

Fabrication and Evaluation of Platinum/Diamond Composite Electrodes for Electrocatalysis

Preliminary Studies of the Oxygen-Reduction Reaction

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A catalytic electrode was prepared using a new electrically conducting and corrosion resistant carbon support material, borondoped diamond. Fabrication of the composite electrode involves a three-step process: (i) continuous diamond thin-film deposition on a substrate, (ii) electrodeposition of Pt catalyst particles on the diamond surface, and (iii) short-term diamond deposition to entrap the metal particles into the surface microstructure. The process results in a conductive, morphologically, and microstructurally stable composite electrode containing metal particles of somewhat controlled composition, size, and catalytic activity. The metal catalyst particles were galvanostatically deposited from a K₂PtCl₆/HClO₄ solution, with the metal particle size (50-350 nm) and distribution ($\sim 10^9$ cm⁻²) being controlled by adjusting the galvanostatic deposition and secondary diamond-growth conditions. For a 300 s Pt deposition time, the estimated loading was 75.8 μ g/cm², assuming a 100% current efficiency. The composite electrode was extremely stable, both structurally and catalytically, during a 2 h polarization in 85% H₃PO₄ at 170°C and 0.1 A/cm². The electrode's catalytic activity was evaluated using the O₂ reduction reaction at room temperature in 0.1 M solutions of H_3PO_4 , H_2SO_4 , and $HClO_4$. The kinetic parameters (Tafel slope and exchange current density) were obtained by cyclic voltammetry and were found to be comparable to those for a polycrystalline Pt electrode in the same media. Tafel slopes of -63to -80 mV/dec were observed at low overpotentials, with the lowest slope in HClO₄ and highest in H₃PO₄. The exchange current density ranged from 10^{-12} to 10^{-10} A/cm², and increased in the order of $H_3PO_4 < H_2SO_4 < HCIO_4$. The potential advantages of the composite electrode, as compared with commercial sp^2 carbon electrodes, are (i) the corrosion resistance of the diamond support, resulting in highly stable reaction centers at high potentials, current densities, and temperatures, and (ii) the fact that all of the catalyst particles are strongly anchored at the film surface and are not contained inside pores. © 2002 The Electrochemical Society. [DOI: 10.1149/1.1524612] All rights reserved.

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Electrodes consisting of supported metal catalysts are used in electrosynthesis and electrochemical energy conversion devices (*e.g.*, fuel cells). The metal catalysts are typically impregnated into the porous structure of an sp²-bonded carbon support material. Typical carbon supports include chemically or physically activated carbon, carbon black, and graphitized carbons.¹ The primary role of the support is to provide a high surface area over which small metallic particles can be dispersed and stabilized. The porous support should also allow facile mass transport of reactants and products to and from the active sites.² Several properties of the support are critical, porosity, pore size distribution, crush strength, surface chemistry, and microstructural and morphological stability.¹

A limitation of sp²-bonded carbon supports is their susceptibility to corrosion and microstructural degradation during anodic polarization. One possible carbon electrochemical corrosion reaction is³

$$\mathrm{C} + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{CO}_2 + 4\mathrm{H}^+ + 4\mathrm{e}^-$$

The corrosion rate is strongly dependent on the electrode potential, electrode microstructure, electrolyte composition, and pH. The rate is also affected at a given potential by other factors, such as temperature and vapor pressure.³ In general, high temperature, high pressure, and high operating potentials result in an increased rate of corrosion. Importantly, electrochemical corrosion produces microstructural degradation and surface chemical changes, which generally lead to lost catalytic activity or even catastrophic electrode failure.

Conductive sp³-bonded diamond is a new type of carbon electrode that has attracted much attention recently.⁴⁻⁷ Boron-doped diamond thin-film electrodes possess excellent properties, such as electrical conductivity and chemical inertness. But, two of the most attractive features of diamond are its extreme corrosion resistance and dimensional stability. Compared with more commonly used sp²-bonded carbon materials, diamond is highly resistant to electrochemical corrosion. For example, polycrystalline diamond can withstand anodic current densities of 0.1 A/cm², or greater, for 12 h in an acidic chloride media (E = 3.4 V vs. SCE), without any structural degradation.⁸ The microstructure is also very stable during polarization in 0.1 M HNO₃ + 0.1 M NaF at 50°C, conditions that lead to catastrophic failure of highly ordered pyrolytic graphite (HOPG), GrafoilTM, and glassy carbon.⁹ This makes diamond an ideal electrode for high-current density electrolysis, particularly under demanding conditions (*i.e.*, complex matrix, high-current density and potential, high temperature, extremes in pH, etc.).

