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Optimization of cathode flooding in scaled-up microfluidic fuel cells

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Abstract

The scaling up of microfluidic fuel cells (MFC) with enlarged electrode area can be very advantageous for their stacking, which will, however, aggravate the cathode flooding problem due to the intensified fuel crossover. In this paper, we first validate the cathode flooding phenomenon in a scaled-up MFC prototype which has a hydrogen-breathing anode and an air-breathing cathode. To optimize the flooding issue, cracking the cathode catalyst layer is found to be remarkably effective. The cathode outer surface is found to be free from water after six polarization cycles, and the degradation rate of current density is as low as $1.3mAcm^{-2}h^{-1}$ when the cell is discharged at 0.4V for five hours. This is probably attributed to the pressure variation inside the cathode induced by the cracks, which alters the water transport direction from gas diffusion layer to the electrolyte channel.

1. Introduction

Microfluidic fuel cell (MFC) generally employs two laminar flow electrolytes instead of using a solid membrane electrolyte, with all its cell components confined in a micro-channel [1, 2]. Benefited from the small channel size, the laminar flow interface is kept stable in the middle channel and works as a virtual membrane for fuel & oxidation separation purpose, which brings distinct advantages to MFCs including cost-efficiency, fuel & oxidant flexibility, adjustable electrolyte pH, inherent heat & water management, etc. However, the small channel size has also restricted the electrode area, leading to insufficient power output. Therefore, it is necessary to stack multiple MFCs together in order to achieve a practical power output [3, 4].

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A MFC stack generally exhibits sophisticated fluid management and great system complexity due to the large amount of single cells. As a consequence, its efficiency will be dragged down due to the shunt currents between adjacent cells [3, 4], and its stability is also questionable as the failure of one single cell will cause a chain-effect to the whole MFC stack. In consideration of these, the scaling up of MFCs with enlarged electrode area is highly promising for stacking purpose, leading to a much reduced number of single cells for a specific power demand. However, enlargement of electrodes in MFCs may bring some intractable issues such as the intensified fuel crossover, leading to an aggravated flooding problem to the cathode.

Electrode flooding is a common issue in low-temperature fuel cells, such as the proton exchange membrane fuel cell (PEMFC). The accumulated water in gas diffusion electrode (GDE) has negative effects on cell performance due to the elevated mass transport resistance, which is especially associated with the cathode side where water is continuously generated via both the oxygen reduction reaction (Eq.1) and the oxidation of crossovered H_2 fuel (Eq.2), as shown in the following chemical equations:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (1)$$
$$2H_2 \text{ (crossovered)} + O_2 \rightarrow 2H_2O \quad (2)$$
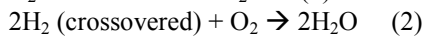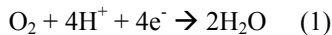
If not removed in time, the generated water will accumulate inside the porous cathode first, and finally emerge on the cathode gas diffusion layer (GDL) surface, i.e. cathode flooding occurs. As for MFCs, cathode flooding can be greatly alleviated because the continuous electrolyte flow can not only suppress fuel crossover, but also remove the generated water from the catalyst layer (CL) efficiently [1, 2]. However, as for scaled-up MFCs, since fuel crossover is intensified, whether cathode flooding can still be suppressed remains to be seen, which has not been studied yet to the best of our knowledge.

In this study, a scaled-up MFC prototype with H_2-breathing anode and air-breathing cathode is utilized to study the issues of cathode flooding. This phenomenon is first experimentally verified, which proves that cathode flooding can be quite severe in scaled-up MFCs. In order to suppress the flooding issue, an optimization strategy has been proposed and testified, which is proved to be remarkably effective on flooding control.

