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Short communication

In situ analysis of voltage degradation in a polymer electrolyte membrane fuel cell with a dead-ended anode

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ABSTRACT

In this paper, the impact of dead-ended anode (DEA) operation on the liquid water management of polymer electrolyte membrane fuel cells (PEMFCs) was investigated using X-ray synchrotron radiography. The fuel cell voltage and concurrent through-plane liquid water saturations in anode and cathode gas diffusion layers (GDLs) were measured during DEA and open anode operation. It was observed that DEA operation led to significant increases in liquid water content in both anode and cathode GDLs, along with fuel cell power output degradation. A strong correlation was observed between the buildup of the liquid water in the anode and the cathode, and as a result, the liquid water transport in the cathode was also significantly impacted by this DEA operation.

1. Introduction

Polymer electrolyte membrane fuel cells are electrochemical energy conversion devices which are considered to be a promising alternative to internal combustion engines for the next generation of automobiles. Cost reductions in both fuel cell components and balance of plant accessories are critical for meeting the Department of Energy (DOE) target for automotive application by 2017 [1]. One approach to reduce the cost per kW is to operate the fuel cell in dead-ended anode (DEA), where the hydrogen fuel is not exhausted. However, compared to the classical open-ended anode design, DEA operation typically leads to lower fuel cell power output and lifetime [2].

Fuel cell voltage drops in DEA operation have been typically attributed to two phenomena: (i) the buildup of the liquid water in the anode [3–7], referred to as anode flooding, and (ii) nitrogen accumulation in anode channels [5,8–11]. Both liquid water and nitrogen, originally present in the cathode, permeate through the membrane and accumulate in the anode, which leads to hydrogen starvation. Pulsating the hydrogen feed was proposed as a strategy to mitigate nitrogen accumulation [8,9]. However, the buildup of the liquid water in the fuel cell induced by DEA operation remains a major, unresolved issue.

Liquid water transport in the anode has been a focus of DEA operation studies. Siegel et al. [4] and Lee et al. [3] visualized the liquid water in anode channels using neutron imaging and a transparent fuel cell, respectively. More recently, it was reported that the overpotentials of both the anode and cathode concomitantly increased or decreased at the same time during DEA operation [12], and that the relative humidity of the cathode plays a significant role in fuel cell voltage degradation rates [3,4]. Therefore, understanding water transport in both anode and cathode is critical for determining the impact of DEA operation on the global water management of the fuel cell.

In this work, the impact of DEA operation on fuel cell water management was investigated by comparing the liquid water transport in open anode and DEA operation. The liquid water in an operating fuel cell was visualized in situ using synchrotron X-ray radiography. This technique has been recognized as a powerful method for studying fuel cell liquid water transport behaviour at high spatial resolutions between 2 and 10 μm and temporal resolutions with minimal alteration to the original hardware [13–18], providing advantages over other in-situ visualization techniques [19]. This study is focused on the fuel cell voltage degradations associated with the buildup of liquid water in the anode and cathode GDLs during DEA operation. Voltage degradations refer to recoverable degradations throughout this paper.

2. Methodology

The fuel cell hardware, operating conditions, synchrotron imaging setup, and the calculation of the liquid water saturation in the GDLs are described in the following sections.

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2.1. Fuel cell setup

The fuel cell used in this study, designed to optimize imaging capabilities, had an active area of 0.68 cm^2 with 0.6 mm-wide parallel channels and ribs. This cell was specifically designed for in-plane liquid water visualizations via X-ray radiography [15,18]. The membrane electrode assembly (MEA) was composed of a thin membrane (thickness of 15 μm) and two 10 μm-thick catalyst layers. TGP-H-060 (Toray Industry©) carbon paper was used as anode and cathode GDLs without a microporous layer (MPL). Both GDLs were compressed to 65% of their original thickness once assembled within the cell. A Scribner 850e Fuel Cell Test Station (Scribner Associates Inc., Southern Pines, NC) was used to control the cathode operating condition: air was fully humidified at 60° C under a relative pressure of 1 bar and a mass flow rate of 0.2 L/min was used at the cathode. For DEA operation, the anode was directly connected to the hydrogen cylinder, therefore dry hydrogen was supplied at the ambient temperature. In open anode conditions, high mass flow rates were used in the anode at atmospheric pressure. During DEA conditions, the hydrogen stoichiometry was equal to one and the relative pressure was 1 bar. The cell temperature was controlled by a watercooling circuit maintained at 60 °C. A schematic of the fuel cell is given in Fig. 1(a).

A solenoid valve monitored by a process controller was set up downstream from the fuel cell at the anode to achieve the DEA operating conditions. This valve was closed when the cell voltage was above 0.2 V. If the voltage dropped below 0.2 V, the valve switched to the open position until the cell recovered to a voltage of 0.6 V (where the valve closed again). In this experiment, cathode experimental conditions (humidity, pressure, temperature, and air flow rate) were held constant for open anode and DEA operation. The cell current was held constant at 0.6 A.

