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Synthesis and Characterization of Fly Ash/ Chitosan/ PVA Composite Bio Membrane for Low to Moderate Temperature Fuel Cell Applications

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Abstract

Now days, the demand of petroleum based energy resource gradually increases. But due to its limited availability, high toxic emission and adverse effect to the environment, forced us to development of potential alternatives. In recent year, fuel cell technology received more attention because of its high efficiency and lower toxic emission. Fuel cell is a device that continuously converts the chemical energy from a fuel like hydrogen, methanol etc. into electricity through an electro chemical reaction. PEMFC is an efficient electro chemical conversion device for stationary and portable applications. In PEMFC, a proton conducting polymer is used as an electrolytes . In PEMFC, proton transport plays a vital role for achieving more power density. Proton Exchange Membrane (PEM) is one of the important components of a PEMFC for achieving high power density. It is a selective permeable membrane which allows the transport of protons from anode side to cathode side and separate reactant gases from each other. For achieving high power density, PEM should have better proton conductivity, low reactant permeability, excellent electron insulation property, low cost, easily prepared, better mechanical, thermal and hydrolytic stability. Perfluorinated sulfonic acid membranes (PFSA) like Nafion (Dupont®) are considered as a conventional PEM membrane because of their high proton conductivity, good mechanical and thermal stability at low temperatures.

Keywords: Proton exchange membrane; Alkaline Solid Polymer Electrolyte; quaternized polyvinyl alcohol

Introduction

But their applications are restricted because of their high cost, low proton/vanadium ion selectivity, poor mechanical properties at swollen condition and dramatic reduction of proton conductivity above 80°C. Poor performance at higher temperatures is due to the loss of water by evaporation, high fuel cross over, poor thermal stability and possibility of environment contamination [1]. As the wide potential applications in electrochemical devices, such as batteries and supercapacitors, Alkaline Solid Polymer Electrolyte (ASPE) has been considerably investigated have reported studies about alkaline solid polymer hydrogel electrolytes based on poly(ethylene oxide) for application on Ni–Cd, Ni–Zn, and Ni–MH secondary battery systems. The ionic conductivity of alkaline poly(ethylene oxide)-based polymer electrolytes was further reported around 103 S cm1 at room temperature. prepared polymer hydrogel electrolyte with high conductivity from acrylic acid and KOH(aq) solution. The semi-crystalline polyvinyl alcohol, PVA, is also an attractive material for the use as a polymer hydrogel electrolyte. Series results about the preparation and characterization of PVA-based polymer electrolytes and application for Zn–air batteries, rechargeable Ni–MH batteries and direct methanol fuel cell have been reported [2]. Chitosan (CS), [poly-b(1–4)-D-glucosamine], a cationic polysaccharide, is obtained by alkaline deacetylation of chitin, the principal exoskeletal component in crustaceans. As the combination of properties of chitosan suchwater binding capacity,fat binding capacity, bioactivity, biodegradability, nontoxicity, biocompatibility, and antifungal activity, chitosan and its modified analogs have shown many applications. As chitosan membranes have been found to have excellent film-forming properties and high mechanical strength, they are suitable for haemodialysis, ultrafiltration, reverse osmosis, pervaporation and fuel cells. Blending of chitosan with PVA or Quaternized Chitosan With Quaternized Polyvinyl Alcohol (QAPVA) had been reported to improve mechanical stability and the evaluation of methanol permeability and proton conductivity; whereas the electrochemical performance for the direct methanol fuel cell was not reported. In alkaline DMFCs, it is critical to both overcome methanol permeability and enhance ionic conductivity. Numerous researchers have utilized different polymers in the synthesis of alkaline ion-exchange membranes; consequently, the mechanical and electrochemical properties of ion-exchange membranes have been significantly improved. In this study PVA modified by chitosan to get modified PCS membrane and their performances for alkaline direct methanol fuel cell are reported. The homogeneous, nonporous PCS membranes were prepared by casting the polymer solutions with different PVA/ CS ratio and drying at room temperature at least 24 hrs. In order to improve the stability of PCS membrane in KOH(aq) solution, PCS membrane was crosslinked with glutaraldehyde to get PCS-G membrane. The structures of these membranes are identified with azocarmine G.

