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Preparation and Proton Conductivity of a Novel Polymer Composite Membrane PVDF- $CsAl(SO_4)_2 \cdot 12H_2O$

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Abstract: *A novel polymer composite membrane PVDF-*$CsAl(SO_4)_2 \cdot 12H_2O$ *with high conductivity within a wide temperature range (30-140 °C) is synthesized by composing PVDF and conductors* $CsAl(SO_4)_2 \cdot 12H_2O$*. A sharp increase of the conductivity has been observed at around 90 °C, which was due to the release of the crystal water in the* $CsAl(SO_4)_2 \cdot 12H_2O$*. The highest conductivity of* 0.45×10^{-3} $S \cdot cm^{-1}$ *was obtained at 140°C , The novel polymer composite membrane PVDF-*$CsAl(SO_4)_2 \cdot 12H_2O$ *described here can be an attractive candidate as electrolyte in the low and medium fuel cell.*

Keywords: Proton exchange membrane fuel cells; Polymer composite membrane; Proton conductivity

1. INTRODUCTION

The interest of developing fuel cell arises from its relatively high efficiencies in energy conversion and low-level pollutant emission in comparison to the fossil fuel based internal combustion engines. Nafion-based proton exchange membrane fuel cells (PEMFCs) are generally considered to be the promising approach for mobile application in the future [1, 2]. Currently the most studied membranes include perfluorosulfonic acid membranes, non-fluorinated membranes, polymer blends and anhydrous polymer acid-base complex membranes. However, the application temperature of these membranes is less than 100°C. Furthermore, they are permeable to methanol and hydrogen, which lowers the fuel efficiency [2]. Recently, many novel proton-conducting solid acids electrolytes working at mediate temperatures (100-300°C) without external humidification have been developed because of their high proton conductivities and phase-transition behaviors. However, solid acids have not been considered as viable fuel-cell electrolyte alternatives owing to their water solubility and poor mechanical behavior. To address these issues, composite membranes containing inert polymers such as polyvinylidene fluoride (PVDF) and inorganic materials with high proton conductivities have been widely studied [3-5].

In our previous research, the mesoporous alumina with a high protonic conductivity at low temperature has been synthesized [6, 7]. In the present study, A novel polymer composite membrane was prepared by compositing the proton conductor $CsAl(SO_4)_2 \cdot 12H_2O$ with PVDF. The crystal structure, proton conductivity and thermal stability were investigated. Results indicate that the conductivity of the composite membrane is improved within the low-temperature range and has a sharp increase at 90°C, which indicates its viability for use as a low and medium proton exchange membrane.

2. EXPERIMENTAL

Polycrystalline $CsHSO_4$ was obtained by the evaporation of an aqueous solution containing equimolar amounts of Cs_2SO_4 (ACROS, purity > 99%) and H_2SO_4 at 80°C for 1 day. The X-ray diffraction (XRD) pattern confirms the formation and purity of $CsHSO_4$.

Mesoporous Al_2O_3 was synthesized using a sol-gel method described in the literature [8]. The $CsAl(SO_4)_2 \cdot 12H_2O$ conductor was prepared by mechanically mixing the polycrystalline $CsHSO_4$ powders and mesoporous Al_2O_3 powders with the molar ratio 2:3, followed by thermal treatment at 250 °C for 10 h. The prepared $CsAl(SO_4)_2 \cdot 12H_2O$, $CsHSO_4$ and mesoporous Al_2O_3 were chosen

