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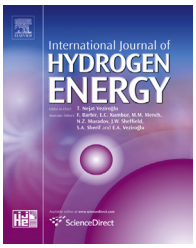

Mechanisms of reverse current and mitigation strategies in proton exchange membrane fuel cells during startups

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ABSTRACT

Understanding the dynamic behaviors of proton exchange membrane (PEM) fuel cells during startups is crucial for their proper operations to minimizing the detrimental effects of reverse current. In this study, the fuel cell is initially filled with nitrogen at both sides, and then reactants are supplied to the cell and the load is imposed simultaneously. Experimental results show that reverse current still occurs even though nitrogen purging is employed before the startup and hydrogen/air boundary is eliminated at the anode. The magnitude of reverse current density increases with the startup voltage. Analysis shows that the reverse current is proportional to the difference between the startup voltage and the open circuit voltage, and it occurs only when the open circuit voltage is lower than the startup voltage, which is due to the charging of the electrical double-layer on the cathode. Thus a startup strategy of air pre-filling is devised and the experimental results show that reverse current can be completely avoided or significantly reduced by pre-filling the cathode with air before startups. Another startup strategy, a linear startup mode, is also tested and the results show that it is effective in reducing the reverse current.

Introduction

The durability of PEM fuel cells is one of the critical issues in its commercial application. In order to enhance durability of PEM fuel cells, it is necessary to investigate the cell performance under dynamic working conditions. Startup is a dynamic process that the PEM fuel cell inevitably experiences in its commercial applications [1–4] and startup may induce air/hydrogen boundary at the anode [5–8] and high potential at the cathode side [9–11], causing reverse current and performance degradation [12–20]. Thus, the study of dynamic characteristics of the cell during startup process is critical and

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may lead to optimal startup strategies, thus improving durability of fuel cells.

When a PEM fuel cell starts up from an initial state and air is used to purge the cell at both sides, hydrogen/air boundary forms at the anode flow field and cathode potential can increase up to about 1.4 V [5,10,11]. With the high potential at the cathode side, carbon corrosion, oxygen evolution, Pt oxidation and dissolution occur at the catalyst layer [6,12,15,16,19,21], leading to significant decreases in both cell performance and durability. Therefore, many research efforts have been focused on reverse current during startups.

The description of the reverse-current decay mechanism of PEM fuel cells was first presented by Reiser et al. [5]. They established a one-dimensional model to simulate the change of electrolyte potential and corrosion current when the anode was partially filled with oxygen during startup process. The modeling results showed that the membrane potential where hydrogen was absent dropped to −0.59 V, resulting in high interfacial potential difference at the cathode and reverse current occurred. With the increase of cathode potential, performance degradation of the fuel cell became severe due to carbon corrosion and dissolution or accumulation of Pt in the cathode catalyst layer. The dynamic behavior of the cell during startup process has also been analyzed in detail by obtaining the changes of electrode potentials [8,10,11]. Baumgartner et al. [8] developed a reference electrode method to measure electrode potentials and showed that cathode potential in the downstream increased due to the presence of significant undersupply at the anode. Shen et al. [11] found that potential difference between the membrane inlet and outlet and the interfacial potential difference of cathode/membrane outlet were about 0.8 V and 1.6 V, respectively. Meanwhile, their results showed that increasing hydrogen flow rate and purging with nitrogen during startup could effectively reduce the degradation of the fuel cell performance. Kim et al. [10] explored the relationship between the cathode potential and carbon dioxide concentration by utilizing a dynamic hydrogen electrode and a FT-IR spectrometer at the cathode outlet. The experimental results suggested that a high cathode potential lead to the oxidation of carbon support causing the fuel cell performance to degrade.

Besides, *in situ* potential measurements, electrochemical characterization methods were used to illustrate the degradation phenomena during startup processes [6,15,17,19,21]. Tang et al. [6] measured cathode electrochemical active surface area by cyclic voltammetry (CV) and the thickness of cathode catalyst layer through scanning electron microscopy (SEM) in corrosion cycles. Their experimental results showed that the cathode lost very large amount of active surface area and the cathode catalyst layer thickness was reduced to about 1/3 of its original value after 80 corrosion cycles. Ishigami et al. [19] studied oxygen pressure distribution by visualization technique during startup process and found that the time to replace air by hydrogen was longer than the predicted value, which would cause serious degradation of the cathode catalyst layer. Meanwhile, scanning transmission electron microscope (STEM) images of cathode catalyst layer showed that the degradation mainly occurred near the inlet and outlet regions. Kim et al. [10] measured electrochemical impedance spectra and the results showed that with the increase of operating temperature, charge transfer resistance increased significantly, due to the high oxidation rate of carbon at high temperature. Moreover, membrane resistance also increased, indicating membrane deterioration.

Transient behavior of PEM fuel cells during startup process has been also studied by numerical modeling [7,22,23]. Gu et al. [7] incorporated an electrode's pseudo-capacitance into their previous startup model [24] and the modeling results showed that with decreasing residence time of hydrogen/air boundary at the anode flow channel, effects of pseudo-capacitance on carbon corrosion became significant. Mishra and Wu [23] established a 3D unsteady two-phase non-isothermal model to study two different startup conditions. Their results suggested that variation trends of temperature and saturation were different along the flow direction under purged initial condition.

Some efforts have been dedicated to develop strategies to mitigate the performance loss during startup process [20,25–29]. Perry et al. [25] pointed out that the voltage control during the fuel introduction at startup caused the performance loss decreased from 100 μV per cycle to 4 μV per cycle. Kim et al. [26] applied a dummy load during startup process and studied the performance degradation via electrochemical techniques. They found that the decrease in electrochemical active surface area and the increase in charge transfer resistance were significantly reduced, indicating an improvement in the cell durability. Then they utilized physicochemical methods to continue to investigate the effect of the dummy load during startup [28], and their experimental results showed that the application of the dummy load could significantly mitigate the Pt particle size growth/agglomeration/oxidation/dissolution and carbon corrosion in the cathode catalyst layer.

One method to avoid the formation of hydrogen/air boundary in the anode side is to fill the anode with nitrogen first [9,22]. However, very limited studies have focused on the reverse current during such startup process. In this study, initially nitrogen was fed into the cell in order to avoid the formation of hydrogen/air boundary at the anode and then reactants and load were imposed on the cell simultaneously to study the reverse current phenomena during startups. Then, detail information of the transient behavior of the cell during startup process was studied, and analyses were performed to understand the fundamental mechanisms of this type of reverse current. Based on the analyses, startup strategies that to reduce or eliminate the reverse current were devised and tested. The experimental results using these strategies are presented.

Experimental

In the experiments, a single PEM fuel cell was used. It consisted of a catalyst coated membrane (Nafion 115) and two gas diffusion layers with micro-porous layer (Spectracarb 2050-L carbon paper). The active electrode area was 16 cm^2 and thickness of the membrane and gas diffusion layer was 125 μm and 200 μm, respectively. Graphite flow field plates were identically placed at both anode and cathode sides and channel width, channel depth and shoulder width were 2 mm,