The performances of the cells with various Pd and Pt anodes for electrochemical reactions were compared. Modification with SnO$_2$ increased the performance of Pd/C anode, while the modification decreased that of Pt/C anode. Second, the effect of temperature on the performance of the cell with the Pt/C/SnO$_2$ anode was examined in 500-ppm CO-contaminated H$_2$. Regeneration of the Pt/C/SnO$_2$ performance with an increase in the cell temperature suggests that the CO molecules adsorbed on active sites were easily desorbed at high temperature. Finally, the effect of SnO$_2$ addition on the performances of the cell with the Pd anode in 500-ppm CO-contaminated H$_2$ was examined. The cell with the Pd/C/SnO$_2$ anode in pure H$_2$ was 0.4 V at current density of 0.15 A-cm$^{-2}$, while that in CO-contaminated H$_2$ was 0.35 V. The Pd/C/SnO$_2$ anode exhibited excellent tolerance to CO poisoning.

INTRODUCTION

Polymer electrolyte fuel cell (PEFC) is the system which can convert the chemical energy to electricity efficiently, since the efficiency of fuel cells is not restricted by Carnot’s theorem. The system is attractive power source as new clean power generator for domestic use or automobiles. PEFC can generate electricity on site to decrease the transmission loss. When PEFC is applied as domestic use, the high energy utilization is expected because the heat waste can be used as air conditioners and hot water by co-generation systems. However, there are a lot of tasks to be solved in PEFC systems; one of the most important tasks is to lengthen the life of the system. High reliability and durability are required to spread the domestic-use PEFC system. At present, the voltage of PEFC at the same current density gradually decreases with time in use; therefore, it is being aimed for the declining rate to be less than 2.0 mV per 1000 h in the current density range from 0.1 to 0.3 A-cm$^{-2}$. This target is expected to be achieved under the following conditions: the entrance temperature of the cell ranges from 70 to 80$^\circ$C; the fuel utilization ranges from 70 to 80%; air utilization ranges from 30 to 60%. At the rate of 2.0 mV per 1000 h, the voltage declines by 70 mV for 40000 h. It is corresponding to 10-year operations including 10-h operations a day (1).
In contrast the addition of small amounts of HPA to sulfonated perfluorinated polymers such as Dupont's Nafion® by infusion from aqueous solution under gentle reflux for 24 h dramatically increases the performance of the membranes at temperatures up to 150 °C depending on the HPA. The polarization for Nafion® doped with four different HPA at 120 °C with ca. 25% RH are shown in Figure 3. All doped samples show improved performance relative to the control membrane; the best performance is seen with 21-HAsW21. Unfortunately it is not clear exactly which species in the 21-HAs2W case is responsible for the improved performance as the 21-HAsW HPA equilibrates to several other HPA structures under the imbibing conditions and so this result is hard to reproduce.

Figure 3. Polarization curves for HPA doped Nafion® at 120 °C using H₂ and O₂ humidified at 80 °C.

These membranes have been studied in terms of understanding the interaction of the HPA with the polymer to enable a full understanding of this beneficial interaction. Proton conductivities of the membranes generally appear to be improved but the amount of HPA doped into the sample is critical and this concentration relationship is not well understood. The ATR-IR spectra of the hydrated membranes show no difference in the doped versus undoped Nafion®s, but subtle differences are observed in the ATR-IR spectra of membranes that have been placed in a vacuum oven overnight, Figure 4. When the Nafion® spectrum is subtracted from the 12-HPW Nafion® spectrum the HPA bands are observed, 1200 – 700 cm⁻¹ as well as changes to some of the Nafion® bands and new δ(OH) bands at ca. 1600 cm⁻¹, Figure 4. SAXS shows that the HPA are mono-dispersed and do not form clusters in the membrane. The HPA do not appear to be chemically reduced by hydrogen in these systems but are not immobilized and so may be
leached from the membrane over time. One approach to the leaching problem is to use the approach of Savadogo\textsuperscript{22} in which the doped Nafion\textsuperscript{®} is heat treated at 150 °C for 4 h followed by refluxing in water for 24 h. We have repeated this work with 12-HPW using a large excess of the HPA, almost all of which is recovered from the refluxing solution. However, ATR-IR does reveal that a small amount of 12-HPW is immobilized in the membrane. Because a number of sulfonic acid groups are lost this is not seen as a practical approach.

Another approach to the leaching problem is to immobilize the HPA in a nanocomposite membrane as reported by Honma using silicate sol-gel chemistry.\textsuperscript{1-3} Rather than rely on encapsulating 12-HPW in the silica matrix we have used the lacunary 11-HPW to covalently bond the HPA to silica end capped polyethylene glycol($M_n = 400$). Films cast from this precursor appeared to have superior mechanical properties as compared to the 12-HPW.\textsuperscript{3} Proof of the W-O-Si bond is shown in the IR spectrum, where new sharp bands are observed at 1594 and 1429 cm$^{-1}$ assigned to $\nu$(SiO$_2$W), and in the MAS $^{29}$Si NMR spectrum. Dry samples showed no self-diffusion as measured by PFGSE-NMR, but wet samples showed fast and slowly increasing self diffusion coefficients as the sample swelled eventually stabilizing at 1.2 x $10^{-6}$ cm$^2$/s, corresponding to 50 % of the sample. Ion exchange capacities were measured at 2.0-2.5, twice that of Nafion\textsuperscript{®} 117. The HPA are stable in these systems to leaching in hot water as shown by IR spectroscopy. SAXS indicates that the HPA are entrapped in the silica network, but the HPA are monodispersed. TEM analysis indicates that there is no ordering of proton conducting channels in these systems. The DC conductivity measurements, Figure 5, show that the conductivity is lower than for Nafion\textsuperscript{®} but

Figure 4. ATR-IR spectra for vacuum dried Nafion\textsuperscript{®} 112, 12-HPW doped Nafion\textsuperscript{®} 112 and the result of subtracting the Nafion\textsuperscript{®} spectrum from the 12-HPW doped Nafion\textsuperscript{®}.

