

Pulsed Galvanostatic Deposition of Electrocatalysts on
Conductive Diamond Supports

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Electrodes consisting of supported metal catalysts are used in a variety of electrochemical technologies, including electrosynthesis and electrochemical energy conversion devices (e.g., fuel cells). The electrocatalyst support material is extremely important for the operational performance. The primary role of the support is to provide a high surface area over which highly-dispersed nanometer-sized metal particles can be dispersed and stabilized. Supported catalysts enable a decrease in expensive catalyst loading while increasing the electrochemically-active surface area of the catalyst. Platinum is the best electrocatalyst for the oxygen reduction reaction (ORR) – an important reaction in biological systems and fuel cells.

Current electrocatalyst support materials are generally porous, sp^2 -bonded carbon materials (e.g., physically or chemically activated carbon or carbon black). These materials are susceptible to oxidation and/or corrosion in the presence of oxygen, or in aggressive chemical environments. The oxidation/corrosion can lead to decreased catalytic activity due to catalyst detachment, aggregation, and/or fouling by gasification products. Complete electrode failure can result if the degradation is severe enough.

Advanced electrocatalyst support materials are needed for demanding applications where conventional sp^2 -bonded carbon supports fail. Our group has been investigating the use of electrically conducting polycrystalline diamond as an advanced electrocatalyst support material – so called metal/diamond composite electrodes (1-3). There are two technical challenges in this endeavor: development of conductive diamond powders with high surface area, and development of a protocol for depositing highly dispersed electrocatalyst particles on the diamond powder surface. Thus far, we have focused much of our work on (i) determining the dimensional stability of diamond under a variety of electrochemical conditions and (ii) studying metal nucleation and growth on such surfaces. Diamond possesses properties that make it a potentially useful new support material: dimensional stability, resistance to corrosion, and the ability to operate for extended periods of time in harsh chemical environments at high potential, current density, and temperature without microstructural or morphological degradation.

We report on the pulsed galvanostatic deposition of nanometer-sized Pt particles on electrically conducting microcrystalline (BMD) and nanocrystalline (BND) diamond thin films. The deposition was investigated as a function of pulse number (10 – 50) and current density ($0.50 - 1.50 \text{ mA cm}^{-2}$) at two morphologically different forms of diamond. Deposition of catalyst particles using ten 1-s pulses (duty cycle 50%) at a current density of 1.25 mA cm^{-2} (geometric area) produced the most highly dispersed particles on both diamond surfaces. Pulsed deposition is superior to fixed potential deposition in terms of minimizing the particle size and maximizing the

particle density. Secondary electron micrographs (SEM) revealed a nominal particle size of $43 \pm 27 \text{ nm}$ for BMD and $25 \pm 25 \text{ nm}$ for BND, and a nominal particle density of $7.48 \pm 0.92 \times 10^9 \text{ cm}^{-2}$ for BMD and $1.92 \pm 1.00 \times 10^{10} \text{ cm}^{-2}$ for BND. The catalytic activity of these surfaces was evaluated using the oxygen reduction reaction in an acidic medium. Deposition under these conditions resulted in the most efficient utilization of the metal catalyst, judging from the electrochemically-active Pt surface area normalized to the metal loading, the latter estimated by atomic absorption spectroscopy.

Figure 1 shows a scanning electron micrograph of a microcrystalline diamond film decorated with Pt electrocatalyst. Pulsed galvanostatic deposition was employed to form the electrocatalyst particles using 25 pulses at 0.5 mA/cm^2 and a 1 s pulse duration in 1 mM potassium hexachloroplatinate (IV) dissolved in 0.1 M HClO_4 . The metal particles decorate most of the surface (grains and grain boundaries) and the nominal particle size is ca. 50 nm and the partial density is ca. $5 \times 10^9 \text{ cm}^{-2}$.

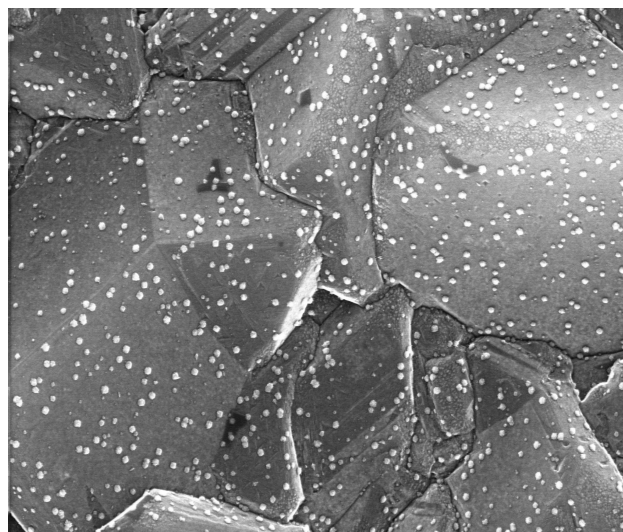


Figure 1. Scanning electron micrograph of a metallized polycrystalline diamond thin-film surface.

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3. J. Wang and G. M. Swain, *J. Electrochem. Soc.*, **150**, E24 (2003).