Protonic Conductivity Measurements of $CsHSO_4/SiO_2$ Composite Electrolyte for Intermediate Temperature Fuel Cell

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1. Introduction

Protonic conductivity measurements in pure $CsHSO_4$ and $CsHSO_4/SiO_2$ systems were carried out in the temperature range of 350 K to 460 K, aiming at developing a solid inorganic electrolyte for intermediate temperature fuel cell. We discuss the influence of heterogeneous SiO_2-doping into $CsHSO_4$ salt on the protonic conductivity as a function of mol ratio of SiO_2 by AC impedance spectroscopic measurements.

2. Experimental

$CsHSO_4/SiO_2$ composites were prepared by grinding in an agate mortar for 30 minutes, and then pressed at 3t/cm^2 and finally calcined at 470 K for 1 h in an air. SiO_2 with meso-pores (particle size: 1.3μm, meso-pore diameter: 22 nm, specific surface area: 300 m^{2}g^{-1}) was used in the present experiments. The conductivity measurements were carried out with Ag-electrodes in Ar atmosphere by Hewlett Packard 4192A impedance analyzer over frequency range of 10Hz-10MHz.

3. Results and Discussions

3-1 Conductivity of $(1\text{-}x)CsHSO_4/xSiO_2$ composite

The temperature dependencies of conductivity of $CsHSO_4/SiO_2$ were presented in Fig.1. The mol ratio of SiO_2, x, of $(1\text{-}x)CsHSO_4/xSiO_2$ composites was varied from 0 to 0.65. The conductivities in both the pure and composites systems abruptly changed at around 410 K from low temperature phase (350-390 K) to high temperature phase (420-460 K). In pure $CsHSO_4$, the conductivity-increase of about 3 magnitudes was observed at around 410 K, which was accompanied by a structural phase transition (monoclinic → tetragonal). In $CsHSO_4/SiO_2$ composites systems, at any mol ratio of SiO_2, the conductivity at the low temperature phase increased about one magnitude in comparison with pure $CsHSO_4$. The maximum conductivity at the high temperature phase was observed at x = 0.15, while the conductivity at the high temperature phase became smaller with an increase of SiO_2 mol fraction.

3-2 Impedance spectra

The impedance plots at 403 K with various mol ratios were shown in Fig.2. While the impedance of the pure $CsHSO_4$ and the composites with low mol fraction of SiO_2 (x = 0.15) showed one semicircle, two semicircles appeared in the composites with high mol ratio of SiO_2 (x = 0.45, 0.60). Thus, we tried to separate and assign the impedance spectra, assuming an equivalent circuit consisted of a series circuit of two parallel circuits of a resistance and a capacitance. As seen in the Fig.2, the high frequency semicircles became smaller with the increase of SiO_2 additives. On the contrary, low frequency semicircles became bigger. It was considered that this trade-off relation for resistances of high and low frequency semicircles resulted in the maximum conductivity at a relevant mol ratio of SiO_2. The values of capacitance of high frequency semicircles are similar to that of pure $CsHSO_4$ (5.2×10^{-10}F), and those of the low frequency semicircles are larger by 1-2 orders, compared with pure $CsHSO_4$. Therefore, it is considered that high frequency semicircles are derived from the proton conduction of bulk and interface transfer between $CsHSO_4$ and SiO_2. This interface phase probably enhances the protonic conductivity. Low frequency semicircles are associated with the slow proton conduction at the boundary inhibited by the SiO_2 particles. Thus, by controlling the dispersed structure of the SiO_2 particles, protonic conductivity can be improved. We consider that further investigations are necessary with the samples prepared with a variety of SiO_2-characteristics, mixing methods, and structures in $CsHSO_4/SiO_2$ systems.

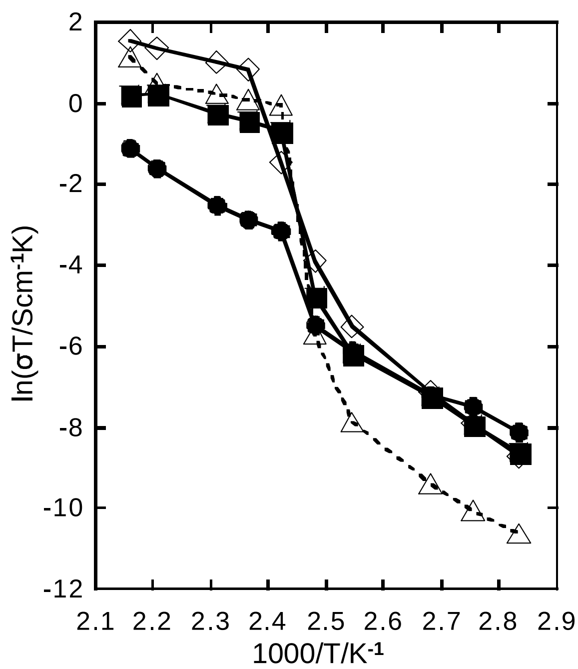

Fig.1 Temperature dependences of the conductivity of $(1\text{-}x)CsHSO_4/xSiO_2$ composites with different SiO_2 contents and pure $CsHSO_4$ on cooling process. △ : Pure $CsHSO_4$ ◇: x = 0.15 ■: x = 0.40 ●: x = 0.65

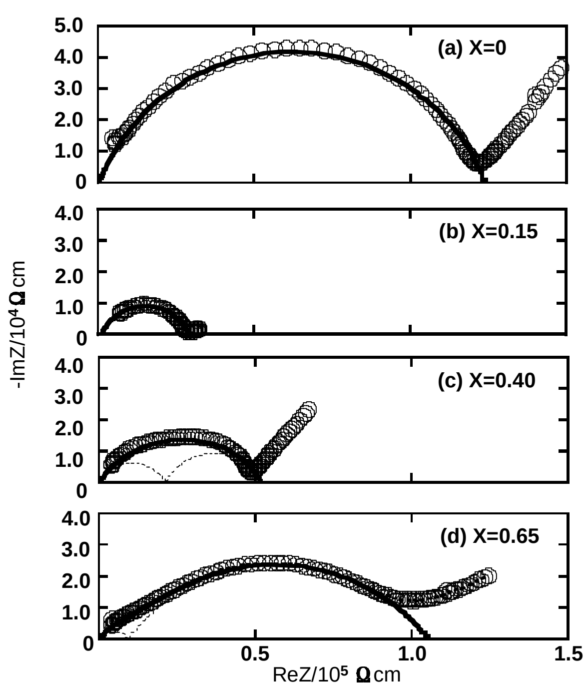

Fig.2 Typical impedance plots of $(1\text{-}x)CsHSO_4/xSiO_2$ composites at 403 K in Ar atmosphere. Open circle: experimental value; Solid line: fitting curve; Dotted line: deconvoluted semicircles of the fitting curve
(a) Pure $CsHSO_4$ (b) x = 0.15 (c) x=0.40 (d) x = 0.65