

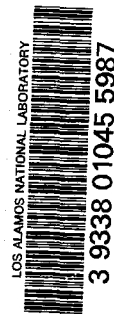
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OPTIMIZATION OF CARBON-SUPPORTED PLATINUM CATHODE CATALYSTS FOR DMFC OPERATION

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ABSTRACT

In this paper, we describe performance and optimization of carbon-supported cathode catalysts at low platinum loading. We find that at a loading below 0.6 mg cm^{-2} carbon-supported platinum outperforms platinum black as a DMFC cathode catalyst. A catalyst with a 1:1 volume ratio of the dry NafionTM to the electronically conducting phase (platinum plus carbon support) provides the best performance in oxygen reduction reaction. Thanks to improved catalyst utilization, carbon-supported catalysts with a platinum content varying from 40 wt% to 80 wt% deliver very good DMFC performance, even at relatively modest precious metal loadings investigated in this work.

INTRODUCTION

Until alternative electrocatalysts are developed, the most active anode and cathode catalysts for polymer electrolyte membrane (PEM) fuel cells, including the direct methanol fuel cell (DMFC), are likely to be platinum-based (1,2). Consequently, the need for limiting precious metal loading while maximizing catalyst utilization, with the emphasis on the optimization of electrode structure, may remain one of the primary goals of PEM fuel cell research for the foreseeable future. Thanks to a significant progress in electrocatalysis and membrane-electrode assembly (MEA) research over past 10-15 years, the total Pt loading required by the H₂/air fuel cells has been reduced by more than an order of magnitude, from *ca.* 4.0 mg cm^{-2} (with unsupported Pt blacks) to as low as 0.2 mg cm^{-2} (with well-dispersed carbon-supported Pt catalysts) (3,4,5). In most cases, this impressive decrease in the required precious metal loading has been achieved with catalyst formulations containing no more than 20 wt% of Pt.

DMFCs suffer from the methanol permeation (crossover) through the polymer electrolyte membrane that kinetically burdens the cathode catalyst (5,7,8). As a consequence, the DMFC cathode loading needs to be much higher than that of an H₂/air fuel cell, reaching levels quite comparable to that of the anode loading and bringing the total cell Pt loading to $\sim 10 \text{ mg cm}^{-2}$ or even more.

In this work, we demonstrate that respectable DMFC cathode activity can be achieved with carbon-supported platinum catalysts having Pt-to-C ratios higher than used for the cathode in H₂/air fuel cells. Good performance will be demonstrated with cathode Pt loading not exceeding 0.6 mg cm^{-2} . It will also be shown that careful optimization of

platinum content in the cathode catalyst can offer substantial improvements in DMFC performance at the low catalyst loading.

EXPERIMENTAL

All cathode catalysts used in this work were supported on carbon black, with the platinum content varying from *ca.* 30% to 80% by weight. The anode catalyst was a Pt-Ru black from Johnson Matthey, UK, and was used at a high loading of *ca.* 9.0 mg cm⁻². The anode and the cathode catalyst inks were made by dispersing appropriate amount of the catalyst powder in water with added 5 wt% suspension of Nafion™ in a mixture of alcohols (Solution Technology Inc., USA). The inks were then applied to Nafion™ 117 membranes. The experimental techniques employed in this work for measuring fuel cell performance and high-frequency membrane resistance have been described in detail elsewhere (9). In this study, both upward and downward voltage scans were used for each polarization curve measurement. Polarization plots were taken using a voltage interval of 50 mV and 25 s waiting time between points. The curves in the two scan directions were averaged and presented here as a single curve. To measure the high-frequency cell resistance, a sinusoidal wave perturbation at 2.4 kHz was applied to the fuel cell load, resulting in a few millivolt cell voltage variation and the associated cell current variations. At such a high frequency, the imaginary part of the impedance was verified to be negligible.

MEAs with different Pt/C catalysts were typically conditioned in an H₂/air operating mode for 2-5 hours. Hydrogen-air cell polarization plots were then recorded as an initial test of cathode activity, followed by DMFC tests. In all experiments, 1.0 M methanol solution was pumped through the DMFC anode flow field at 2 mL min⁻¹ at a zero back-pressure. The cathode air was humidified at 95°C, and flown through the cathode at 460 mL min⁻¹ (standard flow conditions). The anode hydrogen was humidified at 105°C and flown at a rate of 150 mL min⁻¹. Both electrodes were back-pressurized to ~2.0 atm resulting in a total cathode pressure of 2.8 atm (exactly, 2.04 atm back pressure plus 0.76 atm, the atmospheric pressure at the altitude of Los Alamos). The cell operating temperature was 80°C. The geometric active area of the MEAs used in this work was 5 cm².

In order to make sure that the cathode catalyst comparison was not affected by the individual anode performance, all anodes had the same loading of the Pt-Ru black catalyst. The anode activity was independently verified by measuring anode polarization plots. In these experiments, 1.0 M methanol was flown through the anode at a rate of 2.0 mL min⁻¹, with the fuel cell cathode serving as a combined reference/counter electrode (a dynamic hydrogen electrode, DHE). The rate of hydrogen gas flow through the cathode was 110 mL min⁻¹ at a backpressure of 0.7 atm (1.4 atm total pressure). The hydrogen was humidified at a temperature that was 10°C higher than the cell temperature. The potential scan rate was 2.0 mV s⁻¹.

RESULTS AND DISCUSSION

Low Loading Operation of the Pt Black and 40% Pt/C Cathodes

In the first part of this work, the performance of a 40% Pt/C catalyst (De Nora E-Tek, USA) and unsupported Pt black catalyst (HiSPEC 6000, Johnson Matthey) was compared as a function of Pt loading. A series of fuel cell tests were conducted by using different cathode Pt loading. H₂/air fuel cell performance as a function of the catalyst loading is shown for the Pt black and 40% Pt/C catalysts in **Figure 1**. The performance was determined at 0.8 V, often used as a reference voltage in the PEM fuel cell technology. The two plots cross at a point corresponding to a cathode Pt loading of 0.6 mg cm⁻². Carbon supported catalyst performs better at lower loadings while the Pt black catalyst provides an overall performance advantage at higher loadings. At the Pt loading higher than 2.0 mg cm⁻², the performance of the carbon-supported catalyst begins to decrease, likely due mass transport limitations in the carbon-rich – and therefore relatively thick – layer of the catalyst material.