Our group has previously demonstrated that electrically conducting diamond is a good electrocatalyst host/support.^{10,11} Nanometersized Pt particles can be incorporated into the surface microstructure of boron-doped microcrystalline diamond thin-films via a sequential diamond growth/Pt magnetron sputtering/diamond growth fabrication procedure. The dispersed Pt particles are stabilized by the growth of a very thin diamond film around their base and are in good electrical communication with the current collecting substrate through the boron-doped diamond support. While the catalyst particles are stably anchored, the magnetron sputtering approach affords poor control over the particle size and distribution.

We report presently on another method for more controllably fabricating Pt/diamond composite electrodes, in terms of the metalparticle size and distribution. In this approach, the Pt particles are galvanostatically electrodeposited from 1 mM K₂PtCl₄ + 0.1 M HClO₄ at 0.5 mA/cm² (geometric area). Control of the particle size (30-500 nm) and distribution ($\sim 10^8$ to 10^9 particles/cm²) is achieved through adjustments in the electrodeposition (current density and time) and secondary diamond growth conditions (C/H ratio, pressure and time). Potentiodynamic deposition of the metal was also investigated, and is briefly discussed herein, but was found to be inferior to galvanostatic deposition. The morphology, microstructure, and catalytic activity of the composite electrodes were examined by atomic force microscopy (AFM), Raman spectroscopy, and cyclic voltammetry (CV), respectively. The Pt-coated electrodes were also characterized, before and after the secondary diamond growth, by AFM, scanning electron microscopy (SEM), energy-

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dispersive X-ray analysis, and CV. The resulting Pt/diamond composite electrodes have metal-catalyst particles that are well anchored into the surface microstructure, all exposed at the surface, and are extremely stable with unchanging catalytic activity even after 2 h of anodic polarization in 85% H_3PO_4 at 170°C and 0.1 A/cm.^{11,12} An acid etching experiment and cross-sectional SEM measurements confirmed that the secondary diamond film grows around the base of the metal deposits, stably anchoring them into the surface microstructure.

Platinum is the best known electrocatalyst for the oxygenreduction reaction and it is widely used in electrochemical energy conversion devices. Pt particles are generally dispersed onto a high surface area conductive support, such as carbon powder or a porous membrane, in order to obtain high electrocatalytic activity and optimized Pt utilization. The electrode kinetics for the oxygenreduction reaction have been extensively studied at Pt-supported catalytic electrodes in both acidic and alkaline electrolytes.¹³⁻²⁷ The electrocatalytic activity of the Pt/diamond composite electrodes for oxygen reduction was investigated in 0.1 M H_3PO_4 , H_2SO_4 , and HClO₄ at room temperature. Tafel slopes and exchange current densities were determined as a function of the electrolyte composition and Pt loading.

Experimental

Preparation of Pt/diamond composite electrodes .-- Diamond thin-films were deposited by microwave-assisted, chemical-vapor deposition (CVD, 1.5 kW, 2.54 GHz, ASTeX, Inc., Lowell, MA) on highly conducting p-Si(100) substrates ($\sim 10^{-3} \Omega$ cm). The substrates (0.1 cm thick \times 1 cm² in area, Virginia Semiconductor, Inc.) were pretreated by rinsing in toluene, methylene chloride, acetone, isopropanol, and methanol. They were then etched in concentrated HF for 60 s, rinsed with ultrapure water, and air dried. The cleaned substrates were then sonicated in a diamond powder/acetone slurry (0.1 µm diam, GE Superabrasives, Worthington, OH) for 20 min followed by a rinse with clean acetone. The sonication scratches the surface and leaves seed crystals (>10⁸ particles/cm²), both of which serve as nucleation sites during film growth. The seeded substrates were then placed in the CVD reactor, and the system pressure reduced to about 10 mTorr. Ultrahigh purity (99.999%) methane and hydrogen were used as the source gases. The hydrogen flow rate was 200 sccm and the methane flow rate was 0.70 sccm during the deposition. Prior to introducing methane, the substrates were heated to the growth temperature in a hydrogen plasma for 10 min. The plasma was formed with a system pressure of 40 Torr and a power of 1000 W. The substrate temperature was approximately 850°C, as measured using a disappearing filament optical pyrometer. The films were doped using solid-state boron dopant sources, a boron diffusion source (GS-126, BoronPlus[™], Techniglas, Inc., Perrysburg, OH) and a small piece of boron nitride (Goodfellow, Ltd., England). Boron-dopant concentrations were estimated to be approximately 10^{19} to 10^{20} B/cm³ (300-3000 ppm B/C), based on boron nuclear reaction analysis of other films deposited using similar conditions. The apparent in-plane film resistivities ranged from 0.1 to 0.01 Ω cm, and were measured using a tungsten four-point probe (0.1 cm probe spacing) with the diamond film attached to the conducting Si substrate

