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Durability and stability of vapor-feed microfluidic fuel cells, a preliminary study

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Abstract

Vapor-feed microfluidic fuel cell (VF-MFC) can achieve much higher energy density than conventional liquid-feed microfluidic fuel cell, but its durability and stability have never been investigated yet. In this work, a preliminary experimental study is conducted specifically on this issue. First, the long-term durability of VF-MFC is studied by consecutively discharging the cell at its peak power point for ten times in total and 5hrs for each time. It is found that the relative degradation rate for each discharge is similar, which is ~3.6%/h. Also, the cell performance keeps identical throughout the durability test. Therefore, it is concluded that no irreversible degradation such as catalyst poisoning or contact resistance increment occurs and the cell durability is satisfactory. Next, several possible mechanisms responsible for the short-term stability degradation are investigated separately, including the effect of fuel dilution, the effect of carbonate precipitation on the anode side, and the effect of water flooding on the cathode side. These issues will be further optimized in the future in order to obtain a much better discharge stability.

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Keywords: Durability; stability; microfluidic fuel cell; fuel dilution; carbonate precipitation; water flooding

1. Introduction

Microfluidic fuel cell (MFC) is a novel type of fuel cell which generally employs two laminar flows, one dissolved with fuel (anolyte) and the other dissolved with oxidant (catholyte), as electrolyte to replace the conventional expansive solid membrane [1]. Benefited from its membraneless configuration, MFC has achieved many appealing features, such as low cost, high power output, reactant flexibility, easy heat and water management,

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and so on, which are especially advantageous for miniwatt applications [2]. During the past 15 years, great efforts have been made on the R&D of this technology. Many laboratory prototypes with different cell structures have been proposed to optimize the power output [3], fuel utilization [4] and energy density [5] of the single cell. In addition, different stacking strategies have also been proposed to unite multiple single cells together in order to provide more practical power output [6]. Furthermore, the numerical modeling of MFC has provided more fundamental understanding of its working mechanism and instructions on its further optimization [7]. Despite of these achievements, one of the obstacles impeding the practical application of this technology is the storage of bulk electrolyte in the MFC system, which not only decreases the system energy density, but also consumes much parasitic energy for electrolyte delivery.

Previously we have developed a vapor-feed MFC (VF-MFC) which achieved much higher energy density than its conventional liquid-feed counterpart [5]. This is because that the VF-MFC utilizes neat methanol to provide methanol vapor as fuel, so the liquid storage is reduced by half due to the elimination of anolyte. In addition, the VF-MFC can tolerate an electrolyte flow rate as low as $50 \mu\text{Lmin}^{-1}$, which further decreases the electrolyte storage and the parasitic energy loss. In conclusion, the VF-MFC might be more competitive for practical applications than the LF-MFC, but its durability and stability have not been investigated yet to the best of our knowledge. Due to the change of the fuel feeding mode, the VF-MFC may encounter different stability problems compared with the LF-MFC. Therefore, in this study, both the long-term durability and the short-term stability of the VF-MFC have been investigated preliminarily by the potentiostatic discharge method. Here, the short-term stability is defined as 5hrs' discharge of the VF-MFC after a single inject of fuel into the reservoir, while the long-term durability is defined as multiple times of 5hrs' discharge with fresh fuel injected before each time of discharge. This research method is reasonable considering the fact that MFC is generally targeted for miniwatt applications which do not require long-term continuous operation. First, durability of the cell was studied to exclude the possibility of any permanent degradation such as catalyst poisoning or contact resistance increment. Next, various possible reasons behind the stability degradation have been explored separately, including the effects of fuel dilution, carbonate precipitation and cathode flooding. Possible solutions to these issues have also been proposed for stability optimization in the future.