The DMFC performance of the two cathode catalysts was compared at a selected cell voltage of 0.45 V. As shown in **Figure 2**, once again the carbon-supported Pt performs better at the lowest catalyst loading, below 0.6 mg_{Pt} cm⁻². Both catalysts allow to generate similar cell current density in the loading range from ~0.8 to ~1.6 mg_{Pt} cm⁻², with the unsupported catalyst beginning to outperform the carbon-supported material at higher loadings. There may be several possible reasons for the better H₂/air and DMFC performance of the carbon supported than the Pt black catalyst at low loadings, with the most likely being (i) smaller catalyst particle size, (ii) better catalyst utilization, and (iii) reduced tendency to particle agglomeration.

The results presented so far in Figures 1 and 2 were obtained at a high flow rate (“stoichiometry”) and a high total pressure of the air, 460 mL min⁻¹ and 2.8 atm, respectively. In case of cells with the Pt black catalysts, a reduction in the flow rate from 460 to 51 mL min⁻¹ at a constant total pressure of 2.8 atm leads to a significant performance drop (**Figure 3**). The cell current density drops further upon lowering of the cathode air pressure (from 2.8 atm to ~1.4 atm, **Figure 3**). The performance of the carbon-supported cathode is even more sensitive to the changes in the flow rate and pressure of the air (**Figure 4**). While relatively little effect of the cathode feed conditions can be seen at ultra-low loadings of Pt, 0.2-0.3 mg cm⁻², the situation changes as the loading increases. For example, at 1.6 mg_{Pt} cm⁻², the DMFC current density measured at a high flow and pressure of the air, 460 mL min⁻¹ and 2.8 atm, respectively, is nearly twice that measured at a low flow and pressure of the air (50 mL min⁻¹ and 1.4 atm, respectively). Lowering the flow and pressure of the air possibly results in an increased flooding and in a drop of the mixed potential of the cathode. The mixed potential, a direct result of methanol crossover, is strongly dependent on the air flow and tends to become more apparent under conditions of a limited supply of the air to the cathode catalyst layer (5,7,8,10). Both the catalyst flooding and mixed-potential effects could be augmented as the layer of the carbon-supported catalyst becomes thicker.

Cathode Performance vs. Nafion™ Content in the Catalyst Layer

Traditionally, the reason for replacing Pt black with a carbon-supported Pt catalyst was to extend the three-dimensional reaction zone, raise catalyst utilization and, effectively, reduce the amount of the precious metal needed to generate practically viable currents (11,12,13). One important parameter to be optimized is the content of a proton-conducting ionomer, typically Nafion™, in the catalyst layer. This is done to minimize ohmic losses, facilitate mass transport to and from the reaction site, preserve good electronic and ionic conductivity in the catalyst layer and, ultimately, achieve the highest possible utilization of the Pt catalyst. The effect of the Nafion™ content on DMFC performance of the 40% Pt/C cathode catalyst is shown in **Figure 5**. The cell performance improves until Nafion™ content in the cathode reaches ~41 wt%. At an even higher ionomer content the performance drops, likely due a gradual loss in the electronic conductivity in the catalyst layer as the individual catalyst particles become electronically isolated from one another and cease to participate in the electrode process. Interestingly, the optimum weight percent of the Nafion™ ionomer in the catalyst layer (~41 wt%) corresponds to approximately 52% by volume. This may suggest that the best performing formulations of the cathode catalyst are those with a balanced content of ionic (recast ionomer) and electronic (Pt, carbon support) conductors.

Cathode Catalysts with Different Pt-to-C Ratios

Even with low Pt cathode loading of *ca.* 0.6 mg cm^{-2} , the H_2/air cell voltage measured with the 56% Pt/C catalyst at a current density of 0.2 A cm^{-2} is *ca.* 0.84 V, indicating high activity of the catalyst in the oxygen reduction reaction, ORR (**Figure 6**). For a comparison, the cell voltage obtained with 40% Pt/C catalyst at a similar loading is no more than 0.78 V under identical H_2/air test conditions. The 60% Pt/C catalyst performs similarly to 80% Pt/C but not as good as 56% Pt/C. By comparison with other catalysts, 30% Pt/C does not show good H_2/air performance.

In order to make sure that the cell performance is affected by the cathode performance only, anode polarizations were recorded for the cells with different Pt-to-C cathode ratios. In this case, the cells were operated in a 'driven mode', with methanol being oxidized at the fuel cell anode and the fuel cell cathode acting as a counter/quasi-reference hydrogen-evolving electrode (a dynamic hydrogen electrode, DHE). As demonstrated in **Figure 7**, the performance of the anodes is very similar in all five tested cells.

The DMFC performance plots obtained with different Pt/C catalysts at 80°C are shown in **Figure 8**. Polarization plots shown in this figure, recorded for the same Pt loading and cell operating conditions, reveal that 56% Pt/C and 60% Pt/C provide the best performance at the cathode loading of $0.6 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. The DMFC performance recorded with 80% Pt/C is not as good as that of 56% Pt/C and 60% Pt/C, yet better than that of 40% Pt/C and 30% Pt/C. The difference between two best performing catalysts and the 80% Pt/C catalyst is more significant in DMFC operation than H_2/air operation (**Figure 6**). This may indicate that, in addition to somewhat lowered activity in ORR, the high-Pt-content catalyst may be less effective in handling the methanol crossover.

The performance of a DMFC cathode catalyst for a specific application is often a result of a compromise between required precious metal loading and acceptable cost. For certain cost-sensitive applications, the Pt-to-C ratio in a cathode catalyst may depend on the Pt loading that can be afforded. As already demonstrated above, at a cathode loading of $0.6 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$, 60% Pt/C is potentially a good choice. Earlier presented data on the loading dependence of the DMFC performance, obtained with 40% Pt/C (Figure 2), show a decrease in the catalyst performance at loadings in excess of $1.6 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ that results from mass transport limitations as the catalyst layer gets thicker. A comparison of the data obtained with cathode catalyst of different Pt-to-C ratios implies that at higher required Pt loadings better performance may be generated by catalysts with a higher Pt content.

