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# DIRECT METHANOL FUEL CELLS AT REDUCED CATALYST LOADINGS

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## ABSTRACT

We focus in this paper on the reduction of catalyst loading in direct methanol fuel cells currently under development at Los Alamos National Laboratory. Based on single-cell DMFC testing, we discuss performance *vs.* catalyst loading trade-offs and demonstrate optimization of the anode performance. We also show test data for a short five-cell DMFC stack with the average total platinum loading of  $0.53 \text{ mg cm}^{-2}$  and compare performance of this stack with the performance of a single direct methanol fuel cell using similar total amount of precious metal.

## INTRODUCTION

Prospective applications of a direct methanol fuel cell (DMFC) range from replacing batteries in portable electronic devices to providing power for automobiles of the future. Thanks to high energy density of methanol,  $6.1 \text{ kWh kg}^{-1}$  at  $25^\circ\text{C}$ , DMFC offers significant advantage over today's batteries, particularly at longer operating times. After accounting for the fuel cell stack and system power losses (balance-of-plant losses), the realistic energy density of DMFCs for portable power applications is expected to reach at least  $1.0 \text{ kWh kg}^{-1}$ , *i.e.*, 5-10 times higher than the energy density of advanced batteries. In addition to portable use, DMFCs are being considered for automotive applications as a source of main and/or auxiliary power. In either case, by eliminating the reformer, direct methanol fuel cells promise simpler system design and potentially higher overall efficiency than the reformate-fed fuel cells.

DMFC research at Los Alamos National Laboratory (LANL) has focused on two potential applications: (i) portable power source for the military (50-100 W power level) and consumer electronics (*e.g.*, cellular phones), and (ii) primary and/or auxiliary power for automotive transportation. Depending on specific application, the temperature and pressure of cell operation, catalyst loading and cell design may differ, however, most factors affecting DMFC performance are likely to remain the same regardless of the intended DMFC use. In earlier communications [1-3], we were able to demonstrate the first LANL five-cell DMFC stack, operating at conditions relevant to automotive applications, *i.e.*, at elevated temperature ( $90\text{-}100^\circ\text{C}$ ) and above-ambient pressure of air (up to 2.8 atm). The stack, which had originally been built for portable power

applications (DARPA-funded research project), generated maximum power density per active stack volume of  $1.1 \text{ kW L}^{-1}$ , yet at high Pt loading, corresponding to  $54 \text{ mg Pt W}^{-1}$  at the point of maximum aerial power density ( $0.21 \text{ W cm}^{-2}$ ). In this presentation, we show significant power densities obtained with substantially reduced precious metal loading in the anode and cathode catalyst layers. This research, aimed specifically at prospective high-power applications of DMFC in automotive transportation, has been performed in single cells with a total platinum loading as low as  $0.2 \text{ mg cm}^{-2}$  and in a short five-cell stack containing  $0.53 \text{ mg}$  of Pt per  $\text{cm}^2$  of the membrane-electrode assembly (MEA).

## EXPERIMENTAL

45- $\text{cm}^2$  membrane-electrode assemblies were used in all single cells and a short stack studied in this work. Pretreatment of the Nafion<sup>®</sup> 117 membrane and MEA preparation have been previously described [3,4], as has the cell testing system used [5,6]. The anodes were prepared using developmental samples of either Pt-Ru black or 67% (wt.) Pt-Ru supported on carbon (Johnson Matthey). Anode inks were made by dispersing appropriate amounts of the Pt-Ru catalyst in the Millipore purity water and adding 5% Nafion<sup>®</sup> solution (1200 in equivalent weight, Solution Technology Inc.). Cathode inks contained either unsupported Pt black ( $30 \text{ m}^2 \text{ g}^{-1}$ , Johnson-Matthey) or 40% (wt.) Pt on carbon (E-Tek, Inc.) mixed with Millipore water and 5% Nafion<sup>®</sup> solution (1200 equivalent weight, Solution Technology Inc.). In some cases, rather than using the decal technique [3], catalyst layer preparation involved direct application of catalyst inks to the membrane.

Methanol solutions, between 0.2 and 2.0 M in concentration, were pumped through the DMFC anode flow field at precisely controlled rates using a Shimadzu LC-10AS HPLC pump in case of single-cell testing and a Masterflex L/S peristaltic-digital pump for feeding the short stack. Anode exhaust was pressurized to 1.0-2.0 atm to ensure that the membrane would be in contact with a liquid solution of methanol at the cell operating temperature. The backpressure of air was typically between 1.0 and 2.0 atm. The air was pre-humidified at the same or slightly higher temperature than the cell operating temperature.

