

Short communication

## Investigation of acidic methanol solution as a fuel for microchannel fuel cells

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### Abstract

Acidic methanol solutions have been investigated for use in direct methanol microchannel fuel cells. The increased proton conductivity of a methanol solution containing sulfuric acid enables the anode to be constructed with the catalyst separated from the proton exchange membrane. This approach could be especially useful in the fabrication of thin-film microchannel fuel cells where a more complex carbon fabric electrode is not possible. The performance of sequential build-up fuel cells was shown to be improved by depositing an additional layer of Pt/Ru on the side-walls of the anode microchannels opposite the membrane. Results from anode half-cell and full cell experiments are reported.

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*Keywords:* Fuel cell; PEM; Micro-fuel cell

### 1. Introduction

Low temperature direct methanol fuel cells (DMFCs) convert liquid methanol (MeOH) and water into electrical energy and are a promising technology for portable devices. Compared with other fuel cell systems, the liquid-feed DMFC is relatively simple and could be easily miniaturized since it does not need a fuel reformer, complicated humidification, or thermal management system [1–3]. Furthermore, methanol has a high energy density in comparison with lithium polymer and lithium ion polymer batteries [4]. The main challenges associated with the development of DMFCs include poor electro-oxidation kinetics of methanol, high methanol crossover through the proton exchange membrane (PEM), carbon dioxide removal from the anode, and high overpotentials at the air cathode [5–9]. To date, Pt–Ru alloy catalysts are still the most efficient anode catalysts for methanol electro-oxidation [10–12]. The addition of Ru to the Pt catalyst enhances the rate of methanol electro-oxidation because

the Ru provides a site for water oxidation and OH adsorption needed in oxidation of methanol to CO<sub>2</sub>. The availability of adsorbed OH on the Ru lowers the number of CO intermediates on the Pt [13–16]. In a typical DMFC, the anode catalysts are generally present in the form of nanoparticles supported on high surface area carbon in contact with the membrane [13,17–19].

Direct methanol microchannel fuel cells (DMMFC) based on using a sacrificial polymer to form microchannel structures are being investigated to meet the energy needs of microsensors, microelectromechanical systems (MEMS), and microfluidic devices [20]. The integration of a fuel cell into the build-up structure of an electronic device (e.g. sensor or integrated circuit) can be accomplished through a sequential build-up process, as shown in Fig. 1. That is, a fuel flow channel is first fabricated, followed by catalyst deposition and membrane deposition. The membrane needs to be a thin-film material (e.g. 1 μm thick), so that the other electronic features (sensor or integrated circuit) can also be processed [20,21]. Due to this thin-film, sequential build-up limitation, the anode Pt–Ru alloy catalysts in the DMMFC must be directly deposited (e.g. sputtering or evaporation)

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on a relatively flat surface. Hence, the anode catalyst is composed of a relatively porous, smooth layer directly on the membrane as compared to Pt–Ru nanoparticles on high surface area carbon supports in the typical DMFC and has a much lower surface area than the carbon supported fuel cell anode [22]. In the DMMFC, the catalyst layer itself serves as part of the current collector (Fig. 1a) and provides in-plane conductivity for electron transfer as well as proton transfer to the membrane. The porosity of the catalyst layer on the membrane is a key issue for proton generation and transport to the membrane. A denser anode catalyst layer (lower porosity) has improved electrical conductivity at the expense of proton conductivity. Thus, an optimum anode catalyst loading is necessary in the DMMFC to maintain low current collector electrical resistance and provide high catalytic activity.

In this work, a conductive analyte was used so that the surface area of the anode catalyst layer could be increased without having to decrease the porosity of the catalyst layer on the membrane or change the membrane-electrode configuration, as shown in Fig. 1b. Although the anode catalyst extends to regions not in contact with the membrane, an acidic methanol solution could provide sufficient conductivity for proton transfer to the membrane. In the present work, the electro-oxidation of acidic methanol on the sputtered Pt–Ru alloy was investigated. A fuel cell using an acidic methanol solution as the fuel and proton transport medium was fabricated to examine the contribution of Pt–Ru catalyst lining the anode chamber to the overall anode reaction. The power density of the fuel cell and the ability of the acidic methanol solution to transfer the protons are reported.