Once the Pt loading is increased to 2.0 mg cm^{-2} , the H_2/air fuel cell voltage obtained with the 80% Pt/C cathode raises to *ca.* 0.84 V at 0.2 A cm^{-2} , attesting to good overall cell performance (Figure 9). Thus, at a higher Pt loading, the performance offered by 80% Pt/C becomes very similar to that of 60% Pt/C and Pt black and approaches that of the best-performing 56% Pt/C (0.86 V at 0.2 A cm^{-2}). The performance advantage offered at a higher loading by the higher Pt-content catalyst in H_2/air operation is also seen in the DMFC (Figure 10). For example, the DMFC current density measured with 56% Pt/C cathode catalysts reaches 0.34 A cm^{-2} at 0.45 V, not much below the current density obtained with a Pt black catalyst at a very high loading (greater than $5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$). This result demonstrates that, thanks to the right dispersion of the catalyst particles, a very promising DMFC performance can be accomplished with high-Pt content Pt/C catalysts at a relatively low platinum loading.

As stated earlier, a practically viable approach to lowering precious metal loading in fuel cells is to support electrocatalysts on high surface area graphitic carbons. Generally, this approach allows for making effective membrane-electrode assemblies with low and moderate catalyst loadings. At high loadings, like those required for DMFCs under development for portable applications, the condition of maintaining catalyst layers thin is impossible to meet with most commercially available carbon-supported catalysts. These catalysts, developed for H_2/air fuel cell operation, typically contain $\sim 20 \text{ wt\%}$ of platinum. Based on the experimental evidence presented above, this is far too low a Pt-to-C ratio for DMFCs. In order to effectively operate, direct methanol fuel cells need much higher catalyst content in the cathode, just as for the anode (14). Unfortunately, achieving a good dispersion of the metal nanocrystallites in catalyst materials with high Pt content catalysts remains a big challenge. Designing a good cathode catalyst becomes more complex at the presence of methanol crossover that significantly raises the demand for the active catalyst sites and makes the task of lowering the cathode catalyst loading even more challenging. Clearly, the most effective approach to lowering the cathode catalyst loading in today's DMFCs would be to either lower the methanol crossover through advances in the membrane technology or to develop a well-performing methanol-tolerant cathode catalyst. In spite of a very significant effort invested in these two areas of the DMFC research the progress to date on the way to replacing the Nafion™ membrane and the Pt cathode catalyst with a better performing and/or less expensive materials has been rather limited. For as long as practically viable replacements of the presently used materials are not available, the research on cathode electrode structure will remain a prudent course of action.

CONCLUSIONS

Reducing the cathode catalyst loading results in fewer active sites available to oxygen reduction and limits the electrode ability to handle methanol crossover, thereby leading to a drop in the (mixed) potential of the DMFC cathode. Depending on the loading, various carbon-supported cathode catalysts can provide right density of active reaction sites, distributed in the catalyst layer of an appropriate thickness and volume. This study has shown that through careful optimization of the catalyst composition a very good DMFC cathode performance can be achieved with carbon-supported platinum catalysts. Depending on the total required cathode loading, a Pt content between 40 and 60 percent by weight is the best suited for DMFC operation.

Another important factor affecting the DMFC cathode performance is the amount of recast ionomer in the catalyst layer. This study has revealed that the approach of preserving a 1:1 volume ratio between the ionic and the electronic conductors in the cathode layer helps maximize the catalyst performance.

ACKNOWLEDGEMENTS

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FIGURES

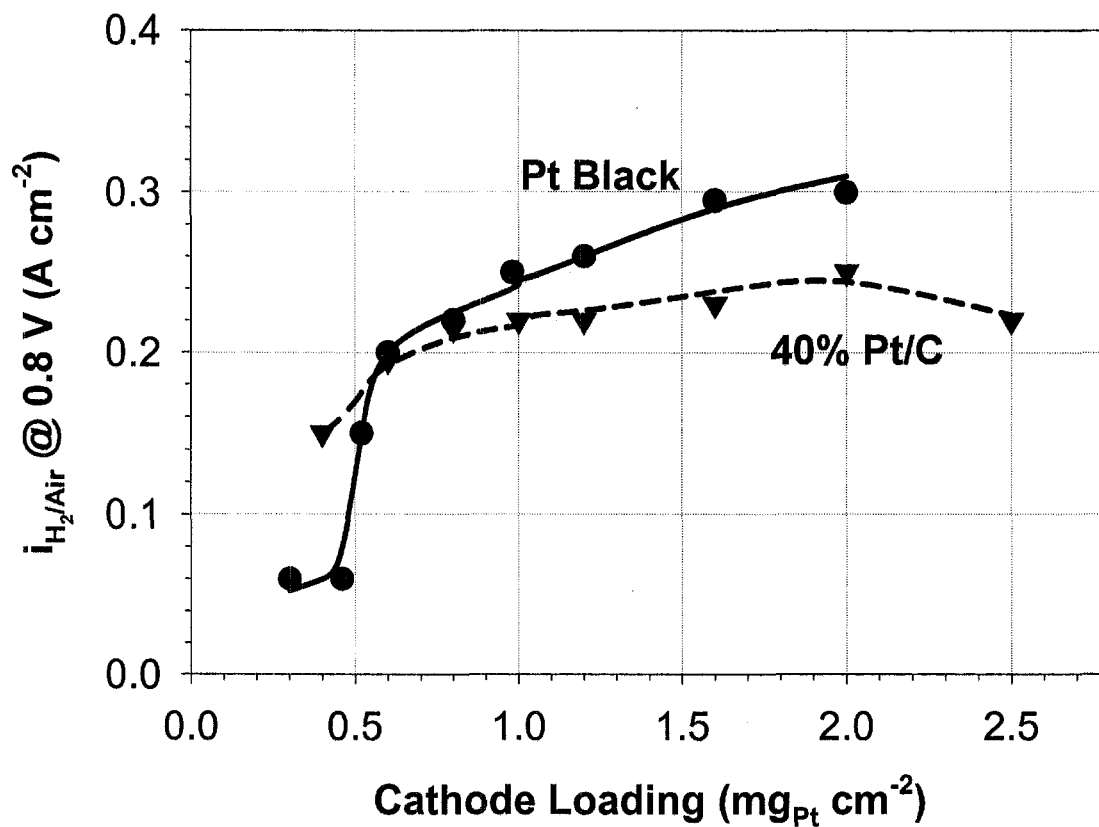


Figure 1 H_2/air fuel cell performance at low cathode Pt and Pt/C loadings at 80°C . Pt-Ru black anode: H_2 , 300 mL min^{-1} , 2.8 atm total pressure. Pt black or 40% Pt/C cathode: Air, 460 mL min^{-1} , 2.8 atm total pressure.

