

## Effect of Nano-fillers on the Conductivity and Structural Properties of EMIHSO<sub>4</sub>-based Polymer Electrolytes

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A non-fluorinated ionic liquid (IL)-polymer electrolyte has been developed for flexible electrochemical capacitors. Thermal and structural characterizations of this polymer electrolyte revealed a positive effect of IL on reducing the crystallinity of the polymer electrolyte [1]. To further enhance its performance at ambient temperature, we investigated the effect of inorganic nano-fillers on the ionic conductivity and structure stability of the polymer-IL electrolytes.

1-Ethyl-3-methylimidazolium hydrogensulfate (EMIHSO<sub>4</sub>) was integrated with polyethylene oxide (PEO) to form PEO-EMIHSO<sub>4</sub> electrolytes. The ionic liquid composition is reported as weight ratio with respect to the polymer, referred as (PEO:EMIHSO<sub>4</sub>). Nanosized silica (SiO<sub>2</sub>, amorphous) and titania (TiO<sub>2</sub>, anatase) fillers in 3 wt% of the total polymer and IL weight were dispersed in PEO-EMIHSO<sub>4</sub> mixture. The solution-cast PEO-EMIHSO<sub>4</sub> thin films were sandwiched between stainless steel electrodes for electrochemical characterization. Differential scanning calorimetry (DSC), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) were used for thermal and structural analyses.

The effect of fillers on the ionic conductivity was investigated for PEO-EMIHSO<sub>4</sub> at 1:3 composition. SiO<sub>2</sub> and TiO<sub>2</sub> fillers showed a different impact on the ionic conductivity of PEO-EMIHSO<sub>4</sub>. Figure 1 shows the temperature dependence of ionic conductivity for filler-free PEO-EMIHSO<sub>4</sub> and PEO-EMIHSO<sub>4</sub> electrolytes containing 3 wt% SiO<sub>2</sub> and TiO<sub>2</sub>. The addition of SiO<sub>2</sub> increased the ionic conductivity of PEO-SiO<sub>2</sub>-EMIHSO<sub>4</sub> more than 2-fold and reached 1.82 mS/cm, comparable to that of liquid EMIHSO<sub>4</sub> at room temperature [1]. On the other hand, the trend of conductivity for PEO-TiO<sub>2</sub>-EMIHSO<sub>4</sub> electrolytes remained almost the same as that of filler-free electrolyte. Figure 1 also shows the activation energy of ionic conduction for temperatures below and above the melting point of crystalline phase of PEO. At low temperatures, the higher activation energy of PEO-TiO<sub>2</sub>-EMIHSO<sub>4</sub> implies that the ionic conduction was hindered compared to that of filler-free electrolyte. In the case of PEO-SiO<sub>2</sub>-EMIHSO<sub>4</sub>, the increase in ionic conductivity throughout the entire temperature range suggests that the addition of SiO<sub>2</sub> was not only effective in retaining the amorphous phase at lower temperatures but also improved the ionic conduction. The DSC thermograms of all three PEO-EMIHSO<sub>4</sub> electrolytes are shown in Figure 2. With the addition of SiO<sub>2</sub> filler, the crystallinity of PEO-SiO<sub>2</sub>-EMIHSO<sub>4</sub> decreased slightly compared to that of filler-free electrolyte, and no obvious T<sub>g</sub> was found. In contrast, the crystallinity of the electrolyte with TiO<sub>2</sub> increased by ca. 10%. The effect of fillers on the conductivity of PEO-EMIHSO<sub>4</sub> can be attributed to the difference in their structure.

Thermal and structural characterizations support the notion that the crystalline TiO<sub>2</sub> may act as a

nucleation center for crystallinity [2], whereas the amorphous SiO<sub>2</sub> can restrain the recrystallization of polymer in PEO-EMIHSO<sub>4</sub> system. Detailed analyses on the effect of these nano-fillers on ionic conduction and polymer structure will be discussed.

### References:

- [1] S. Ketabi, K. Lian, *Solid State Ionics*, 227, 86, 2012.
- [2] B.-K. Choi, Y.-W. Kim, K.-H. Shin, *J. Power Sources*, 68, 357, 1997.

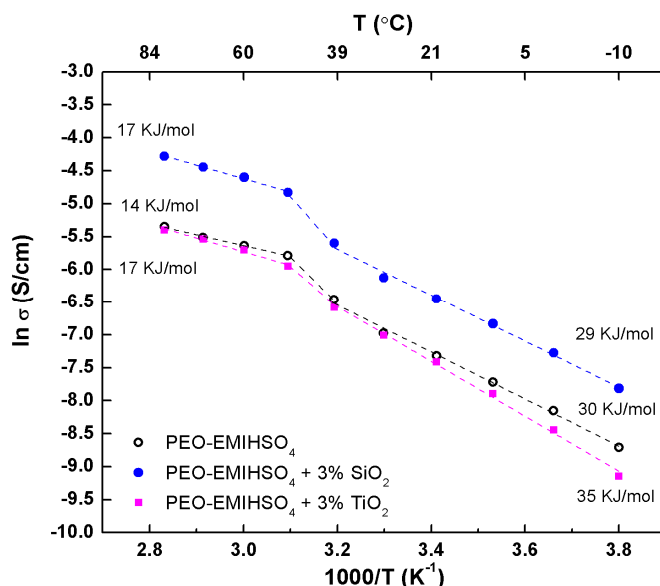


Figure 1. Temperature dependence of ionic conductivity for PEO-EMIHSO<sub>4</sub> (1:3) electrolytes: filler-free, with 3wt% SiO<sub>2</sub> and TiO<sub>2</sub>.

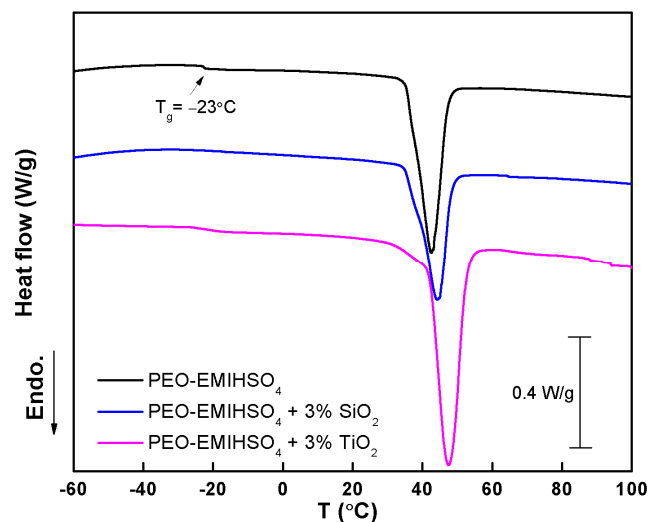


Figure 2. DSC thermograms for PEO-EMIHSO<sub>4</sub> (1:3) electrolytes: filler-free, with 3wt% SiO<sub>2</sub> and TiO<sub>2</sub>.