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Newly developed sol-gel derived P_2O_5 - ZrO_2 - TiO_2 - SiO_2 proton conducting glass electrolyte for fuel cell applications

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ABSTRACT

Proton conducting sol-gel P_2O_5 - ZrO_2 - TiO_2 - SiO_2 glass is synthesized and characterized with specific focus on the structural characterization of material which enable proton conductivity and on testing the stability of the glass under fuel cell conditions. The chemical structure of the synthesized glass was characterized by using FTIR (Fourier Transform Infra-red) spectroscopy and X-Ray diffraction studies and the stability of the P_2O_5 - ZrO_2 - TiO_2 - SiO_2 glass was probed through the TGA and hydrogen permeation techniques. The amorphous phase of our glass was confirmed by the XRD analysis. The presence of hydro phosphate groups in the material responsible for the high conductivity and the Si, Zr and Ti bonded with the main backbone of Si and P-O were identified by the FTIR spectral data. The decomposition of surface adsorbed water and organic matters occur in the temperature range of 30-400°C. Pore distribution analysis shows that the average pore size of the synthesized glass is 2.65nm and pore volume and surface area are around 0.27cm³/g and 410m³/g respectively. The conductivity of the synthesized proton conductor was examined through electrochemical impedance analysis, conductivity is increased with increase in temperature and it was 10⁻⁴S/cm at room temperature and 10⁻³S/cm at elevated temperatures. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Fuel cell;
Proton conductor glass;
Electrochemical impedance;
Membrane stability;
H₂ permeation;
XRD.

INTRODUCTION

Fuel cells produce a direct electric current by the chemical reaction of hydrogen and oxygen without the emission of any harmful pollutants. To produce energy with high efficiency, membranes with high proton conductivity are necessary as the electrolyte through which the protons move from the anode to cathode of the fuel cell. Proton exchange membrane fuel cells (PEMFC)

are extensively studied as one of the new energy conversion devices^[1,2]. Attention on PEMFC mainly focused for the mobile, stationary and portable electrical and electronic devices^[3]. Perfluoro sulfonate ionomers such as Nafions (Dupont), Aciplexs (Asahi Chemicals) and Flemions (Asahi Glass) have been used as the electrolytes in the PEMFCs because of their good mechanical strength, chemical stability and high proton conductivity^[4,5]. However, the use of the PEMFC is largely

restricted by the complex water management, CO poisoning of catalyst and high cost^[6].

The high proton conducting inorganic glasses are alternative to the polymers^[7]. For this purpose, sol-gel method has become an attractive route to design into thin film as well as bulk forms, porous glasses and homogeneous particles with controllable sizes^[8]. The sol-gel properties depend strongly on the interaction of these two components (substance that contains a solid skeleton enclosing a continuous liquid phase). The liquid prevents the polymer network from the collapsing into a compact mass while the network prevents the liquid from flowing away. Most of the gels are solid but exhibit liquid-like characteristics due to the presence of a large number of liquid filled micropores. The mesoporous structure of gels are likely to provide channels for ion migration^[9].

The sol-gel chemistry of phosphosilicate has been intensively studied, showing that the choice of the phosphorous molecular precursor plays a fundamental role in the characteristics of the final product, such as the extent of copolymerization between the silicate and phosphate units. Compared with Si-OH, phosphate glasses are more efficient for high proton conduction because of the hydrogen ions are more strongly bounded to the non-bridging oxygen. The hydrogen in the P-OH group is more hydrogen-bonded with molecules, resulting high temperature is necessary to remove the water from P-OH. Simultaneously, the silicate network improves the mechanical strength and chemical durability. The introduction of Zr⁴⁺ into the silico phosphate gel improves the chemical stability^[10]. The titanium phosphates functionalized to titanium sulfo phenylphosphonate showed higher proton conductivity^[11]. Recently, a series of phosphosilicates, zirconium and titanium phosphates have been exploited for their use as electrolyte in PEMFCs^[12-21]. However, there is no report on the presence of Zr and Ti in the phosphosilicate glasses for the PEMFC applications.

The presence of Zr and Ti in one another film, could improve both the conductivity and stability. With this view in mind, for the first time the present investigation has been focused on the sol-gel synthesis of Zr and Ti doped phosphosilicate thin film synthesis and its structural characterization. We also demonstrated a fuel cell using our glass as the electrolyte membrane.

