

Short communication

Flexible graphite-based integrated anode plate for direct methanol fuel cells at high methanol feed concentration

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Abstract

An integrated anode plate suitable for operating direct methanol fuel cells (DMFCs) at a high methanol feed concentration is reported. This anode structure which was made of flexible graphite materials not only provides dual role of liquid diffusion layer and flow field plate, but also serves as a methanol blocker by decreasing methanol flux to the interface of catalyst and membrane electrolyte. DMFCs incorporating this new anode structure exhibited a much higher open circuit voltage (OCV) (~ 0.51 V) than that (~ 0.42 V) of a conventional DMFC at a 10 M methanol feed. Cell polarization data show that this new anode structure significantly improves the cell performance at high methanol concentration scenarios (e.g. 12 M or above). Moreover, this new design greatly simplifies the anode structure and offers a promising approach in running passive-mode DMFC at high methanol feed concentrations.

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising power generators for consumer electronics applications. Major obstacles that prevent a widespread commercial application of DMFCs include low activity of anode catalysts and methanol crossover through the membrane electrolyte. On the issue of catalysts, studies were made to explore new catalysts with a higher catalytic activity for methanol oxidation [1–2]. Despite of many years' investigations, PtRu alloy catalyst is still recognized as the most active and reliable catalyst for the anodic oxidation of methanol in DMFC. The issue of methanol crossover, on the other hand, is a totally different challenge. It arises from the inability of DMFC to block methanol permeating from anode to cathode through the perfluorosulfonic acid membrane (e.g. Nafion®) electrolyte. Methanol crossover would severely reduce the cell voltage and limit the oxygen access to the cathode catalyst. To reduce the performance impact of methanol crossover, DMFC usually runs at a methanol feed concentration of 1–5 M.

At a higher concentration condition, cell performance could be dramatically reduced. To achieve a high energy capacity in a fuel cell system, a dilute methanol solution would require a larger fuel reservoir, which could increase the total fuel volume and reduce the energy density of a DMFC. Moreover, low concentration of methanol would further reduce an already slow kinetics of methanol oxidation [3] and a feed of high methanol concentration or pure methanol feed is much desired for consumer electronics' applications.

To address the crossover issue, most of the studies reported so far focused on the modification of Nafion® based membranes [4,5] or development of new membrane materials [6,7]. Although most of the reported data demonstrated that methanol crossover could be effectively reduced, nonetheless, other electrochemical and mechanical properties (e.g. proton conductivity, mechanical strength and cost) of the new membranes were unavoidably compromised.

In this study, we attempt to tackle methanol crossover issue by controlling methanol transport in a newly designed anode plate without changing Nafion® membrane. Several related studies that utilize methanol diffusion characteristics to improve fuel cell performance were recently reported. Oedegaard and Hentschel [8] presented a portable DMFC stack operating in

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a passive mode with an interesting methanol feeding concept where a continuous methanol supply to compensate the methanol consumption could be achieved in the feed loop by having a permeable tube in a concentrated methanol storage tank to facilitate methanol diffusion. Ali Abdelkareem and Nakagawa [9] introduced a porous carbon plate between the anode current collector and methanol fuel tank. The CO_2 gas formed between the anode and porous plate could reduce the mass transport flux of methanol and subsequently retard the methanol crossover. One advantage of this interesting approach is the achievability of running DMFC at high methanol operations, yet the formation and retention of a stable CO_2 layer might not be an easy task for a long term operation. In another recent paper published by Kim et al. [10], a similar concept of restricting the mass transport of methanol was studied. Instead of using CO_2 , their approach utilized hydrogel based fuel cartridges as a way to control methanol diffusion flux through the membrane, which consequently improved the DMFC performance at high methanol concentrations, e.g. 8 M.

Our approach highlights the use of a flexible-graphite based anode, which serves both as liquid diffusion layer and methanol flow field plate, to replace the traditional concept of gas diffusion layer (e.g. carbon paper and cloth) and anode current collector. Our method eliminates carbon paper based anode diffusion layer [11], which was an indispensable component in the conventional membrane-electrode-assembly (MEA) unit of a fuel cell and our approach simplifies the assembly process of an MEA. Moreover, this unique design simultaneously addresses methanol crossover issue by taking advantage of pore structure in layered graphite materials, which behave very nicely as a methanol blocker, making our approach an attractive one for DMFC at high methanol concentrations. Flexible graphite plate usually used as sealed materials has properties of high temperature resistance, good chemical resistance, high electric conductivity, good porosity, layered structure and low cost. These characteristics make flexible graphite a possible alternative to the conventional carbon graphite plate. Our results will show that DMFC incorporating this integrated anode structure offers a much higher cell performance than that of the conventional counterparts at high methanol feed concentrations (>8 M).

