

Phosphorus-doped glass proton exchange membranes for low temperature direct methanol fuel cells

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Abstract

Phosphorus-doped silicon dioxide thin films were used as ion exchange membranes in low temperature proton exchange membrane fuel cells. Phosphorus-doped silicon dioxide glass (PSG) was deposited via plasma-enhanced chemical vapor deposition (PECVD). The plasma deposition of PSG films allows for low temperature fabrication that is compatible with current microelectronic industrial processing. SiH_4 , PH_3 and N_2O were used as the reactant gases. The effect of plasma deposition parameters, substrate temperature, RF power, and chamber pressure, on the ionic conductivity of the PSG films is elucidated. PSG conductivities as high as $2.54 \times 10^{-4} \text{ S cm}^{-1}$ were realized, which is 250 times higher than the conductivity of pure SiO_2 films ($1 \times 10^{-6} \text{ S cm}^{-1}$) under identical deposition conditions. The higher conductivity films were deposited at low temperature, moderate pressure, limited reactant gas flow rate, and high RF power.

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1. Introduction

Silicate glasses deposited by plasma-enhanced chemical vapor deposition (PECVD) have traditionally been used as low-loss electrical insulators in microelectronic devices. However, in recent years it has been reported that introducing minority additives into the silicate matrix allows researchers to tune the physical properties of these glasses, making them attractive for a variety of applications. It has been shown that introducing limited amounts of a secondary oxide in the glass can tailor its structure, mechanical strength, and both the electrical and ionic conductivity [1]. One possible application of silicate glasses with increased ionic conductivity is fully inorganic electrolyte materials for low temperature proton exchange membrane fuel cells. Silicate glasses with adequate proton conductivity are ideal because they are inexpensive, reliable, easily fabricated over a wide range of thicknesses and can serve as a methanol barrier layer to lower the fuel crossover rate in direct methanol fuel cells (DMFCs).

Silicate glasses have a tetrahedral structure where defect –OH terminated silicon groups assist in ion transport by providing nano-porous regions that are tens of angstroms in diameter. These imperfections retain the high electrical loss characteristics of the structure, while providing a surface-site ionic pathway along the length of the pores. The ionic conductivity is achieved by liberation of the protons from silanol hydroxyl groups in the glass structure pores [2]. Abe et al. have shown that oxides prepared at low temperature incorporate a large number of hydroxide and water impurities that impart high porosity to the glass as compared to those formed at high temperature [3].

It has been shown that doping of silicate glasses with group V elements, such as phosphorus, increases the conductivity of the silicate glasses. This is accomplished by introducing gaps in the tetrahedral glass network as the requisite Si–O–Si bond formation is sterically hindered and replaced by either –Si–OH or –Si–O–POH surface groups. This increases both the free volume and pore wall surface area, thus increasing the ion-exchange capacity of the prepared glass. It should also be considered that the group V hydroxyl groups have a higher acidity when compared to silanol. This indicates that the associated proton in the P–OH group is more strongly bonded with neighboring water molecules [1], which should increase its mobility.

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Further studies in this area have shown that proton mobility is also a function of the hydrogen bonding that occurs between the hydroxyl groups attached to a network-forming cation ($X = \text{Si}^{4+}$ or P^{5+}) and a hydroxide ion ($X\text{--O--H}\cdots\text{O--X}$) [4,5]. It has been shown that the strength of the hydrogen bond between the hydroxyl groups depends on the type of counter ion it is bonded to. The hydrogen bonding is extremely weak in cases where the counter ion is of the bridging type ($X\text{--O--X}$) compared to those where the counter ion is of the non-bridging type ($X\text{--O}^-$). Uma et al. found that in phosphorus-doped silicate glasses (PSG), the phosphorus is bonded to one bridging and three non-bridging oxygen atoms [6]. It is believed that the increase in non-bridging oxygen bonds increases the ion conduction sites, leading to higher conductivity for phosphorus-doped silicate glasses.

Additional enhancement in the ionic conductivity of silicate glasses occurs by water absorption into the pores. The defect sites located within the glass film provide a high local charge density and electrostatic field, promoting the chemisorption of water molecules that provide a bulk transport mechanism for the charge carrying protons. Therefore, the magnitude of the ionic conductivity in phosphorus-doped silica glasses depends on free volume and pore surface area (for ion transport), chemical structures in the glass (e.g. --Si--OH and --P--OH concentration), intermediate range order and the local bonding environment in the glass network [3,7,8].

It has been well established that high quality phosphorous-doped silicate glasses can be fabricated by melt-quenching techniques. However, the high processing temperature of melt casting makes it incompatible with many microelectronic and electrochemical applications. Also, glasses fabricated by this technique have low proton conductivity, making it undesirable as an electrolyte material [9,10]. Therefore, alternative fabrication methods have been explored in order to deposit the proton-conducting silicate glasses, including sol-gel and plasma-enhanced chemical vapor deposition (PECVD). Sol-gel processes have been commonly used, though they often suffer from low mechanical strength and stability [10–12].

