

*Ryan Reed received his B.S. in Chemical Engineering from the University of Washington in the spring of 2004. As an undergraduate, Ryan worked with Dr. Stuart Adler on solid oxide fuel cell cathode materials. Their work focused mainly on chemical expansion of ceramic materials in high vacuum. Following graduation, he participated in the Science Undergraduate Laboratory Internship (SULI) at the National Renewable Energy Laboratory (NREL). While at NREL, the focus of his project was testing new proton exchange membrane materials for use in fuel cell. Specifically, the project was looking at ionic conductivity. Advising him on the project was Dr. John Turner (NREL). Ryan is currently a graduate student at the University of Washington under the tutelage of Dr. John Berg, who specializes in colloidal and interfacial science. Ryan is currently devoting his research time to looking at the mechanical optimization of composite materials through chemical modification.*

*John A. Turner, Ph. D., is a Principal Scientist at the National Renewable Energy Laboratory. He received his B.S. degree from Idaho State University, his Ph.D. from Colorado State University, and completed a postdoctoral appointment at the California Institute of Technology before joining the Laboratory (then the Solar Energy Research Institute) in 1979. His research is primarily concerned with enabling technologies for the implementation of hydrogen systems into the energy infrastructure. This includes direct conversion (photoelectrolysis) systems for hydrogen production from sunlight and water, advanced materials for high temperature fuel cell membranes, and corrosion studies of fuel cell metal bipolar plates.*

## CONDUCTIVITY ANALYSIS OF MEMBRANES FOR HIGH-TEMPERATURE PEMFC APPLICATIONS

R. REED, J.A. TURNER

### ABSTRACT

Low-temperature operation requirements for per-fluorinated membranes are one factor that limits the viability of current fuel cell technology for transportation and other uses. Because of this, high-temperature membrane materials are being researched. The protonic conductivity of organic/inorganic hybrid composites, Nafion® analog material, and heteropoly acid doped Nafion membranes were studied using a BekkTech® conductivity test cell as a hydrogen pump. The goal was to find a high-temperature membrane with sufficient enough conductive properties to replace the currently implemented low-temperature membranes, such as Nafion. Four-point conductivity measurements were taken using a hydrogen pump experiment. Results showed that one of the organic/inorganic membranes that we tested had similar protonic conductivity to Nafion. Nafion analog membranes were shown to have similar to slightly better conductivity than Nafion at high-temperatures. However, like Nafion, performance dropped upon dehydration of the membrane at higher temperatures. Of the heteropoly acid doped Nafion membranes studied, silicotungstic acid was found to be, overall, the most promising for use as a dopant.

### INTRODUCTION

Proton exchange membrane fuel cells (PEMFC) have been shown in the literature to be viable options for replacing petroleum-based power generation applications such as diesel generators and internal combustion engines [1-8]. However, economic competitiveness, fuel choice, and system integration difficulties are hurdles that must be cleared in order for the technology to become widely accepted. One factor that addresses all of these issues is membrane material technology.

A majority of commercially available fuel cell systems today use Nafion®, produced by DuPont®. Nafion is a perfluorinated sulfonic acid polymer that is manufactured into a membrane. As a fuel cell membrane, Nafion has long been known to produce high power densities at low-temperature operation (< 100°C). One reason for the high power density is that, at low-temperatures (e.g. 80°C) and

high relative humidity, Nafion conducts protons very efficiently, 75 mS/cm (Nafion 117) [9, 10]. Because of this, Nafion currently is the most common fuel cell electrolyte. However, due to the dependence of hydration for conductivity, Nafion is not designed for high-temperature (low relative humidity) operation [11]. At high relative humidity (high water activity), water is absorbed into hydrophilic regions of Nafion, which in turn conduct protons, necessary for generating the PEMFC reactions [12]. When the water required for proton conduction is eliminated from the system, membrane proton conductivity decreases rapidly [13].

