High Performance of H_2/O_2 Fuel Cells using Pt/C Electrodes and P_2O_5 - SiO_2 -PMA Glasses as an Electrolyte in Low Temperature

Thanganathan UMA and Masayuki NOGAMI

Department of Material Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya-shi 466-8555

P_2O_5 - SiO_2 -PMA 系ガラスを電解質にした H_2/O_2 燃料電池の低温動作特性

Thanganathan Uma · 野上正行

名古屋工業大学, 466-8555 名古屋市昭和区御器所町

Heteropolyacid containing phosphosilicate glasses were prepared by the sol-gel technique and were studied in relation to their structural, thermal, and textural properties. These glasses are mechanically, thermally, chemically stable and have proton conductivity. It was found to be a suitable potential electrolyte for H_2/O_2 fuel cells. The average pore size of up to 3 nm was observed from a N_2 adsorption-desorption analysis. The electrical conductivity was measured under humidity and temperature conditions. The glasses showed the proton conductivity values in the order of 10^{-3} – 10^{-2} S cm^{-1} , especially, 9.8×10^{-2} S cm^{-1} at 90°C and 70% RH. The cell performance is mainly determined by the higher conductivity characteristics of the electrolyte. We have successfully achieved a high power density value of 17.2 mW/cm² using P_2O_5 - SiO_2 -PMA (7–89–4 mol%) glasses as an electrolyte and 0.1 mg/cm² of Pt/C loaded on the electrode at 30°C and RH 30%.

[Received May 8, 2006; Accepted July 20, 2006]

Key-words : Sol-gel, Glass, PMA, Proton conductivity, H_2/O_2 fuel cells, Power density

1. Introduction

Phosphosilicate glasses exhibit interesting technological and structural properties. In particular, they find uses in energy generating applications, such as hydrogen fuel cells and proton exchange membrane fuel cells, because of their ability to act as fast proton conductors.^{(1),(2)} The main advantage of sol-gel processing is the high degree of compositional and homogeneity control inherent with them in the solution syntheses of multi-component inorganic materials. A H_2/O_2 fuel cell is an electrochemical energy device which converts some fuels and oxidants into electricity, water and heat. This device is poised to become a leading power source for mobile and transportation applications. Low temperature fuel cells have promising characteristics for application in vehicle traction and portable devices.

Heteropolyacids and their metal salts are well known acidic and oxidative catalysts. A heteropoly compound has acidic and redox catalytic properties.⁽³⁾ It also shows characteristic sorption behavior⁽⁴⁾ depending on the properties of the adsorbates. Most non-polar chemicals like alkenes are adsorbed only on its surface (surface area is less than 10 m²/g), while polar compounds like alcohols, water, pyridines and ethers mostly penetrate into its bulk to form a pseudo-liquid phase.⁽⁵⁾ Thus, some reactions occur only on the surface, whereas others occur in the bulk of the heteropolyacid. On the other hand, Tatsumisago and Minami⁽⁶⁾ made a protonic conductor by incorporating phosphomolybdic acid (PMA) (42% by weight) into silica gel and film using tetraethoxysilane as precursor. PMA was initially investigated by Nakamura et al.^{(7)–(9)} as solid protonic electrolyte in fuel cells. These authors evidenced a strong influence of relative humidity on the protonic conductivity of solid electrolyte together with the difficulty to maintain the 29-hydrate form during the fuel cell operation. Among the various heteropolyacids, phosphotungstic (PWA) and phosphomolybdic (PMA) acid, in their 29-water molecules hydrate form ($H_3PW_{12}O_{40} \cdot 29H_2O$ and

