

## Low Pt Content DMFC Catalyst Discovery Using Combinatorially-Deposited Nanoscale Thin Films

Jay F. Whitacre, and S.R. Narayanan

Jet Propulsion Laboratory/California Institute of Technology  
4800 Oak Grove Drive, Pasadena, CA 91109

To minimize the costs associated with mass-producing fuel cells, it is desirable to limit or even eliminate the amount of precious metal necessary for sufficient PEM catalyst performance. To this end, we have conducted a set of experiments aimed at understanding the DMFC anodic catalytic reaction process via the study of carefully controlled catalyst surface compositions and structures.

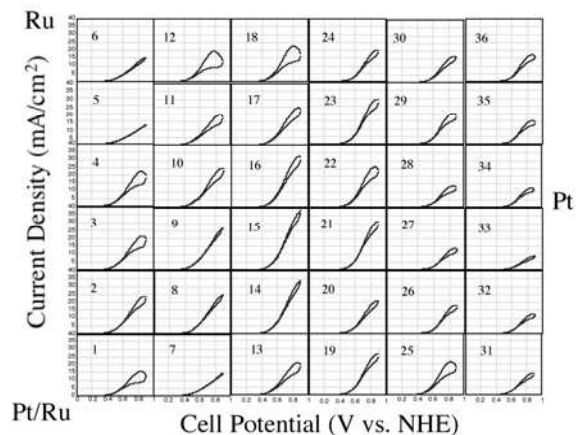
To reduce the effects of surface/bulk segregation and variable surface morphologies, extremely thin (less than 80Å) catalyst layers were sputter-deposited onto flat Au electrode structures. To facilitate the rapid examination of many compositional variations, a 36-cell combinatorial substrate (patterned Ti/Au on polished glass) was used in conjunction with three 2" sputter targets. All films were deposited at room temperature using simultaneous sputtering from all 3 targets. This ensured atomic-level mixing though the bulk and surface of the film while the low deposition temperature mitigated any significant thermally motivated segregation effects. Hundreds of test cells containing various levels of Pt, Ru, Ni, and Zr were fabricated and rapidly screened electrochemically at temperatures ranging from 23°C to 60°C using a 36-channel pseudo-potentiostat (cyclic voltammetry and potentiostatic analyses). X-ray diffraction (XRD), scanning electron microscopy (SEM), x-ray energy dispersive spectroscopy (XEDS), Rutherford backscattering spectroscopy (RBS), and x-ray photoelectron spectroscopy (XPS) were used to study composition and structure.

To establish experimental validity, the industry-standard Pt/Ru catalyst system was examined. The optimal Pt/Ru ratio was determined to be 91/9, and potentiostatic current levels at 0.45 vs. NHE in a 1 M H<sub>2</sub>SO<sub>4</sub>/1 M methanol were similar to those reported in the literature (about 0.15 mA/cm<sup>2</sup> after 300 seconds at room temperature). Figure 1 shows some of the data from this set of experiments.

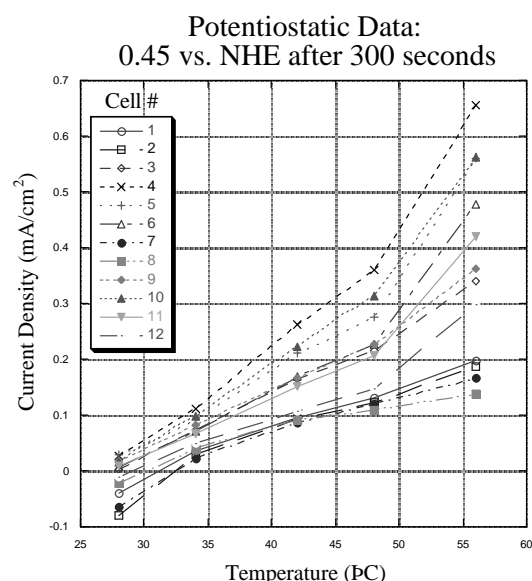
The Ni/Zr/Pt/Ru system was then examined. It was found that a catalyst with as little as 30 atomic % Pt can exhibit nearly the same catalytic activity as the industry standard 91/9 Pt/Ru. Figure 2 shows the potentiostatic collected from some low Pt-content cells at temperatures ranging from 25 to 60 °C.

X-ray diffraction analyses showed that those films that contained greater than 50% Pt were typically single phase (substitutional FCC Pt-like) and nanocrystalline. Lower Pt content films contained multiple phases and were partially amorphous.

These results will be discussed in the context of several methanol catalysis models. In particular, it will be shown that the ensemble model of methanol catalysis used to describe the Pt/Ru system is not applicable to the novel quaternary Ni/Zr/Pt/Ru alloy studied here. Implications for further work and industrial insertion will be addressed.



**Figure 1:** C-V data from 36 electrode Pt/Ru array collected at 58°C in H<sub>2</sub>SO<sub>4</sub>/1 M methanol. The general location of the Pt, Ru, and Pt/Ru sputter targets are indicated in the figure. Data indicate that cell 15 exhibited the highest current densities. Correlating potentiostatic data with composition showed that the best Pt/Ru ratio was 91/9. The current density was calculated based on electrode area (did not vary significantly from electrochemical area).



**Figure 2:** Potentiostatic data from 12 cells composed of the quaternary alloy Ni/Zr/Pt/Ru. Cell #4, which contained about 30 atomic % Pt, exhibited the highest current density at all temperatures. This performance was similar to that of the best Pt/Ru materials. The current density was calculated based on electrode area (did not vary significantly from electrochemical area).