2. Experimental

2.1 Fuel cell fabrication

The VF-MFC prototype employed in the present study was very similar to the one described in our previous work [5], which was mainly composed of the fuel cell part and the fuel reservoir part as shown in Fig. 1(a). To conveniently remove electrodes out of the cell for rinsing and drying, a detachable prototype was fabricated by using bolts and nuts. In addition, soft silicon rubber (SR) layers were utilized between the solid poly(methyl methacrylate) (PMMA) layers for better sealing purpose. From the midmost to the outermost, the fuel cell part included one 0.5mm-thick channel layer (SR), two 0.5mm-thick electrode layers (PMMA), two 0.2mm-thick gas diffusion electrodes (GDE), two 0.5mm-thick sealing layers (SR) and two 2mm-thick substrate layers (PMMA). The electrode area was 3mm x 3mm and the electrode distance was 1mm. As for the fuel reservoir part, it contained a 15mm x 15mm x 15mm cavity for methanol storage purpose and a fuel feeding hole on the back. In addition, an extra sealing layer (SR) was requisite to combine them together. For comparison purpose, a LF-MFC prototype with exactly the same cell parameters was also fabricated. GDEs used in the MFCs were all commercial products bought from Shanghai Hesens Co. 10mgcm^{-2} Pt-Ru (1:1 atomic ratio, Hispec 6000, Johnson Matthey) and 2mgcm^{-2} Pt/C (60wt.% Pt, Hispec 9100, Johnson Matthey) were used as anode and cathode catalysts, respectively, while carbon paper (HCP120, Hesens) was employed as the gas diffusion layer (GDL) to support the catalyst layer (CL).

2.2 Fuel cell testing

Fig. 1(b) shows the fuel cell testing facilities used in the present study. Since the ambient temperature can dramatically influence the methanol evaporation rate in the VF-MFC, the cell itself, the syringe containing the electrolyte solution and the reference electrode were all put inside an incubator (SPX-150-Z, Shanghai Botai), which was set at a constant temperature of 25°C. In addition, a temperature sensor was added on the top of the VF-MFC to

record the real-time temperature of the cell, which was collected by a UNO R3 board. The electrolyte solution was delivered into the cell by a syringe pump (LSP02-1B, LongerPump) and the exit fluid was collected in a beaker, inside which a reference electrode (Ag/AgCl in saturated KCl, Shanghai Leici) was placed. To test the cell performance and discharge stability, an electrochemical workstation (CHI660E) and a multimeter (Fluke 116C) were employed, which were put outside the incubator with only their wires connected to the cell and the reference electrode. Based on our previous experimental experience, a standard test condition was utilized for the durability and stability study, that is, neat methanol as fuel, 1M KOH solution as electrolyte and an electrolyte flow rate of $50 \mu\text{min}^{-1}$. As for the LF-MFC, 0.5M methanol, dissolved in 1M KOH, was used as anolyte and 1M KOH was used as catholyte. The flow rate of both the anolyte and catholyte was also kept at $50 \mu\text{min}^{-1}$.

To study the long-term durability, the VF-MFC was discharged for ten times in total and 5hrs for each time at its peak power point, that is, 0.3V. After each discharge, the cell was purged by 50mL DI-water, and the electrodes were detached from the cell, fully rinsed by DI-water and dried at 60°C for 1h. In addition, the fuel was refreshed before the next time of discharge. As for the short-term stability, different methods were adopted to explore possible reasons behind its degradation. To validate the effect of fuel dilution, fuel concentration after 5hrs' OCV test was measured by Chemical Oxygen Demand (COD) analysis using Hach method 8000 with ultralow range digestion vials. To investigate the effect of carbonate precipitation, the VF-MFC was discharged continuously for 50hrs without water purge and electrode processing, in order to exacerbate the carbonate accumulation. To study the effect of cathode flooding, a conventional LF-MFC was adopted to exclude any possible influences from the anode side. In addition, degradation rate of the VF-MFC was also compared with that of the LF-MFC.