The need to maintain a high relative humidity makes high temperature operation difficult due to the energy losses associated with humidifying feed streams. The need for low-temperature operation poses a problem when attempting to integrate current fuel cell and automotive technologies. Automotive cooling systems are designed to operate at temperatures around 120°C. Lowering

the operating temperature to accommodate a Nafion PEMFC stack requires either a retrofit or a complete redesign of the automotive cooling system. In both cases, the total system cost could increase significantly. Ideally, membrane materials that could conduct at higher temperatures (120°C) and lower relative humidity could be employed so that current automotive cooling systems could be employed without excessive energy losses due to reactant stream humidification.

In addition to the system costs associated with low-temperature integration, fuel choice is also limited by operation with Nafion and other perfluorinated membranes. The low-temperature requirements of these systems cause the catalyst to be highly sensitive to carbon monoxide (CO) poisoning [14]. Because of this, a system using Nafion requires that the CO content of the fuel be extremely low. In most cases, the fuel must be additionally filtered after production, as in the case of hydrogen obtained via reformation of hydrocarbons [14]. Post-reformation filtration also increases the overall system cost. Higher temperature operation decreases the poisoning effect of CO on the catalyst [14], and eliminates some, if not all, of the need for post-reformation filtration of fuel. For these reasons and more, high-temperature membrane materials are being studied.

Conductivity analysis of alternative membrane materials at high-temperature operation was the focus of this paper. Specifically three types of membranes were studied. The first were organic/inorganic hybrid composite membranes. Secondly, an analog of Nafion was studied. Finally, Nafion doped with various heteropoly acid proton-conductors were investigated. In each of these studies Nafion control samples were also compared to our test membranes.

Organic/Inorganic hybrid composite membranes of the type studied here are defined as having polymer complexes (organic) that have been doped with a proton-conducting material (inorganic) in order to obtain an optimized combination of physical and chemical properties. The synergy between the thermo-mechanical stability of the polymer “backbone” and the conductive properties of the dopant provide a possibility for higher efficiency, high-temperature, proton exchange membranes to be developed [11, 17-21]. Heteropoly silicotungstic acid and sulfonic acid were the two groups of conductors studied. They were chosen because both display high protonic conductivity in their solid states compared to Nafion. A special type of polypropylene oxide named BSPPO was used as the polymer complex in both cases. The composition of BSPPO is proprietary. In addition to the membrane compositions discussed here, other organic/inorganic composite membrane studies can be found in the literature [15, 16].

Analog membranes are materials that have similar composition to an existing membrane; however, they are different enough to be categorized as their own material. Two thicknesses of a Nafion analog that were designed and manufactured in Russia were tested under high-temperature operation. The purposes of these tests were to see if the slight modification to the composition yielded improved performance at high-temperatures.

The third membrane type studied was Nafion doped with proton-conducting inorganic heteropoly acids. Membranes of these types have been studied elsewhere and have shown promising results [13]. By doping Nafion with highly conductive heteropoly acids it is theorized that conductivity will be increased and become

less dependent on hydration. This lack of dependence on hydration would open the door for high-temperature operation. The specific membrane/dopant combinations studied were Nafion 112 doped with the following: heteropoly silicotungstic acid (HSiW), heteropoly arsenotungstic acid (HAS<sub>2</sub>W), and both Dawson and Keggin structures of heteropoly phosphotungstic acid (12-HPW and HP<sub>2</sub>W, respectively). In addition to the membranes studied in this paper, Savadogo has provided a summary of other types of high-temperature membranes currently being researched [14].