MEAs were usually conditioned in the H<sub>2</sub>/air fuel cell operating mode for between two to four hours before being used in a DMFC. In addition to full-DMFC testing, the activity of the anode was determined from the anode polarization plots. In this case, rather than in fuel cell mode, the cell was operated in a “driven mode”, with well-humidified hydrogen gas flown through the cathode chamber. A linear potential scan was then applied to the cathode at a rate of  $2 \text{ mV s}^{-1}$  in a typical potential range of 0.1-0.5 V, with the fuel cell cathode serving as a dynamic hydrogen reference/counter electrode, DHE.

The  $iR$ -corrected current density of methanol oxidation at 0.35 V vs. DHE was then used as a measure of the DMFC anode activity at various catalyst loadings.

All measurements reported in this paper were performed at either 100 or 110°C.

## RESULTS AND DISCUSSION

### Single Cell Performance at Low Catalyst Loading

A trade-off between the peak power density and total platinum loading is demonstrated in **Figure 1** for two single 45-cm<sup>2</sup> DMFCs. Unsupported Pt-Ru and Pt black were used only in the cell with the highest total Pt loading (16.6 mg cm<sup>-2</sup>). In all other cases, carbon-supported catalysts were used. As reported earlier by Witham *et al.* in their work with sputtered Pt-Ru DMFC anodes [7], a reduction in the catalyst loading leads to noticeably diminished, yet by no means insignificant, fuel cell performance. In this work, more than a twenty-fold drop in the amount of platinum, from 16.6 to 0.8 mg cm<sup>-2</sup>, resulted in a tolerable 32-33% decrease in the maximum power density at either 100 or 110°C. The obtained cell performance with a total Pt loading of 0.8 mg cm<sup>-2</sup> corresponds to 5.5 and 4.9 mg of Pt per one watt of peak power at 100 and 110°C, respectively.

Lower values of mgPt/W(peak) were measured at further reduced total platinum loading, however at a more substantial penalty in the peak power density (**Tables 1** and **2**). In the most extreme case of total platinum loading close to 0.2 mg cm<sup>-2</sup>, the amount of Pt required to generate one watt of power was found to be 1.6 mg at 100°C and 1.4 mg at 110°C. Corresponding peak power density values drop in this case to 0.115 W cm<sup>-2</sup> (100°C) and 0.130 W cm<sup>-2</sup> (110°C), *i.e.*, to only a little more than half of the peak power measured with the highest total platinum loading of 16.6 mg cm<sup>-2</sup>. Although a 360-fold drop in the amount of precious metal between the cells with the highest and the lowest loading is very significant, the decrease in the maximum power density by almost half may render the use of this and similar ultra-low catalyst loadings unpractical, at least at the present stage in the development of DMFC technology. Based on the data presented in Figure 1 and Tables 1 and 2, cells with the total platinum loading in the vicinity of 1 mg cm<sup>-2</sup> may offer a better choice overall, especially at longer cell operating times (not reported in this work).

Cathode air pressure has a significant effect on the cell performance. The current density drops by as much as a factor of two when the backpressure changes from 0.7 to 2 atm (**Figure 2**). In the case shown in Figure 2, platinum was approximately equally distributed between the anode and the cathode. Considered that total Pt loading in the cell was 0.53 mg cm<sup>-2</sup>, the cathode loading did not exceed *ca.* 0.25 mg cm<sup>-2</sup>. Consequently, the number of reaction sites at the cathode to simultaneously reduce oxygen from the air and oxidize methanol permeating through the membrane was very

limited. At 100-110°C and 1.0 M feed concentration of methanol, the crossover can easily reach a level that, expressed in terms of the equivalent current density, should give 0.15-0.17 A cm<sup>-2</sup> at the open cell voltage. Although crossover drops once current is drawn from the cell, it remains relatively high in the cells with reduced catalyst loadings compared to the cells significantly greater catalyst loading. Consequently, DMFC cathodes operated at low Pt loading are likely to be more sensitive to the changes in the air pressure than electrodes with containing large amount of the Pt catalyst.

**Table 1**  
**Single cell performance data at 100°C**

Other than the highest loading case (shown in italic) all cells used carbon-supported anode and cathode catalysts, as described in the Experimental section above.

Total Pt Loading (mg cm <sup>-2</sup> )	mg / W(peak)	Peak Power (W cm <sup>-2</sup> )
<i>16.6</i>	73.8	0.225
1.1	6.2	0.180
0.8	5.5	0.150
0.5	3.8	0.140
0.4	2.8	0.135
0.2	1.6	0.115

**Table 2**  
**Single cell performance data at 110°C**

Other than the highest loading case (shown in italic) all cells used carbon-supported anode and cathode catalysts, as described in the Experimental section above.

