

Characterization of Unsupported Platinum Nanoparticulates produced via Combustion Chemical Vapor Deposition

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Over the past four years, MicroCoating Technologies (MCT) has developed its patented Combustion Chemical Vapor Deposition (CCVD) technology for the synthesis of Pt nanoparticles for use in proton exchange membrane fuel cell (PEMFC) applications. The ability to continuously produce nanoparticles coupled with a spray polymer deposition strategy that utilizes both micron-sized droplet formation and extremely flexible solution composition limits has tremendous promise. The large-scale fabrication of low Pt loading / high performance composite electrode layers is widely accepted as one of the most crucial requirements for the successful commercialization of fuel cells.

The development focus at MCT has been on composite electrode layer production and process scale-up; however, fundamental information on the structure and activity of the flame-produced Pt nanoparticles is necessary in order to establish baseline kinetic performance. This paper captures some of the ongoing efforts underway at MCT and Brookhaven National Laboratory to more thoroughly characterize Pt nanoparticles produced via CCVD.

Recent advances at MCT have allowed for the collection of nanopowders on the grams per hour scale. This now allows for the structural and electrochemical characterization of the unsupported nanoscale electrocatalyst particles, without complications due to ionomer or support materials.

Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurements are used to structural characterize the unsupported catalyst particles. A variety of precursor compositions, combustion parameters and nanoparticle collection conditions are utilized in the nanopowder fabrication/collection process. Thus particle size, particle size distributions, degree of agglomeration and surface oxidation states can now be, in effect, 'dialed in.'

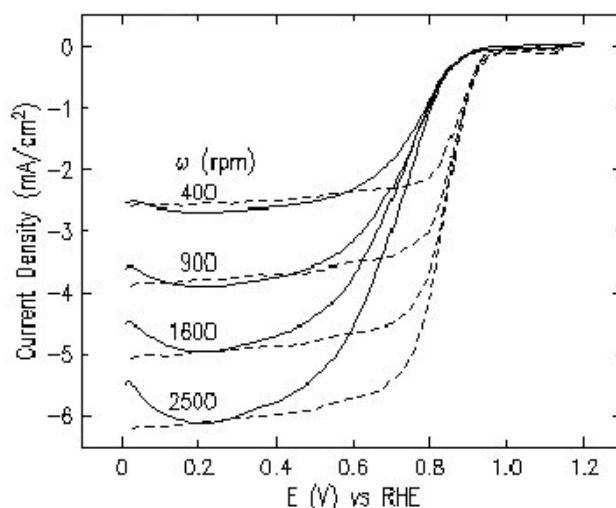
Rotating disc electrode measurements with electrocatalysts deposited on glassy carbon electrodes and both uncovered and covered with a thin Nafion® layer are used to investigate the mass specific activity for oxygen reduction.

Fig. 1 compares the rotating disk electrode (RDE) measurements for two different Pt loadings of a particular Pt nanoparticle (*vide infra*). For this nanopowder production run, a slurry collection

scheme was utilized, with several liters of slurry collected with a Pt particle concentration of 14 g/L.

Polarization curves obtained with RDE measurements shown in Fig. 1 indicate a high catalytic activity of this unsupported catalyst. Particularly important is the high onset potential of O₂ reduction. A considerably lower half-wave potential for the reaction on the catalyst with lower Pt loading is indicative of inadequate catalyst dispersion. Rotating disk-ring measurements will provide additional insights on the catalytic properties of this catalyst.

Figure 1. Comparison of hydrodynamic polarization curves for two different Pt loadings, ----- 500 $\mu\text{g}/\text{cm}^2$, ——— 50 $\mu\text{g}/\text{cm}^2$, dispersed on a glassy carbon electrode. The thin active layer consists of Pt nanoparticles only. The electrolyte solution was oxygen-saturated 0.1 M HClO₄ and the sweep rate was 10 mV/s



The presentation will compare a series of CCVD-produced Pt nanoparticles with respect to formation conditions, structural characterization and electrocatalytic activity. For example, for the unsupported catalyst used in the electrochemical measurements shown in Fig. 1, the TEM data indicate an average particle size of ~8 nm with both very small, < 2 nm and large, ~ 30 nm, particles present. From the XRD peak widths, a 5 nm crystallite size can be calculated. The XPS shows ~15% of the surface atoms in the +2 oxidation state with chemical shifts consistent to a mix of PtO and Pt(OH)₂.

Other nanopowder production runs under different sets of conditions have produced smaller (and larger) particle sizes, less (and more) agglomeration and undetectable (to nearly complete) surface oxidation.