Electrochemistry Communications 13 (2011) 638–641

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Soft X-ray visualization of the liquid water transport within the cracks of micro porous layer in PEMFC

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ARTICLE INFO

Article history:
Received 15 December 2010
Received in revised form 25 March 2011
Accepted 28 March 2011
Available online 3 April 2011

Keywords:
Soft X-ray radiography
Micro porous layer
Crack
Surface morphology
Liquid water transport
PEMFC

ABSTRACT

In order to investigate the effect of the cracks on the MPL on liquid water transport, the cross-sectional imaging (cell membrane parallel to the beam) of liquid water behavior in the operating PEMFC was carried out by laboratory-based soft X-ray radiography technique. The spatial and temporal resolutions of the visualization were 0.5 um and 2 s/frame, respectively. The carbon cloth GDLs with the cracked MPL were used and each layer of the PEMFC and the crack on the MPL were clearly visualized. The results clearly showed that the liquid water mainly flows through the crack on the MPL to the substrate layer, and no liquid water was observed in the MPL. Because the MPL is highly hydrophobic, the MPL can limit the liquid water access to the substrate layer. On the other hand, liquid water tends to be stored in the interface between the CL and the MPL. These results suggest that the larger pores (e.g. cracks) on the MPL function as the liquid water pathway to the substrate layer, and the smaller pores on the MPL function as the gas transport path, and the surface morphology of the MPL might affect the liquid water transport in the PEMFC.

1. Introduction

The proton exchange membrane fuel cells (PEMFCs) are regarded as a promising alternative clean power source for automobile application. For successful implementation of PEMFCs for automobile application, cost reduction and downsizing of the PEMFC stack are necessary. In order to meet these demands, further improvements of cell performance is required. The accumulation of excessive product water in the cathode side is an important limiting factor of PEMFC performance under high current density operation. The liquid water generated by the cathode reaction blocks the porous pathways in the catalyst layer (CL) and gas diffusion layer (GDL). Therefore, a fundamental understanding of liquid water transport in the PEMFC porous layers (CL and GDL) and its effect on fuel cell performance is essential to improve the PEMFC performance [1–3].

A bilayer GDL, consisting of a coarse substrate layer and a finer micro porous layer (MPL), has been employed to improve the PEMFC performance under high current density operation. The MPL typically consists of carbon powder bound with a hydrophobic polymer (e.g., polytetrafluoroethylene: PTFE) and must be applied between the CL and the substrate layer. A number of studies have been reported about the transport through the cathode MPL, but the actual function of this layer is still under debate. Some works [4,5] conclude that the MPL acts as a capillary barrier to water entering the cathode GDL and forces water to permeate from the cathode to the anode, yet other works [6,7] conclude that the MPL has no impact on back diffusion.

Recently, some works [8–11] on the effects of the MPL and CL surface morphology have been reported. Hizir et al. [8] developed optical profilometry, and characterized the surfaces of the MPL and CL. Swamy et al. [9] developed an analytical model for investigating the effects of the MPL and CL surface morphology, and they concluded that the cracks on the MPL and CL might act as the significant water pool and strongly affect the water management in the PEMFC.

In this study, we have visualized the liquid water flow through the cracks of the MPL by soft X-ray radiography technique. The soft X-ray radiography technique [12] made it possible to visualize the liquid water distribution in the operating PEMFC with high temporal and spatial resolution. The visualization results clearly show that the liquid water mainly flows through the crack to the substrate layer, and no liquid water was observed in the MPL itself. It is suggested that the surface morphology of the MPL might strongly affect the water transport in the PEMFC.

2. Experimental

Fig. 1 shows the mass attenuation coefficients of the materials used for the PEMFC. Conventional X-ray radiography technique uses the relatively high beam energy. In this range, the mass attenuation coefficient of metal (platinum) is much higher than that of light element (liquid water and carbon), and detection of the liquid water in the PEMFC by X-ray radiography technique was difficult. Meanwhile, the mass attenuation coefficient of platinum and liquid water

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doi:10.1016/j.elecom.2011.03.033

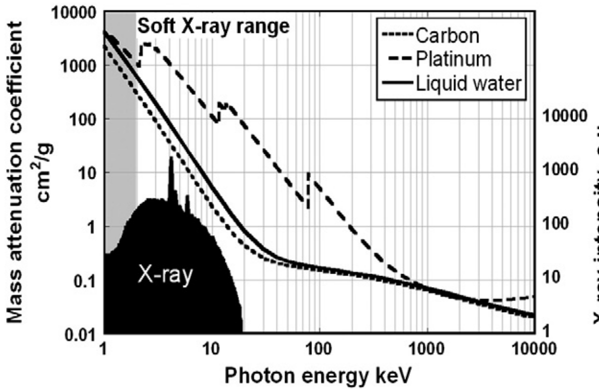

Fig. 1. Mass attenuation coefficients of water and selected elements used in the PEMFC.

becomes closer in the range of low photon energy of less than 2.0 keV (soft X-ray range). Therefore, optimizing the wavelength of the X-rays (using the soft X-ray range) makes it possible to detect the liquid water in the PEMFC by X-ray radiography technique.

Laboratory-based transmission soft X-ray microscope system (Tohken, TUX-3110FC) was developed for the visualization of the water accumulation and discharge behavior in the operating PEMFC. The X-ray generated from a thin film target irradiated by an electron beam was not monochromated but consists of a broad spectrum of low energy X-ray. The X-ray spectrum generated by using a vanadium target clearly showed the strong peak corresponding to the characteristic X-ray (4.95 keV) and the other broad low energy X-ray peak (Fig. 1). In this system, the high geometric magnification imaging is possible by changing the distance between the X-ray source and the sample. Furthermore, the electron beam is focused on the target to produce a point X-ray source of a diameter less than 1.0 μm, and the spatial resolution of 0.5 μm was carried out. In this study, to improve the signal to noise ratio, the accelerating voltage of 15 kV, and the temporal resolution of 2 s/frame were used.