The three-step fabrication procedure for the composite electrodes is shown diagrammatically in Fig. 1. A boron-doped diamond thinfilm was initially deposited on a Si(100) substrate for 12 h. The film thickness, at this stage, was about 4-6 μ m. The diamond growth was then stopped, and the substrate cooled to less than 300°C in the presence of atomic hydrogen. After completely cooling to room temperature, the coated substrate was removed from the reactor. Metal particles were then electrodeposited on the surface. Galvanostatic deposition was performed in 1 mM K₂PtCl₆ + 0.1 M HClO₄ at a current density of 0.5 mA/cm². Both diffusion and convection influenced the magnitude of the current, as nitrogen was slowly bubbled



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Figure 1. Fabrication process for the Pt/diamond composite electrodes.

through the solution during the deposition. This current, and all others in the text, unless otherwise stated, is normalized to the geometric area of the electrode (0.2 cm^2) . Four diamond films from the same batch were examined, using deposition times of 100, 200, 300, and 400 s each. Some experiments involved potentiodynamically depositing the metal particles from the same solution while scanning the potential from 0.8 to -0.3 V vs. Ag/AgCl at 50 mV/s. The Pt-coated diamond film electrode is then placed back in the reactor and boron-doped diamond deposited for an additional 3 h, using the same conditions as described above. The secondary growth film thickness is much less than 1 μ m (on the order of 0.3 μ m) and entraps the metal particles, anchoring and stabilizing them within the microstructure. Diamond will nucleate and grow on both the Pt and the surrounding diamond matrix, however, the growth rate on the diamond is much greater than on the Pt. Undoubtedly, some of the smaller Pt particles can be completely covered during the process, as has recently been confirmed in cross-sectional SEM measurements, but if the conditions are optimized, then the complete coverage of particles is minimized. Hydrocarbon deposits also accumulate on the Pt surface, but these can be effectively removed by potential cycling, as discussed below.

Film characterization.—The atomic force microscopy (AFM) was performed with a Nanoscope II instrument (Digital Instruments, Santa Barbara, CA) in the contact mode. Pyramidal-shaped Si₃N₄ tips mounted on gold cantilevers (200 μ m legs, 0.38 N/m spring constant) were used to acquire topographical images in air. Raman spectra were obtained at room temperature with a Chromex Raman 2000 system (Chromex, Inc., Albuquerque, NM) consisting of a diode-pumped, frequency-doubled CW Nd:YAG (500 mW at 532 nm, Coherent), a Chromex 500is spectrometer (f/4, 600 grooves/mm holographic grating), and a thermoelectrically cooled 1024 × 256 charge coupled device (CCD) detector (Andor Tech., Ltd.). Spectra

were collected with an incident power density of *ca*. 500 kW/cm² (100 mW at the sample and 5 μ m diam spot size).

