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Full Length Article

Design of stable and durable polymer electrolyte membrane fuel cells by embedding hydrophobic cage-structured material in cell components

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ABSTRACT

Performance stability and durability of polymer electrolyte membrane fuel cells (PEMFCs) depend on many factors of cell assembly that in turn determines the commercial applicability of PEMFC technology. In this study, an economically viable solution to improve the stability of PEMFCs at variable power is achieved with tailored membrane electrode assemblies (MEAs) by the incorporation of hydrophobic, cage-structured octasilane polyhedral oligomeric silsesquioxanes, (OSP) to Nafion™ in the MEA construction. In the Durability and Stability Dynamic Stress Testing (DST) studies over an operating time of 250 h; OSP modified MEAs exhibited a higher peak power density of 0.60 W cm^{-2} which dropped only 45%, compared to peak power density of neat Nafion™ which dropped 70% from the initial peak power density of 0.37 W cm^{-2}. The H$^+$ conductivity of OSP/Nafion™ composite MEAs remains stable during the full course of study and demonstrated sustained performance in harsh DST environment. The results illustrated that small amount of OSP (~3%) in the MEA does prevent excess water accumulation in MEA and simultaneously allocate enough humidity for transporting H$^+$, thus it advances the stability and durability of Nafion™ for manufacturing PEMFC and Direct Methanol Fuel Cells (DMFC).

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have great promise as environmentally friendly power sources because of their quick start and low temperature operation, especially for vehicles applications [1–3]. The polymer electrolyte membrane (PEM) is a critical component of the PEMFC which separates the H_2 and air/O_2 for preventing electronic conduction, and conversely conducts protons, vital role on cell performance. Similarly, ionomer with the same composition in the electrodes predictably reduces the standing water in the triple-phase boundary thereby increasing the utilization of Pt and assists to conduct protons and electrons simultaneously through the electrodes matrices [4]. In conventional PEMFCs, membrane and ionomer in the electrodes contain sulfonic acid groups which create hydrophilic domains for transporting both protons and water respectively [5]. These sulfonic acid groups in their conventional form require controlled hydration [6–9] to maintain efficient proton conductivity without excess flooding [10], which often happens during high current PEMFC operation, and that is much more severe at freezing and cold-start conditions [11].

Water accumulation is a well-established factor known as flooding in PEMFCs, [9,12–14] and is a complex problem for fuel cell system designing. Retained water physically block: (i). the micro-pores present within the catalyst layers (CLs) and prevents/slows the diffusion of reactant gasses from reaching active sites; (ii). the gas diffusion layers (GDLs); and even (iii). the flow-field channels that are typically designed with millimeter-sized dimensions. It has been recognized that water droplets in channels, in the pores of GDL and electrodes can potentially decrease the cell performance from efficient reactants flow and thus, reduce the stability of the PEMFC; and affecting the lifetime/durability [15–19]. The referred problem intensifies when PEMFC is operating at higher current densities as the electrical current density of the cell is proportional to water production, which, naturally condenses in the micro-pores of the gas diffusion electrodes (GDE) and more severely at the cathode/GDE interface. From a mechanistic point of view; water transports with protons from the anode to the cathode through electro-osmotic drag [9,12], and the generated water at the cathode of the PEMFC usually back-diffuses to the electrolyte [12] which triggers water buildup [20,21] across MEA components. Therefore, regulated water retention within the cell is extremely important to sustain the electrochemical and physical stability of PEMFCs, particularly, at high current densities and cooler operating conditions.

For minimizing water retention problem in PEMFCs Numerous approaches have been considered by various research groups as, X. Li et al. and Antolini et al. respectively changed the physical and chemical properties of the flow channels within the bipolar plate [22,23]. In

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addition, to correct the water standing problem, a series of methodologies were investigated to modify the chemical properties of microporous GDLs by adjusting the ratio of hydrophobic and hydrophilic zones [23–25]. For instance incorporation of polytetrafluoroethylene (PTFE) into certain parts of the PEMFC, another strategy has been tested to increase the hydrophobicity for components to repel/expel water towards the exhaust of the fuel cell as it is produced. These strategies have reportedly improved the capability of the PEMFC system to remove water while avoiding any negative effects on the reactant gasses flowing into the catalytic sites of the GDEs [23–26] by adding between 5 and 40 wt% of PTFE into the GDLs structure are typical for minimizing water retention [26,27]. PTFE is electrically an insulator, thus, reducing the electrical conductivity of the components possibly hinders overall cell performance by increasing electrical resistance and thus does not provide a perfect solution to the problem. Molaeimanesh et al. [28] studied the dynamic behavior of water droplets formed in GDLs containing PTFE coated glass fibers and neat glass fibers by injecting internally water vapor with the reactant gases. Their study suggested that the addition of PTFE in the GDL matrices did not provide any noticeable differences in preventing water accumulation.

The present investigation specifically focuses on a novel method in improving the stability and durability of PEMFC without hampering the electronic transport by utilizing a very minimal amount cage-structured, hydrophobic oligomeric silsesquioxane polyhedral (OSP) in the cell components of PEMFC. This is so that water content would be good enough for maintaining the reasonable hydration level required for steady H^+ conductivity at the same time preventing excess accumulation of water in the components of the cell. In order to enable facile adaptation to already established manufacturing processes of PEMFC components, present study exhibit the stabilized cell performance in its maximum limits and sturdiness of the cell by adding 1–3 wt% of OSP in MEA construction and tested through stop and go duty DST cycles. Finally, the controlled water transport behavior of the OSP-modified PEMFC is demonstrated through a schematic representation based on the result obtained in this course of study. To reveal the effect of OSP nano-filler for maintaining the regulated hydration and quantify the performance adjustment, both control MEAs (without OSP) and MEAs with OSP were prepared, and were tested through accelerated degradation testing [29,30] referred to as dynamic stress testing (DST).