$H_3PMo_{12}O_{40} \cdot 29H_2O$) are characterized by high protonic conductivity, i.e., 0.17 and 0.18 Ohm⁻¹ cm⁻¹, respectively.⁽⁷⁾ Abe et al.^{(10),(11)} reported that protons are very mobile when they are strongly hydrogen-bonded in glasses, and the magnitude of proton conductivity is primarily determined by the degree of hydrogen bonding and the concentration of mobile protons in the glass structure. Park et al.⁽¹²⁾ reported that the effect of acid concentration with silica phosphate gels [SiP-PMA (PWA)] on proton conductivity was successfully fabricated via a sol-gel method. Staiti et al.⁽¹³⁾ reported on a fuel cell fed with H_2/O_2 utilizing PWA as solid electrolyte and produced a maximum power density of 0.738 W/cm² at room temperature. These efforts are stimulating us to achieve the high performance for H_2/O_2 fuel cells at low temperatures using a novel class of heteropolyacid glasses as an electrolyte with a Pt/C electrode. Previously, we reported the preparation of proton conducting P_2O_5 - SiO_2 glass with the highest conductivity (10^{-2} S cm^{-1}) at 50°C,⁽¹⁴⁾ this glass was applied for the first time to H_2/O_2 fuel cell operated at 50°C and 90% RH, and found the output power was approximately 6 mW/cm². Heteropolyacids such as PMA and SiMA are considered as the most dopants in the sol-gel matrix. The dissociation energy of the proton is dependent on the degree of strength of the hydrogen bonding between the hydroxyl bond and the water molecules. On this basis, we prepared a new class combination of P_2O_5 - SiO_2 -PMA glasses with a higher proton conductivity which could be potential substitutes for electrolytes in fuel cells. The scope of this present work is the evaluation of electrochemical activity of the H_2/O_2 fuel cells based on the proton conducting glasses as electrolytes and electrodes and their characterization.

2. Experimental procedure

The glass membrane and Pt/C electrode prepared by following procedure was previously reviewed.⁽¹⁵⁾ Tetraethoxysilane (TEOS, 99.9%, Colcote) was hydrolyzed with a solution

of H_2O (as 0.15N-HCl aq) and $\text{C}_2\text{H}_5\text{OH}$ (4:1 mol%). Trimethylphosphate (98.0%, Nacalai Tesque) (5, 7, 9 and 11 mol%) was added drop wise under continuous magnetic stirring. After a period of 1 h, Phosphomolybdic acid (PMA, Kishida chemicals) was completely dissolved in ethanol and water then mixed with the total amount of the solution under stirring. After hydrolyzing, HCONH_2 (N-N Dimethyl formamide) (1 ml) was added into the solution followed by more stirring for 1 h. The HCONH_2 is effective in changing the porosity of the glass, in order to obtain 5 g of glass. The obtained solution was kept at room temperature for one month to form a gel glass. It was water-treated at 150°C for 30 h and then heat-treated at 600°C for 2 h to obtain the final glass. Upon heating, the gel liberates the water molecules and shrinks due to dehydration-condensation of the hydroxyl groups.

Two different structures of electrodes have been prepared with a Nafion[®] ionomer, PTFE (polytetrafluorethylene) and the Pt/C powder. The electrodes were prepared by directly mixing the Nafion[®] ionomer and the PTFE at room atmosphere with magnetic stirring for about 30 min. The Pt/C powder (0.1 and 0.15 mg/cm²) was added with solvent ethanol and water to obtain a catalyst ink. The ink was smoothly painted on a carbon sheet and then dried at 100°C for 1 day to remove the solvents from the catalyst layer. The thickness of the electrodes varied with the amount of Pt/C powder that occurs in the catalyst ink. The catalyst layer thickness ranged from 0.21–0.23 mm. The catalyst layer porosity and electrolyte volume fraction depends directly on the preparative conditions, while the agglomerate porosity and the macropore porosity are not influenced significantly.

The glass membrane electrode assemblies (MEAs) were prepared with two electrodes attached on the two faces of the electrolyte (glass) by hand-pressing with the catalyst ink at room atmosphere. This MEA preparation is not the same as compared to hot-pressing as used for the Nafion membrane. Firstly, a small drop of the catalyst ink was injected onto one side of the glass surface, and then attached to the electrode by hand-pressing on the active region of the electrolyte. Another, similar attachment was made on the other side of the electrolyte at room temperature. Finally, the MEAs were dried at room temperature for 30 mins. This attachment plays in an important role in the electrochemical behavior. The electrode/electrolyte unit is the heart of the fuel cell. The active area of electrode was 0.25 cm² and the thickness of the MEA was approximately 1.1 mm.