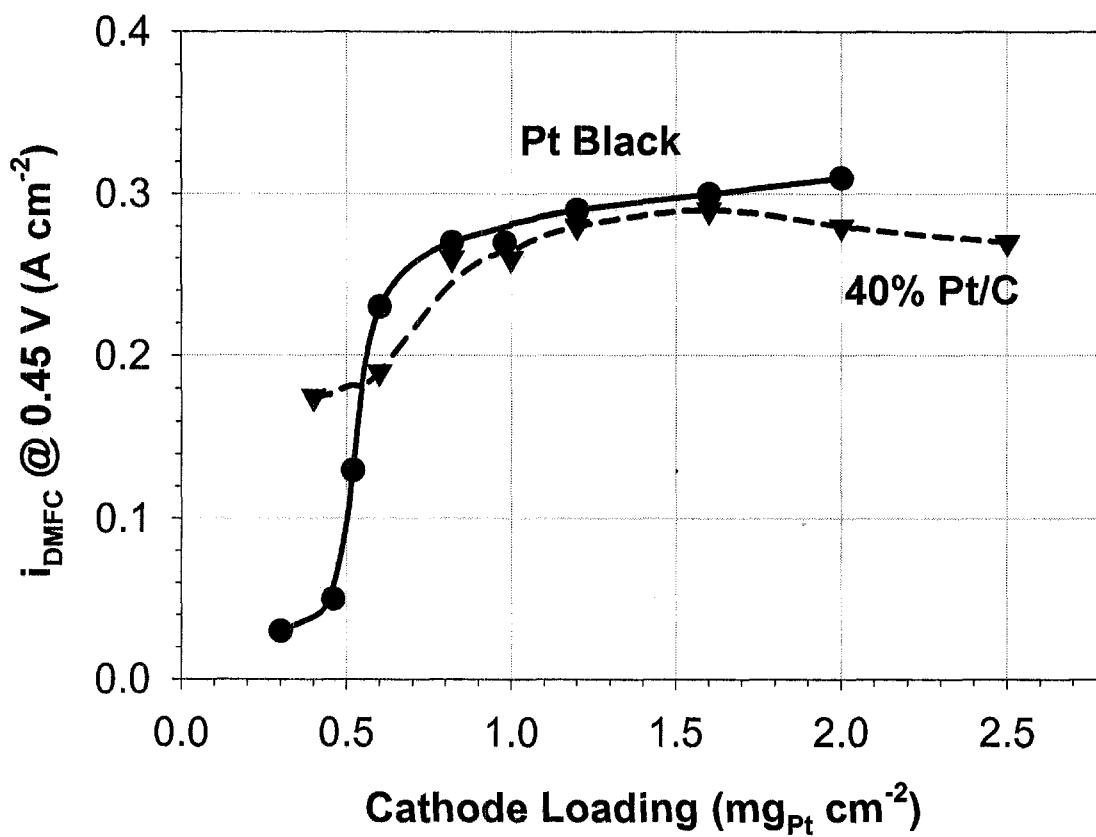


Figure 2 DMFC performance at low loading of Pt black and Pt/C cathode catalysts at 80°C. Pt-Ru black anode: 1.0 M MeOH. Pt black or 40% Pt/C cathode: Air, 460 mL min⁻¹, 2.8 atm total pressure.