Total Pt Loading (mg cm <sup>-2</sup> )	mg / W(peak)	Peak Power (W cm <sup>-2</sup> )
<i>16.6</i>	66.0	0.250
1.9	10.0	0.190
1.1	6.1	0.185
0.8	4.9	0.170
0.4	2.7	0.140
0.2	1.4	0.130

Thanks to high quality air cathodes designed at LANL, good DMFC performance can be still achieved in spite of greatly reduced cathode catalyst loading and low flow of air. As shown in **Figure 3**, 90% of maximum power density is reached with the air flow only 3

times stoichiometric. A sharp drop in the cell performance is observed only after the air flow is reduced below 2.8 times stoichiometric at 110°C and below 2 times stoichiometric at 100°C.

Achieving good fuel cell performance required careful selection of the anode and the cathode catalysts for DMFC operation with low catalyst loading. It also required a thorough optimization of the catalyst composition and structure. Unlike applications that focus on the maximization of DMFC performance with less attention being paid to lowering precious metal loading (generally, low-power portable cells), fuel cells operating at reduced catalyst loading seem to benefit from the use of carbon-supported catalysts. As shown by the anode polarization data in **Figure 4**, this is clearly the case for the DMFC anodes. In this figure, current density of methanol oxidation at a reference potential of 0.35 V vs. DHE has been plotted against the loading of platinum in the catalyst layer. Comparison of the activity of an unsupported 1:1 Pt-Ru catalyst (Johnson Matthey) with the activity of three different formulations using carbon-supported Pt:Ru catalyst (45% carbon by weight, Johnson Matthey) shows that carbon-supported anodes outperform the unsupported one as long as Pt loading remains below *ca.* 1 mg cm<sup>-2</sup>. This is likely due to better catalyst utilization in case carbon-supported catalyst. Metal particles supported on carbon are expected to agglomerate less than particles of the unsupported catalyst thus leaving more surface area (higher number of electrocatalytic sites) accessible to methanol. This advantage is lost at higher loadings of the carbon-supported catalyst because of mass transport limitations resulting from the fact that the thickness of a carbon-supported catalyst increases much faster than that of its unsupported counterpart.

Optimization of the catalyst layer composition and structure is often as important as choosing the right catalyst material. Also, separate optimization procedures may be required for various intended catalyst loadings. For example, out of three different Pt-Ru/C catalyst formulations shown in Figure 4, formulation (3) performs the best in the Pt loading range between 0.3 and 1.1 mg cm<sup>-2</sup>, while formulation (1) appears to offer an edge at the lowest anode catalyst loadings, below 0.2 mg of Pt per cm<sup>2</sup>.

#### Operation of a Five-Cell DMFC Stack at Low Catalyst Loading

Short five-cell DMFC stack was built using membrane-electrode assemblies like those used in single-cell testing above. Platinum loading of the stack MEAs was  $0.53 \pm 0.02$  mg cm<sup>-2</sup>. Platinum was equally distributed between the anode and the cathode, with the respective loadings equal to  $0.26 \pm 0.01$  mg cm<sup>-2</sup> and  $0.27 \pm 0.01$  mg cm<sup>-2</sup>. When operated on pressurized air at 100°C, the stack generated almost 0.2 A cm<sup>-2</sup> at 2.0 V and the maximum power density of 26 W at a current density of *ca.* 0.45 A cm<sup>-2</sup> (**Figure 5**). For comparison, power density achieved at 100°C by a similar stack with a high Pt loading of nearly 12 mg cm<sup>-2</sup> was found to be 48 W under very similar cathode operating conditions [3]. Thus, the decrease in the platinum loading by a factor of about 23 has led to the 46%

reduction in the maximum power density of the stack. The five-cell stack performance near the maximum power point corresponds to approximately 5 mg of Pt per one watt of generated power (**Figure 6**).

As shown in **Figure 7**, the average cell performance in the stack is below that of a single cell with the same total platinum loading,  $0.53 \text{ mg cm}^{-2}$ . For example, the difference in the measured cell voltages at a current density of  $0.2 \text{ A cm}^{-2}$  is around 40 mV, which represents a noticeable performance loss. This loss results from non-uniform operation of the individual cells in the stack (**Figure 8**). Performance of the cells was found to vary continuously, with different cells showing better performance than others at various times of stack operation. This phenomenon, not observed before at much higher stack catalyst loading [3], is likely related to the extremely low amount of catalyst used in the present stack. With limited number of available reaction sites, the cathode becomes highly sensitive to any mal-distribution in the air flow and other effects, such as the flooding of the oxygen reduction sites. Planned modification of the stack hardware is expected to help rectify the problem and achieve further improvement in the performance of the future stacks with ultra-low catalyst loadings.