2. Experimental design

2.1. Preparation of MEAs

In the preparation of the MEAs, the hydrophobic, cage-structured OSP ($(RSiO_{3/2})_8$, R = HMe_2SiO, SH1310, Hybrid Plastics) was added to both the membrane and the CLs, named as OSP-Nafion™ hybrid MEA, and will be referred hereafter as MEA-2. Another set was prepared from that of neat Nafion™ and without any additions of OSP to act as a control and will hereafter be referred to as MEA-1. Additions ranging from 1 to 3 wt% OSP relative to that of the ionomer present were evaluated in the CLs and in the electrolyte membrane during the fabrication of MEA-2.

For the fabrication of both sets of MEA-1 and MEA-2, membranes were crafted using the solution prepared from 2.0 g of dry Nafion™ dissolved into 44 mL dimethylformamide (DMF). In house, dry Nafion™ was obtained by purging N_2 over 20 wt% Nafion™ (D2021, DuPont) solution. For MEA-2, a desired amount of OSP was first dissolved in tetrahydrofuran and then dispersed into the bulk of the in-house prepared Nafion™ solution for preparing the membrane of MEA-2. Membranes representing MEA-1 and MEA-2 were casted via a standard solvent evaporation method [30]. The thicknesses of the membranes were measured with a Brunswick Metrology Processor and Apparatus, and were approximately 50 μm thick.

The catalyst inks were prepared similarly as described in a previous publication [31]. In short, the catalyst ink for both sets of MEAs, MEA-1 and MEA-2, was prepared by dispersing 20% Pt/C (Alfa Aesar, HiSPEC 3000) catalyst powder into a mixture of water, isopropanol and a commercial Nafion™ solution (Nafion™ D2021, DuPont). In the catalyst inks for CLs of MEA-2, a specific amount of OSP was added in the ink slurry by maintaining same weight-ratio of OSP:Nafion™ used in the membrane. The catalyst ink was aerosol-sprayed directly onto the membranes [30] to form the catalyst coated membranes (CCMs). The CCMs were then sandwiched between the GDL (SGL 10BC) in both sets of MEAs and hot-pressed [31] to form MEAs with active areas of 5 cm^2 for the electrochemical evaluation. The obtained catalyst loadings for all MEAs were approximately 0.20 and 0.25 mg Pt cm^{-2} at the anode and cathode, respectively.

2.2. Membrane characterization

The water uptake of the membranes were calculated as flows; membranes were soaked in DI water either at 25 °C or 65 °C for 24 h. These membranes were taken out, excess water were removed with the help of kim wipes and wet weights were recorded (W_{wet}). The membranes were then dried in a vacuum oven for 10 h and dry weight was recorded (W_{dry}). Water uptake was calculated based on the Eq. (1),

$$Water\ uptake,\ \% = \frac{(W_{wet}-W_{dry})}{W_{dry}} \times 100 \tag{1}$$

The contact angles of the neat Nafion and composite membranes measured by an optical approach. Water droplet was placed on the membranes and images were captured using DSLR camera fitted with a micro lens after 10 s stabilization time. The contact angles values were then obtained using ImageJ software.

2.3. Performance testing

The performance of the MEA was evaluated on a fuel cell test station (850e, Scribner Associates). The humidified hydrogen and oxygen gases at relative humidity (RH) of 80% were fed (0.2/0.2 L min^{-1}) into the anode and cathode, respectively. The cell was operated at temperature of 80 °C and the polarization curves were potentiostatically recorded by the electrical load bank of the fuel cell test station. Electrochemical impedance spectroscopy (EIS) was employed to conduct proton conductivity measurement over a frequency range of 0.1 Hz to 100 kHz in full cell configuration. EIS data were collected after each duty-on cycle on a frequency response analyzer (Solartron 1260) coupled with an electrochemical potentiostat/galvanostat (Solartron SI 1287) in potentiostatic mode.

2.4. Design cell testing: start and stop cycling

The in housed prepared MEAs were evaluated in a standard planar single cell testing fixture (active area = 5 cm^2, having serpentine channels, provided by Fuel Cell Technologies) using a fuel cell testing station (850e, Scribner Associates). The performances of fuel cells were characterized by voltage–current density (V–i) and power density curves. Further, the fuel cells were evaluated using the official Durability and Stability Testing (DST) protocol established by the U.S. Department of Energy (DOE) in order to represent operating conditions expected for fuel cells used in automobiles [29,30]. The DST test protocol involves cyclically stepping through a series of electrical loads that generate specific currents imposed on the cell over a 12 h period (running time per day referred to as “duty-on”) and periodic interruption of the cycling via a shutdown of operation (off-time of 12 h per day referred to as “duty-off”). The duty-on and duty-off cell testing was completed over a total of 250 h of cycling and is presented in the results and discussion section. During the duty-on period, DST protocols were programmed at 367 s/cycle and included a total of 118 cycles which was equivalent to a period of 12 h. MEA-1 and MEA-2 both were