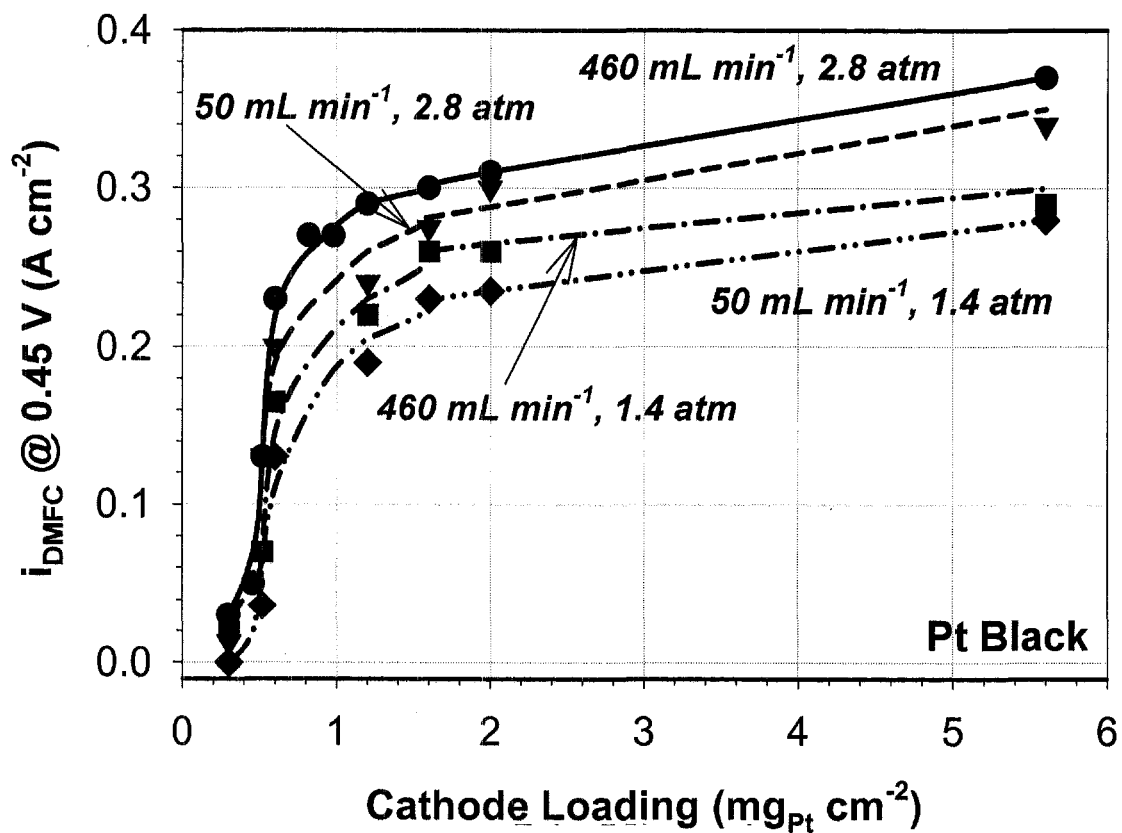


Figure 3 DMFC performance with different Pt black cathode loadings at 80°C. Pt-Ru black anode: 1.0 M MeOH. Pt black cathode: Air (flow and total pressure indicated on the graph).

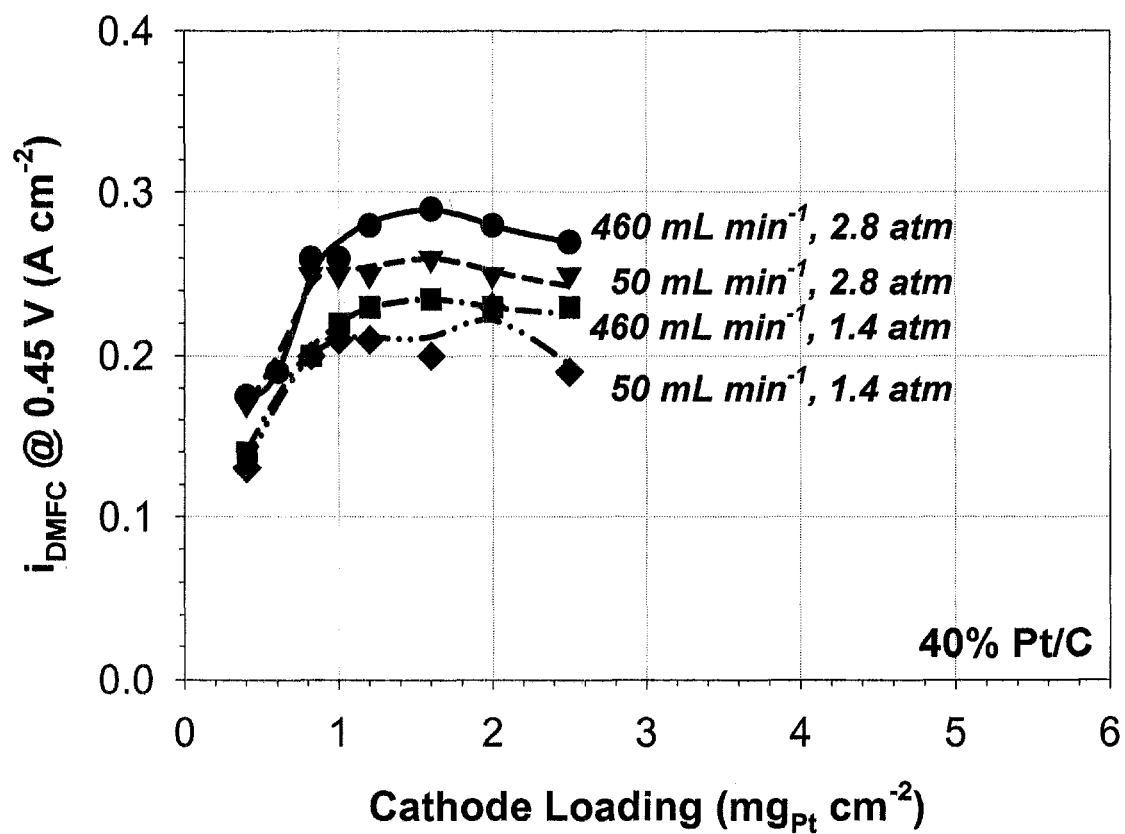


Figure 4 DMFC performance with different 40% Pt/C cathode catalyst loading at 80°C. Pt-Ru black anode: 1.0 M MeOH. 40% Pt/C cathode: Air (flow and total pressure indicated on the graph).