## SUMMARY

Thanks to the earlier progress in the anode electrocatalysis, improvements in the MEA fabrication techniques, new hardware design and optimization of the backing material properties, there is a real chance for operating direct methanol fuel cells with a significantly reduced precious metal loading. As follows from the present study, the catalyst loading in a single DMFC and short stack can be reduced by as much as one order of magnitude. The performance penalty brought about by such a reduction in the catalyst loading, although significant, may ultimately be judged acceptable, depending on specific application.

As found in this work, once the amount of the catalyst is substantially reduced, the anode and cathode composition and structure need to be optimized. This optimization is likely to involve a selection of different catalysts than those used in the cells with higher loading, in particular moving away from the unsupported metallic blacks, typically used in DMFCs for prospective low power applications, to carbon supported catalysts. For as long as the amount of the carbon-supported catalyst remains low, the mass-transport hindrance is insignificant thus allowing the system benefit from the generally better catalyst utilization achieved with carbon-supported materials.

Although cells operating with as little as  $0.2 \text{ mg cm}^{-2}$  of platinum have been fabricated and successfully tested in this work, it appears that the corresponding performance penalty and, even more importantly, poor long-term-stability of the single cell/stack may render an extreme reduction in the catalyst loading impractical. With the current state-of-the-art in DMFC research and development, somewhat higher platinum loadings, in the

range between 0.5 and 1.0 mg cm<sup>-2</sup>, may represent a compromise between cell performance and catalyst cost. Further lowering of the loading will most likely become contingent upon the increase in the intrinsic activity of the anode catalyst and lowering of methanol crossover that, at present, limits the performance of the cathode. This closely ties the catalyst loading reduction with the progress in the research specifically targeting the development of a methanol-impermeable (and high-temperature) proton exchange membrane. Finally, in the context of observed unevenness in the operation of individual cells in the short five-cell stack, a careful design of the cell hardware may turn out to have considerable impact on the performance of DMFC stacks with reduced total precious metal loadings, much more so than in the case of stacks with higher platinum content, so far demonstrated by various research groups [3,8-10].

## ACKNOWLEDGMENTS

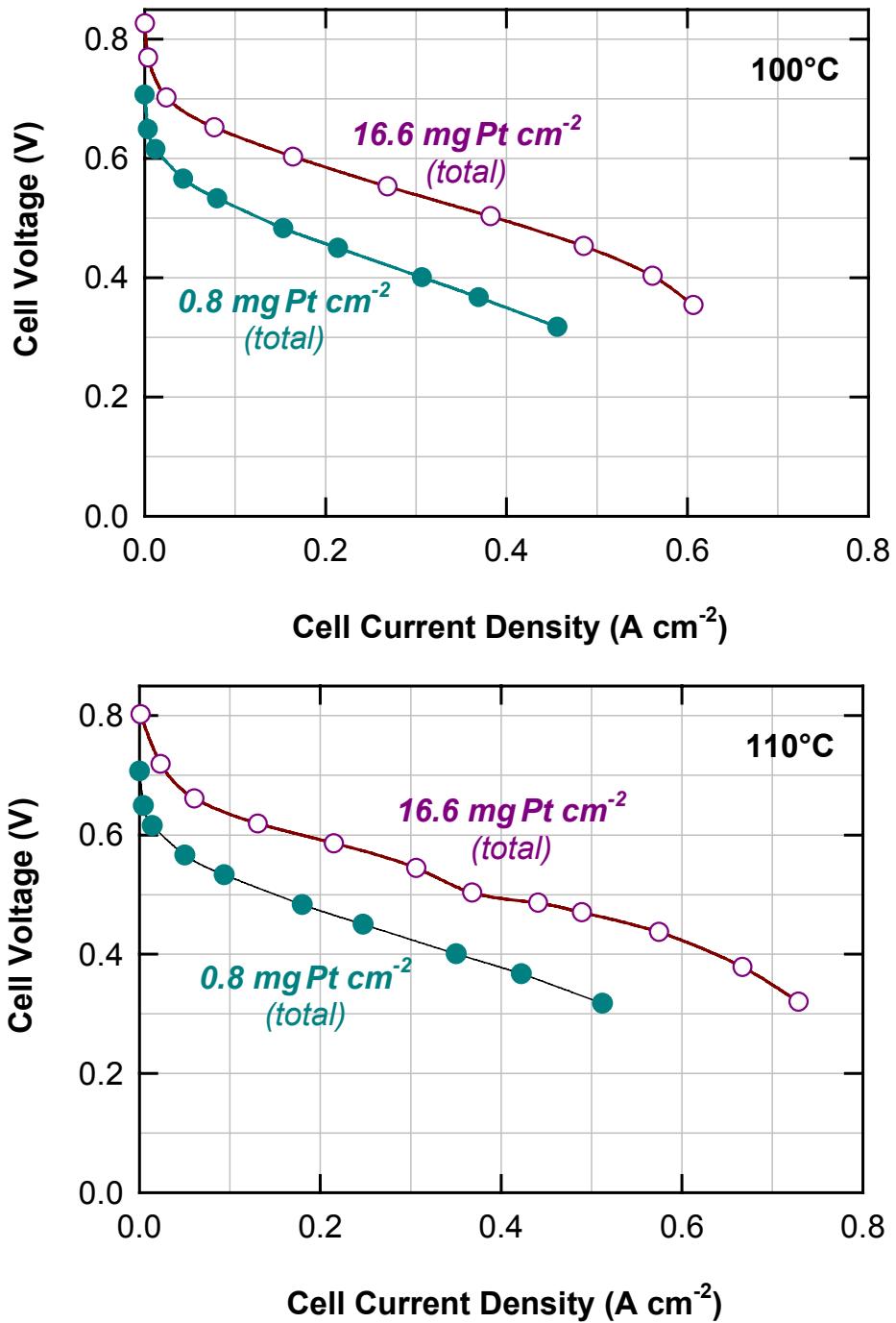
This work was supported by the U.S. Department of Energy through the Office of Advanced Automotive Technology and by the Defense Advanced Research Projects Agency (DARPA) through the Defense Sciences Office.