Experimental Materials

The chemicals used in this study were polyvinyl alcohol, (Mw¼70,000–100,000 g) obtained from Sigma. Chitosan was purchased from Chitin, Chitosan Inc, Taiwan. The molecular weight is about 635,000 with 85% deacetylation. Acetic acid was reagent grade for the study. Fly ash collected from Nalco ,Angul used in cross-linking process. Hydrochloric acid, sodium,sodium hydroxide and phenolphthalein indicator used for titration was availed in our laboratory.

Membrane preparation

Preparation of Bio-membrane(chitosan/PVA composite membrane) take place using chitosan solution and PVA(poly vinyl alcohol) solution in different ratio. Here chitosan solution is prepared using 1% acetic acid solution.1% acetic acid solution prepared by adding 1ml acetic acid into 99ml of distilled water.

90/10

PVA solution was prepared adding 5gm of PVA powder in 50ml of distilled water in beaker. Then beaker was placed in magnetic stirrer for 2hr at 60°c [3]. Simultaneously CS solution was prepared using 0.15 gm of chitosan and 50ml of acetic acid. As previously mentioned in case of PVA solution , this CS solution also placed in magnetic stirrer for 2hr at room temperature. After 2 hr time span both the solution mixture added in one beaker and placed in magnetic stirrer for another 2 hr at room temperature. After complete mixing the solution kept in a petri dish for 24 hr at room temperature. Then these petri dish was kept in oven for 24hr at 50°C.

80/20

Similar procedure was followed in case of 80/20. Only quantities of chitosan and PVA was different than previous procedure. Here 0.3 gm of chitosan and 4.5 gm of PVA was taken.

70/30

Only dissimilarity in this procedure was 0.45gm of chitosan and 4gm of PVA was taken.

Cross-Linking of Bio-Membrane

Cross-linking with h2so4

0.5M H2SO4 solution was prepared . Then Bio-membrane was immersed in the prepared solution for 24hrs. After 24hrs membrane is rinsed with deionized water.

Then immersed in 1.5ml aqua solution of NaOH for 5min(1.5M NaOH solution prepared by adding 2.4gm of NaOH pellets in 40ml of distilled water). Then finally dried at 28°C.

Cross-linking with glutaraldehyde solution

Previously prepared Bio-membrane rinsed in distilled water, then immersed in 40 ml of GA solution for 24 hr.

After 24 hr the Bio-membrane taken out of the solution and kept in a dried petri dish at room temperature.

Crossing with fly ash(90/10)

100ml of both CS and PVA solution was prepared as previously discussed procedure for 90/10 composite bio membrane.

Then both the solution added together in a beaker and kept in magnetic stirrer for 2 hr at room temperature. After complete mixing solution was separate in a beaker (each 100 ml).

Fly ash was added in each beaker in different amount for preparation of different % cross-linked composite Bio-membrane [4].

% of cross-linking	Fly ash content(gm)
1	0.05
2	0.103
4	0.206
8	0.412

Table 1: Fly ash was added in each beaker in different amount for preparation of different % cross-linked composite Bio-membrane.

Preparation of Zelotile

NaOH solution was prepared by adding 8.35gm of NaOH pellets in 37.5 ml of deionized water, mixed with magnetic stirrer at room temperature.

Silicate solution was prepared by adding 5.62gm of silicate powder in 20ml of previously prepared NaOH solution this solution was prepared in a Teflon bottle and mixed manually [5].

Then sodium aluminate solution was prepared by adding 6.54gm of sodium aluminate in 20ml of distilled water. This solution was kept in magnetic stirrer at room temperature with 200 rpm. Both the solution (silicate & sodium aluminate) was mixed together and placed in sonicator for 30min at 40°C. Then the final solution mixture kept in oven at 90°C for 24 hrs.

Ion Exchange Capacity and Degree of Sulfonation

Ion exchange capacity of the composite membrane was measured by standard titration method. Composites membrane with film thickness 120µm, were cut into circular shape (surface area: 11.342 cm^2) by using die cutting machine. Before testing, sample was dried in a hot air oven for 30 minutes at 60°C. Dry Sample was immersed in a 0.1M of Hydrochloric acid for 24 hour to ensure H+ ion transport. After protonation, surface of membrane was washed with distilled water till there is no free proton present on it. Then acidified membrane is immersed in a 0.1M of NaCl solution for exchange of proton (H$^+$) with Na+ ions. The IEC is measured by the following expression

$$IEC(meqg^{-1}) = \frac{V_{NaOH}C_{NaOH}}{W_d} \qquad (1)$$

VNaOH is the volume (ml) of NaOH consumed by titration, CNaOHis the concentration (mol/l) of NaOH used for titration and Wd is the weight (gm) of dry membrane.

