Synthesis, Characterization And Performance Study Of Phosphosilicate Gel-Sulfonated Poly (Ether Ether Ketone) Nanocomposite Membrane For Fuel Cell Application

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ABSTRACT

Phosphosilicate gel – SPEEK (Sulfonated Poly Ether Ether Ketone) hybrid nano-composite membranes are proposed for performance enhancement of polymer electrolyte fuel cell. The nanocomposite membranes are synthesized and characterized at 60 weight percent of inorganic loading. Phosphosilicate gel particles of varying size (sub micro to nanometer) are synthesized using sol gel approach followed by grinding using planetary ball mill for different time. Transmission Electron Microscopy (TEM) reveals less than 10 nm particle size for 20 hr grinding. Nanocomposite membrane having inorganic particles of size less than 10 nm exhibits higher values of proton conductivity, ion exchange capacity and water uptake compared to composite membrane comprising of larger (400 nm and above) inorganic particles. The membrane is assembled with the electrode in the unit cell and the polarization characteristics are measured at different operating temperatures. Performance study reveals that between 65 to 75 $^{\circ}$C the membrane offers best performance in terms of peek power generation and of allowable load current. For the same conditions 40% nano-enhancement of peek power generation is achieved by reducing the average gel particle size from sub micro to less than 10 nm. At medium temperature (between 65 to 75ºC) the nanocomposite membrane offers more than 75% enhancement of peek power generation compared to that generated by SPEEK membrane.

Key words: Organic-inorganic nanocomposite, Fuel cell, Phosphosilicate gel, SPEEK, Performance enhancement

INTRODUCTION

In the wake of the emerging market potential for fuel cell based energy generation using hydrogen as raw material, it becomes imperative to research upon the development of nanomaterials to improve its real-life performance.

The proton exchange membrane fuel cells (PEMFC) are today in the focus of interest as one of the most promising power generator for a wide range of applications in transportation and in portable electronics [1, 2]. These fuel cells convert the chemical energy of the fuel and oxidant into electrical energy releasing the balance as heat. The major material components are the proton conductive electrolyte membrane and the electrodes. The performance of PEMFC

is crucially dependent on the proton conductivity, ion exchange capacity and water uptake of the electrolyte membrane.

Inorganic–organic hybrid nanocomposite membranes generated substantial research interest due to their potential of having a wide range of physical, chemical, thermal and mechanical properties. The nanocomposite membranes comprising of nanosize inorganic phase/building block often demonstrate interesting properties due to nano scale of constituent phases, high interfacial area and synergetic properties [3]. The structural and physicochemical properties and hence the performance of such composite membranes depends on their composition, size of the inorganic particle, interfacial interactions etc. [4].

It has been reported in literature that sol-gel derived phosphosilicate gel has served as a very promising proton conductor with high proton conductivity in the low and medium temperature range, which is attributed to phosphoric acid and thermally stable inorganic silica networks [5]. Presence of phosphosilicate gel provides phosphoric acid functionalised, inorganic silica network electrolytes having solid pores for water to be absorbed. Pores having smaller diameters become filled with water even at lower humidity and act to form the pathways for proton transfer. The organic component, Poly (ether ether ketone) is a thermally stable and mechanically tough polymer. On sulfonation, the polymer becomes hydrophilic and ionically conductive. Due to these properties, SPEEK membranes find application as polymer electrolyte membrane in proton exchange membrane fuel cell (PEMFC).

The synthesis, characterization and performance of hybrid nanocomposite (phophosilicate gel-SPEEK) membrane for the application in fuel cells has hardly been explored in literature. The present paper describes the experimental synthesis, characterization and performance studies for the novel hybrid nanocomposite membranes. The enhancement of performance of proton exchange membrane fuel cells, as demonstrated in this publication, highlights the promising potential for their commercial exploitation.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

Synthesis of phosphosilicate gel nano particle:

The phosphosilicate gel was prepared by sol-gel process [6] using tetraethoxysilane and ortho phosphoric acid at a molar ratio of P/Si = 1.5. Tetraethoxysilane (TEOS) was diluted with ethanol (EtOH) and hydrolyzed with water (H_2O) containing HCl with stirring at room temperature for 10-15 min. An appropriate amount of ortho-phosphoric acid was added drop by drop under constant stirring. After stirring for another 50-60 min, a homogeneous gel was formed. The mole ratio of $TEOS:EtOH:H_2O:HCl:H_3PO_4$ was fixed as 1:4:4:0.01:1.5. The gel formed was further dried at 80^0C for 24 h. The dried gels, which were pulverized into powders with an agate mortar and a pestle, were heat treated in muffle furnace at high temperatures of $150-600^0C$ for 6-7

h. The dried gel powders were further ground into fine powders using a planetary ball mill. Grinding time is varied from 8 hrs to 20 hrs to obtain sub-micro to nanometer sized particles, respectively.

Synthesis of phosphosilicate gel –SPEEK nano composite membrane by precursor method:

Poly(ether ether ketone) was first sulfonated. 15 wt% SPEEK (Sulfonated Poly ether ether ketone) was dissolved in DMAc (N,N Dimethyl Acetamide) using magnetic stirrer, and subsequently it was mixed with finely ground phosphosilicate gel powder. After dissolving the polymer in solution, appropriate amount of gel powder was mixed. It was stirred periodically using a magnetic stirrer and an ultra-sonicator until the gel powder became completely miscible. The obtained slurry was then cast on transparent sheet and was dried under ambient condition until it became fully dried. Subsequently, it was then peeled off from the sheet. Membranes were casted for 80 % inorganic weight loading for different average particle size varying from sub-micrometer to nanometer scale.

