Mixed-Molecular Weight Nanocomposite Polymer Electrolytes

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Introduction

Polymer electrolytes are attractive for rechargeable lithium batteries since they promise improved safety and reliability, better electrode/electrolyte stability, and mechanical strength compared to traditional liquid electrolytes.[1] Polymer electrolytes consisting of poly(ethylene oxide) (PEO) and lithium salts have been extensively studied.[2-3] However, electrolytes based on high-molecular weight (MW) PEO do not possess sufficient conductivity to be operated at ambient temperature. Fumed silica-based composite electrolytes developed in our lab show improved mechanical strength, interfacial stability with lithium for both low-MW and high-MW PEO.[4-5] In this study, we investigate mixed-MW (low- + high-MW) fumed silica-based polymer electrolytes to evaluate the effects of adding low-MW component to high-MW PEO on ionic conductivity, thermal, and rheological properties.

Experimental

PEO (MW= 6 × 10^5, DOW), polyethylene glycol dimethylether (PEGdM, MW=250, Aldrich), lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 3M), and silanol-terminated fumed silica (Aerosil A200) were dried prior to use. Samples were prepared by weighing stoichiometric amounts of the components and then dissolving in acetonitrile (Aldrich). The slurry was cast onto Teflon plates, and the solvent was evaporated at room temperature.

Conductivity was measured using ac impedance spectroscopy with an EG&G 273 potentiostat and EG&G 5210 lock-in amplifier. The conductivity cell is a sealable vial with two platinum wires. Thermal properties were measured using a TA instrument DSC Q100. Rheological measurements were conducted using a TA AR2000 stress rheometer.

Results and Discussion

Conductivity was measured for $P(EO)_{20}LiTFSI$ + 10% A200 composites with different mass ratios of PEO (600K) to PEGdM (250): 100/0, 80/20, 67/33, 50/50, 33/67, and 20/80. The conductivity increases with amount of low-MW PEG-dM from 15 to 90 °C (Figure 1), with the increase being more pronounced in the low-temperature range.

Differential scanning calorimetry (DSC) measurements were performed for the above composite mixed-MW PEO electrolytes. The melting and crystallization temperatures decrease with amount of low-MW PEGdM, and the heat of fusion follows the same trend.

The dynamic rheology was measured for composite electrolytes with high-to-low-MW mass ratios of 100/0, 80/20, 67/33, 50/50 at 80°C. We did not measure the 33/67 and 20/80 compositions since they do not form a continuous film. A significant aspect of our findings is that the corresponding moduli of the blends are higher than the composite consisting of the high-MW component (Figure 2). Dynamic rheological results for the composite mixed-MW systems reveal that the elastic modulus increases and goes through a maximum as the concentration of PEGdM increases in the blends. These results are impactful and interesting since it was expected that the low-MW component would plasticize the high-MW component and produce a monotonic decrease in elastic modulus. We have dynamic strain sweep results (Figure 3), which show the same trend as the above dynamic frequency sweep results. It is found that the yield stress is also increased by adding suitable amount of low-MW component. There seems to be a synergistic mechanism of network formation among the high-MW PEO, fumed silica, and low-MW PEGdM than what occurs in the presence of only one of the polymer components.

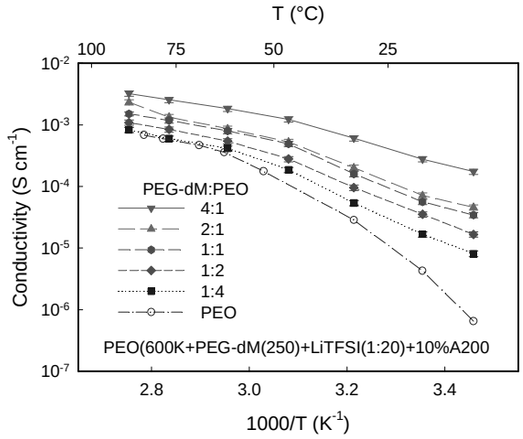

Fig 1. Conductivity of mixed-MW nanocomposite polymer electrolytes.

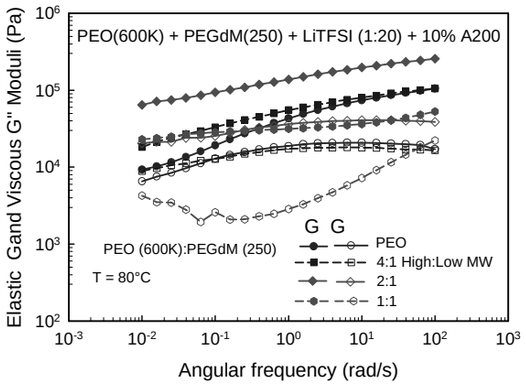

Fig 2. Dynamical frequency sweep of mixed-MW nanocomposite polymer electrolytes.

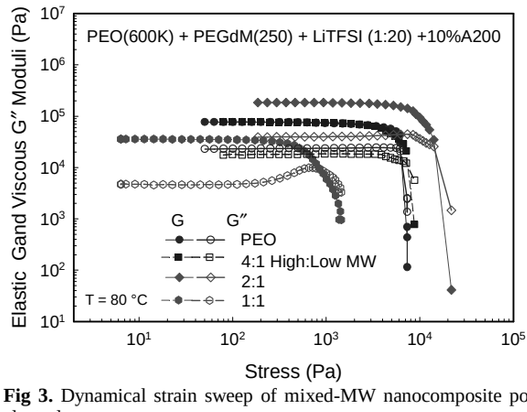

Fig 3. Dynamical strain sweep of mixed-MW nanocomposite polymer electrolytes.

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