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Mechanisms of voltage spikes and mitigation strategies for proton exchange membrane fuel cells with dead-ended anode under pressure swing operation

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ABSTRACT

In proton exchange membrane fuel cells with dead-ended anode, water and nitrogen can accumulate in the anode, causing cell performance decrease and cell degradation. The anode pressure swing operation can reduce the local accumulation of water and nitrogen by generating an oscillatory flow in the anode channel. However, sharp spikes are observed in cell voltage and these spikes are especially large near the end of a purge period. Thus the mechanisms of these voltage spikes are studied through dynamic voltage and local current measurements. The measurement results show that even though the average current density is maintained constant, local current densities also experience sharp spikes and these spikes occur at exactly the same time as the voltage spikes. By examining the spikes in local current densities, it is found that in the upstream the spikes are upward and in the downstream downward. Further detailed study show that the periodical spikes of cell voltage and local current densities are due to the backflow of liquid water and nitrogen in the anode channel from the outlet tube. Based on the mechanism, a novel approach to alleviate the cell voltage spikes is proposed - adding an anode exit reservoir. The experimental results with the anode exit reservoir show that it is very effective in reducing the spikes of cell voltage and local current densities by storing accumulated liquid water and nitrogen and enhancing the backflow of hydrogen. With the anode exit reservoir, the effect of the pressure pulsation amplitude on the cell performance is also studied. The experimental results show that there is a threshold of the pressure pulsation amplitude for a specific fuel cell system and the threshold for the experimental fuel cell is around 0.05 bar. © 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) have been recognized as one of the most promising energy conversion devices due to their high power density, low emission, fast start-up and quiet operation. However, high cost remains to be one of the primary challenges for their commercialization. To simplify fuel cell systems and reduce system cost, deadended anode (DEA) is widely used [1-4]. In DEA configuration, a pressure regulator is installed at the anode inlet to supply hydrogen and a normally-closed solenoid valve is installed at the anode outlet to conduct DEA operations [1,3,5–8]. Without the anode recirculation system, the fuel cell system weight, cost and volume are all reduced. However, nitrogen and water can transfer from cathode to anode and their accumulation in anode can cause local fuel depletion or starvation, leading to decrease in cell performance [9-11]. Meanwhile, local fuel starvation can cause cathode catalyst carbon corrosion, which is a type of irreversible cell degradation [12-15]. To remove the accumulated water and nitrogen, anode purge is conducted during DEA operation. The anode purge is conducted by opening the solenoid valve at the anode outlet.

The accumulations of water and nitrogen in anode have been observed through various technologies and the effects of operating parameters have been studied. Chevalier et al. [9] investigated liquid water accumulation in different layers of a PEMFC with DEA using X-ray synchrotron radiography. Significant increases in liquid water content in GDLs were observed. Lee et al. [10] observed liquid water distribution in the dead-ended anode channel with a transparent single fuel cell and the results showed that water accumulation decreased as air stoichiometry increased. Siegel et al. [11] studied the water management in a PEMFC with DEA using neutron radiography technology and their results showed that water accumulation in the anode increased with operating current density. Himanen et al. [2] studied the effect of hydrogen supply pressure on liquid water accumulation in a planar free-breathing PEMFC and their results showed that the anode flooding was reduced as the hydrogen pressure increased. Strahl et al. [16] investigated the nitrogen accumulation by measuring mole fractions of nitrogen and hydrogen in purge gas using gas chromatograph and their results showed that nitrogen accumulation in the anode increased significantly with operating current. Yu et al. [5] and Manokaran et al. [17] studied the effects of operating conditions on local cell performance in PEMFCs with DEA through measuring current distributions. Their results showed that liquid water and nitrogen accumulated near the outlet first and progressed upstream. Asghari et al. [7] studied the effect of cell temperature on performance of PEMFCs with DEA and found that the cell performance increased with cell operating temperature up to a certain value. McKahn [8] studied the effects of channel design parameters in PEM fuel cells with DEA and found that the channel depth was very important. Yang et al. [18] systematically studied the overall and local effects of operating parameters in PEMFCs with DEA through measuring local current distributions. The results showed that rates of water and nitrogen accumulation increased with

the increase in cathode inlet humidity and operating current density, while the rates decreased with hydrogen pressure and air stoichiometry up to a certain value.

Anode purges are essential to remove the accumulated water and nitrogen. The anode purge strategy, including the purge duration and purge frequency should be carefully designed to reduce hydrogen waste [19-21]. To optimize anode purge strategy, Chen et al. [22] and Yang et al. [23] investigated the nitrogen accumulation in anode under various operating current densities using a dynamic model. Based on the simulation results, they suggested an optimal purge strategy under various operating current load. Chen et al. [24] studied the rate of carbon corrosion in cathode during DEA operation with a mathematical model and optimized the anode purge process considering both carbon corrosion rate and fuel utilization. Sasmito et al. [25] developed a mathematical model to investigate the transient behavior of a PEMFC during DEA operation and studied the effects of anode purge frequency and purge duration on the cell performance. Belvedere et al. [19] suggested an optimal purge strategy considering the cell voltage drop, water flooding and fuel efficiency. Nikiforow et al. [21] studied the effects of cathode humidity, purge duration and purge triggering criteria on fuel efficiency through measuring purged gas volume and composition. The results showed that fuel efficiency could reach 99.9% with optimized anode purge strategy. Okedi et al. [6] developed an effective anode purge strategy considering the purge interval and dead-ended duration under various operation loads. Hu et al. [20] investigated effects of different purge strategies on stack performance with DEA using cell voltage measurement system and the mass spectrum. The results showed that the diameter of the purge valve was also a key parameter in optimizing anode purge strategy.

To further reduce local liquid water and nitrogen accumulation, novel anode supply modes are developed [26,27]. Choi et al. [26] introduced hydrogen pulsations in anode channel in PEMFCs with DEA to reduce local liquid water accumulation. The results showed that the hydrogen pulsation could significantly reduce anode flooding and improve cell performance. Ichikawa et al. [27] developed a pressure swing gas supply mode in a PEMFC stack with DEA. In their pressure swing configuration, a normally-opened solenoid valve was added between the hydrogen pressure regulator and the anode inlet. Hydrogen was supplied intermittently as the inlet solenoid valve was closed periodically. Thus, an oscillatory flow was generated in anode channel. The results showed that the nitrogen concentration distribution in anode channel became much more uniform with the oscillatory flow. The local current distribution was much more uniform than that under constant pressure operation as well.

Pressure swing supply has been proven to improve cell performance during DEA operation through the oscillatory flow in anode channel [26,27]. However, the novel anode supply mode can cause other problems. As shown in the literature [27], there are sharp fluctuations, or spikes, in cell performance under pressure swing operation. Hence, in this study, experiments are conducted to investigate the mechanism of such fluctuations and to find strategies to eliminate or minimize them.

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