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Understanding of temperature-dependent performance of short-side-chain perfluorosulfonic acid electrolyte and reinforced composite membrane

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ABSTRACT

The short-side-chain (SSC) perfluorosulfonic acid (PFSA) membranes are important candidates as membrane electrolytes applied for high temperature or low relative humidity (RH) proton exchange membrane fuel cells. In this paper, the fuel cell performance, proton conductivity, proton mobility, and water vapor absorption of SSC PFSA electrolytes and the reinforced SSC PFSA/PTFE composite membrane are investigated with respect to temperature. The pristine SSC PFSA membrane and reinforced SSC composite membrane show better fuel cell performance and proton conductivity, especially at high temperature and low relative humidity conditions, compared to the long-side-chain (LSC) Nafion membrane. Under the same condition, the proton mobility of SSC PFSA membranes is lower than that of the LSC PFSA membrane. The water vapor uptake values for Nafion 211 membrane, pristine SSC PFSA membrane and SSC PFSA/PTFE composite membrane are 9.62, 11.13, and 11.53 respectively at 40 °C and they increase to 9.89, 12.55 and 13.09 respectively at 120 °C. The high water content of SSC PFSA membrane makes it maintain high performance even at elevated temperatures.

Introduction

High temperature proton exchange membrane fuel cells (PEMFCs) have great advantages including improved gas transport, simplified water and thermal management system, enhanced cathode kinetic, and improved CO tolerance of catalyst [1]. Thus, many efforts have been made on high-temperature operation of proton exchange membrane (PEM) [2]. One kind of PEM applied for high temperature applications is the modified perfluorosulfonic acid (PFSA) PEM [3,4]. The PFSA PEM was commonly modified by hydroscopic compound, such as SiO_2 and TiO_2 to enhance its water retention ability and thus ensuring a satisfactory conduction performance at high temperature and low humidity condition. Other sulfonated polyaromatic polymers-based PEMs, such as PEEK membrane [5], which have excellent chemical resistance, high thermo-oxidative stability, good mechanical properties and low cost, also show high conductivities and good fuel cell performance at high temperature. In addition, the inorganic acid based PEM,

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such as the phosphoric acid doped PBI membrane [6], which was also studied by many researchers, could be a potential PEM applied for high temperature fuel cell operation because of their outstanding thermal, oxidative, chemical, and hydrolytic stability under fuel cell operating conditions, and particularly at high temperatures.

In addition to the work mentioned above, short-side-chain (SSC) PFSA membranes have attracted considerable attention as membrane electrolytes for high temperature PEMFC applications due to their high resistance to chemical and electrochemical degradation as well as good proton conductivity under low relative humidity [7–13]. It was found that the lower equivalent weight (EW) SSC PFSA membrane showed superior proton conductivity and good fuel cell performance under high temperature and low humidity conditions [14–16]. Recently, the new SSC PFSA named Aquivion™ was commercialized by Solvay Solexis. The Aquivion™ membranes exhibited good mechanical stability, high water retention capability and high proton conductivity at high temperature and/or low relative humidity conditions as reported in literature [17,18]. Besides from experimental studies, many simulation works have also been conducted to have a better understanding on the performance of membrane with respect to its structure, water and proton transfer [19–24]. From the simulation results, it was concluded that the superior performance of SSC PFSA membrane was closely related to their microstructure and the according proton transfer through the membrane. These excellent properties of the SSC PFSA membrane ensured its good performance in high temperature PEMFCs applications [25].

We have previously reported the synthesis and basic performance of reinforced SSC composite Aquivion/PTFE polymer electrolyte membranes. The results proved that Aquivion/PTFE composite membrane possesses superior physical stability and better single cell performance compared to long-side-chain (LSC) Nafion 211 membrane under high temperature and low relative humidity condition [18]. The prepared composite membrane inherit the excellent electrochemical property of the SSC PFSA membrane, and improve its dimensional stability due to the adding of polytetrafluoroethylene(PTFE) matrix, suggesting that it could be potential membrane electrolyte applied for high temperature and/or low relative humidity (RH) fuel cells. However, the electrochemical property under various temperatures and RH values wasn't studied in detail to figure out why it performs better at high temperature conditions compared to LSC PFSA membranes.

In this paper, we continuously focus on studying the electrochemical performance of the SSC membrane and reinforced SSC composite membrane in comparison with LSC Nafion 211 membrane, to make it clear why the SSC PFSA membranes have the advantage for application in high temperature and/or low temperature environment. We studied the dependence of proton conductivity and fuel cell performance of three different membranes on temperatures and analyzed their difference with the data of water absorption and proton transfer. The results suggested that SSC PFSA membranes, especially the reinforced composite membrane have great potential as membrane electrolytes to be applied in high temperature fuel cells.

Experimental

Preparation of membranes

The Nafion 211 membrane was purchased from the Dupont Company. The Aquivion cast membrane and Aquivion/PTFE composite membranes were prepared as reported previously [18]. Briefly, the Aquivion cast membrane was prepared as follows: A Petri dish with a certain volume of as-received Aquivion® SSC PFSA (Solvay Solexis) solution was put into the oven by solvent evaporation at 70 °C for 2 h. Then the membrane was annealed at 100 °C and 150 °C for 30 min and 20 min, respectively. To prepare the Aquivion/ePTFE composite membrane, a mixture of Na form Aquivion® SSC PFSA (5 wt% *in* isopropyl alcohol, EW ~ 790, Solvay Solexis) and Triton X 100 (5 vol%, Sigma–Aldrich) was first prepared. Then, the above-prepared suspension was impregnated into the matrix membrane, PTFE mounted plastic frame (10 × 10 cm^2, Dagong Co. Shanghai, porosity of 80%) under vacuum for 2 min. Next, the membrane was dried at 260 °C for 1 min. To control the thickness of composite membrane, the impregnation and drying process were repeated several times. Finally, the membrane was soaked in water and isopropanol to remove the Triton X100 and converted into H-form by immersing in 0.5 M sulfuric acid for 30 min and then washed in demonized water for 30 min. The Aquivion/ePTFE composite membrane consists of 73.4 wt% of Aquivion polymer electrolyte and 26.6 wt% of PTFE.

The EW (equivalent weight) value of Aquivion cast membrane, reinforced Aquivion/PTFE composite membrane and Nafion membrane were calculated from titration results to be 790, 1080 and 1100 g mol^{-1}, and the thicknesses of membranes were 26, 16 and 26 μm, respectively.

Three membranes were pretreated as follows before using: first soaked in H_2O_2 for 1 h and then in 0.5 M sulfuric acid for another hour, finally immersed in 80 °C demonized water for 1 h.

Characterization of membranes

The water vapor absorption was measured when the membranes were equilibrated with saturated water vapor under variable temperatures. We used a home-made cell to control the temperature and added different volume of water at different temperatures into cell to control the RH of environment. The temperature of membranes was controlled by electric heating and the volume of water was calculated with ideal gas state equation at different temperatures using equation (1):

$$\varphi PV_{cell} = VRT/18 \qquad (1)$$

where φ is the humidity of membrane in the cell; P is the saturated pressure of water; V_{cell} is the volume of the whole cell, that is 510 cm^{-3}; V is the volume of water adding into the cell; R is ideal gas constant and T is the temperature of membrane.

The temperature and humidity of membranes were detected by temperature and humidity sensor.

The prepared membranes were cut into 3 cm × 3 cm and dried in oven for 3 h, and weighed with electronic balance