Thermoanalytical measurements were performed on the glass powder using a model SSC-5200 (SEIKO Instrument) at a temperature ranging from 30 to 800°C to gather information on the thermal stability and weight loss. The IR absorption spectra was measured by using a JASCO (FTIR-460) Fourier, which transforms infrared spectroscopy in the range of 400–4000 cm⁻¹. N_2 adsorption isotherms were measured using a nitrogen-gas adsorption analyzer (NOVA-1000, Quantochrome). And isotherms were obtained in both adsorption and desorption modes. Specific surface areas were determined by the BET (Brunauer-Emmett-Teller)¹⁶⁾ and the pore size distribution was established using the BJH (Barrett-Joyner-Halenda)¹⁷⁾ method. Electrical conductivity was measured by an impedance analyzer (Solartron 1260). Before the resistance was measured, the samples were kept for 3 h in an atmosphere controlled humidity ranging from 30 to 90%. The values of resistance registered at the bridge were corrected for the resistance of the connecting wires. The thicknesses of samples were measured at the end of conductive measurements. The

Fig. 1. TG-DTA curves for the P_2O_5 - SiO_2 -PMA glasses heat treated at 600°C : (M1) 5-91-4 (mol%), (M2) 7-89-4 (mol%) and (M3) 9-87-4 (mol%).

electrochemical characterization of the fuel cells was performed by measuring a polarization versus the current curve using a Solartron 1287 electrochemical interface and a Solartron 1260 frequency response analyzer. The electrochemical test was conducted at 30°C with 30% relative humidification and one atmospheric pressure. To evaluate the performance of the H_2/O_2 , a single cell was fed with a gaseous H_2 and O_2 , with a flow rate ca. 10–100 mL/min, over the anode and cathode stations, respectively.

3. Results and discussion

The TG and DTA analysis of the P_2O_5 - SiO_2 -PMA glasses in Fig. 1 shows the thermal dehydration changes indicating that the glass materials have been present in a non-crystalline phase. Two different regions of weight loss were obtained via thermal treatment for all samples. The first region corresponds to temperatures below 150°C ; this was associated to a loss of structural water. The second region occurs at temperature above 200°C . Fig. 1 (c) highlights the three different regions of weight losses. For temperatures below 150°C and temperatures between 250 and 400°C , which is due to the loss of structural water; and above 400°C , which is due to the simultaneous loss of carbon residues and also to the loss of structural water in the form of silanol groups. A small endothermic peak was observed in all samples, which can be attributed to evaporation of molecular water adsorbed on the glass surface. There was no exothermic peak up to 600°C , which indicates that there was no phase change. The information obtained with the DTA analysis confirmed the results obtained by the TGA. No exothermic peak was visible on the DTA curve of P_2O_5 - SiO_2 -PMA glass in the temperatures ranging from 200 to 800°C . This means that the secondary structure of water between α -Keggin units in the clathrates of HPAs, the characteristics for pure acids, has been destroyed and replaced with interactions of individual α -Keggin units with silica. The thermal stability of α -Keggin units thus substantially increased. It can be seen that all the samples show a thermal stability at 150°C with a weight loss between 8–20%,

Fig. 2. FTIR plots of P₂O₅-SiO₂-PMA glasses heat treated at 600°C: (M1) 5-91-4 (mol %), (M2) 7-89-4 (mol %), (M3) 9-87-4 (mol %) and (M4) 11-85-4 (mol %).

which was the operating temperature at 800°C. Above 100°C, the weight loss of all samples show below 20%, can be attributed to the loss of absorbed water and isolated trimethyl-phosphate. The total weight loss observed was restored by the adsorption of water molecules in air humidity.¹⁸⁾ The observed loss of water at higher temperatures for heteropoly acids supported on silica with respect to the heteropoly acids will have probably a beneficial effect on proton conductivity above 100°C. This result suggests that the all samples are thermally stable up to 800°C.

