

Experimental study on porous current collectors of PEM electrolyzers

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ABSTRACT

Experimental study on proton exchange membrane (PEM) electrolyzer was carried out focusing on the effect of pore structural properties of current collectors, such as porosity and pore diameter. Various titanium (Ti)-felt substrates with different porosities and pore diameters (measured by capillary flow porometry) were used as the anode current collector. Results show that when the mean pore diameter of the current collector was larger than 10 μ m, the electrolysis performance improved with decreasing pore diameter. In contrast, changes in porosity had no significant effect on the cell performance when the porosity exceeded 0.50. The flow pattern of two-phase flow in the flow channel was discussed in terms of its relationship to bubble size and to pore diameter of the current collector. Finally, correlation between the calculated membrane resistance and the measured pore diameter of the current collectors suggest that larger bubbles generated from larger pores tend to become long bubbles in the channel, thus hindering the water supply to the membrane.

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1. Introduction

Hydrogen production linked to renewable sources is a critical process for establishing a "hydrogen society" with zero environmental impact. The integration of renewables (hydro, wind, photovoltaic) with water electrolysis is an attractive option to achieve such a society [1,2]. A proton exchange membrane (PEM) water electrolyzer has recently attracted attention because of its wide range of current density and high conversion efficiency [3–6].

The configuration of a PEM electrolyzer is similar to that of a PEM fuel cell (PEMFC) in that it consists of a membrane electrode assembly (MEA), current collectors, bipolar plates with flow channels, bus plates, manifolds, and end plates. The current collector is a porous medium placed between the MEA and bipolar plate at both electrode sides. The two major roles of a current collector are similar to those of gas diffusion layers (GDLs) of a PEMFC, namely, electric conduction between the electrode and the bipolar plate and efficient gas transport from the electrode to the flow channels. In a typical PEMFC, carbon paper or carbon cloth is used as the GDL at both sides of the electrodes. However, in a PEM electrolyzer, carbon material cannot be used for either the oxygen electrode (anode) or for the GDL (i.e., current collector), because the potential of the anode

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during electrolysis operation is so cathodic that carbon material tends to corrode. Thus, in a PEM electrolyzer, the anode current collector is typically titanium (Ti) in the form of sintered porous media, expanded screen mesh, or felt (unwoven fabric).

At the anode of a PEM electrolyzer, liquid water is transferred through the current collector from the flow channel and dissociated into molecular oxygen. Produced oxygen gas diffuses back to the flow channel by diffusion through the anode current collector. Liquid water acts as a reactant in the anode reaction while simultaneously humidifying the membrane to maintain high proton conductivity. If the produced oxygen cannot be removed efficiently, the anode channel will be blocked, thus limiting the mass transport. Therefore, efficient mass transport of liquid (water) and gas (oxygen) through the anode current collector is crucial for stable operation of a PEM electrolyzer. Despite its importance, however, correlation between electrolysis performance and the properties of the current collector such as porosity, pore size, and hydrophobicity, has not been extensively studied. Grigoriev et al. [7] presented an optimization of the current collector from the view point of mass transport. Based on their experimental data using a porous plate of sintered Ti-powder, they determined that the optimum pore size of a current collector is $12-13 \,\mu m$. However, a definitive correlation between cell performance and pore size has not yet been clearly presented. Hwang et al. [8] carried out electrolysis experiments using unitized reversible fuel cells (URFCs) with different Ti-felt current collectors, and concluded that when the mean pore diameter (MPD) of a porous current collector is smaller than about 60 µm, electrolysis performance is not noticeably affected by changes in either the polytetrafluoroethylene (PTFE) content or porosity, whereas when the MPD $>100 \,\mu m$, cell performance is degraded at a high current density (>0.5 A/cm²). In a previous study [9], we focused on the flow pattern of twophase flow in the flow channel and investigated the relation of flow pattern and electrolysis performance.

