Performance of polymer nano composite membrane electrode assembly using Alginate as a dopant in polymer electrolyte membrane fuel cell

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Abstract. Polymer membrane and composite polymer for membrane electrode assembly (MEAs) are synthesized and studied for usage in direct methanol fuel cell (DMFC). In this study, we prepared 3 type of MEAs, polystyrene (PS), sulfonated polystyrene (SPS) and composite polymer SPS-alginat membrane via catalyst hot pressed method. The performance and properties of prepared MEAs were evaluated and analyzed by impedance spectrometry and scanning electron microscopy (SEM). The result showed that, water up take of MEA composite polymer SPS-alginate was obtained higher than that in SPS and PS. The proton conductivity of MEA-SPS-alginate was also higher than that PS and PSS. SEM characterization revealed that the intimate contact between the carbon catalyst layers (CL) and the membranes, and the uniformly porous structure correlate positively with the MEAs prepared by hot pressed method, exhibiting high performances for DMFC.

1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) has great potential for movable and stationary power supply application wherein the fuel cell must be capable of operating at high power density with low content of catalyst to reduce its cost. In order to reduce the prime cost of PEMFC, the performance improvement of membrane electrode assembly (MEA) becomes a key point. MEA typically consists of proton exchange membrane (PEM), catalyst layers and gas diffusion layers (GDLs), in which the electrolyte, catalytic particles and reactants have a close contact with each other. The GDLs facilitate transport of reactants and products between fuel cell flow in the field and the ionomer electrolytes-catalysts interface. The state-of the art MEA consists of perfluorosulfonic acid (PFSA) polymer membranes such as Nafion® and Pt/C electrocatalysts. In spite of good physical and chemical stability and high proton conductivity, PFSA suffers from limited operation temperature, high cost and environmental concerns [1-2]. Therefore, significant effort has been made to develop nonfluorinated hydrocarbon polymers based on aromatic plastics, such as sulfonated

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polystyrene (SPS), sulfonated polysulfone (SPSf), sulfonated poly(ether ether ketone) (SPEEK), sulfonated polybenziimmidazole (SPBI) and sulfonated poly (aryl ether kethone) (SPAEK) as an alternative proton exchange membranes for PEMFCs. These sulfonated aromatic polymers possess excellent chemical resistance, high thermo-oxidative stability, good mechanical properties and low cost [3-4].
MEA for PEMFCs is generally fabricated by the hot pressing method, wherein a PEM is sandwiched between an anode and a cathode electrode and pressed at a high temperature. However, the MEAs fabricated by the conventional hot pressing method are usually inclined to delamination both at anode and cathode interfaces after long-term operation, leading to degradation in cell performance. Thus, conventional hot-pressing method can only offer physical contact, rather than achieving a true interfacial contact between the PEM and the electrodes during the MEAs fabrication process. Some researchers faced delamination problem in hot-pressing method in case of using liquid methanol as a fuel in a direct methanol fuel cell (DMFC), because swelling of the PEM in methanol solution which can greatly affect the intimate contact between the PEM and electrodes in MEAs. In this context, it is essential to mention some of the recent studies in which effort has been made to improve the interfacial contact in the MEAs for DMFC. Liang *et al.*[5] introduced a simple method for fabricating the MEAs as compared to dry