2. Experimental

2.1 Fuel cell fabrication

The present single-flow MFC prototype shared a similar structure with the one described in our previous work [5]. It was mainly composed of two parts, i.e. the fuel cell part and the H_2 flow field part, which were combined together by six pairs of bolts&nuts in their periphery and a silicon rubber gasket in between. As shown in Fig.1, the fuel cell part had a multi-layer structure, including four poly methyl methacrylate (PMMA) layers, three silicon rubber layers, two GDEs, and two silver foil curent collectors. In its middle, a 0.5mm-thick silicon rubber layer with a mico-channel was sanwiched and sealed by two 0.5mm-thick PMMA layers which had electrode windows (7mm x 7mm) and circular grooves around it. The 0.3mm-deep grooves were used to embed the GDEs while the electrode windows were employed to expose the catalyst surfaces to the electrolyte channel. Therefore, the reaction area used to calculate power and current densities was 7mm x 7mm in the following study. 20μm-thick Ag foils were pressed onto electrode edges in order to collect the generated current. Next, two 0.5mm-thick silicon rubber layers with electrode windows were utilized to seal the GDEs. At the outmost, two 2mm-thick PMMA layers with electrode windows were employed to fix the exsiting layers. For the three layers on the cathode side, electrolyte inlet and outlet were drilled at their bottom and top, respectively, where plastic tubes were

inserted for electrolyte delivery. As for the H_2 flow field part, an unidirectional H_2 channel (19mm long, 7mm wide, 5mm deep) was employed, with H_2 entered from the top and exited from the bottom.

Pt/C (60wt.% Pt, Johnson Mattey) was employed as both anode and cathode catalyst, which was dispersed by a dispersion solution (ethanol and water, 1:1 volume ratio) and 5wt.% Nafion solution first, then sonicated for one hour, and finally sprayed on a carbon paper GDL (HCP120, Hesen). The catalyst loading was 2mgcm^{-2} for both electrodes.
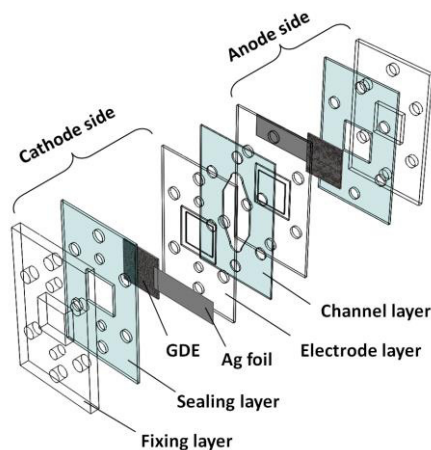

Fig. 1. Composition of the present scaled-up MFC prototype.

2.2 Instrumentations and testing procedures

A CHI660E electrochemical workstation (Shanghai Chenhua) was employed in the present study. To obtain the polarization curve, potentiostatic technique was applied to cycle the cell from 0.9V to 0V with an interval of 0.1V. Each step lasted for 30s which was enough for current stabilization. To obtain the single electrode polarization curves, a reference electrode (Ag/AgCl in saturated KCl, Shanghai Leici) was placed at the electrolyte exit and connected to the cathode through a multimeter (Fluke 116C) [6]. The cell was placed in an incubator (SPX-150-Z, Shanghai Botai) at 25℃. Before the test, electrolyte solution of 1M sulfuric acid (H_2SO_4, Sigma Aldrich) was flowed through the cell at 100μlmin^{-1} and H_2 was provided to the anode side at 2sccm, which were controlled by two syringe pumps (LSP02-1B, LongerPump), respectively. All solutions were prepared by 18MΩ deionized-water (Barnstead, NANOpure Diamond™).

To study the effect of cathode flooding on cell performance degradation, each test consisted of six continuous polarization cycles, during which images of cathode GDL surface were captured after each cycle by a digital microscope (Supereyes A005+). After each test, electrodes would be detached from the cell, fully rinsed by de-ionized water, and dried in an oven at 60℃ for two hours, after which the electrodes were repeatedly used for the next test. Each test was repeated for at least three times to ensure experimental repeatability. The image of cathode CL surface was also captured by a low-power digital microscope (Supereyes A005+) and a high-power scanning electron microscope (SEM, Hitachi S-3400N).

