

Performance Enhancement of the Direct Methanol Fuel Cell

2. Improved Low Temperature Electrical Performance Employing a Pt/nano-Cobalt Cathode Electrode

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High surface area nanometal particles of nano-cobalt (90 m²/g), produced at QuantumSphere Inc., were used in conjunction with finely divided platinum in direct methanol fuel cell cathode electrodes to determine if platinum loading could be reduced while increasing power. Total Pt loading was reduced by one-third, with an increase in electrical performance. Cells were investigated using a Nafion®-117 proton exchange membrane at fuel concentrations ranging from 0.5-10 M methanol at 22-30 °C. In the concentration ranges of 0.5-5M methanol, the cells employing a Pt/Co cathode outperformed a standard Pt cathode having a peak power density of 6.1 mW/cm² versus 2.3 mW/cm² for the standard. In addition to this electrical performance increase, cost of cathode catalyst was reduced by 30%.

Introduction

Since inception of the direct methanol fuel cell (DMFC)¹, significant gains have been made in power output. Intensive study around the world has resulted in improved proton exchange membranes, cell design and hardware, and catalysts for methanol oxidation and oxygen reduction. In recent years, the DMFC has shown excellent promise for the augmentation and replacement of batteries in portable devices. As the next generation laptops, PDAs, cell phones, and media players reach the market, the use of current battery technology will result in decreased device run time before recharge. Unlike a battery, the DMFC offers instant rechargeability by direct fuel injection of cartridges, and longer operation time by virtue of increased energy density of the fuel. Currently, the largest barrier for fuel cells to reach commercialization is their cost relative to current batteries. The largest contributing cost to a DMFC is the significant amount of platinum catalyst necessary (usually 4-8 mg/cm²). Currently, the price of Pt ranges from \$75-\$125.00/gram, and is only expected to rise in the future due to its limited quantity. Ideally, platinum should be replaced with a less costly material while maintaining or increasing current performance.

Catalytic enhancement of the oxygen reduction reaction has become critically important for the operation of high performance direct methanol fuel cell cathodes, which is considered to be the limiting side of the cell due to slow oxygen reduction kinetics. To date, platinum and Pt/C cathodes have given the highest performance. However, considerable effort is being dedicated to non-platinum catalysts using transition metal macrocycles.² Also, Pt-M alloys where M = Ni, Co, Cr, and Fe are showing great promise.³⁻⁷ These alloys are typically prepared by sputtering or chemical reduction⁸ of metal salts on carbon to achieve small particle size and good dispersion. Unlike these

methods, vapor condensation of bulk metal yields unsupported metal nanoparticles with high purity. Most importantly, the vapor condensation process is scalable. If a candidate is found which can reduce or eliminate platinum, mass quantity production can occur. These nanoparticles, by virtue of their increased surface area, can be physically blended with Pt and prepared as an effective catalytic ink for electrodes. It is well established that the electrode fabrication procedures play a large role in absolute power output⁹⁻¹¹. A conventional method of electrode preparation was used to construct the MEA, by directly painting the catalyst ink onto carbon supports. However, the high surface area metals prepared on site are prepared by a vapor condensation process which is also conducive to direct deposition of the material.

Objectives

- Determine electrical performance and power output of a 25 cm² single cell DMFC operating under near-ambient conditions and elevated methanol concentration using a Pt/n-Co cathode eliminating one-third of the platinum, compared to a standard Pt cathode
- Determine if performance is stable over 6-12 hour run cycles

