

Short communication

## Fabrication of electrocatalyst layers for direct methanol fuel cells

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### Abstract

To optimize the performance of the membrane electrode assembly (MEA), a manufacturing process for electrocatalyst layers is systematically studied by controlling physical parameters such as electrocatalyst loadings at each electrode, electrocatalyst compositions, and layer thickness. The MEA is evaluated in an air-breathing direct methanol fuel cell (DMFC) with various methanol concentrations. The investigation focuses on finding the best compromise between electrocatalyst loadings and utilization of methanol concentration. Surprisingly, the power density is influenced more by the Pt loading than by the Pt–Ru loading, and can be increased further by using a methanol concentration above 3 wt.% for a certain level of electrocatalyst loading. Current–voltage characteristics indicate that increasing Pt and Pt–Ru loadings at each electrode can reduce the activation overpotentials, but the respective variation of current density with cell voltage differs in the voltage range (0.3–0.8 V). Although MEA performance can be improved by increasing the Pt (and Pt–Ru) concentration, a penalty is paid due to the tendency towards increased nanoparticle aggregation. The MEAs are also applied to a small pack of air-breathing DMFCs to assess their operability in mobile phones.

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*Keywords:* Direct methanol fuel cell; Membrane electrode assembly; Electrocatalyst loading and layer; Mobile phone; Power density; Methanol cross-over

### 1. Introduction

Fuel cells are promising power sources because of their potential suitability for many different applications, e.g., power stations, road transportation and small power-supply units [1–4]. Recently, many researchers [5–7] have returned to the direct methanol fuel cell (DMFC) because of its low operating temperature, use of liquid fuel, existing supply infrastructure, and less safety concerns compared with the proton-exchange membrane fuel cell (PEMFC). These advantages are particularly appropriate for portable electronic devices, which are widely seen as the first major commercial application for fuel-cell systems. Nevertheless, DMFCs suffer from the key problems of low power density and low fuel utilization, which are related respectively, to poor reaction kinetics and methanol permeation through the membrane (namely methanol cross-

over). Consequently, the performance of DMFCs must be enhanced by developing better MEA microstructures. That is, methanol cross-over has to be reduced by modifying the structure of Nafion membranes [8–10] or by designing new proton-conducting polymers [11], and the poor reaction kinetics have to be improved by finding more active electrocatalysts or by optimizing electrode structures. With respect to the electrode structure, physical parameters such as the electrocatalyst loading, the composition of the electrocatalyst itself and the porosity and thickness of the electrocatalyst layers have to be controlled. Although numerous studies [5,12,13] have examined the influence of these physical parameters on the performance of the DMFCs, a systematic study of the interaction of these physical parameters and their effect on cell performance appears to be lacking. For example, investigations are necessary of the effect of each electrocatalyst loading using different methanol concentrations, the effect of catalyst-layer thickness under different electrocatalyst compositions, and the effect of methanol concentrations at various electrocatalyst loadings. Therefore, this work explores

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the optimisation of MEA performance by adjusting the electrocatalyst loading, layer thickness and methanol concentration, as well as by correlating these controlled changes in the physical parameters with the results from cell tests.

The MEA performance is analyzed by measuring the maximum power density based on current–voltage characteristics. Also, four MEAs mounted in an air-breathing DMFC cell pack have been fabricated in-house to supply power, via a d.c.-to-d.c. converter, for a mobile phone operating in talk mode.

## 2. Experimental

### 2.1. Electrode inks

Catalysts of 40 wt.%Pt–20 wt.%Ru and 60 wt.%Pt were supported on a conductive carbon black with a high surface area. These, together with 60 wt.%Pt–30 wt.%Ru and 100 wt.%Pt catalysts, were purchased from Johnson Matthey, Inc. The mean particle size of the catalysts ranges between 2.5 and 4 nm. The anode ink was made by mixing 40 wt.%Pt–20 wt.%Ru/carbon black catalyst with 60 wt.%Pt–30 wt.%Ru catalyst and a fixed amount of 5 wt.% Nafion solution (DuPont) to enable the electrodes of the MEA to be fabricated at various electrocatalyst concentrations. The cathode ink was obtained from a mixture of 60 wt.%Pt/carbon black, 100 wt.%Pt and a fixed amount of 5 wt.% Nafion solution. The catalysts were rigorously stirred until the mixture became a smooth paste. These electrode inks were then applied directly on the membrane.