Electrochemical measurements.-The Pt electrodeposition and cyclic voltammetry were performed in a single-compartment glass cell, using a CYSY-2000 computer-controlled potentiostat (Cypress Systems, Inc., Lawrence, KS). A Ag/AgCl (saturated KCl) electrode was used as the reference and a large-area carbon rod served as the counter electrode. The Pt/diamond composite working electrode was pressed against the bottom of the glass cell, using an Al plate current collector with the fluid being contained by a Viton® O-ring. Silver paste was applied to the center portion on the back side of the Si substrate, after cleaning. The composite electrodes were cleaned, once mounted in the cell, by a thorough rinse with ultrapure water $(>17 \text{ M}\Omega \text{ cm}, \text{ Barnstead E-Pure})$, a 20 min soak in distilled isopropanol, followed by another thorough rinse with ultrapure water. The electrolyte was deoxygenated with nitrogen (99.9%, BOC Gases) for 20 min prior to any electrochemical measurements, and the solution was blanketed with the gas during the measurements. For the oxygen reduction experiments, the solution was saturated with oxygen gas (99.9%, BOC Gases) by bubbling for 30 min prior to any electrochemical measurement.

Chemicals.—All chemicals were reagent grade quality or better and used without additional purification. The acids, HClO₄ (Aldrich), H₂SO₄ (Aldrich), and H₃PO₄ (Aldrich), were all of ultrahigh purity (99.999%). The K₂PtCl₆ (Aldrich) was reagent grade quality. All solutions were prepared with ultrapure water from a Barnstead E-Pure purification system (>17 M Ω cm).

Results and Discussion

Electrodeposition of Pt on diamond thin films.—The Pt electrodeposition was performed by both potentiodynamic and galvanostatic electrolysis, and the results are compared herein. Figure 2A shows cyclic voltammetric *i*-*E* curves obtained during the metal deposition in 1 mM K₂PtCl₆ + 0.1 M HClO₄. A total of twenty-five potential sweeps were made, and the *i*-*E* curves for 1st, 5th, 10th, 20th, and 25th scans are presented. The potential sweep was initiated at 800 mV and scanned in the negative direction to -300 mV at a scan rate of 50 mV/s. During the first cycle (innermost curve), the cathodic current for the metal deposition begins to gradually increase at *ca.* 350 mV *vs.* Ag/AgCl, with the significant current onset at 0 mV. Based on the redox reaction²⁸

$$PtCl_4^{2-} + 2e^- \rightleftharpoons Pt + 4Cl^ E^0 = 561 \text{ mV } vs. \text{ Ag/AgCl}$$

This represents an overpotential of some 200 mV for the deposition of Pt on diamond. A deposition overpotential has also been observed for Ag and Hg on diamond,^{29,30} the cause of which has been attributed, in a very general way, to the inertness of hydrogen-terminated diamond surface. The metal deposition likely proceeds by two irreversible reactions, corresponding to sequential two-electron transfers $(Pt^{4+} \rightarrow Pt^{2+} \rightarrow Pt \text{ or } PtCl_6^{2-} \rightarrow PtCl_4^{2-} \rightarrow Pt)$, as has been proposed for Pt electrodeposition on carbon fiber electrodes.³¹ The reactions occur at potentials sufficiently close such that each step is not well resolved at diamond (50 mV/s). The reduction peak at -240 mV is attributed to the adsorption of hydrogen on the electrodeposited Pt particles, a reaction that is occurring simultaneously with the metal deposition. The current crossover seen during the reverse sweep is a characteristic feature of metal nucleation and growth.³² The voltammetric currents grow with cycle number (the 25th scan is the outermost curve) due to the progressive increase in metal particle size and distribution. All voltammograms, after the initial one, show the characteristic current features for Pt, Pt oxide formation (700-1200 mV), oxygen evolution (1200 mV), Pt oxide reduction (500 mV), hydrogen adsorption and desorption (0 to -300 mV), and hydrogen evolution (-300 mV).

Figure 2B shows a top-view, $10 \times 10 \,\mu$ m AFM image (force mode, air) of the diamond surface after 25 potential cycles. The



B



Figure 2. Successive potentiodynamic *i*-*E* curves for a boron-doped diamond thin-film in 1 mM K₂PtCl₆ + 0.1 M HClO₄ (A). Arrows indicate the current increase with increasing cycle number. Scan rate = 50 mV/s. AFM force mode image (air) of the diamond thin film after 25 potential cycles (B). The white arrows indicate the position of some of the metal deposits.