Experimental

Membrane-Electrode Assembly Preparation

Nafion®-117 (Ion-Power) was pre-treated by boiling in 3 vol% H₂O₂ for 1 hour, DI water for 1 hour, 3 vol % H₂SO₄ for 1 hour, then in DI water for a final hour before use. Anode catalyst ink was prepared by blending 50:50 atomic wt.% Pt:Ru, DI water, and 5 wt % Nafion® solution, sonicating for 30 minutes, then directly painted onto a plain carbon paper support. Total Pt/Ru loading was 8 mg/cm². Cathode catalyst ink was prepared by blending Pt black, DI water, and 5 wt% Nafion® solution, sonicating for 30 minutes, then directly painted onto a 6% Teflonized carbon paper support. Total Pt loading was 6 mg/cm². Finally, the Pt/n-Co cathode was prepared by blending Pt black, QSI-Nano® cobalt, DI water, and 5 wt% Nafion® solution, sonicating for 30 minutes, then directly painted onto a 6% Teflonized carbon paper support. Total Pt loading was 4 mg/cm², and total n-Co loading was 2 mg/cm². Electrodes were hot pressed to Nafion®-117 at 120 °C for 20 minutes at 300 psi. Prior to cell installation, the MEA was placed in a 60 °C water bath for 12 hours under light compression to rehydrate the membrane. After the MEA was placed in the cell, the anode and cathode were circulated with water at 60 °C before testing was initialized.

Cell Testing

Polarization and power output of a single cell was tested using a Scribner 850C Fuel Cell Test System. Cell was tested using a fuel flow rate of 10 mL/min of methanol and 0.1 L/min oxygen at room temperature to 30 °C. Durability tests were performed at

30 °C using an amperostatic measurement and monitoring voltage over 6-12 hour periods. All data corrected for ohmic resistance as a function of current.

Results and Discussion

Low Fuel Concentration (0.5M)

Figure 1 compares the iR-corrected electrical performance and power density of a 6 mg/cm² Pt loaded cathode to a cathode loaded with 4 mg/cm² Pt with 2 mg/cm² n-Co in a cell operating at room temperature with 0.5M methanol. Across the entire range of operating current density, the Pt/n-Co cathode outperforms the standard Pt cathode. Although no increase in open circuit voltage (OCV) is observed, performance is enhanced in the catalytic activation region of the polarization curve, indicating that n-Co may enhance the kinetic performance of platinum, in addition to increasing the apparent electrochemical surface area. In addition, based upon the increase in performance throughout the ohmic resistance-limiting portion of the curve, it is clear the n-Co does not impede electron flow through the catalytic layer, and may in fact promote conduction. Peak power increased over 2 mW/cm². Figure 2 plots voltage as a function of time. The Pt/n-Co cathode operated, on average, 90mV higher than the Pt standard cathode for a power advantage of 29%. Both electrodes are stable over time after equilibrium was achieved.

Figure 1. DMFC operated at 22 °C, 0.5 M Methanol, 0.1L/min O₂ (iR Corrected).