### 2.2. Fabrication of membrane electrode assembly

Nafion 117 membranes (DuPont) were used as membrane materials. After cleansing the membrane, a thin layer of electrode was coated on each surface by screen printing with the prepared catalysts. The MEAs, which consist of the electrocatalyst layers and the electrolyte membrane, were then hot pressed at 120 °C and 5–30 kg cm<sup>-2</sup> for 1–2 min. The electrode area of the MEA was 4 cm<sup>2</sup> and was coated with various Pt loadings at the cathode, while the Pt–Ru loadings at the anode were kept constant, and vice versa. This enabled assessment of the optimum content of the electrocatalyst loadings at each electrode. An MEA with an area of 25 cm<sup>2</sup> was also fabricated for an air-breathing DMFC cell pack to power a mobile phone.

### 2.3. Single-cell testing

The MEA was sandwiched between carbon cloths (purchased from ElectroChem. Inc. and used as diffusion layers) and then installed in a single-cell test fixture with two current-collectors. The current-collectors were made from 1.2 mm stainless-steel plates with a series of 3-mm diameter holes drilled to enable the passage of fuel or ambient air. The cell

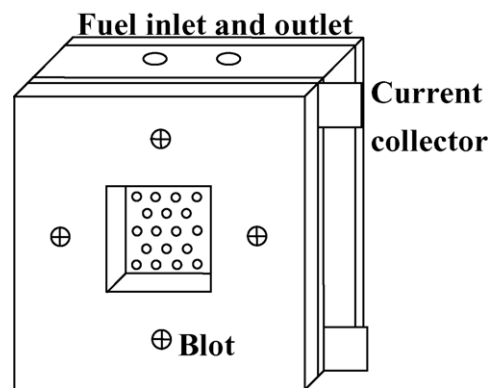


Fig. 1. Schematic diagram of experimental DMFC.

was held together between acrylic plates by means of a set of four retaining bolts that were positioned at the periphery of the cell. The experimental DMFC is shown schematically in Fig. 1. Tests on air-breathing DMFCs were performed at room temperature (~22 °C) with three different methanol concentrations (3, 6, and 9 wt.%). Current–voltage (polarization) curves were obtained with a test station equipped with a Chroma 63030 electronic load. The maximum power density of each MEA was determined from the fifth cycle of current–voltage curves to avoid the instability of the first few cycles. Each MEA was tested over several days (with one test per day) to assess the effect of time and environment on cell performance. The data indicated that the standard errors of the power densities ranged from ~5 to ~10% (note, the reported power density of each MEA was the average value of five to seven test points).

## 3. Results and discussion

### 3.1. Effect of electrocatalyst layer thickness on DMFC performance

This study evaluates the effect of the thickness of electrocatalyst layers fabricated with two different sets of electrocatalyst compositions, based on 40 wt.% Pt–20 wt.% Ru/C and 60 wt.% Pt/C, and on 50 wt.% Pt–25 wt.% Ru/C and 80 wt.% Pt/C, respectively. The maximum power density of each MEA was measured with a 3 wt.% methanol concentration at 22 °C and was normalized in terms of the total amount of Pt per cm<sup>2</sup> in both electrodes (here called specific power density, W g<sup>-1</sup> Pt). This procedure allows the performance of each MEA to be compared independent of the various amounts of Pt in the electrodes. The variation of specific power density is shown in Fig. 2 as a function of the total thickness of the electrocatalyst layers. As expected, the specific power density increases with decreasing total thickness for the same electrocatalyst composition. About a two-fold increase in specific power density is obtained when the total thickness is decreased from 177 to 70 μm. On the other hand, the specific

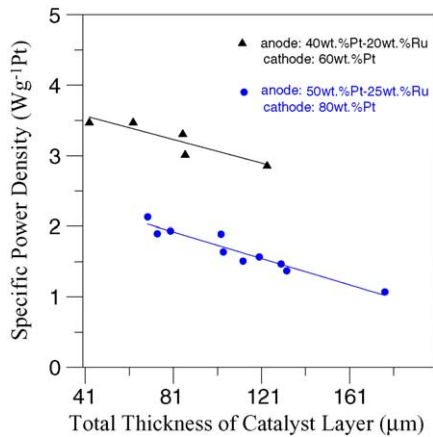


Fig. 2. Variation of specific power density with total thickness of electrode for air-breathing DMFC tested with 3 wt.% MeOH at room temperature (22 °C).

