

# Effects of Inorganic Fillers on Electrochemical and Rheological Properties of Composite Polymer Electrolytes

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## Introduction

Composite polymer electrolytes (CPEs) with significant lithium-ion conductivity, enhanced ion-transport properties, and good compatibility with lithium metal electrodes have attracted attention for rechargeable lithium batteries.<sup>1,2</sup> Conventional CPEs are normally formed by dispersing ceramic fillers (e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ) into high-molecular weight (MW) poly(ethylene oxide) (PEO) polymers doped with lithium salts.<sup>1,2</sup> Our group, however, is developing a new type of CPE based on low-MW PEO with fumed silica ( $\text{SiO}_2$ ) fillers.<sup>3-5</sup> Our CPEs yield a much higher conductivity ( $>10^{-3}$  S/cm at room-temperature)<sup>3</sup> than conventional CPEs ( $10^{-5}$  to  $10^{-4}$  S/cm at room-temperature) due to less rigidity of the polymer chain. Solid-like mechanical strength (elastic modulus  $G' > 10^5$  Pa) and a significant improvement of lithium interfacial stability with incorporation of the fumed silica is also observed during cell cycling.<sup>3-5</sup>

The purpose of this work is to investigate the effects of varied inorganic fillers such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and mixtures of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  on electrochemical and rheological properties of CPEs. One common feature of above-mentioned fillers and fumed silica is that they all have hydroxyl surface groups that may allow them to flocculate or form three-dimensional networks through hydrogen bonds. In addition, their surface chemistry can be modified by replacing these hydroxyl groups with other functional groups through chemical reactions. The ultimate purpose of this work is to explore the underlying mechanism that determines the effects of fillers on performance of composites and further optimize the properties of the composites.

## Experimental

Four types of fillers, all commercially available from Degussa, are employed in this work:  $\text{TiO}_2$  P25,  $\text{Al}_2\text{O}_3$  C, and two types of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  mixtures (Aerosil COK84 and Aerosil Mox 170). All materials are dried at  $110^\circ\text{C}$  under vacuum for 2 days prior to use. Composite polymer electrolytes are prepared by dispersing fillers in the solution of poly(ethylene glycol) dimethyl ether ( $M_n = 250$ ) and lithium bis(trifluoromethylsulfonyl)imide ( $\text{Li}[\text{N}(\text{SO}_2\text{CF}_3)_2]$ , LiTFSI) (Li:O=1:20) in an Argon-filled glove box. The water content of electrolytes is about 20 ppm. Ionic conductivity of CPEs was measured using AC impedance spectroscopy controlled by EG&G 273 potentiostat and EG&G 5210 amplifier. The frequency and temperature ranges are 100 mHz to 100Kz and  $0^\circ\text{C}$  to  $100^\circ\text{C}$ , respectively.

## Results and Discussion

Preliminary conductivity data of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  composites are shown as a function of temperature in Figures 1 and 2. The addition of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  fillers up to 20 wt% shows very little effect on conductivity: there is virtually no difference between base liquid electrolyte and 5 wt% composites for both cases; conductivity decreases slightly with the additional

increase of filler concentration. Both  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  composites show very high room-temperature conductivity, which is greater than  $1.6 \times 10^{-3}$  S/cm even for the worst scenario (i.e., 20 wt% composites). Little effect of fumed silica on composites' conductivity were also reported previously,<sup>3</sup> which gives us a leverage to improve other properties of composites without diminishing their conductivity significantly.

Work is underway to investigate the effects of inorganic fillers on other electrochemical and rheological properties of composite polymer electrolytes. We are in the process of investigating lithium transference number, interfacial stability, and cell-cycling of these composites and correlate them with the rheological properties of materials to gain a better understanding of the filler-filler and filler-base electrolyte interactions and how these interactions affect the performance of the composites.

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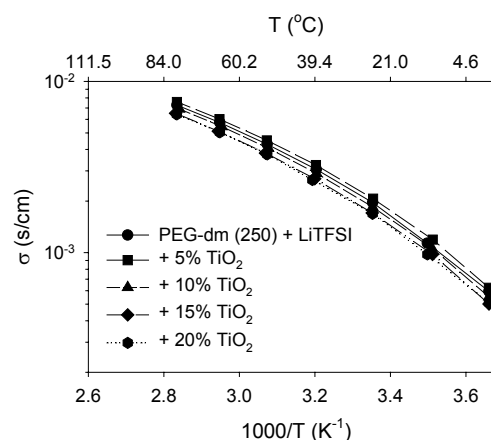


Figure 1. Ionic conductivity of  $\text{TiO}_2$  composite polymer electrolytes and base-liquid electrolyte.

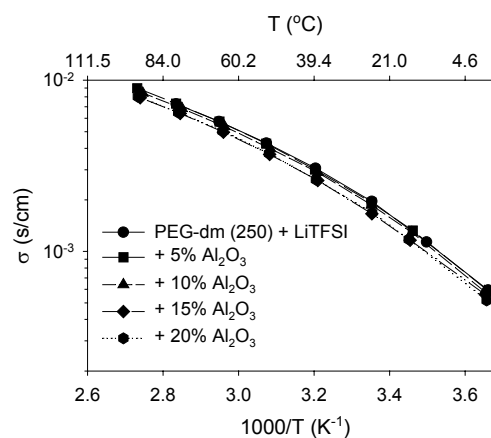


Figure 2. Ionic conductivity of  $\text{Al}_2\text{O}_3$  composite polymer electrolytes and base-liquid electrolyte.