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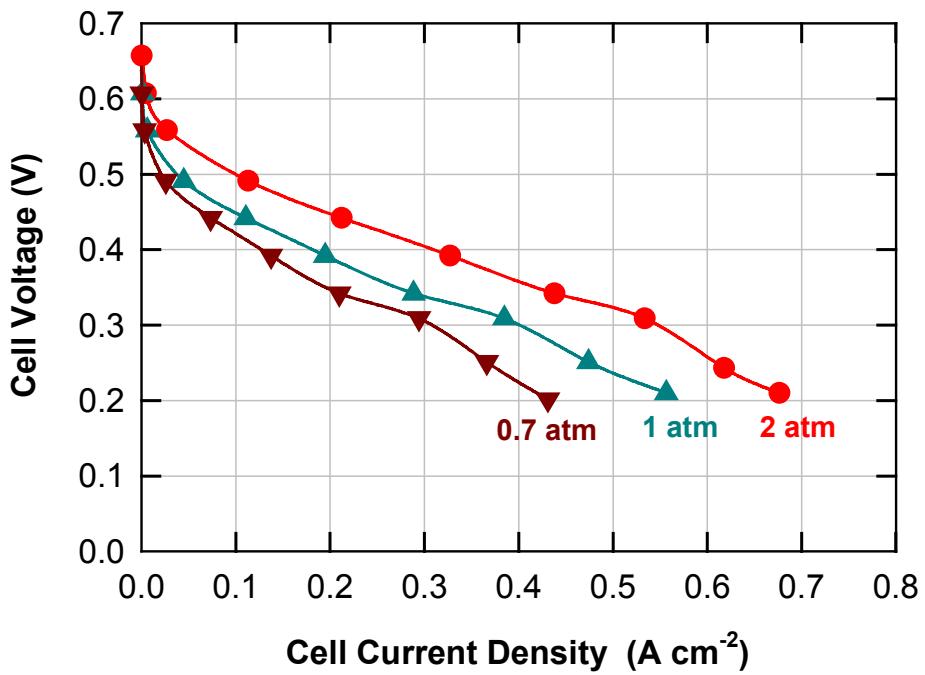
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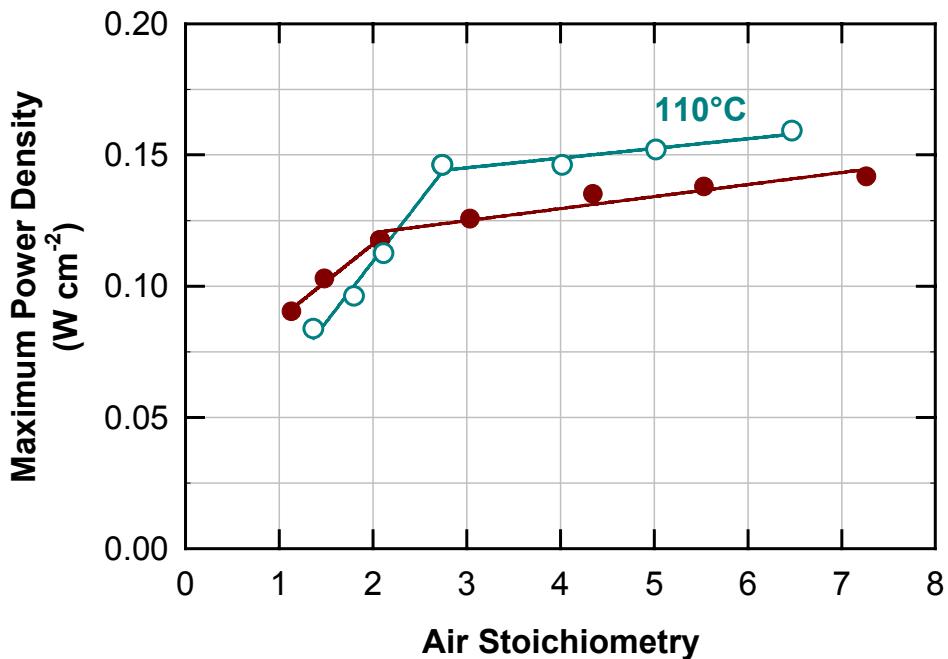
## FIGURES



