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Carbon corrosion and performance degradation mechanism in a proton exchange membrane fuel cell with dead-ended anode and cathode

Ben Chen [a, b], Jun Wang [b], Tianqi Yang [a], Yonghua Cai [a], Caizhi Zhang [c], Siew Hwa Chan [c], Yi Yu [d], Zhengkai Tu [b, c, *]

[a] Hubei Key Laboratory of Advanced Technology for Automotive Components, Wuhan University of Technology, Wuhan, 430070, China
[b] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, 430070, China
[c] Energy Research Institute @ Nanyang Technological University, 50 Nanyang Avenue, 637553, Singapore
[d] Research & Advanced Technology Department, SAIC Motor, Shanghai, 201804, China

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ABSTRACT

This paper presents the work on a PEMFC (proton exchange membrane fuel cell) with DEAC (dead-ended anode and cathode) to achieve high hydrogen and oxygen utilization. Gas purging is an effective way to remove the excess water and maintain normal operation of fuel cell while the voltage drops to the set value chosen arbitrarily due to accumulation of generated water. However, serious carbon corrosion has been observed in MEA (membrane electrode assembly) under this purging model. Voltage degradation process during one purging cycle can be divided into three stages: dehydration of membrane induced ohmic loss, quasi-equilibrium state, and flooding induced concentration polarization. To improve the lifespan of PEMFC, gas purging should be conducted before water flooding. The operation time till the quasi-equilibrium state is suggested as the purging duration in the subsequent research. The results show that with the introduction of time regulator purging strategy, the decay rate of the carbon corrosion is greatly reduced. Moreover, it has also been found that the cell performance and purge cycle duration increase with increasing operating pressure, whereas they decrease with the increase in current density.

1. Introduction

PEMFC (proton exchange membrane fuel cell) has been considered as one of the most promising clean energy sources in the 21st century for transportation, steady power stations, submarines, spacecraft etc, due to its high energy conversion efficiency, high power density, and zero environment pollution [1–5]. PEMFC systems usually work with dead-ended mode or flow-through configuration. Compared with the flow-through system, dead-ended mode operation can improve hydrogen utilization and simplify the fuel cell system, thus leading to great reduction in costs, volume, weight and risk [6–8]. PEMFC with dead-ended mode relies on pressure regulation rather than mass flow control to supply the hydrogen or oxidant at a regulated inlet pressure to maintain the electrochemical reaction, and it is therefore considered to be a promising operating way due to its simply configuration and security operation [9–13]. Flow-through fuel cell system can maintain stable performance by optimizing flow channel geometry and operating parameters, or even applying new material to enhance the uniformity of gas distribution and avoid water flooding. Carton [14] pointed out that water flooding can be avoided by having geometry changes in the flow fields. What's more, they used the open pore cellular foam material as flow plate for PEMFC, and found that this kind of flow plates could manage gas distribution, water and temperature better than the conventional flow field [15]. However, performance will gradually degrade due to the accumulation of liquid water and impurity gas inside the cell. Thus, periodical purging, especially in the cathode, are often required to maintain fuel cell running normally [16–18]. Ramiar [19] investigated the effect of pulsation of air flow at the cathode

* Corresponding author. State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, 430070, China. Tel.: +86 (0) 15102756731; fax: +86 27 87879468.
E-mail address: tzklq@whut.edu.cn (Z. Tu).

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Abbreviation

PEMFC	proton exchange membrane fuel cell
DEAC	dead-ended anode and cathode
MEA	membrane electrode assembly
GDL	gas diffusion layer
CPS	conventional purging strategy
EPS	enhanced purging strategy
MPL	micro-porous layer
HFR	high frequency resistance
CV	cyclic voltammetry
SEM	scanning electron microscopy
RHE	reversible hydrogen electrode
OER	oxygen evolution reaction
CCL	cathode catalyst layer
HOR	hydrogen oxidation reaction
ECSA	electrochemical surface area
PTFE	Polytetrafluoroethylene