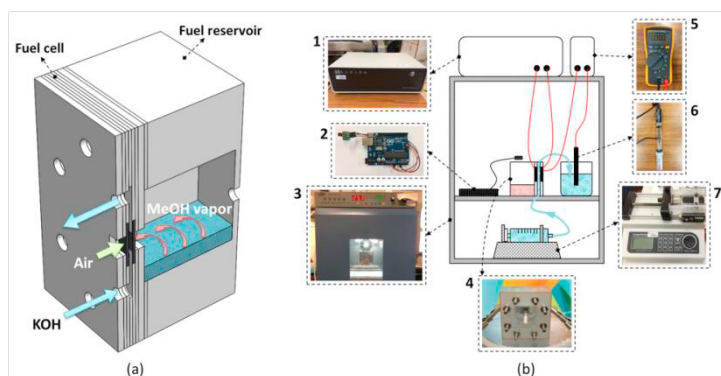


Fig. 1 Schematic diagrams in the current study: (a) Cross-sectional view of the VF-MFC prototype; (b) Testing facilities (1-electrochemical workstation, 2-temperature sensor, 3-incubator, 4-fuel cell, 5-multimeter, 6-reference electrode, 7-syringe pump).

3. Results & Discussion

3.1 Study of long-term durability

Before studying its short-term stability, long-term durability of the VF-MFC was investigated in order to exclude the possibility of any permanent degradation such as catalyst poisoning or contact resistance increment. Otherwise, results from the study of short-term stability could be inaccurate. Fig. 2(a) shows one typical discharge process. In general, the current density gradually dropped from 85.1 to 56.3 mAcm^{-2} in 5hrs, with a quick drop at the beginning and then a constant degradation after about 1h. This phenomenon was due to the temperature variation inside the incubator as shown in Fig. 2(a). At the beginning of the discharge, the incubator would encounter an over-heating effect and the temperature would rise above the set value. After that, the temperature would go back to 25°C . Therefore, to remove this over-heating effect, the relative degradation rate was calculated using the next 4hrs' discharge curve only. In addition, it was observed that the ambient temperature would oscillate periodically due to the heat & rest working mode of the incubator, which also made the discharge current oscillating as shown by the inset. To remove this interference, only the current density values collected exactly at 25°C were employed to obtain a smoothed discharge curve. Fig. 2(b) exhibits the 1st, 4th, 7th and 10th discharge curves, which all show a similar

degradation trend. This phenomenon indicates that the VF-MFC faces no permanent degradation within 50hrs' discharge. Corresponding degradation rates were calculated and compared in Fig. 2 (c), which were all similar to each other with an average degradation rate of 3.6%/h. Fig. 2(d) further confirms the high durability of the VF-MFC by comparing the cell polarization curves after different times of discharge. Both the anode and cathode performance kept identical throughout the test. In the future, more extended discharge time (such as 1000hrs) should be conducted in order to better prove the high durability of the VF-MFC.

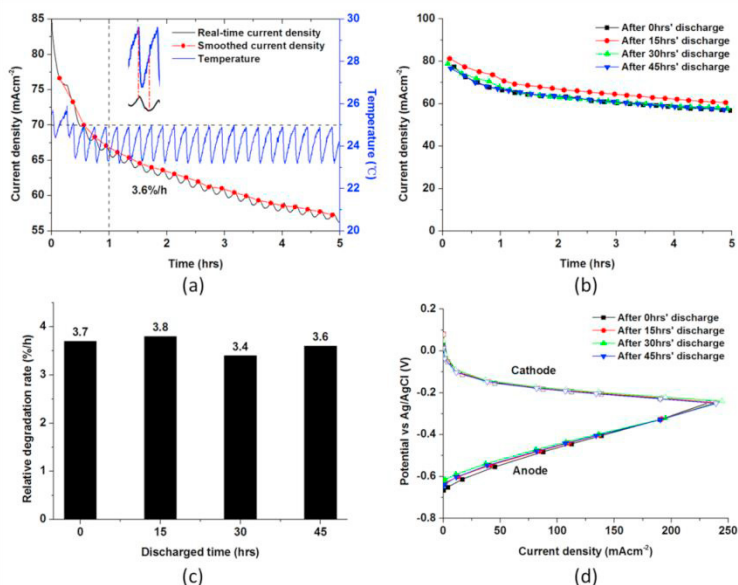


Fig. 2 Long-term durability test of the VF-MFC: (a) 5hrs' discharge of the cell at 0.3V; (b) Discharge curves after different testing time; (c) Relative degradation rate of the current density after different discharge time; (d) Variation of polarization curves after different discharge time.