EXPERIMENTAL

Synthesis of thin glass film

The sol-gel method was used to synthesis pure inorganic thin film membrane using SiO₂ backbone. Tetraethyl orthosilicate (Aldrich) was diluted with acidified (diluted HCl) ethanol by stirring one hour at room temperature. PO(OCH₃)₃, Zr(OC₄H₉)₄ and Ti(OC₄H₉)₄ were diluted with ethanol with respect to their alkoxide and they were added to the hydrolyzed solution one by one every 30 minutes stirring interval. An appropriate amount of formamide and water were added to the hydrolyzed propoxide solution and allowed for continuous stirring until to get clear solution. The final colorless solution was transferred to closed petri-dish and allowed for one month to form gel-thin film at constant temperature of 25°C. The sol-gel derived P₂O₅-ZrO₂-TiO₂-SiO₂ thin film was examined for their structural and performance studies^[19,22]. The P⁵⁺ ions rapidly decreases with increasing ZrO₂ content (P⁵⁺ ions bonded with four non-bridging oxygen atom). The P⁵⁺ ions bound to one or two bridging oxygen are increase with the ZrO₂ content.

Characterization

The Fourier Transform Infra-red (FTIR) spectrum for the synthesized glass was obtained using X Caliper Spectrometer to analyze the formed P₂O₅-ZrO₂-TiO₂-SiO₂ glass. X-ray diffraction measurement was performed by using a Rigaku miniplex operating at 30kV and 15mA at a scan speed of 1.2 S per point using Cu-K α radiation. Thermogravimetric analysis (TGA) for the synthesized P₂O₅-ZrO₂-TiO₂-SiO₂ glass film was studied in a Perkin-Elmer Diamond thermal analyzer instrument with a heating/cooling rate of 10°C/min in an O₂/air atmosphere (temperature range 30-800°C. Brunauer-Emmett-Teller and BJH tests were made on the synthesized P₂O₅-ZrO₂-TiO₂-SiO₂ glass film to analyze its pore size, surface area and pore volume at a bath length of 77.35K, with warm and cold free space of 16.61145cm³ and 50.8341 cm³ respectively, using Micromeritics, ASAP-2010 instrument. The stability of the glass was examined by hydrogen permeation test at different temperature (20-250°C) at 1Mpa hydrogen gas pressure.

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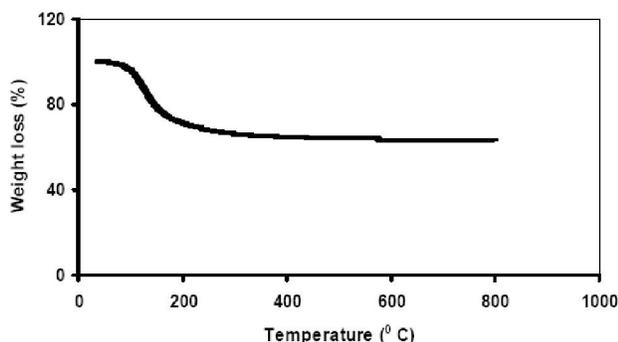


Figure 1 : Thermogravimetric analysis of sol-gel derived $P_2O_5-ZrO_2-TiO_2-SiO_2$ proton conductor

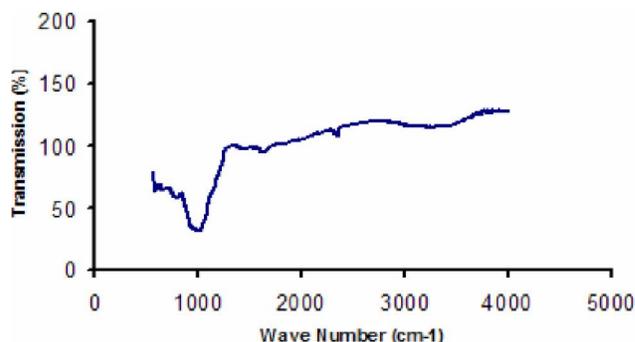


Figure 2 : FTIR – spectrum of sol-gel derived $P_2O_5-ZrO_2-TiO_2-SiO_2$ proton conductor