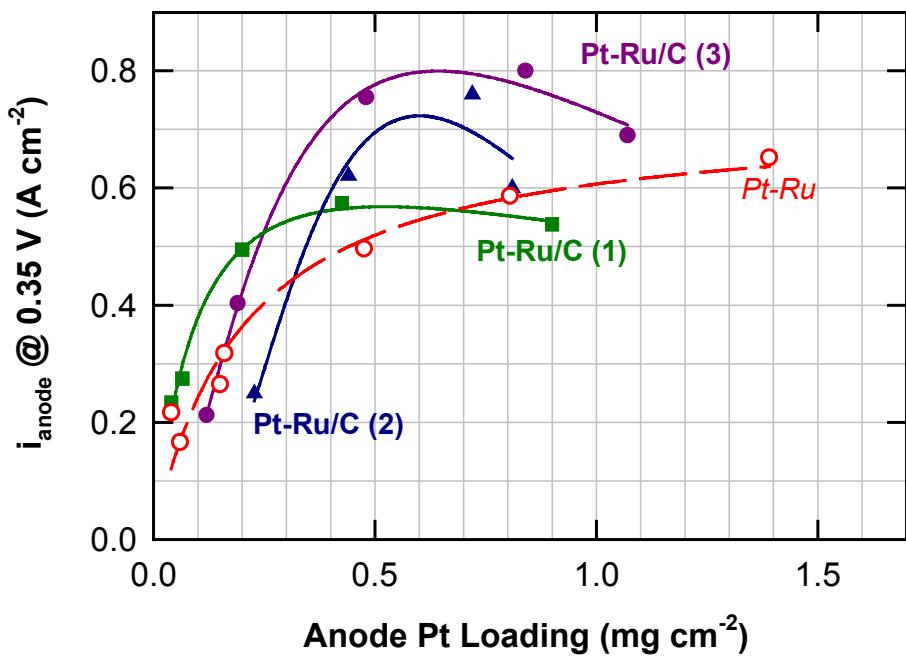
**Figure 1.** DMFC performance with different total Pt loadings at 100°C and 110°C. 1.0 M MeOH at  $7 \text{ mL min}^{-1}$ ;  $0.4 \text{ L min}^{-1}$  air flow at 2.0 atm cathode backpressure.