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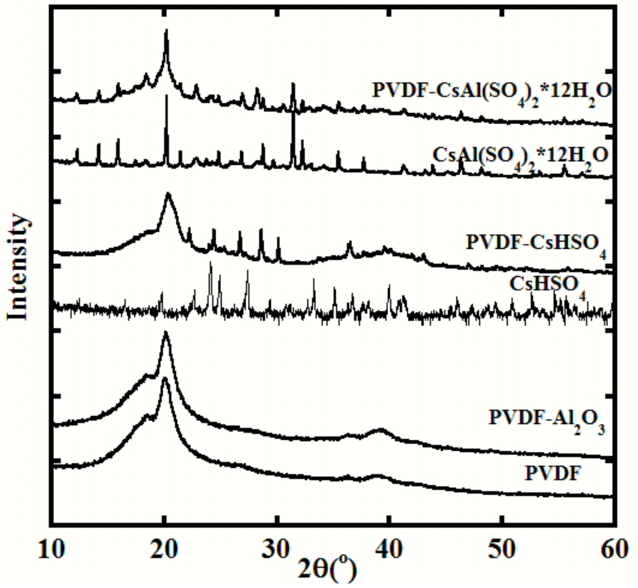

Figure 1. X-ray powder diffraction patterns of membranes.

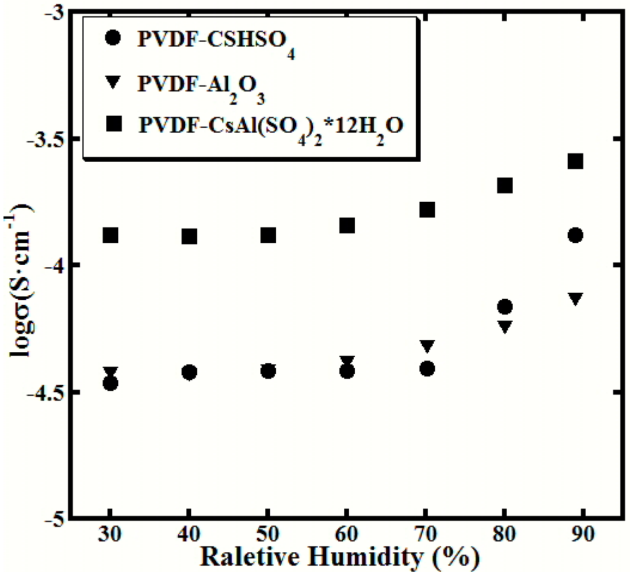

Figure 2. The humidity dependence of conductivities for different membranes at 30℃.

as conductors. The novel polymer composite membranes were prepared by composing PVDF (Shanghai 3F FR921) and conductors. 3 g PVDF powder was dissolved in 25 mL dimethylacetamide (DMAC) by stirring at 50°C. The conductor was then ultrasonically dispersed into the solution. The weight ration of PVDF to conductor was controlled as 3:1. After physical stirring for 30 min and ultrasonic oscillation for 10 min, the white colloidal solution obtained was cast onto a glass plate using an adjustable coating instrument to produce the membrane, which was then dried in vacuum at 50 °C for 24 h. The thickness of the membrane can be controlled within a range of 50 μm-200 μm [9].

The crystal structure of the prepared composite membrane was characterized by using XRD instrument (X'Pert Pro Holland, CuK$_\alpha$ radiation) operating at 40 kV and 30 mA. The 2θ range in the XRD patterns was measured from 10° to 80° with interval of 0.02° at a constant scan rate of 8° min^{-1}. The analysis of thermogravimetric and differential scanning calorimeter (TG-DSC) was performed with a METTLER TOLEDO STAR instrument at a heating rate of 2 °C min^{-1} from room temperature to 300 °C. The proton conductivity of membrane was measured by AC impedance spectroscopy with Agilent 4294A impedance spectroscopy instrument in the range of 40 Hz to 30 MHz. The membrane was sandwiched between two stainless steel electrodes and placed in a constant temperature and humidity chamber to measure the proton conductivity. The temperature and the humidity in the chamber can be controlled within the range of -20 °C ~+150 °C and 20 ~ 98%RH.

3. RESULTS AND DISCUSSION

3.1. Structure analysis

The X-ray diffraction patterns of composite membranes are shown in Fig. 1. In the sprectrum of PVDF-CsAl(SO$_4$)$_2$·12H$_2$O, diffraction, peaks are present both from PVDF and CsAl(SO$_4$)$_2$·12H$_2$O. In the sprectrum PVDF-Al$_2$O$_3$ and PVDF-CsHSO$_4$, the diffraction peaks from PVDF are still existed. No Al$_2$O$_3$ diffraction peaks are found because Al$_2$O$_3$ is amourphous [6]. No typical diffraction peaks of CsHSO$_4$ are observed, which demonstrates that the structure of CsHSO$_4$ crystal has been changed.