## MATERIALS AND METHODS

Hydrogen pump experiments were performed on three types of membranes, organic/inorganic hybrids, Nafion analogs, and heteropoly acid doped Nafion. Organic/Inorganic hybrid membranes were solution-cast consisting of a polymer host and a SiO<sub>2</sub>-based proton-carrier composite that was synthesized via a sol gel approach using a functional silane and tetraethoxysilane (TEOS) in acidic conditions [22]. In total, two organic/inorganic membranes were studied. The first organic/inorganic hybrid membrane was composed of a polymer backbone of special polypropylene oxide (BSPPO) and doped with heteropoly silicotungstic acid (W12-STA). Sulfonic acid (SFA) that was thermo-oxidatively converted from a mercapto (-SH) group was used along with the same BSPPO backbone in the second organic/inorganic hybrid membrane. These membranes have been characterized in previous work, using diffusion reflectance Fourier transform infrared spectroscopy (DRIFT), differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA) [22].

Analog membranes were provided from an Armenian company; however, the membranes themselves were designed and produced in Russia. Membranes of multiple thicknesses were supplied for the study; samples of 80 μm and 150 μm were tested. Exact composition of the membranes is proprietary.

Heteropoly acid (HPA) doped Nafion membranes were prepared by submersing pure Nafion membranes in aqueous solutions of HPA or HPA salts for 24 hours at 80°C. The amount of acid in solution varied according to the amount of material available and the solution density. A more detailed description of the fabrication method may be found in literature [26]. Membranes were characterized using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), diffusion reflectance Fourier transform infrared spectroscopy (DRIFTS), small-angle x-ray scattering (SAXS), and thermo-gravimetric analysis (TGA). The procedure and results of these tests have been published elsewhere [10].

Four-point conductivity measurements were taken of all three types of membranes using the BakkTech® conductivity test cell in conjunction with a PGZ 301 Dynamic EIS Voltammeter®. The BakkTech cell functioned as the hydrogen pump with sense wires set up along the transverse direction. Temperature and humidification were controlled using the Globe Tech CompuCell® GT fuel cell test stand. Strips of membrane material approximately 5 cm x 2 cm were cut and placed into the BakkTech conductivity test cell in order to test for protonic conductivity.

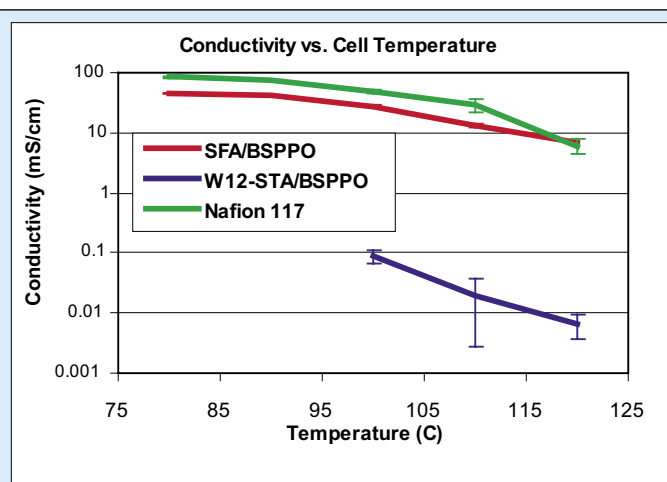
Four-point conductivity measurements involved the use of four electrodes placed around the cell to obtain resistance values. First, two electrodes were attached to the current collectors of the test cell. Two additional electrodes were then attached directly to the membrane material via platinum sense wires in the BekkTech cell. The electrodes being attached directly to the membrane material allowed for compensation of the interfacial and material resistances due to the existing fuel cell hardware. Current was then measured as a function of applied voltage; from this, a membrane resistance could be calculated via Ohm's Law. Length, width, and thickness of samples were then recorded in order to calculate conductivity. While the length and width could always be accurately determined using calipers, the thickness of the membranes was found to vary occasionally upon inspection with a micrometer. When this was the case, average thickness values were recorded. Conductivity was then calculated using the equation was provided with the BekkTech test cell manual.

