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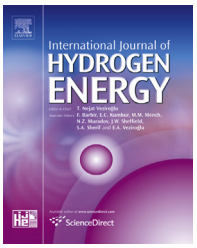

Experimental and theoretical analysis of ionomer/carbon ratio effect on PEM fuel cell cold start operation

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ABSTRACT

The effect of ionomer/carbon (I/C) ratio on proton exchange membrane (PEM) fuel cell cold start is investigated experimentally with theoretical water transport analysis. The scanning electron microscope (SEM) images show larger agglomerates and smaller effective reaction area by increasing the I/C ratio from 0.7 to 1.7. For normal operation, increasing the I/C ratio can improve the humidity tolerance, especially in the cathode. For cold start >−10 °C, a lower I/C ratio leads to better performance because the core reaction area is shifted towards the membrane, leading to more membrane water absorption and slower ice formation. For <−15 °C, the total water production is low and almost the same for the different I/C ratios because the ice formation takes place before effective membrane water absorption; and although the cathode catalyst layer (CL) and micro-porous layer (MPL) can provide sufficient space to store all the ice, higher I/C ratios (e.g. 1.2) still cause more ice formation in GDL and flow channel because the core reaction area becomes closer to GDL. The results show that the CL design has significant effect on the cold start performance, and there is a potential for further improvement.

Introduction

With the rapid increase of worldwide energy demand and reduction of traditional fossil fuels, proton exchange membrane (PEM) fuel cell that converts chemical energy directly into electrical energy has attracted much attention due to its high power density, fast dynamic response, low operating temperature and zero emission [1–6]. However, there are still several challenging tasks for its widespread use, in which the capability of starting up from subzero temperature (also called cold start) is vital for PEM fuel cell in low temperature operation (lower than the freezing point of the water).

During the cold start operation, the water produced in the cathode catalyst layer (CL) will quickly freeze into ice, which reduces the effective reaction area, prevents the reactant transport and even causes the fuel cell shutdown [7,8]. Recently, there have been many experimental investigations on the cold start operation. Mishler et al. [9] pointed out that more ice is formed in the cathode side of the membrane electrode assembly (MEA) than that in the anode side. Lin et al. [10] found that the region with the highest current density moves from the inlet area to the middle of flow channel if the fuel cell can start up from subzero temperature successfully, but it moves to the upper-left area (between the inlet and middle area) when it fails. Hirakata et al. [11] adopted a new

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gas diffusion layer (GDL) with three-layer structure, namely micro-porous layer (MPL), carbon paper (CP) and hydrophobic layer (HL). It was observed that inserting HL can enhance the water removal during the cold start operation, and improve the performance at both low and high humidity under normal condition. In addition, some new purging methods have been developed to improve the water removal. The hydrogen addition and pressure reduction purging methods adopted by Kim et al. [12,13] showed superior water removal and weakened cell degradation after cold start operation. It was also shown that changing the Pt/carbon ratio and ionomer fraction in CL has significant effects on cold start performance [14].

In addition to experimental investigations, numerical simulation of cold start also acts as an important role in further understanding the ice formation mechanism under cold start operation. The three-dimensional (3D) multiphase modeling work conducted by Jiao et al. [15] showed that the CL parameters, membrane thickness and Nafion ionomer volume fraction, are all the important factors in reducing the ice formation. Luo et al. [16] developed a 3D multiphase PEM fuel cell stack model, revealing that the region of faster ice formation in the CL is shifted from bipolar plate (BP) to membrane side with the increment of current density. Gwak et al. [17] numerically described the three water uptake increase stages during the cold start operation. At the beginning, the product water freezes into ice due to the low water vapor saturation pressure. Then, with the increase of cell temperature, more product water evaporates. The final increase stage belongs to the hydration with the electrolyte because of the ice melting. In addition, to improve the capability of starting up from subzero temperature, many numerical strategy models were developed, such as the gas purge model by Ding et al. [18], the maximum power cold start model by Du et al. [19], the three-layer GDL cold start model developed by Ko et al. [20] and so on.

