$ ) was computed using the DSC data and the following equation, assuming that pure PEG was 100% crystalline.

$$X_c = \left( \frac{\Delta H_m}{\Delta H_m^0} \right) \times 100\%$$

where  $\Delta H_m^0$  is the standard enthalpy of fusion of pure PEG (i.e., 204.3 J g<sup>-1</sup>) and  $\Delta H_m$  is the enthalpy of fusion of the solid polymer electrolyte.  $X_c$ ,  $\Delta H_m$  and the crystalline melting temperature ( $T_m$ ) for all polymer electrolytes are presented in Table 1. It is clear that the values of  $X_c$  and  $\Delta H_m$  decreased with increasing CH<sub>3</sub>COONa salt concentration, and low values were obtained for optimum conducting composition (80:20). In addition, the melting endotherm was found to widen with increase of CH<sub>3</sub>COONa concentration. The decreasing of the  $T_m$  and expanding of the melting endotherm are clear indications of lessen in the degree of crystallinity and the dominant presence of amorphous phase.

Table 1. DSC results of PEG- CH<sub>3</sub>COONa solid polymer electrolytes.

Sample PEG- CH <sub>3</sub> COONa	Melting point ( $T_m$ ) (in °C)	$\Delta H_m$ (J/g)	$X_c$ (in %)
Pure PEG	59.42	204.3	100
90:10	57.82	145.2	71.1
80:20	56.76	112.4	55.02
70:30	56.08	120.8	59.1

### 3.2. Conductivity analysis

The complex impedance plot for PEG: CH<sub>3</sub>COONa (80:20) at various temperatures is shown in Figure 2. This graph shows a high frequency semicircle that corresponds to bulk resistance and a spike (lower frequency region) caused by the electrode/electrolyte interface. Vertical spikes at the low frequency end should have been obtained if the electrodes and electrode/electrolyte interaction were perfect. As shown in Fig. 2, semicircles are greatly expanded, and electrode spikes at the low frequency end of the spectrum are conspicuously non-vertical. Because of the roughness of the electrode/electrolyte contact, spikes angled at less than 90° to the actual axis were obtained in this investigation [12]. The bulk resistance ( $R_b$ ) where the semicircle crossed the  $Z'$ -axis was used to calculate ionic conductivity. The conductivity of the

sample was estimated using the formula  $=L/R_pA$ , where  $L$  is the electrolyte thickness and  $A$  is the electrode area, respectively.

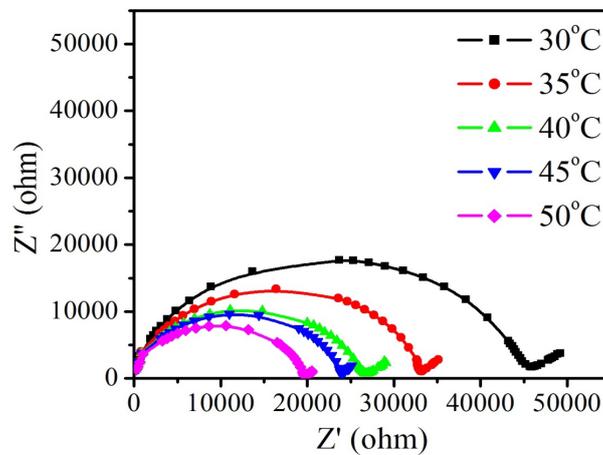


Fig. 2. Complex impedance plots for the [PEG:  $\text{CH}_3\text{COONa}$ ] (80:20) polymer electrolyte at different temperatures.

Temperature-dependent conductivity of the PEG-  $\text{CH}_3\text{COONa}$  polymer electrolytes is shown in Figure 3 at temperatures ranging from 303 to 333 K. At normal temperature (303 K), pure PEG has a modest ionic conductivity ( $\sim 5.41 \times 10^{-8} \text{ S cm}^{-1}$ ). The ionic conductivity is increased to  $7.9 \times 10^{-6} \text{ S cm}^{-1}$  with the addition of 20 wt% of  $\text{CH}_3\text{COONa}$  salt. The Arrhenius trend was observed in the polymer electrolytes, as the ionic conductivity increased almost linearly with the increase in temperature (Fig. 3). According to Miyamoto and Shibayama [13], the ionic conductivity increased with increasing temperature as a result of the free volume model, in which the polymer electrolyte expands readily and produces free volume as the temperature rises. As a result, ions, solvated molecules, or polymer segment might enter the free volume, increasing it [12]. This improves ion and polymer segmental mobility, resulting in improved ionic conductivity.

