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Abstract (Doctor)

Title of Thesis	Effects of Inorganic Additives on Properties of Polybenzimidazole Electrolyte Membranes for Medium Temperature Fuel Cells
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Approx. 800 words

Fuel cells are electrochemical cells that directly convert the chemical energy of a fuel (eg. hydrogen) and an oxidizing agent (eg. oxygen) into electrical energy with high efficiency and low pollutants through the redox reaction (oxidation and reduction). The working principle or the performance of fuel cells are quite different from most of the batteries, which need a continuous source of fuel and oxygen (usually from air) to prolong the chemical reaction, whereas in a battery the chemical energy usually comes from metals and their ions or oxides that are commonly already present in the battery, except in flow batteries. Fuel cells can yield electricity continuously for as long as fuel and oxygen are supplied. In the proton-exchange membrane fuel cell (PEMFC) systems, the electrolyte works as a proton conductor during fuel cell operation, which prevents the electron flowing through it from direct fuel gas mixing. In this research, the fabrication of inorganic solid composite materials was performed using mechanochemical dry milling, wet milling, and liquid-phase shaking to achieve potential proton conductors with high proton conductivities. Especially, in the fabrication of inorganic solid acid composite materials, the effect of *N,N*-dimethylacetamide (DMAc) solvent was clearly seen in these composite materials fabricated using mechanochemical wet milling and liquid-phase shaking because the dispersing solvent DMAc will perform to weaken/break the precursor materials bonds by partial or complete dissolution without using high impact energy; and by extension the formation of the new bonds. In addition, with a highly mobile liquid dispersing medium it was expected that reacting species will easily locate one another and could easily attain the right orientations for effective reactions and also possibly cause a reduction in activation energies needed for effective reactions.

Inorganic solid acid composite materials were synthesized using inorganic solid acid salts CsHSO₄ (CHS), and heteropoly acid (HPAs). These high proton conductive composite materials were applied as inorganic additive fillers in the fabrication of inorganic-organic composite electrolytes, to improve the physicochemical and electrochemical performances of organic polymer electrolytes. Phosphoric acid doped polybenzimidazole (PA-PBI) was selected as a polymer membrane to obtain high proton conducting state, since proton conduction mechanism and chemical interaction in this polymer matrix under anhydrous condition at medium temperatures were well understood.

In the fabrication of cesium substituted-silicotungstic acid composite materials, high proton conductive $x\text{CsHSO}_4\text{-(1-x)H}_4\text{SiW}_{12}\text{O}_{40}$ (CHS-WSiA) composite materials with molar ratio $x = 0.5, 0.7,$ and 0.9 were successfully prepared via mechanochemical dry milling, mechanochemical wet milling, and liquid-phase shaking method. Ion-exchange reactions and strong chemical interactions were occurred between precursor CHS and WSiA during the mechanochemical milling treatments and liquid-phase shaking. X-ray diffraction characterization confirmed that mechanochemical treatments and liquid-phase shaking induced an ion-exchange reaction between Cs⁺ ions in CHS and H⁺ ions in WSiA to produce a new class of composite materials. The proton conductivities of composite materials were significantly improved over their precursor materials, especially at low temperatures, below the superprotic phase-transition temperature (141 °C) of CHS. Among these composite materials, the 0.9CHS-0.1WSiA (in mole ratio)

composites fabricated via dry milling, wet milling, and liquid-phase shaking showed the highest conductivities of around 10^{-3} S cm^{-1} at 170 °C under dry nitrogen atmosphere. The enhanced anhydrous proton conductivities of the Cs-substituted WSiA composite materials were also corroborated with shortening of the hydrogen bonding distance in these composites for fast proton hopping transport mechanism via ^1H -MAS-NMR evaluation. The proton conductivities of composite materials obtained by wet milling and liquid-phase shaking were remarkably higher than those of the composites fabricated via dry milling, especially for the composites with a lower CHS content (0.5CHS-0.5WSiA and 0.7CHS-0.3WSiA). Thus, wet milling and liquid-phase shaking methods cooperated with DMAc effectively promoted the high chemical interaction between CHS and WSiA, which increased the proton conductivities of the obtained inorganic composites. Additionally, inorganic solid $\text{CsHSO}_4\text{-H}_3\text{PW}_{12}\text{O}_{40}$ composites (CHS-WPA) were also fabricated via mechanochemical dry milling and wet milling, and CHS-WPA doped-PBI electrolyte membranes were studied for the improvement of acid and water retention properties in the medium temperature fuel cells.