DS of the pure Biomembrane is calculated by following expression

$$DS = \frac{M_{SPEEK} \times IES}{1-(IES \times M_{SO_3H})} \times 100 \qquad (2)$$

Mbio is the molecular weight (288) of Bio membrane without functional group, MSO3H is the molecular weight (81) of sulfonic group present in Biomembrane and IEC is in meqg-1. IEC and DS of the all composite membrane were determined by using equation-1 and 2.

Water Uptake and Diffusivity

Before water uptake study; composite membrane was dried in a hot air oven for 30 minute at 60°C [6]. Dry weight of the membrane was measured by a digital balance and noted. Then dry membrane is immersed in distilled water till equilibrium weight of the membrane achieved. During absorption process, at a particular interval of time membrane is kept out from the container and surface water is cleaned properly by tissue paper. Then immediately weight of wet membrane is taken. The above procedure is continued for different interval of time till membrane achieved equilibrium value. Water uptake capacity of the different composite membrane was measured at different temperature. Water uptake capacity (WU) is measured by using following expression

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{wet}} \qquad (3)$$

Wwetis the equilibrium weight (gm) of the membrane and Wdry is the dry weight (gm) of the membrane. The number of water molecule absorbed per sufonate group (-SO3H group) present in composite membrane is calculated by using following expression

$$\lambda = \frac{10 \times WU}{IEC \times MW_{H_2o}} \qquad (4)$$

Where λ is the number of water molecule absorbed per sulfonate (SO3-) group, WU is the water uptake capacity (%), IEC is the ion exchange capacity (meqg-1) and MWH2O is molecular weight of water (18 gmmol^{-1}). Experimental λ value for different composite membrane at different temperature is determined by using equation-4.

The rate of water absorption in the membrane is controlled by diffusion. The behavior of water diffusion was well explained by Fickian diffusion. Several Fickian model was proposed by different researchers for measuring water diffusivity but the model proposed by Takamatsu et al. and Morris and Sun is more effective for analysis. The model equation used for measuring water diffusivity is

$$\frac{M_t}{M_\infty} = \exp(-kt) \qquad (5)$$

Mt is the water uptake at time t, M” is the equilibrium water uptake, k is the effective rate constant and t is the duration of time. By plotting moisture ratio (Mt/M”) with time, slope of the curve provides effective rate constant, k. After estimating k, diffusivity value is calculated by using following expression

$$D(cm2/s) = kL2 \qquad (6)$$

D is the water diffusivity, cm^2/s and L is the thickness of membrane. The water uptake study is performed at different temperature and at a particular temperature; diffusivity is measured by using equation-5 and 6.

Methanol Permeability

Methanol permeability (P) of the composite membrane was determined by using a glass diffusion cell separated by two compartments. One compartment filled with methanol concentration are called donor reservoir and the other compartment which was initially filled up with deionized water are called receiver reservoir. The composite membrane was sandwiched between the two compartments. Before performing test, proper hydration of the composite membrane was obtained by immersing it in distilled water for 24 hours. The methanol transported through the composite membrane into water compartment was measured at a regular interval of time using a density meter (model: DA-130N, Kyoto Electronics

Manufacturing Co., Ltd., Kyoto, Japan). At a particular interval of time, 0.25 ml of sample was collected from the receiver compartment and weighed. Then concentration of solution was determined by density meter. During experiment both compartments were agitated continuously. The methanol permeability (P) was calculated from following equation.

$$C_B = \frac{A}{V}\frac{DK}{L}C_A(t - t_0) \qquad (7)$$

Here CB and CA are the concentration of methanol in water and methanol compartment (mol L^{-1}) respectively; L is the thickness of the membranes (cm), A is the effective diffusion area (cm^2) and V is the volume of deionized water in water compartment (mL), D is the methanol diffusivity (cm^{2}s^{-1}), K is the partition coefficient between membrane and solution, t is the duration time (minute) and t0 is the time lag, related to diffusivity as t0= . The product “DK” is called membrane permeability in cm^{2}s^{-1}. Methanol permeability is obtained from the slope of curve plotted between permeated methanol concentrations with time.