2. Experimental Methods

Polymer material used in the study was prepared from styrofoam (PS) waste and it's synthesized by sulfonation reaction. Membranes were prepared by dissolving a known amount of sulfonated poly styrene (SPS) in dichloromethane (10%) under constant stirring. Polymer SPS-Na-alginate nanocomposite membranes were prepared by mixing SPS and Na-alginate and dissolving in dichloromethane with ultrsonication process.Three types of proton exchange membranes PS, SPS and SPS-Na-alginate were used as the polymer electrolyte membrane for MEA preparation. Before use, the membranes were pretreated in hydrogen peroxide solution (5 wt.%) at 80℃ for approximately 1 h; after being flushed with deionized water, it was transferred into a 0.5M sulphuric acid solution and boiled at 80℃ for an additional 1 h, then washed with deionized water [8].
The catalyst inks were prepared by dispersing catalysts powder into a mixture of dichloromethane and membrane solution. The catalyst used for anode and cathode layers were Ag/C (20 wt.% Ag/AgCl) and 5% membrane solution. The mixture was ultrasonically dispersed for 30 min before being used. All MEAs used in this study were prepared using hot pressing method at 120-125℃ for approximately 5 min.
Electrochemical impedance was conducted for a single cell by feeding 1.0M methanol at a flow rate of $1 mlmin^{-1}$ using a high-pressure piston pump and by purging dry oxygen gas into the cathode at a flow rate of $20 mlmin^{-1}$ at 40°C at a constant dc potential controlled by the potentiostat with applying a small alternating voltage (10mV) and varying the frequency of the alternating voltage from 1×10^{4} to 1×10^{-2} Hz.
Scanning electron microscope (SEM) was used to evaluate the cross section of the MEA. The sample with gold sputter coatings was carried out on the desired membrane samples at pressure ranging between 1 and 0.1 Pa. The DMFC performance test was conducted at 40.0℃ by feeding 1.0M methanol at a flow rate of $1 mlmin^{-1}$ using a high-pressure piston pump and by feeding dry oxygen gas into the cathode at a flow rate of $20 mlmin^{-1}$ at ambient pressure by fixing the load current, which was controlled with an electric load system.

3. Result and Discussion

The DMFC performance was evaluated through by polarization curve, also known as a voltage–current density (V-I) curve, is commonly used to evaluate fuel cell performance. Figure 1 is a representation of typical polarization compares the performance of the single cells with the membrane PS, SPS, SPS-alginate and MEA-PS, MEA-SPS, MEA-SPS alginate with 1.0 M methanol at 50℃. The Figure 1 shows that all of the MEA membranes have better fuel cell performance than that in single membrane. This suggests that

the membrane with this type of membrane electrode assembly can improve fuel cell performance. These results also reveal that in the very low current density region, the cell using MEA-SPS exhibited a slightly lower open circuit voltage (OCV) and performance than the cell with the MEA-PS and MEA-SPS-alginate. This can be attributed to the fact that the rate of methanol cross over for the MEA-SPS is higher than that in the MEA-SPS and MEA-SPS-alginate.
However, in higher current density region particularly above 500 mA/cm2 the cell using MEA-SPS-alginate showed much better performance as compared to the cell with MEA-PS and MEA-SPS. This indicates that the MEA-SPS-alginate has a lower mass transfer resistance than the MEA-PS and MEA-SPS. The lower mass transfer resistance for the MEA-SPS-alginate might be related to the possible formation of hydrophilic pores in the MEA fabrication process. Chaudry and Sengawa [6] have reported increase in hydrophylicity properties and also the conductivity with addition of small inorganic polymer such as monmorilonite, alginate, silica, etc. Earlier reports suggest that sulphonated of polystyrene has ability to increase the hydrophilicity properties of the membrane.