3. Results and discussions

3.1 Verification of cathode flooding in scaled-up MFCs

In order to validate the cathode flooding phenomenon in scaled-up MFCs, the six-cycle polarization test was conducted. As shown in Fig.2(a), the polarization curve from each cycle is quite consistent at low current densities, but gradually drops when entering the high current density region (>300mAcm^{-2}). In addition, cell performance from the initial cycle is found to be weaker than those from the next five cycles at low current region, which might be due to cell activation during the first cycle. Fig.2(b) further illustrates that the anode performance is identical throughout the six cycles, while the cathode loss is the main reason behind the gradual performance degradation. This loss is mainly due to the aggravated water flooding, as can be seen from the images of cathode GDL surface in Fig.2(c). Tiny droplets appear immediately after the first cycle and gradually grow up, which finally merge together into large droplets and severely block the gas pores of the cathode. As a consequence, after only six cycles, the short-circuit current density drops by more than 15% from 474.3mAcm^{-2} to 402mAcm^{-2}. As for the anode surface, no flooding is ever found throughout the test (not shown in figure), which is consistent with the identical anode performance.
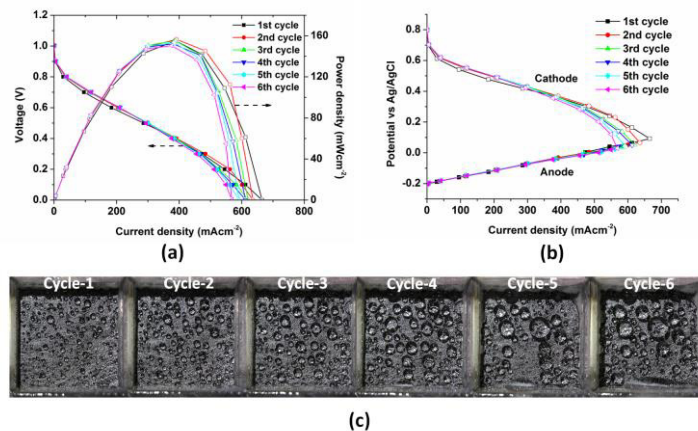

Fig.2. Evidence of cathode flooding in the present scaled-up MFC: (a) cell performance variation during the six-cycle polarization test; (b) single electrode polarization curves; (c) images of cathode GDL surface after each cycle.

3.2 Cathode flooding optimization

During the study, it was found that the morphology of electrode CL is not always consistent. As shown in Fig.3(a), the flat and dense CL from a new electrode gradually turned into a cracked one. This process generally takes dozens of tests followed by electrode rinse and drying, which are believed to crack the CL cooperatively. SEM image of the cracks further shows that the crack width is generally between 10 to 50μm, with thick ones connecting with each other as arteries and thin ones spreading as branches throughout the CL. Fig.3(b) exhibits the single electrode polarization curves tested with the cracked cathode, which shows negligible cathode loss during the six cycles. Moreover, the cathode GDL surface is totally free from water after the test, as shown in the inset. To quantify the extent of cathode flooding, degradation rate of short-circuit current density (I_{sc}) was calculated by dividing the I_{sc} obtained from each cycle to the I_{sc} obtained from the first cycle. As shown in Fig.3(c), the I_{sc} degradation rate from the final cycle is only 2.5% for the cracked cathode compared with 15% for the un-cracked cathode. All these results indicate that the cathode CL cracks can effectively suppress the cathode flooding issue.

To further testify this effect, a 5hrs' potentiostatic discharge test at 0.4V had been conducted. As shown in Fig.3(d), the MFC with an un-cracked cathode runs into a fast drop of current density from 311.2 to 217.3mAcm^{-2} during the first one hour, which finally reaches 190.8mAcm^{-2} in the end. By cracking the

cathode CL, current stability is remarkably improved during the 5hrs' discharge, except for two times of interruption due to pump failure. However, when the pump is reset to work, the current can soon recover to its normal value. The degradation rate of current density is 24.1 and 1.3mAcm^{-2}h^{-1} for the un-cracked and cracked cathode, respectively, of which the latter one is only 5.4% of the former one.
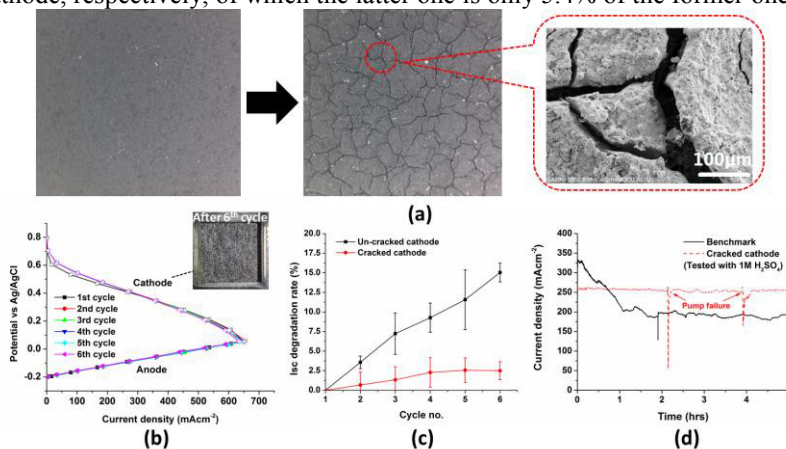

Fig.3. Effect of cathode CL cracking on flooding control: (a) Crack formation after couples of tests; (b) Single electrode polarization curves during the six-cycle test; (c) I$_{sc}$ degradation rate; (d) 5hrs' discharge at 0.4V.

