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Performance improvement of the open-cathode proton exchange membrane fuel cell by optimizing membrane electrode assemblies

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ABSTRACT

The oxidant supply coupled with the cooling task in open-cathode proton exchange membrane fuel cells (PEMFCs) creates a simple system configuration. Based on a simulated condition which was previously established for evaluating cell performance of different membrane electrode assemblies, this work has conducted performance optimization by altering electrocatalysts, thickness of micro-porous layer (MPL) and membranes. The thickness of the catalyst layers was around ~35 μm with 20 wt% Pt/C, and reduced to only 12 μm with 60 wt% Pt/C. Although a thick catalyst layer resulted in a stable performance at various air stiochiometric ratios, especially under high temperatures where cell performance decreased due to a low Pt utilization and poor mass transport of proton and reactants in the cathode. The cathode with 2 mg cm^{-2} carbon loading in the MPL gave the best performance and the cell voltage varied between 0.71 and 0.62 V at 800 mA cm^{-2} in the temperature range from 50 °C to 60 °C. Finally, different membranes were investigated, and a thin composite Nafion/PTFE membrane around 17 μm showed better performance comparing to Nafion 211, which can be attributed to a good water retention capacity owing to easy crossover of hydrogen and water through the membrane.

Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered as promising energy sources for vehicles and portable power applications, due to their high power densities, high efficiency and clean energy conversion [1]. Open-cathode PEMFCs have attracted attention for portable applications in a wide power range [2–15]. The air-breathing PEMFC, which

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relies on natural air from atmosphere directly, is useful for low-power devices up to 10 W [3,14,15]. The forced-air convection PEMFC could feed more air to the cathode and cool down the stack temperature, so its output power can be as high as hundreds of watts.

The membrane electrode assembly (MEA) used in the fuel cell, which is composed of a proton exchange membrane (PEM), two catalyst layers (CLs), and two gas diffusion layers (GDLs) usually covered with micro-porous layer (MPL), plays a vital role in its output performance. The PEM is a barrier between the oxidant and hydrogen, also enables proton to pass through from the anode to the cathode. The CL is the place where the oxidation and reduction reactions occur. The GDL allows the diffusion of hydrogen and oxygen to the catalyst layer, and conduction of electrons to and from the catalyst layer. The water and heat generated from the electrochemical reactions in the catalyst layer are discharged through the GDL, too [12]. There are a lot of studies focusing on the influence of MEA components on cell performance. Different kinds of membranes (perfluorinated, partially fluorinated and non-fluorinated) and preparation methods (supported composite membrane and others) [16] have been studied to improve the single cell performance or lifetime. Researchers from W.L. Gore [17–19] and others [20–22] used porous ePTFE to reinforce Nafion as PEM. Other researchers reported membranes without Nafion resins, such as disulfonated poly-(arylene ether sulfone) (SPSU) [23], sulfonated polyimide (SPI)/PTFE [24], Sulfonated poly-(sulfide sulfone) (SPSSF)/PTFE [25]. About catalyst layers, some researchers changed the morphology, such as using multi-layer structure [26–28], adding pore forming agents [29], while others optimized the content of Nafion ionomer [30,31] and Pt [15,32] in CL. Other studies were conducted with different electrocatalysts, such as non-platinum catalysts [33] and Pt-nanowire catalysts [34]. In addition, the influence of GDL structure has been studied as well. Kitahara [35] studied the cathode GDL with a hydrophilic MPL layer. Park [36] reported the effect of carbon loading in the MPL, and obtained the best single cell performance with a carbon loading of 0.5 mg cm^{-2}. However, the above-mentioned optimization on MEA was aiming at the automobile application with an air stoichiometry fewer than 3.0 and cell temperature below 80 °C accompanied by nearly full humidification. The open-cathode PEMFC is exposed to conditions quite different from and more critical than that in automobile vehicles, such as low operating temperature, low relative humidity (RH), large air flow rate and dry hydrogen feed. Therefore, the existing results based on single-cell tests might not perfectly apply to an open-cathode PEMFC stack. So far researchers have been mainly focusing on the cathode structure, including the fan's configuration and the geometric parameters of the flow fields, to study the open-cathode PEMFC stack with respect to the influence of stack temperature [2] and the performance of different cells in a stack [3]. It should be noted that the fans' speed not only determines the air flow rates to the cathode electrode, but also prevents the stack from over-heating [5]. Furthermore, the geometry (depth, width and length) of the flow field channels has a strong impact on the reactant distribution over the gas diffusion layers and water dragging [7]. On the other hand, the common dead-ended anode configuration of the open-cathode PEMFC stack will lead to excess water and nitrogen due to crossover in the anode which in turn causes performance losses [13]. A regular release of the gas stream by an electromagnetic valve is needed for the anode, however, this will cause a continual performance fluctuation. The MEA is also very important to a PEMFC stack. Yuan [37,38] evaluated four different MEAs in one stack, showing that different cells in the same open-cathode PEMFC stack would be exposed to different conditions, such as cell temperature and air flow rates [3,6]. It is hard to conclude that the difference in cell performance can exactly be attributed to the MEA difference.

In our previous work [39,40], we had developed a method to evaluate the performance of different MEAs for forced-air convection PEMFC stack in single cells instead of a real stack. This method can eliminate the performance fluctuations caused by the anode, and cathode air supply and cell temperature. In this study, an experimental analysis of MEAs with 20 wt%, 40 wt% and 60 wt% Pt/C in the cathode catalyst layer, different carbon loadings in the cathode GDLs, and different membranes operating at simulated open-cathode conditions is presented. The dynamic responses of cell voltage under constant-current discharge to air flow rate (varying air stoichiometry from 3 to 100) and cell temperature (from 30 °C to 60 °C) are examined. The results indicate that the water generated in the cathode is very important to the cell performance for the forced-air convection open-cathode PEMFC. A better water holding capacity is needed for higher and more stable output performance by either modulating membranes or the cathode.

Materials and methods

Preparation of MEAs

The catalyst ink was prepared by ultrasonically dispersing the catalyst powders (Pt/C, Johnson Matthey, UK) and Nafion solution (5 wt%, EW 1100 g mol^{-1}) in iso-propanol. Then a catalyst-coated membrane (CCM) was made by spraying the catalyst ink onto a Nafion 211 (Dupont, USA) membrane using an ultrasonic spraying coating system (EXACTA COAT, SONO TEK Corp, USA). The membrane was heated at 110 °C during the spraying to quickly evaporate the solvent. For the anode side of all MEAs, 60 wt% Pt/C was used. For the cathode side, 20 wt%, 40 wt%, and 60 wt% Pt/C were used for a comparison purpose. The Pt loading was kept at 0.5 mg cm^{-2}, and the loading of Nafion at 0.24 mg cm^{-2}.

Lab-made GDLs were prepared to compare the performance of different MPLs at the cathode side. The carbon paper (Toray 060, Japan) was soaked into 2.0 wt% PTFE slurry until its PTFE content reached 1.0 mg cm^{-2}, then the MPL was coated on the GDL by brushing carbon ink onto the hydrophobic carbon paper by a screen printing method. The carbon ink was prepared by dispersing 90 wt% XC-72 and 10 wt% PTFE slurry in deionized water. The carbon paper was sintered at 340 °C for 2 h twice, both after the hydrophobic treatment and after the screen printing of the MPL. A commercial hydrophobic gas diffusion layer (Sunrise Power Corp., China) was used in this work for the comparison experiments of catalyst layers and membranes.