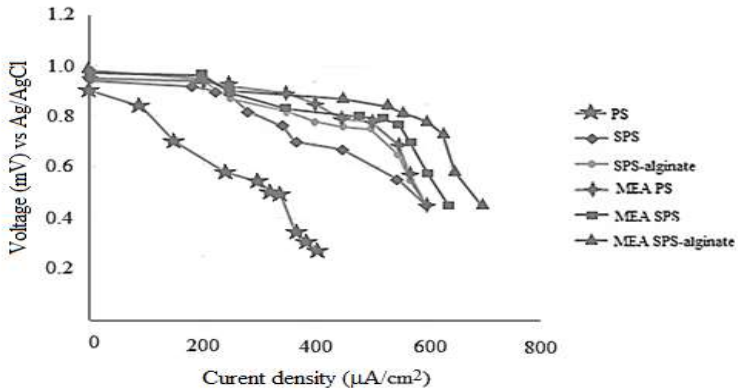


Figure 1. Polarization of comparison of cell performance for membrane

Generally with sulfonated acid membranes, there is no preferential permeation of water or methanol; both decrease with increasing sulfonated content. For PS membranes the total flux of methanol and water increases with increasing temperature and feed methanol concentration. Therefore, sulfonated membranes seems promising and worth investigating for DMFC application. Figure 2 exhibit the result of proton conductivity in different electrode such as carbon, cuprum and iron. In order to provide enough hydration to the membrane and activated the anode catalyst activation of the prepared membranes is necessary. MEA SPS alginate activated membrane appeared to have higher proton conductivity than that the MEA SPS activated membrane. Alginate as a dopants incorporated into the pores of membrane of MEA will affect the high conductivity of membrane. The effect of incorporating alginate as inorganic dopants in the membrane depends on the nature of the dopant in question. If the dopant is not acidic it simply acts as a barrier to both proton and methanol flow. The dopant in this case is non-conducting and acts as a barrier to both vehicular diffusion and Grotthuss diffusion. It obstructs the former by preventing the vehicular transport of hydronium ions, and it also obstructs the latter by disturbing the hydrogen bond network. Apparently this should be particularly effective in blocking ing methanol flow as methanol molecules are much larger than protons, but it also affects proton conductivity adversely.

Another effect of higher conductivity of MEA SPS-alginate membrane is due to its contents of sulfonate group in the SPS. The particle has an SO_4^{2-} group attached which attracts protons and continues the hydrogen bond network. This particle would still block vehicular diffusion but will only slightly reduce Grotthuss diffusion, if at all. Depending on the acidity of the particles, it might even increase the proton exchange sites and Grotthuss diffusion and the overall conductivity.

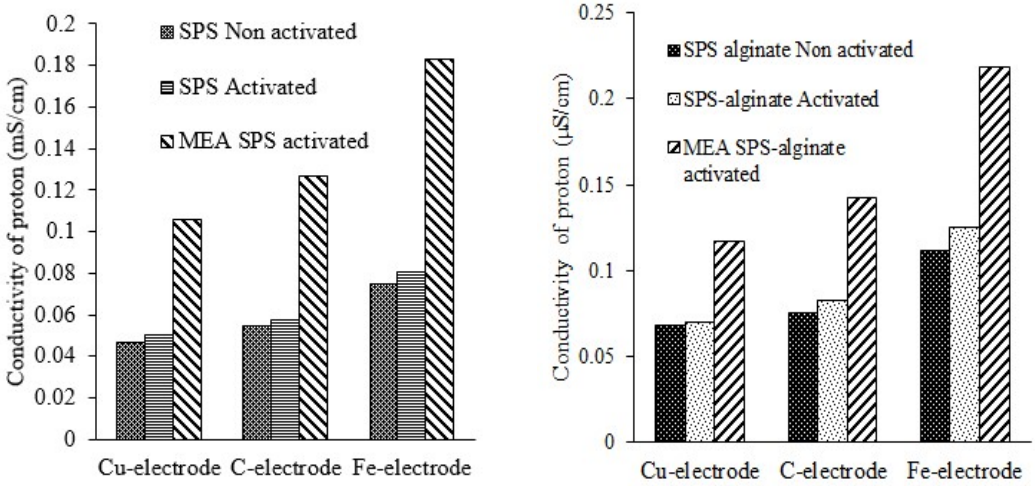


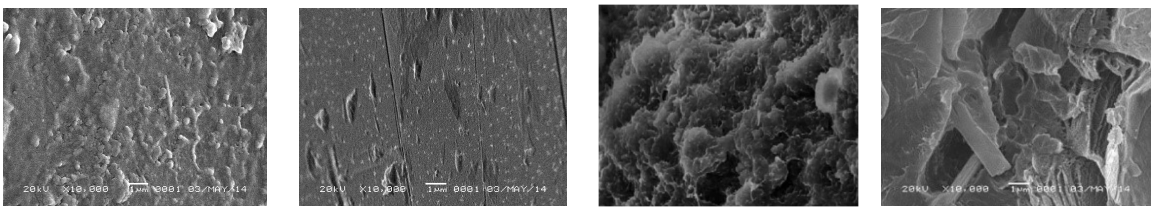
Figure 2. Proton conductivity of SPS and SPS-alginat

Sulfated dopants, such as sulfated zirconia and sulfated silica are especially popular in current research [11] and extensive research has been done with these inorganic particles in PEMFCs. Incorporation of sulfated zirconia particles (ZrO_2/SO_4^{2-}) into Nafion via the sol-gel method has shown increased water uptake and proton conductivity in hydrogen/oxygen fuel cells due to the additional acid sites [12]. However, due to methanol crossover, increased water uptake is undesirable in DMFCs. The acidity of the membrane should be such that overall methanol crossover is reduced while maintaining conductivity. The results revealed that the water up take of MEA SPS (13.68%) was higher compared to SPS (5.15%) and PS (0.69%). The contribution of alginate and sulfonate in the MEA-SPS-alginate membrane would increase proton conductivity and water uptake. While the water up take might increase methanol crossover in the membrane, sulfonate group increases the proton exchange site.

