Fabrication and Characterization of Sulfonated Poly(vinyl alcohol-co-ethylene glycol) Electrolyte Membranes

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Abstract—In this study, poly (vinyl alcohol-co-ethylene glycol) was sulfonated and cross-linked with different amounts of sulfosuccinic acid (SSA) to prepare the polymer electrolyte membrane for direct methanol fuel cell. In addition, phosphoric acid was added to the sulfonated membranes to further promote the proton conductivity. The synthesized membranes were characterized by measuring their gel content, water uptake, ion exchange capacity and methanol permeability to determine how these properties varied with composition. The results showed that the gel content first increased with the amount of SSA, and then decreased after reaching a maximum value. The addition of phosphoric acid only slightly increases the gel content. The properties such as water uptake, ion exchange capacity and methanol permeability are closely related to the gel content. Finally, in the single cell test, the membrane electrode assembly fabricated with phosphoric acid-doped sulfonated membrane has a better performance over that with the undoped sulfonated membrane.

Indexed Terms—poly (vinyl alcohol-co-ethylene glycol), proton exchange membrane, membrane electrode assembly, direct methanol fuel cell

I. INTRODUCTION

Fuel cells have the advantages of low pollution, high efficiency, high energy density, no need to charge and a wide range of fuel sources. They can be used to replace traditional batteries. A fuel cell is an energy conversion device with an electrochemical working principle similar to that of a traditional battery. But unlike a traditional battery which stores the active reactants inside the battery, a fuel cell transports external fuel and oxidant into the cell as active reactants, and directly converts the chemical energy of the fuel and the oxidant into the electrical energy inside the cell according to the electrochemical principle. A direct methanol fuel cell (DMFC) is also a polymer electrolyte fuel cell, which uses methanol as fuel to provide electrons [1]–[4]. At the anode inlet, methanol in the form of an aqueous methanol solution is fed to the anode catalyst layer, where the oxidation half-reaction of the anode takes place:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$
$$E_a^o = -0.046V \tag{1}$$
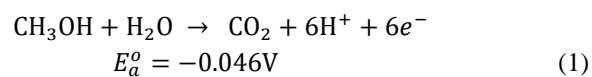
In this half-reaction, one methanol molecule will generate six electrons and six protons. The electrons will be conducted to the cathode through the external circuit, while the protons will be conducted to the cathode through the middle polymer electrolyte membrane, and then conducted to the cathode. At the cathode, the protons will react with the electrons conducted to the cathode from the external circuit and the oxygen molecules supplied from the outside, and the reduction half-reaction of the cathode will occur in the cathode catalyst layer:

$$\tfrac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad E_c^o = 1.229V \tag{2}$$
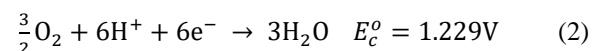
Water and heat will be produced in this half-reaction. The net cell reaction is:

$$CH_3OH + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \quad E_{cell}^o = 1.183V \tag{3}$$
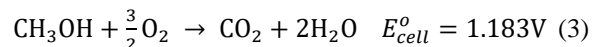
The standard electromotive force for the cell is 1.183V. Methanol has the advantages of low price, easy transportation and storage. In addition, compared with the high operating temperature of other reformate fuel cells, DMFC systems save the cost of the reformer and can operate at a temperature below 80 °C. Low temperature and high safety make DMFC systems the top choice for portable applications.

In a fuel cell, the anode and cathode are separated by a polymer electrolyte membrane, and the protons