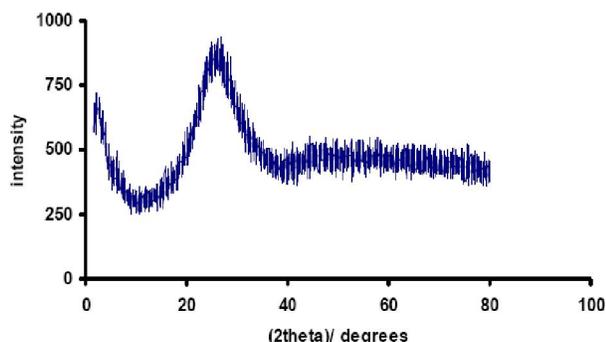


Figure 3 : XRD spectrum of sol-gel derived $P_2O_5-ZrO_2-TiO_2-SiO_2$ glass

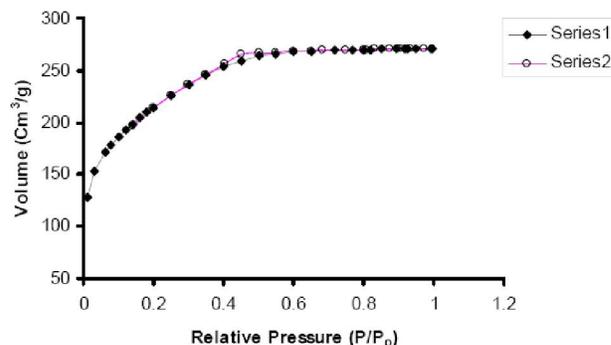


Figure 4 : Nitrogen gas adsorption (Series 1)-desorption (Series 2) isotherm of $P_2O_5-ZrO_2-TiO_2-SiO_2$ glass

PEMFC assembly and impedance analysis

A Pt/Ru nano colloidal catalyst was loaded on the Au coated nickel Foam, which was used as the catalyst on the anode and cathode side of the fuel cells. Externally humidified oxygen and hydrogen gases were passed into the respective channels of the fuel cell assembly. The temperature of the cell was maintained by the thermostat (leads/Coils). Synthesized $P_2O_5-ZrO_2-TiO_2-SiO_2$ thin film was made into opt size to fix into the place of the membrane in the cell and closed tightly without any damage to the membrane and also no gas leakages. A H_2/O_2 cell was constructed with the above mentioned assembly, which consists the glass ($P_2O_5-ZrO_2-TiO_2-SiO_2$) electrolyte and Pt-Ru/C loaded on Au coated nickel foam as electrode catalyst. The flow rate of hydrogen and oxygen over anode and cathode were 50 and 100mL/min. respectively. Using the above cell assembly and operating conditions, the temperature dependant performance was examined. The conductivity of the thin glass at different temperature was also investigated by collecting impedance spectra in the frequency range of 0.1Hz to 1mHz using GAMRY Instrument impedance analyzer.

RESULTS AND DISCUSSION

Thermal studies

The synthesized glass material was in the form of non-crystalline phase, it was confirmed by the XRD analysis. TGA thermogram of $P_2O_5-ZrO_2-TiO_2-SiO_2$ glass is presented in figure 1. The TGA curve can be divided into four different regions. An initial weight loss of 4% is observed in the temperature range of 30-100°C, which is mainly due to the de-sorption of physically adsorbed water. The second and major weight loss is (16%) occurred in the temperature between 100-200°C. In this region, the residual solvent from the sol preparation, elimination of water and alcohol formed from condensation reactions are evaporated. This apparent weight loss can be attributed to the decomposition of silane molecule chain that is bonded to the silica net work. It is clear that the water de-sorption results decrease of conductivity. A third region between 200°C and 400°C is attributed to the decomposition of alkoxides at around 280°C, indicating that the alkoxide in the gel was completely hydrolyzed^[19]. And also, de-