power density decreases to half of its initial value when the Pt–Ru and Pt concentrations are increased from 40–20 wt.% and 60 to 50, 25 and 80 wt.%, respectively, for a given layer thickness. Further examination of the data reveals that the power density increases slowly with total Pt loading, even if different electrocatalyst concentrations are used at each electrode, as illustrated in Fig. 3. Based on the experimental curves in Figs. 2 and 3, increasing electrocatalyst concentrations may slightly increase power density, but considerably decrease the specific power density for a given layer thickness. Thus, this investigation indicates that a high concentration of electrocatalyst in a thin electrocatalyst layer improves MEA performance, but suffers from the use of larger amounts of noble metals because of the greater tendency for nanoparticle aggregation at higher electrocatalyst concentrations. The lack of utilization of the electrocatalysts increases the cost of fabricating the MEA and therefore lowers the commercial viability of DMFCs. Accordingly, finding optimum electrocatalyst layers for MEAs not only requires maximizing cell performance, but also minimizing the utilization of noble-metal electrocatalysts.

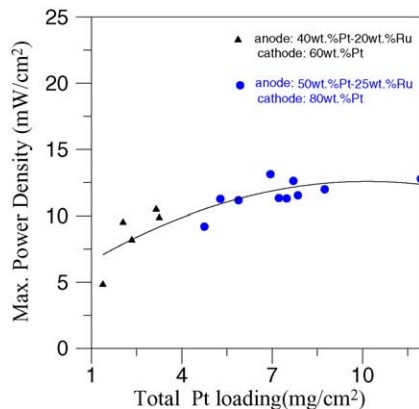


Fig. 3. Variation of maximum power density with total Pt loading on both electrodes for air-breathing DMFC tested with 3 wt.% MeOH at room temperature (22 °C).

### 3.2. Effect of Pt–Ru loading

The variation of maximum power density with Pt–Ru loading at the anode is shown in Fig. 4 for a given Pt loading at the cathode. The power density increases as the Pt–Ru loading is raised to 7.8 mg cm<sup>-2</sup>, and changes little at high Pt–Ru loadings. The slow increase in power density may result from concentration polarization (that is from slow transport of reactants/products to/from the electrochemical reaction sites) since the thickness of the catalyst layer becomes larger with increasing Pt–Ru loading. Notably, the power density of each MEA tested with 3 wt.% methanol concentration (MeOH) is higher than that tested with 6 wt.% MeOH for a low Pt loading of 2.6 mg cm<sup>-2</sup>, whereas the power density tested with 6 wt.% methanol concentration is higher than that tested with 3 wt.% for a high Pt loading of 7.6 mg cm<sup>-2</sup>. These observations suggest that the MEA performance can be improved by increasing the Pt loading at the cathode and simultaneously using a higher methanol concentration (i.e., 6 wt.% instead of 3 wt.% for the Nafion 117 membrane used in this study).

Close inspection of the current–voltage curves for MEAs with various Pt–Ru loadings, indicated in Fig. 5, shows that the current density in the high voltage range ( $\geq 0.5$  V) increases with the Pt–Ru loading. This phenomenon indicates that the activation overpotential (polarization), at the anode, which dominates at high cell voltages (i.e., low current densities), reduces with increasing Pt–Ru loading, whereas concentration polarization dominates at low cell voltages (i.e., high current densities). Interestingly, a recent study conducted at 80 °C [12] showed that the current density at a low cell voltage increased with increasing Pt–Ru loading, but abruptly decreased when the loading exceeded 3.75 mg cm<sup>-2</sup> due to mass-transfer resistance through the thicker catalyst layer at the cathode (i.e., concentration polarization). In the present investigation of an air-breathing DMFC tested at 22 °C, however, the current density at a low cell voltage increases with increasing Pt–Ru loading even when it reaches about 7.8 mg cm<sup>-2</sup>. This difference in behaviour from that reported by Nakagawa and Xiu [12] is not surprising since

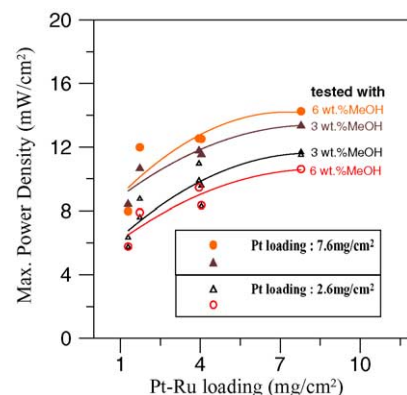


Fig. 4. Variation of maximum power density with Pt–Ru loading at anode tested with 3 wt.% MeOH and 6 wt.% MeOH for given Pt loading at cathode.

