Osaka University Knowledge Archive

Title	Synthesis and properties of hybrid-type polymer membranes for fuel cells
Author(s)	Yogo, Toshinobu
Citation	Transactions of JWRI. 2010, 39(2), p. 266-267
Version Type	VoR
URL	https://doi.org/10.18910/24815
rights	
Note	

Osaka University Knowledge Archive : OUKA

https://ir.library.osaka-u.ac.jp/

Osaka University

Synthesis and properties of hybrid-type polymer membranes for fuel cells†

YOGO Toshinobu *

KEY WORDS: (Fuel Cell) (Hybrid) (Membrane) (Proton Conductivity)

1. Introduction

Fuel cell technology has been considered a promising alternative source for future energy. Growing attention has been focused on proton exchange membrane fuel cells (PEFCs) for mobile, stationary and portable electrical devices because of their high energy efficiency and clean exhaust. Perfluorosulfonic polymers including Nafion have many attractive properties including good mechanical strength, good chemical stability and high proton conductivity, and they are widely used in commercial applications. However, the perfluorosulfonic membranes have several drawbacks such as complex water management, CO poisoning of Pt anode catalysts and high cost. An increase in PEFCs operation temperature would allow for increased reaction kinetics of the fuel cell, lower consumption of the platinum catalyst, and a decrease in the size of the heat management system. Thus, proton-conducting materials of high conductivity at the intermediate temperature range from 100 to 200 ˚C are required.

This paper describes the synthesis and characterization of silica-based inorganic/organic hybrid membranes with chemically bound phosphonic acid. The structure, thermal stability and proton conductivities of hybrid membranes were analyzed. The H_2/O_2 fuel cell performances of membrane–electrodes assemblies (MEAs) were also studied.

2. Synthesis of Hybrid Membranes

Starting compounds for membranes are styryl-substituted alkoxysilanes and a derivative of acrylic phosphonic acid (EPA). The styryl-substituted alkoxysilanes used in this study contain organosilyl groups of $-Si(CH_3)(OCH_3)_2$ and $-Si(CH_3)_2(OCH_3)$, which are called difunctional (MDMSMS(D)) and monofunctional DMMSMS(M), respectively. The $Si\text{-}OCH_3$ group undergoes acidic hydrolysis affording a Si-O-Si linkage. Therefore, the structure of the hybrid membrane can be controlled by the number of alkoxy groups. On the other hand, a derivative of acrylic phosphonic acid used in this study has an acrylic ester group and a phosphonic acid group. The acrylic ester group allows copolymerization with other polymerizable groups and the phosphonic acid group is expected to contribute to proton conduction.

Hybrid membranes were prepared through copolymerization reaction followed by sol-gel reaction. Each styryl-substituted alkoxysilane (DMMSMS(M) or MDMSMS(D)) was copolymerized with EPA in various monomer ratios using a radical initiator (AIBN). The samples were labeled with their monomer feed ratios such as DMMSMS(M) (or MDMSMS(D))/EPA = x/y. The ratio of x/y = 1/2, 1/4, 1/6 were investigated in this study.

3. Properties of Hybrid Membranes

Figure 1 shows the DTA-TG curves obtained for DMMSMS(M)/EPA(=1/2) and MDMSMS(D)/EPA(=1/2) hybrid membranes with a solid line and a dashed line, respectively. Both TG curves for DMMSMS(M)/EPA and MDMSMS(D)/EPA hybrid exhibit first weight losses up to around 100ºC. This weight loss is attributed to the loss of absorbed water molecules. The second step ranging from 100ºC to 300ºC shows a gradual weight loss attributed to the loss of chemically bound water. Above 200ºC, water generated from the condensation of $-P(O)(OH)_2$ groups is also lost from the hybrid. The decomposition of membranes starts above 280ºC. The exothermic peaks are also observed with rapid weight losses for both membranes.

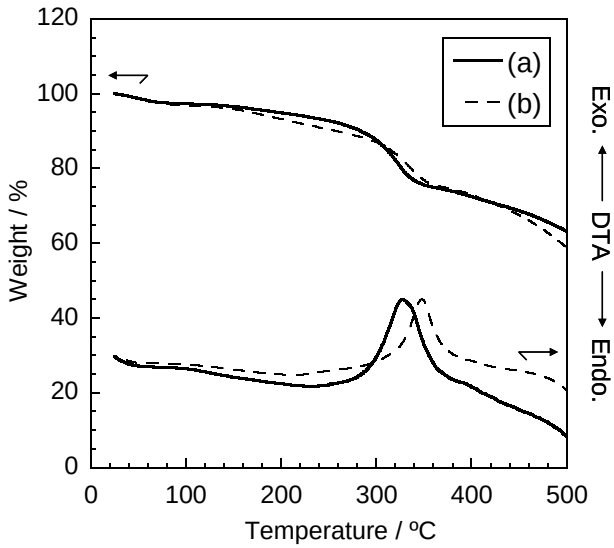

Fig. 1 DTA-TG curves of hybrid membranes:
(a) DMMSMS(M)/EPA=1/2 and
(b) MDMSMS(D)/EPA=1/2.