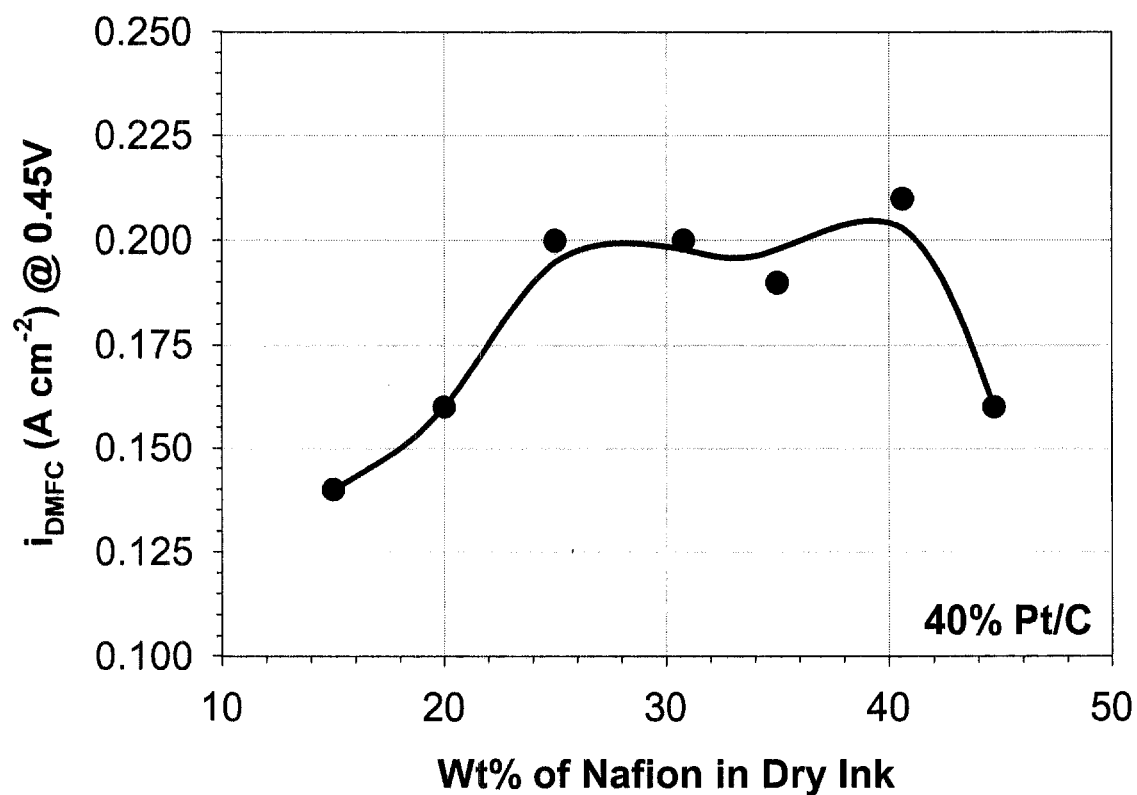


Figure 5 Relationship between DMFC performance at 0.45 V and the weight percent of NafionTM in the cathode catalyst layer. Pt-Ru black anode: 1.0 M MeOH. 40% Pt/C cathode: Air, 460 mL min⁻¹, 2.8 atm total pressure, 0.6 mg_{Pt} cm⁻².

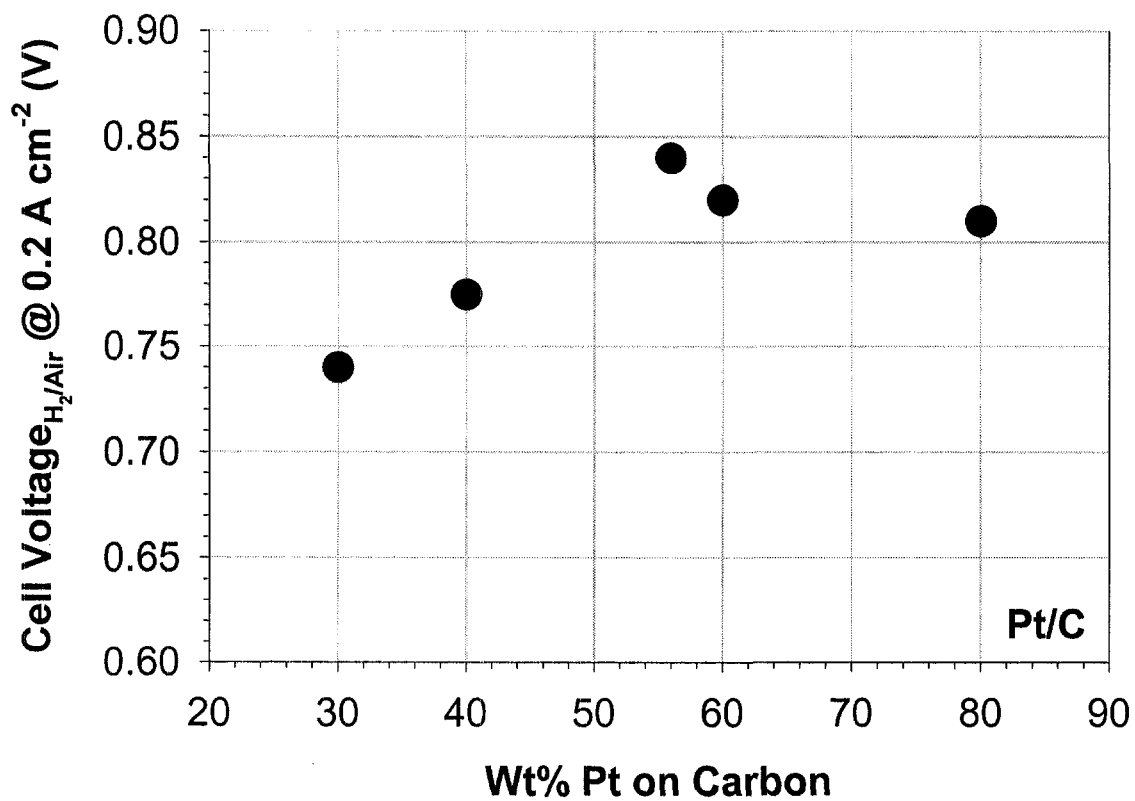


Figure 6 H₂/air performance of fuel cells with different Pt/C cathode catalysts at 80°C. Pt-Ru black anode: H₂, 150 mL min⁻¹, 2.8 atm total pressure. Pt/C cathodes: Air, 460 mL min⁻¹, 2.8 atm total pressure, 0.6 mg_{Pt} cm⁻².