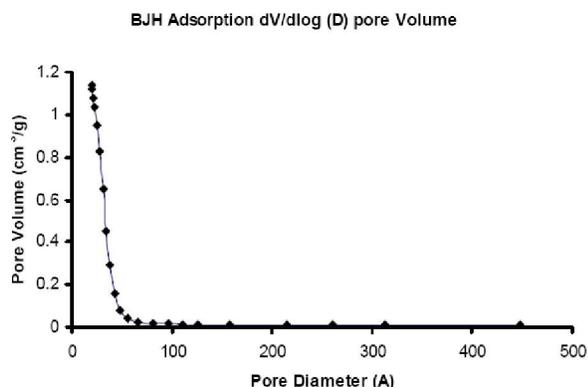


Figure 5 : BJH distribution curve of P_2O_5 - ZrO_2 - TiO_2 - SiO_2 glass

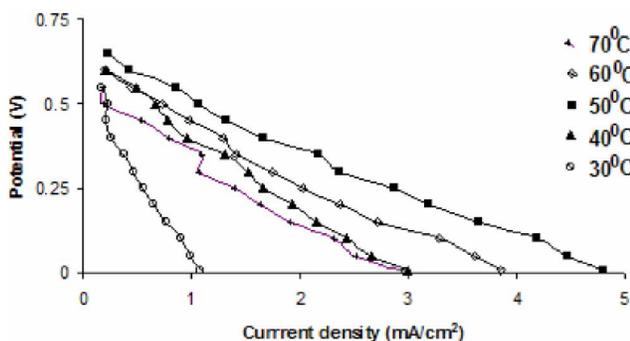


Figure 7 : Performance of P_2O_5 - ZrO_2 - TiO_2 - SiO_2 thin film at different temperatures (30-70°C) with 100% humidity at a gas flow rate of 50mL/min. and 100mL/min. H_2 and O_2 gas respectively

composition of organic residues from unhydrolyzed ligands bound to metals and combination of formamide. Above 400C, obviously, there is no change in weight. The proton is strongly bonded the POH group than in the SiOH^[23]. The result confirmed that the synthesized P_2O_5 - ZrO_2 - TiO_2 - SiO_2 is thermally stable than elsewhere reported.

Structural characterization

The FTIR spectrum of the synthesized P_2O_5 - ZrO_2 - TiO_2 - SiO_2 glass is presented in figure 2. The addition of ZrO_2 in the P_2O_5 - SiO_2 glass, results P^{5+} ion strongly react with the ZrO_2 components during the gel synthesis^[22]. The $PO(OH)_3$ species are decreased rapidly with the addition of ZrO_2 content more than 5%. And also, the P^{5+} ion bound to one and two bridging oxygens increased with increasing ZrO_2 content. In the present glass, 5% ZrO_2 was used for the synthesis to get the cent percent gel formation of P_2O_5 with the other doped material. The P_2O_5 content increases on increasing ZrO_2 to a nominal composition of below 7% ZrO_2 . These

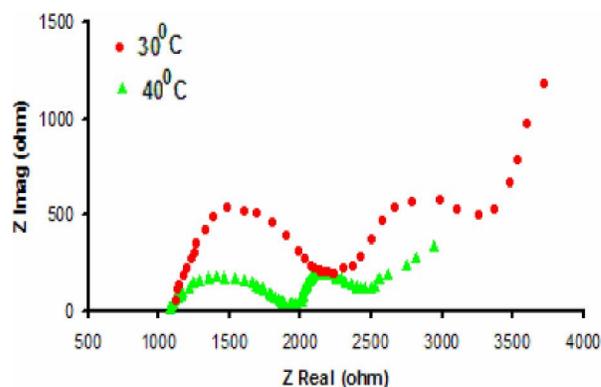


Figure 6a : Impedance spectra of P_2O_5 - ZrO_2 - TiO_2 - SiO_2 thin film at different temperatures (30 & 40°C)

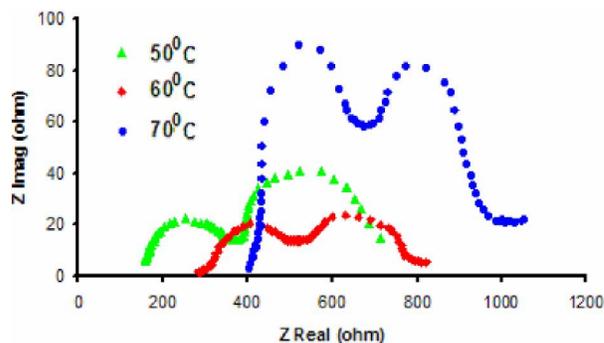


Figure 6b : Impedance spectra of P_2O_5 - ZrO_2 - TiO_2 - SiO_2 thin film at different temperatures (50-70°C)