3.3 Further study on cathode CL cracking

To further verify the effect of cathode CL cracking, a manually half-cracked electrode was employed as cathode as shown in Fig.4(a). The cracks were produced randomly by the tip of a blade and their widths are quite regular, all around 10μm. Fig.4(b) shows the images of cathode GDL surface after each cycle during the six-cycle polarization test. It is observed that the surface of the un-cracked half still suffers from aggravating flooding as the test proceeds, while the surface of the cracked half is almost free from water. This phenomenon proves that the cracks do have the ability to suppress cathode flooding. It is also worthy to mention that there are still a few tiny droplets observed on the cracked-half of cathode GDL surface, which is probably due to the insufficient density of the manual cracks, compared with the above naturally-formed cracks. As a consequence, local areas away from the manual cracks can still transport the generated water to the GDL surface.
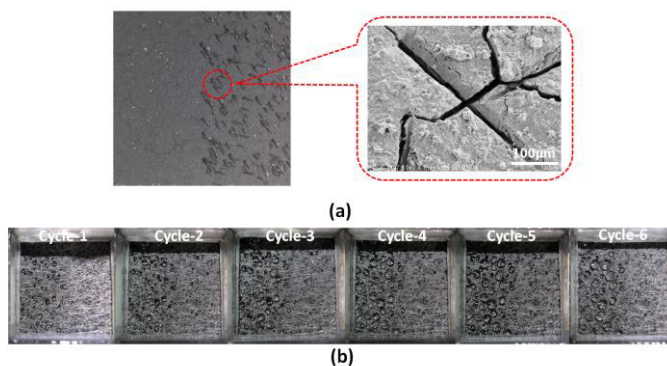

Fig.4. Effect of the manually half-cracked cathode on flooding control: (a) image of the CL surface and SEM image of the cracks; (b) Images of the cathode GDL surface after each cycle.

The positive effect of cathode CL cracking on flooding control could be explained by the pressure variation inside the porous electrode. During cell operation, the generated water inside the cathode CL will continuously accumulate, leading to an elevated local pressure. The un-cracked CL is a dense layer composed of catalyst nanoparticles and Nafion polymer, which impedes water transport into the flowing electrolyte. Therefore, the generated water is forced through the GDL and appears on its outer surface, i.e. cathode flooding occurs. By cracking the CL, its dense structure is broken, providing multiple "easy" passages for water transport into the flowing electrolyte. As a consequence, water is less likely to pass the hydrophobic GDL, i.e. the flooding is effectively suppressed. Eccarius et al. [7] also found that by partially ablating the cathode CL using laser in their PEMFC, water in the cathode could be better transported to the electrolyte side, which is very similar to the finding in the present study. Therefore, the present cathode CL cracking technique may also be applicable to PEMFCs for flooding control purpose.

4. Conclusion

In this paper, we have investigated the cathode flooding phenomenon in scaled-up MFCs. The enlargement of electrode area was found to aggravate the cathode flooding problem, leading to a great extent of performance loss especially at high current densities. By cracking the cathode CL, the flooding was found to be remarkably suppressed. This is because that the cracks can break the dense structure of the cathode CL, lowering down its inside water pressure on the channel side. As a consequence, the generated water can be efficiently transported into the flowing electrolyte instead of towards the GDL side, leaving the GDL surface free from flooding. Future research works will be focused on optimizing the crack pattern in the cathode CL, including crack density, width, depth, spacing, etc.

Acknowledgements

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Biography

Prof. Dennis Y.C. Leung received his Ph.D in 1988 from the Department of Mechanical Engineering at the University of Hong Kong. He joined the same department in 1993 and is now a full professor of the department specializing in renewable energy and energy conservation. He has published more than 400 articles including 210+ peer reviewed SCI journal papers. Prof. Leung is one of the top 1% highly cited scholars in energy field.