2.2. Liquid water visualization

The *in situ* X-ray visualizations were performed at the Biomedical Imaging and Therapy (BMIT) bending magnet beamline (0505B1-1) at the Canadian Light Source Inc. in Saskatoon, Canada. A Hamamatsu C11440-22CU charge-coupled device camera with a scintillator was used for imaging with a beam energy level of 24 keV. The pixel resolution was 6.5 μm and the temporal resolution was 3 s. Raw radiographs (Fig. 1(b)) were processed according to the Beer–Lambert law [14,20] to measure the liquid water thickness. A detailed description of the image processing can be found in our previous work [15]. Only the central region of the radiograph (defined by the white dotted rectangle in Fig. 1(b)) was used for our analysis, since this was the most focused region of the radiograph and exhibited the highest spatial resolution. An example of the liquid water thickness pattern is presented in Fig. 1(c).

2.3. Calculation of through-plane liquid water saturation profiles in GDLs

Through-plane liquid water saturation profiles were calculated according to the following relationship:

$$s = \frac{X_w}{\varepsilon_c . l_z}, \tag{1}$$

where s is the saturation profile, X_w is the in-plane liquid water thickness quantified by averaging the liquid water thicknesses along the x direction in Fig. 1(c), and l_z is the GDL in-plane depth in the z direction, i.e. 0.85 cm. The bulk compressed porosity ε_c is given by

$$\varepsilon_c = 1 - \frac{1}{R}(1 - \varepsilon_0), \tag{2}$$

where R is the compression ratio of the GDLs used in our fuel cell and ε_0 is the uncompressed porosity given by the manufacturer for TGP-H-060 carbon paper; respectively 0.65 and 0.78.

3. Results and discussions

3.1. Analysis of fuel cell voltage degradations in DEA operation

The temporal evolution of the fuel cell voltages is presented in Fig. 2. Steady fuel cell voltage was observed in open anode condition, but was significantly lower compared to DEA operation between 0 and 150 s. This difference was attributed to the higher hydrogen pressure when the anode was closed [5].

During DEA operation, periodic fuel cell voltage drops were recorded after 150 s. Every 30 s, the fuel cell voltage reached 0.2 V, which triggered the opening of the solenoid valve, symbolized by the vertical red segments in Fig. 2. Fuel cell voltage degradation with a similar rate was reported previously [7] and can be explained by several parameters of our study; such as the relatively small channel size (0.6 mm wide), thin membrane (15 μm thickness), and fully humidified air [3]. These parameters are known to accelerate nitrogen and water permeation from cathode to anode [21]. Moreover, the short time lapse observed between two fuel cell voltage drops, i.e. ~ 30 s, was not compatible with any significant accumulation of nitrogen in the anode channels [5,8–11]. Water accumulation in the GDLs is more likely the origin of our observed voltage degradation.

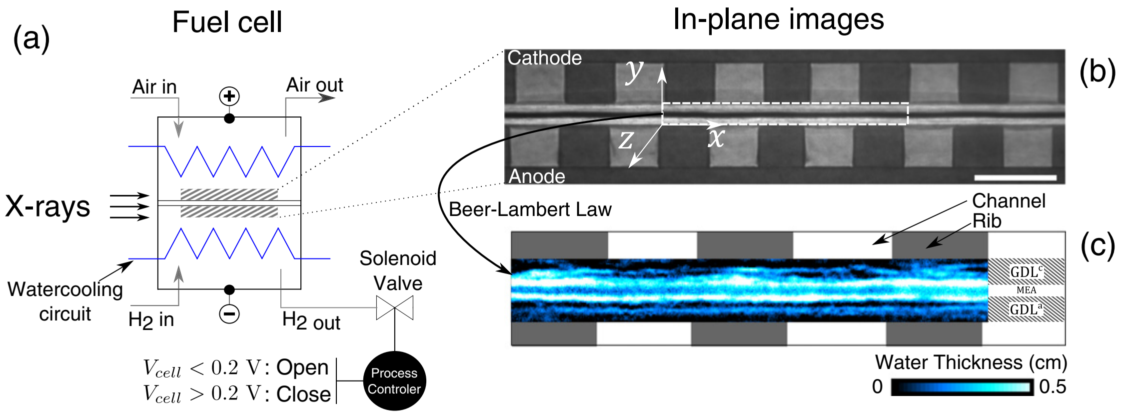

Fig. 1. Schematic of the fuel cell setup (a). Raw radiograph (b) and image processed by the Beer–Lambert law (c). The length of the scale bar in (b) is 1 mm.