2. Experimental

2.1. Preparation of a catalyst coated membrane

Nafion[®] (DuPont, USA)115 membranes were purified by three sequential boiling steps in the solutions of (1) 3 wt% H_2O_2 , (2) de-ionized water and (3) 0.5 M H_2SO_4 . Each step took 2 h. Finally, the membrane was rinsed in boiling deionized water for 2 h. Catalysts at anode and cathode were unsupported Pt/Ru black (4 mg cm^{-2} metal loading) and Pt black (2.5 mg cm^{-2} loading), respectively. The catalyst ink was made by ultrasonically mixing 5 wt% Nafion, water-wetted catalysts and appropriate amount of ethanol. The weight ratio between catalyst and Nafion was 85:15 for the anode and 90:10 for the cathode, respectively. The well-dispersed inks were sprayed onto the Teflon blanks. Then the catalyzed layer was transferred

onto the Nafion[®] 115 membrane by thin film decal method [12].

Catalyst-coated-membrane (CCM) can be obtained by treating the membrane at 140°C for 90 s to remove the water and then hot-pressed at 140°C and 10 atm for 120 s.

2.2. Fabrication of an integrated anode electrode and membrane electrode assembly

Flexible graphite sheet materials were obtained from Qing-Dao Advanced Seals Inc., China. One side of the graphite was mechanically molded to form a parallel flow field pattern for methanol transport; while the other side was in direct contact with the anode catalyst layer. Bulk region of the layered graphite sheets served as the methanol diffusion layer. Gas diffusion layer at the cathode was made on Toray[®] paper with thickness of 0.4 mm (Toray Industrials Inc., Japan) by a homogeneous brushing of a mixture containing a desired amount of carbon particles (Vulcan XC-X72), polytetrafluoroethylene (PTFE) and ethanol. The total content of PTFE at the diffusion layer was 20 wt% and the loading of carbon was 1 mg cm^{-2} . The diffusion layer coated paper was then heated at 340°C for 50 min at N_2 atmosphere. Finally, the catalyst-coated membrane was sandwiched between a flexible-graphite anode and cathode diffusion layer at a hot-pressing condition of 135°C and 70 atm for 90 s to form a MEA unit of an active geometric area of 4.5 cm^2 .

A stainless steel mold of the flexible-graphite anode was used as a support to prevent the channel from being broken during the hot-pressing process. A conventional MEA containing traditional anode structure with the same loading of PTFE and carbon as cathode diffusion layer was made for comparison in cell performance.

A schematic diagram of the MEA with a detailed integrated anode structure is shown in Fig. 1. Unlike the cathode electrode with an additional gas diffusion layer, the integrated anode plate provides the function of current collector, flow field and liq-

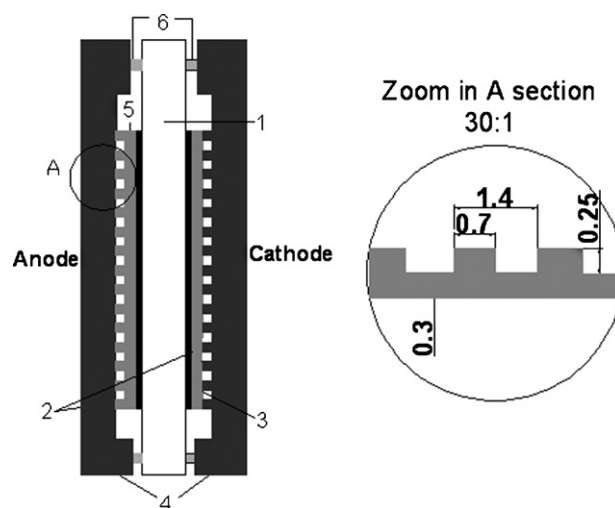


Fig. 1. Schematic diagram of MEA with integrated anode structure: (1) Nafion 115 membrane; (2) catalyst layer; (3) cathode gas diffusion layer; (4) graphite end plate; (5) anodic integrative structure; (6) sealed silicon rubber sheet. The circle region is an enlarged view of the integrated anode (dimensions in mm).

uid (i.e. methanol) diffusion. The adoption of flexible-graphite based anode greatly simplifies the design of the fuel cell system and interesting properties of the flexible graphite (e.g. porosity and conductivity) provide a unique opportunity to operate DMFC at high methanol concentrations. Mechanical strength of the flexible graphite anode can be improved by the support of carbon-based end plate. In a conventional DMFC, the anode structure closely mimics the structure of the cathode.

