Mitigation strategies for hydrogen starvation under dynamic loading in proton exchange membrane fuel cells

Fei Jia [a,b,*], Liejin Guo [b], Hongtan Liu [c]

[a] School of Mechano-Electronic Engineering, Xidian University, Xi'an, Shaanxi 710071, China
[b] International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China
[c] Clean Energy Research Institute, Department of Mechanical and Aerospace Engineering, University of Miami, Coral Gables, FL 33124, USA

A B S T R A C T

Hydrogen starvation in a proton exchange membrane (PEM) fuel cell during dynamic loading can have detrimental effects to cell performance, causing significant degradations to cell components and reduce stack durability. In this study, mitigation strategies for hydrogen starvation are proposed and effectiveness of the approaches is studied by measuring variations of local current densities and temperatures *in situ* under various load change scenarios. A two-step startup strategy is studied and the experimental results show that current undershoots in the downstream and the region with zero current at the outlet can be completely eliminated. Experimental studies have also been conducted to examine the effectiveness of a hydrogen reservoir at the anode outlet and the results show that it can significantly reduce the fluctuations in both local current densities and temperatures under both potentiostatic and galvanostatic modes.

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1. Introduction

Durability is one of critical barriers in proton exchange membrane fuel cells (PEMFC) commercialization [1,2]. When hydrogen starvation of PEM fuel cells occurs, degradation of components [3–8] caused by carbon corrosion and water electrolysis, can result in loss of cell performance [9] and durability [10,11]. Therefore, it is crucial to developing strategies [3,4,7,12,13], such as alternative catalyst supports [14–21] and system strategies [22–27], to mitigate the detrimental effects of hydrogen starvation. Thus, studying dynamic characteristics of a cell during load changes under hydrogen starvation and devising mitigation strategies are of great importance to improving fuel cell performance and durability [10].

As mentioned above, hydrogen starvation could cause carbon corrosion, leading to agglomeration of platinum particles [28] and irreversible degradation of the anode [29], and thus many efforts have been dedicated to developing new materials as catalyst support to avoid carbon corrosion and reduction in electrochemical active surface area under hydrogen starvation. Natarajan and Hamelin [15] studied and compared the durability of different catalyst supports under simulated PEMFC cathode environments. Their results showed that carbon nanostructure

(CNS) with high graphitic content and long-range order exhibited higher corrosion resistance and better performance than carbon black (CB), indicating that CNS was more electrochemically stable and would be a good candidate for catalyst support. Owejan et al. [17] introduced graphitized carbon in the micro-porous layers (MPL) to increase carbon oxidation resistance. Their experimental results showed that graphitized carbon in the MPL reduced voltage degradation rate by 25% during accelerated start-up/shut-down tests and decreased the current density loss more than 50% under high potential hold testing. Cerri et al. [14] developed titanium niobium oxide as a new support for platinum to overcome carbon corrosion and investigated the effect of the support composition on its electrical conductivity and stability. The results showed that the conductivity of support sharply increased with the increase of niobium content and the stability was also enhanced. Ioroi et al. [16] prepared Ti_4O_7 as catalyst support and examined the effect of high potential on the activity and stability of Pt-deposited Ti_4O_7 catalyst. They found that polarization curves, electrochemical active surface areas and platinum particle size of Pt/Ti_4O_7 kept unchanged after potential holding at 1.5 V for 1 h, indicating a significant higher stability of the Ti_4O_7 support. Chhina et al. [18] applied tungsten oxide in a PEM fuel cell to replace conventional carbon as the catalyst support. The results showed that during accelerated oxidation cycles the stability of Pt/tungsten remained high, implying that it was feasible as a catalyst support material. Steinbach et al. [19] reported that nanostruc-

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tured thin film PtCoMn catalyst-based MEAs showed less performance loss under start/stop cycling and found that most of loss was recoverable by shutting down the cell and restarting the tests. Suzuki et al. [30] synthesized S-ZrO$_2$ and utilized it as cathode catalyst support to prevent degradation of the electrocatalysts. They found that S-ZrO$_2$ could reduce the content of ionomer in the catalyst layer due to its high proton conductivity and provide sufficient thermal stability.

Besides, system strategies were proposed and studied to alleviate hydrogen starvation and improve the durability of the cell. Pei et al. [26] studied the effect of operating condition factors on fuel cell lifetime and presented an arithmetic equation for fuel cell lifetime. They pointed out that decreasing load-changing time and quickly dispelling open circuit voltage after the cell stops operating could prolong fuel cell lifetime. Kim et al. [31] investigated the relationship between the cathode inlet humidity and durability of the cell. With the decrease of cathode inlet humidity, the loss of electrochemical active surface area and the increase in charge-transfer resistance became slower, leading to a significantly better performance and durability of the cell. Jo et al. [25] studied the effect of operating temperature on performance degradation under hydrogen starvation and found that carbon corrosion and Pt dissolution were accelerated at higher operating temperature, resulting in significant decay of cell performance. Kim et al. [22,23] found that applying a dummy load during startup process could greatly reduce the decrease in electrochemical active surface area, the increase in charge transfer resistance and carbon corrosion rate at the cathode, thus increased the durability of the cell. Perry et al. [24] pointed out that voltage control during hydrogen introduction at startup could decrease the performance loss by about 25 times.

