

Highly Dispersed Pt on Mo₂C: Durable Catalyst for Oxygen Reduction Reaction

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State-of-the-art Pt/C catalysts for PEMFC cathodes have been shown to suffer from limited durability due to electrochemical oxidation of the carbon support [1]. As an alternative, high surface area transition metal carbides have been investigated as corrosion resistant support materials due to their resistance to electrochemical oxidation. Specifically, molybdenum carbide is of significant interest as high degrees of platinum dispersion and strong catalyst-support interactions between platinum and molybdenum carbide have been reported [2]. It is our goal to further stabilize Pt supported on β -Mo₂C by dispersing Pt prior to the formation of passivation oxide on the carbide surface, allowing for a more direct Pt-Mo₂C interaction, which is believed to stabilize Pt and provide for a more durable catalyst.

Previously, we reported a novel synthesis method which focuses on the controlled decomposition of magnesium containing precursors under syngas to yield a high surface β -Mo₂C phase [3]. In the present work, this method has been modified to allow for an *in situ* approach to achieve high levels of platinum dispersion on β -Mo₂C. A newly developed Pt-Mo salt has been prepared by adding chloroplatinic acid hydrate (CPA) to a solution of (NH₄)₂Mg(MoO₄)₂. A precipitate is formed from the solution by using ammonium hydroxide which produces an insoluble salt containing platinum, magnesium, and molybdenum. The molybdenum salt is then reacted in syngas at elevated temperature producing a solid solution of Pt and β -Mo₂C as well as MgO, which serves as a sacrificial support.

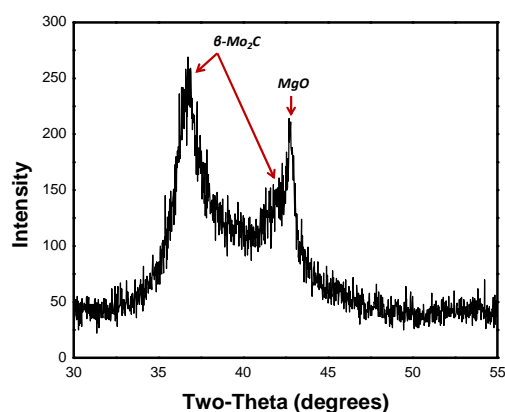


Figure 1. XRD pattern for 8% Pt/ β -Mo₂C + MgO

Figure 1 shows the XRD pattern for 8wt% Pt/ β -Mo₂C produced from this reaction. The absence of crystalline platinum suggests a possible solid solution of Pt and β -Mo₂C. Cyclic voltammetry also shows that platinum is likely not on the surface or is otherwise inaccessible. A strategy was developed to draw platinum

to the surface of the carbide using CO adsorption in a cyclic voltammetric process.

For the electrochemical activation of Pt, a rotating disk electrode (RDE) was prepared using 8%Pt/ β -Mo₂C. CO was sparged into the cell and the electrode potential was cycled from -50mV to 1000mV vs. RHE for 5 minutes. After CO cycling multiple CV's were performed to observe CO desorption and subsequent H₂ adsorption on the newly formed surface Pt. The cell was then saturated in O₂ and CV data was recorded for ORR. CO cycling has shown to improve oxygen reduction performance significantly through improvements of both limiting current as well as in the half wave potential for ORR. However, a large overpotential associated with this catalyst is attributed to the presence of low conductivity MgO which was not leached from the catalyst prior to electrochemical measurements.

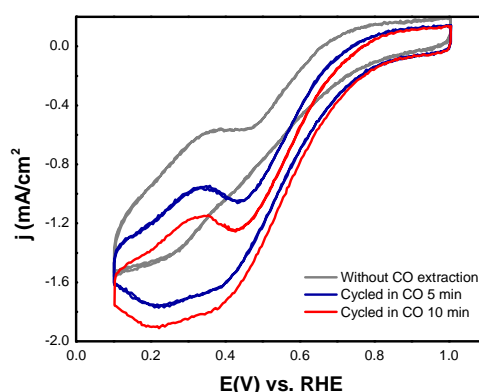


Figure 2. Cyclic voltammetry in 0.1M HClO₄ in saturated O₂ for 8%Pt/ β -Mo₂C without CO cycling, after cycling in CO for 5 min, and after cycling in CO for an additional 5 min.

This early work suggests that *in situ* methods of platinum dispersion on β -Mo₂C can be used without forming highly crystalline, i.e. large particle size, platinum. Additionally, CO adsorption/desorption can be employed to draw otherwise inactive platinum particles to the surface of β -Mo₂C. The use of *in situ* dispersion methods are believed to result in increased catalyst durability, homogeneously distributed platinum particles, a more efficient and cost effective catalyst synthesis, and a more efficient use of platinum by the formation of highly active nano-particles. Future work will focus on exploring the effect of Pt loading and ultimately investigating the durability of these catalysts for PEMFC applications.

This work is supported by Los Alamos National Laboratory through the U.S. Department of Energy Hydrogen and Fuel Cell Technology Program and in conjunction with the UNM Center for Emerging Energy Technologies

References:

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