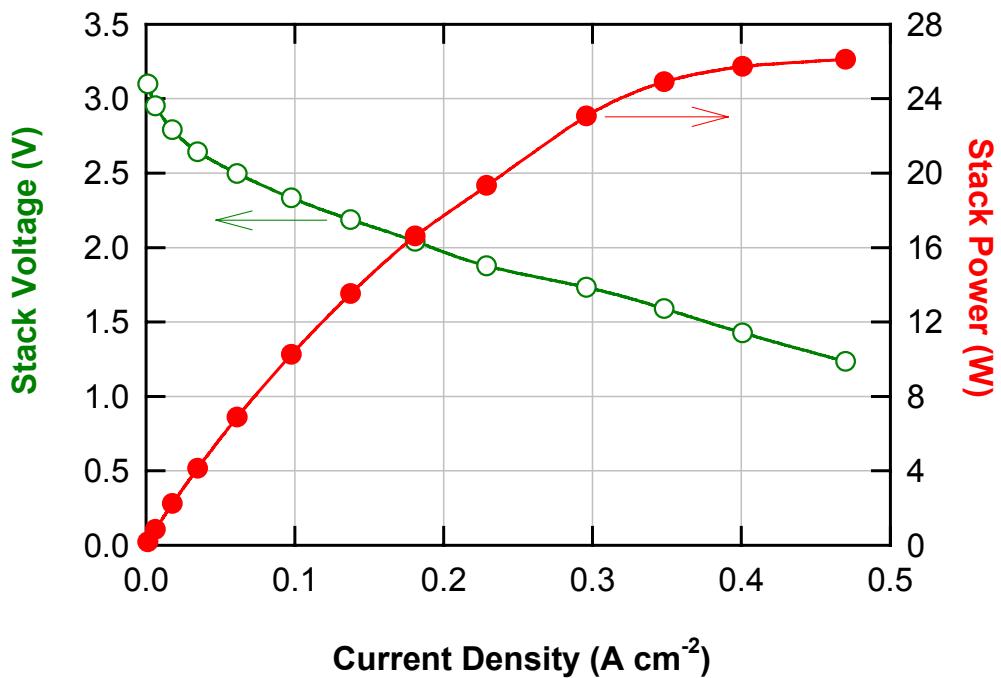
**Figure 2.** Effect of backpressure of air on DMFC performance at 110°C. Total Pt loading 0.53 mg  $\text{cm}^{-2}$ ; 1.0 M MeOH at 7  $\text{mL min}^{-1}$ ; air flow 0.4  $\text{L min}^{-1}$ .



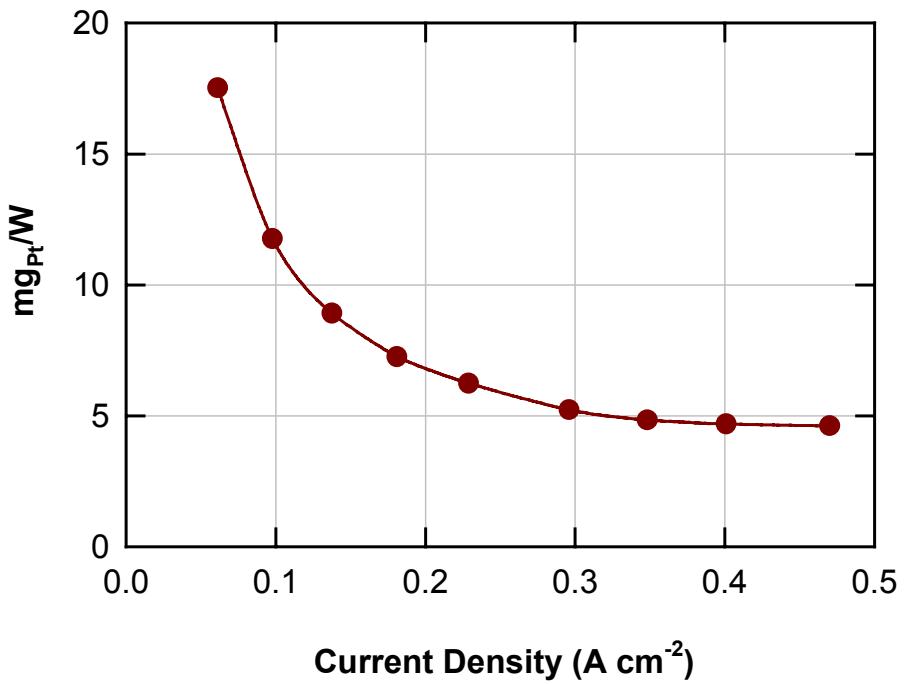
**Figure 3.** Maximum power density as a function of air stoichiometry at 100°C and 110°C. Total Pt loading 0.53 mg  $\text{cm}^{-2}$ ; 1.0 M MeOH at 7  $\text{mL min}^{-1}$ ; 2.0 atm backpressure of air.