On the other hand, the low temperature, PECVD yield high mechanical strength and stable glasses using a fabrication technique that is compatible with state-of-the-art microelectronic materials and processes. Plasma-deposited oxides can also have higher porosity than high-temperature sol-gel glasses due to increased silanol concentration and water impurities, especially when deposited at low temperature [13], which should provide enhanced ionic conductivity. Furthermore, the PECVD technique provides better control of the surface reactions, adsorbate mobility, and desorption of reaction byproducts by controlling the number of active radicals and ions in the plasma, which may be adjusted by control of several variables, including substrate temperature, chamber pressure, RF power and reactant flow-rate [2].

In this study, we have characterized the ionic conductivity of PECVD, phosphorus-doped silicate glasses by parametrically adjusting the plasma deposition conditions in order to optimize its properties for use as a proton-conductor for low-power DMFCs. It was found that undoped, plasma-deposited

silicon dioxide has an ionic conductivity in the range of $1 \times 10^{-6} \text{ S cm}^{-1}$, which is inadequate for use as a solid electrolyte material in low-power proton exchange membrane (PEM) fuel cells due to resistive losses in the membrane. For example, a low-power fuel cell operating at $100 \mu\text{A}$ and 0.5 V with a $1 \mu\text{m}$ thick silica membrane (1 cm^2 area) would have a 20% resistive energy loss with a $1 \times 10^{-6} \text{ S cm}^{-1}$ membrane. Therefore, the goal of this study is to characterize plasma deposition conditions for the fabrication of phosphorus-doped silicate glasses (PSG) that have higher ionic conductivity such that the fuel cell energy loss is less than 0.1%. For low-power applications, the ionic conductivity should be at least $1 \times 10^{-4} \text{ S cm}^{-1}$, which is two orders of magnitude higher than dense silicate glass. For this purpose, thin-film PSG membranes were prepared on a metallized substrate by reacting silane, phosphine and nitrous oxide. A systematic variation of critical deposition parameters (substrate temperature, RF power, pressure, and gas composition) was performed in order to investigate their effect on the ionic conductivity of PSG films. Additional experiments were carried out in order to compare the performance of passive DMFCs fabricated with PSG-Nafion composite and single-component Nafion membranes.

2. Experimental

Thin films of phosphorous-doped SiO_2 were deposited on (100) n-type silicon substrates. The first step in preparing the silicate glasses involved metallization of the silicon substrate to provide a conductive plane underneath the glass. For this purpose, a thin layer (200 \AA) of aluminum metal was deposited on the substrate by DC sputtering. Oxide deposition was carried out using a Unaxis 78324 RF PECVD (plasma-enhanced chemical vapor deposition) system operating at a frequency of 13.56 MHz. The semiconductor grade reaction precursors were 5% SiH_4 in He, 1% PH_3 in He and pure N_2O . The SiH_4 and PH_3 flow rates were both kept constant at 200 sccm in order to maintain a molar ratio of phosphorus to silicon at 1:5 in the plasma chamber. The N_2O flow rate was set to one of the two values: 80 and 450 sccm.

In this study, three deposition parameters: RF power of plasma, substrate temperature and chamber pressure were investigated. First, the temperature of the metallized silicon substrate was varied from 100 to $200 \text{ }^\circ\text{C}$ while holding the chamber pressure and RF power constant at 400 mTorr and 400 W, respectively. Next, the RF power was adjusted between 100 and 400 W at constant substrate temperature ($100 \text{ }^\circ\text{C}$) and chamber pressure (400 mTorr). Finally, the chamber pressure was varied from 400 to 800 mTorr with a substrate temperature of $100 \text{ }^\circ\text{C}$ and a chamber pressure of 400 mTorr.

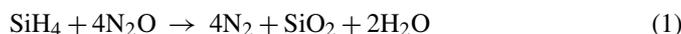
The thickness of the deposited phosphorus-doped glass film was typically 2–3 μm for a 30 min deposition time. The resulting thin oxide membranes deposited were amorphous in nature and formed translucent films. The ionic conductivity of the films was measured by ac impedance spectroscopy using a Perkin-Elmer PARSTAT 2263 electrochemical system with a MSI Electronics Model Hg-412 mercury probe. The frequency range of the impedance measurement was 100 mHz to 1 MHz with an ac signal amplitude of 10 mV. Phosphorus concentration in the films

was determined by X-ray photoelectron spectroscopy (XPS) using the Perkin-Elmer 540 XPS system. A Perkin-Elmer 1600-FTIR was used to obtain the infrared spectra. Refractive index measurements were carried out with a Woollam Ellipsometer.