Although many efforts have been focused on alleviating detrimental effects of hydrogen starvation during dynamic processes, it will be very valuable to develop strategies that can avoid hydrogen starvation in the first place, or to mitigate its negative effects. Since hydrogen starvation and its negative effects can occur locally even the cell voltage and average current density are normal [27]. Thus mitigating strategies for hydrogen starvation based on detail information of the local transient responses of the cell will be more valuable. In this study, transient responses of local current densities, temperatures and cell voltage were measured *in situ* to study hydrogen starvations under dynamic loading and strategies to alleviate or eliminate hydrogen starvation are proposed and the effectiveness of mitigation strategies are evaluated based on the experimental results.

2. Experimental

2.1. Experimental system

The single PEM fuel cell used in this study is similar to the one in a previous work [32]. The active area of the cell was 16 cm^2 and it consisted of the MEA with a catalyst coated membrane (CCM) and two identical gas diffusion layers with microporous layer (Spectracarb 2050-L, carbon paper). Thickness of the membrane, catalyst layer and gas diffusion layer was 0.125 mm, 0.01 mm and 0.2 mm, respectively. The single serpentine flow pattern was machined on the graphite plate and flow field plates were arranged identically at both anode and cathode sides.

The experimental system included three parts: a fuel cell test station (FCT-16, USA), an electrochemical workstation (Bio-Logic SA, France) and a data acquisition system (MX-100, Yokogawa, Japan). During experiments, reactants flow rates, humidification temperature, cell operating temperature and back pressure were controlled by the fuel cell test station and the cell voltage and discharging current density were controlled by the electrochemical workstation. Meanwhile, the data acquisition system was used to record all experimental data at a time interval of 100 ms.

2.2. Measurement methods

Measurement methods of local current density and temperature were similar to the previous works [32,33]. A current distribution measurement gasket [34,35] was placed between the gas diffusion layer (GDL) and the flow field plate at the anode side to accurately measure local current density along the flow direction and the anode GDL was segmented in the middle of each channel [32,36] to reduce the effect of lateral current [33,37,38]. T-type thermocouples were placed between GDL and CCM at the cathode side due to the main heat source was at the cathode catalyst layer [39], as shown in Fig. 1.

2.3. Experimental procedures

Under dynamic loading, especially for each startup experiment, the fuel cell was initially fed with humidified hydrogen and air for 5 min to ensure a steady open circuit condition. Then, under potentiostatic mode, the cell voltage was suddenly changed from the open circuit voltage (OCV) to the start voltage and local current densities and temperatures were measured *in situ*. Under galvanostatic mode, the average current density was suddenly changed from initial operating condition to a predetermined value.

In all the experiments, the cell was fed in co-flow with pure hydrogen (99.99%) and air, and the anode/cathode gases were humidified at 50%/100%, respectively. The reactants flow rates were kept constant and the back pressure was atmospheric pressure. Meanwhile, the fuel cell operating temperature was always maintained at 333 K.

3. Results and discussions

3.1. Two-step startup

A simple two-step startup procedure is shown in Fig. 2 and compared with the single-step startup. For the single-step startup, or the instant startup, the cell voltage was reduced instantly from the open circuit voltage (OCV) to the operating voltage (0.6 V). For the two-step startup, the startup process was divided into two stages: first, the cell voltage was changed from OCV to an intermediate value, 0.75 V in this case, and was maintained at this level for a period of time, about 2 s in this case, and then the cell voltage was further reduced to the operating voltage (0.6 V).

Fig. 3 shows transient responses of local current densities under different startup modes. It is clearly shown that though local current densities under both startup modes showed overshoot phenomena, the overshoots under the two-step mode were much lower. Since the cell was initially filled with hydrogen before starting up, hydrogen concentration was high and local current densities were all high [40] at the startup. As time progressed, local current densities under the two cases all decreased to their steady state values. However, variation trends of local current densities under the two startup modes were very different along the flow direction. From Fig. 3, it can be seen that in the upstream, transient responses of local current densities in both startup modes are similar and decreased gradually to reach their equilibrium states. However, in the downstream variation patterns of local current densities were very different for the two cases.

The most important difference is that the two-step startup has completely avoided local hydrogen starvation. Under the instant startup mode, local current densities experienced very large under-