Ultrahigh Surface Area Catalyst Nanospheres of Pt and Pt/Ru Formed by Electrodeposition

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Uniquely nano-structured platinum and platinum/ruthenium fuel cell catalysts have been electrodeposited[1] and characterized. The catalysts were deposited directly onto carbon black (Ketjen Black) via potentiostatic methods and monitored coulometrically for loading. The process resulted in highly porous 230 nm catalyst spheres forming throughout the carbon black matrix. Characterizations include SEM micrographs, surface area measurements by hydrogen adsorption/desorption in acid solution, bulk chemical composition by chemical analysis and quantitative loadings, all as a function of deposition progress.

SEM micrographs were taken at several coulombic loadings. Interestingly, the size of the catalyst spheres did not change with increased loading, only the number density within the carbon matrix changed. This presents a peculiar phenomenon where individual nano-spheres nucleate and grow rapidly to approximately 200 nm in diameter, then slow down, forcing others to nucleate and grow. Very slow growth was noted once the catalyst particles reached about 200 nm, and a maximum size of 230-250 nm was present at higher loadings. Low loadings showed the initial growth of the first spheres, and high loadings forced agglomeration of spheres and eventual "skinning" at the free surface of the carbon layer. High-resolution SEM micrographs revealed pores on the order of 2-4 nm at the surface of all the spheres, and cleaved spheres showed porosity throughout the bulk of the spheres.

Hydrogen adsorption/desorption measurements on Pt nano-spheres demonstrated an electrochemically active specific surface area in excess of 100 m^2/g of Pt catalyst over a range of loadings. Lower specific surface areas were seen at earlier stages of deposition and can be explained by the change in porous structure as the spheres undergo the final slow growth process. A sharp decrease at high loadings was caused by agglomeration and skinning.

Chemical analysis of the Pt/Ru spheres showed a constant ratio of 78% platinum to 22% ruthenium with our given deposition conditions over the entire range of loadings studied. Also, post-deposition, quantitative mass measurements showed a deposition efficiency (current efficiency) of 35-50%. The deposition was done potentiostatically just positive of hydrogen adsorption and the background current measured was very small. SEM micrographs revealed nearly identical porous morphology to that of the Pt spheres described above. We note that a similar morphology for Pt/Ru catalyst spheres was reported recently.[2] However, surfactants were utilized for that synthesis, and the surface areas reported were lower by more than a factor of two.

Ultimately, it is desirable to control the morphology of these platinum and platinum/ruthenium nano-spheres. The Pt/Ru catalysts have been tested successfully as anode materials in a direct methanol fuel cell and exhibit specific power densities of 34 mW/mg and 130 mW/mg at room temperature and 90°C, respectively. If the growth of these spheres can be arrested at smaller particle sizes, the area of electrochemically accessible catalyst surface, while still supporting high current, could be increased. We are continuing to study this aspect of catalyst deposition and control.

References:

1. S. C. Kelley, G. A. Deluga and W. H. Smyrl, *Miniature Fuel Cells Fabricated on Silicon Substrates*. AIChE Journal, May 2002, **48**(5), p. 1071-1082.
2. Junhua Jiang and Anthony Kucernak, *Mesoporous Microspheres Composed of PtRu Alloy.* Chemistry of Materials, November 2003, **16**, p. 1362-1367.

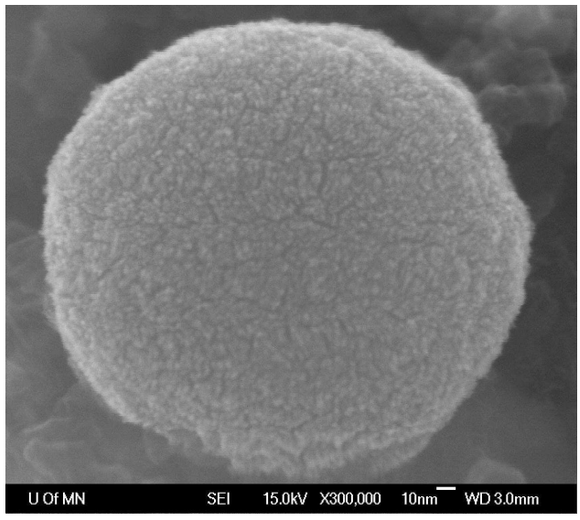

Figure 1: SEM micrograph of a fully developed 250nm diameter Pt/Ru catalyst sphere clearly showing surface porosity.