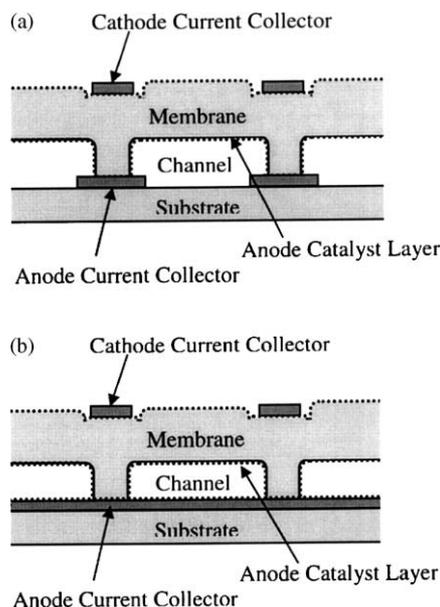


Fig. 1. Cross-sectional view of the microchannels in the microfabricated direct methanol fuel cell (a) and the microfabricated direct acidic methanol fuel cell (b).

## 2. Experimental

The electrochemical experiments were performed using a Perkin-Elmer PARSTAT 2263. The scan rate for linear sweep voltammetry was  $1 \text{ mV s}^{-1}$ . The electro-oxidation of methanol in the acidic solution was studied in a three electrode system. The working electrode was a solid Pt–Ru alloy layer deposited on titanium by sputter-deposition at room temperature. The deposition rate was  $3.0 \text{ \AA s}^{-1}$  and the deposition time was 6 min. The atomic ratio of the Pt–Ru alloy layer was 1:1, as confirmed by XPS analysis. The counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE). Deionized water and  $\text{H}_2\text{SO}_4$  were used to prepare the acidic methanol solutions. The conductivity of the solutions was measured using impedance spectroscopy. The frequency range for the impedance measurement was from 100 mHz to 1 MHz, with an ac signal amplitude of 10 mV. During each test, the acidic methanol solution was purged with nitrogen gas.

The structure of the cell with the acidic methanol solution as the fuel and proton transport medium is shown in Fig. 2. The anode was a Pt–Ru alloy layer with  $1080 \text{ \AA}$  thickness on the Ti board. The cathode was a Pt/C gas diffusion electrode with a Pt loading of  $0.5 \text{ mg cm}^{-2}$  from E-TEK Inc., and the membrane was Nafion 117 from DuPont. The membrane (after pretreatment) and the cathode were hot-pressed to form a membrane cathode assembly at  $130^\circ\text{C}$  and 2 MPa for 3 min. The distance between the anode Pt–Ru alloy catalyst layer and the membrane was 20 mm. The anode half-cell behavior at the same condition in the cell was evaluated using 1 M  $\text{H}_2\text{SO}_4$  solution with SCE and a platinum wire counter electrode in the cathode compartment.

The effectiveness of the Pt–Ru alloy catalysts deposited on the current collector on the bottom (or opposite side) of the microchannel was tested in a microfabricated anode half-cell. The detailed microfabrication process has been described elsewhere [20,21,23]. The  $3.0 \text{ \mu m}$ -thick  $\text{SiO}_2$  was used as the membrane and fabricated by plasma enhanced chemical vapor deposition (PECVD) at  $100^\circ\text{C}$ . The size of the microchannels was  $0.30 \text{ mm} \times 0.018 \text{ mm} \times 15.0 \text{ mm}$ .

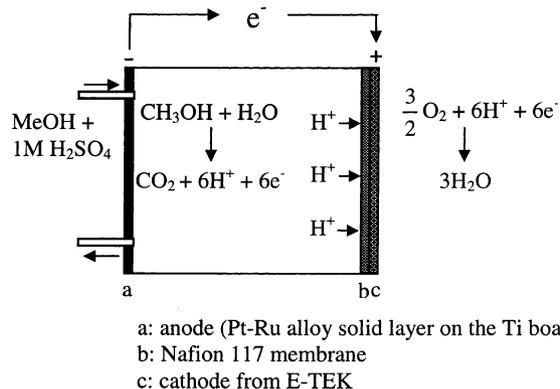


Fig. 2. Schematic of the fuel cell using acidic methanol solution as the fuel and proton transport medium.