## RESULTS

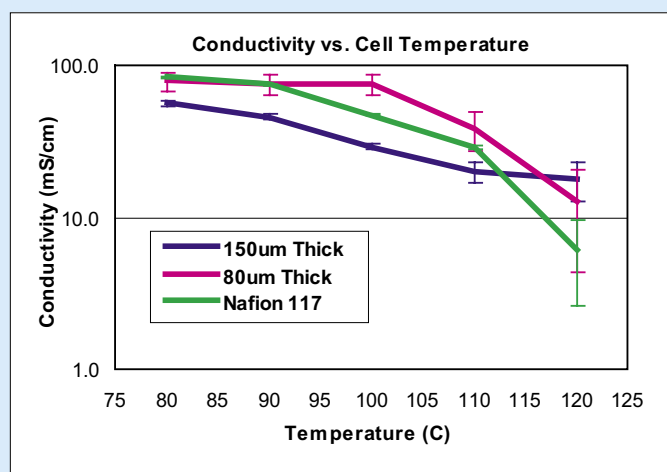
Figure 1 shows the conductivity verses cell temperature results obtained for the organic/inorganic hybrid composite membranes using the BekkTech cell. Membrane materials were cut and placed in the conductivity test cell, as mentioned above. All measurements were obtained in a pure hydrogen (99.999%) environment, keeping with the standard operating procedure of the BekkTech cell provided in the manual. Values were taken at a constant humidification temperature of 80°C, a hydrogen flow rate of 0.2 slpm, and a hydrogen backpressure of 30 psig. Results are presented along with a conductivity sweep of Nafion 117, to provide a baseline for comparison. Nafion 117 was chosen due to the similarity that the membranes shared in thickness. Results were consistent with those of a typical hydrogen pump experiment using the BekkTech cell.

Figure 2 compares the conductivity verses cell temperature of the Russian analog membrane to Nafion 117. Again, Nafion 117 was chosen because of the similarity in thickness to the analog membranes. Measurements were obtained in a pure hydrogen (99.999%) environment, keeping with the standard operating procedure of the BekkTech cell provided in the manual. Values were taken at a constant humidification temperature of 80°C, a hydrogen flow rate of 1.0 slpm, and a hydrogen backpressure of 30 psig.

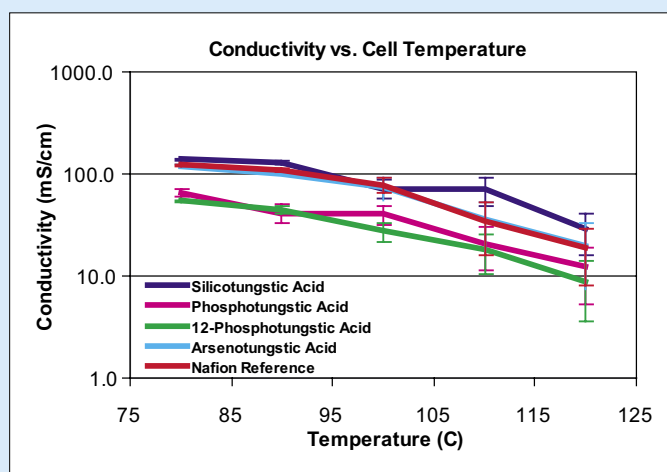
Figure 3 displays the conductivity verses cell temperature of various heteropoly acid doped Nafion membranes. The membrane base in each case was Nafion 112. For that reason, results are shown along with a control membrane of pure Nafion 112. Measurements were obtained in a pure hydrogen (99.999%) environment, keeping with the standard operating procedure of the BekkTech cell provided in the manual. Values were taken at a constant humidification temperature of 80°C, a hydrogen flow rate of 1.0 slpm, and a hydrogen backpressure of 30 psig.



**Figure 1.** Conductivity measurements obtained for SFA/BSPPO 0.41wt% and W12-STA/BSPPO 0.44wt% at various cell temperatures ranging from 80-120°C. All measurements were taken at a humidification temperature of 80°C, hydrogen flow rate of 0.2 slpm, and a hydrogen backpressure of 30 psig. Note that units of conductivity are in milli-Siemens/cm.