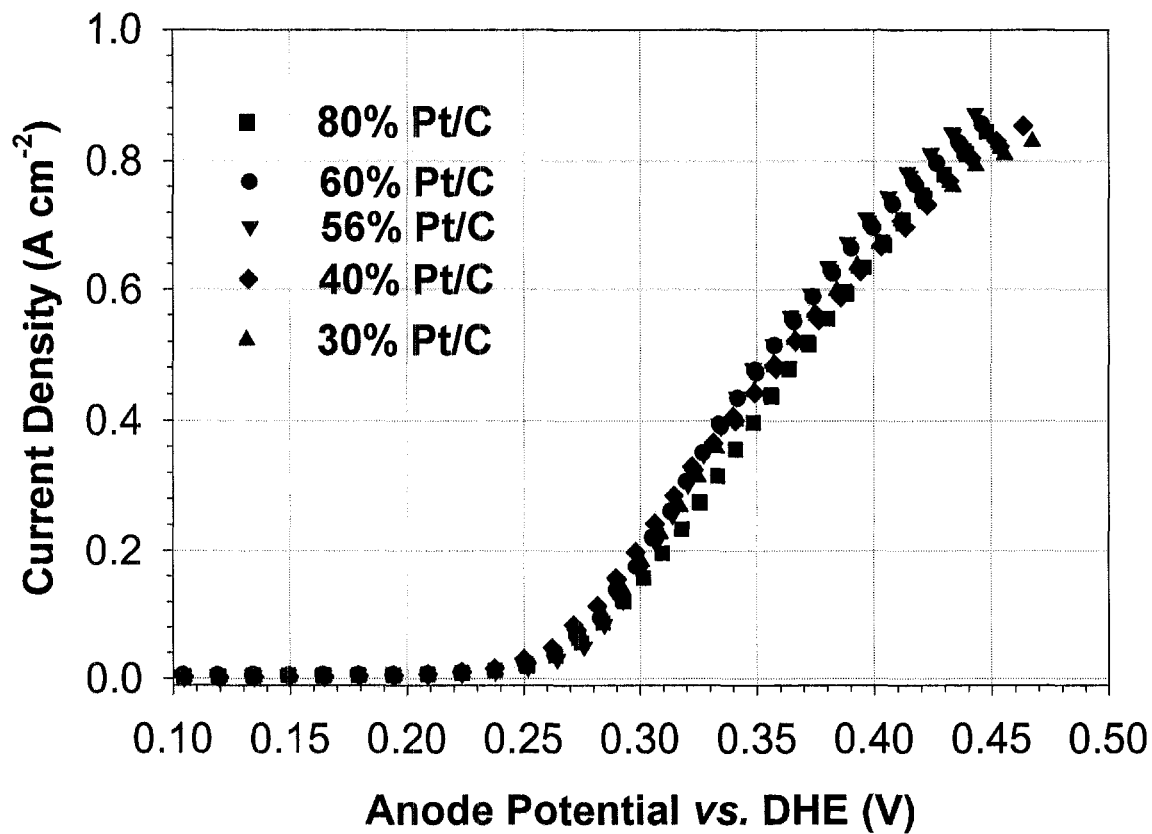


Figure 7 Anode polarization plots with cells using different Pt/C cathode catalysts at 80°C. Pt-Ru black anode: 1.0 M MeOH. Pt/C “cathodes”: H₂, 110 mL min⁻¹, 1.4 atm total pressure, 0.6 mg_{Pt} cm⁻².

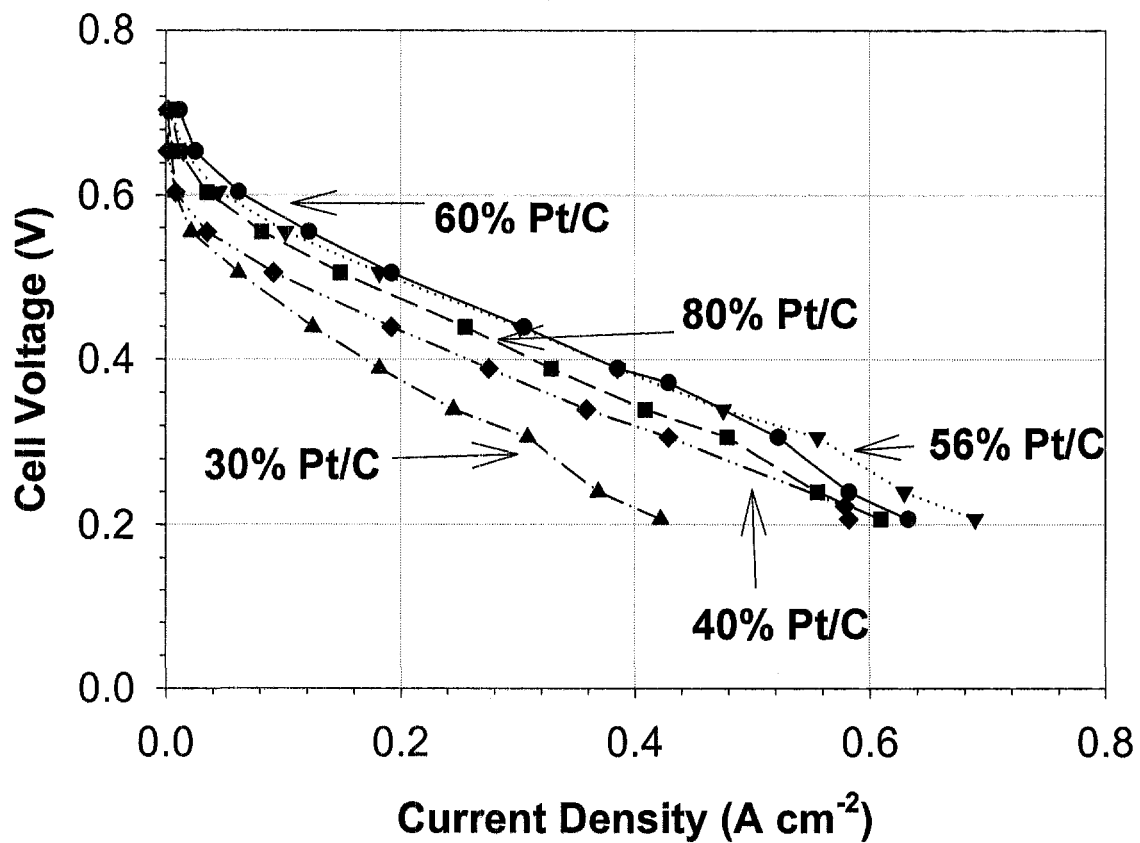


Figure 8 DMFC performance of different Pt/C cathode catalysts at 80°C. Pt-Ru black anode: 1.0 M MeOH. Pt/C cathodes: Air, 460 mL min⁻¹, 2.8 atm total pressure, 0.6 mgPt cm⁻².