The performance of a passive DMFC with Nafion-PSG hybrid electrolyte was tested using a Perkins Elmer PARSTAT 2263 potentiostat. Linear sweep voltammograms were obtained at room temperature and a scan speed of 10 mV s^{-1} under ambient conditions. Chronopotentiometric curves were also obtained and the steady-state performance of the fuel cell under ambient conditions was evaluated for a period of 2 days. The cell was refueled as required during testing.

3. Results and discussion

Fig. 1 shows the ionic conductivity of PECVD deposited PSG thin films as a function of substrate temperature at constant RF power and chamber pressure. The samples were prepared at an RF power of 400 W and a pressure of 400 mTorr. The trend observed in Fig. 1 indicates that increasing the deposition temperature leads to a decrease in the conductivity of PSG films. This trend can be explained by two factors. First, it has been well established that the silane oxidation reaction can proceed through two reaction pathways, the complete oxidation to SiO_2 , Eq. (1), or the so-called non-bridging defect SiOH structure, where at least one of the oxygen bonds is not condensed.



Since the ionic conductivity of the silicate glasses is a function of the defect content of the prepared film [2], the reaction selectivity is a key control parameter. Due to differences in the activation energy of these two reactions, if a typical Arrhenius expression is assumed, the selectivity will be an exponential function of the temperature, shown in the following equation

$$S \equiv \frac{r_{\text{SiOH}}}{r_{\text{SiO}_2}} = A \exp \left[\frac{E_{\text{SiO}_2} - E_{\text{SiOH}}}{RT} \right] \quad (2)$$

where S is the reaction selectivity, r_i the overall reaction rate, R the ideal gas constant, T the reaction temperature in Kelvin and

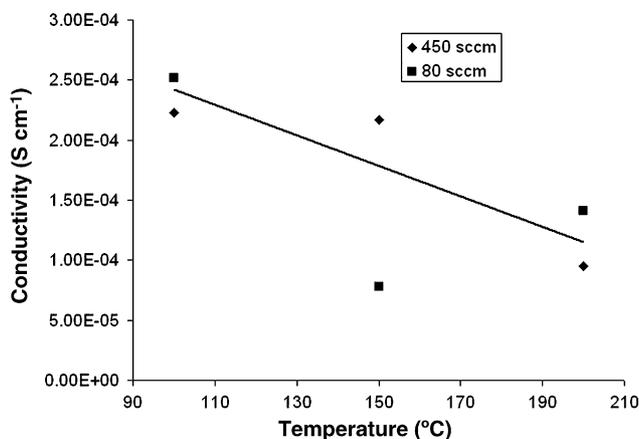


Fig. 1. Ionic conductivity of P-doped SiO_2 thin films as a function of substrate temperature at 400 mTorr chamber pressure, 400 W RF power and N_2O flow-rates of 80 and 450 sccm.

E_i is the reaction activation energy. Since the activation barrier for the complete condensation reaction is greater than that for silanol, it is clear from Eq. (2) that at low temperatures the selectivity increases, leading to an increase in the ionic conductivity, which is in agreement with previous observations by Abe et al. [3].

Second, it has already been established that the ionic conductivity of silicate glasses is enhanced by the presence of secondary oxides formed by doping with group V elements including phosphorus and the amount of phosphorus that gets incorporated in the glass matrix directly influences the ionic conductivity of the deposited PSG films. Similar to the previous discussion, the relative reaction rates for the phosphorus and silicon precursor species is also a function of the substrate temperature due to changes in the selectivity between the total reaction rate of silane and phosphine, Eqs. (1) and (3), at the surface. However, it should be noted that during the phosphorus oxidation, incomplete condensation can also occur, forming defect P-OH bonds that may increase the ionic conductivity [14].

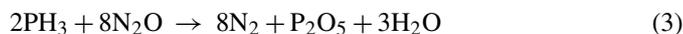


Fig. 2 shows the phosphorus content of the prepared films as a function of substrate temperature. It is observed that as the temperature of the substrate increases, the phosphorus content in the film decreases, leading to a decrease in the number of defect sites at elevated temperature and, hence, the ionic conductivity.