**Figure 2.** Conductivity verses operating temperature results for Russian analog membranes at varying thicknesses. All measurements were taken at a humidification temperature of 80°C, hydrogen flow rate of 1.0 slpm, and a hydrogen backpressure of 30 psig. Note that units of conductivity are in milli-Siemens/cm.



**Figure 3.** Conductivity verses operating temperature results for heteropoly acid doped Nafion membranes. All measurements were taken at a humidification temperature of 80°C, hydrogen flow rate of 1.0slpm, and a hydrogen backpressure of 30psig. Note that units of conductivity are in milli-Siemens/cm.

## DISCUSSION AND CONCLUSIONS

Conductivity results of the organic/inorganic hybrid membranes showed that SFA/BSPPPO has a much higher protonic conductivity than W-12 STA/BSPPPO at all temperatures measured. As discussed in the literature, the decreased performance of W-12 STA as a dopant for organic/inorganic hybrid membranes is likely due to the fabrication process of the membrane [20]. Further research on membrane fabrication has been undertaken. SFA/BSPPPO was not as conductive as Nafion at 80°C; however, there are multiple reasons for considering it a viable replacement option. First, at 80°C, the normal operating temperature of Nafion, SFA/BSPPPO showed conductivity near 50 mS/cm, two-third the values of Nafion. This conductivity gap became smaller as temperature was increased. Secondly, SFA/BSPPPO showed increased thermo-mechanical and conductive stability at elevated temperatures when compared to Nafion. These are promising results when compared to current literature on organic/inorganic hybrid composite membranes [15, 16]. It is suspected that by continuing research on the effect of dopant concentration and by optimizing the fabrication method, that overall performance of organic/inorganic hybrid composite membranes can be increased to a point that may make them a viable replacement material in the future.

Conductivity results for the Nafion analog appeared to show that as membrane thickness increased, the conductivity of the material decreased. Most likely, the higher performance was caused by superior water retention in the thicker analog membrane. Evidence of this increased performance can be seen in Figure 2. At +100°C operation the 150  $\mu\text{m}$  thick membrane had a slower drop in conductivity than the 80  $\mu\text{m}$  sample, most likely corresponding to better water retention. However, it is believed that the superior performance is to be due to the transient nature of water retention at short operating times. Long term operation would need to be performed to confirm this theory. Regardless, both samples showed similar to slightly better conductive properties compared to reference Nafion samples. Both the 150  $\mu\text{m}$  and 80  $\mu\text{m}$  membranes had superior high-temperature conduction values than Nafion, as can again be seen from Figure 2. Additionally, the thermo-mechanical properties of the analog membranes were superior to Nafion in the sense that the material did not disintegrate at 120°C, as was the case with the Nafion studied. Increased conductivity performance and improved thermo-mechanical properties make this material another possible option for replacement of Nafion in high-temperature applications.

Heteropoly acid doped Nafion 112 membranes showed promising results when compared to pure Nafion 112 at elevated temperatures. Specifically, the membrane doped with heteropoly silicotungstic acid (HSiW). At 120°C, the HSiW doped Nafion had a recorded conductivity of 12.6 mS/cm, a 17% improvement over Nafion 112. In addition to the membrane doped with heteropoly silicotungstic acid, the membrane doped with heteropoly arsenotungstic acid (HAS<sub>2</sub>W) also showed slightly better conductivity at 120°C, when compared to Nafion 112. From these results, heteropoly acid doped Nafion membranes certainly seem to be a viable possibility for use as high-temperature proton exchange fuel cell membranes.