generated by the anode are sent to the cathode through this membrane. In the membrane, there are two mechanisms for the conduction of protons, one is the vehicle mechanism, that is, the protons are transported through the water channel in the membrane in the form of hydrated proton complexes (Zundel $H_5O_2^+$ and Eigen $H_9O_4^+$ cations), and the water molecules are brought to the cathode simultaneously (called electro-osmosis). Another mechanism of proton conduction is the dynamic rearrangement of covalent and hydrogen-bonds involving neighboring hydrated proton complexes. The hydrated proton bonds an oxygen atom and another proton at the other end on the same hydrated proton complex is released simultaneously by forming a bond with oxygen at the neighboring complex and the proton is transferred from one complex to another complex (proton hopping), forming proton transport channel (proton wire). This mechanism is called the Grotthuss mechanism. The polymer electrolyte membrane is a key component of the entire DMFC. A good DMFC electrolyte membrane should have good proton conductivity, good electronic insulation, good chemical and thermal stability, and the ability to prevent methanol crossover. A single fuel cell is mainly composed of a membrane electrode assembly (MEA), flow field plates and current collector plates. To test the performance of the polymer electrolyte membrane, it is necessary to make a self-made membrane electrode assembly, while other parts can be assembled with commercial accessories. MEA mainly includes three major components, in addition to a polymer electrolyte membrane [5], there are two catalyst layers and two gas diffusion layers [6], [7]. The main function of the catalyst layers is to accelerate the methanol oxidation at the anode and the oxygen reduction reaction at the cathode. At present, the most commonly used anode catalyst is Pt-Ru black or 80wt% Pt-Ru/C, while the catalyst at the cathode end is Pt black or 80wt% Pt. The main function of the gas diffusion layer is to effectively and uniformly disperse the methanol aqueous solution at the anode and the air or oxygen at the cathode. At the same time, it must also effectively discharge the carbon dioxide generated at the anode and the water at the cathode. The materials of the gas diffusion layer are mainly carbon paper and carbon cloth. Using the MEA made from the synthesized membrane and feeding it with aqueous methanol solution, the fuel cell is ready for use.

We have used sulfonated polyvinyl alcohol (PVA) as a proton exchange membrane. The proton conductivity of its dry membrane is quite low. The presence of hydrogen bonding interactions involving hydroxyl functional groups in PVA results in a higher glass transition temperature of 80 °C. The rate of its segmental rotation, and consequently its proton conductivity, is thus limited. To improve the proton hopping capability, the rotating rate of sulfonic group bearing segments is very important. Therefore, if we can incorporate a soft and proton-conducting chain to PVA, we can synthesize a balanced dry-wet proton exchange membrane. Polyethylene glycol (PEG) can form complexes with salts [8], and the oxygen atoms on its chain can dissociate with salts to form cations to form coordination bonds, and ion transport is assisted by the segmental motion of polymer chains [9]. When the fuel cell is in operation, the MEA must be adequately humidified to fully hydrate the membrane to maintain proton conduction. Because of the hydrophilic nature of the of the sulfonic acid which is covalently bonded to the backbone of the polymer, the sulfonic group behave as the hydrophilic proton exchange group. Protons can move freely within the membrane. In the cathode reaction, the sulfonic group near the cathode dissociates the proton to participate in the electrochemical reaction to generate water, and after the proton leaves, the adjacent proton will quickly fill the vacancy on $-SO_3^-$ due to electrostatic attraction. Protons in the membrane can only move from the anode to the cathode caused by the potential difference. The water molecules in the exchange membrane will solvate protons with protons on $-SO_3H$, thereby weakening the attraction between $-SO_3^-$ and proton and facilitating the conduction of protons. After the proton leaves $-SO_3^-$, it either hops quickly the through the channel formed by sulfonic groups along the polymer backbone, the solvated proton complexes and free water molecules, or migrates in the form of a solvated proton complex through the channel. These two mechanisms make hydrated proton exchange membranes good conductors of protons.

In this study, poly(vinyl alcohol-co-ethylene glycol) copolymer (PVAEG) was selected as the polymer to fabricate the proton exchange membrane, and then cross-linked with sulfosuccinic acid to achieve the

purpose of sulfonation. In addition, phosphoric acid was added to form coordination complex to greatly increase the proton concentration in the polyelectrolyte membrane and improve the conductivity, and it still has a considerable conductivity when the water content is reduced, which reduces the burden of water management in the battery system.