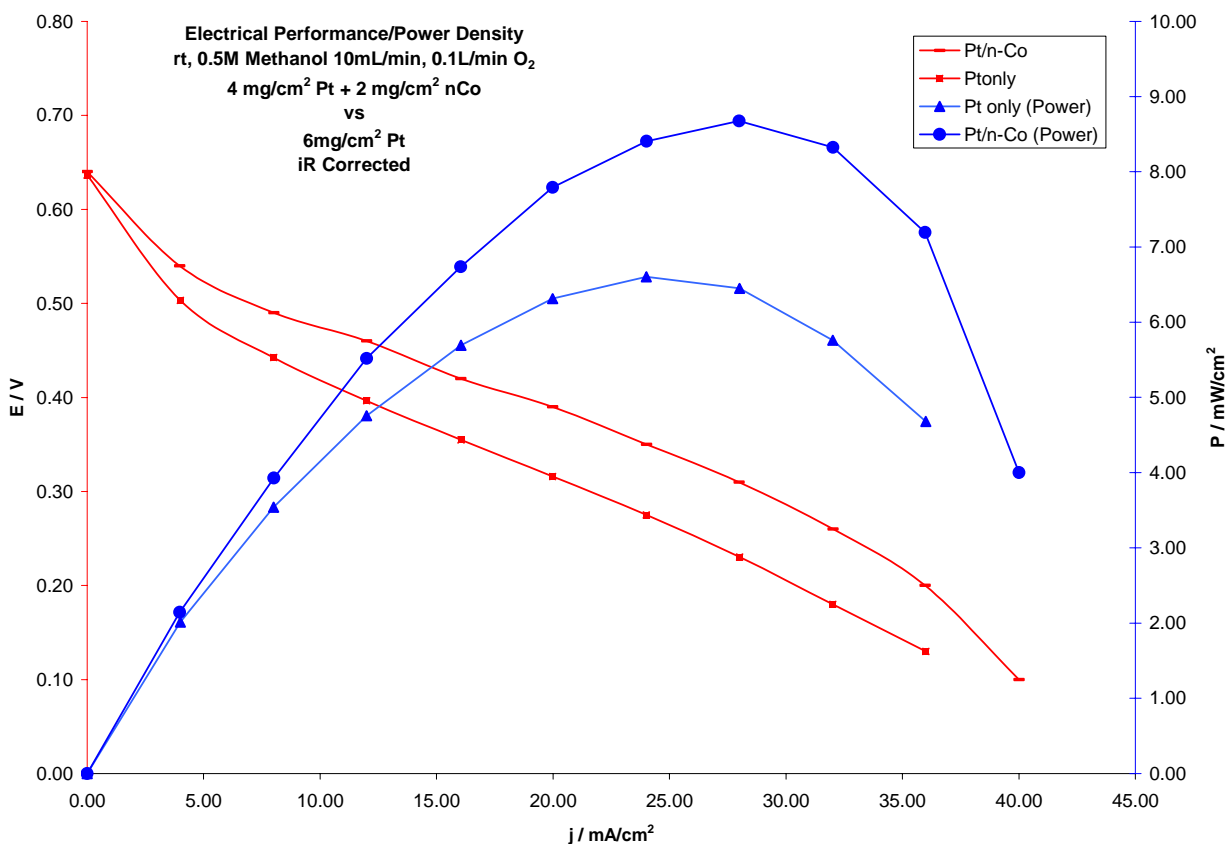
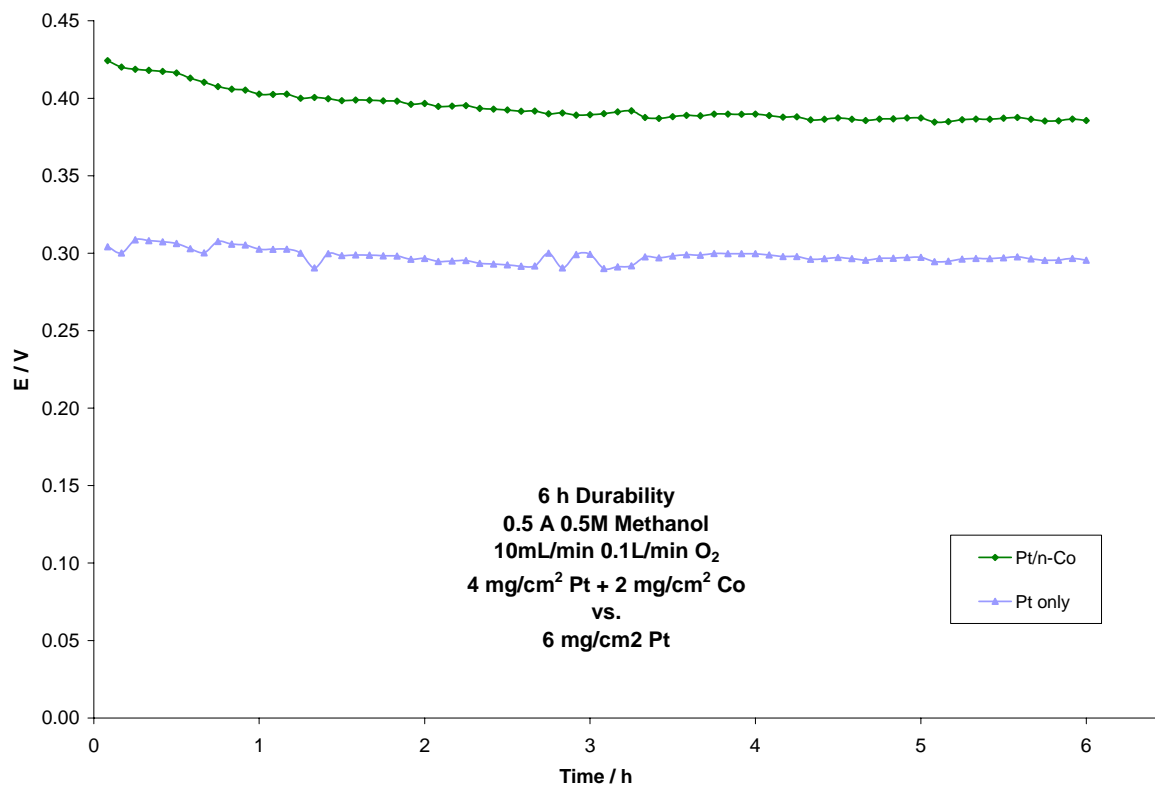