Figure 2 demonstrates the FTIR spectra of the PMA in phosphosilicate glasses. In the absorption spectra of P₂O₅-SiO₂-PMA glass, the absorption bands at 1043 cm⁻¹ due to the Si-O-P bonds that were observed and was heat-treated at 600°C. The presence of Si-O-P bonds was expected to enhance the retention of the hydrated water and thus improve the proton conductivity even in a dry atmosphere at relatively high temperatures. The weak IR shoulder around 1010 cm⁻¹ (due to low-silica contents) was assigned to the asymmetric stretching vibration (ν_{as}) of the silicon-oxygen bond in the [SiO₄] tetrahedral network.^{19),20)} In the FTIR spectra, it was noticed that in the range of 1064 cm⁻¹ the band intensity was higher than other samples. This may be due to the SiO₂ concentration effects or due to the free OH stretching occurrences in glass. The main characteristic of the glass was in the presence of Si-O-Si and PM-O-Si bonds, which can be identified by the FTIR analysis. Bands at 1115 cm⁻¹ were assigned to the asymmetric stretching vibrations of the Si-O bond in a tetrahedral network. Bands at 704 cm⁻¹ were due to the symmetric stretching of the Si-O-Si (bridging oxygen atoms between the tetrahedral). The vibrations of the Si-O-Si, PM-O-PM or PM-O-Si bonds were located at 642 cm⁻¹. The origin of the band at 2316 cm⁻¹ can be found in trapped CO₂ gas inside the remaining closed porosity. This may be due to the degradation of the hydrogenocarbonates (CO₂ + OH⁻ → HCO₃⁻) or of the bidentate C=O linkages.²¹⁾ The band at 2915 cm⁻¹, observed in the glass containing P₂O₅ whose intensities increase with an escalating P₂O₅ content, was assigned due to the OH groups bound with the P⁵⁺ ions. This may be assigned due to the OH stretching. It was known that the position of the OH absorption bands depends on the degree of strength of the hydrogen bonding and shifts to a lower wave number with an increasing strength of the hydrogen bonding.²²⁾ The phosphorous ions were bound with the silica network consisting of the core structure. Therefore, pore sur-

Fig. 3. N₂ adsorption isotherms (a)–(b) and BJH pore-size distributions (c)–(d) for P₂O₅-SiO₂-PMA glasses (M2 and M3) heat treated at 600°C.

Table 1. Pore Properties of P₂O₅-SiO₂-PMA Glasses Heat Treated at 600°C

Sample	P ₂ O ₅ -SiO ₂ -PMA glasses (mol %)	Average pore size (nm)	Average pore volume (cm ³ /g)	Specific surface area (m ² /g)
M2	7-89-4	2.33	0.27	471 ± 2
M3	11-85-4	2.32	0.32	562 ± 2

faces of the obtained glasses were rich in POH groups; the phosphorous ions consisting of the POH bonds and were dissolved into the silica matrix. Protons in the POH bonds were easily dissociated and transferred between the POH bonds and the adsorbed water, resulting in high conductivity.

The N₂ adsorption-desorption isotherms curves are presented in **Fig. 3**. The pore size distribution was obtained by the analysis of the nitrogen adsorption-desorption isotherms and all the calculations were performed with the help of a BET program.¹⁶⁾ All data listed in **Table 1**. Figure 3 shows that the surface area of 562 m²/g was observed for the M2 sample. The specific surface area and pore volume changes, which is due to the polycondensation reaction between the hydroxyl groups of the pore surfaces. Upon heating, the water and solvents in pores evaporated at around 100°C, followed by the gradual removal of water produced by the dehydration-condensation reaction between the hydroxyl groups on the pore surfaces. The porous properties are strongly linked with the preparation of the glass composition and the amount of formamide used

Fig. 4. Humidity dependence of the proton conductivity for P_2O_5 - SiO_2 -PMA glasses heat treated at $600^\circ C$: (M1) 5-91-4 (mol %), (M2) 7-89-4 (mol %), (M3) 9-87-4 (mol %) and (M4) 11-85-4 (mol %).

in the gel synthesis. The incorporation of formamide in the sol-gel glasses could be responsible for the significant improvement in the protonic conduction for the $600^\circ C$ heat treated glass, and can be attributed to the higher porosity of the glass.²³⁾ In this case, the surface hydroxyls can involve more and stronger hydrogen bonds due to the shorter interionic distance of the neighboring sites. Strong hydrogen bonding makes the proton of the OH group very mobile and a large amount of water adsorbed on the pore surface. Although the pore formed by the stack of primary gel particles sounds in the presence of formamide, the glasses heat treated at $600^\circ C$. The pore properties strongly reflect the glass composition and the amount of formamide used in the gel synthesis.

