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Efficient hydrogen production from aqueous methanol in a PEM electrolyzer with porous metal flow field: Influence of PTFE treatment of the anode gas diffusion layer

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ABSTRACT

In a proton exchange membrane (PEM) methanol electrolyzer, the even supply of reactant to and the smooth removal of carbon dioxide from the anode are very important in order to achieve a high hydrogen production performance. An appropriate design of flow field and gas diffusion layer (GDL) is a key factor in satisfying the above requirements. Previous research has shown that hydrogen production performance of the PEM methanol electrolyzer cell was largely improved with a porous flow field made of sintered spherical metal powder compared with a conventional groove type flow field. Based on this improvement, the current study investigated the influence of polytetrafluoroethylene (PTFE) treatment of the anode GDL on hydrogen production performance of the PEM methanol electrolyzer with porous metal flow fields. Influences of operating conditions such as methanol concentration and cell temperature with the flow field were also investigated.

1. Introduction

Hydrogen is one of the most promising energy carriers for the future owing to its clean and sustainable energy. Among many methods to produce hydrogen, water electrolysis with a proton exchange membrane (PEM) [1–9] is one of the most convenient ways since it offers a number of advantages for the hydrogen production such as high gas purity and compatibility with renewable energy sources (e.g. wind, solar). Besides the water, aqueous methanol can also be electrolyzed to generate hydrogen [10–14]. With lower Gibbs free energy for methanol, hydrogen production performance in the aqueous methanol electrolysis proceeds at much lower voltage than that in the water electrolysis [10–14]. Fig. 1 describes an aqueous methanol electrolysis process with the following reactions:

$$\text{Anode}: CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad E_a^0 = -0.016\,\text{V vs. SHE} \tag{1}$$

$$\text{Cathode}: 6H^+ + 6e^- \rightarrow 3H_2 \quad E_c^0 = 0\,\text{V vs. SHE} \tag{2}$$

$$\text{Overall}: CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad E^0 = -0.016\,\text{V vs. SHE} \tag{3}$$

The standard potential for the methanol oxidation reaction (MOR) shown in Reaction (1) is only −0.016 V vs. the standard hydrogen electrode (vs. SHE) at 298 K, while that for hydrogen reduction reaction (HRR) shown in Reaction (2) is 0 V (vs. SHE).

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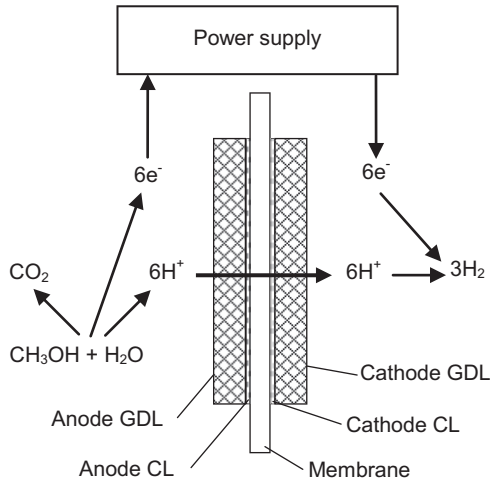

Fig. 1 – Aqueous methanol electrolysis.

As a result of the substantially reduced operating voltage, the energy requirement from methanol electrolysis can be reduced significantly. In addition to this, the corrosion in the PEM methanol electrolysis is less severe than that in the PEM water electrolysis which needs more than 1.23 V to start producing hydrogen. Carbon-based and stainless steel materials, therefore, can be used in the PEM methanol electrolysis, while these materials which are vulnerable to corrosion at high operating voltage cannot be used in the anode section of the PEM water electrolysis [7].