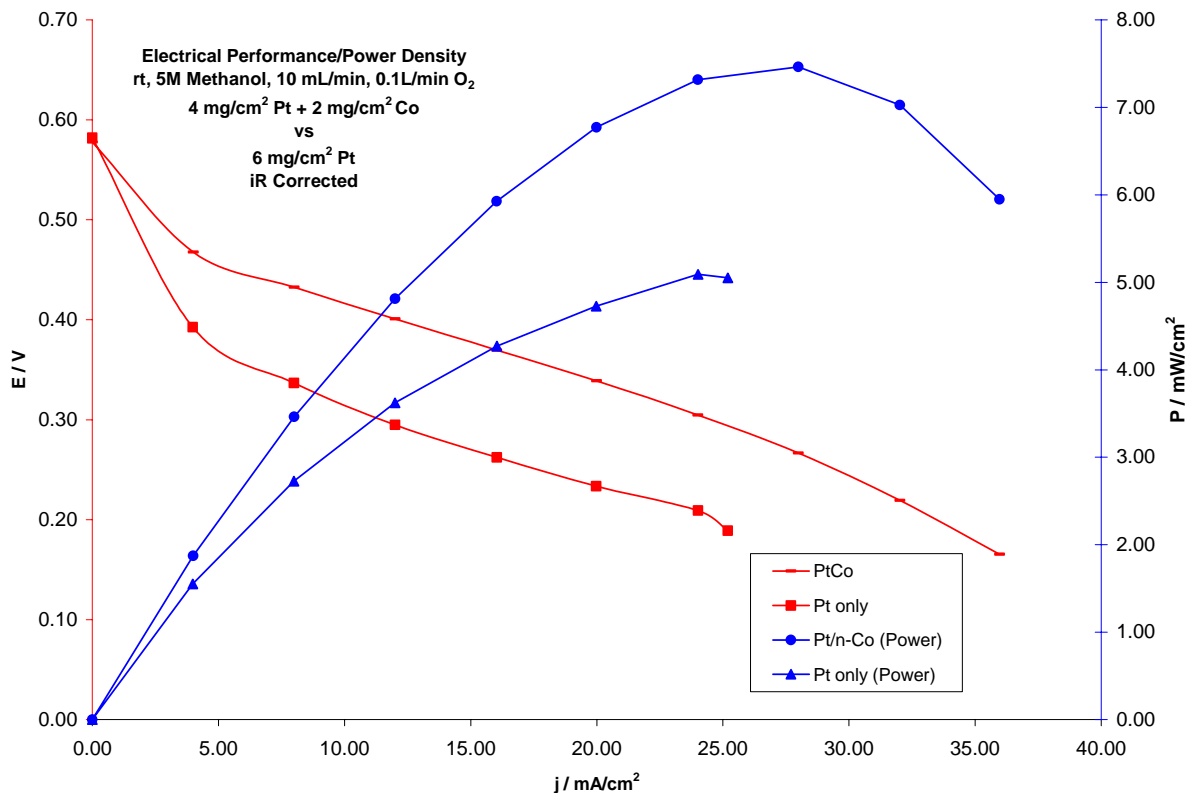
Figure 2. DMFC operated at 26 °C, 0.5 M Methanol, 0.1L/min O₂ (iR Corrected) fixed at 0.5A for 6 hours.