Characterization

Structural characterization of the phosphosilicate gel particles were done by TEM analysis. The surface morphology of the membrane was obtained using SEM analysis of the composite membrane.

Proton Conductivities of the composite membranes were determined by impedance data taken at different constant temperatures. Potentiostat (AUTOLAB PGSTAT 302 n manufactured by Ecochemie, BV, Netherland) was used to obtain the impedance data in a frequency range of 100 KHz to 1MHz. Ion exchange capacity and water uptake of the membrane were recorded at room temperature.
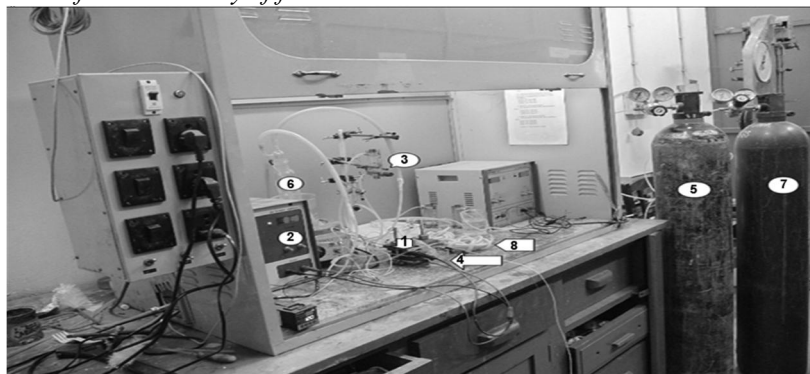
Performance Study of fuel cell

Fig. 1 – Experimental setup for performance study of PEMFC unit cell [Specifications: 1) PEMFC unit cell 2) Constant current source 3) Flow meters 4) Probes connected to cell 5) H_2 cylinder 6) Humidifier 7) O_2 cylinder 8) Adsorbers]
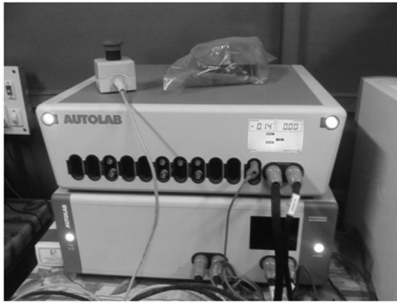
Fig. 2 – Electrochemical Workbench

The single fuel cell tests were carried out for the membrane/electrode assemblies (MEAs) which consisted of the composite sheets as an electrolyte and commercially available Pt-loaded carbon paper sheets as electrodes. The current vs. voltage characteristic (DC polarization) of the fuel cell was measured at different temperatures. From the polarization data power versus current data were evaluated. The enhancement of peak power generation with respect to the particle size was investigated and reported. The relevant TEM and SEM results are also appended in the present work. *Figures 1* and *Figures 2* represent the experimental setup and the electrochemical workbench setup for the present study.

RESULTS AND DISCUSSION

TEM analysis reveals that grinding of material for 20 hrs produces less than 10 nm size of particles; while grinding for less than 8 hr produces average particle size more than 500 nm.
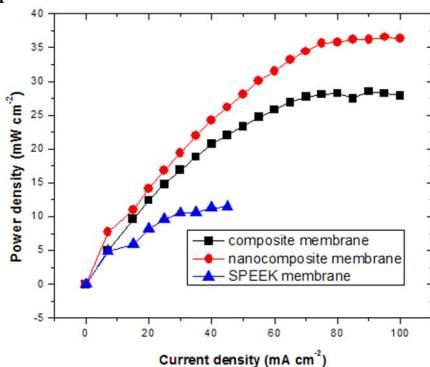

Fig. 3 – Power density versus Current density for the fuel cell at $70^{\circ}C$

Figure 3 depicts the performance enhancement achieved in a fuel cell using nanocomposite phosphosilicate gel-SPEEK membrane comprising of less than 10 nm particle size at $70^{\circ}C$. Data analysis reveals that the composite membrane offers best performance at $70^{\circ}C$. For 60 weight percent inorganic loading of the membrane almost 40% nano enhancement of peak power generation is obtained by varying the gel particle size from sub micrometer to nanometer (Fig. 3). Reduction in particle size from submicro to nanometer range causes enhancement of water uptake, ion exchange capacity and the proton conductivity; thus enhances the performance. The performance study also reveals that at medium cell temperature (65 to $75^{\circ}C$) Phosphosilicate gel-SPEEK hybrid nanocomposite membrane offers more than 75% enhancement of peak power generation compared to that offered by SPEEK membrane.

CONCLUSION

Phosphosilicate gel – SPEEK (Sulfonated Poly Ether Ether Ketone) hybrid nano composite membranes are proposed for performance enhancement of polymer electrolyte fuel cell at low to medium cell temperature. Almost 40% enhancement in power generation is achieved by replacing the composite hybrid membrane with coarse submicro or micrometer size phosphosilicate particles by a nanocomposite membrane comprising of less than 10 nm particles. The present paper standardizes the procedure for experimental synthesis, characterization and performance studies for the novel hybrid nanocomposite membranes. The study highlighted the promising potential for using hybrid nanocomposite membrane for the enhancement of performance of proton exchange membrane fuel cells.

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