# Structural and Compositional Control of Mesostructured Thin Film Electrocatalysts

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Our fundamental understanding of commercially relevant electrocatalytic processes, particularly those related to fuel cells (oxygen reduction (ORR) and hydrogen oxidation (HOR)) to date has been greatly aided by the use of single crystal metal electrodes. Single crystals have allowed a direct correlation of surface structure such as steps, kinks and flat atomically ordered domains with electrochemical activity. Modulation of this structure, through selection of different low index crystallographic orientations or vicinal stepped surfaces, along with introduction of transition metal alloying components toward optimized compositional gradients (Pt-skinned alloys) has given valuable insight leading to development of extended (bulk) surfaces with dramatically enhanced activity [1]. Moving forward, the challenge is to mimic this bulk, compositionally optimized architecture in high surface area, practical electrocatalysts.

Single crystal electrodes, especially those composed of precious metals can be very cost prohibitive. Here we demonstrate a process by which sputtered metal thin films (~20 nm thick) on glassy carbon substrates are transformed from a small grained (~5 nm), polycrystalline surface to a structurally ordered electrode that while still polycrystalline, displays a strong (111) texture. Through thermal annealing, grain growth and ordering driven by surface energy reduction produce a surface whose electrochemical signature is nearly identical to that of highly oriented, bulk single crystal electrodes, see Figure 1. Atomically flat domains on these mesostructured thin films have been identified by STM to be on the order of hundreds of nanometers wide. Ease of fabrication, negligible amount of precious metal use and the high quality surface produced make these mesostructured thin films ideal for electrocatalytic investigations.

In addition we will use these mesostructured thin films to move beyond planar surfaces and develop unique 3D nanoporous architectures with electrochemically active surface areas equivalent to nanoparticles but with electrochemical and electrocatalytic properties that directly mimic those of bulk electrodes. Through annealing in various gas mixtures of as-sputtered alloys and dealloyed metals we can create ordered domains on the ligaments of the porous metal and tune the compositional gradient giving optimized electrocatalytic activity as well as durability.

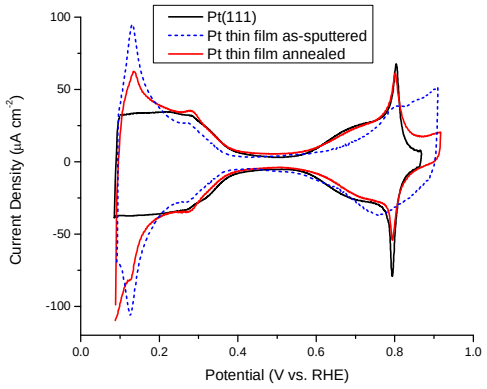


**Figure 1:** Cyclic voltammograms of Pt(111) (black line), as-sputtered Pt-thin film (blue dotted line) and annealed, Pt(111)-like thin flim (red line) recorded in 0.1 M $HClO_4$ with a sweep rate of 50 mV $s^{-1}$.

References

[1] V. Stamenkovic, B. Fowler, B. Mun, G. Wang, P. Ross, C. Lucas, N. Markovic, *Science* **315** (2007) 493.