Mid-Fuel Concentration (5M)

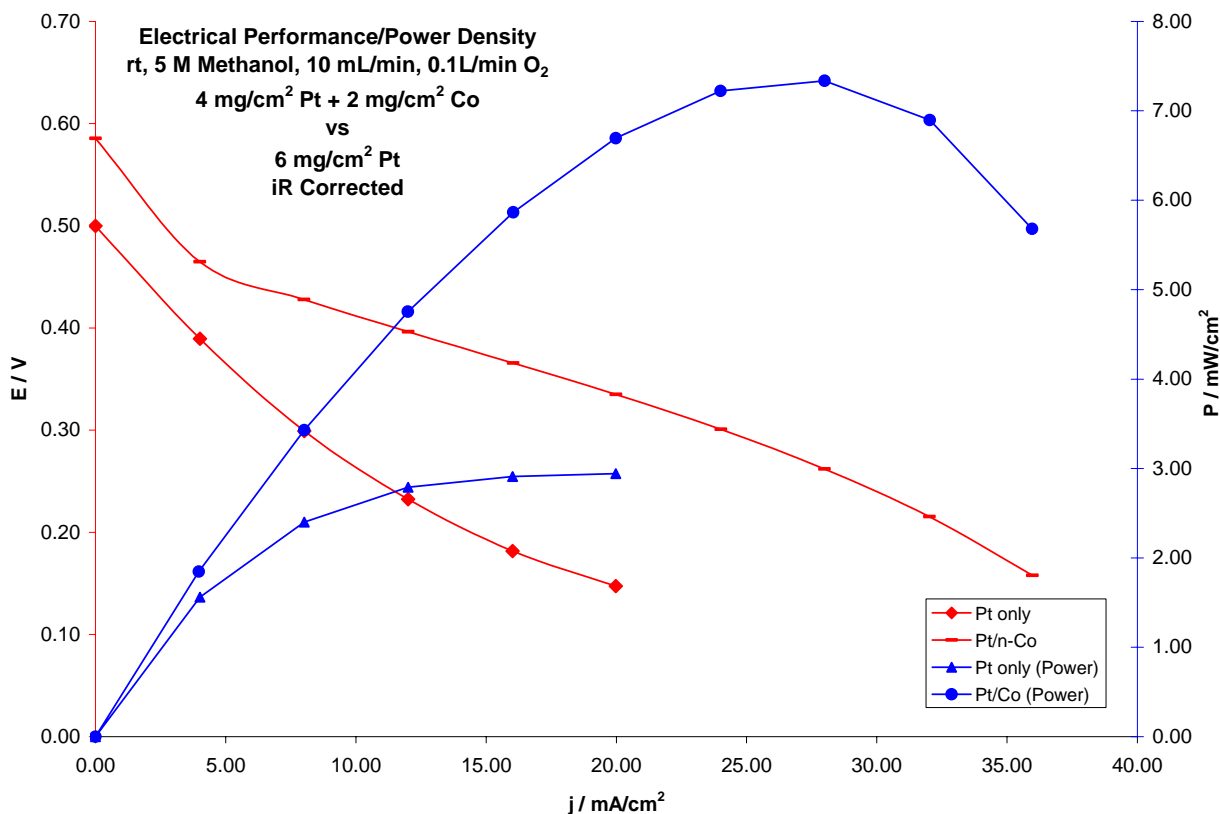
Figure 3 compares the iR-corrected electrical performance and power density of a 6 mg/cm² Pt loaded cathode to a cathode loaded with 4 mg/cm² Pt with 2 mg/cm² n-Co in a cell operating at room temperature with 5M methanol. Across the entire range of operating current density, the Pt/n-Co cathode outperforms the standard Pt cathode. As expected, the OCV of both the standard and the Pt/n-Co sample decreased by approximately 80 mV. However, the overall power increase of the Pt/n-Co sample relative to the standard is maintained at higher fuel concentrations, indicating that the presence of an increased amount of methanol at the cathode does not adversely affect nano-cobalt.