The proton conductivity study was carried out under humidification ranging from 30 to 90% and a temperature of $30^\circ C$ (Fig. 4). It is apparent that the conductivity increases with the rising humidity level and this behavior suggests that the pores in the samples are completely filled with water molecules. The conductivity is proportional to the adsorbed water concentration.²⁴⁾ It was previously determined that the proton conduction is promoted by the proton hopping between the hydrogen bond and the adsorbed water molecules. The humidity dependent conductivity in such systems arises from the protonic transport in the water molecules adsorbed on the wide surface separating the porous oxide and the atmosphere. The principal transport mechanism is known as the Grotthuss chain reaction. Protons are transported through the membrane by two pathways. The first is a proton shuttling (or Grotthuss) mechanism that involves the formation and breaking of hydrogen bonds between the proton and the water.^{25),26)} The second pathway for proton conduction is equivalent to traditional cation conduction where the hydrated proton diffuses through the aqueous media in response to an electrochemical gradient.^{27),28)} The proton conductivity via the Grotthuss mechanism is considerably faster than the hydronium ion diffusion, and it is estimated that approximately 90% of the proton conductance occurs via the Grotthuss pathway.²⁵⁾

The temperature dependence of the proton conductivity was evaluated in the temperatures ranging from 30 to $90^\circ C$ with a relative humidity of 70% (Fig. 5). The temperature increases with the increasing proton conductivity was found to be in the

Fig. 5. Arrhenius plot of log conductivity against reciprocal temperature for P_2O_5 - SiO_2 -PMA glasses heat treated at $600^\circ C$: (M1) 5-91-4 (mol %), (M2) 7-89-4 (mol %), (M3) 9-87-4 (mol %) and (M4) 11-85-4 (mol %).

order of 10^{-3} - 10^{-2} $S\ cm^{-1}$. The Arrhenius behavior is typically observed with a higher proton conductivity (9.8×10^{-2} $S\ cm^{-1}$), suggesting a well-ordered structure capable of effective proton transportation. The glasses have been found to be thermally stable up to $400^\circ C$ and possess protonic conductivities of approximately 10^{-2} $S\ cm^{-1}$ at $30^\circ C$ and RH. The magnitude of proton conductivity is primarily determined by the hydrogen-bonding strength of the OH. It means that the proton conductivity rises with an increasing number of the adsorbed water molecules and is dependant upon the pore properties. When used with the glass membrane, the membrane was set under a humidified atmosphere. This may influence on the amount of water and the physical state of the OH groups in the membrane. It could be strongly suitable as a potential electrolyte for fuel cells.

The high proton conductivity showing P_2O_5 - SiO_2 -PMA (7-89-4 mol%) glass membrane was used for cell test. The 0.1 mg/cm² of Pt/C was loaded on the electrode with P_2O_5 - SiO_2 -PMA (7-89-4 mol%) glasses as electrolyte attained the current density value of 55 mA/cm² (Fig. 6(a)) and a high power density value of 17.2 mW/cm² (Fig. 6(b)) at 0.2 V at $30^\circ C$ and RH 30% for a 7 h experiment. The cell potential is about 1 V. During the operation, the cell performance rises with an increasing humidity level with respect to the time period. A similar trend was observed in Figs. 7(a) and (b), where the current density value of 60 mA/cm² and the power density value of 9.1 mW/cm² at 0.2 V for a 12 h experiment. This output is not sufficient at present, but it is comparatively higher than our previous result.¹⁴⁾ Both plots, each curve line (V1, V2... and PO1, PO2,...) indicates the time variation during the cell operation. From electrochemical measurements, the low amount of the Pt/C loaded on the electrode shows a good performance compared to the high amount of Pt/C loaded on the electrode. This may be due to the electrode microstructure and interface contact between the electrode-electrolyte. Therefore, the densities of the electrocatalyst sites are higher in Fig. 6 than in Fig. 7 which results in an improved electrocatalyst-membrane electrolyte contact. Such contact may lead to the improved performance. The size of the MEA varied with respect to the thickness of the catalyst layer and the electrolyte, and also the amount of the Pt/C powder embedded on the electrolyte. Consequently, the Pt/C particles embedded in the membrane played an important role in enhancing the