II. EXPERIMENTALS

A. Materials

Poly(vinyl alcohol-co-ethylene glycol) (PVAEG, Kollicoat IR with VA:EG=3:1, BASF), sulfosuccinic acid (SSA, 70 wt% solution in water, Sigma-Aldrich), methyl alcohol (99.9%, Mallinckrodt Baker Inc.), phosphoric acid (Shimakyu), Nafion solution (5wt%, Sigma-Aldrich), Carbon black powder (Vulcan XC 72, Cabot), Pt-Ru black (50wt%Pt-50wt%Ru, Alfa Aesar), Pt black (100%, Alfa Aesar), carbon paper (Toray TGP-H-090, E-TEK), gas diffusion layer (GDL, ELAT LT2500W, E-TEK) were purchased and used as received.

B. Membrane

8% aqueous solution of PVAEG was prepared by adding PVAEG powder to deionized water, shaking in a 90 °C water bath for 6 h and cooling to room temperature. Various amounts of SSA, SA and phosphoric acid were then added to the solution, stirred until homogeneous, and the stirring speed was then reduced to prevent formation of foams. Membranes were prepared by casting the solution on stainless steel plates and drying at room temperature for several days. The obtained membranes were sandwiched between two glass plates and then placed in a vacuum oven for sulfonation and crosslinking at 70 °C for 24 h, then 90 °C for 2 h. The designation and composition of the fabricated membranes are listed in Table 1.

C. Membrane Electrode Assembly

The catalysts used for anode and cathode are Pt-Ru black and Pt black, respectively. To fabricate the catalyst layers, the precursor solutions of the two electrodes are first prepared. Pt-Ru black or Pt black was adding to an appropriate amount of deionized water, and the catalyst mixtures were dispersed with an ultrasonic shaker for 10 min. The precursor catalyst solutions (Pt-Ru 15wt%–Nafion 85%wt for anode, Pt

10 wt%–Nafion 90 wt% for anode) were then obtained by adding an appropriate amount of Nafion solution to the above mixtures and dispersing with an ultrasonic shaker for 10 min. The precursor solution was brushed onto a piece of carbon paper and then dried in a convection oven at 60 °C; the brushing and drying steps were repeated about 20 to 30 times until the

Table 1. Sample designation and composition of the polymer electrolyte membranes.

Designation	Composition (molar ratio)				
	VA	EG	SSA	SA	H₃PO₄
1SSA	100	33.3	1		
2SSA	100	33.3	2		
3SSA	100	33.3	3		
4SSA	100	33.3	4		
5SSA	100	33.3	5		
5SSAQPA	100	33.3	5		8.3
5SSAHPA	100	33.3	5		16.7

weight of the catalyst on the carbon paper reached the desired weight to obtain a catalyst layer.

The sulfonated PVAEG membrane was then sandwiched between the anode and cathode catalyst layers and pressed at 60 °C under a pressure of 50 kg/cm^2 for 90 s. The MEA was then fabricated by further sandwiching the above membrane/catalyst laminate with two sheets of ELAT LT2500W carbon cloth.

D. Characterization and Testing

The values of gel content were obtained using the reflux extraction method with water as the solvent. The values of water uptake were obtained by immersing the samples in deionized water at 30 and 80 °C, respectively for 24 h, and then measuring the weight gain. The values of IEC were obtained by NaOH titration of the NaCl solution that had been used to convert the membrane from the H$^+$ form to the Na$^+$ form. The permeation coefficients were obtained by measuring the concentration of methanol permeating the membranes as a function of time. Single cell discharge tests were performed on an Arbin BT-2043 electrical load with 1 M methanol solution fed at 4 ml/min and oxygen fed at 20 SCCM.

