

# Carbon Supported Pt Nanomaterials For Fuel Cell Applications Using Combustion Chemical Vapor Condensation

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## ABSTRACT

We have successfully demonstrated PEM fuel cell cathode performances at Pt loadings below  $0.2 \text{ mg/cm}^2$  using our Combustion Chemical Vapor Condensation (CCVC) technology. The supported catalyst produced by the CCVC process has shown unique microstructure, which may have contributed to the high power performance at very low loadings. We have also benchmarked our CO-tolerant anode to Johnson Matthey HISPEC catalysts. By modifying process parameters to control the alloying of Pt-Ru, we have correlated the oxidation state of catalysts to CO oxidation overpotentials. Lastly, we have shown a seven to tenfold increase in limiting methanol oxidation current over standard Pt-nafion-carbon electrodes using refractory additive. This promises further breakthroughs in DMFC technology, which suffers from reduced rate capability and energy efficiency compared with PEMFCs.

**Keywords:** cathode, DMFC, PEMFC, CCVC, fuel cell

## 1 INTRODUCTION

The CCVC process was used to produce electrocatalysts with particle sizes as low as 3 nm. The plume of CCVC catalyst vapor (nanoclusters) can be directly deposited onto a substrate or mix the vapor stream with other materials before depositing onto a substrate. In the fabrication of electrocatalyst layers (electrocatalyst/carbon particle/ionomer composites), the CCVC catalyst fabrication scheme is coupled to carbon particles and ionomer introduction schemes to produce continuously electrocatalyst layers on the appropriate substrates. The resulting electrocatalyst layer has a unique structure and the process is easily scaleable. This process is shown schematically in Figure 1. The microimages for the electrocatalyst layer and the supported Pt are shown in Figure 2.

## 2 CATHODE ELECTROCATALYST LAYERS

We have made Pt-carbon-ionomer electrocatalyst composite layers on gas diffusion carbon paper using the CCVC process.

Figure 3 shows comparative half cell slow sweep polarization curve results for these samples. The comparison is made between our CCVC cathode and conventional screen-printed Johnson-Matthey HISPEC catalyst.

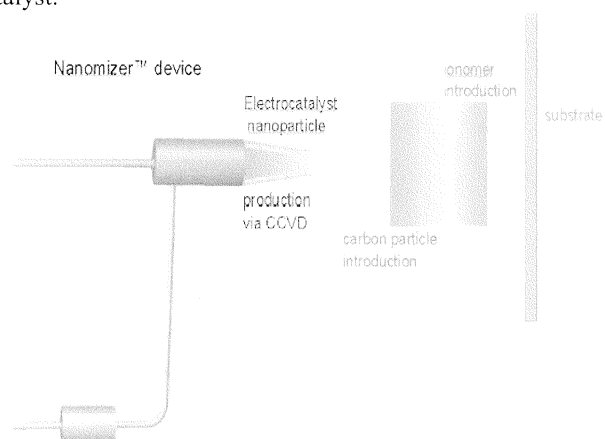


Figure 1: Schematic representation of the continuous deposition process for forming electrode layers for PEMFC applications.

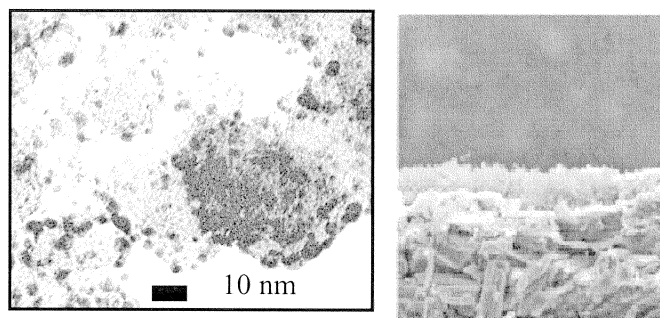


Figure 2 The micrographs for the supported Pt (TEM image, left) and the electrocatalyst layer (SEM cross-sectional image, right) produced by the CCVC process.

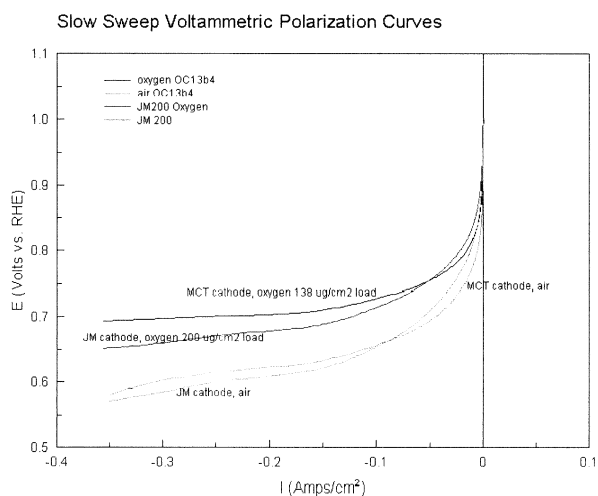


Figure 3 Slow sweep voltammetric “polarization” curve comparing conventional screen printed Johnson-Matthey HISPEC catalysts with CCVC grown materials. Conditions: 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte, Pt counter electrode, RHE at 40°C.

It is apparent from the Figure 3 that CCVC cathodes, with lower platinum and ionomer loading (0.138 mg/cm<sup>2</sup>; Johnson Matthey loading=0.200 mg/cm<sup>2</sup>) perform with similar power output in basic electrochemical tests. The performance of fuel cell load tests on MCT client test stands verified comparable performance between MCT representative samples (>0.15-0.25 mg/cm<sup>2</sup> loading) and commercially available electrocatalyt layers at about 0.3 mg/cm<sup>2</sup> Pt loadings.

