

## 3D Transmission X-ray Microscopy Characterization of PtNi Extended Surface Catalyst Electrodes

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Platinum catalysts with extended surfaces have demonstrated much promise as catalysts for the oxygen reduction reaction (ORR) in polymer electrolyte membrane fuel cells (PEMFCs) with higher specific activities than the current state of the art catalysts composed of platinum nanoparticles supported on high surface area carbon (Pt/HSC). The main limitation of these catalysts is low mass activities due to low surface areas.

In this work we focus on Pt-Ni nanowires synthesized by galvanic displacement. Through optimization of morphology, structure, surface and bulk composition high Pt surface areas ( $> 90 \text{ m}^2/\text{g}$ ) were achieved. Pt-Ni nanowires demonstrated initial specific activity 7 times higher than Pt/HSC and showed high durability with 97% of the initial activity being retained after durability testing.

Our current efforts focus on optimization of the performance of these extended surface electrode structures in membrane electrode assemblies (MEAs), which requires detailed information about electrode composition and structure. XAS (XANES and EXAFS) and TXM at SSRL was used to analyze a series of electrodes to explore the effects of ink formulations (i.e. amount of ionomer, amount and type of carbon, addition of poly(acrylic acid) (PAA)) on electrode structure). The results showed clear differences in the cathode electrode structure with the various ink compositions and post-treatments. Addition of graphitized carbon nanofibers (GCNFs) resulted in significantly less densely packed, but more homogeneous nanowire distribution. 3D reconstruction of the MEA confirms the observed structure persists throughout the MEA. Changes in the electrode structure were also observed after leaching the electrode in acid with the goal of removing unalloyed nickel from the bulk of the nanowires. EXAFS studies confirmed that Pt is alloyed to Ni and leaching removes unalloyed Ni while the alloyed Ni remains. TXM and XAS were correlated with analysis from other microscopy techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning TEM (STEM) combined with energy dispersive elemental mapping. The results from these studies provide guidance for further optimization of extended surface catalysts and electrodes.