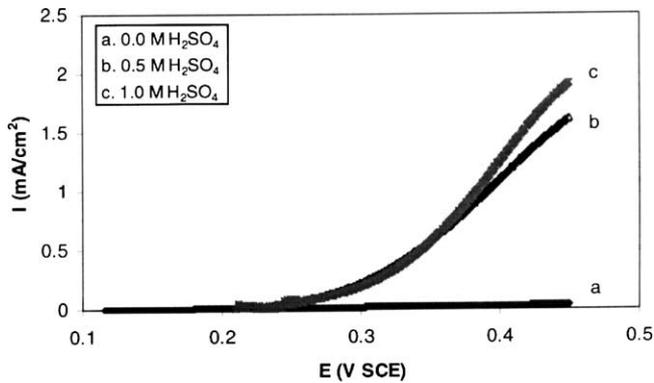


Fig. 3. Oxidation of 1 M methanol solution with different H<sub>2</sub>SO<sub>4</sub> concentration on the sputter-deposited Pt–Ru alloy.

The Pt–Ru loading on the inner wall of the membrane of the microchannel was 38 μg cm<sup>-2</sup> and the thickness of the Pt–Ru alloy layer on the bottom side of the microchannel was 1080 Å. The current collector was Au, and a 45 Å thick Ti layer was deposited between Pt–Ru alloy and Au to improve adhesion. A reservoir was built on the top of the channel for the 1 M H<sub>2</sub>SO<sub>4</sub> solution. The SCE reference electrode and a platinum wire counter electrode were used for the anode current–voltage curve measurements.

### 3. Results and discussion

The oxidation behavior of the methanol on the Pt or Pt–Ru alloy catalyst has been studied in acidic electrolytes because the addition of acid can improve the solution conductivity [24–26]. The linear sweep voltammetry curves for the oxidation of a 1 M methanol solution with different H<sub>2</sub>SO<sub>4</sub> concentrations on a sputter-deposited Pt–Ru alloy at 60 °C are shown in Fig. 3. It can be seen that the current density for methanol oxidation on the Pt–Ru alloy without H<sub>2</sub>SO<sub>4</sub> in the solution was very low. When 0.5 M H<sub>2</sub>SO<sub>4</sub> was mixed with the methanol solution, the oxidation current increased significantly because H<sub>2</sub>SO<sub>4</sub> increased the conductivity of the methanol solution. Table 1 lists the conductivity of the 1 M methanol solution with different H<sub>2</sub>SO<sub>4</sub> concentration at room temperature. The dependence of the methanol oxidation current on the acid concentration in the solution is consistent with the conductivity of the solution. There was little difference in the oxidation current with H<sub>2</sub>SO<sub>4</sub> con-

Table 1  
Conductivity of 1 M methanol solution with different sulfuric acid concentration at room temperature

Concentration of H <sub>2</sub> SO <sub>4</sub> (M)	Conductivity (s cm <sup>-1</sup> )
0.00	0.00003027
0.25	0.0126
0.50	0.2509
1.00	0.4420
1.50	0.5619
2.00	0.6589

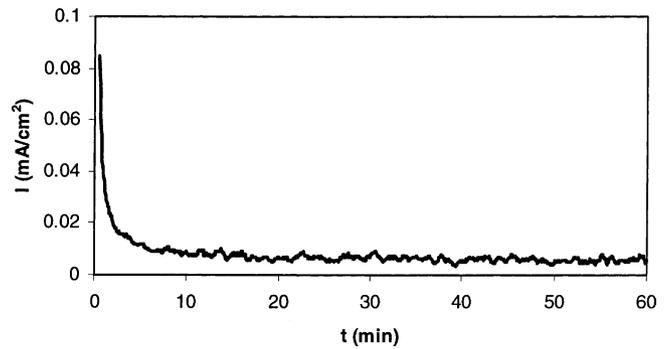


Fig. 4. Current–time curve for 1 M methanol oxidation in 1 M H<sub>2</sub>SO<sub>4</sub> solution at 0.25 V SCE and 60 °C on the sputter-deposited Pt–Ru alloy.