Fig. 6. Cell voltage vs. current density of H_2/O_2 fuel cell using $\text{P}_2\text{O}_5\text{-SiO}_2\text{-PMA}$ (7-89-4 mol %) glass membrane with Pt/C electrodes: (a) 0.1 and (b) 0.15 mg/cm^2 at 30°C and RH 30%.

proton conductivity in the proton conducting glass electrolyte. The preparation of MEA strongly influenced the electrochemical performance of oxygen and hydrogen electrodes.^{29)–33)} These results indicate that the glass membrane and the MEA preparation conditions are key factors in the fuel cell performance. The resistance of the catalyst layer was connected to the amount of catalyst in the catalyst layer. The resistance of the electrodes varied depending on the amount of the catalyst. The Pt/C particles were conceived to provide sites for the catalytic recombination of hydrogen and oxygen reactant gases permeated from the anode and cathode, thereby producing water inside the membrane. In general, as the amount of Pt/C powder embedded in the membrane increases, the resistance of the glass membrane is increased due to the hindrance of proton conduction through the membrane. The proton conductivity in the membrane decreased with an increase in the Pt/C particle doping. The cell resistance with 0.15 mg/cm^2 Pt/C loaded was still large resulting in a poor cell performance. This indicates that the water content in the glass membrane cell with 0.1 mg/cm^2 Pt/C loaded was higher than that of the other cell and that the rate of proton conduction through the glass membrane with 0.1 mg/cm^2 of Pt/C loaded was faster than through the other. The $\text{P}_2\text{O}_5\text{-SiO}_2\text{-PMA}$ (7-89-4 mol%) glass membrane with 0.15 mg/cm^2 of Pt/C loaded shows a lower performance than that with 0.1 mg/cm^2 of Pt/C loaded. Furthermore, the fabrication of electrodes needs to be delivering high energy efficiency with heteropolyacid glass membrane for a low temperature H_2/O_2 fuel cell.

Fig. 7. Power density vs. current density of H_2/O_2 fuel cell using $\text{P}_2\text{O}_5\text{-SiO}_2\text{-PMA}$ (7-89-4 mol %) glass membrane with Pt/C electrodes: (a) 0.1 and (b) 0.15 mg/cm^2 at 30°C and RH 30%.

4. Conclusions

$\text{P}_2\text{O}_5\text{-SiO}_2\text{-PMA}$ glass membrane should be a promising candidate as an electrolyte for the H_2/O_2 fuel cell. The glasses have a high thermal stability, mechanical stability and proton conductivity. A maximum power density value of 17.2 mW/cm^2 as well as current density value of 55 mA/cm^2 was obtained at 30°C and RH 30%. Our group will be focusing on the development of the cells performance with fabrication of electrode/electrolyte and MEA to achieve a high efficient energy.

Acknowledgements This work was supported by a grant from the Japan Society for the Promotion of Science (JSPS) fellowship program in Japan.

References

- 1) Nogami, M., Goto, Y., Tsurita, Y. and Kasuga, T., *J. Am. Ceram. Soc.*, Vol. 84, pp. 2553–2556 (2001).
- 2) Chandra, S., Sekhon, S. S., Srivastava, R. and Arora, N., *Solid State Ionics*, Vol. 154 & 155, pp. 609–619 (2002).
- 3) Komata, T. and Misono, M., *Chem. Lett.*, pp. 1177–1180 (1983).
- 4) Misono, M., *Mater. Chem. Phys.*, Vol. 17, pp. 103–120 (1987).
- 5) Misono, M., Mizuno, N., Katamura, K., Kasai, A. and Konishi, Y., *Bull. Chem. Soc. Jpn.*, Vol. 55, pp. 400–406 (1982).
- 6) Tatsumisago, M. and Minami, T., *J. Am. Ceram. Soc.*, Vol. 72, pp. 484–486 (1989).
- 7) Nakamura, O., Kodama, T., Ogino, I. and Miyake, Y., *Chem. Lett.*, Vol. 1, pp. 17–18 (1979).
- 8) Nakamura, O., *Progress in Batteries & Solar Cells*, Vol. 4, pp. 230–243 (1982).
- 9) Nakamura, O., Ogino, I. and Kodama, T., “Proceedings of the