strongly suggest that the P^{5+} ions react with the ZrO_2 components either by gel-synthesis or by heating^[7]. A broad peak with three different small transmission bands is appeared in the band range of 550-1260 cm^{-1} . The bands in the range of 960-980 cm^{-1} , 1040-1090 cm^{-1} and 1000-1030 cm^{-1} corresponds to the $(HPO_4)^{2-}$, $(H_2PO_4)^{-1}$ and P-OH respectively^[24,25]. The spectrum is characterized by a broad peak at around 950-1200 cm^{-1} and at 800 cm^{-1} , indicating the presence of extensive network structure of Si-O-Si group. Further, the bands at ~1350 and 1650 cm^{-1} are assigned to stretching modes of P = O and O = P-OH, respectively. The Si-O-Ti net work band appears at ~900 cm^{-1} . The Ti^{4+} ions are preferentially bonded with the hydrolyzed SiOH groups, forming the Ti-O-Si bonds. The presence of Zr in the glass structure could be identified by assigning the transmission bond around 2200 cm^{-1} . The P^{5+} ion easily reacts with the ZrO_2 . Crystal water in the pores of the glass is observed by the appearance of the broad bond at 3000-3500 cm^{-1} . These bands clearly indicate the formation of glass.

The XRD pattern of the P_2O_5 - ZrO_2 - TiO_2 - SiO_2 sol-

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TABLE 1 : Hydrogen permeation property of $P_2O_5-ZrO_2-TiO_2-SiO_2$ thin film at different temperatures at 1Mpa hydrogen pressure

Sl.No.	Temp.(°C)	H ₂ permeation (mL/10min.)
1	20	
2	30	
3	50	
4	75	
5	100	
6	125	
7	150	Until 175°C no gas was found
8	175	
9	200	0.15
10	225	0.20
11	250	0.25

gel synthesized material is presented in figure 3. The glass material exhibit amorphous phase and the heat treatment does not influence on the structure of the material. The well defined and broad peak appeared at 2θ value 25 and 26 are assigned for the SiO_2 and P_2O_5 respectively. A small hump like peak at 47 and 75 are for the TiO_2 and for the presence of ZrO_2 , the peak at 2θ value 49 can be assigned. Because of the well dispersed P_2O_5 , ZrO_2 and TiO_2 in the SiO_2 matrix or the small size of the semi-crystalline nature of the material, respective crystalline peaks could not mark legibly. The existence of non-crystalline nature of material, which is corroborate with the earlier report^[19,21].

Stability and pore characterization

The stability of the synthesized $P_2O_5-ZrO_2-TiO_2-SiO_2$ glass is examined at different temperature (20-250°C). A 1Mpa hydrogen was passed through the glass and the H₂ permeation of the glass was noted at different temperature and the results are presented in TABLE 1. No gas flow was found until the temperature at 175°C, beyond that, slow gas flow was observed, which may be due to the adsorbed water molecules in the micro-pores of the glass membrane are desorbed at higher temperature and further opening of pores allows easy hydrogen permeation. Hence, the synthesized glass can be used for the moderate temperature applications below 200°C.

For the proton conduction in the glass or membranes, pores characteristics plays an important role. The obtained glass was interrogated for its pore char-

TABLE 2 : Resistance and conductivity of $P_2O_5-ZrO_2-TiO_2-SiO_2$ thin film at different temperatures

Sl.No.	Temp.(°C)	Resistance (ohm)	Conductivity (S/cm)
1	30	1121	3.67×10^{-4}
2	40	1070	3.85×10^{-4}
3	50	163	2.53×10^{-3}
4	60	285	1.45×10^{-3}
5	70	408	1.01×10^{-3}

acteristics by nitrogen gas adsorption- de-sorption measurements. The N₂ adsorption- de-sorption isotherm of the synthesized glass is presented in figure 4. It is evident that the adsorption isotherm of the glass exhibits a large adsorbed volume at low relative pressure and a plateau in the adsorbed volume after the intermediate pressure. The curve seems to be flat and the glass compositions are completely micro porous and mechanically stable and it reiterates the TGA results. There is a higher de-sorption observed in the relative pressure range of 0.4-0.5. However, there is no hysteresis formed in desorption or adsorption cycle, which indicates that the pores are smooth and cylindrical in shape. The pore volume, diameter and surface area of the film (glass) are derived from the BJH Figure 5 and they are 0.272315cm³/g, 26.5343A and 410.5097m²/g respectively. The pore size obtained from BET analysis is 21.7383A and the surface area is 771.6470m²/g. However, the Langmuir surface area is 1059.1970m²/g, which is little higher than the others.

The pore properties are related to water absorption and further proton conduction and relaxation of proton transfer. At low humidity, the water molecules filled in the small pores and they act to form the pathways for proton transfer.