3.2. Proton conductivity of membranes

Figure 2 shows the relative humidity (RH) dependence of proton conductivity for composite membranes at 30 °C. The conductivities of all composite samples increase with increasing humidity, which demonstrates that adsorbed physical water has contribution to the proton conductivity of these membranes in the low temperature. At 30 °C, PVDF-CsAl(SO$_4$)$_2$·12H$_2$O apparently has the highest conductivity within humidity range 30%-90% RH.

Figure 3 shows the temperature dependence of the conductivities for different membranes. The relative humidity is about 55% RH below 100 °C and 10% RH above 100 °C, respectively. The conductivities of all membranes increased with increasing temperature. Membrane PVDF-CsAl(SO$_4$)$_2$·12H$_2$O showed the highest conductivity within the whole temperature range (30-140 °C) and the conductivity at 30 °C and 55% RH was approximately 0.5 magnitude higher than that of other samples , which is accordant with the data reported in fig.2. In particular, the conductivity of PVDF-CsAl(SO$_4$)$_2$·12H$_2$O had a sharp increasing around 90 °C and then kept a steady increase trend in the higher temperature and lower humidity range. The highest conductivity of 0.45×10^{-3} S·cm^{-1} was obtained at 140°C. For the membrane PVDF-CsHSO$_4$, no rapid increase of the conductivity was observed within the range of 140-150 °C.

3.3. Thermal analysis

The results of TG (a)-DSC (b) analysis are shown in Fig. 4. The TG curves of all samples had a weight loss below the boiling point of physically water. And for the sample PVDF-CsAl(SO$_4$)$_2$·12H$_2$O,

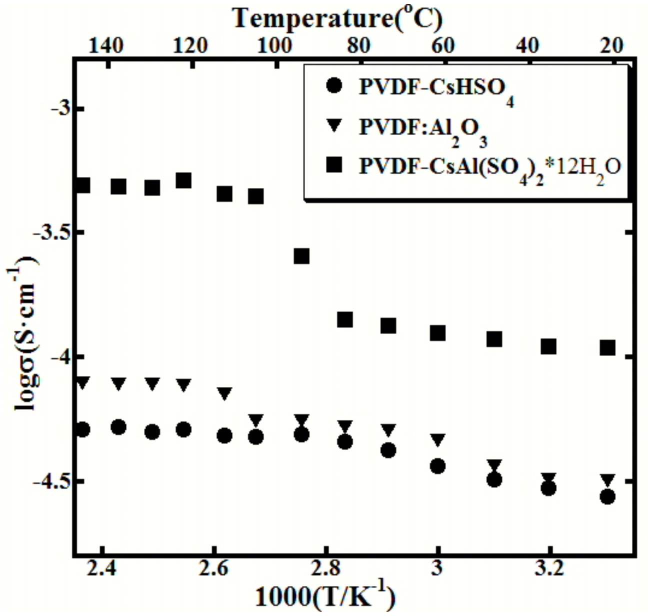

Figure 3. The temperature dependence of conductivities for the different membranes. The relative humidity is around 55%RH below 100℃ and around 10%RH above 100 ℃.

a deep weight loss between 60 °C and 80 °C was observed.

The DSC plot shown in Fig. 4b confirms the melting of PVDF around 165°C. A DSC endothermic peak around 72 °C of PVDF-$CsAl(SO_4)_2 \cdot 12H_2O$ fits well with weight-loss step in Fig. 4a. From the literature [13], the MAS-NMR result showed that the remarkable change near 350 K is related to decomposition due to the loss of H_2O, which demonstrates that a probably crystal water molecule release near 77 °C in the membrane PVDF-$CsAl(SO_4)_2 \cdot 12H_2O$ do take place. No endothermic peak for superprotonic transition of PVDF-$CsHSO_4$ around 141 °C was found, which should be the reason that the conductivity has no rapid increase in the range of 140-150°C.

