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Sulfosuccinic Acid-Modified Polyvinyl Alcohol Electrolyte Membrane for Direct Methanol Fuel cells

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Abstract- ***In this study, a proton exchange membrane with excellent methanol barrier properties was prepared by simultaneously performing sulfonation and crosslinking through the esterification reaction of polyvinyl alcohol (PVA) and succinic acid (SSA). A fabricated membrane electrode assembly was then developed for application in a direct methanol fuel cell. The swell ratio experiments revealed that the degree of molecular crosslinking tends to increase with increasing SSA dosage, and the anode and cathode electrode membranes exhibit a certain degree of crosslinking. In the AC impedance experiments, the proton conductivity of the membrane also increases with increasing SSA dosage. Ion exchange capacity increases with increasing SSA dosage. In the methanol permeability experiment, methanol permeability increased with increasing temperature. However, as the SSA dosage increased, the accompanying increase in crosslinking reduced the rate of methanol crossover. The methanol permeability of sulfonated PVA membranes was two orders of magnitude lower than that of Nafion. For the single cell, the steps to fabricate a membrane electrode assembly have been developed, and both increased temperature and methanol concentration contribute to improved current density.***

Index Terms- ***Direct Methanol Fuel Cell, Methanol Crossover, Poly (Vinyl Alcohol), Proton Exchange Membrane***

I. INTRODUCTION

The rapid development and widespread use of portable electronic products (such as laptops, tablets, and mobile phones) have led to a surge in consumer demand for high-energy-density, small batteries. As an emerging electrochemical power generation device, fuel cells are considered a major revolution in the field of green energy because they can directly convert the chemical energy of fuel and oxidant into electrical energy, are not limited by the Carnot cycle, and have the characteristics of high efficiency, low pollution, and fast refueling. Among various fuel cells, the direct methanol fuel cell (DMFC), evolved from the proton exchange membrane fuel cell, uses a methanol aqueous solution as fuel, directly eliminating the need for a bulky and complex reformer device. This not only solves the safety risks associated with hydrogen production, high-pressure storage, and transportation but also makes refueling extremely simple. Therefore, DMFC demonstrates unparalleled unique advantages and commercial potential in applications such as mobile power supplies of portable electronic products. A DMFC is essentially a complex electrochemical system consisting of end plates, current collectors, bipolar plates, a gas diffusion layer, a catalyst layer, and, most importantly, a proton exchange membrane. Its basic operating mechanism involves the continuous external supply of methanol fuel to the anode catalyst layer, where an electrocatalytic oxidation half-reaction occurs on the anode surface, converting methanol into carbon dioxide, protons, and electrons. The protons released in the reaction pass through the proton exchange membrane to the cathode, while the electrons, after performing work through the external circuit, flow to the cathode. At this point, oxygen, protons, and electrons at the cathode undergo a reduction reaction under the action of a catalyst to produce water. The theoretical total potential difference between the two electrodes is 1.183 V [1].

The most well-known proton exchange membrane material traditionally is the Nafion® membrane developed by DuPont. However, the interconnected hydrophilic ion channels within this membrane structure, when in contact with a methanol aqueous solution, can facilitate the easy diffusion of methanol molecules along with water molecules to the cathode, resulting in a significant methanol crossover effect [2]. This will cause a loss of fuel efficiency and reduce the effective potential generated. This research team chose polyvinyl alcohol (PVA), which has good selectivity for alcohols and water, high

methanol barrier properties, and low cost, as the base polymer membrane material [3]. The hydrophilic PVA used has hydroxyl groups on its molecular chain. By introducing sulfosuccinic acid (SSA), a bifunctional nucleophile containing both carboxyl and sulfonic acid groups, the carboxyl groups of SSA and the hydroxyl groups of PVA can undergo esterification under heterogeneous conditions. In this way, SSA acts as a hydrophilic proton carrier, providing a large number of sulfonic acid groups to the non-conductive PVA, constructing an ion-conducting network and significantly improving the ion exchange capacity (IEC) and proton conductivity of the membrane. Furthermore, SSA acts as a three-dimensional crosslinking agent, creating a dense crosslinked network structure between the PVA molecular chains. This cross-linking effect can significantly restrict chain segmental movement, reduce its swelling rate in aqueous solution, and greatly limit the size of the porous structure inside the material, thereby constructing a high-density hydrophilic barrier that effectively prevents the crossover of larger methanol molecules at both physical and chemical levels. Finally, we hope to combine this newly synthesized membrane with a suitable catalyst slurry formulation and optimize the hot pressing process of the fuel cell membrane electrode assembly (MEA) using a membrane transfer printing method. Our goal is to obtain the core technology for fabricating fuel cell single cells with lower polarization losses and higher current densities.