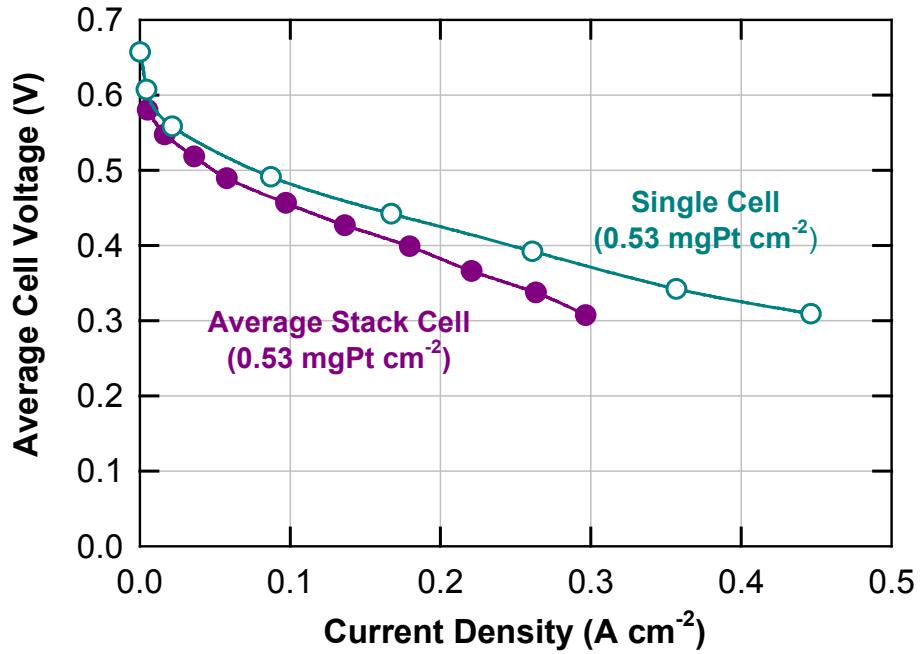
**Figure 4.** Electrocatalytic activity of different Pt-Ru anodes as a function of Pt loading in the catalyst layer. Current density of methanol oxidation was determined from the anode polarization plots at a potential of 0.35 V vs. DHE.



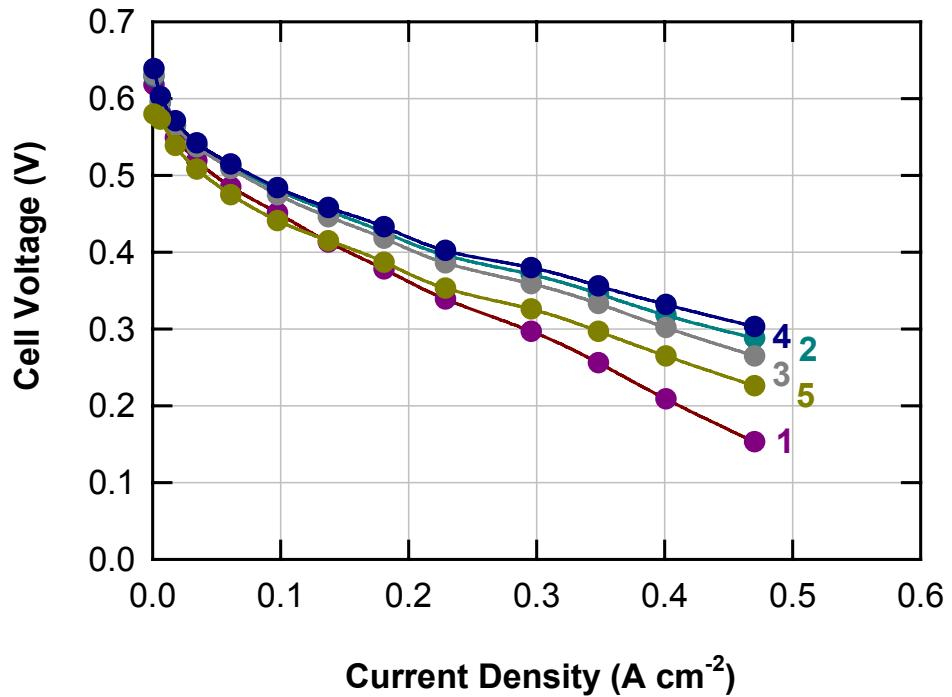
**Figure 5.** Performance of the five-cell DMFC stack at 100°C. Total Pt loading 0.53 mg cm⁻²; 1.0 M MeOH at 35 mL min⁻¹; air flow 2.0 L min⁻¹.



**Figure 6.** Platinum loading per one watt of generated power as a function of the stack current density at 100°C. Stack operating conditions as in Figure 5.



**Figure 7.** Comparison of the average cell performance in the five-cell stack with the performance of a single-cell DMFC of the same total Pt loading ( $0.53 \text{ mg cm}^{-2}$ ) at 100°C. Stack operating conditions as in Figure 5. Anode and cathode feeds in the single cell were one-fifth of those used in the stack.



**Figure 8.** Individual cell performance in the five-cell stack at 100°C. Stack operating conditions as in Figure 5.