3.2 Study of short-term stability

After 5hrs' discharge, it was found that both the anode and cathode performance degraded from its original state. Since effects of both catalyst poisoning and contact resistance increment were already excluded, the rise of mass transport resistance might be the major reason behind this reversible degradation. As shown in Fig. 3, on the cathode side water flooding inside the porous GDL can greatly impede the oxygen diffusion, which may be generated from the oxidation of crossovered methanol. As for the anode side, carbonate precipitation inside the porous GDL can block the delivery of methanol vapor, which may be produced from the reaction between the generated CO₂ and the alkaline electrolyte. Furthermore, the gradual dilution of the stored fuel may be an extra issue in the VF-MFC.

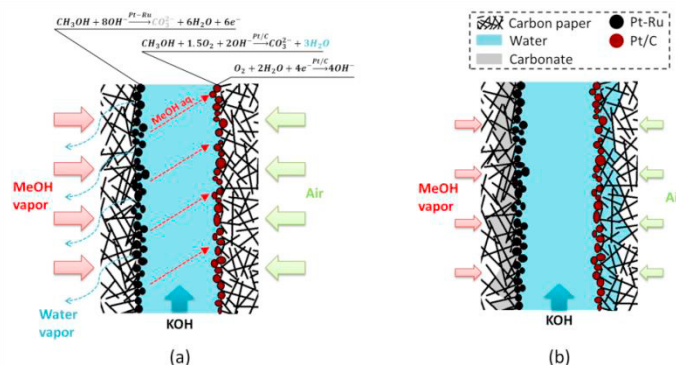


Fig. 3 Schematic diagram of possible reasons behind the degradation of VF-MFC: (a) Before discharge; (b) After discharge.

3.2.1 Effect of fuel dilution

To study the effect of fuel dilution, the VF-MFC was held at OCV for 5hrs. In this manner, no reaction products would be produced in the electrodes, excluding the possible influence from either water flooding or carbonate precipitation. As shown in Fig. 4(a), after 5hrs' OCV test the cathode performance kept identical but the anode performance degraded, indicating that the concentration of methanol vapor in the anode decreased. By refreshing the stored fuel, the anode polarization curve went back to its original state. These results have validated the fuel dilution effect in the VF-MFC. To further prove this conclusion, concentrations of the stored fuel before and after the OCV test were measured by COD analysis. 30 μ l of the fuel was dissolved in 1L DI-water. Theoretically the COD value for neat methanol is 35.6 mgL⁻¹ while the tested value was 35.4 mgL⁻¹, indicating the accuracy of the COD analysis. After 5hrs' exposure to the flowing electrolyte, the COD value decreased to 31.6 mgL⁻¹, which verified the fuel dilution process. As illustrate in Fig. 3(a), water vapor from the aqueous electrolyte can diffuse through the porous anode into the fuel reservoir and be absorbed by neat methanol. To alleviate this issue, a pervaporation membrane can be adopted to separate the neat methanol from the water vapor, which may greatly retard the dilution of fuel.

3.2.2 Effect of carbonate precipitation

Since alkaline electrolyte was employed in the present study, one of the methanol oxidation products, CO₂, can react with KOH and generate K₂CO₃ inside the porous anode, where the flowing of electrolyte is greatly impeded by the microstructure. Therefore, the K₂CO₃ may accumulate along with the discharge and precipitate once exceeding its saturation point, which will block the transport of methanol vapor through the GDL thus degrade the anode performance. To intensify this effect, a 50hrs' continuous discharge was conducted as shown in Fig. 4(b). After every 5hrs, the fuel was refreshed and the water droplets on cathode surface were removed in order to keep current density high. As shown in the figure, after 50hrs' discharge even though the fuel was refreshed to exclude the effect of fuel dilution, the anode polarization curve still could not recover, indicating an extra degradation mechanism on the anode side. By purging the cell with 50ml DI-water and rinsing & drying the electrodes, the anode performance could fully recover to its original state. This is probably because that the precipitated carbonate can be dissolved and removed by the water purge and electrode rinse, so the diffusion path of methanol vapor is clear again. To further validate this hypothesis, SEM proof of the carbonate precipitation is needed in the future. This issue of carbonate precipitation should be addressed in order to achieve a better operational stability. For instance, the micro-structure and the hydrophilicity of the porous anode could be optimized to increase the water exchange rate inside. In addition, macro-scale cracks may be introduced to the anode CL to obtain faster removal of the generated carbonate.