Figure 3. DMFC operated at 26 °C, 5 M Methanol, 0.1L/min O₂ (iR Corrected).



After 14 days of daily testing with 10 M methanol, polarization and power density were measured again for the 5 M study. As shown in figure 4, the Pt/n-Co cathode maintained original performance, however the Pt standard peak power declined from 5 mW/cm² to 2.75 mW/cm². Based on this observation, n-Co, in the form of cobalt oxide, may aid the in the removal of carbon monoxide produced from methanol oxidation at the cathode by conversion to CO₂. This reaction is otherwise irreversible on the standard Pt cathode under these testing conditions.

Figure 4. DMFC operated at 26 °C, 5 M Methanol, 0.1L/min O₂ (iR Corrected) after 2 weeks of testing.



High Fuel Concentration (10M)

Figure 5 shows the power density and polarization for a cell operating with 10M fuel. In the ranges of 0-8mA/cm², the Pt standard outperforms the Pt/n-Co cathode, but above 9 mA/cm² the Pt/n-Co cathode gives greater electrical performance. At this concentration and especially at lower current density, an excessive amount of methanol permeates Nafion®-117 such that catalyst sites become blocked to the extent that even the addition of n-Co cannot prevent poisoning and performance degradation.

Figures 6 and 7 show the durability of a cell operating with 10 M methanol at 0.1 and 0.5 A respectively, for 12 h. At low current, the Pt standard outperforms the Pt/n-Co cathode. However at 0.5A, the Pt/n-Co cathode gives a 21% higher voltage. Both cathodes are stable over 12 hours of operation. If methanol saturation at the cathode is the primary factor in the performance of Pt/n-Co, use of a membrane with reduced crossover characteristics should yield larger performance changes similar to that observed in Figures 1-4.

Figure 5. DMFC operated at 30 °C, 10 M Methanol, 0.1L/min O₂ (iR Corrected).