2.3. Measurement of limiting permeation (methanol crossover) current

The flux of methanol crossover through the membrane could be obtained by measuring the transport-controlled limiting current occurred at the membrane/cathode catalyst interface. A similar procedure was used based on what was previously reported [4]. Methanol solutions were fed to the anode at a volumetric flow rate of 0.8 mL min^{-1} and a humidified N_2 stream at a flow rate of 100 mL min^{-1} was fed to the cathode. Using the Autolab PSTAT20 potentiostat (Eco Chemie, the Netherlands) with a dynamic potential range from 0.1 to 1.2 V at the scanning rate of 3 mV s^{-1} , the limiting current of crossover methanol was recorded. The anode where H_2 evolution took place served as dynamic hydrogen reference electrode (DHE) and counter electrode.

2.4. Measurement of open circuit voltage (OCV) and Cell polarization testing

The cell performance of DMFCs was measured by a FCT-2000 fuel cell testing station (ElectroChem, USA). A single fuel cell unit was operated at an active mode where a peristaltic pump was used to drive methanol aqueous solution at the flow rate of 0.8 mL min^{-1} to the anode flow field with 0 atm back pressure and oxygen humidified at 65°C was fed to the cathode at 0.35 L min^{-1} with 1 atm back pressure. The operating pressure of anode and cathode was maintained at zero and 1 atm, respectively.

3. Results and discussion

Fig. 2 shows the evolution of OCV in a DMFC with and without an integrated anode structure at a methanol concentration of 0.25–18 M. The OCV reading might take several minutes to get stabilized upon the change of methanol concentration [13]. It can be seen that OCV value drops along with the increase of methanol concentration for both types of DMFCs (Fig. 2(a and b)). However, OCV of the DMFC with an integrated anode was much higher than that of a conventional DMFC with a traditional anode structure (i.e. carbon paper diffusion layer and carbon-graphite flow field) at the same methanol concentration. For example, OCV of the new structure was 0.51 V at 10 M compared to an OCV of 0.425 V by a conventional counterpart. In measuring membrane methanol diffusion coefficient, Barragán and Heinzl established a nice equation to delineate the relationship between OCV and methanol concentration [14]. Using a similar derivation and incorporating the additional mass trans-

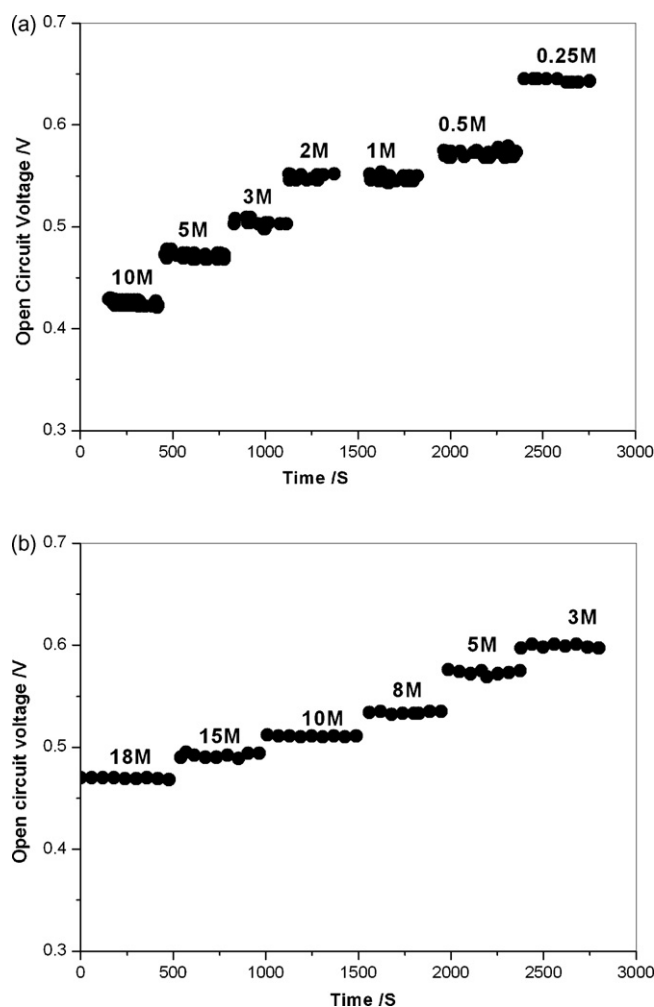


Fig. 2. OCV of DMFCs at different methanol concentrations: (a) conventional DMFC and (b) DMFC with an integrated anode structure.