Schematic diagram of the cross-sectional imaging cell is shown in Fig. 2. Because the X-ray beam goes through parallel to the membrane (Fig. 2(a)), cross-sectional imaging can resolve the distribution of liquid water between the different layers composing the PEMFC. To permit the penetration of the low energy X-ray through the cell, the length of the gas channel (penetration length) was set at 0.2 cm. The cell has an active area of 0.4 cm^2 (2 × 0.2 cm) with straight channels (Fig. 2(b)). The channel width and depth were 1.0 and 0.5 mm, respectively, and the rib-to-channel ratio was 1. The number of channels was 10. The carbon cloth GDL with the cracked MPL (ELAT®LT1400-W) was used for both the anode and the cathode side. Hydrogen and oxygen were used as the fuel and oxidant gas with the flow rate of 1.0 NL/min. To promote water accumulation in the cell, the cell was operated under room temperature (25 C), and the bubbler temperature was 20 C (relative humidity: 60%). In this study, the current density of the cell was kept constant (0.8 A/cm^2).

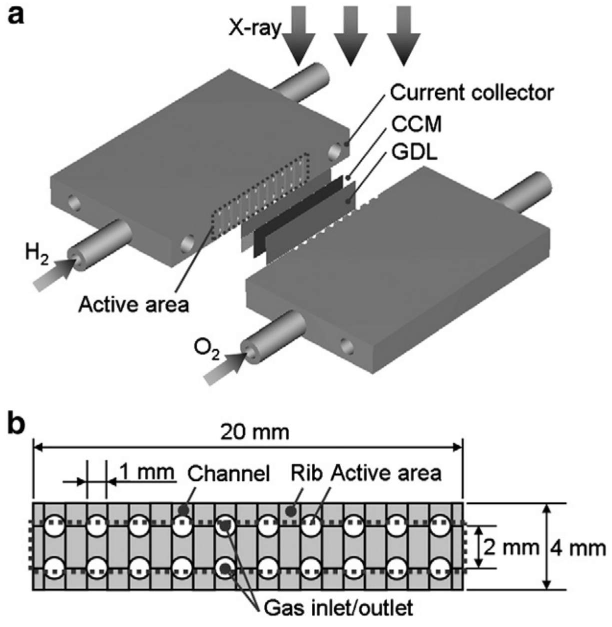

Fig. 2. Schematic diagram of the cell for the cross-sectional imaging. (a) The cross-sectional imaging cell. (b) The flow field configuration.

Fig. 3 shows the scanning electron microscope (SEM) images of the MPL. From the surface image (Fig. 3(a)), a number of cracks on the MPL surface were observed, and they were randomly oriented with variable width. The detachment of the MPL from the substrate layer was also observed. The depth of the cracks seemed different from each other, and some cracks passed through the MPL (Fig. 3(b)).

3. Results and discussion

Fig. 4 shows the original images of the cross-sectional visualization. In Fig. 4(a), the channel and the rib structure of the current collectors are observed. To investigate the effect of the rib and the channel structure, this imaging area is useful. But, in this study, to investigate the effect of the crack on the MPL on liquid water transport, the area shown in Fig. 4(b) was chosen. The imaging area of Fig. 4(b) was ca. 600 × 600 μm, and each layer of the PEMFC and the crack on the MPL were clearly visualized.

In this study, the current density of the cell was raised directly from 0 A/cm^2 (OCV) to 0.8 A/cm^2. The results of cross-sectional imaging of liquid water in the operating PEMFC are shown in Fig. 5. Fig. 5(a)–(f) shows the liquid water distribution in the PEMFC after 5, 7, 9, 11, 30, and 60 s after the beginning of power generation, respectively. To clarify the liquid water in the PEMFC, the images have been subtracted from the image of water free cell (obtained under OCV condition), and the liquid water was represented by the white color.

In Fig. 5(a), the liquid water was only observed at the interface between the CL and the MPL. Because the MPL is highly hydrophobic, the liquid water cannot penetrate it. This is the reason why the liquid water tends to be stored in the CL/MPL interface, and this tendency is remarkable under the channel area of the anode side. Hartnig et al. [13] reported the similar result obtained by the synchrotron X-ray radiography, and this result suggests that the CL/MPL interfacial morphology strongly affects the liquid water transport in the PEMFC.

In Fig.5(b)–(d), liquid water flowing through the MPL to the substrate layer was clearly observed, and no liquid water was observed in the MPL itself. The widths of the cracks were ca. 10 μm, and the pore diameter of the MPL is reported as ca. 60 nm. [14] Therefore, the Young–Laplace equation reveals that the breakthrough pressure of the crack should be much lower than the MPL itself. Therefore, the liquid water mainly flowed through the crack on the MPL and could not penetrate the MPL. Recently, Owejan et al. [14] measured the breakthrough pressure of the crack-free GDL and that of the cracked GDL ex-situ. Their result revealed a drastic contrast in the liquid water pressure to initiate flow through the MPL. In this paper, we successfully visualized the liquid water flow in the crack on the MPL in-situ, and the same tendency was observed. This result suggests that the crack on the MPL significantly affects the liquid water transport in the PEMFC.

Furthermore, the liquid water discharge behavior from the area under channel was observed in Fig. 5(e),(f). The liquid water mainly flowed from the crack on the MPL into the substrate layer, and the liquid water flowed along the fiber bundle and effectively discharged from the larger pore (the weave of the fiber bundle). Gostick et al. [15] reported that liquid water injection into the GDL from a point source