Furthermore, Digiovanni et al. have shown that at high temperature, the thermal activity of phosphorus causes it to volatilize into the gas phase, thus decreasing the overall content of P-OH bonding in the glass network [15]. Since the P-OH moiety is more acidic in nature than silanol (Si-OH), a decrease in phosphorus content could lead to a decrease in the conductivity of the deposited film, other factors remaining equal. Also, Nogami and coworkers have shown that the activation energy of proton disassociation from Si-OH bonds is much higher than that of P-O-H making P-OH a more acidic unit [16]. Visual inspec-

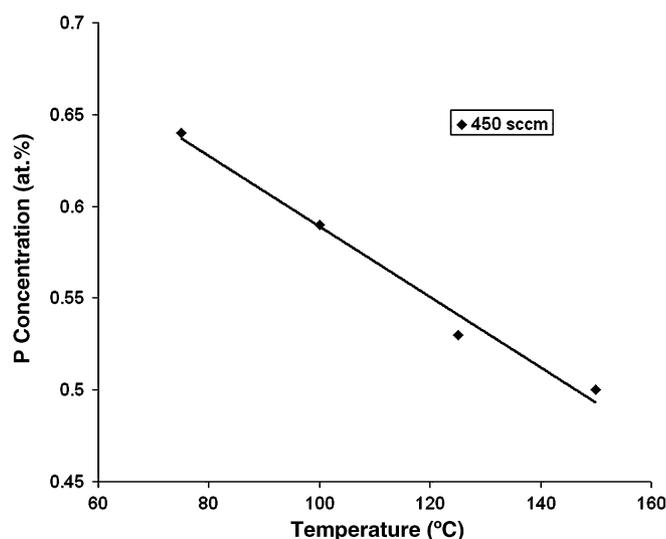


Fig. 2. Phosphorus content of PSG films as a function of substrate temperature at 400 mTorr chamber pressure, 400 W RF power and 450 sccm N_2O flow-rate.

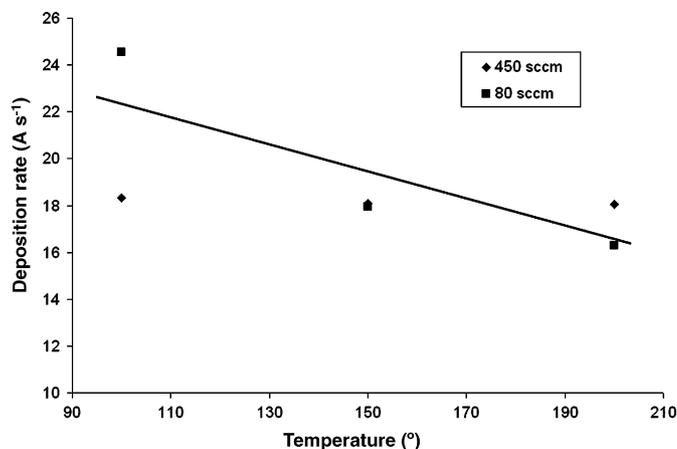


Fig. 3. PSG deposition rate as a function of substrate temperature at N₂O flow-rates of 80 and 450 sccm, 400 mTorr chamber pressure, 400 W RF power.

tion of the PSG samples also showed that films deposited at higher temperature tended to crack due to thermal expansion mismatches with the metallized substrate.

Finally, at higher temperatures, the substrate surface is activated, leading to an increase in the kinetic energy of the reactive ions on the surface. Chapple-Sokol et al. showed that in the plasma deposition of pure silicon dioxide at elevated temperature, the formation of hydroxyl bonds might be inhibited due to thermal activation of the surface [2]. Also as the temperature increases, the residence time of the reactants on the surface decreases due to the accelerated rate of collisions and high kinetic energy of moieties at the heated substrate. This low residence time of the reactants on the substrate forces the reaction to take place in the gas phase and the depletion of reactants at the growing surface of the substrate causes a decline in the overall deposition rate of glass at higher temperature, as shown in Fig. 3. Thus, low temperature deposition results in thinner films with higher intrinsic conductivity.

Next, the effect of the RF plasma power on the film properties was investigated by depositing glass films at two N₂O flow rates, 80 and 420 sccm, while maintaining the same silicon to phosphorus ratio. The plasma chamber pressure was held at 400 mTorr and the substrate temperature was set to the optimum value obtained in Fig. 1, 100 °C. Increasing the RF plasma power results in a steady rise in the conductivity of the deposited PSG films, which is presented in Fig. 4.

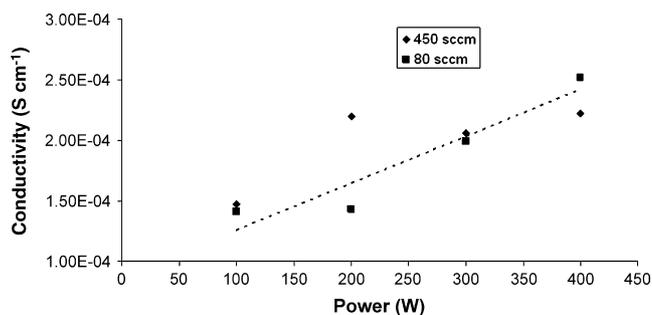


Fig. 4. Ionic conductivity as a function of PECVD RF power at 100 °C substrate temperature, 400 mTorr chamber pressure and N₂O flow-rates of 80 and 450 sccm.

