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# Effect of sodium salt in poly(ethylene oxide) electrolyte on initial discharge capacity of Na/poly(ethylene oxide)/S battery

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To investigate the effects of sodium salt in a poly(ethylene oxide) (PEO) electrolyte on the initial discharge properties of a Na/ S cell, various concentrations of NaCF<sub>3</sub>SO<sub>3</sub> from 0.1 to 2.0 m were added to the electrolyte. Scanning electron microscopy and differential scanning calorimetry results showed a continuous decrease in the crystallinity of the PEO electrolyte with increasing amounts of sodium salt. The ionic conductivity of the PEO electrolyte at 70 °C increased with increasing sodium salt concentration up to 0.33 m, at which point the highest ionic conductivity of  $1.732 \times 10^{-4}$  S cm<sup>-1</sup> was obtained. However, the ionic conductivity decreased at 2.0 m sodium salt. The same trend was seen in the initial discharge capacity, in that the highest value of 435 mAh g<sup>-1</sup> was achieved at a sodium salt concentration of 0.33 m. These results demonstrate that 0.33 m of sodium salt is the optimum composition for Na/S batteries.

Keywords: A. organic compounds, B. microstructure, D. electrochemical properties, D. ionic conductivity, D. energy storage.

# Introduction

Motivated by the safety issues of high-temperature Na/S batteries [1], low-temperature solid-state Na/ poly(ethylene oxide) (PEO)/S batteries have generated significant interest because they are safe and inexpensive and because they have a high theoretical energy density of 1270 Wh kg<sup>-1</sup> [2]. As a key component, PEO solid electrolytes [especially the (PEO)NaCF<sub>3</sub>SO<sub>3</sub> electrolyte system] have a number of advantages, such as fast ion transport below the melting temperatures of sodium and sulfur, flexibility, safety, and compactness [3-7].

Previously, many studies have focused on the charge carrier transport mechanism in PEO electrolytes [8, 9]. For example, Rhodes *et al.* reported cation-anion and cation-polymer interactions in (PEO)<sub>n</sub>NaCF<sub>3</sub>SO<sub>3</sub> ( $1 \le n \le 80$ ) electrolytes with different sodium salt concentrations [9]. Researchers have also investigated solutions to the drawbacks of PEO polymer electrolytes, such as their poor mechanical properties and low ionic conductivity below the melting temperature of sodium, which are to decrease the crystallinity of the polymer in order to improve the polymer chain mobility and increase the mechanical properties through the use of inorganic ceramic nanosized fillers [10, 11] and increase the

concentration of charge carriers such as lithium salt in the polymer electrolyte [6]. In other words, previous reports have focused on the physical properties of the PEO electrolytes themselves. It is also necessary to investigate an optimum PEO electrolyte for Na/S batteries. However, there are no studies on the relationship between the sodium salt concentration in the PEO electrolyte and the electrochemical properties of solid-state Na/PEO/S cells.

In this work, therefore, we studied the changes in the initial discharge properties of a solid-state Na/PEO/S cell as a function of the sodium salt concentration of NaCF<sub>3</sub>SO<sub>3</sub> in the PEO electrolyte.

# **Experiments**

The PEO electrolyte was prepared by dissolving PEO powder (MW =  $4 \times 10^6$  g mol<sup>-1</sup>, Aldrich) and NaCF<sub>3</sub>SO<sub>3</sub> in acetonitrile for 2 h. Then the solution was cast onto a glass dish and dried in a vacuum oven at 50 °C for 12 h [12]. The sodium salt content was varied through a [EO] : [Na<sup>+</sup>] ratio, which is the stoichiometric proportion of PEO ether units, ether oxygen (EO), to Na ions. The stoichiometric proportion in molality of NaCF<sub>3</sub>SO<sub>3</sub> per unit mass of PEO polymer was varied at 0.1, 0.12, 0.20, 0.33, and 2.0 m. The sulfur cathode for the Na/PEO/S battery consisted of sulfur, PEO, and carbon in a weight ratio of 60 : 20 : 20, and it was prepared as described previously [13]. The Na/PEO/S cells were discharged at 70 °C at a current of 50 mA g<sup>-1</sup>-sulfur

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(WBCS3000, WonATech). For the ionic conductivity measurement, an AC impedance test was carried out in a frequency range of  $10^5$ -0.1 Hz at 70 °C (CMS100 system, Gamry Instruments Inc.). The glass transition temperature ( $T_g$ ) of the polymer electrolyte was measured through differential scanning calorimetry (DSC, DSC2010, TA Instrument Inc.) under an argon stream of 80 mL min<sup>-1</sup> and a heat flow rate of 2 °C min<sup>-1</sup>. The morphologies of the polymer electrolytes were observed by scanning electron microscopy (SEM, JSM6400, JEOL).

## **Results and Discussion**

Fig. 1 shows SEM images of the surface morphologies of the PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>n</sub> electrolytes (0.1  $\leq n \leq 2.0$  m). The PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>0.1</sub> electrolyte had clear radial comb patterns several hundred micrometers in diameter, as indicated by the dashed circle in Fig. 1(a). However, these patterns became less visible and smaller with increasing sodium salt content, results that are well matched to those reported by Sreekanth et al. [14]. At n = 0.33 m, the polymer electrolyte had a spherulitic pattern several tens of micrometers in diameter, which decreased significantly to a few micrometers in size for n = 2.0 m. According to MacCallum and Vincent, [15]

spherulitic growth starts via sporadic nucleation and continues radially until the individual spherules impinge upon each other at straight boundaries. These results could indicate that the nucleation sites grew and the crystallinity of the PEO electrolyte decreased as the sodium salt content increased. The dimensions of spherulitic patterns depend on various factors that may control the nucleation density per unit area, such as the purity of the solution, film thickness



**Fig. 2.** DSC curves of PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>*n*</sub> electrolytes for *n* of (a) 0.1, (b) 0.12, (c) 0.20, (d) 0.33, and (e) 2.0 m.