At the cathode, hydrogen gas is produced and diffuses through the current collector to the flow channel. Contrary to the anode reaction, the cathode reaction does not require liquid water, although liquid water is transferred (by electroosmosis) from the anode and is accompanied by protons in the membrane. Thus, hydrogen gas and liquid water are simultaneously transported to the channel through the current collector during electrolysis operation. Because the activation overpotential of the cathode reaction is small [10,11], the effect of the properties of the cathode current collector on the cell performance is limited.

Similar to the anode of a PEM electrolyzer, the anode of a direct methanol fuel cell (DMFC) has simultaneous mass transport of the supply of liquid reactant and the release of gas product through the porous media. In a DMFC where carbon paper or carbon cloth is used as the GDL the same as in a PEMFC, carbon dioxide (CO₂) generated at the anode diffuses through the GDL and flows into the channel flow of methanol. The twophase flow of methanol and CO₂ gas in the anode channel has been visualized using a transparent DMFC [12–20]. Argyropoulos et al. [12,13] noted that carbon paper is not suitable as a GDL of a DMFC due to its poor gas removal properties, whereas carbon cloth has relatively good gas removal properties. Lu and Wang [15] also concluded that carbon cloth is more suitable than carbon paper for GDL and that CO_2 bubbles produced by hydrophilic carbon cloth are more uniform and smaller than those produced by hydrophobic carbon cloth. These flow visualization studies on DMFC generally revealed that the minimum bubble size is comparable to the size (i.e., width or depth) of the channel (~1 mm) and thus, dispersed bubbly flow is rarely observed and the presence of slug flow in the channel leads to a smaller effective mass transport area between methanol and the GDL and to degradation in cell performance.

In this work, the effect of pore structural properties (i.e., porosity and pore diameter) of the anode current collector on the performance of a PEM electrolyzer was investigated experimentally. Various Ti-felt substrates with different porosities and pore diameters (measured by capillary flow porometry) were used as the anode current collector in a PEM electrolyzer. Electrolysis performance was measured for each cell set-up. Results revealed that the measured pore diameter of the current collector was correlated with cell performance and with ohmic resistance of the cell.

2. Experimental

2.1. PEM electrolysis

The experimental set-up of the PEM electrolyzer and the balance of plant (BOP) used in this present study has been described previously [9]. This electrolyzer was a small single cell (27 cm²) that had the commonly used PEMFC configuration, consisting of a membrane electrode assembly (MEA), porous current collectors, and separators (bipolar plates) with flow channels. The MEA used here was designed for a URFC and was developed by Takasago Thermal Engineering Co. and Daiki Ataka Engineering Co. For the MEA fabrication, catalytic electrodes were hot pressed to both surfaces of the membrane (Nafion 115). An iridium oxide (IrO₂) and platinum (Pt) mixed electrocatalyst was used for the oxygen electrode, and a Pt catalyst was used for the hydrogen electrode. Carbon paper (Toray TGP-H-090) with a porosity of 0.78 was used for the current collector of the cathode. Table 1 summarizes the types of Ti-felt prepared and used as the current collectors. First, three types of Ti-felt of different fiber diameter (ϕ) and porosity (ε) were prepared, in which A1 and A3 had the same ϕ (20 μ m) and A1 and A2 had the same ε (0.75). Then, to change their pore structure (ϕ and ε), three substrates (B1–B3) were prepared by loading Ti-powder (20 µm average diameter) onto bare substrates of A1-A3. The Ti-powder loading process was similar to conventional carbon-powder MPL loading for GDL of a PEMFC, that is, a slurry containing PTFE, Ti-powder, distilled water and a surface active agent was prepared by mixing with an impeller blade-type mixer, and then spread onto the substrate using a bar coating machine. (The wt% ratio of Tipowder and PTFE binder in the slurries was 99 to 1.) The B1, B2, and B3 substrates were then dried at 180 °C for 30 min to evaporate the remaining solvent, and finally sintered at 360 °C in vacuum condition for 1 h. In the cell set-up, the flow field of the bipolar plates at both sides was 26 channels in parallel and each channel had a square cross-sectional area of 0.01 cm² [9].

The cell temperature was controlled by a thermocouple inserted in the body of the cell and by electric heaters on the Download English Version:

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