Templated Vapor Synthesis and Thermally-Induced Evolution of Platinum-Group Metal Nanotubes

Robert W. Atkinson III[1,*], Alexander B. Papandrew[1], Thomas A. Zawodzinski, Jr.[1,2]

[1]Chemical and Biomolecular Engineering
University of Tennessee
Knoxville, TN 37996

[2]Physical Chemistry of Materials Group
Oak Ridge National Laboratory
Oak Ridge, TN 37831

Unsupported metallic nanotubes are extraordinarily active, durable materials for electrocatalysis and electrochemical device applications. High aspect ratio morphology nanotubes composed of platinum thin films exhibit high specific activity for the oxygen reduction reaction while limiting sacrifices in electrocatalytic surface area[1]. Substituting platinum by palladium in these nanotube structures and alloys of the two metals may be promising catalysts for the electrooxidation of alcohols.

Typical synthesis routes for these materials include template electrodeposition[2] or galvanic displacement[3]. Here, we detail an alternate route to metallic and alloy nanotubes based on a chemical vapor deposition (CVD) process.

The metalorganics platinum acetylacetonate ($Pt[acac]_2$) and palladium acetylacetonate ($Pd[acac]_2$) are used to deposit conformal nanoparticle films of platinum, palladium, or platinum-palladium within the pores of anodic alumina (AAO) templates by decomposition of the precursors by a heat treatment at 180°C. As-synthesized Pt, Pd, or Pt-Pd nanotubes can be liberated by dissolution of the template to yield freestanding nanotubes. Alternatively, the thermally stable templates can be annealed to induce structural evolution of the nanotube structures, including crystallite growth and the development of nanoscale porosity.

The Pt, Pd and PtPd nanotubes were characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD) and energy dispersive spectrometry (EDS). Prior to heat treatment, the nanotubes are nanoparticulate aggregates composed of 3 to 3.5 nm crystallites. The tubular structures have 200 nm outer diameters and range in length from 1 to 20 µm. Annealing the nanotubes induces crystallite growth, development of porosity and thinning of the walls. In the case of the annealed PtPd nanotubes, we have confirmed that the metals are alloyed by XRD.

We have demonstrated that annealed platinum nanotubes are highly active catalysts for oxygen reduction[1]. Pd and Pt-Pd nanotubes may display similarly high specific activities for the oxidation of alcohols and more complex liquid fuels.

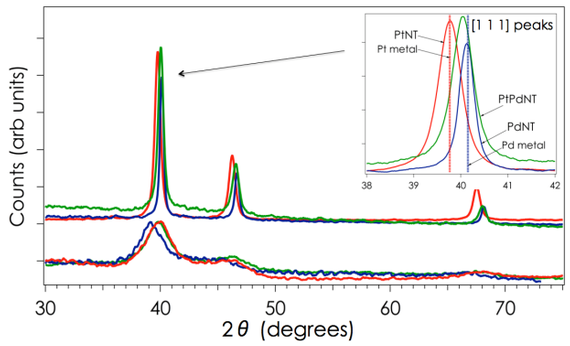

Figure 1. XRD patterns of PtNTs, PdNTs and PtPdNTs.

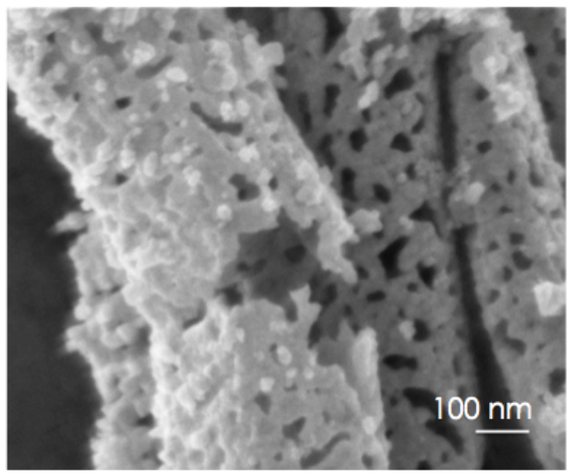

Figure 2. Scanning electron micrograph of platinum-palladium nanotubes (58% palladium) annealed at 500°C.

References

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