Evaluation of sulfonate group in the sulfonation process of the PS was confirmed qualitatively by FTIR. The process, which occurs exclusively in the phenyl rings should be manifested by the appearance of new vibration characteristic of sulfonic acid groups; by changes in the aromatic C–H out of plane bending region and perhaps by splitting of some bands (e.g. the C–O stretch of the substituted rings), which is due to the reduced symmetry and direct influences of sulfonic acid groups vibration frequencies after the sulfonation process.

Significant differences in FTIR spectra of sulfonated PS were observed compared to pure PS. The peak identified at 1500 cm^{-1} proved the presence of C–C aromatic ring in the PS, which referred to the 2, 4-substitution aromatic ring indicating that only first substitution was involved in this study. As sulfonated PS became water-soluble when the sulfonation degree was approaching 100% the first type of substitution reaction is more favorable. Therefore, the study followed first type substitution. The sulfonation process decreased the intensity of the aromatic C–C vibration and the peak was observed to split to two absorption bands at 1495 and 1475cm^{-1}. These two bands increase with the increasing concentration of sulfonic acid

group in the sulfonated PS membranes. Occurrence of a new absorption band at 1028.35 cm^{-1}, 1181.27cm^{-1}, 1275 $cm^{-1}$and 1069 cm^{-1} upon sulfonation indicated presence of the sulfonic acid groups in PS. In summary, the changes observed in the FTIR spectra indicated the presence of $–SO_3H$ groups.
The cross section of membrane morphology was evaluated to support the performance of DMFC. Figure 3 shows the SEM cross-sectional images of membrane PS, SPS, SPS-alginate and MEA SPS-alginate, respectively. It is clear from the SEM images that for the MEASPS-alginate, by hot pressing, the interfacial contact between the membrane and the electrodes proves to be good. However, for the membrane SPS-alginate, which was activated, alginate seems algomerated in the membrane. Dopant of alginate increased both proton conductivity and the strengthen of hot pressing method to reduce the delamination problem that occurred at the interfaces of the MEAs. Liang *et al* reported that delamination problem seems to be more serious both at the anode and cathode interfaces of the conventional MEA; in fact, this could be the main cause for the low performance of the cell with the MEA after being operated for 4 days. The existence of a better interfacial contact at the cathode interface for the MEA SPS-alginate explains why it yielded more stable performance than that of MEA SPS after operating the cell. The prevalence of a good interfacial contact at the cathode interface of the MEA SPS-alginate can be attributed to the effect of alginate as an inorganic dopant into membrane. In addition, the alginate presence in the MEA SPS-alginate also roughens the surface of the membrane, which enhances the contact region of the MEA-SPS-alginate membrane with the electrodes during the fabrication of the MEA. It is pertinent to mention that the solvents methanol/water present in the membrane dispersion play an important role while fabricating the MEA by the hot pressing method.



(a) (b) (c) (d)

Figure 3 Cross section morphology of membranes (a) PS, (b) SPS (c) SPS-alginate, dan (d) MEA SPS-alginate

In conclussion, a kind of polymer electrolyte composite inorganic dopant was introduced between the PEM and the electrodes during the MEA fabrication process to achieve a better interfacial contact. The dopant provides a better resistant and stronger binding force between the membrane and the electrodes. The performance of the cell using the MEA-SPS-alginate was found to be more stable. The cross-sectional analysis of the MEAs after the long-term operation revealed that the MEA-SPS-alginate retained a better interfacial contact between the membrane and the electrodes as compared to the MEA-SPS. The proton conductivity results revealed that the MEA-SPS-alginate exhibited a higher value than the MEA-SPS, confirming that the MEA-SPS-alginate had a better interfacial contact between the electrodes and the membranes. The inorganic content needed for the right balance varies. Sulfonate group attached in PS and alginate doped into MEA-SPS-alginate membranes seems to have potential advantages for DMFCs over plain Nafion membranes.

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