

Flame Based Synthesis of Core-Shell Structures using Pd-Ru and Pd Cores Prepared from the Vapor Phase with Reactive Spray Deposition Technology

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The oxygen cathode in proton exchange fuel cells still dominates catalysis research due to the slow kinetics of electrochemical oxygen reduction. Even as the automotive industry is making plans to put large numbers of fuel cell powered cars on the road, researchers are focusing their efforts on this critical cost component of the cell. At present, the most promising near-term electrocatalysts for the oxygen reduction reaction (ORR) appears to be the platinum-based bimetallic systems, and it is likely that these will be used in electric vehicles in the future.

Core-shell catalyst structures, having a shell thickness of only a monolayer, have garnered enormous attention because they simultaneously reduce cost and tune catalyst activity. The core composition shifts the electronic structure at the surface of the active shell material. Core-shell structured nanoparticle catalysts can be tailored to optimize the surface activity and/or product selectivity for many applications. Adzic et al. pursued this concept initially to produce monolayers of Pt on Ru for anodic fuel cell reactions such including a CO-tolerant hydrogen oxidation reaction (HOR) and the methanol oxidation reaction (MOR) [1,2]. This concept has now been extended to ORR catalysis [3,4]. Cores formed from various bimetallic alloys including Pd-Ru and having a monolayer shell of Pt produce increased activity, ration the total Pt use and show durability improvements [5,6].

Reactive spray deposition technology (RSDT) has been developed by Maric et al. to produce nanoparticles in vapor phase for catalysts comprised of Pt [7], $\text{Ir}_x\text{Pt}_{1-x}\text{O}_{2-y}$, and $\text{Ir}_x\text{Ru}_{1-x}\text{O}_{2-y}$ [8]. Figure 1 shows a representation of the RSDT process. As a first step in producing a non-oxidized and non-phase separated Pd-Ru core, the RSDT processing conditions must be optimized with feedback from microscopy and chemical analysis. Feasibility in this approach has been demonstrated with the bimetallic Pd-Pt system prepared by the analogous flame spray pyrolysis process [9]. In this study, glassy carbon rotating disk electrodes and gas diffusion layers are coated directly by the RSDT process. Next, a Pt monolayer is synthesized using galvanic displacement of an underpotentially deposited (UPD) Cu monolayer. The Pt attached on the surface is then tested for electrochemical surface area and activity toward the oxygen reduction reaction. Additionally, representative TEM grids (removed at several timed intervals) will be used to examine the evolution of the growing film before thickness effects obscure imaging. Examples of the particle (size and crystallinity) and film (morphology and thickness) properties produced by the RSDT process will be examined. Representative morphologies are shown in Figure 2 using Pt as the reference catalyst. The individual

nanoparticles will be counted to determine the average particle size and distribution. Phase segregation will be examined by XEDS, the crystal structure examined by bulk (powder diffraction) and spatially (TEM) resolved diffraction methods.

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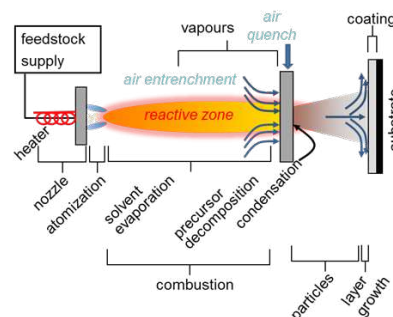


Figure 1. Schematic diagram of the RSDT process showing the atomization, combustion and film formation sections of the process.

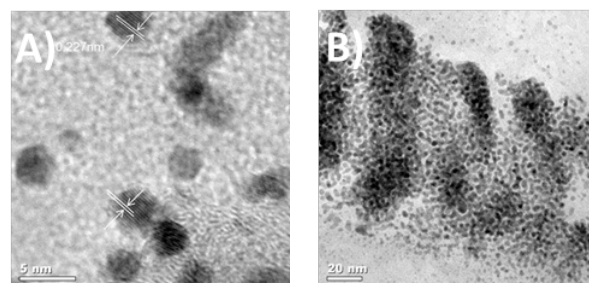


Figure 2. A) Individual particles of Pt deposited directly onto a Cu grid and onto a Vulcan XC-72R carbon particle (lower right corner) and B) A 100 nm film of Pt formed directly onto a Nafion® electrolyte