III. RESULTS AND DISCUSSION

A. Gel Content

The hydroxyl group (−OH) on PVAEG will undergo an esterification reaction with the carboxyl group (−COOH) on SSA. If the SSA molecules reacts with two different PVAEG chains, a crosslink will form. Since PVAEG is water-soluble, a high degree of cross-linking will help keep the material intact during fuel cell operation. However, if the crosslink density in the polymer electrolyte membrane is too high, it will reduce the water uptake, which will adversely affect proton conduction. Gel content is a common measure of crosslinking level among polymer chains. Figure 1 shows that when only SSA was used, the gel content
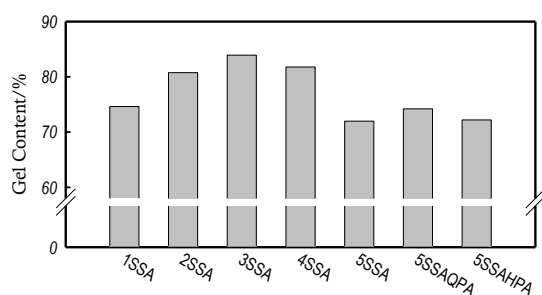

Figure 1. Gel content of the synthesized membranes.

initially increased with the amount of SSA. That was, more crosslinks were created by adding more SSA. But when the VA/SSA molar ratio was higher than 3%, the gel content started to decrease. This might be caused by excess SSA carboxyl groups in the system, many of which reacted with only one PVAEG chain without creating a crosslink. The addition of phosphoric acid slightly increased the gel content, since the acid acted as a catalyst for esterification and made the reaction more complete.

B. Water Uptake
Water plays a crucial role in proton conduction associated with the dynamics of hydrated proton complexes. The membrane needs water to maintain good proton conductivity. However, excessive water uptake causes dimensional swelling, leads to delamination between the electrode layer and the membrane inside a MEA, thereby reducing cell durability [10]. Water uptake is highly correlated with gel content. For membranes with high gel content, the high crosslink density limits the flexibility of the polymer chains, and it will be difficult for water molecules to permeate into the membrane. Figure 2

shows the water uptake of the proton exchange membranes crosslinked at 90 °C with different amounts of SSA added to PVAEG. The uptake value
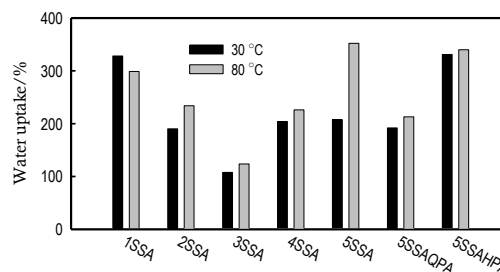

Figure 2. Water uptake of the synthesized membranes.

decreases initially and then increase with the amount of SSA because the gel content also increases initially and then decrease. The 30 °C water uptake value of 5SSAHPA is higher than expected because phosphoric acid is highly hygroscopic, and hydrated phosphoric acid effectively plasticizes PVAEG, making 5SSAHPA highly hydrated. The 80 °C uptake values are also generally higher than those of 30 °C. At higher temperatures, the chains of PVAEG are more flexible, and thus capable of a higher hydration level.

C. Ion Exchange Capacity
Ion-exchange capacity (IEC) is defined as the number of incorporated ions that is responsible for ion exchange in a polymer electrolyte membrane, and is usually expressed in mmol ions per gram of dry membrane. In this study, the functional groups or active sites responsible for proton exchange in the membrane are sulfonic acid and phosphoric acid. It can be seen from Figure 3 that when the amount of SSA increases, the sulfonic acid groups attached to PVAEG also increase, consequently the IEC value also increases as well. However, we found that the actual IEC values of 4SSA and 5SSA are much larger than their corresponding theoretical values. This is because many SSAs had one end attached to the PVAEG chain, while the carboxyl group at the other end did not react. When titrating in IEC measurements, H^+ on the carboxyl group was also titrated. It should be noted that the dissociation degree of the carboxyl group is too low to contribute to the membrane proton conductivity. The addition of phosphoric acid also significantly increased the IEC value, and the IEC value also increased with the increase in the amount of phosphoric acid added, indicating that the phosphoric acid was not lost, and it

