

## Temperature Tolerant Proton Conducting Organic/inorganic Hybrid Membranes

Je-Deok Kim, and Itaru Honma

Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, 305-8568, Japan  
Kim-1167@aist.go.jp

Polymer electrolyte membrane fuel cells (PEFC) using hydrated perfluorosulfonic polymers such as NAFION have been developed in the past years. However, the high materials cost and complicated water managements are major obstacles for practical applications of PEFC. Also, CO poisoning of Pt alloy electrodes requires the complicated reforming system, which purify the hydrogen rich gas down to the CO contamination level of few ppm. One of the technological challenges is to develop an electrolyte membrane that can be operated at higher temperatures (100-200°C) and lower humidity level, which drastically improve the electrode performance and the cell efficiency. Synthetic approaches of temperature tolerant proton conducting membranes based on acid-base blends or organic/inorganic hybrids are reported [1-10], and successful application in single fuel cells has been shown in many cases.

In this paper, we have investigated the structure and proton conductivities of organic/inorganic hybrid membranes synthesized by sol-gel processing with polydimethylsiloxane (PDMS) or polytetramethylene oxide (PTMO) and metal (zirconium, titanium) alkoxides. The hybrid membranes have been found to be temperature tolerant and stable even at higher temperature with acidic condition. The membranes become a proton conducting electrolytes by the soaking of phosphoric solution or adding heteropolyacids such as 12-phosphotungstic acid (PWA). Various polymer membranes by incorporated acids can release mobile protonic carriers to afford the conductivity of the membrane. The hybrid membranes showed good protonic conductivities at intermediate temperatures up to 150°C. Fig. 1 shows the  $^{31}\text{P}$ -MASNMR spectra of zirconia/PTMO soaked with 1M phosphoric acids. It shows the one strong peak at -22ppm and two small peaks at -13 and -28ppm. On the other hand, it has been known that the chemical shift of zirconium phosphate such as  $\epsilon\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  and  $\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ -gel appears between -19 and -21ppm. Therefore it is speculated that zirconia phase is chemically bound to phosphoric acid through P-O-Zr bonding [Fig. 2] and/or to be complex compound with phosphate, resulting in immobilizing acidic groups in the hybrid matrix. The NMR results indicate the phosphate moieties are strongly binding to inorganic phase.

The structures of the hybrid membranes have been characterized by infrared absorption (IR), thermal analysis (TG-DTA), proton conductivity and cell properties, and will be presented.

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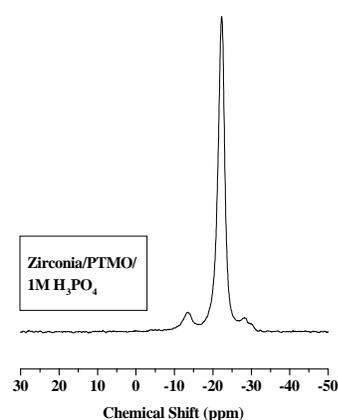


Fig. 1.  $^{31}\text{P}$  NMR spectra of Zr/PTMO/ $\text{H}_3\text{PO}_4$  membrane.

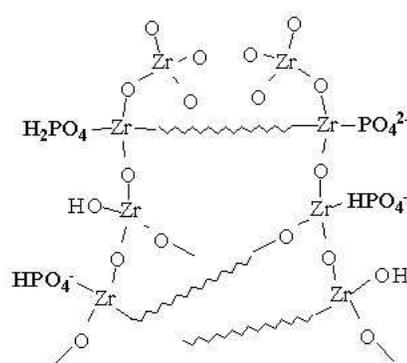


Fig. 2. Molecular schematic diagram of Zr/PTMO/ $\text{H}_3\text{PO}_4$  membrane.