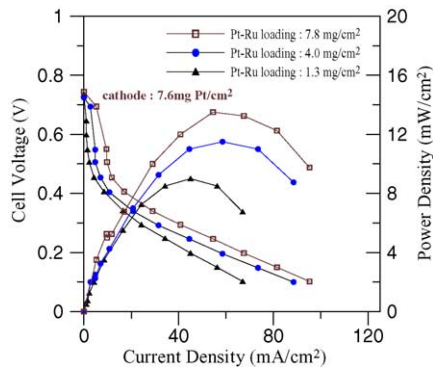


Fig. 5. Effect of Pt–Ru loading on performance for an air-breathing DMFC tested with 3 wt.% MeOH at room temperature (22 °C).

concentration polarization is known to depend on the electrode microstructures, and these are probably quite different in the two studies.

### 3.3. Effect of Pt loading

The variation of maximum power density with Pt loading at the cathode is shown in Fig. 6 for a given Pt–Ru loading at the anode. The power density increases with the Pt loading up to about 7 mg cm<sup>-2</sup>, and then declines as the Pt loading is raised to 10.5 mg cm<sup>-2</sup>. The latter behaviour is due to concentration polarization, as described in the previous section. Again, when cells are tested using different methanol concentrations, the power density of each MEA with 3 wt.% MeOH exceeds that with 6 and 9 wt.% MeOH if the Pt loading is <5 mg cm<sup>-2</sup>, and vice versa if the Pt loading is >5 mg cm<sup>-2</sup>. This is in good agreement with the results in Fig. 4 that showed that DMFC performance can be improved by increasing the Pt loading at the cathode and by using a higher methanol concentration. It is also inferred from Fig. 6 that a maximum power density of about 20 mW cm<sup>-2</sup> might be obtained at 22 °C from a MEA with commercial noble-metal loadings of about 7 mg cm<sup>-2</sup> at each electrode by using a 6 wt.% methanol concentration. Notably, the power density

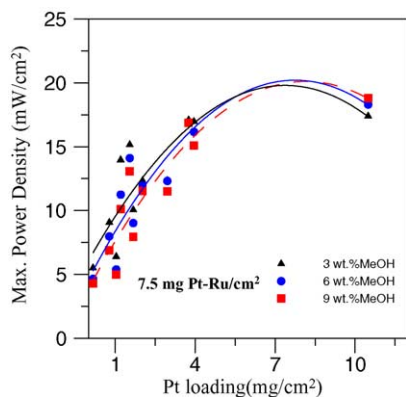


Fig. 6. Variation of maximum power density with Pt loading at anode tested with 3, 6 and 9 wt.% MeOH for a given Pt–Ru loading at anode.

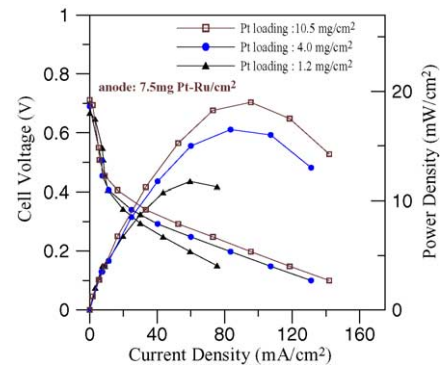


Fig. 7. Effect of Pt loading on performance for air-breathing DMFC tested with 6 wt.% MeOH at room temperature (22 °C).

is influenced more significantly by the Pt loading than by the Pt–Ru loading, as clearly indicated by the steep rise in power density in Fig. 6 and the gentle rise in Fig. 4.

