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Behavior of Current Density Redistribution and Voltage Drop under Hydrogen Starvation Conditions for a Polymer Electrolyte Membrane Fuel Cell

Zhifeng Xia, Huicui Chen*, Wanchao Shan, Tong Zhang

School of Automotive Studies, Tongji University, Shanghai, China

ABSTRACT

Hydrogen starvation is an essential limiting factor of lifetime for commercial polymer electrolyte membrane fuel cell (PEM fuel cell) stack. In this paper, a segmented single 25 cm2 PEM fuel cell is utilized to investigate hydrogen starvation phenomenon. The current distribution under different hydrogen stoichiometry conditions is characterized based on contour maps, and the voltage drop phenomenon is tracked constantly during the whole duration until the cell reversal occurs. The results approve that voltage drop becomes more rapid and more severe with the decreasing number of hydrogen stoichiometry. Furthermore, hazardous carbon support oxidation induced by hydrogen starvation causes current density redistribution in the voltage drop process, reflecting irreversible performance degradation and component deterioration of PEM fuel cell.

Keywords: PEM fuel cell, segmented fuel cell, current density distribution, printed circuit board, hydrogen starvation, cell reversal

NONMENCLATURE

Abbreviations	
CD	Current Density
CL	Catalyst Layer
COR	Carbon Oxidation Reaction
DAQ	Data Acquisition System
GDL	Gas Diffusion Layer
HOR	Hydrogen Oxidation Reaction
MEA	Membrane Electrode Assembly
OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction
PEM	Polymer Electrolyte Membrane
PEM Fuel Cell	Polymer Electrolyte Membrane Fuel Cell
Symbols	
SLPM	L min^{-1}

1. INTRODUCTION

Due to its own advantages of high efficiency and zero pollution, polymer electrolyte membrane (PEM) fuel cell is considered to have the potential to become the next generation of vehicle power[1]. Many researchers have paid much attention on PEM fuel cell to prolong its lifespan for future large-scale commercial utilization. Among many urgent problems, hydrogen starvation is an essential limiting factor of PEM fuel cell lifetime. The frequent working condition switch in dynamic cycling, uneven gas distribution led by unsuitable flow field design, control failure of hydrogen supply system and fuel reformer and some other reasons may cause hydrogen starvation[2].

Severe consequences caused by hydrogen starvation, including corrosion of carbon support and carbon substrate[3-9], catalyst particle agglomeration and Ru dissolution[3, 7, 8, 10], cell reversal[4, 8], etc., is hazardous to output performance and electrochemical characteristics of PEM fuel cell. In order to mitigate hydrogen starvation phenomenon, a lot of effective measures including but not limited to electrode design modification[11], control[12-14] and purge[14, 15] strategy optimization, dummy loading[16] were adopted.

In this regard, a rapid and robust diagnostic strategy to detect hydrogen starvation is need to fulfill real-time reactant gas starvation determination. In this paper, a segmented 25 cm^2 single PEM fuel cell was conducted to investigate detailed evolution process of electrochemical parameters (e.g. current density, output voltage) under different anode stoichiometric ratio conditions. The real-

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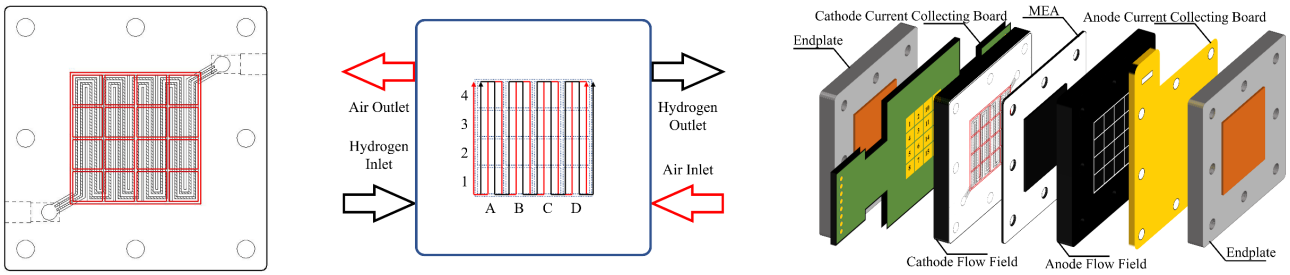
time output voltage is monitored until the cell reversal occurs, and the current density (CD) distribution at several certain moments are captured to characterize voltage drop process. The current redistribution and voltage drop phenomenon is analyzed and explained to shed the light of future further study.

