The effect of nano-fillers on a silicotungstic acid-based polymer-in-salt electrolyte

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INTRODUCTION

Polymer electrolytes are key enabling materials for energy storage devices that require light weight, thin and flexible form factors. High solid-state conductivity (0.01 Scm⁻¹ to 0.02 Scm⁻¹) of silicotungstic acid (SiWA)-H₃PO₄-poly(vinyl alcohol) (PVA) polymer electrolytes was demonstrated for solid electrochemical capacitors (ECs) [1, 2]. However, their environmental stability needs to be further improved. Inorganic nano-fillers could be used as additives to enhance the properties of polymer electrolytes. In this work, we performed a comparative study of the effect of nano-TiO₂ and nano-SiO₂ fillers on the proton conductivity of such SiWA-H₃PO₄-PVA electrolytes.

EXPERIMENTAL

Aqueous polymer electrolyte precursor solutions with a mixture of PVA, SiWA, H₃PO₄ were prepared first. Nano-TiO₂ or nano-SiO₂ was added as the inorganic oxide filler. The processed SiWA-H₃PO₄-PVA/TiO₂ (or SiO₂) films had a composition of 80 wt. % SiWA, 10 wt. % H₃PO₄, 5 wt. % PVA, and 5 wt. % TiO₂ (or SiO₂). For comparison, a SiWA-H₃PO₄-PVA film with the same content of ionic conductive materials and 10 wt. % PVA was studied as well.

Stainless steel foils were used as planar metallic electrodes. The cell was assembled through a lamination process [1, 2]. AC impedance was measured under different temperatures.

RESULTS AND DISCUSSION

The conductivity of electrolytes with and without fillers was monitored under ambient conditions over time as shown in Fig. 1. SiWA-H₃PO₄-PVA had an average conductivity of 0.011 Scm⁻¹. However, it showed a strong fluctuation with relative humidity compared with the electrolytes with fillers. Although the SiO₂-containing electrolyte was slightly more resistive than the other two, it demonstrated a much better stability (i.e. the lowest fluctuation over time) in Fig. 1.

Arrhenius plots of proton conductivity (σ) for all three electrolytes are shown in Fig. 2. The proton conductivity of all electrolytes increased with temperature. The activation energy of SiWA-H₃PO₄-PVA was 9.15 kJmol⁻¹ from 273 K to 323 K. The addition of TiO₂ or SiO₂ increased the activation energy within this temperature range, especially for the electrolyte with SiO₂. The higher activation energy in the SiO₂-containing electrolyte could be related to a more pronounced barrier effect on proton transportation. Nevertheless, the low activation energy of all electrolytes confirmed the presence of a proton hopping mechanism.

However, an increase in activation energy for all three electrolytes was observed for temperature below 273 K. The activation energy of SiWA-H₃PO₄-PVA increased to 33.21 kJmol⁻¹, reflecting a diffusion controlled proton transportation in the matrix. However, TiO₂ and SiO₂ had different effect on the activation energy. The one with TiO₂ had a slight decrease to 32 kJmol⁻¹ while the one with SiO₂ had an increase to 34 kJmol⁻¹. The causes of these effects will be discussed. In addition, structural characterization and solid EC cell performance based on these electrolytes will also be presented.

REFERENCES


Fig. 1. Proton conductivity tracking of solid polymer electrolytes SiWA-H₃PO₄-PVA (■), SiWA-H₃PO₄-PVA/TiO₂ (▲), and SiWA-H₃PO₄-PVA/SiO₂ (▲) over time under ambient conditions

Fig. 2. Temperature dependence of proton conductivity of solid polymer electrolytes SiWA-H₃PO₄-PVA (■), SiWA-H₃PO₄-PVA/TiO₂ (▲), and SiWA-H₃PO₄-PVA/SiO₂ (▲) at 50% RH