- 3rd World Hydrogen Energy Conference," Vol. 119, Tokyo (1980).
- 10) Abe, Y., Hosono, H., Ohta, Y. and Hench, L. L., *Phys. Rev. B*, Vol. 38, pp. 10166–10169 (1988).
 - 11) Abe, Y., Hosono, H., Lee, W. H. and Kasuga, T., *Phys. Rev. B*, Vol. 48, pp. 15621–15625 (1993).
 - 12) Park, Y. I., Kim, J. D. and Nagai, M., *J. Mater. Sci. Letts.*, Vol. 19, pp. 2251–2253 (2000).
 - 13) Staiti, P., Hocevar, S. and Giordano, N., *Int. J. Hydrogen Energy*, Vol. 22, pp. 809–814 (1997).
 - 14) Nogami, M., Matsushita, H. and Goto, Y., *Adv. Mater.*, Vol. 12, pp. 1370–1372 (2000).
 - 15) Uma, T., Izuhara, S. and Nogami, M., *J. Eur. Ceram. Soc.*, Vol. 26, pp. 2365–2372 (2006).
 - 16) Brunauer, S., Emmett, P. H. and Teller, E., *J. Am. Chem. Soc.*, Vol. 62, pp. 309–319 (1938).
 - 17) Barret, E. P., Joyner, L. G. and Halenda, P. H., *J. Am. Chem. Soc.*, Vol. 62, pp. 1723–1732 (1940).
 - 18) Nogami, M. and Abe, Y., *Phys. Rev. B*, Vol. 55, pp. 12108–12112 (1997).
 - 19) Merzbacher, I., McGrath, K. J. and Higby, P. L., *J. Non-Cryst. Solids*, Vol. 136, pp. 249–259 (1991).
 - 20) Merzbacher, C. I. and White, W. B., *J. Non-Cryst. Solids*, Vol. 130, pp. 18–34 (1991).
 - 21) Colomban, Ph. and Bruneton, E., *J. Non-Cryst. Solids*, Vol. 147 & 148, pp. 201–205 (1992).
 - 22) Scholze, H., *Glastech. Ber.*, Vol. 32, pp. 81–88, 142–152, 314–320 (1959).
 - 23) Wang, C. and Nogami, M., *Mater. Lett.*, Vol. 42, pp. 225–228 (2000).
 - 24) Nogami, M. and Abe, Y., *Phys. Rev. B*, Vol. 18, pp. 12108–12112 (1997).
 - 25) Bockris, J. O. M. and Reddy, A. K., "Modern Electrochemistry," Vol. 1, 2nd ed., Plenum Press, New York (1998).
 - 26) Marx, D., Tuckerman, M. E., Hutter, J. and Parrinello, M., *Nature*, Vol. 397, pp. 601–604 (1999).
 - 27) Zawodzinski, T. A., Davey, J., Valerio, J. and Gottesfeld, S., *Electrochim. Acta*, Vol. 40, pp. 297–302 (1995).
 - 28) Eikerling, M., Kornyshev, A. A. and Stimming, U., *J. Phys. Chem. B*, Vol. 101, pp. 10807–10820 (1997).
 - 29) Uchida, M., Aoyama, Y., Eda, E. and Ohta, A., *J. Electrochem. Soc.*, Vol. 142, pp. 463–468 (1995).
 - 30) Paganin, V., Ticianelli, E. and Gonzalez, E., *J. Appl. Electrochem.*, Vol. 26, pp. 297–304 (1996).
 - 31) Lee, S. J., Mukerjee, S., McBreen, J. and Rho, Y. W., *Electrochim. Acta*, Vol. 43, pp. 3693–3701 (1998).
 - 32) Antolini, E., Giorgi, L., Poizo, A. and Passalacqua, E., *J. Power Sources*, Vol. 77, pp. 136–142 (1999).
 - 33) Passalacqua, E., Lufrano, F., Squadrito, G., Patti, A. and Giorgi, L., *Electrochim. Acta*, Vol. 46, pp. 799–805 (2001).