

## Fine Tuning Highly Active Pt<sub>3</sub>Ni<sub>7</sub> Nanostructured Thin Films for Fuel Cell Cathodes

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Polymer electrolyte membrane fuel cells (PEMFCs) are under intense research and development for transportation applications. It has been shown that a highly active, lower cost, oxygen reduction reaction (ORR) catalyst can be made by replacing a portion of the costly Pt catalyst with a transition metal, in this case Ni [1]. Further gains can be achieved through dealloying the PtNi alloy catalyst to create a Pt-rich skin or shell, although spontaneous dealloying during fuel cell operation poses a significant durability issue [2]. While usually deployed in nanoparticle form, highly active Pt<sub>3</sub>Ni<sub>7</sub> nanostructured thin films (NSTF) have also been demonstrated, and the substantial increase in both the specific activity and specific surface area has been attributed to a complex interplay between composition, grain size, lattice strain, and the catalyst nanoparticle morphology, e.g., Pt-skin, -shell or -skeleton structures [3].

In this work, dealloying and annealing pre-treatments have been performed on Pt<sub>3</sub>Ni<sub>7</sub> NSTF aimed at improving the specific activity and area, as well as operational durability. The effect of these pre-treatments on catalyst morphology at the nanoscale has been characterized by quantitative scanning transmission electron microscopy (STEM) techniques including energy dispersive X-ray spectroscopy, selected area electron diffraction, and electron tomography. These results are correlated with X-ray diffraction, X-ray fluorescence, and cyclic voltammetry measurements to understand structure-activity relationships, which direct further process development for enhanced performance. These measurements were performed following five major stages of the catalyst preparation and performance testing: growth, dealloying, annealing, conditioning, and voltage cycling. High-angle annular dark-field (HAADF)-STEM images of the PtNi NSTF catalyst at each of these stages is shown in Figure 1.

The dissolution of Ni from the as-deposited Pt<sub>3</sub>Ni<sub>7</sub> catalyst via dealloying and annealing treatments resulted in a Pt-rich surface layer. Fuel cell conditioning, an activation process performed by cycling the fuel cell on and off, induced the largest change in the NSTF catalyst whiskers, which are transformed into a nanoporous Pt<sub>7</sub>Ni<sub>3</sub> alloy. The voltage-cycled electrode was further studied by electron tomography to reveal an open-pore network (Figure 2). The available surface area (electrochemically active surface area) was quantified and compared with an annealed whisker to show that the pore network and loss of the whisker interior may provide additional catalytically active sites in the cycled NSTF electrodes [4].

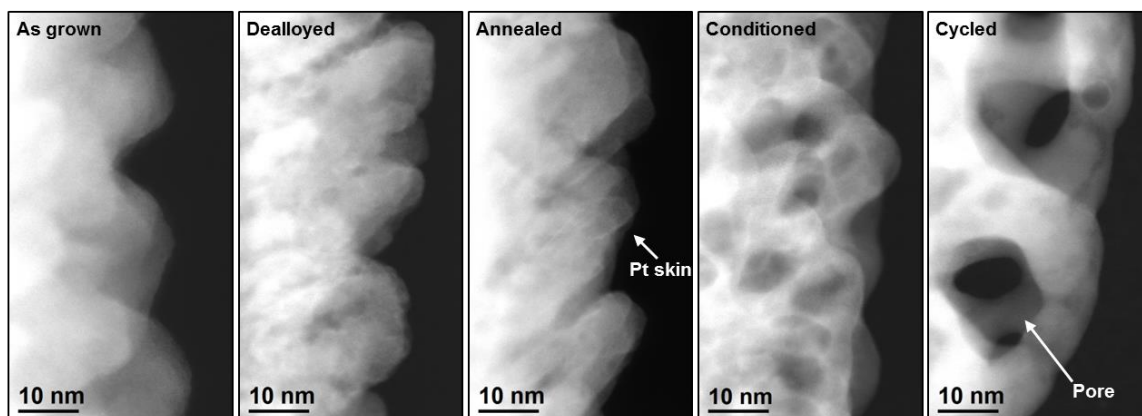
### References:

[1] V.R. Stamenkovic *et al.*, Nat. Mater. **6** (2007) p. 241.

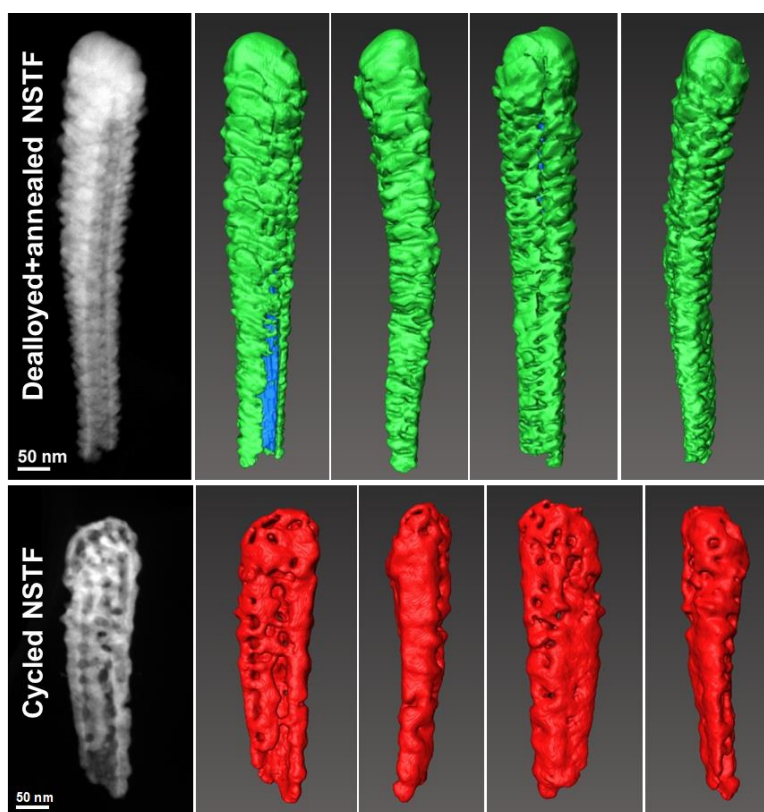
[2] J. Synder. I. McCue, K. Livi, J. Erlebacher, J. Am. Chem. Soc. **124** (2012) p. 8633.

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**Figure 1.** HAADF-STEM images of PtNi NSTF alloy catalyst during various stages of treatment and testing.



**Figure 2.** HAADF-STEM images and 3D rendered surface of individual NSTF whiskers following pretreatment and voltage cycling. The surface area and Pt loading were quantified, allowing for an estimation of the specific area, which could be compared with cyclic voltammetry measurements. Color scheme: blue=perylene-red core, green/red= $\text{Pt}_3\text{Ni}_7$  catalyst