



## High Concentration Direct Methanol Fuel Cell Using QSI-Nano® Pd

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*A significant hurdle to decrease the \$/W of direct methanol fuel cells (DMFC) is to reduce the precious metal content in the electrode layers, while also using high fuel concentration. This, in addition to use of a low cost proton exchange membrane, will aid in DMFC commercialization. Herein, we report the replacement of 50% of the platinum at the cathode of a DMFC with high surface area palladium. QSI-Nano® Palladium has shown to suppress methanol oxidation for cathode operation in a DMFC, allowing for the use of higher fuel concentration. Operating at 60 °C using 10M methanol and air, this low Pt content cathode more than doubled the peak power output to 15.5 mW/cm<sup>2</sup>. Increased methanol tolerance was observed in all cases by a higher OCV.*

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### INTRODUCTION

Since early development of the direct methanol fuel cell (DMFC), vast 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. Under low fuel concentration operating conditions, single cell power densities exceed 100mW/cm<sup>2</sup>. However, in miniature devices, higher fuel concentrations should be utilized to minimize size. Over the past several years, DMFC has shown good promise for the augmentation of batteries in portable devices, and will make further strides as miniaturization engineering is improved. As 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; fuel cells have the potential to play a critical role as renewable recharger. Unlike a battery, the DMFC offers instant ability to recharge by direct fuel injection using 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 for high power (typically from 2-4mg/cm<sup>2</sup>), and this cost is only expected to

increase as demand for Pt increases. Platinum loading needs to be minimized, and most ideally replaced with a less costly material while maintaining or increasing current performance. Catalytic enhancement of the oxygen reduction reaction has become critically important for efficient operation of direct methanol fuel cell cathodes, which is considered to be the limiting side of the cell due to slow oxygen reduction kinetics. This is especially true under DMFC operating temperatures, typically between 30-70 °C, and is compounded at higher fuel concentrations, wherein a higher proportion of methanol passes through the proton exchange membrane resulting in a mixed potential at the cathode. While the use of high surface area, highly active catalysts improves the ORR reaction, it also provides increased surface area for methanol oxidation at the cathode, giving lower power densities.

High surface area fuel cell catalysts are typically prepared by sputtering, sol-gel, or chemical reduction of metal salts on carbon to achieve small particle size and good dispersion. Alternative to these methods, vapor condensation yields unsupported metal nanoparticles with high purity. Upstream, these particles are coated with a controlled oxide shell to prevent agglomeration. Several of these nanometals have already

exhibited orders of magnitude improved performance in metal-air battery cathodes.

## EXPERIMENTAL

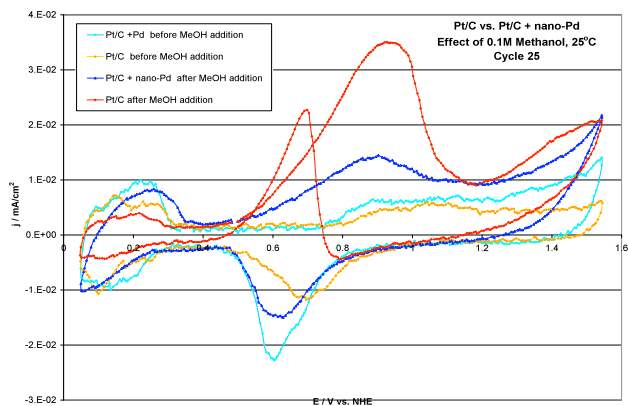
Cyclic voltammograms data was collected on a Solartron SI1287 at room temperature in 1M H<sub>2</sub>SO<sub>4</sub> after 25 cycles. Catalyst inks were prepared by the combination of catalyst, water, and 5% Nafion<sup>®</sup> ionomer solution in alcohol. Catalyst used was 50% Pt-Ru/C and 50% Pt/C (Alfa). Nano-palladium having a surface area of 70.2 m<sup>2</sup>/g was manufactured at QuantumSphere. Catalyst, water and Nafion<sup>®</sup> ionomer were blended on a vortex mixer for 30 seconds, followed by one hour of sonication and another 30 seconds of vortex mixing. Anode catalyst was directly painted on plain carbon paper and cathode catalyst was painted on 6% teflonized carbon paper. Catalyst was painted in thin layers and allowed to dry between each layer. Final anode loading was 2 mg/cm<sup>2</sup> Pt (in PtRu/C) and 4 mg/cm<sup>2</sup> Pt at the cathode for the standard MEA. Final anode loading was 2 mg/cm<sup>2</sup> Pt (in PtRu/C) and 2 mg/cm<sup>2</sup> Pt + 1 mg/cm<sup>2</sup> nano Pd loading at the cathode, to represent a 50% reduction in Pt use at the cathode. After both electrodes were fully dried, a final layer of Nafion was coated on top of the catalyst and allowed to dry at 100 °C for five minutes. Next, they were hot-pressed at 140 °C for four minutes onto a Nafion<sup>®</sup>-117 proton exchange membrane (Ion-Power, Inc.). The completed MEA was then placed between two porous plates under light compression and placed in a DI water bath at 80 °C for 14 hours. The MEA was then placed in a 25cm<sup>2</sup> fuel cell and water was circulated through both the anode and cathode at 80 °C for another three hours. Cell was re-gasketed and torqued before electrochemical tests. Cell was conditioned by running galvanostatically at 2A for 6 hours at 80 °C before testing was initiated. Cell resistance was measured in both cases to be ~ 26 milliohms at 0.5V. Cell anode was operated with 5 to 10 M methanol, flowing at 10-50 mL/minute. Cell cathode was operated with air, flowing at 0.5-1 L/min without back pressure. To determine electrical performance and power density, cell was run at 30 and 60 °C with current steps of

0.5A/minute until the voltage dropped below 0.1 V. Polarization and power output of a single cell was tested using a Scribner 850C Fuel Cell Test System.