For the fabrication of mixed alkaline-substituted phosphotungstic acid composites, MHSO_4 ($\text{M} = \text{K}, \text{Cs}$) and phosphotungstic (WPA) solid acids were applied to produce anhydrous proton conductive composite materials via mechanical planetary dry ball milling. Very fast proton conducting irreversible new phase composites were obtained, with 90(50KHS-50CHS)-10WPA (mol %) mixed metal ions composite exhibiting the highest performance with conductivity from 4.9×10^{-2} to 1.4×10^{-3} S cm^{-1} at 160 to 40 °C, respectively; compared to those of the precursor materials (CHS and KHS) on the order of 10^{-3} to 10^{-8} under the same temperature regime. The XRD, FT-Raman, ^1H -MAS-NMR and HR-TEM results of the composites revealed the formation of an amorphous nano-interface proton-conducting pathway shell around an M-substituted WPA crystalline core, resulting in a nanoionics effect leading to the high conductivities observed; in addition to preferred sites of alkali metal ions substitution into the WPA with different stabilities and conductivities with respect to type of ion.

Inorganic-organic composite membranes were fabricated using partially cesium-substituted silicotungstic acid (CHS-WSiA) and polybenzimidazole (PBI, MRS0810H) for medium temperature polymer electrolyte fuel cells (MT-PEFCs). 0.5CHS-0.5WSiA composites fabricated via dry milling/wet milling were selected to apply inorganic composite fillers in the electrolyte membrane preparation. The flexible and homogeneous composite membranes with several phosphoric acid doping levels (PADLs) were prepared. A high maximum power density of 378 mWcm^{-2} and a good constant current stability test (200 mAcm^{-2}) with stable voltage of 0.61 V were obtained from a single cell test using the PBI composite membrane containing 20 wt% of CHS-WSiA from wet milling and phosphoric acid doping level (PADL) of 8 mol, at 150 °C under an anhydrous condition. Wet milling CHS-WSiA crystallites were highly dispersed in PBI matrix to give homogenized membranes and played a significant role in the enhancement of acidity by increasing the number of proton sites in the electrolyte membrane. After adding CHS-WSiA into PBI membrane, the acid and water retention properties were significantly improved and incorporated as new proton conduction path by adsorbing phosphoric acid in these composite electrolyte membranes. These observations suggested that composite membranes with 8 mol of PADL are good promising PA doped-membranes with effective electrochemical properties for the medium temperature fuel cells.

In addition, metal oxide particles (TiO_2) possessing high affinity for phosphoric acid are added to the electrolyte membrane so that the PBI composite electrolyte membrane could retain phosphoric acid retention for a longer period measurement. The proton conductivity of the electrolyte membranes by these added particles and the influence on the fuel cell power generation characteristics in the medium temperature range were investigated. Chemically stable TiO_2 nano-powders were added to the PBI electrolyte membrane at various concentrations (2, 10, 20 wt%) to increase the retention of phosphoric acid and water. The TiO_2 /PBI electrolyte membrane was achieved output characteristics more than twice that of the pure PBI electrolyte membrane. It was observed that the addition of TiO_2 improved the phosphate holding power of the electrolyte membrane. TiO_2 /PBI membrane retained high conductivity values at the higher temperatures as a result of its high doping level and high water retention capacity. TiO_2 (2 wt%)/PBI composite membrane showed the best performance with a power density of 434 mWcm^{-2} . These results suggest that TiO_2 /PBI-based composite membranes are promising electrolytes for MT-PEFCs.