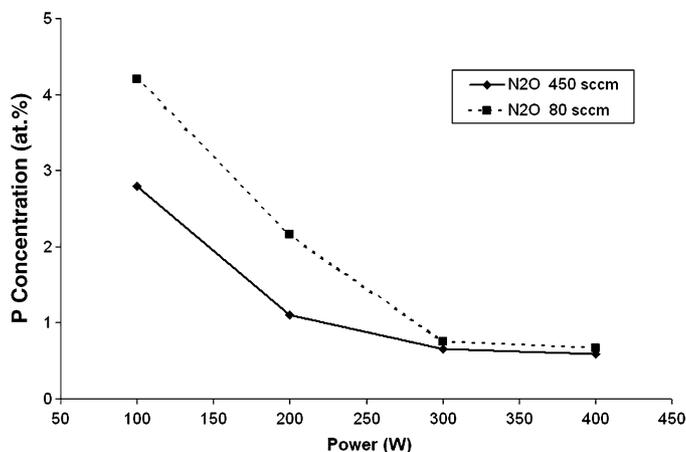


Fig. 5. Phosphorus concentration determined by X-ray photoelectron spectroscopy as a function of RF power at 100 °C, 400 W and N₂O flow-rate of 80 sccm.

The phosphorus concentration, estimated by XPS, as a function of RF power is shown in Fig. 5. It is observed that the phosphorus content in the prepared films decreases as plasma power increases. The decrease in phosphorus content at higher RF power likely originates from the differences in the disassociation energy between SiH₄ and PH₃. Phosphorus is more electronegative than silicon meaning that the bond disassociation energy of PH₃ is higher than that of SiH₄. At high RF power, the fraction of SiH₄ undergoing disassociation is comparatively higher than PH₃; hence, the overall phosphorus concentration decreases. It is also observed that the ionic conductivity of the film increases with decreasing phosphorus content. This appears to be a direct contradiction to earlier results; however, it was previously noted that imperfections in pure silicate glass from incomplete oxidation also lead to the formation of conductive species in the form of –OH. Therefore, the hydroxide concentration in the films was analyzed by examining the –OH stretch in the FTIR spectra.

Fig. 6 shows the FTIR spectra for PSG films prepared with 80 sccm N₂O flow rate at 200, 300 and 400 W. Two important

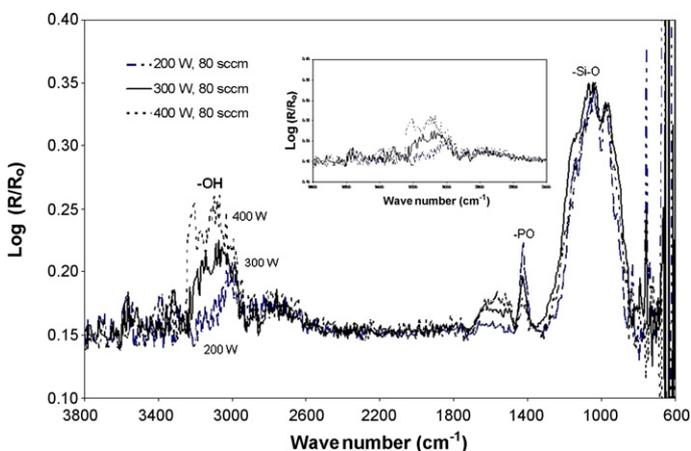


Fig. 6. Fourier transform infrared spectra of PSG films prepared with RF powers of 200, 300 and 400 W with a 100 °C substrate temperature, 400 mTorr chamber pressure and 80 sccm N₂O flow rate.

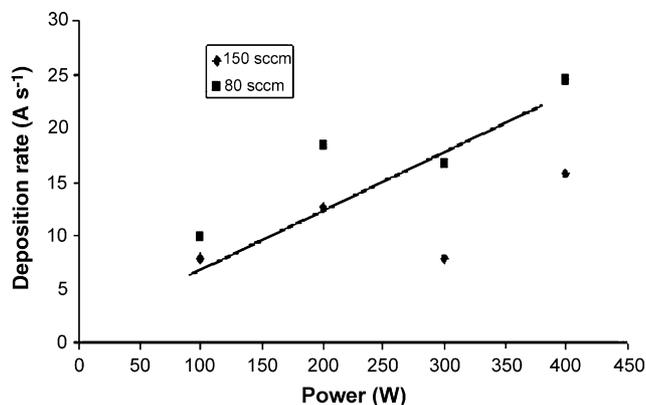


Fig. 7. P-doped glass deposition rate as a function of RF power at 100 °C, 400 mTorr and N₂O flow-rates of 80 and 450 sccm.

observations can be made. First, the P=O stretch at 1400 cm⁻¹ decreases with increasing power, in agreement with the XPS results that the phosphorus content decreases with RF power. Second, the films deposited at higher power showed a greater hydroxide concentration, as evidenced by increased area under the broad peak observed for all samples in the 3000–3300 cm⁻¹ range.