At the anode of a PEM methanol electrolyzer cell, aqueous methanol is transferred to the catalyst layer and decomposed to carbon dioxide molecules. Because of having the same function of the anode, the setup for the PEM methanol electrolyzer cell can be quite similar to that for a direct methanol fuel cell (DMFC) as shown in Fig. 3. It is well known that the sluggish kinetics of the MOR [15–18], the permeation of methanol from the anode to the cathode (i.e. methanol crossover) [15–18], and cathode flooding [15] are key barriers that has hampered the development of DMFC technology. Especially, the crossover of methanol causes a severe problems including a mixed potential on the cathode (i.e. decreasing the cathode potential), low fuel utilization efficiency, etc. Because of this, most DMFCs uses relatively thick membrane (e.g. Nafion 117) [19,20] and low methanol concentration (i.e. <10 wt%) [21] to lower the methanol crossover. Unlike the DMFC, water is not produced in the cathode of PEM methanol electrolyzer cell and the flooding is not a problem. Therefore, the major challenges for better performance in the PEM methanol electrolyzer cell exist only on the anode side. Besides improving the sluggish kinetics of the MOR, the mass transport related to supply of aqueous methanol and removal of CO_2 is also highly concerned as in the DMFC. Previous research has shown that hydrogen production performance of the PEM methanol electrolyzer cell was largely improved with a porous flow field (PFF) made of sintered spherical metal powder (SMP) compared with a conventional groove type flow field [14]. This is attributed to an increase in effective electrode area by using the porous material which enables the flow field to supply reactant evenly to the electrode and remove carbon dioxide smoothly. A lower interfacial contact resistance with the SMP is also a reason for the improvement.

Besides the flow field, an appropriate design of the anode gas diffusion layer (GDL) shown in Fig. 1 is also an interesting topic for better performance in the PEM methanol electrolyzer cell. Since having the same setup as above mentioned, a membrane electrode assembly (MEA) for DMFC has been used in the previous research by the authors [14]. While the GDLs on both sides of MEA for DMFC are usually coated with a polytetrafluoroethylene (PTFE), there have been attempts to optimize the amount of PTFE in the anode GDL in order to improve the cell performance of DMFC [22–26]. Scott et al. [22] and Oedegaard et al. [23] found that adding PTFE to the anode GDL might lead to better gas transfer in the liquid phase and have a positive effect on the cell performance of a DMFC. Krishnamurthy and Deepalochani [24] concluded that anode microporous layer and anode GDL should be coated with an appropriate amount of PTFE to achieve an ideal cell performance. Meanwhile, Gogel et al. [25] and Xu et al. [26] found that the anode GDL of a DMFC need not be wet-proofed with PTFE from the view point of enhancing the mass transport of aqueous methanol solution. So far, there has been no clear consensus showing whether the PTFE content in the anode GDL of DMFC is needed or not. To our knowledge, the influence of PTFE treatment of the anode GDL on the hydrogen production performance of the PEM methanol electrolyzer cell has not been addressed yet. In this study, the MEAs with different amount of PTFE in the anode GDL were used in experiments to analyze their influence on hydrogen production performance of the PEM methanol electrolyzer cell with porous metal flow field. Moreover, the influences of operating conditions such as the methanol concentration and the cell temperature on the performance with the flow field were also investigated.

2. Experimental

2.1. *Membrane electrode assembly*

Specifications of the MEAs tested in this research are shown in Table 1. The MEAs were made with 5 layers including anode GDL, anode catalyst layer (CL), electrolyte membrane, cathode CL, and cathode GDL as depicted in Fig. 1. Carbon paper (Toray TGP-H-90) with the thickness of 0.28 mm was used as GDL on both sides of the three MEAs. The PTFE contents in the

Table 1 – Specification of the MEAs.

	MEA1	MEA2	MEA3
Polymer membrane	Nafion 117 (175 μm)		
Reaction area	25 cm^2 (5 × 5 cm)		
Anode catalyst	Pt–Ru 1.0 mg/cm^2		
Cathode catalyst	Pt 1.0 mg/cm^2		
PTFE content in the anode GDL	0 wt%	5 wt%	10 wt%
PTFE content in the cathode GDL	10 wt%		