The reason why MEA performance can be improved by increasing the Pt loading can be explained by a close examination of current–voltage curves presented in Fig. 7. These reveal that current density increases with Pt loading in the medium voltage range of 0.3–0.5 V. In other words, the voltage increases with Pt loading in the low current density range of 10–20 mA cm<sup>-2</sup>, which suggests that an increase in Pt loading at the cathode also reduces the activation polarization. Accordingly, increasing Pt loadings at the cathode and Pt–Ru loadings at the anode can reduce the activation polarization, but with a different variation in current density with cell voltage in the range of 0.3–0.8 V. While the current density increases with the Pt–Ru loading in the high voltage range (>0.5 V), as illustrated in Fig. 5, the current density increases with the Pt loading in the medium voltage range (0.3–0.5 V), as illustrated in Fig. 7. By comparing Figs. 5 and 7, it can be easily understood how the Pt–Ru loading at the anode and Pt loading at the cathode affect the activation polarization. The positive influence of cathode Pt loading on activation polarization can be further explained by the methanol crossover that forces high Pt loadings on the cathode. A large part of the catalyst becomes inhibited by the methanol so that an excess of catalyst has to be provided to sustain the oxygen reduction reaction.

### 3.4. Effect of methanol concentration

The methanol concentration at the anode has a crucial influence on DMFC performance. If the methanol concentration is too high, methanol cross-over through membrane will be increased so that the methanol is oxidized at the cathode. This in turn reduces the cell voltage due to the formation of a mixed potential at the cathode. Therefore, methanol cross-over will decrease mass efficiency as well as voltage efficiency [14,15]. Typical current–voltage characteristics at methanol concentrations of 3 and 6 wt.% are shown in Fig. 8 for an air-breathing DMFC with high electrocatalyst loadings. As expected, a high methanol concentration of 6 wt.%



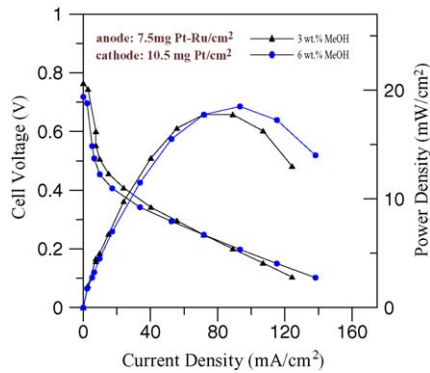


Fig. 8. Effect of methanol concentration on performance for air-breathing DMFC tested with 3 and 6 wt.% MeOH at room temperature (22 °C).

reduces the cell voltage in the low current density range ( $\leq 20 \text{ mA cm}^{-2}$ ), due to the higher methanol cross-over; but leads to a higher cell voltage in the high current density range ( $\geq 70 \text{ mA cm}^{-2}$ ). This is because the methanol permeation rate decreases with increasing current density due to the elevated fuel consumption in the anode catalyst layer. The mechanism results from the methanol cross-over being affected by diffusion through the membrane and by additional electro-osmotic drag due to proton transport through the membrane [15,16]. The diffusive fraction of the methanol cross-over is influenced by a concentration difference between the anode and the cathode. The electro-osmotic fraction, on the other hand, is influenced mainly by the current density and the methanol concentration at the interface between the anode catalyst layer and the membrane [17]. Therefore, the maximum power density with 6 wt.% methanol concentration is higher than that with 3 wt.%. A further increase of methanol concentration from 6 to 9 wt.% only slightly increases the maximum power density, as shown in Fig. 9. Another reason for the increase in the maximum power density with concentration is the reduced mass-transport limitations at the anode with more concentrated methanol.

The typical variation of maximum power density with methanol concentrations at various Pt loadings is shown in Fig. 10. The maximum power density declines as the

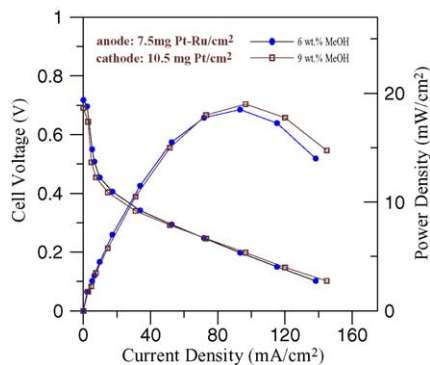


Fig. 9. Effect of methanol concentration on performance for air-breathing DMFC tested with 6 and 9 wt.% MeOH at room temperature (22 °C).