Hybrid sol-gel HPA polymers.

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increases exponentially with temperature under 100% RH. In addition, preliminary data from MEA testing of these materials indicate that significant optimization of the membrane/electrode interface will be required for these membranes to exhibit their full potential. This is manifested in the polarization curves, which lack a clear kinetic loss region and show little improvement with the addition of Nafion® paint to the electrode surface. The performance is modest, Voc = 0.85 V, limiting currents of 40 mA cm⁻² under 100 % RH at 47 °C.

Figure 5. DC conductivity of membrane samples Vs. temperature all at 100% humidity. Trendline for Nation® 117, for the hybrid membranes, M-1, stirred and M-2, not stirred, during preparation is exponential.

CONCLUSIONS

HPA are thermally stable to ca. 400 °C and depending on their structure may retain water molecules to ca. 200 °C. Fast self diffusion coefficients can be observed in these systems but the hydrogen bonding environment between the HPA is more important than the water content of the HPA. Very high current densities can be observed with simple HPA non-interacting polymer composite membranes using dry gases at room temperature, but only modest activity is observed at elevated temperatures, the HPA are also water soluble and are eventually washed out, in addition in permeable membranes H₂ cross over may eventually lead to chemical reduction of the HPA and cell shorting. Small amounts of HPA can dramatically improve the performance of Nafion® membranes at elevated temperatures, but the concentration effects and nature of this interaction is poorly understood. Polymer/silica/HPA nano-composites can be fabricated in which the HPA is immobilized but the resultant membranes are poorly organized and

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require fully hydrated conditions to give reasonable proton conductivities. In addition, fabricating MEAs from such materials will require the further development of these ionomers for incorporation into the catalyst layer.

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REFERENCES

1. Honma, I.; Nakajima, H.; Nishikawa, O.; Sugimoto, T.; Nomura, S. J. Electrochem. Soc., 150, A616 (2003).
2. Honma, I.; Takeda, Y.; Bae, J. M. Solid State Ionics, 120, 255 (1999).
3. Vernon, D.; Meng, F.; Dec, S. F.; Williamson, D. L.; Turner, J. A.; Herring, A. M. J. Power Sources, in press (2004).
4. Kim, Y. S.; Wang, F.; Hickner, M.; Zawodzinski, T. A.; McGrath, J. E. J. Membr. Sci., 212, 263 (2003).
5. Ramani, V.; Kunz, H. R.; Fenton, J. M. J. Membr. Sci., 232, 31 (2004).
6. Staiti, P. J. New Materials for Materials for Electrochemical Systems, 4, 181 (2001).
7. Pope, M. T.; Müller, A., Eds. Polyoxometalate Chemistry: From Topology Via Self-Assembly to Applications; Kluwer Academic Publishers: Dordrecht, 2001.
8. Nakamura, O.; Kodama, T.; Ogino, I.; Miyake, Y. Chem. Lett., 1, 17 (1979).
9. Tourne, C. M.; Tourne, G. F.; Malik, S. A.; Weakley, T. J. R. J. Inorg. and Nucl. Chem., 32, 3875 (1970).
10. Mehta, V.; Cooper, J. S. J. Power Sources, 114, 32 (2003).
11. Dec, S. F.; Herring, A. M. J. Phys. Chem., B, 108, 12339 (2004).
12. Ganapathy, S.; Fournier, M.; Paul, J. F.; Delevoye, L.; Guelton, M.; Amoureux, J. P. J. Am. Chem. Soc., 124, 7821 (2002).
13. Slade, R. C. T.; Pressman, H. A.; Skou, E. Solid State Ionics, 38, 207 (1990).
14. Slade, R. C. T.; Barker, J.; Pressman, H. A.; Strange, J. H. Solid State Ionics, 28-30, 594 (1988).
15. Pressman, H. A.; Slade, R. C. T. Chem. Phys. Lett., 151, 354 (1988).
16. Hardwick, A.; Dickens, P. G.; Slade, R. C. T. Solid State Ionics, 13, 345 (1984).
17. Slade, R. C. T.; Omana, M. J. Solid State Ionics 58, (1992), 195.
18. Uchida, S.; Inumaru, K.; Misono, M. J. Phys. Chem., B, 104, 8108 (2000).
19. Nakamura, O. Progress in Batteries and Solar Cells, 4, 230 (1982).
20. Staiti, P.; Hocevar, S.; Giordano, N. Int. J. Hydrogen Energy, 22, 809 (1997).
21. Staiti, P.; Hocevar, S.; Passalacqua, E. J. Power Sources, 65, 281 (1997).
22. Savadogo, O. Journal of New Materials for Electrochemical Systems, 1, 47 (1998).