2. EXPERIMENTAL

2.1 Setup

As illustrated in Fig. 1, a single 25 cm^2 single PEM fuel cell with triple serpentine parallel flow field is segmented into 16 (4×4) subzones by grooving method. The geometry of flow field is presented in Fig. 1(a). The dashed line indicates the inlet and outlet screw holes of reactant gas, the 8 circles distributed around the bipolar plate represents screw hole for PEMFC assembling, and the red line marks the route of groove which is filled with dried insulating adhesive. In this research, data acquisition system (DAQ) consisted with components of National Instruments is conducted to current density sampling. Fig. 1(b) demonstrates the arrangement of gas flow direction and numbering of segments. It can be seen that the anode hydrogen and cathode air are arranged in accordance with counter flow. Whereas D1 and A4 are close to air inlet and outlet, and meanwhile A1 and D4 are close to hydrogen inlet and outlet, respectively. Fig. 1(c) illustrates the detailed structure of single PEM fuel cell in this research. The physical parameters of utilized MEA (produced by Wuhan WUT New Energy Co., Ltd) is given in Table 1. Fuel cell test system produced by Ningbo Baite Green Energy Technology Co., Ltd is used for voltage monitoring and gas supply.



(a) (b) (c)

Fig. 1. Schematic diagram: (a) geometry of flow field; (b) counter flow distribution and numbering of segments; (c) structure of segmented PEM fuel cell

2.2 *Experimental details*

In the experiment process, hydrogen stoichiometry is controlled artificially by manipulating the fuel cell test system. In order to completely avoid the influence of cathode reactant, the volume flow per unit time is set to 1.5 SLPM. Table 2 gives the operation parameters in the experiment under conditions of 1.0 A cm^{-2} (25 A).

Table 1 Physical Parameters of MEA

Parameter	Amplitude
Surface of active area	25 cm^2
Thickness of PEM	Gore, 15 μm
Thickness of GDL	190 μm
Pt loading of anode	0.1 mg cm^{-2}
Pt loading of cathode	0.4 mg cm^{-2}

Table 2 Operating parameters of segmented PEM fuel cell

No.	Fuel flow rate (SLPM)	Hydrogen stoichiometry
1	0.087	0.5
2	0.139	0.8
3	0.174	1.0
4	0.209	1.2
5	0.348	2.0
6	0.522	3.0

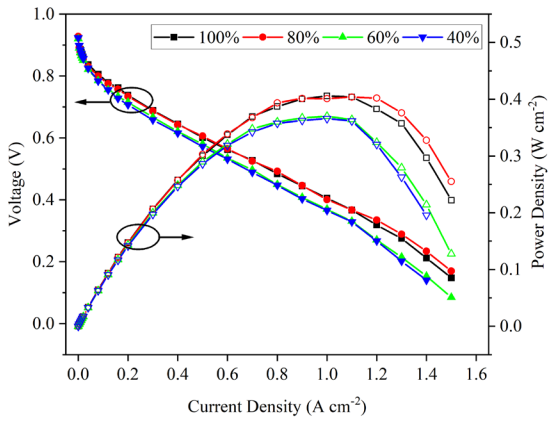


Fig. 2. Polarization and power density curves under different relative humidity conditions

Fig. 2 shows the polarization curves of the assembled PEM fuel cell. In order to work under the best conditions, the relative humidity of reactant gas is set to 80%.

3. RESULTS AND DISCUSSION

3.1 Voltage evolution

Fig. 3 illustrates time-dependent change in the output voltage during the experiment process under different conditions of hydrogen stoichiometry. It can be figured out that the cell reversal phenomenon does not

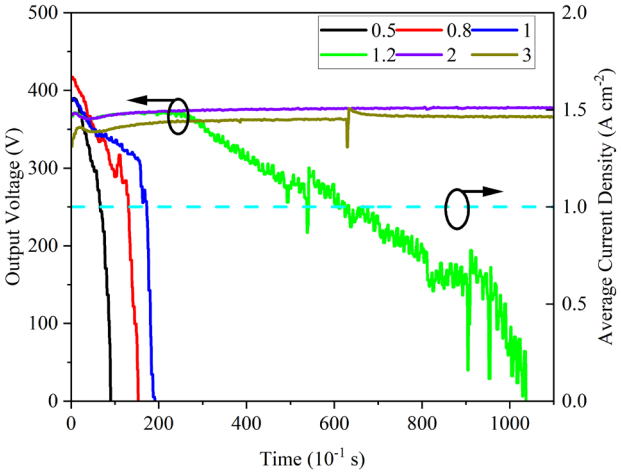


Fig. 3. Voltage evolution during the conditions under different hydrogen stoichiometry

appear under conditions of 2 and 3. This is because sufficient hydrogen supply is enough to provide protons which consume oxygen to generate H_2O at the catalyst layer (CL) of cathode for promoting hydrogen oxidation reaction (HOR).