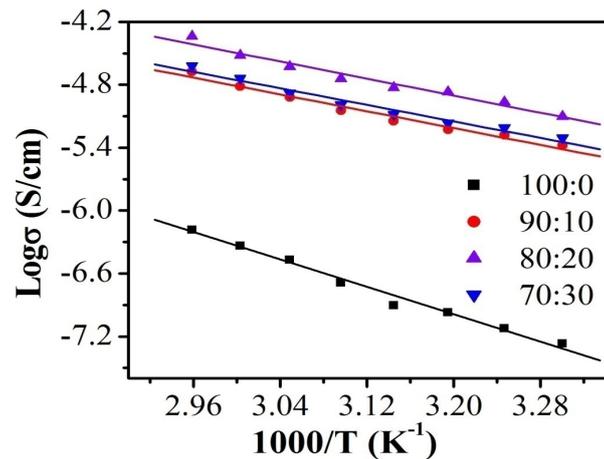


Fig. 3. Temperature dependent conductivity of PEG-  $\text{CH}_3\text{COONa}$  polymer electrolytes.

#### 4. Conclusion

In the present investigation, PEG modified by sodium acetate electrolytes were synthesized. The  $T_m$  of polymer electrolytes is lower than the pure PEG. Polymer electrolytes have a lower  $T_m$  than pure PEG. The lower  $T_m$  and lower heat of melting,  $H_m$ , are responsible for the drop in  $X_c$ . The percentage of salt loaded connected to a better ionic conductivity mechanism. The ionic conductivity rises linearly as a function of temperature reaching maximum to  $10^{-5} \text{ S cm}^{-1}$  near the melting point. The conduction mechanism was based on an Arrhenius-type thermally activated process, as evidenced by the temperature-dependent ionic conductivity.

#### References

- [1] M.B. Armand, Ann. Rev. Mater. Sci. 16 (1986) 245; <https://doi.org/10.1146/annurev.ms.16.080186.001333>
- [2] L. Jorissen, J. Garche, Hydrogen and Fuel Cell, Springer, 2016, pp 239-281; [https://doi.org/10.1007/978-3-662-44972-1\\_14](https://doi.org/10.1007/978-3-662-44972-1_14)
- [3] J.R. Mac Callum, C.A. Vincent (Eds.), Polymer Electrolyte Reviews, Elsevier, Amsterdam, 1987.
- [4] A.A. Latoszynska, P.L. Taberna, P. Simon, W. Wieczorek, Electrochim. Acta 242 (2017) 31; <https://doi.org/10.1016/j.electacta.2017.04.122>
- [5] T. Dam, N.K. Karan, R. Thomas, D.K. Pradhan, R.S. Katiyar, Ionics 21 (2015) 401; <https://doi.org/10.1007/s11581-014-1181-5>
- [6] A. Yoshino, Angew. Chem. Int. Ed. 51 (2012) 5798; <https://doi.org/10.1002/anie.201105006>
- [7] D. E. Fenton, J. M. Parker, P. V. Wriath, Polymer 14 (1973) 589; [https://doi.org/10.1016/0032-3861\(73\)90146-8](https://doi.org/10.1016/0032-3861(73)90146-8)
- [8] M. P. Armand, J. M. Chabagno, M. Diadat, Fast Ion Transport in Solids (Eds.) P. Vashistha, J.M. Mundy and G.K. Shen, North Holland, 1979, p. 135.
- [9] R. C. Agrawal, G. P. Pandey, J. Phys. D: Appl. Phys. 41 (2008) 223001; <https://doi.org/10.1088/0022-3727/41/22/223001>
- [10] A. R. Polu, R. Kumar, Bull. Mater. Sci., 37 (2014) 309; <https://doi.org/10.1007/s12034-014-0654-5>
- [11] Ch.V. Subba Reddy, A.K. Sharma, V.V.R. Narasimha Rao, Polymer 47 (2006) 1318; <https://doi.org/10.1016/j.polymer.2005.12.052>
- [12] D.F. Shriver, M.A. Ratner, Chem. Rev. 88 (1988) 109; <https://doi.org/10.1021/cr00083a006>
- [13] T. Miyamoto, K. Shibayama, J. Appl. Phys. 44 (1973) 5372; <https://doi.org/10.1063/1.1662158>