† Received on 30 September 2010
* EcoTopia Sci. Inst., Nagoya University, Nagoya, Japan

Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

The results confirm that the hybrid membranes possess sufficient thermal stability up to 200ºC. It is worth noting that the exothermic peak temperatures vary according to the functionality of the membrane. The DTA curve for DMMSMS(M)/EPA=1/2 membrane exhibits a peak at 328ºC, whereas the curve for MDMSMS(D)/EPA=1/2 membrane shows a peak at 348ºC. MDMSMS(D)/EPA hybrid membrane has a linear siloxane linkage and a higher thermal stability than that of DMMSMS(M)/EPA above 280ºC. This result reveals that siloxane chain formed in the membrane improves the thermal stability of the hybrid membrane.

Figure 2 shows the proton conductivities under different relative humidities for the hybrid membranes of DMMSMS(M)/EPA=1/6 and MDMSMS(D)/EPA=1/6. The conductivities of Nafion 112 measured under the same humidified conditions are also shown in Fig. 2. Obviously, the conductivity strongly depended on the relative humidity and decreased with decreasing relative humidity. The proton conduction for hydrated membranes generally occurs via a proton hopping mechanism (Grotthuss mechanism) and a diffusion mechanism (vehicle mechanism) [1]. It should be noted that the activation energy of the proton conduction is dependent on the relative humidity and increases with decreasing the relative humidity. The activation energies for DMMSMS(M)/EPA=1/6 and MDMSMS(D)/EPA=1/6 membranes are 0.14 and 0.26 eV at fully hydrated state, 0.40 and 0.48 eV at about 65 %RH and 0.75 and 1.05 eV at about 20 %RH, respectively. At the fully hydrated state, the activation energy for proton conduction in the hybrid membrane is comparable to that of Nafion [2]. This result suggests that water molecules absorbed in the membrane contribute to the proton conduction like usual water-cooperative proton conductive membranes by both Grotthuss and vehicle mechanisms in the fully hydrated state. The increase in activation energy with decreasing relative humidity is reported for Nafion [2]. Similarly, the increase in activation energy for the current membrane derives from the decrease in water content used for proton conduction. The conductivities of hybrid membranes were considerably low compared to that of Nafion 112 in the range from 40 to 120ºC (Fig. 2). However, the conductivity of Naffion 112 drastically decreased above 120ºC. In contrast, the conductivity of hybrid membranes increases with temperature up to 140ºC under any humidified conditions. Also, no decrease in conductivity by water evaporation was observed up to 140ºC even at low humidified conditions. The results indicate that the membrane is superior in water retention to Nafion above 120ºC.

4. Conclusions

Proton conducting hybrid membranes consisting of organic polymer chains containing phosphonic acid groups and Si-O linkage were successfully synthesized via the copolymerization and sol-gel reaction. A phosphonic acid group was immobilized to polymer chain by radical polymerization of styryl-substituted alkoxysilane and a derivative of acrylic phosphonic acid (EPA) via a stable C-P bond. The membranes exhibited good thermal stability, which depended on the degree of inorganic chain in the hybrid membrane. The proton conductivity depended on the temperature and relative humidity. The membranes synthesized from monomethoxysilane derivative were found to show higher conductivities than those from the dimethoxysilane derivative. The membrane exhibited good conductivities up to 140ºC at various humidities. The hybrid membranes immobilizing phosphonic acid groups have a potential for a PEFC application operated at intermediate temperatures.

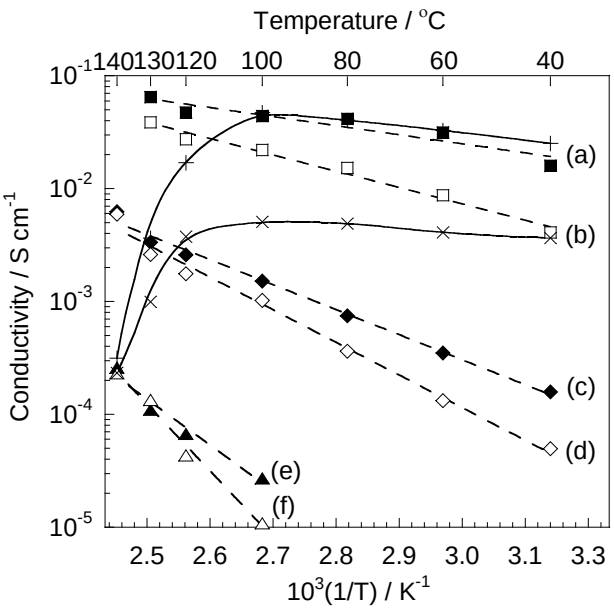

Fig. 2 Temperature dependencies of proton conductivities for the hybrid membranes of DMMSMS(M)/EPA=1/6 (solid symbols) and MDMSMS(D)/EPA=1/6 (open symbols) under different relative humidities: (a) and (b) 100 %RH, (c) and (d) from 63.5 to 67.7 %RH humidified with NaCl solution, (e) and (f) from 19.3to 20.8 %RH, humidified with $MgCl_2$ solution.The conductivities of Nafion 112 are also plotted for comparison; (+) humidified with NaCl solution, (×) humidified with $MgCl_2$ solution.

References

[1] W.H.J. Hogarth, J.C.D. da Costa, G.Q. Lu: J. Power Sources, 142 (2005), pp.223-237.

[2] Z. Siroma, R. Kakitsubo, N. Fujiwara, T. Ioroi, S. Yamazaki, K. Yasuda: J. Power Sources, 189 (2009), pp.994-998.