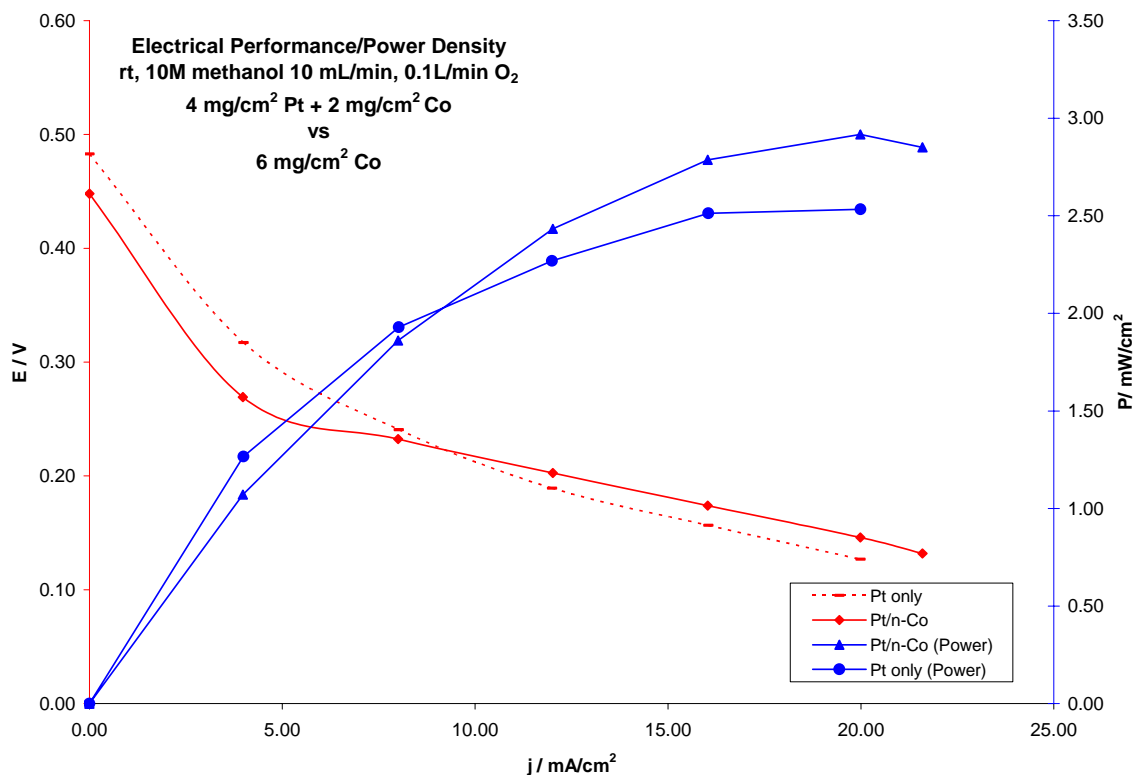


Figure 6. DMFC operated at 30 °C, 10 M Methanol, 0.1A for 12h.