### 3 ANODE ELECTROCATALYST LAYERS

We have demonstrated the ability to make Pt and Ru containing electrocatalyst layers using our CCVC technology that has similar performance to commercially available Etek Pt-Ru materials. Figure 4 shows comparative half cell slow sweep ignition potential data for samples on gas diffusion electrode substrates. This method is similar to that used by Gasteiger et. al.[1] using rotating disk studies. We observe from the Figure 4 that the overpotential associated with CO oxidation differs by less than 20 mV for samples of similar Pt loading. It is also shown that significant “preignition” current exists for Ru containing samples but not for Pt only electrocatalyst layers. This current is usually associated with formation of Pt-O or Pt-OH species, which may play an important role in CO oxidation. Recent work by Rolison et. al.[2] discusses the relationship between CO tolerance and the oxidation state of ruthenium. Mukerjee et. al.[3] have examined the structure of the Pt-Ru electrocatalyst and determined that the lower oxidation state of Ru and the presence of the Pt-Ru alloy is critical to CO tolerance behavior. The effect of Ru oxidation state on the ignition potential is demonstrated in Figure 5, which shows the ignition potential as a function

of the Ru metallic ratio in Ru-RuO catalyst (analyzed with XPS). The different oxidation state of Ru in Pt-Ru was controlled by adjusting the CCVC parameters.

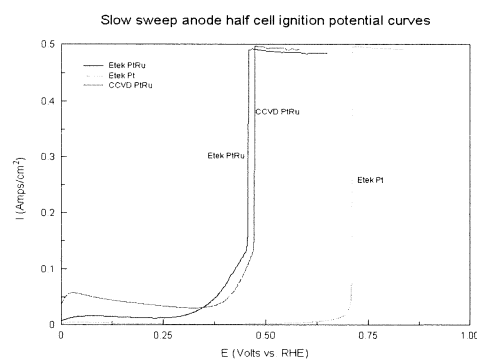
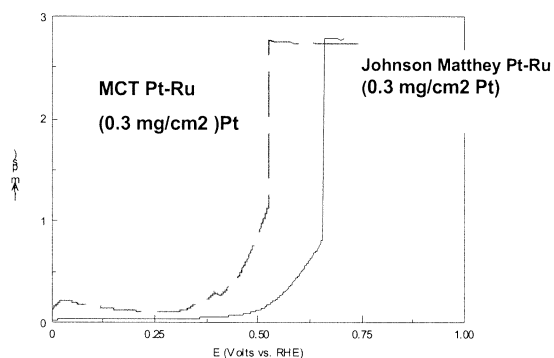


Figure 4 Slow sweep ignition potential curves at 40°C for samples prepared by CCVC and by conventional screen-printing techniques with different catalyst compositions. Electrolyte: 0.5M H<sub>2</sub>SO<sub>4</sub>.

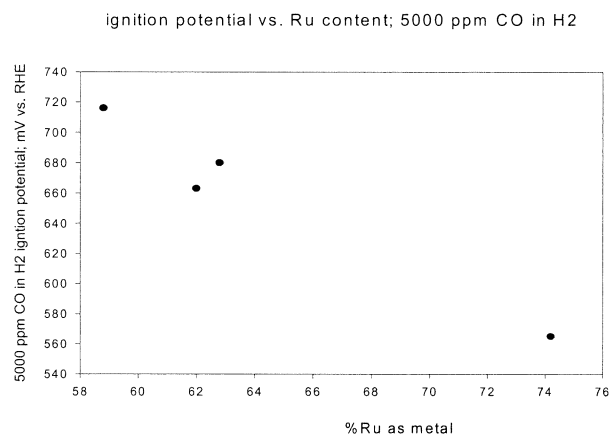


Figure 5 Ignition potential of Pt-Ru anode as a function of Ru metallic content in the CCVC formed catalyst.

## 4 DIRECT METHANOL ELECTROCATALYSTS

We have also used CCVC technique to make direct methanol fuel cell electrocatalysts. Figure 6 shows preliminary cyclic voltammetric data of CCVC catalysts with our proprietary additive vs. that prepared without with similar ionomer and platinum loading. We can see an increase of nearly an order of magnitude in the limiting current, suggesting enormous potential for rate capability increases in DMFC technology. These results are promising and will be further explored in future efforts. Recent work by Leddy et. al.[4] show enhancements in CO and methanol oxidation by incorporation of magnetic nanoparticles in the electrocatalyst layer. Recent work by Anderson et. al.[5] also shows improvements in methanol oxidation limiting current by use of silica “nanoglue” in an aerogel type electrocatalyst matrix.

Comparison of Pt and Pt with MCT additive methanol oxidation limiting currents

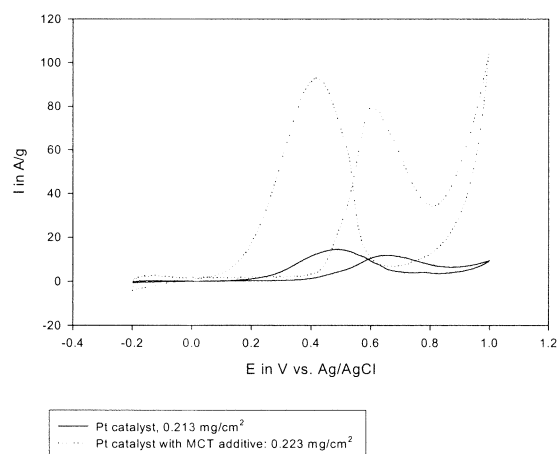


Figure 6 Comparative cyclic voltammogram data showing differences in methanol oxidation performance between Pt only electrocatalysts and those using our proprietary additive. Electrode size: 1 cm<sup>2</sup>; N<sub>2</sub> purge, 0.5 M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte.

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