Fig. 1. SEM images of surface morphologies of PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>n</sub> electrolytes for n of (a) 0.1, (b) 0.12, (c) 0.20, (d) 0.33, and (e) 2.0 m.

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**Fig. 3.** Ionic conductivities of PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>*n*</sub> electrolytes and the initial discharge capacities of Na/PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>*n*</sub>/S cells with a current density of 50 mAg<sup>-1</sup> at 70 °C for *n* of (a) 0.1, (b) 0.12, (c) 0.20, (d) 0.33, and (e) 2.0 m.

and growth rate, and uniformity of solvent removal [3]. It is believed that the concentration of sodium salt also significantly affects the structure of PEO solid electrolytes.

The thermal behavior of the PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>n</sub> electrolyte for various concentrations of sodium salt was characterized through DSC from 40 to 90 °C and the results are given in Fig. 2. There was an endothermic



**Fig. 4.** Initial discharge curves of Na/PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>*n*</sub>/S cell with current density of 50 mAg<sup>-1</sup> at 70 °C for *n* of (a) 0.1, (b) 0.12, (c) 0.20, (d) 0.33, and (e) 2.0 m.

peak at 69 °C for pure PEO, similar to results previously reported [16]. This endothermic peak is attributed to the glass transition of crystalline PEO. The glass transition temperature continuously decreased from 64.01 to 59.70 °C as the amount of sodium salt increased. This phenomenon may have been due to changes in the local structure of PEO from an ordered to a disordered arrangement by the



**Fig. 5.** SEM micrographs of sulfur electrodes for Na/PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>n</sub>/S cell after initial discharge: (a) Before test and for *n* of (b) 0.1, (c) 0.12, (d) 0.20, (e) 0.33, and (f) 2.0 m.

introduction of sodium salt, along with a decrease in the mechanical strength of the PEO electrolyte.

The ionic conductivity of the PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>n</sub> electrolyte and the initial discharge capacity of the Na/ PEO/S cell were then investigated as a function of the concentration of sodium salt at 70 °C and the results are presented in Fig. 3. The PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>n</sub> electrolyte showed a continuous increase in ionic conductivity to up n = 0.33 m, but the last concentration of 2.0 m produced a lower ionic conductivity as compared to the previous concentration of 2.0 m, which showed the highest value of  $1.732 \times 10^{-4}$  S cm<sup>-1</sup>. This tendency was different from the DSC results, which showed continuous decreases in the crystallinity. The ionic conduction in a PEO electrolyte is demonstrated by the movement of polymer chain segments. These mean that the addition of sodium salt made it easier through the decrease in the crystallinity of PEO polymer to some degree, as seen in the results of Figs. 1 and 2. However, there is another factor that controls the ionic conduction of sodium ions. Melchiors et al. [17] reported that, at high salt concentrations, ion clusters form and the polarity of the medium increases. The formation of ion clusters reduces the charger carrier number and their mobility, whereas the increase in polarity decreases the ion mobility. We believe that these phenomena took place for n = 2.0 m, resulting in a decrease in ionic conductivity.

The initial discharge curves of the Na/PEO (NaCF<sub>3</sub>SO<sub>3</sub>)<sub>n</sub>/S cell at a current density of 50 mA g<sup>1</sup> and a temperature of 70 °C are shown in Fig. 4. At n = 0.33 m, the Na/S cell showed the highest initial discharge capacity of 435 mAh g<sup>-1</sup>. The discharge curve of the Na/PEO (NaCF<sub>3</sub>SO<sub>3</sub>)<sub>n</sub>/S cell at this concentration had two clear plateau regions at 2.3 and 1.75 V. These results imply that the ionic conductivity of the PEO electrolyte is very important to the electrochemical properties of the Na/PEO/S cell at this current density.

Changes in the surface morphology of the sulfur electrode as a function of the amount of sodium salt in the PEO electrolyte after the initial discharge are shown in Fig. 5. The surface morphology of the sulfur electrode with a PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>0.1</sub> electrolyte was similar to that of the original sulfur electrode. However, agglomeration of discharge products on the sulfur electrode with the PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>0.12</sub> electrolyte was observed, and the agglomeration increased gradually with increasing sodium salt concentration. However, at the final composition of PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>2.0</sub>, large agglomeration was observed . This means that the interactions between the PEO electrolyte and the sulfur electrode strongly depend on the concentration of sodium salt.

#### Conclusions

A PEO(NaCF<sub>3</sub>SO<sub>3</sub>)<sub>n</sub> electrolyte was successfully prepared

using concentrations of sodium salts from 0.1 to 2.0 m. As the concentration of the sodium salt increased, the crystallinity of the PEO electrolyte continuously decreased. The ionic conductivity of the PEO electrolyte continuously increased up to n = 0.33 m but it decreased at n = 2.0 m. The highest ionic conductivity of  $1.732 \times 10^{-4}$  S cm<sup>-1</sup> was obtained for n = 0.33 m. The initial discharge capacity of the Na/PEO/S cell was 435 mAh g<sup>-1</sup> for n = 0.33 m. After the initial discharge, the surface morphology showed an agglomeration on the sulfur electrode, which is believed to have resulted from discharge products and the PEO electrolyte. These results demonstrated that PEO(NaCF<sub>3</sub> SO<sub>3</sub>)<sub>0.33</sub> was the optimum composition for Na/S batteries.

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