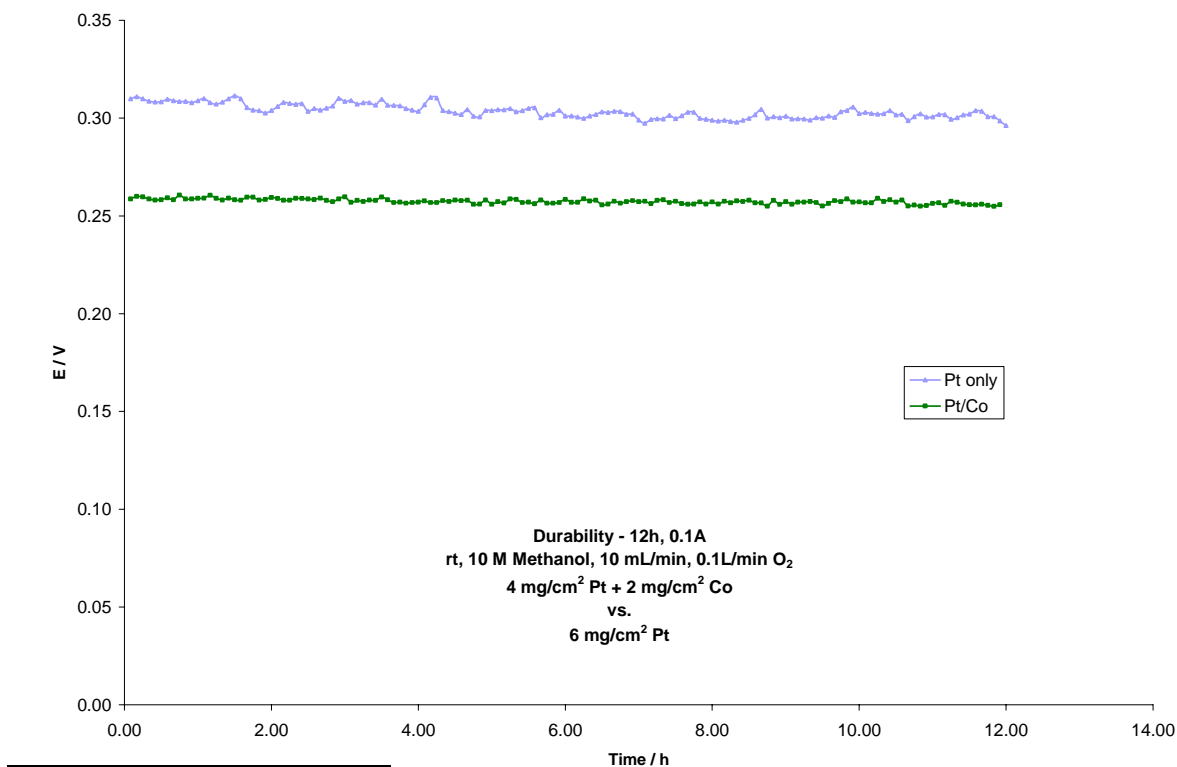
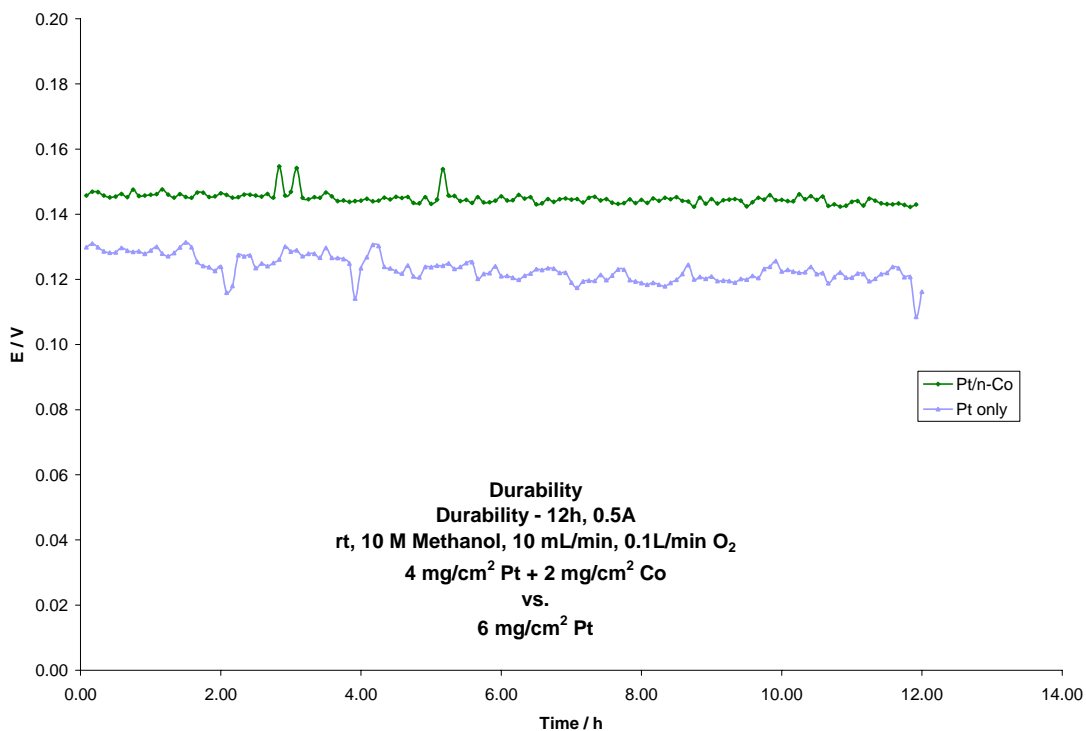


Figure 7. DMFC operated at 30 °C, 10 M Methanol, 0.5A for 12h.



Conclusion

At all fuel concentrations and under most operating currents, a cathode painted with Pt/n-Co ink outperforms the standard Pt cathode. This performance increase can be attributed to an increase in the kinetic activity of Pt by n-Co, and an increase in the apparent electrochemical surface area due to efficient dispersion of Pt on high surface area n-Co without sacrifice of electrical conductivity. In addition to an increase in power, the Pt/n-Co electrode drops the cost of cathode catalyst by 30% (Pt = \$75.00/gram, n-Co = \$15.00/gram).

Future studies will include the use of a low-crossover membrane for testing higher fuel concentrations. If methanol saturation at the cathode is the primary factor in the performance of Pt/n-Co, use of a membrane with reduced crossover characteristics should yield larger performance changes similar to that observed for 0.5-5M fuels. Reduction in Pt loading to ½ and ¼ loading and replacement with n-Co is in progress to determine if increased electrical performance can be maintained while reducing cost further.

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