3.2.3 Effect of water flooding

To study the effect of water flooding, a conventional LF-MFC was employed instead of the VF-MFC for the 5hrs' discharge test, in order to exclude the influences from the anode side. As shown in Fig. 4(c), the cathode polarization curve dropped after 5hrs' discharge, especially at high current density region where more oxygen was needed to support the reaction. This is probably due to water flooding on the cathode surface which impedes the diffusion of oxygen from the ambient air into the cathode GDL, which is shown in the inset. By actively removing the water droplets on cathode surface, the cathode performance was fully recovered to its original state. This water flooding is probably produced by the oxidation reaction of crossover methanol. As shown in Fig. 3, the oxygen reduction reaction will consume water instead of generating it, so the only possible source of water generation is from the crossover methanol. Due to the dense cathode CL compared with the porous GDL, the generated water will be pushed to the GDL side, thus blocking the oxygen diffusion path and causing the degradation of cathode performance. As for its anode side, the polarization curve was quite stable during the discharge. Fig. 4(d) compares the discharge stability of the VF-MFC and the LF-MFC, of which the latter achieved a lower degradation rate of 2.3%/h. Therefore, it is concluded that the effect of cathode flooding may be the major reason behind the stability degradation of VF-MFC. Possible solution to this issue includes the introduction of CL cracks to the cathode CL, which has been proved to be effective in our previous work [8].

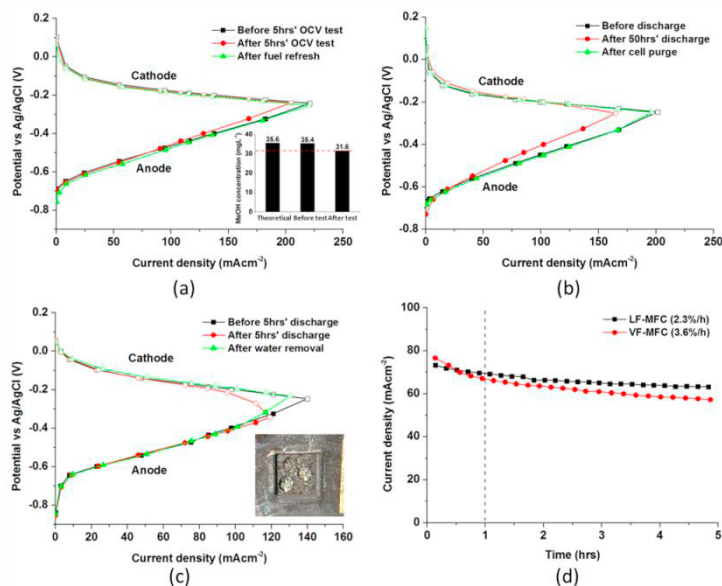


Fig. 4 Short-term stability test of the VF-MFC: (a) Effect of fuel dilution after 5hrs' OCV test; (b) Effect of carbonate precipitation after 50hrs' discharge; (c) Effect of water flooding after 5hrs' discharge using a LF-MFC; (d) Stability comparison between the VF-MFC and the LF-MFC.

4. Conclusion

VF-MFC can achieve much higher energy density than the conventional LF-MFC by eliminating the anolyte and employing low electrolyte flow rates, which is more competitive for practical applications. Nevertheless, its operational durability and stability have not been studied yet, which is the main purpose of the current work. Before studying its discharge stability, the long-term durability of VF-MFC was investigated, which shows that no permanent degradation was introduced during the 50hrs' discharge. As for the short-term discharge stability, an averaged degradation rate of 3.6%/h was observed during 5hrs' discharge at 0.3V. This reversible degradation is mainly attributed to the aggravated mass transport resistance, including the effect of fuel dilution, carbonate precipitation on the anode side, and the effect of water flooding on the cathode side. Future works will focus on the optimization of its short-term stability and the study of its long-term durability with extended testing time.

Acknowledgements

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