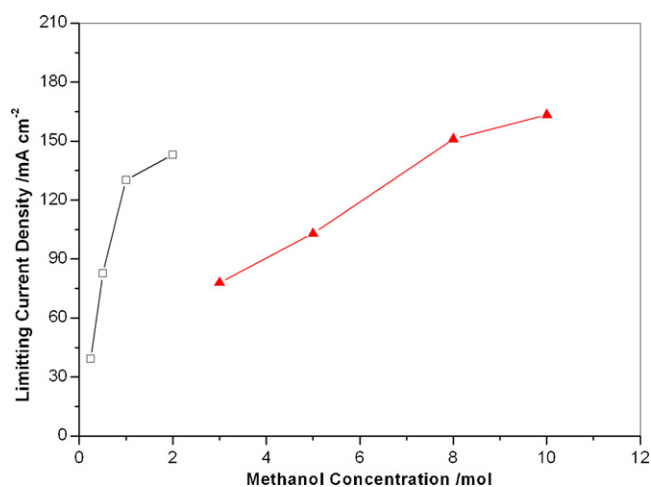


Fig. 3. Limiting permeation current density of methanol at the cathode with and without an integrated anode structure at different methanol concentrations; open square points: conventional DMFC; triangular points: integrated anode based DMFC; cell temperature was controlled at 70°C with the supplies of 0.8 mL min^{-1} methanol solution and 0.1 L min^{-1} N_2 humidified at 65°C onto anode and cathode, respectively. The scanning rate was 3 mV s^{-1} .

fer barrier of methanol due to the integrated anode structure (region 5, Fig. 1), OCV can be expressed as Eq. (1):

$$OCV = E_{cell} - \chi \cdot J_{MeOH}$$

$$= E_{cell} - \chi \left(\frac{C_o}{(\delta_a/D_{Me,a}) + (\delta_m/D_{Me,m}) + (1/k) + A^* \Delta P} \right) \quad (1)$$

where E_{cell} is the cell potential, χ an empirical constant, J_{MeOH} the methanol crossover flux, $D_{Me,a}$ and $D_{Me,m}$ the diffusion coefficients of methanol in membrane integrated anode and electrolyte, respectively, δ_a and δ_m the thickness of integrated anode and membrane, respectively, C_o is the feed methanol concentration, k the mass transfer coefficient for the cathode side, A the empirical constant and ΔP is the pressure difference between cathode and anode.

As it can be seen from Fig. 2, the integrated anode plays an important role in limiting the methanol crossover flux and it offers a much higher OCV at the same feed methanol concentration compared to the conventional DMFC. Moreover, it opens up the possibility of operating DMFC at a high methanol feed concentration (e.g. 10–18 M). The reason of the OCV increase for the “new” DMFC could be easily explained by Eq. (1). Although a high methanol feed concentration (C_o) would adversely affect the OCV, nevertheless, the increase in mass transfer resistance (i.e. a higher value of $\delta_a/D_{Me,a}$) provided by the flexible-graphite based integrated anode structure effectively compensates the high feed concentration effect and maintains the high OCV value. The value of $\delta_a/D_{Me,a}$ can be engineered by controlling the thickness, density and porosity of the flexible graphite materials.

Fig. 3 shows the limiting methanol permeation current density at the cathode at different methanol concentrations. The methanol permeation current is an indication of methanol flux across the membrane [4]. Consistent with the OCV result shown in Fig. 2, the integrated anode based DMFC can sustain a much higher methanol feed concentration (8 M versus 2 M) at a methanol crossover flux (i.e. methanol permeation current density) comparable to the conventional DMFC.

Performance curves of DMFCs with and without integrated anode structure operating at high methanol concentrations (8–20 M) are shown in Fig. 4. The integrated anode one clearly outperforms the cell polarization data of conventional DMFC at low current densities. It was because methanol crossover can be effectively reduced for DMFC with the integrated anode. On the other hand, at high current density conditions, a mass transfer limitation was seen for the integrated-anode based DMFC (e.g. at 8 M operation) and the performance of DMFC with the integrated anode dropped faster than that of a conventional DMFC. However, as it can be seen from Fig. 4b, because of the copious supply of methanol (15 M or above), the integrated anode-based DMFC shows a better polarization characteristics even at high current densities. An interesting study of maintaining a constant