It is well-known that the electrode design, especially the catalyst optimization, is an important factor affecting the PEM fuel cell performance [21–25]. In general, a typical CL is composed of electrocatalyst mixed with Nafion ionomer (conducting proton), carbon support (conducting electron) and void region (conducting gas and liquid), which together form the three-phase boundary surface, also called the effective reaction area. The Nafion content in CL is usually represented by the I/C ratio (weight ratio of Nafion ionomer to carbon support):

$$\text{I/C ratio} = \frac{M_{\text{nafion}}}{M_{\text{carbon}}} \tag{1}$$

where M_{nafion} (mg cm^{-2}) and M_{carbon} (mg cm^{-2}) are the weight per unit area of Nafion and carbon, respectively. Generally, increasing the Nafion content in CL contributes to the reduction of the ohmic loss, but the effective reaction area may thus be decreased, which increases the activation loss. With the proper I/C ratio, the CL can provide sufficient paths for protons, electrons, reactant gas and product liquid, and hence improve the performance of PEM fuel cell. Lopez-Haro et al. [26] indicated that excessive Nafion content would lead to a thicker ionomer layer, which weakens oxygen diffusion in micro level. However, too low ionomer coverage degree will also limit the proton conductivity. Similar conclusions were experimentally obtained by Kim et al. [27] and the best ionomer contents (25 and 30 wt.% in the anode CL and cathode CL) were given. Suzuki et al. [28] further investigated the effect of CL thickness and porosity due to I/C ratio change on the cell performance and concluded that thickness mainly depends on the carbon content and the porosity mainly depends on the ionomer content.

Meanwhile, in order to optimize the electrode design, many researchers choose to develop numerical models. The 2D steady-state model developed by Srinivasarao et al. [29] showed that PEM fuel cell of a four-layer CL with non-uniform Pt distribution performs better. Roshandel et al. [30] developed a 2D mathematical model and pointed out that the catalyst content distribution should match the current density distribution in CL, which strongly depends on the BP configuration, GDL/CL parameters and external loading mode.

Although much work has been done, more in-depth researches are still needed to gain a better understanding of the ice formation mechanism under cold start operation. In the previous work, the studies of CL microstructure were mainly limited to the normal condition and rarely related to the subzero condition. However, it is conceivable that the change of microstructure in the CL inevitably affects the cold start performance of PEM fuel cell. Therefore, in this study, the effect of different I/C ratios (0.7, 1.2 and 1.7) in cathode CL under cold start operation is investigated with the help of high-resolution scanning electron microscope (SEM). The results presented in this paper can also provide some recommendations for the electrode microstructure design and then improve the capacity of starting up from subzero temperature.

Experiment

In this study, three different I/C ratios (0.7, 1.2 and 1.7) in the cathode CL were considered and the microstructure images of CL surfaces obtained by SEM in two resolutions (25 μm and 2 μm) are shown in Fig. 1, from which it can be observed that the most uniform structure is obtained for I/C ratio 0.7, and with the increment of I/C ratio, the catalyst will be agglomerated and thus reduce the effective reaction area, and the higher the I/C ratio, the larger the agglomerate and the smaller the effective reaction area. In general, the CL thickness should increase with the increase of I/C ration. However, the excessive agglomeration of catalyst at higher I/C ratio (e.g., I/C ratio 1.7) may reduce the CL thickness, which may lead to a phenomenon that the CL thickness does not necessarily increase with the increment of I/C ratio, and this is verified by the CL thickness shown in Table 1.

Meanwhile, it can be noticed in Table 1 that the CL porosity (ε_{cl}) decreases obviously with the increment of I/C ratio, in fact, it is theoretically calculated by the equations below [28]:

$$\varepsilon_{cl} = \frac{t_{cl} - t_0}{t_{cl}} \tag{2}$$

where t_{cl} (μm) is the CL thickness and t_0 (μm) the hypothetical CL thickness under zero porosity which can be calculated by the following equation:

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