Under condition of 1.2, voltage fluctuation is obvious throughout the whole experiment until cell reversal occurs. On the one hand, stoichiometry 1.2 meets the requirements of HOR theoretically from a mathematical point of view. On the other hand, the slightly excess hydrogen may be stuck in the process of mass transport due to blockage of GDL and flow channel. Simultaneously, insufficient mass transfer concentration gradient cannot guarantee the arrival of reactant gas to the surface of three-phase boundary where ORR occurs. Therefore, output voltage exhibits fierce fluctuation because of the competition of transit local starvation and short-term reactant supplement, which does not have the ability to prevent the final occurrence of cell reversal.

Under conditions of 0.5, 0.8 and 1, the cell reversal unsurprisingly happens due to insufficient hydrogen supply. It can be concluded from Fig. 3 that voltage drop becomes more rapid and more severe with the decreasing of number of

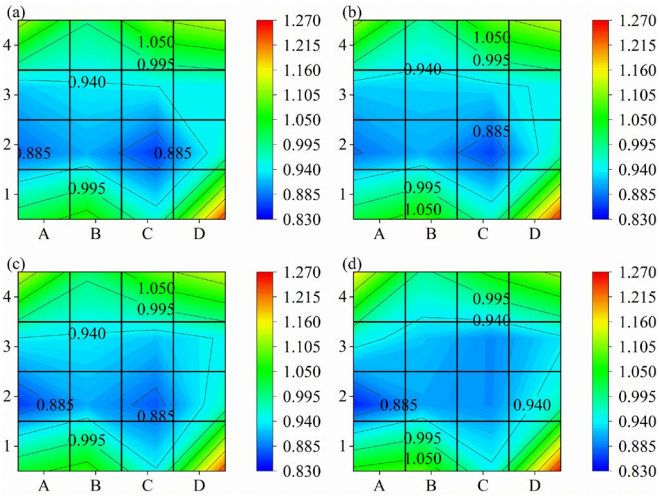


Fig. 5. Current distribution variation during the voltage drop process under condition of hydrogen stoichiometry 0.8 (A cm^{-2})
(a) 3.9 s; (b) 7.7 s; (c) 11.5 s; (d) 15.3 s

hydrogen stoichiometry, which is accordance with Fick's first law[17].

3.2 *Current redistribution*

Fig. 4 demonstrates the current redistribution process during the voltage drop process under condition

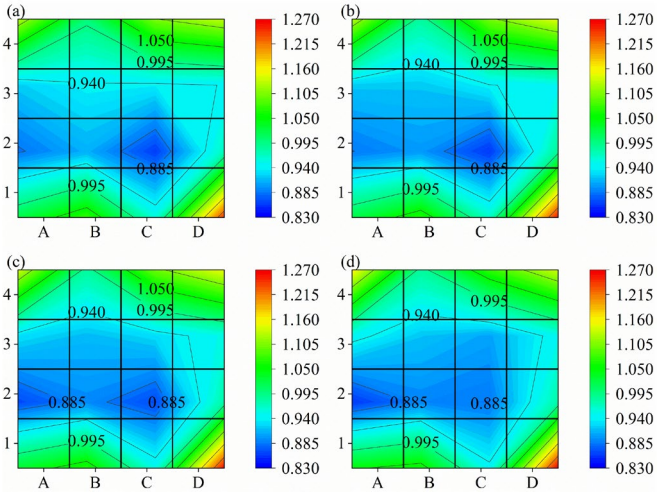


Fig. 4. Current distribution variation during the voltage drop process under condition of hydrogen stoichiometry 0.5 (A cm^{-2})
(a) 2.3 s; (b) 4.6 s; (c) 6.8 s; (d) 9.0 s

of 0.5. The time point of contour map is chosen every 25% during the time period before the cell reversal. It can be seen that the lowest CD region moves from region C2 to region A2. This is because region A2 is adjacent to region A1 where water is easier to accumulate due to the appearance of U-turn flow channel, and A2 is also one of several subareas where the hydrogen is depleted due to the consumption of ORR along the anode flow direction.

Fig. 5 exhibits the current redistribution process during the voltage drop process under condition of 0.8. It is obvious that the color of contour map becomes lighter, which means CD distribution is more even than that under condition of 0.5, indicating strengthened ORR. It can also be seen that "vacuum effect" phenomenon noticed in the literature[17] does not appear due to the manufacture difference between a stack and a single PEM fuel cell, the absence of manifold in the condition of single PEM fuel cell causes different voltage drop time[4].