II. EXPERIMENTALS

A. Materials

PVA (98 – 99 % hydrolysed, MW : 85000 – 124000, Sigma-Aldrich), SSA (70% solution in water, Sigma-Aldrich), methanol (99.9%, Mallincrodt Baker), carbon black (Vulcan XC 72, Cabot), 20% platinum on Vulcan XC 72 catalyst (E-TEK), 20% HP platinum-ruthenium on Vulcan XC-72 catalyst (E-TEK), carbon cloth (Teflon treated, Fuel Cell Scientific), Teflon® PTFE DISP 30 (Du Pont) were purchased and used as received.

B. Proton Exchange Membrane

First, a predetermined weight of PVA powder was placed in an Erlenmeyer flask, and then deionized water was added to prepare an 8 wt% PVA aqueous solution. The Erlenmeyer flask was placed in a 90°C water bath and continuously shaken for 6 h. After cooling to room temperature, a homogeneous PVA aqueous solution was obtained. Next, the required amount of SSA was added to the solution, and the mixture was vigorously stirred with a magnetic stirrer for 12 h, followed by low-speed stirring to remove air bubbles from the solution. Finally, a PVA/SSA membrane with controllable thickness was prepared using this PVA aqueous solution via solution casting. The cast membrane was dried at room temperature for 24 h, and then placed in a vacuum oven for esterification at 130°C for 2 h. After that, it was taken out for later use.

C. Catalyst Electrodes

The anode catalyst electrode used a Pt-Ru-C:PVA/SSA:PTFE ratio of 54:36:10 (wt%), and the cathode catalyst electrode used a Pt-C:PVA/SSA:PTFE ratio of 54:23:23 (wt%). First, a measured amount of catalyst was added to the PVA/SSA aqueous solution and stirred for 10 min to mix, followed by ultrasonic agitation for 10 min. Then, PTFE dispersion was added and stirred for 10 min, followed by ultrasonic agitation for another 10 min. This mixture was then dried at room temperature using a casting method to form a membrane. Finally, this membrane was sandwiched between two glass plates and placed in a vacuum oven, first dried at 70°C for 24 h and then at 130°C for 2 h to obtain the electrode membrane.

D. Membrane Electrode Assembly and Single Cell

The pre-cut catalyst anode, proton exchange membrane, and catalyst cathode were sandwiched between two PET release films, then placed in a stainless steel mold. The mold is then placed in a 90°C hot press and pressed under a pressure of 6.2 MPa for 120 s. After cooling, the self-made MEA was obtained. The fabricated MEA was then placed in Asia Pacific Fuel Cell Technologies' SCTF 2.5x2.5 single-cell pack, ready for cell performance testing.

E. Characterization and Testing

The values of swell ratio were obtained using the reflux extraction method with water as the solvent. The proton conductivity of each membrane was measured using a Wayne Kerr 6440B impedance

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analyzer at a test frequency range of 20 - 3×10^6 Hz. The membrane resistance was then calculated using the Nyquist plot method and converted into the proton conductivity. The experimental details of measuring IEC values, methanol permeability values and testing the single cell performance were the same as those described in [4].

III. RESULTS AND DISCUSSION

A. Swell ratio

After sulfonation with SSA, the molecular chains of the PVA/SSA membrane are simultaneously constrained by crosslinking. Therefore, during the reflux extraction experiment, when the membrane was immersed in water, the crosslinked molecules in the membrane could only expand in a swelling manner and would not dissolve in the aqueous solution. However, the uncrosslinked PVA molecules would be extracted by the aqueous solution, and the swell ratio was related to the degree of crosslinking of the membrane. Figure 1 shows that as the SSA dosage increases, the swell ratio decreases significantly (4.68 at 2 phr and 3.75 at 10 phr), indicating that the degree of crosslinking of the membrane increases with increasing SSA dosage. The anode membrane has a ratio of 4.34, while the cathode membrane has a ratio of 3.96. DMFCs require a hydrophilic anode and a hydrophobic cathode. Therefore, Figure 1 shows that both the anode and cathode membranes have a certain degree of crosslinking. Furthermore, because the cathode contains more PTFE dispersion and is more hydrophobic, its swell ratio is lower than that of the anode.

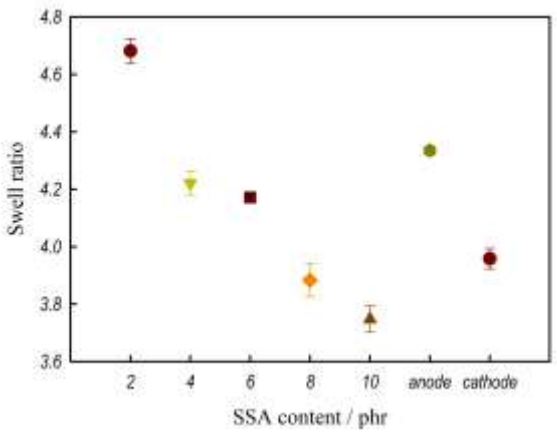

Figure 1. Swell ratio of PVA/SSA membranes with different SSA contents and anode/cathode membranes.