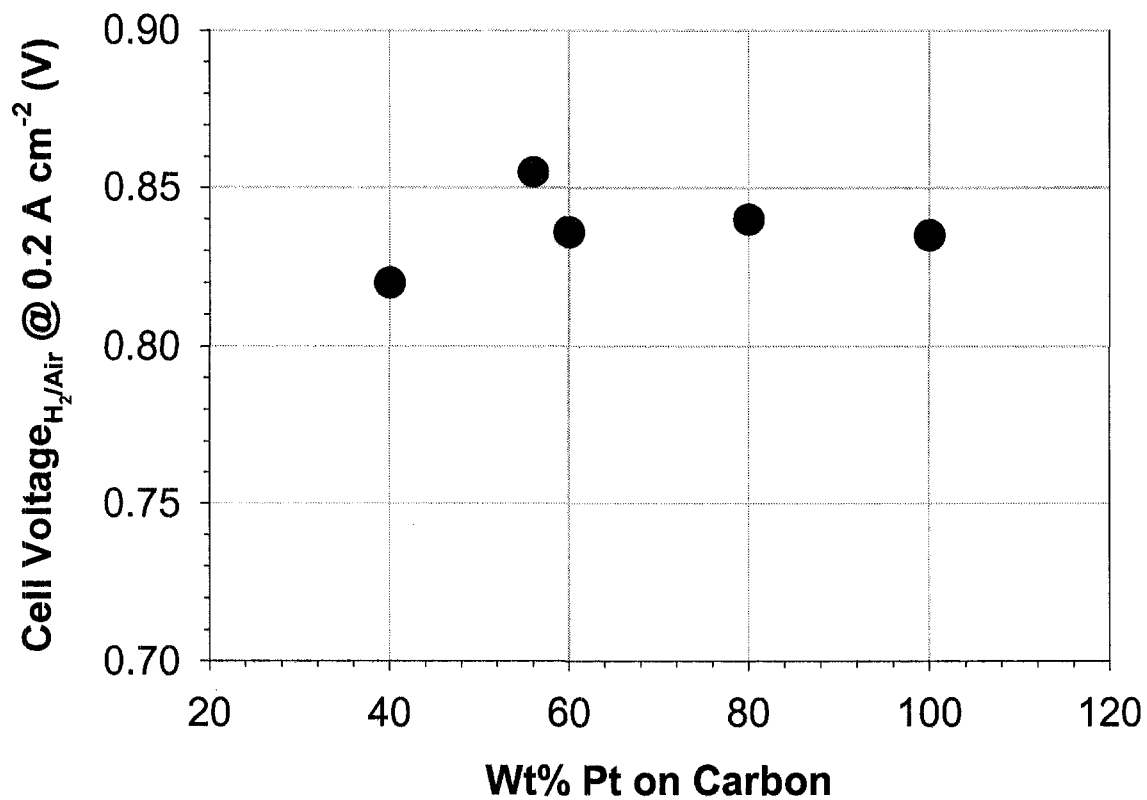


Figure 9 H₂/air performance of cells with different Pt/C cathode catalysts at 80°C. Pt-Ru black anode: H₂, 150 mL min⁻¹, 2.8 atm total pressure. Pt/C cathodes: Air, 460 mL min⁻¹, 2.8 atm total pressure, 2.0 mg_{Pt} cm⁻².

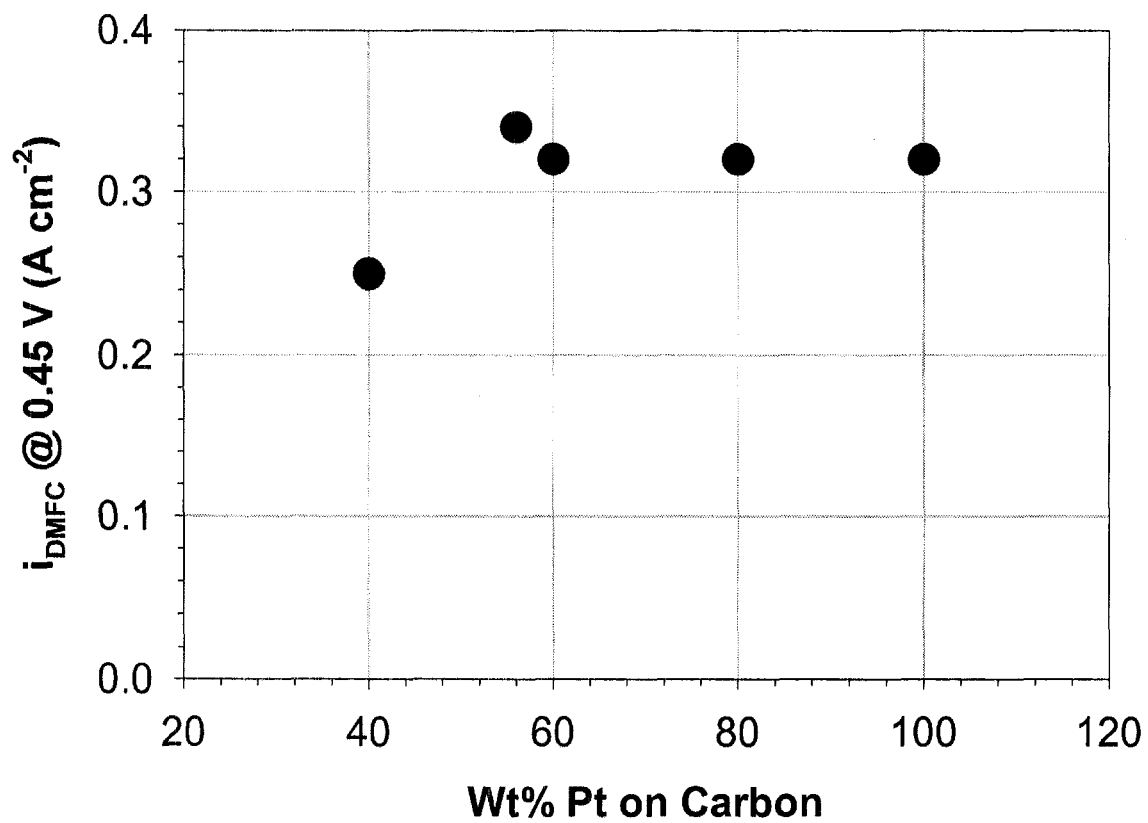


Figure 10 DMFC performance of different Pt/C cathode catalysts at 0.45 V and 80°C. Pt-Ru black anode: 1.0 M MeOH. Pt/C cathodes: Air, 460 mL min^{-1} , 2.8 atm total pressure, 2.0 $\text{mg}_{Pt}\ \text{cm}^{-2}$.