centrations above 1 M because of the modest change in the solution conductivity. It has been reported that the decomposition/electrooxidation process of methanol on the Pt–Ru alloy can be explained by a bifunctional reaction mechanism; the methanol oxidation activity mainly depends on the surface structure of the Pt–Ru alloy and the Pt:Ru composition [13,27–28]. Fig. 4 shows current–time curve for 1 M methanol oxidation in a 1 M H<sub>2</sub>SO<sub>4</sub> solution at the electrode potential of 0.25 V SCE and 60 °C on the sputter-deposited Pt–Ru alloy. The oxidation current had a steep decrease during the first 10 min of the experiment, reaching a steady-state value. In the acidic solution, the catalytic activity of the sputter-deposited Pt–Ru alloy is lower than that of the carbon supported and unsupported Pt–Ru alloy catalyst reported in the literature [10,28].

Fig. 5 shows the performance of the acidic methanol fuel cell utilizing 1 M methanol as the fuel and 1 M H<sub>2</sub>SO<sub>4</sub> as the proton transport medium. The cell was operated at 40–80 °C with ambient air for the air cathode. It can be seen that the performance of the cell increased with temperature. The acidic methanol analyte solution does transport protons generated on the Pt–Ru anode catalyst layer to the membrane when the Pt–Ru alloy is remote from the Nafion membrane. The protons are transported through the acidic methanol solution to the membrane, for migration to the cathode. However, the

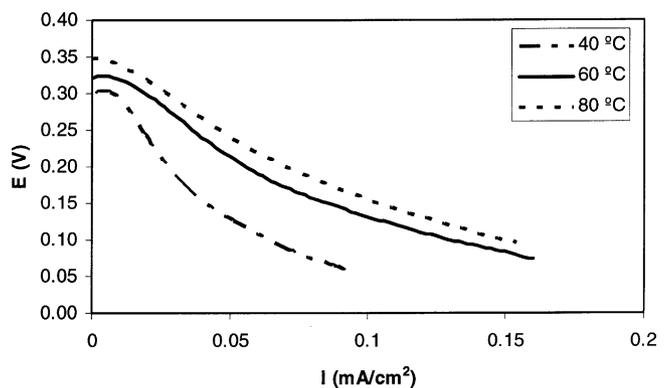


Fig. 5. Performance of the acidic methanol fuel cell utilizing 1 M methanol and 1 M H<sub>2</sub>SO<sub>4</sub> solution as the fuel and proton transport medium at different temperature.

performance of the acid methanol fuel cell was not as good as typical DMFCs where membrane electrode assemblies with high anode surface area are used. For example, typical DMFCs have an open circuit potential of 0.5–0.7 V and a current density of 0.3–0.6 A cm<sup>-2</sup> at 0.2 V and 90 °C [10], although results do vary considerably from study to study. The acidic methanol fuel cell had an open circuit potential of 0.35 V and the current density was about 0.1 mA cm<sup>-2</sup> at 0.2 V and 80 °C.

In order to determine the performance limiting components in the acidic methanol fuel cell, a series of half-cell studies were performed. Fig. 6 shows the current–voltage curves of the anode half-cell under the same condition as the acidic methanol fuel cell (Fig. 5). The performance of the anode is comparable to that of the full acidic methanol fuel cell. Therefore, the performance of the acidic methanol fuel cell appears to be mainly limited by the anode reaction. One reason for the modest anode current is that the sputter-deposited Pt–Ru alloy has a lower catalytic active surface area compared to the carbon supported Pt–Ru alloy particles. Another reason is that the protons generated on the anode have to pass through the interface between the anode and acidic methanol solution, acidic methanol solution, and the interface between acidic methanol solution and the membrane.