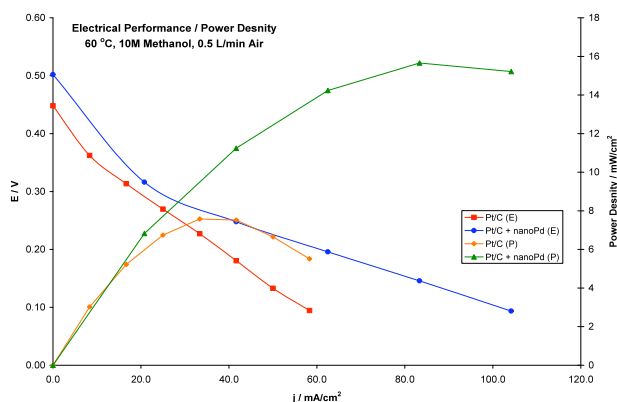
## RESULTS

Using rotating disk electrode voltammetry a Pt/C electrode was compared with a Pt/C electrode with reduced loading but with the introduction of nano-palladium in a cyclic voltammogram experiment. In all cases total Pt loading was 0.25 mg/cm<sup>2</sup>. Electrolyte was 1 M H<sub>2</sub>SO<sub>4</sub>, at room temperature. Referring to the orange and light blue scans in **Figure 1**, the onset of Pt oxide formation begins at about 0.8V, with corresponding peak reduction at 0.7V. At lower potentials strong and weak hydrogen desorption and absorption occurs. Dark blue and red lines are the same scans run after the addition of 0.1M methanol, as a representative of the effect of methanol on the ORR reaction. With respect to Pt/C only (red) we observe a suppression of hydrogen absorption/desorption (likely due to bound CO), along with a substantial CO reoxidation peak at 0.7V as well as oxidation of absorbed methanol by Pt-OH at 0.9V. Also note the suppression of hydrogen adsorption/desorption at low potentials. The increased magnitude of the methanol oxidation and CO peak reflects that Pt has good electrocatalytic activity for methanol oxidation, and as such oxygen competes with methanol for Pt active sites on the catalyst surface. With respect to Pt/C + nano-Pd (dark blue), suppression of the methanol oxidation peak is observed (61% lower than Pt/C), with absence of the CO oxidation peak. It is evident that Pd suppresses methanol oxidation.

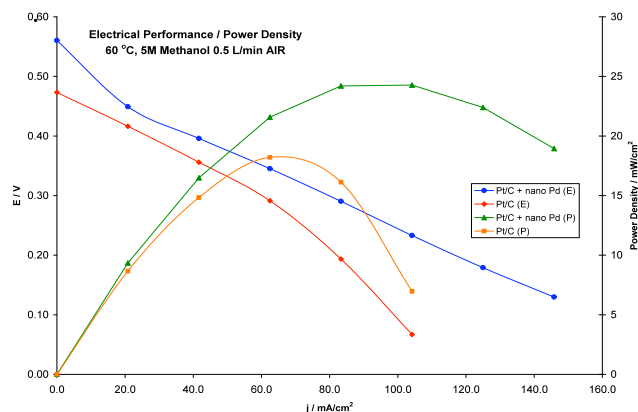
Figure 2 gives the galvanodynamic and power density curves for a DMFC operating at 60 °C with 5M methanol and air. OCV of the MEA containing Pd at the cathode is 90 mV higher than the MEA cathode containing Pt/C alone. In addition, peak power is increased. Perhaps the most compelling difference is at 5 and 10M methanol operation at 30 °C (**Figures 3 and 4**). In this case, peak power density is double using a Pt/C + Pd based cathode.



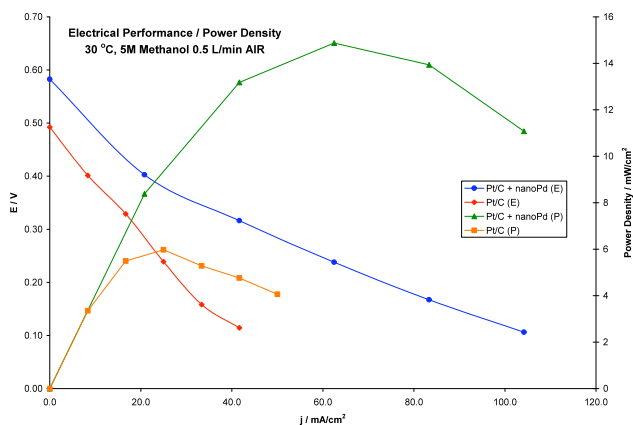
**Figure 1:** Cyclic Voltammograms of Pt/C, Pt/C + Pd before and after 0.1M methanol addition.



**Figure 4.** Comparison of DMFC MEAs operating at 60°C, 10M methanol, 0.5L/min air.



**Figure 2.** Comparison of DMFC MEAs operating at 60°C, 5M methanol, 0.5L/min air.



**Figure 3.** Comparison of DMFC MEAs operating at 30°C, 5M methanol, 0.5L/min air.

## CONCLUSIONS

Through the integration of alternative high surface area, methanol tolerant catalysts such as nano-palladium, it is possible to improve high fuel concentration DMFC performance while minimizing the usage of platinum. By replacing 50% of the Pt in a DMFC cathode with high surface area nano-palladium, a significant increase in power density was achieved operating with 5-10M methanol. By increasing the methanol tolerance of cathode catalysts, and in combination with lower cost, low crossover proton exchange membrane, will aid in the miniaturization and commercialization of DMFCs as a source of portable power.

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