B. Proton Conductivity

The Nyquist plot obtained from AC impedance experiments reveals the impedance value of the proton-conducting membrane from a semi-circular curve. The proton conductivity of the membrane can then be calculated using a formula. The conductivity of polymer materials arises from the movement of internal ions as charge carriers. Therefore, the number of charge carriers, their migration probability, and the amount of charge they carry directly affect the conductivity of the polymer exchange membrane used. As temperature increases, the kinetic energy of the charge carriers also increases, thus enhancing their migration opportunities. Once the migration frequency becomes more frequent, the conductivity of the polymer membrane increases. Figure 2 shows the changes in proton conductivity of PVA membranes with different SSA concentrations at different temperatures. As temperature increases, the mobility of charged ions in the membrane increases, thus increasing the membrane's conductivity. Furthermore, the number of charge carriers is also a major factor affecting conductivity. Therefore, Figure 2 clearly shows that the more SSA added, the more sulfonic acid groups containing proton carriers are present in the proton exchange membrane, and the higher the proton conductivity value. Furthermore, it can be seen that the Nafion membrane has high conductivity, and the conductivity remains almost constant within this temperature range.

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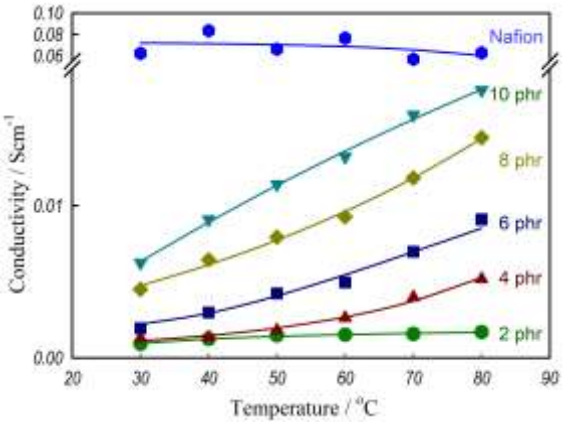

Figure 2. Conductivity of PVA/SSA membranes with different SSA contents and Nafion at different temperatures.

C. Ion Exchange Capacity

After the proton exchange membrane swells with water, it has continuous water channels inside, which can be regarded as the proton transfer channel. When the battery is operating, protons also begin to be conducted from the anode to the cathode through this channel. The synthesized sulfonated PVA membranes all have different numbers of sulfonic acid groups attached to their main chains. When a reaction occurs at the cathode, the sulfonic acid groups near the cathode will actively dissociate to release protons to participate in the electrochemical reaction and water molecules are generated. However, after the protons leave the sulfonic acid groups, the groups that become sulfite ions will attract neighboring protons to fill the vacancies due to electrostatic attraction. This process will create a potential difference, and the ionic attraction will cause the protons generated at the anode to migrate unidirectionally towards the cathode. Since the membrane is in a hydrated state, when protons dissociate from sulfonic acid groups, the hydrated protons at the anode combine with water molecules inside the membrane to form hydronium ions and various hydrated proton clusters, which then rapidly migrate to fill the vacancies. This continuous process of dissociation and association enables the sustained conduction of hydrated protons. Because of this mechanism, protons can be transferred, allowing the electrochemical reactions at the cathode and anode to continue, and maintaining the electrical circuit. In addition, the different proton transfer rates cause different internal resistance within the cell, which significantly affects the power transmission of the fuel cell. Therefore, as shown in Figure 3, when the amount of SSA of the membrane increases, more sulfonic acid groups are attached to the main chains,

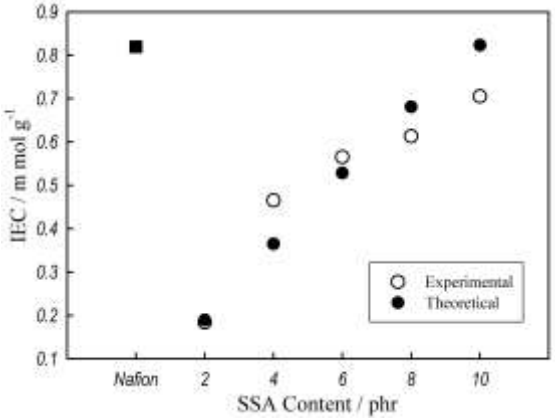

Figure 3. Ion exchange capacity of Nafion and PVA/SSA membranes with different SSA content.

the IEC value will increase, the proton transfer rate will increase, and the battery efficiency will be improved. In comparison, the reported IEC value of Nafion is 0.91 m mol/g [2]. Also noted that the theoretical IEC value of the sulfonated PVA membrane is calculated based on the amount of SSA added.