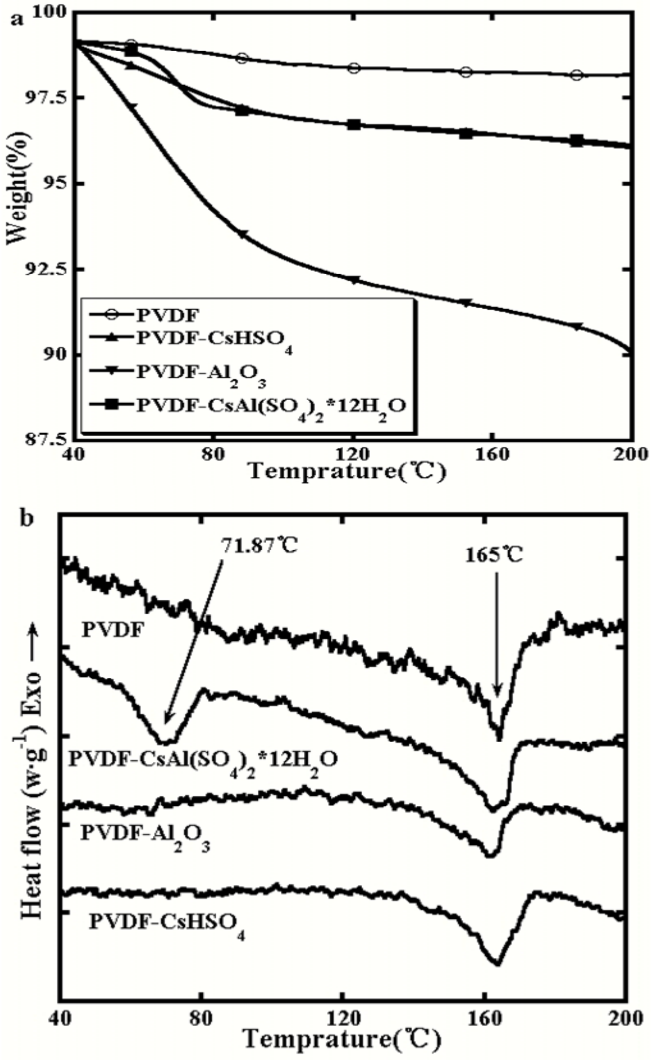

Figure 4. TG (a) and DSC (b) curves of different membranes.

4. CONCLUSIONS

The novel polymer composite membrane PVDF-$CsAl(SO_4)_2 \cdot 12H_2O$ showed a higher proton conductivity within the low-mid temperature range (30-140 °C) was synthesized. It is exciting to find that the high proton conductivity was obtained at the high temperature and low humidity atmosphere. The deep increasing of the conductivity around 90 °C was observed. In any composite system, the conductivity depends on the conductivities of individual components, their volume fractions and their spatial distributions. XRD results suggest that the structure of PVDF and $CsAl(SO_4)_2 \cdot 12H_2O$ were conserved in the composite. The deep increasing of conductivity at 90 °C was due to the release of the crystal water in the $CsAl(SO_4)_2 \cdot 12H_2O$, which demonstrated by TG-DSC and MAS-NMR results [10]. A further study, including Raman and MAS-NMR is under investigation in order to better understand the change of the conductivity.

For the sample PVDF-$CsHSO_4$, the structure of $CsHSO_4$ was changed using the synthesis method in this paper and no typical crystal $CsHSO_4$ exists in the composite from XRD. As a result, phase supertransition was not happened and accordingly no steep increase of conductivity was observed between 140-150 °C.

The novel polymer composite membrane PVDF-$CsAl(SO_4)_2 \cdot 12H_2O$ described here can be an attractive candidate as electrolyte in the low and medium temperature fuel cell.

5. ACKNOWLEDGEMENTS

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