Analysis of the high-temperature conductivity for the various membranes shows that, at temperatures at or near 120°C, many are still relatively conductive. Stable performance at or near 120°C is promising given that system integration problems between the fuel cell and automotive system would be alleviated at this temperature. While the performance of most of the membranes in this temperature range were quasi-stable, it can be seen from error bars in Figures 1, 2, and 3 that reproducibility of results does become increasingly difficult at +100°C operation. It has been theorized in literature [9], that the irreproducibility of conductivity could be caused from the effect of hydration on activation energy for heteropoly acids. The theory points out that activation energy of heteropoly acids change in the presence of even small amounts of water. Building on this theory, instability in conductivity at elevated temperatures could be caused by uneven dopant distribution throughout the membrane. Because the dopants are more capable of retaining water, the variation in concentration would lead to heterogeneous hydration across the membrane and varied conduction pathways. Heterogeneous conduction pathways would lead to irreproducible conductivity values. The theory seems reasonable when considering that the varying dopant concentration would have less effect on the overall conduction when in the presence of highly conductive water, i.e. below 100°C operation, as can be seen in Figure 1, 2, and 3 from the decreased magnitude of the error bars below 100°C.

In conclusion, the organic/inorganic membrane, SFA/BSPPPO, while still inferior to Nafion, appears to show promise as a possible replacement for Nafion and other low-temperature per-fluorinated membranes. In general, for organic/inorganic hybrid composite membranes, the issue of dopant heterogeneity needs to be addressed in order to improve the material. Russian analog membrane samples showed superior conduction compared to Nafion at high-temperature operation. Most promising of the materials types studied were the heteropoly acid doped Nafion membranes. Among them, heteropoly silicotungstic acid and heteropoly arsenotungstic acid showed the most promising results; exceeded the conductivity of the control Nafion 112. Overall, in order to advance the technology of high-temperature membranes, further research is recommended on the effect of dopant levels to conductivity, in order to obtain the optimal balance of mechanical strength and membrane conductivity. Conductivity measurements under long-term operation (above 100 hours) are also recommended to test the durability and consistency of the material properties at high-temperatures. These tests could further validate the possibility of the membranes studied as replacement materials in high-temperature fuel cell applications.

## ACKNOWLEDGEMENTS

I would like to thank the U.S. Department of Energy, Office of Science for giving me the opportunity to participate in the SULI program. Special thanks go to my mentor, Dr. John Turner, for all of his patience and advice. Additionally, I would like to thank Dr. John Pern for supplying the organic/inorganic membrane samples for testing and Dr. Andrew Herring of the Colorado School of Mines for providing the heteropoly acid doped Nafion 112 membranes for this study.