effectively formed complexes with PVAEG. The H+s on phosphoric acid are expected to be involved in proton conduction.
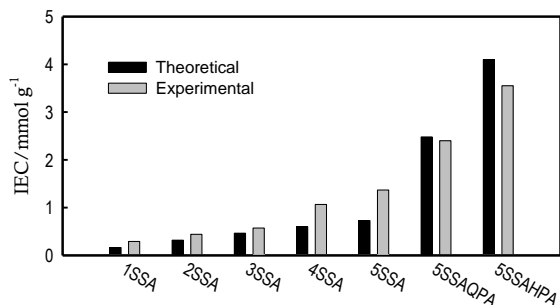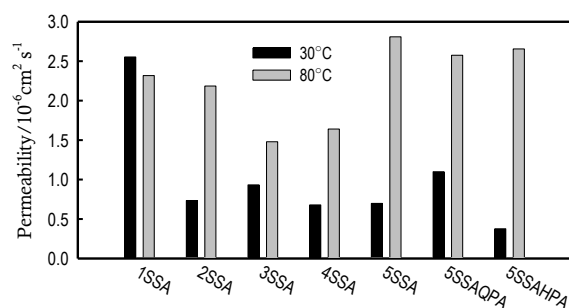

Figure 3. IEC of the synthesized membranes.

Figure 4. Methanol permeability of the synthesized membranes.

D. Methanol Crossover

In DMFC operation, methanol sometimes migrates with water toward the cathode, which in addition to causing fuel loss, also causes methanol to oxidize not only at the anode but also at the cathode, thus resulting in a drop in cell potential. Methanol crossover is one of the major reasons for the performance loss of DMFC. In this study, we evaluated the resistance to methanol crossover of each membrane by measuring the methanol permeability of the membranes. Membranes with low permeability coefficients are considered to have better resistance to methanol crossover. Figure 4 shows the methanol permeability coefficient of each membrane at 30 °C and 80 °C. First of all, it can be seen from the figure that, different from the behavior of the water uptake, at 80 °C, the permeability coefficients of the membrane are much greater than those at 30 °C. Since water uptake is a static equilibrium property, and permeability is a kinetic property, it involves the movement of molecules, and the effect of temperature is more pronounced. The permeability coefficients at 80 °C are also closely related to the gel content. If the crosslink density is higher, the movement of molecules becomes more difficult. Therefore, the membranes 3SSA and 4SSA have the smallest permeability coefficients. In addition, the membranes with higher water uptake also have higher permeability coefficients.

E. Single Cell Testing

Figure 5 shows the polarization curves of a single-cell DMFC with different membranes at an operating temperature of 80 °C. Both the 5SSA and 5SSAHPA MEAs show an initial sharp drop in voltage as current density begins to increase. This is due to the electrochemical activation process related to the electro-oxidation reaction. This region of the
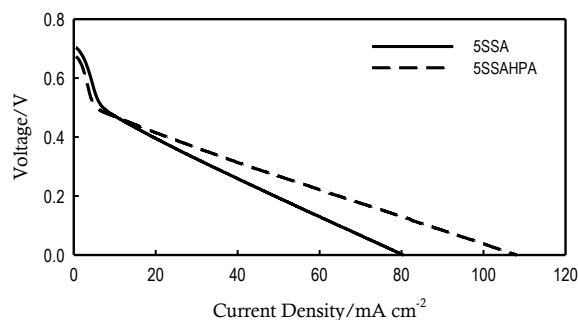

Figure 5. Single cell performance of 5SSA and 5SSAHPA membranes.

polarization curve is usually referred as the activation polarization dominant region. The curves then show a linear decrease of voltage with increasing current density, which is referred as the ohmic polarization region. The polarization is caused by the resistance to flow of ions through the electrolyte membrane and the electrodes. The two membranes have similar values of gel content, water uptake and permeability, while the 5SSAHPA membrane has a significantly larger IEC value. The addition of phosphoric acid to provide more mobile protons certainly helped to promote the performance of the single cell.

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