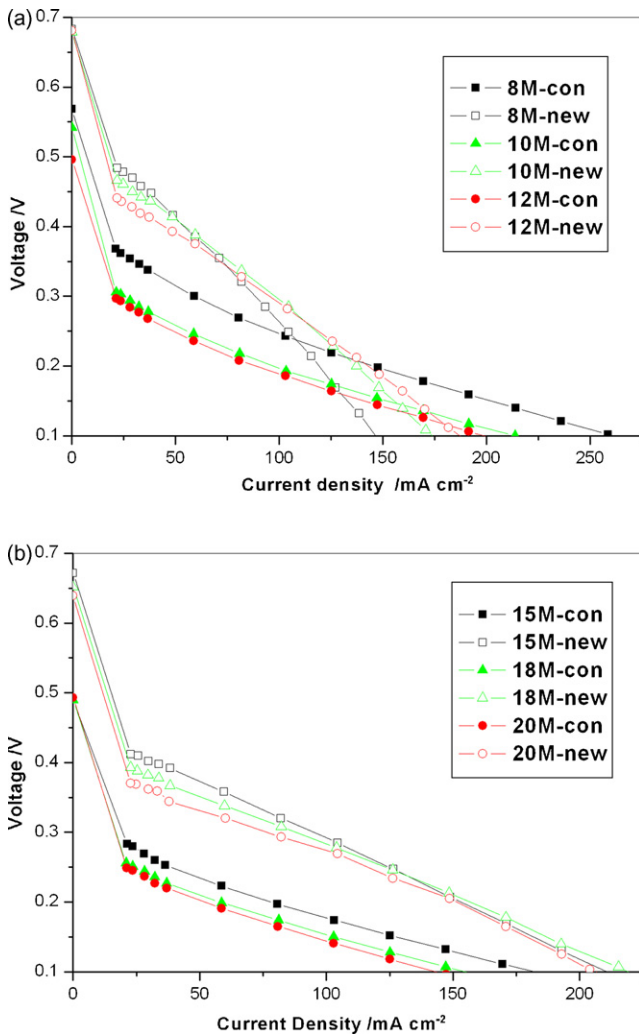


Fig. 4. Cell polarization curves of DMFCs without and with an integrated anode structure at different methanol concentrations: (a) polarization curves for methanol feed at 8–12 M and (b) polarization curves from methanol feed at 15–20 M. Con: DMFC with conventional anode structure; new: DMFC with integrated anode structure. Cell temperature was controlled at 70 °C with the supplies of 0.8 mL min⁻¹ methanol solution and 0.35 L min⁻¹ O₂ humidified at 65 °C onto anode and cathode, respectively.

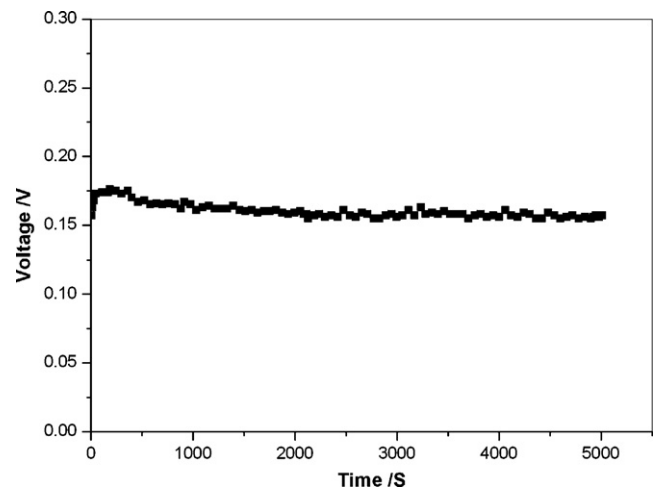


Fig. 5. A continuous operation performance of the integrated anode-based DMFC at a current density of 150 mA cm⁻² and a methanol concentration of 12 M; cell temperature was controlled at 70 °C with the supplies of 0.8 mL min⁻¹ methanol solution and 0.35 L min⁻¹ O₂ humidified at 65 °C onto anode and cathode, respectively.

methanol concentration was recently reported by Xie et al. [15]. An in situ mixing strategy with assistance of methanol sensor was incorporated in the balance of plant (BOP) of their 2 W active-mode DMFC where a variation of methanol concentration could be controlled within 3–6%. A continuous operation of the new DMFC at a current density of 150 mA cm^{-2} and 12 M methanol feed was conducted. As shown in Fig. 5, a stable cell performance was observed for more than 1.5 h.

4. Conclusions

We demonstrated a new DMFC containing an integrated anode structure. This new structure integrates a liquid diffusion layer and a flow field in one single setting and enables the good DMFC operation at high methanol concentrations. The approach presented in this study offers a new strategy to address the methanol crossover issue. Moreover, this new anode structure would contribute to the volume reduction of DMFC systems for portable electronics applications.

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