It is also observed that the density of reactive ions in the plasma is a function of plasma power. At higher plasma power, the numbers of reactive ions present in the plasma increases, which results in a more rapid and imperfect oxide formation. This increase in the glass deposition rate, shown in Fig. 7, points to an increase in the reaction selectivity, Eq. (2), indicating that more non-bridging moieties have been formed. Thus, the faster deposition rate results in an increase in the defect density and the enhancement from the elevated –OH content appears to counteract any decrease in the ionic conductivity that is caused by a decrease in phosphorus content.

The ionic conductivity of the deposited PSG films as a function of chamber pressure at constant substrate temperature and RF power is presented in Fig. 8. The temperature and RF power for each of the experiments was 100 °C and 400 W, respectively,

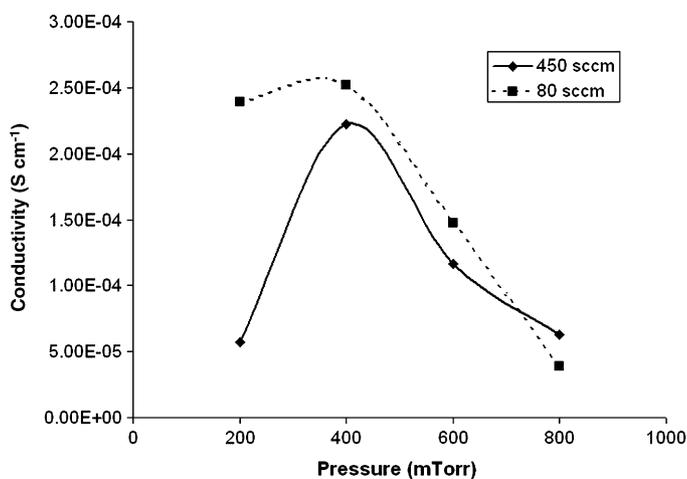


Fig. 8. Ionic conductivity of prepared PSG thin films as a function of chamber pressure at 100 °C substrate temperature, 400 W RF power and N₂O flow-rates of 80 and 450 sccm.

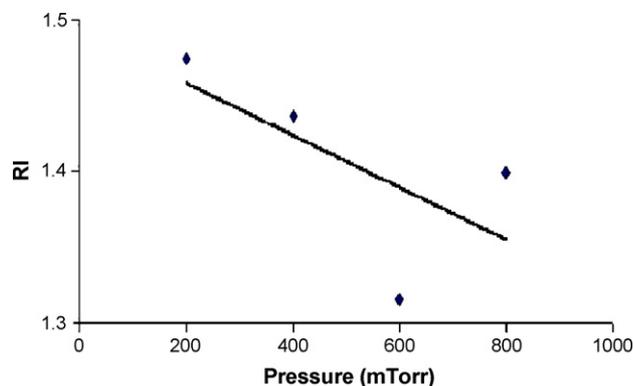


Fig. 9. Refractive index as a function of chamber pressure at N₂O flow rate of 450 sccm, 100 °C and 400 W.

and corresponds to the peak values obtained in Figs. 1 and 4. It is observed that increasing the pressure from 200 to 400 mTorr, results in higher ionic conductivity. However, on further increasing the pressure, the conductivity decreased. It is also observed that increasing the chamber pressure resulted in a decrease in refractive index of the film, shown in Fig. 9. According to Ceiler et al., as the polarity of molecules in a material decreases, the light velocity through the material also decreases, yielding reduced values for the material refractive index [13]. The decrease in refractive index observed at high pressure, as shown in Fig. 9, indicates that as the pressure is increased inside the plasma chamber, the amount of polar species, most likely –OH, incorporated in the glass matrix decreases; thus lowering the conductivity of the films.

The PSG deposition rate with pressure is given in Fig. 10. Apart from the initial increase, the deposition rate was not a strong function of pressure, though a slight decrease was observed. Diffusion models prepared by Dobkin et al. confirms that with increasing pressure, the deposition rate of oxides increases before stabilizing at high pressures [17]. Models prepared by the authors indicate a large increase in deposition rate until pressure reaches approximately 400 mTorr, in agreement with what is observed in Fig. 10. Hey et al. have shown that at higher chamber pressures, the number of collisions between

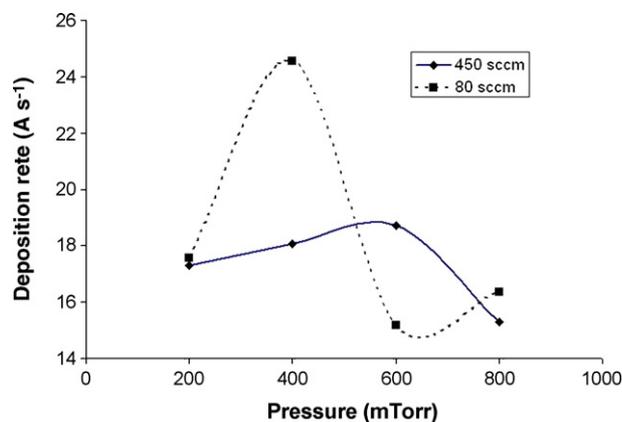


Fig. 10. Phosphosilicate glass deposition rate as a function of chamber pressure at a substrate temperature of 100 °C, 400 W RF power and N₂O flow-rates of 80 and 450 sccm.

