

## Highly Stable and Active Electrocatalysts for Oxygen Reduction : Presynthesized Bimetallic Nanocrystals on Graphitic Carbon

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### Introduction

The commercialization of polymer electrolyte membrane fuel cells (PEMFC) requires activity enhancements for the oxygen reduction reaction (ORR) ~4 times that for pure Pt catalysts<sup>1,2</sup>. Another major challenge is to increase the catalyst stability upon exposure to potential cycling. For Pt supported on traditional amorphous carbons (e.g. Vulcan XC-72), a >50% loss in electrochemical surface area (ECSA) results from potential cycling between 0.5V and 1.2V for 1000 cycles. Graphitic carbon supports would offer resistance to carbon oxidation, however it is difficult to disperse noble metals on these supports as the ionic precursors interact weakly with graphitic sites. In this study we synthesize highly stable catalysts by infusion of presynthesized bimetallic onto graphitic carbons. We achieved 4x mass activity (0.46 A/mg<sub>Pt</sub>) over commercial Pt/C (0.11 A/mg<sub>Pt</sub>) and with ~0% loss in both mass activity and ECSA over potential cycling.

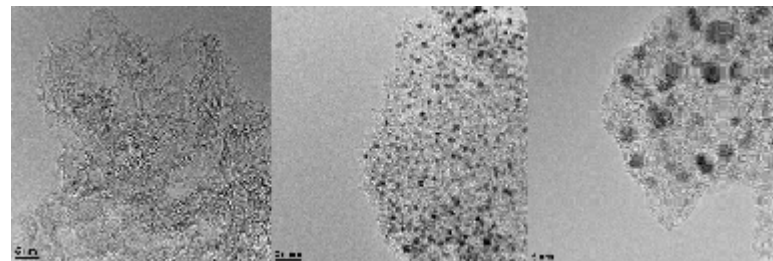
### Materials and Methods

Catalyst Pt-Cu particles were synthesized via a modified polyol process described by Sun et al. and adsorbed onto disordered mesoporous carbon (DMC) graphitized at 850, 2000, and 2600 °C. The catalysts were filtered and calcined at 350 °C. Catalyst loadings were determined using UV-Vis spec. and thermal gravimetric analysis (TGA). X-ray diffraction, SEM-EDX, Raman, and TEM were used for characterization. All electrochemical tests were performed in a 3 electrode cell with 100mL 0.1M HClO<sub>4</sub> on a glassy carbon rotating disk electrode (GC RDE). Catalysts were dealloyed at 200mV/s for 500 cycles from 0.05–1.24V (sat. Ar). The hydrogen desorption peak in the cyclic voltammogram was used to calculate electrochemical area (m<sup>2</sup>/mg<sub>Pt</sub>). RDE measurements were taken in sat. O<sub>2</sub> at 5mV/s at 1600rpm from 0.05-1.24V. An electrochemical accelerated durability test (ADT) was done at 50mV/s for 1000 cycles from 0.5-1.2V(sat. Ar).

### Results and Discussion

We synthesized monodisperse (3.2 nm), nearly single phase (Pt<sub>20</sub>Cu<sub>80</sub>) catalyst particles. Loadings on the graphitic DMC carbon approached ~20 wt% with high dispersion due to a favorable interaction between the graphite and metallic particles (Figure 1). This interaction results from electron delocalization and partial charge transfer between the abundant  $\pi$  electron sites in graphitic carbon (layered sections, Figure 1 left) and platinum, as demonstrated by XPS and electron-spin resonance (ESR)<sup>3</sup>.

The mass activity for commercial Pt on Vulcan carbon and PtCu<sub>3</sub> on DMC 2000 are shown Table 2. The activity is determined at 0.9 V (NHE) to be 4x for the bimetallic catalyst on graphitic carbon. The activity has been hypothesized to be a result of the dealloying process, resulting in the formation of a strained Pt shell on the surface of the particles<sup>2</sup>.



**Figure 1.** TEM of DMC 2000 (left), PtCu<sub>3</sub> on DMC 2000 (center), and dealloyed PtCu<sub>3</sub> on DMC 2000. Average particle size: 3.2 nm. Images taken at ORNL.

Table 2 shows essentially complete stability (no measurable loss) of the DMC graphitic carbon catalyst both in the activity and the ECSA upon the ADT. The losses of >50% in both for the commercial more amorphous Vulcan carbon are commonly observed<sup>4</sup>. The oxidation resistance of graphitic carbon is due to the lack of surface polar oxygen groups which would otherwise act as reactive centers for degradation to CO<sub>2</sub>. The carbon stability prevents nanoparticles from losing electrical contact with the support. Furthermore, the strong metal-graphite interaction also inhibits sintering.

### Significance

The exceptionally high stability of these highly active catalysts will be beneficial for fuel cells, as well as other reactions on graphitic supports. In addition, studies of well-defined nanoparticles on supports with controlled size, morphology and composition provide insight into catalytic mechanisms needed for the design of advanced catalysts.

**Table 2.** Activity (at 0.9V NHE) and stability of dealloyed Pt-Cu on various carbons

Sample	I (A/mg <sub>Pt</sub> ) Before ADT	ECSA Before ADT (m <sup>2</sup> /g <sub>Pt</sub> )	I (A/mg <sub>Pt</sub> ) After ADT	ECSA After ADT (m <sup>2</sup> /g <sub>Pt</sub> )
14% Pt <sub>20</sub> Cu <sub>80</sub> / DMC - 2000	0.45	83	0.45	84
20% Pt <sub>20</sub> Cu <sub>80</sub> / vulcan-XC72	0.42	68	0.20	38
20% Pt/ vulcan-XC72	0.11	69	0.04	21

### References

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