D. Methanol Permeability

In DMFC operation, methanol will diffuse from anode through the membrane to cathode and reacts at both electrodes. When the proton exchange membrane cannot act as an effective barrier to methanol, it will lead to a mixing potential problem, reducing the overall potential of the single cell, and thus reducing the battery efficiency. Furthermore, methanol fuel loss reduces fuel efficiency. To maintain high fuel efficiency and high cell potential, it is necessary to improve the methanol barrier property of the membrane material. Most membrane material studies show that methanol permeation becomes more severe with increasing temperature and methanol concentration. As the dosage of SSA in PVA/SSA membrane increases, the swell ratio decreases, as shown in Figure 2, indicating a greater degree of crosslinking. This restricts molecular chain expansion, reducing the channels through which the

methanol solution can diffuse. Consequently, the methanol permeability coefficient decreases with increasing SSA dosage. Comparing the ratio of the permeability coefficient of the PVA/SSA membrane to that of the Nafion membrane, in Figure 4, the results show that the ratio decreases with increasing SSA content and also decreases with increasing temperature. This means that higher SSA

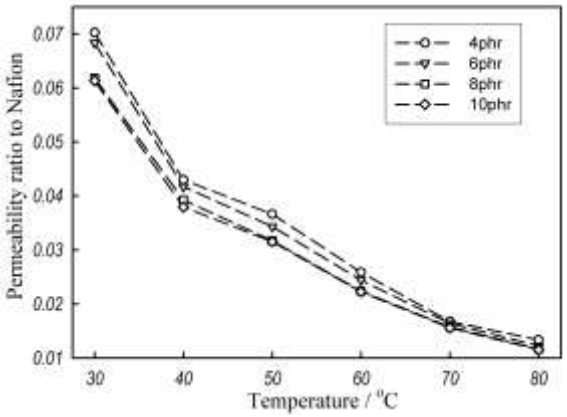

Figure 4. The permeability ratio as compared to Nafion for PVA/SSA with different SSA content.

concentrations and operating temperatures further improve methanol barrier property. For example, at 80°C, the permeability coefficient ratio reaches 0.01. This indicates that the methanol barrier performance of our synthesized sulfonated membrane is far superior to that of the Nafion membrane, which is consistent with the excellent selectivity of PVA for water-alcohol systems.

E. Single Cell Performance

In the single cell discharge test, the proton exchange membrane, combined with catalysts and carbon cloth, was used to fabricate the MEA. We used a PVA/SSA membrane with 10 phr SSA as the proton exchange membrane, and compared it with a Nafion membrane. The anode fuel was a 1M methanol-water solution with a feed rate of 1.0 mL/min. The catalyst content at both electrodes was 1 mg/cm². The cathode oxidizing gas was 99.9% oxygen with a feed rate of 150 SCCM. The cell operating temperatures were 40, 60, and 80°C. Increasing the test temperature accelerates the electrochemical reaction rate and reduces the ohmic impedance within the cell. The limiting current density also increases due to the enhanced mass transfer effect at higher temperatures.

Figure 5 shows that for the PVA/SSA membrane, the cell performance improves with increasing temperatures. As the temperature rises, both the proton conductivity and the methanol diffusion coefficient in the membrane increase. Although methanol crossover increases, the increased temperature enhances catalytic activity and accelerates the electrode reaction rate, thus reducing the ohmic impedance. Therefore, increasing the temperature has a positive effect on the single cell's output voltage. Furthermore, the performance of the MEA with the membrane developed by our team is comparable to that of the MEA with Nafion membrane. This is likely because the main resistance of the single cell is not in the proton exchange membrane itself, but rather at the interfaces between different components.

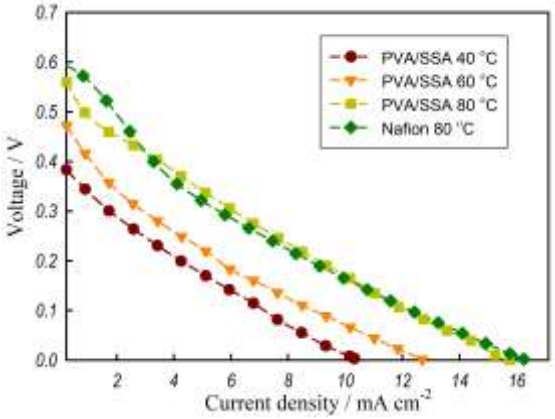

Figure 5. Sigle cell discharge test results for 10 phr SSA-sulfonated PVA and Nafion.

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