Nomenclature

I	operating current, mA
F	Faraday constant, 96,484 C/mol
n	purging number
t	duration of a DEAC cycle, s
Δp	pressure variation in the buffer after the gas purging, Pa
V	volume of the buffer, m^3
R	gas constant, J/(mol K)
T	temperature,°C
p	final pressure after the gas purging, Pa
p_0	initial pressure in the buffer, Pa
σ	proton conductivity, S/cm
R_m	membrane resistance, Ωcm^2
d	thickness of membrane, μm
E_{cell}	reversible cell potential, V
$E_{0,cell}$	reference potential, V
p_{H_2}	pressure of hydrogen, Pa
p_{O_2}	pressure of oxygen, Pa
ΔV_H	voltage variation by hydrogen partial pressure change, Pa
ΔV_O	voltage variation by oxygen partial pressure change, Pa

side of PEMFC and found that using pulsating flow at lower average pressures leads to higher water removal rate from the cell and thus a better PEMFC performance enhancement. Optimization works with respect to the purging interval and cycle duration to balance the relationship between increasing fuel cell efficiency and improving hydrogen utilization were reported in literatures [20–26]. However, the performance fluctuation and carbon corrosion remain unsolved, especially in dead-ended mode. For the application in undersea vehicles, gas flow is avoided and pure oxygen is required as oxidant in PEMFC system, thus water and purging management become more important in the cathode of these fuel cells. Kim [27] carried out a study on the purge characteristics of the cathode dead-end mode PEMFC for the submarine or aerospace applications. The pulsation effect leaded to the decreased voltage decay rate, and made the interval between two purges about three times longer than that without the pulsation effect, which makes the oxidant efficiency of the dead-end mode operation higher. However, the performance degradation after long time operation was not reported in their study. Moçotéguy [28] investigated the dynamic behavior of a 5-cells hydrogen-oxygen PEMFC stack operating in DEAC (dead-ended anode and cathode) both theoretically and experimentally. Voltage declined rapidly to zero in a few seconds, leading to the failure of cell operation. They pointed out that liquid water generated in the cell resulted in the starvation of the active layer from oxygen, and water management was of great importance for a dead-ended PEMFC. In our previous work [29], a modified flow field design combining with assisted gravity water removal technology was introduced into an operated fuel cell under DEAC mode. The generated liquid droplet can flow smoothly on the GDL (gas diffusion layer) surface and drop out the flow channel eventually. In this case, PEMFC can run more than 1 h under DEAC mode with a slight performance decrease, even at 1000 mA cm^{-2}. Although the apparent cell voltage drop was observed directly in that study, the variety in the micro/nano electrode structure and its effect on cell performance remains unclear. As mentioned above, water management was much more important in such fuel cell operating in DEAC mode. In PEMFC, water generated at the catalyst-membrane interface in cathode must be removed from the catalyst layer with the combined roles of evaporation, water-vapor diffusion and capillary force, and finally exhausted out of the fuel cell through the GDL and gas flow field [24,30,31]. However, unlike flow-through mode, the absence of enhanced gas convection will seriously weaken the former two roles in the water transport process in DEAC mode and capillary force becomes the main transport mechanism in liquid water removal from the GDL to the flow channel. Thus, the external liquid droplet on the GDL surface can drop out of the flow channel at the normal speed due to the effect of gravity, whereas the water removal out of the fuel cell as a vapor phase is restrained. Consequently, more water vapor will be condensed into liquid, resulting in a higher water production rate than the removal rate [24]. Thus minor or moderate flooding will occur gradually, leading to the decrease in cell performance. In this case, carbon corrosion and unrecoverable material degradation will occur when fuel cell operates under such condition for a long period of time [32]. Gas purging is an effective way to remove the excess water from the fuel cell [16,18]. Herein, CPS (conventional purging strategy) with voltage indicator for DEAC operation was firstly investigated. It was found that fuel cell would suffer from water flooding during the performance degradation process under this purging mode. EPS (enhanced purging strategy) with time regulator before flooding was conducted subsequently to meet the two strict demands: gas utilization and durability of fuel cells used in underwater applications.

2. Methodology

2.1. Fuel cell and experiment scheme

A single PEMFC with straight flow field was used in the experiment, and the active area was 50 cm^2. The bipolar plates used as current collector were made of commercially graphite material. The geometrical properties of the single cell were listed in Table 1. MEA (membrane electrode assembly) bought from WUT New Energy Company was fabricated using catalyst coated membrane method which composed of the Nafion® XL membrane in combination with platinum loadings of 0.4 mg cm^{-2} per electrode. Carbon paper (TGP-060, Toray) hydrophobically