Scanning Electron Microscopy (SEM)

A different composite membrane surface was well captured by SEM (JEOL; JSM-6480 LV, Japan). Uniformity of the composite membrane is confirmed by SEM images. Before performing SEM test, membrane is chopped into small size. Before performing test, membrane cross section was sputtered with thin layer of gold. Different SEM images were taken for composite membrane at the range of 200-9000 magnification. Dispersion of titanium dioxide particle and its size in a composite is well recognized from the SEM image at high resolution (3000-9000 magnification).

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR of the sample is conducted to find the different functional groups present in it. Particular thickness of dry sample is cut into small piece and kept it in a FTIR machine. Infra red light is passed in the sample and intensity of light is measured in the wavelength range of 400-4000cm-1. Different function group of composite is observed due to appearance of the characteristic peak at different wavelength region.

X-ray diffraction (xrd) analysis

XRD technique is used to identify the phase of crystalline material. Finely ground sample is analyzed by X-ray Diffractometer (Philips, PW1720, USA). Composite membrane is dried and grounded into powder form and placed into the sample holder of machine. X-ray incident light produced by Cu Kα radiation at 40 kV and 30 mA is passed to the sample and scanning is done at different diffraction angle (2θ) ranges between 10-90°.

Dsc and Tga Analysis

The change of the state of the composite membranes with action of heat is studied by DSC (Perkin-Elmer DSC7, MA, USA). Composite membrane is cut into small size and approximately 5 mg of sample is used for analysis. The sample is heated from 29-300°C under nitrogen atmosphere with fixed heating rate of 10°C/ min. The experiment is performed with two heating cycle and one cooling cycle for each sample. The thermal stability of the composite membranes is studied by TGA (Perkin-Elmer TGA, MA, USA). For analysis, 10 mg of sample is used. The sample is heated from 29-800°C under nitrogen atmosphere with fixed heating rate of 10°C/min.

Hydrolytic Stability

The composite membrane is initially dried at 60°C for 2 hour and dry weight of the membrane is measured. Then the sample is submerged in distilled water for one day till equilibrium value achieved. Under equilibrium condition, membrane becomes saturated and that will not absorb water. Then weight of the membrane is measured and kept it in a controlled humidity chamber (RH-78%, 29°C) for 6 days. The rate of weight loss with time is studied focusing on hydrolytic stability. For a particular interval of time, weight of the membrane is measured and the procedure is continued for 6 days.

Proton Conductivity

Proton conductivity of the composite membrane between 30-110°C was studied by two probe method Electrochemical Impedance Spectroscopy (EIS) using a potentiostat (Biologic, SP-150) using the frequency range of 1 to 3×10^6 Hz, applying oscillation voltage amplitude of 10 mV. Before performing test, membrane is fully hydrated by immersing in distilled water for 24 hour. The hydrated membrane is sandwiched between two electrodes and constant electric voltage was supplied. The thickness of the hydrated membrane was measured by screw gauge. The proton conductivity of the sample is calculated by using the following equation

$$\sigma = \frac{L}{R_b A} \qquad (8)$$

Here, σ is proton conductivity (Scm^{-1}), R_b is bulk resistance (ohm) and A is effective area of sample sandwiched between two electrodes during measurement and L is the thickness of membrane (cm). Bulk resistance (R_b) can be obtained at the low intersect of high frequency semicircle region from the complex impedance (Re_Z) plane. Proton conductivity is obtained by two methods: (1) from the Bode plot, (2) from the Nyquist plot.

Mechanical Stability

Mechanical stability of the composite membrane is studied by Universal Testing Machine (UTM3382, Instron, UK). For analysis, Samples were prepared based on ASTM standard (D882-01). The sample is cut into rectangular shape of 2cm × 8cm and the tensile rate is fixed at 10 mm/min.

Conclusion

These membranes were characterized by Differential Scanning Calorimetry (DSC), X-Ray Diffraction (XRD), Thermo Gravimetry Analysis (TGA) and mechanical properties of tensile strength and elongation at breaking. To prepare the alkaline solid polymer electrolyte, these membranes were immersed in 40 wt% KOH(aq) solution to form the KOH containing polymer electrolyte membranes and then the alkaline uptake and swelling ratio in the thickness (SWL) and plane direction (SWA) in membranes are studied. The ionic conductivity, methanol permeability, and selectivity through the membranes were evaluated and compared with the results of other studies. The preliminary results of electrochemical performance for the direct methanol fuel cell were also reported and compared with other studies in the conclusion.

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