Impedance measurement

All the impedance spectra were recorded for the synthesized glass during performance test at 100% relative humidity at different temperature and the resulting spectra are given in figure 6. Each impedance plot is composed of many parts. A first capacitive arc (high frequency end) and a second capacitive arc (low frequency end) appeared in all of the spectra and small diffusion arc is noted for the low temperature plot. They corresponds to mainly charge transfer phenomena (electrons and protons) at high frequencies and are related

to mass and water transport at lower frequencies. The shape of the spectrum taken at the different temperature (30-70°C) is same with various sizes of the high and low frequency impedance arcs. Conductivity of the glass increases with increasing the temperature, however, the trend is reverse after 50°C. The resistance is decreased with increasing the temperature (TABLE 2). At 30°C, the conductivity is 3.67×10^{-4} S/cm and resistance is $1121 \Omega/\text{cm}^2$. These values are increased to 1.01×10^{-3} S/cm and $408 \Omega/\text{cm}^2$ at higher temperature of our study (70°C). The hydroxyl groups bounded in the pores of the glass are highly sensitive to air humidity. At ambient temperature, they adsorb the water and help to improve the proton hopping for proton conduction. The conductivity increases with increasing the adsorbed water. The water molecule is polar and chemically bonded with the hydroxyl groups such as POH, TiOH, SiOH and ZrOH bonds. The glass having small pores size filled with water at low humidity, where the conductivity reaches constant value. On the other hand, the glass with large pore size needed high humidity to get high conductivity. At higher temperature, the adsorbed H_2O molecules in the pores are desorbed and thus decrease the conductivity beyond 60°C. The Grotthuss transport mechanism suggests that charge transportation is controlled through the H_3O^+ and H_5O_2^+ mediated charge transfer. This results shows that the proton transport in the synthesized glass is through the presence of H_2PO_4^- and $(\text{HPO}_4)^{-2}$ groups, which by having free pendent P-OH group attract water and can donate proton to facilitate the charge transfer. Protons dissociated from hydroxyl groups of the glass material from ionic radicals such as H_3O^+ in water and transfer by hopping through the water molecules.

Fuel cell performance studies

The performance of the P_2O_5 -ZrO₂-TiO₂-SiO₂ glass electrolyte has been tested with H_2/O_2 fuel cell at different temperatures. Figure 7 depicts the current-voltage curves of the glass electrolyte at 30-70°C. The open circuit potential (OCP) of the cell is around 0.65-0.7V and the current density is 1.08mA/cm² at 30°C. Current density is slowly increased with temperature upto 50°C, beyond that declining to lower values. The concentration of the active sites (H_2PO_4^- and H_3O^+) is decreased when the temperature increases beyond the

ambient values, these active sites are responsible for the proton conduction process. And also, in the P_2O_5 -ZrO₂-TiO₂-SiO₂ system, the POH bonds are polymerized and / or reacted with Zr^{4+} (Si^{4+}) or Ti^{2+} ions to form P-O-M (M = Zr, Si, Ti) bonds. This causes the density of hydroxyl bonds per phosphorous ion to decrease, resulting, decrease in the proton conductivity. This behavior reveals the impedance results. The output power and performance of the synthesized glass electrolyte could be improved by optimizing the humidity and by reducing the contact problem between the catalyst and electrode and further increasing the proton conduction. Further work will be needed for operation at more higher than 200°C, which could be achieved by controlling the structure of proton conducting glass to densify the electrolyte structure.

CONCLUSIONS

In this work, we have successfully synthesized high proton conducting P_2O_5 -ZrO₂-TiO₂-SiO₂ glass through the hydrolysis of the solution of Zr, Ti and Si alkoxides that reacted with the POH bonds for polymerization. The prepared proton conducting glass is more stable even at higher temperature of 400°C. Through the structural, thermal and XRD studies show that the amorphous nature of glass is chemically and thermally stable. The important characteristic bonds of the Si-O-Si, Si-O-Ti, -P = O and P-Zr-Si are identified by the FTIR analysis. The presence of the phosphorous groups in the glass is expected to contribute higher conductivity of the conductor. A 10^{-4} - 10^{-3} S/cm conductivity is obtained in the temperature range of 30-70°C under 100% relative humidity. Using the synthesized sol-gel glass a fuel cell was constructed, the performance is increased until 50°C and beyond that, performance of the cell is decreased. Our further study in the fuel cell is to be directed towards the stabilization of proton conducting groups in the pores of the glass at moderate temperature ranges.

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