Fig. 6 gives the current redistribution process during the voltage drop process under condition of 1.0. It is clear

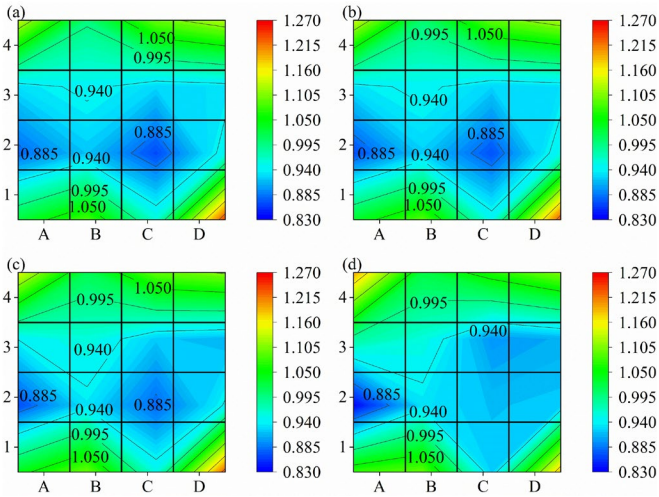


Fig. 6. Current distribution variation during the voltage drop process under condition of hydrogen stoichiometry 1.0 (A cm^{-2})
(a) 4.7 s; (b) 9.5 s; (c) 14.2 s; (d) 19.0 s

that a much more uniform CD comes into being in the voltage drop duration because of more hydrogen supply.

It should be noted that region A4 increases with the development of current redistribution evolution. A4 is located near the cathode outlet where the oxygen concentration is still high enough to perform ORR. Simultaneously, obtuse angle configuration of flow channel entrance/exit enhances local mass transfer to increase local current density. Furthermore, A4 is the region where the first U-turn in the anode flow field appears, which also promotes the transmission of reactant gas. By observing the current density distribution at the four corners, it can be summarized that the design of flow channel entrance/exit plays an essential role in homogeneity of electrochemical reaction.

3.3 Uniform degree under hydrogen starvation

Fig. 7 depicts the standard deviation of current density distribution before cell reversal occurring under conditions of hydrogen starvation. The specific time

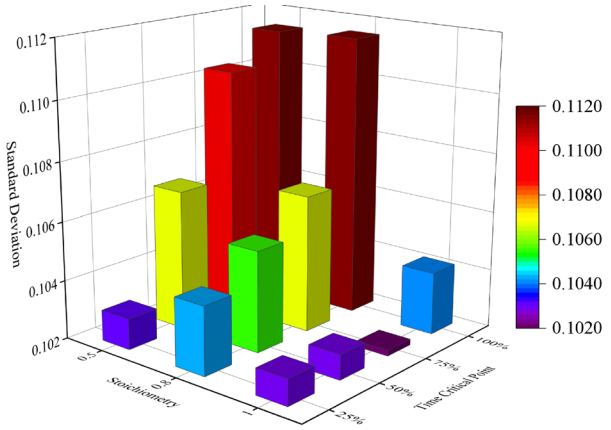


Fig. 7. Standard deaviation at specific time point in voltage drop duration under conditions of hydrogen starvation

point is chosen at 25%, 50%, 75% and 100% of voltage drop interval.

It can be inferred from the figure that heterogeneity of CD under conditions of 0.5 and 0.8 is more obvious than that under condition of 1.0. With the development of voltage drop process, CD uniformity becomes much greater. This is because the anode interface potential varies drastically across the active area due to hydrogen undersupply. In order to meet the need of ORR at the interfacial surface of cathode, oxygen evolution reaction (OER) namely water electrolysis reaction and COR happen at the critical starvation area to produce enough protons, which leads to performance degradation and component deterioration of PEM fuel cell. At the last moment before the reversal happens (100%), the uneven CD exhibits the highest value, indicating that the polarity is about to reverse.

CONCLUSIONS

In this paper, a single 25 cm^2 PEM fuel cell is conducted to investigate voltage drop and current redistribution phenomenon under hydrogen starvation condition. The experiment results indicate that the voltage drop time decreases with the decreasing number of hydrogen stoichiometry. From the contour maps drawn from the specific time point, it can be summarized from the unevenness of CD distribution that the hazardous side reaction is more and more significant with the decreasing number of hydrogen stoichiometry under hydrogen undersupply conditions.

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