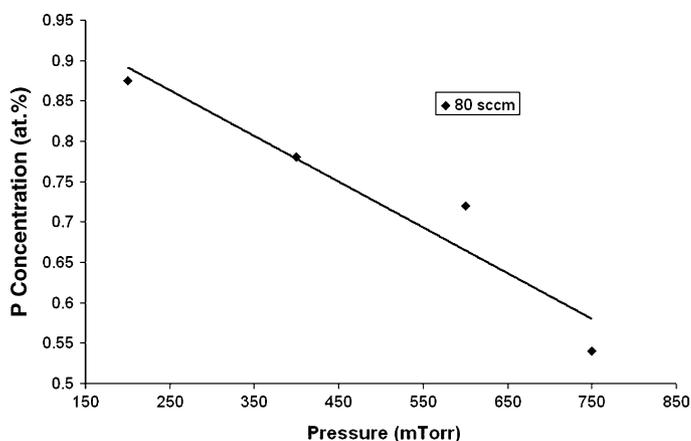


Fig. 11. Phosphorus concentration as a function of chamber pressure at 100 °C substrate temperature, 400 W RF power and N₂O flow-rate of 80 sccm.

reactive ions increases [18]. The authors explain that with every subsequent collision, the reactive ions lose energy and come in close vicinity of each other, thus reducing the mean free path between them. This promotes the reaction to take place in the gas phase in preference to that on the substrate. It also explains the observed decrease in the deposition rate with pressure and the corresponding decrease in conductivity of the films. The phosphorus content of the films was investigated and the results are presented in Fig. 11. It is clear that the phosphorus content of the prepared films steadily decreases with pressure, which further explains the observed decline in conductivity.

In order to characterize the performance of PSG as a proton exchange membrane, DMFCs with Nafion and PSG-Nafion hybrid electrolyte membranes were fabricated. For this purpose, porous glass substrates (1 mm thickness) were first soaked in 5% Nafion solution and cured at 150 °C such that nafion filled the pores of glass substrate to form a well-connected matrix. Some of the Nafion-filled substrates were then exposed to plasma and 3 μm of PSG membrane was deposited at the plasma conditions that showed the maximum ionic conductivity; 100 °C substrate temperature, 400 W RF power and 400 mTorr chamber pressure. The anode (PtRu/C) and cathode (Pt/C) catalyst layers were prepared by painting typical catalyst inks, which contained 30 weight percent Nafion solids on the anode and the cathode side of the impregnated glass substrates (both Nafion only and Nafion-PSG hybrid). Porous gold paint was used as the current collector on both anode and the cathode. The geometric area of the fuel cell was 1 cm². The passive delivery of fuel (methanol) to the electrolyte was achieved by attaching a methanol tank to the composite electrolyte substrate such that the painted anode was in contact with methanol and cathode was exposed to ambient air. To compare the performance of the DMFC made with Nafion-PSG composite membrane to those made with just Nafion, a fuel cell was constructed in the same manner as has been mentioned before except no PSG was deposited on the substrate.

Polarization curves for both Nafion and PSG-Nafion hybrid membrane passive DMFCs are given in Fig. 12. Both polarization curves were measured at room temperature (23 °C) with 12 M aqueous methanol fuel. It is clear from Fig. 12 that the performance of the DMFC is markedly improved with the hybrid

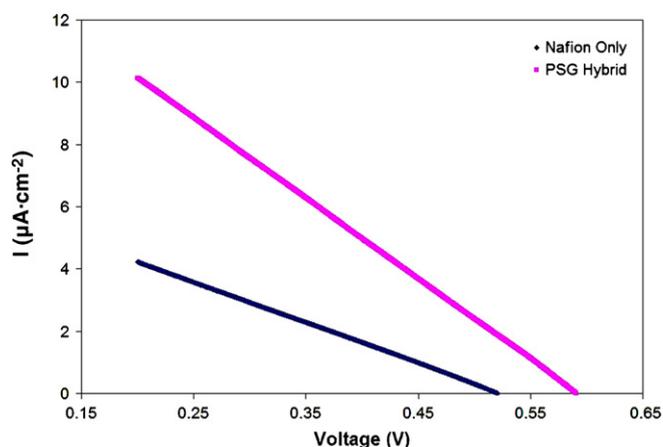


Fig. 12. Polarization experiments for fully passive DMFCs with PSG-Hybrid and Nafion electrolytes; 23 °C, 12 M methanol, 10 mV s⁻¹.

