

Evidence of Enhanced Activity of *In-situ* Formed Pt Nano-rafts on Molybdenum Carbide Support

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The proton exchange membrane fuel cell (PEMFC) is a technology that has the potential to economically replace combustion engines for transportation with high efficiency, and clean (only water emission) energy. The US department of energy (DOE) identifies two remaining major hurdles to the deployment of this alternative: cost and durability of the cathode.¹ Reducing the amount of platinum, still the only material with the needed catalytic activity for oxygen reduction reaction on the cathode, and the most expensive component, will help overcome the first problem and the creation of a new, 'non-carbon', more oxidation-resistant catalyst support material could overcome the second.

At present, carbon is the preferred support, because it exhibits the primary features required: abundant, high surface area, good electrical conductivity, and low cost. However, the use of carbon is clearly problematic. It is well known that the conditions in PEMFCs are oxidizing, especially in the cathode.²⁻⁴ These conditions are detrimental to the carbon and the catalysts which interact with it and shorten the lifetime of PEMFCs.^{5,6} For this reason, electronically conductive ceramic supports are being pursued as alternative supports for PEMFCs.

A novel catalytic synthesis of Pt/Mo₂C, from a physical mixture of precursors, led to the production of unique platinum structures: Nano-rafts, containing less than six atoms of Pt on a molybdenum carbide support (Figure 1). Figure 2 shows the XRD trace of this catalyst; no evidence of nano-crystalline Pt is evident in this XRD trace as one would typically see on Pt/C catalysts (ca. 20–30 Å sized Pt nano clusters). The XRD traces show only a cubic phase Mo₂C (*a*=4.225Å) with an average crystallite size on the order of 22-23Å as determined by full profile fitting methods. Electrochemical half-cell tests (Figure 3) of oxygen reduction demonstrate that nano-raft structures allow for more efficient utilization of platinum, with higher half wave potential than i) traditional, commercial carbon supported catalysts and ii) Mo₂C supports loaded with Pt dispersed post-synthesis using incipient wetness approaches. X-ray photoelectron spectroscopy indicate the Pt nano-rafts have a unique chemistry, specifically there is evidence a strong charge transfer to the support accompanied with the unique morphology. Density functional theory calculations also suggested a strong charge transfer from platinum to Mo₂C should be expected commensurate with enhanced durability when compared to commercial Pt/C catalysts. We will present these data along with other results and discuss the impact that the Nano-raft structure has on support durability in half-cell accelerated stress test (AST) measurements.

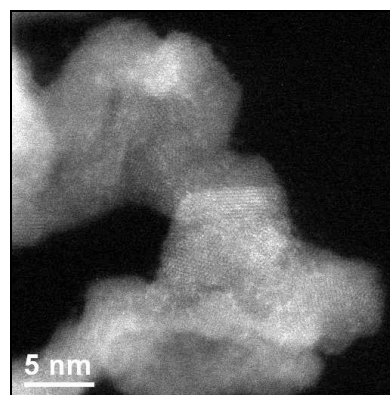


Figure 1. High-angle annular dark field (HAADF) STEM image of Pt imbedded Mo₂C.

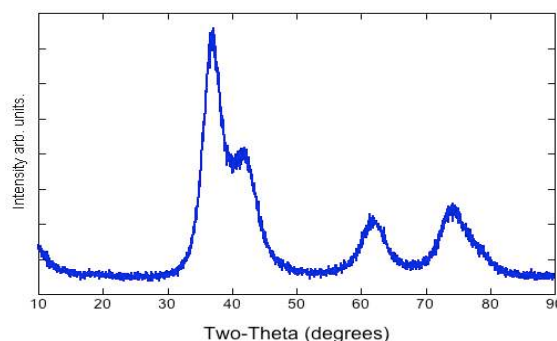


Figure 2. X-ray diffraction trace (XRD) using Cu K_α radiation of a Mo₂C support with 5 wt% Pt dispersed at the time of support formation. Diffraction peaks present are attributable only to the cubic phase molybdenum carbide.

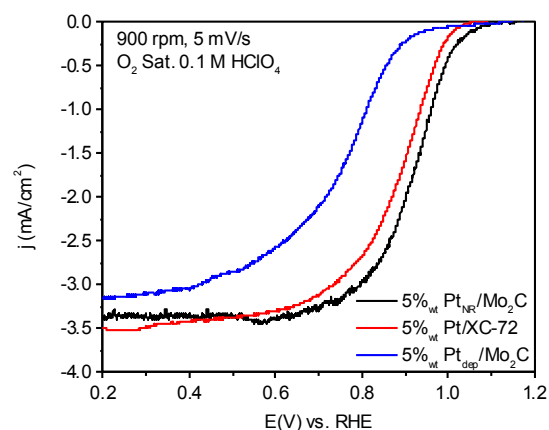


Figure 3. RDE at 900 rpm and 5 mV/s in oxygen saturated 0.1M HClO₄ in DI water of 5% Pt/Mo₂C with imbedded Pt Nanorafts (black curve), 5% Pt deposited on Mo₂C post support synthesis (blue curve), and a commercial 5%Pt/XC-72 for comparison (red curve).

References

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