In the DMMFC using SiO<sub>2</sub> as the membrane, the anode half-cell experimental results indicated that the optimum Pt–Ru alloy catalyst loading on the membrane of the anode was 26–38 μg cm<sup>-2</sup>. The higher catalyst loading on the membrane led to decreased anode current because the porosity of the catalyst layer became lower and blocked proton transport into the membrane. Although the acidic methanol fuel cell described in Fig. 5 has modest performance, it shows that the anode catalyst loading in the DMMFC could be increased by depositing the Pt–Ru alloy on the supporting walls in the microchannel chamber and using the acidic methanol solution as fuel. Fig. 7 shows the performance of the anode half-cells with and without Pt–Ru alloy on the walls of the anode chambers in the microchannels using 1 M MeOH and 1 M H<sub>2</sub>SO<sub>4</sub> or 1 M MeOH as fuel at room temperature. The flow rate of the fuel was 1 ml h<sup>-1</sup>. After depositing more Pt–Ru alloy on

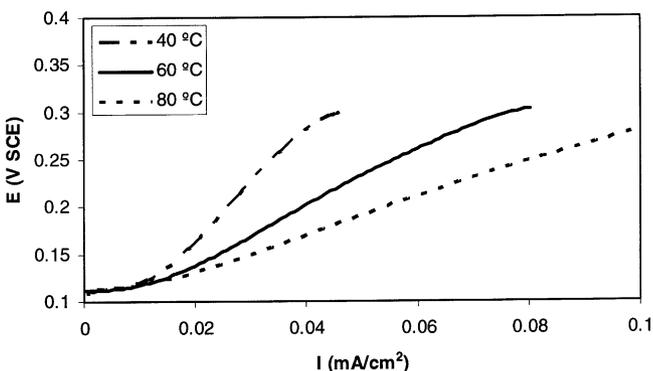


Fig. 6. Performance of the anode in the acidic methanol fuel cell utilizing 1 M methanol and 1 M H<sub>2</sub>SO<sub>4</sub> solution as the fuel and proton transport medium at different temperature.

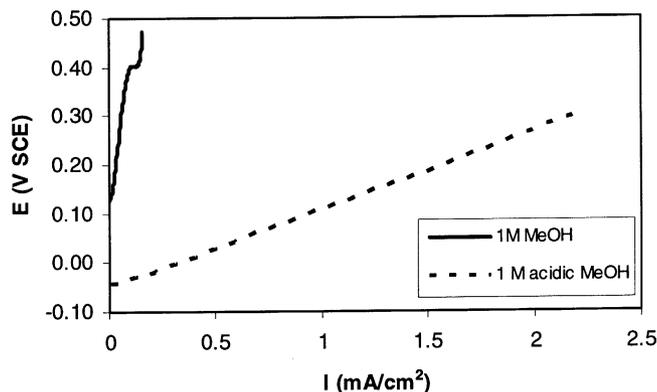


Fig. 7. Performance of the anodes with Pt–Ru alloy on the anode chamber wall in the microchannel using 1 M MeOH and 1 M H<sub>2</sub>SO<sub>4</sub> as the fuel and without Pt–Ru alloy on the anode chamber wall using 1 M MeOH as the fuel at the room temperature.

the anode wall in the microchannel, it can be seen that the performance of the anode improved significantly. The acidic methanol solution effectively increased the anode active surface area from just that on the membrane to that coating the anode-chamber wall. The use of the remote Pt/Ru catalyst and acidic methanol fuel is a particularly attractive option for use in microchannel-based fuel cells. The ability to fabricate an extended anode catalytic area in a DMMFC enables higher currents to be achieved compared to anodes restricted to the membrane surface only. Since steady-state operation would not change the acid content of the analyte, the optimum feed would be a methanol and water mixture.

#### 4. Conclusion

In the direct methanol microchannel fuel cells (DMMFC), SiO<sub>2</sub> was used as the proton exchange membrane, and a solid Pt–Ru alloy layer was directly sputter-deposited on the membrane as the anode catalyst and current collector. The Pt–Ru alloy thus produced has a lower catalytic activity than the carbon supported Pt–Ru alloy in a typical direct methanol fuel cell. For the microchannel fuel cell, the optimum Pt–Ru alloy loading on the membrane is 26–38 μg cm<sup>-2</sup> for compromising the oxidation rate of methanol, electrical conductance, and porosity. The anode catalyst loading in the DMMFC was increased by depositing Pt–Ru alloy on the wall of the channel and using an acidic methanol solution as the fuel. The protons generated on the catalyst on the anode chamber wall can be transported to the membrane through the acidic methanol. The performance of the anode thus made in the microchannel fuel cell is improved significantly.

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