membrane. The open circuit voltage has been increased by approximately 65 mV and the current density at 0.4 V has nearly tripled. The improvement in the performance is likely due to lower methanol permeation through the PSG film when compared to Nafion alone. This is evident in the increase in the open circuit voltage where less internal short circuiting is observed. Also, the current density is improved by the lower crossover by removing methanol and methanol oxidation intermediates from the catalyst surface. The reduced methanol crossover also limits the amount of water that is transported from the anode to cathode, which could lead to local flooding issues within the electrode structure.

The steady-state performance of a DMFC with a PSG-Nafion hybrid membrane was also measured and is presented in Fig. 13. The cell was operated under a constant load of 76 kΩ at room temperature and 12 M methanol fuel. It was observed that the cell performance is quite stable, even following refueling, indicating that the hybrid membrane maintains stable ionic performance over the device life. However, from 700–1300 min of operation, the cell voltage dips by approximately 10%. This is most likely due to entrapped carbon dioxide bubbles at the anode surface, which leads to a reduction in the electrochemically active surface area, and the voltage under constant load declines. As the tank

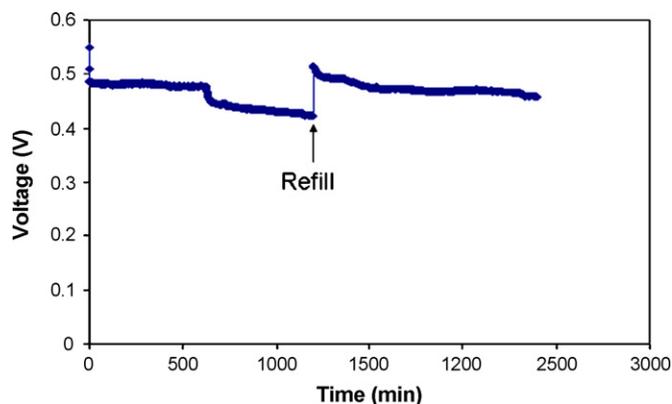


Fig. 13. Steady-state performance of the passive DMFC with PSG-Hybrid proton-conducting electrolyte; 76 kΩ load, 23 °C, 12 M methanol.

is refueled, at ~ 1300 min of operation, the CO_2 bubbles are released and the voltage is increased above the initial operating cell potential. This increase in voltage is most likely a result of catalyst activation over time.

4. Conclusion

PSG films were deposited by PECVD and a systematic variation of deposition conditions was carried out in order to optimize the resulting glass electrolyte for both high film quality and ionic conductivity. The results presented in this study clearly indicate that the plasma deposition conditions play an important role in the oxide growth rate, reaction selectivity and phosphorus content, which directly affect the ionic conductivity of the PSG films. It was observed that increasing the deposition temperature led to a decrease in conductivity of the PSG films due to elevated phosphorus and silanol content. Increasing the plasma chamber pressure had a negative effect on the conductivity since the oxide reaction took place in gas phase in preference to the substrate at higher pressures, which lead to a decrease in the defect density of the prepared films. Finally, increases in RF power lead to an increase in the conductivity. It was found that despite the decrease in phosphorus content of the PSG films, the number of silanol defect sites increased, leading to a substantial increase in the conductivity. It was also observed that the film growth rate was higher with 80 sccm flow rate of nitrous oxide indicating complete oxidation of silicon and phosphorus on the substrate.

Having elucidated the trends in the ionic conductivity as a function of various plasma conditions, a peak conductivity of $2.52 \times 10^{-4} \text{ S cm}^{-1}$ was achieved for PSG deposited at 400 W RF power, 400 mTorr chamber pressure, 100°C substrate temperature and a nitrous oxide flow rate of 80 sccm. This value is 2.5 times greater than the target conductivity value to 1.0×10^{-4} and 250 times greater than the ionic conductivity of pure silicon dioxide films. Therefore, it is clear that doping of silicate glasses with phosphorus significantly improved the ionic conductivity of the oxide films.

The optimized PSG film was then used to make DMFCs with lower methanol permeability than pure Nafion electrolytes. Polarization experiments with both Nafion and PSG-Hybrid membrane passive DMFCs indicated that the presence of the P-doped silicate glass significantly improves cell performance.

The open circuit voltage was increased by approximately 65 mV and the current density at 0.4 V was nearly tripled. The PSG-Hybrid electrolyte DMFC was also exposed to a constant load of $76 \text{ k}\Omega$ and showed excellent stability characteristics at room temperature and 12 M methanol fuel.

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