Nanoparticle Layer-by-Layer Assembly for Fuel Cell Electrodes – Year 3 Summary

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A novel Pt particle synthesis technique has been developed that for the first time in the field permits electrostatic assembly of Pt directly onto porous carbon supports for enhanced electrocatalytic activity and nanoparticles that span the atomic cluster to single crystal transition.

$$(Pt - 3Sn)_{complex} \rightarrow Pt^{0}_{metal} + 2\ Sn^{4+}_{ads} + Sn^{2+}_{ads}$$

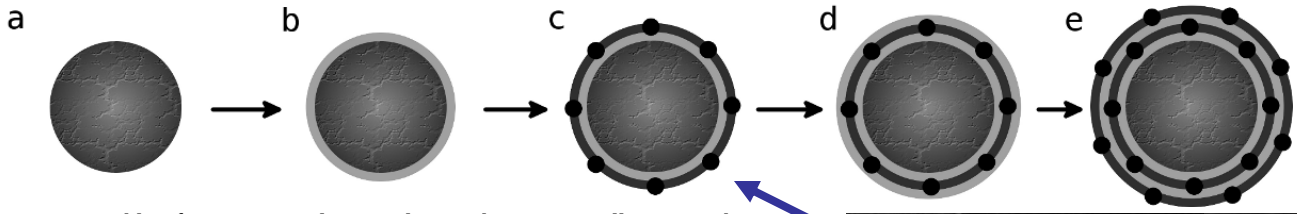

Figure 1: Schematic of electrostatic assembly of Pt nanoparticle on Vulcan carbon support illustrating the individual steps for two overall adsorption cycles: a) bare Vulcan support; b) first cationic polymer layer (light grey) adsorption; c) first Pt nanoparticle layer (dark grey) adsorption; d) second polymer adsorption; and e) second Pt nanoparticle adsorption.

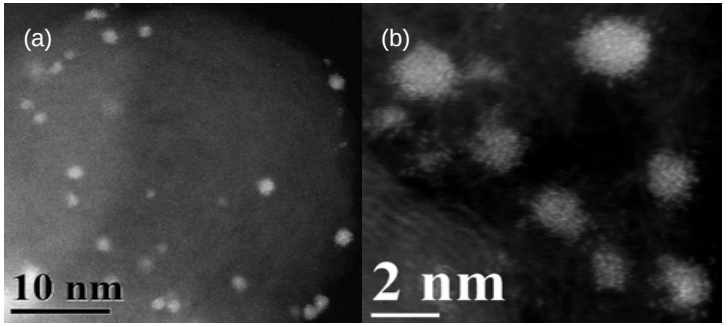

Figure 2: Vulcan supported Pt electrocatalyst. White spots in HAADF-STEM image are transitional (non-crystalline) particles. (a) Magnification illustrates high dispersion formed during electrostatic assembly. (b) Magnification illustrates preservation of particle transitional structure and size during electrostatic assembly.

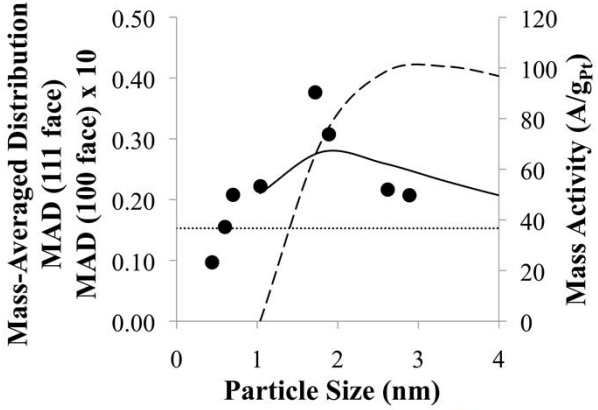

Figure 3: Average mass activity (A/g_{Pt}) plotted versus particle size (circles). Commercial catalyst (TKK) activity indicated by horizontal dotted line. Mass-Averaged Distribution (MAD) is indicated by a solid line – (111) face; and a dashed line – (100) face x 10. based on calculations by Van Hardeveld et al.

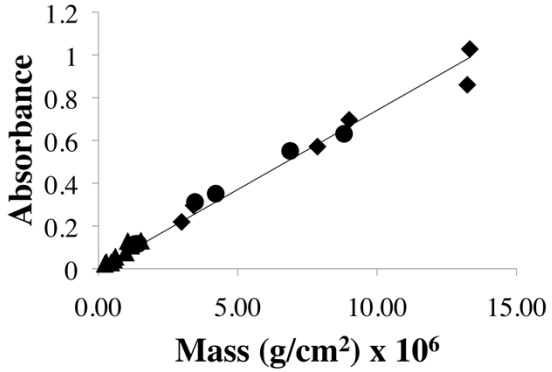

Figure 4: Beer-Lambert analysis of Absorbance versus specific mass data for different electrostatic assemblies of nanoparticles at 352 nm. The different nanoparticle structures are indicated by (▲) atomic clusters; (●) transitional nanoparticles; and (♦) single crystal nanoparticles. Note the overlap in absorbance between the different categories of nanoparticles as the specific mass on the quartz surface varies.

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RESULTS: Enhanced activity is observed with electrostatic assembly of any particle size on Vulcan relative to unsupported or commercial electrocatalyst with comparable durability (see Figure 3). Such enhanced activity is attributed to improved reactant accessibility to the catalyst surface due to the increase in particle dispersion. An extinction coefficient of 7.41m2/g at 352 nm is obtained across the entire cluster to crystal transition from 20 atom clusters to 2.9 nm single crystal nanoparticles (see Figure 4), indicating that observed variation in ORR activity with particle size may be associated primarily with changes in atomic surface structure as opposed to the metallic character of the nanoparticles as assessed by UV-vis spectroscopy.