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#### Abstract

Title	Synthesis of inorganic-organic composite electrolytes using mechanochemical treatment and their application in fuel cell
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(800 words)

Fuel cells are electrochemical devices that directly convert chemical energy in fuels into electrical energy with high efficiency and low environmental impact during the operation. In the proton-exchange fuel cell (PEFC) systems, the electrolyte is a key element, which separates the electrode structures to prevent the direct mixing of fuel and oxidant gases. In the present study, the solid-state mechanochemical treatment was applied to synthesize a new class of proton conductive composites using a planetary ball mill without any solvents in dry nitrogen atmosphere at room temperature. Inorganic solid acid composites were synthesized using oxo-acid salts (MHAO<sub>4</sub>, where M=Cs, K, etc. and A=S, P, etc.) and heteropolyacids (HPAs). These composites were further investigated, as an inorganic filler in inorganic-organic composite electrolytes, to improve the physicochemical and electrochemical performances of organic polymer electrolytes. Sulfonated poly(ether-ether ketone) (SPEEK) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, PA)-doped polybenzimidazole (PA-PBI) are selected as polymeric matrices to comprehend the proton transport mechanism under hydrous and anhydrous conditions, respectively. In addition, the solid inorganic-organic composites were synthesized directly using CsHSO<sub>4</sub> (CHS) and *N*-heterocycle compounds (Azole) by the solid-state mechanochemical treatment without any solvents in dry nitrogen atmosphere at room temperature. The CHS-Azole composites were evaluated as a proton conductor under anhydrous conditions.

In the synthesis of inorganic solid acid composites, various MHAO<sub>4</sub>-HPA composites were synthesized by mechanochemical treatment to clarify the formation mechanism of inorganic solid acid composites. High anhydrous proton conductivity, > 10<sup>-2</sup> S cm<sup>-1</sup>, of various MHAO<sub>4</sub>-HPA composites was achieved regardless of the characteristic of raw materials. Experimental results including transmission electron microscopy (TEM) observations indicated that the phenomenon of high protic conduction of the MHAO<sub>4</sub>-HPA composites clearly differs from those of pure MHAO<sub>4</sub> and pure HPAs under anhydrous conditions. The newly developed hydrogen interaction between CHS and HPA resulted in the formation of the amorphous phase, and it supported anhydrous protic conduction in the composites.

In the study of the proton exchange membrane fabrication, CHS and phosphotungstic acid (WPA) or silicotungstic acid (WSiA) were mechanically milled to synthesize CHS-WPA and CHS-WSiA composites. SPEEK and PBI were used as organic polymeric matrices. The SPEEK composite membranes showed lower water uptake, which largely contributes to proton transport of electrolyte, than that of the pure SPEEK in a temperature range of 60-85 °C as well as sufficient hot water stability in spite of the pure SPEEK and pristine HPA-SPEEK composites electrolytes showing poor stability. Besides these, proton conductivity and fuel cell performance of composite electrolytes were

largely improved by an introduction of the  $\text{MHAO}_4$ -HPA composites in the SPEEK matrix. Maximum power densities of 140, 245 and 247  $\text{mW cm}^{-2}$  were obtained for the pure SPEEK, 50WPA-50CHS- and 50WSiA-50CHS-containing SPEEK (1/5 by weight) composite electrolytes, respectively; from single cell tests at 80 °C with 80 % relative humidity (%RH). It is noteworthy that the composite electrolytes containing CHS-HPA composites showed lower water uptake than that of pure SPEEK, and the fuel cell performances were largely increased under the same conditions. PA-PBI composite electrolytes containing of  $\text{MHAO}_4$ -HPA composites were prepared to study as an electrolyte in medium temperature fuel cells under anhydrous conditions. Current densities at 0.4 V of pure PBI, 50WPA-50CHS- and 50WSiA-50CHS-containing PBI with 120, 87 and 82 wt% PA doping level (PADL) were 223, 203 and 179  $\text{mA cm}^{-2}$  at 160 °C, respectively. Because of the high proton conductivity of  $\text{MHAO}_4$ -HPA composites even under anhydrous conditions, the electrochemical properties of PBI- $\text{MHAO}_4$ -HPAs composite electrolytes with lower PADL were comparable to those of pure PBI. These observations are probably due to the fact that the mechanochemically modified  $\text{MHAO}_4$ -HPA composites added to SPEEK cause a large increase in number of sites in the composite electrolyte for protonation, which consist of hydrogen bonding between the interfacial layer of CHS-HPA composites and hydrocarbon polymer. Moreover, an increase in the amount of CHS-HPA composites allows further improvement of fuel cell performances.

In the study concerning direct mechanochemical preparation of inorganic-organic composites, CHS and Azole were treated by solid-state mechanical milling, in dry nitrogen atmosphere without any solvents. The proton conductivity of the composite electrolytes was largely increased by an introduction of Azole, especially in the low temperature region (below 100 °C). The typical composite consisting of 80 mol% of CHS and 20 mol% of triazole (80CHS-20Tz) showed high proton conductivity ( $6.0 \times 10^{-4}$  to  $1.60 \times 10^{-3}$   $\text{S cm}^{-1}$ ) over a wide temperature range (60-160 °C) in dry atmosphere. These results and the spectroscopic investigations indicate that the solid-state mechanochemical treatment involves ion-exchange between  $\text{Cs}^+$  in CHS for the much larger Azole molecule, and protic solvent effect of Azole provides the CHS-Azole composite systems with high protic diffusion. Furthermore, these observations suggest that proton transfer in the CHS-Azole composite systems includes the proton-hopping and self-dissociation, hence, this phenomenon supports proton diffusion, especially in low temperature regions. Based on all the studies performed, it can be concluded that mechanochemical synthesis is a promising method of improving the physicochemical and electrochemical performances of inorganic solid acids and of synthesizing a new class of inorganic solid acid-based composites.