## REFERENCES

- [1] T. Oi, K. Wada, "Feasibility study on hydrogen refueling infrastructure for fuel cell vehicles using the off-peak power in Japan," International Journal of Hydrogen Energy, vol. 29, 2004, pp. 347-354.
- [2] D. Hissel, M.C. Péra, J.M. Kauffmann, "Diagnosis of automotive fuel cell power generators," Journal of Power Sources, vol. 128, 2004, pp. 239-246.
- [3] K. Agbossou, M. Lal Kolhe, J. Hamelin, É. Bernier, T. Bose, "Electrolytic hydrogen based renewable energy system with oxygen recovery and re-utilization," Renewable Energy, vol. 29, 2004, pp. 1305-1318.
- [4] A. Mills, S. Al-Hallaj, "Simulation of hydrogen-based hybrid systems using Hybrid2," International Journal of Hydrogen Energy, vol. 29, 2004, pp. 991-999.
- [5] "DaimlerChrysler begins deliveries in Japan, US," Fuel Cells Bulletin, vol. 2003 (12), Dec. 2003, pp. 9.
- [6] "Honda FCX demonstrates cold-start performance," Fuel Cells Bulletin, vol. 2004 (4), April 2004, pp. 5.
- [7] "Ebara Ballard 1 kWe generator for field trials, unveils kerosene system," Fuel Cells Bulletin, vol. 2004 (6), June 2004, pp. 3-4.
- [8] "Have Power to install ReliOn fuel cells in Ohio," Fuel Cells Bulletin, vol. 2004 (6), June 2004, pp. 8.
- [9] E.L. Hahn, "Spin Echoes," Phys. Rev. vol. 80, 1950, pp.580-594.
- [10] M.A. Sweikart, "Heteropoly Acids for Use as Proton Conductors in High Temperatures Proton Conducting Membrane Fuel Cells," M.S. Thesis. Golden, CO: Colorado School of Mines, 2004.
- [11] I. Honma, H. Nakajima, S. Nomura, "High temperature proton conducting hybrid polymer electrolyte membranes," Solid State Ionics, vol. 154-155, 2004, pp. 707-712.
- [12] J.J. Fontanella, M.C. Wintersgill, R.S. Chen, Y. Wu, S.G. Greenbaum, "Charge Transport and water molecular motion in variable molecular weight Nafion membranes: high pressure electrical conductivity and NMR," Electrochimic Acta, vol. 40, no. 13-14, 1995, pp. 2321-2326.
- [13] V. Ramani, H.R. Kunz, J.M. Fenton, "Investigation of Nafion®/HPA composite membranes for high temperature/low relative humidity PEMFC operation," Journal of Membrane Science, vol. 232, 2004, pp. 31-44.
- [14] O. Savadogo, "Emerging membranes for electrochemical systems Part II. High temperature composite membranes for polymer electrolyte fuel cell (PEFC) applications," Journal of Power Sources, vol. 127, 2004, pp.135-161.
- [15] Mary Ann Sweikart, Andrew M. Herring, John A. Turner, D. L. Williamson, Bryan D. McCloskey, Sukritthra R. Boonrueng, and Maria Sanchez, "12-Tungstophosphoric Acid Composites with Sulfonated or Unsulfonated Epoxies for High-Temperature PEMFCs", Journal of The Electrochemical Society, vol. 152, 2005, A98-A103.
- [16] D. Vernon, F. Meng, D.L. Williamson, J.A. Turner, A.M. Herring, "Synthesis, Characterization, and Conductivity Measurements of Hybrid Membranes Containing a Lacunary Heteropolyacid for PEM Fuel Cell Applications," Journal of the Electrochemical Society, in Press.
- [17] I. Honma, S. Hirakawa, K. Yamada, J.M. Bae, "Synthesis of organic/inorganic nanocomposites protonic conduction membrane through sol-gel processes," Solid State Ionics, vol. 118, 1999, pp.29-36.
- [18] I. Honma, Y. Takeda, J.M. Bae, "Protonic conducting properties of sol-gel derived organic/inorganic nanocomposite membranes doped with acidic functional molecules," Solid State Ionics, vol. 120, 1999, pp. 255-264.
- [19] I. Honma, S. Nomura, H. Nakajima, "Protonic conducting organic/inorganic nanocomposites for polymer electrolyte membrane," Journal of Membrane Science, vol. 185, 2001, pp. 83-94.
- [20] H. Nakajima, I. Honma, "Proton-conducting hybrid solid electrolytes for intermediate temperature fuel cells," Solid State Ionics, vol. 148, 2002, pp. 607-610.
- [21] I. Honma, H. Nakajima, O. Nishikawa, T. Sugimoto, S. Nomura, "Organic/inorganic nano-composites for high temperature proton conducting polymer electrolytes," Solid State Ionics, vol. 162-163, 2003, pp. 237-245.
- [22] F.J. Pern, J.A. Turner, A.M. Herring, "Hybrid Proton-Carrier Polymer Composites for High-Temperature FCPEM Application," Proceeding of Symposium S: Nanostructured Materials in Alternative Energy Devices, 2004, in Press.
- [23] V. Ramani, H.R. Kunz, J.M. Fenton, "Electrochemical Characterization of Stabilized Heteropolyacid/Ionomer Composite Membranes for High Temperature PEMFCs," Abs. 983, 2004 Meeting. © 2003 The Electrochemical Society, Inc.
- [24] S. Hocevar, P. L. A., V. Antonucci, N. Giordano Fuel Cell Seminar: San Diego, CA, 1994, p 329.