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)-H_3PO_4-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-TiO_2 and nano-SiO_2 fillers on the proton conductivity of such SiWA-H_3PO_4-PVA electrolytes.

EXPERIMENTAL

Aqueous polymer electrolyte precursor solutions with a mixture of PVA, SiWA, H_3PO_4 were prepared first. Nano-TiO_2 or nano-SiO_2 was added as the inorganic oxide filler. The processed SiWA-H_3PO_4-PVA/TiO_2 (or SiO_2) films had a composition of 80 wt. % SiWA, 10 wt. % H_3PO_4, 5 wt. % PVA, and 5 wt. % TiO_2 (or SiO_2). For comparison, a SiWA-H_3PO_4-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-H_3PO_4-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 SiO_2-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-H_3PO_4-PVA was 9.15 $kJmol^{-1}$ from 273 K to 323 K. The addition of TiO_2 or SiO_2 increased the activation energy within this temperature range, especially for the electrolyte with SiO_2. The higher activation energy in the SiO_2-containg 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-H_3PO_4-PVA increased to 33.21 $kJmol^{-1}$, reflecting a diffusion controlled proton transportation in the matrix. However, TiO_2 and SiO_2 had different effect on the activation energy. The one with TiO_2 had a slight decrease to 32 $kJmol^{-1}$ while the one with SiO_2 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

[1] H. Gao and K. Lian, *J. Power Sources*, **196**, 8855 (2011).
[2] H. Gao, H. Wu and K. Lian, *Electrochem. Commun.*, **17**, 48 (2012).

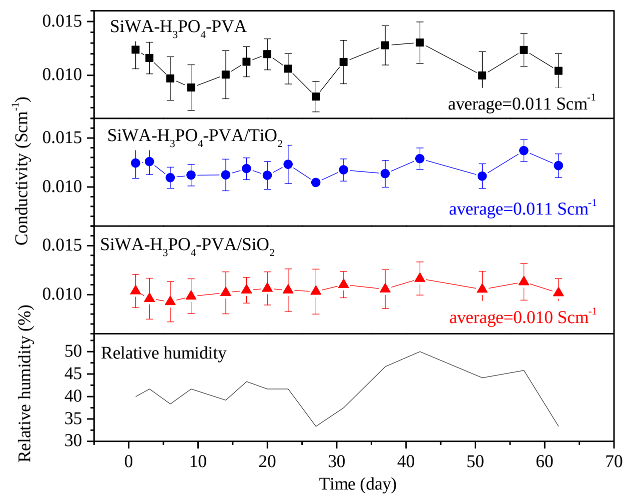

Fig. 1. Proton conductivity tracking of solid polymer electrolytes SiWA-H_3PO_4-PVA (■), SiWA-H_3PO_4-PVA/TiO_2 (●), and SiWA-H_3PO_4-PVA/SiO_2 (▲) over time under ambient conditions

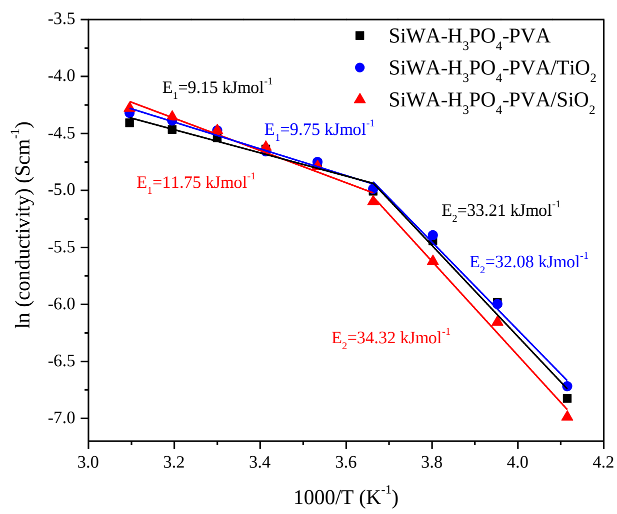

Fig. 2. Temperature dependence of proton conductivity of solid polymer electrolytes SiWA-H_3PO_4-PVA (■), SiWA-H_3PO_4-PVA/TiO_2 (●), and SiWA-H_3PO_4-PVA/SiO_2 (▲) at 50% RH