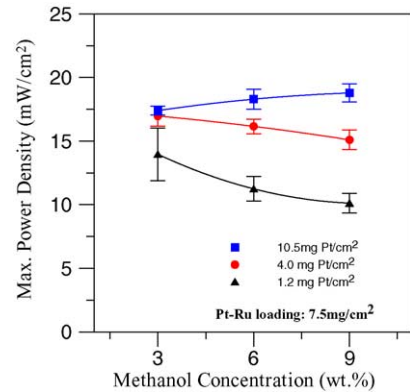


Fig. 10. Variation of maximum power density with methanol concentration at various Pt loadings for air-breathing DMFC tested at room temperature (22 °C).

methanol concentration is increased from 3 to 9 wt.% when the Pt loading is low ( $1.2 \text{ mg cm}^{-2}$ ). By contrast, the curve gently falls with increasing methanol concentration when the Pt loading is increased to  $4.0 \text{ mg cm}^{-2}$  and then turns upward when the Pt loading is further increased to  $10.5 \text{ mg cm}^{-2}$ . This phenomenon occurs because the activation polarization is reduced with increasing Pt loading, and because the rate of methanol permeation declines at the high current density range at which the maximum power density is determined. This is consistent with the results presented in Figs. 4–9 that show the relationships between maximum power density, noble metal loading, and methanol concentration. Given these findings, the methanol concentration can be adjusted to an optimum value that represents the best compromise between Pt loading at the cathode and Pt–Ru loading at the anode in order to improve MEA performance.

### 3.5. DMFC cell pack

Using the fabrication process conditions described above, an attempt was made to fabricate MEAs to evaluate their operability in an air-breathing DMFC cell pack, it should be noted, however, that flooding of the cathode by product water appears to be a major limitation for portable electronic applications, as reported in our previous work [5]. A small air-breathing DMFC cell pack with four unit cells is shown in Fig. 11. The cells are connected in series to meet the voltage requirement of the power conditioning for mobile phones. The outer dimensions of the pack are only  $7.0 \times 8.0 \times 2.5 \text{ cm}$ . The cathodes are on both sides of the pack and are simply exposed to ambient air at room temperature. The 3.0 wt.% methanol solution is stored between the two sub-modules. Each sub-module consists of two unit cells and each cell has an active area of  $25 \text{ cm}^2$ . The maximum power output of this module is  $\sim 1.2 \text{ W}$  at  $0.95 \text{ V}$  and the maximum power density of each MEA is  $\sim 12 \text{ mW cm}^{-2}$ . This fuel cell, via the d.c.-to-d.c. converter, can supply power for continuously operating a mobile phone in talk mode. Fuel utilization is



Fig. 11. Mobile phone powered by air-breathing DMFC cell pack.

measured simply by running a mobile phone of Nokia 3310 in talk mode. A mobile phone can sustain 50 min of talk when 1.0 ml methanol is fed into the cell pack (i.e., the effective energy density of the fuel is about  $800 \text{ Wh l}^{-1}$ ).

#### 4. Conclusions

The performance of MEAs has been studied systematically by adjusting the electrocatalyst loading at each electrode, the composition of the electrocatalyst itself, and the thickness of the electrocatalyst layers. The following conclusions can be drawn.

1. The power density is influenced more significantly by the Pt loading than by the Pt–Ru loading, and can be further increased by using a higher methanol concentration if the noble metal loading is increased to a certain level at each electrode (around  $5 \text{ mg cm}^{-2}$  in this work).
2. Based on current–voltage characteristics, increasing the Pt loading at the cathode and Pt–Ru loading at the anode may reduce the activation polarization, but will give a different variation in current density with cell voltage. The current density increases with the Pt–Ru loading in the high voltage range ( $>0.5 \text{ V}$ ), whereas it increases with the Pt loading in the medium voltage range ( $0.3\text{--}0.5 \text{ V}$ ).
3. Increasing the electrocatalyst concentrations may slightly increase power density, but considerably decrease the specific power density for a given layer thickness.

4. The maximum power density declines as the methanol concentration is increased from 3 to 9 wt.% at low Pt loadings. By contrast, the curve gently falls with increasing methanol concentration and then turns upward when the Pt loading is raised from  $1.2$  to  $4.0 \text{ mg cm}^{-2}$  and then to  $10.5 \text{ mg cm}^{-2}$ . This phenomenon occurs because the activation polarization reduces with increasing Pt loading, and the methanol permeation rate declines at high current densities.

Based on the above results, it is possible to infer that a maximum power density of about  $20 \text{ mW cm}^{-2}$  can be obtained at  $22^\circ\text{C}$  from a MEA with commercial electrocatalysts by using a 6 wt.% methanol concentration. Finally, the MEAs demonstrate that a mobile phone can sustain 50 min of talk when 1.0 ml methanol is fed into an air-breathing DMFC cell pack.

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