image features are influenced by the tip geometry, which is often the case when imaging rough, polycrystalline diamond films with low aspect ratio, pyramidally shaped tips. A well-faceted, polycrystalline film morphology is inferred from the image with cubic, octahedral, and cuboctahedral microcrystallites. This morphology was confirmed by SEM. Also present are the intercrystalline grain boundaries where the microcrystallites join together. The Pt deposits are not uniformly distributed over the surface but rather are located almost exclusively at grain boundaries and other visible, extended defects (see arrows). The particle diameters range from 0.3 to 2 μ m with a distribution density of *ca*. 4×10^7 cm⁻² (geometric area), although the shapes of the deposits are most strongly influenced by the tip geometry. After 25 potential cycles, most of the surface is still void of Pt, and many of the particles have diameters of up to ca. 2 µm. These observations, and others, suggest that the metal deposition preferentially initiates at the grain boundaries, or other surface defects, during the first cathodic scan, with a limited number of Pt nuclei formed. 3D growth of the metal particles from these nuclei then dominates during the successive potential sweeps.

A high degree of metal dispersion is desired when fabricating catalytic electrodes. The deposition method, the deposition condi-





Figure 3. AFM images (air) of boron-doped diamond thin-films after galvanostatic deposition of Pt from a solution of 1 mM $K_2PtCl_6 + 0.1$ M HClO₄. The deposition times are (A) 100, (B) 200, (C) 300, and (D) 400 s, respectively.

tions, and the form of the metal solute complex all play a role in determining the size and distribution of the electrodeposited particles.³³ The potentiodynamic deposition produced particles with large diameters and poor distribution. Therefore, the galvanostatic deposition of Pt was also investigated. A current density of 0.5 mA/cm² was determined to be optimal for the continuous deposition, based on results from other experiments. During the deposi-

A

tion, the electrode potential ranged from -100 to -300 mV vs. Ag/AgCl. Figure 3A-D shows top-view, $5 \times 5 \,\mu$ m AFM images (force mode, air) of diamond surfaces after deposition for 100, 200, 300 and 400 s, respectively. The nominal particle size, variances, and distribution density for each deposition time are summarized in Table I.

Table I. Pt particle size, distribution, hydrogen desorption charge, and roughness factor (RF) for the Pt/diamond composite electrodes before and after the secondary diamond growth.

	Before				After				
Deposition time (s)	Particle size (nm)	Distribution density (10 ⁹ cm ⁻²)	Hydrogen desorption charge (mC/cm ²)	RF	Particle size (nm)	Distribution density (10 ⁸ cm ⁻²)	Hydrogen desorption charge (mC/cm ²)	RF	Surface loss (%)
100	20-200	0.5 ± 0.10	0.51	2.4	30-250	3.0 ± 1.5	0.32	1.5	37.3
200	10-250	0.8 ± 0.04	0.80	3.8	50-300	5.1 ± 0.7	0.56	2.7	30.0
300	50-300	1.0 ± 0.05	1.19	5.7	50-350	8.0 ± 0.3	0.81	3.9	31.9
400	60-500	1.2 ± 0.09	1.43	6.8	60-500	8.5 ± 0.4	0.92	4.4	35.7

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Figure 4. AFM images (air) of Pt-coated diamond thin-films (as indicated in Fig. 3) after a 3 h secondary diamond growth. The corresponding Pt deposition times are (A) 100, (B) 200, (C) 300, and (D) 400 s, respectively.

The metal particles decorate the entire surface with much better distribution than was achieved with the potentiodynamic method. The nominal particle size is also smaller. Both are desirable trends for a catalytic electrode. After 100 s of deposition (Fig. 3A), distinguishable Pt particles are uniformly dispersed over the diamond surface, decorating both the microcrystallites and the grain boundaries. The particle size ranges from 10-200 nm with an average particle distribution of 0.5×10^9 cm⁻². The distribution was determined by manually counting the particles in AFM images from multiple sites on the surface. Slightly larger particles and a higher distribution are observed after 200 s of deposition (Fig. 3B). The particle size ranges from 20 to 250 nm, and the distribution increases to 0.9×10^9 cm⁻². A further increase in the distribution is seen after 300 s of deposition (Fig. 3C). The particle size ranges from 50 to 300 nm and the distribution is 2×10^9 cm⁻². Finally, somewhat larger particles and a higher distribution are observed after 400 s of deposition (Fig. 3D). The particle size ranges from 60 to 400 nm and the distribution is 4×10^9 cm⁻². The image features are consistent with a progressive nucleation, and 3D growth mechanism in which new Pt nuclei progressively form, as a function of time, while the existing nuclei increase in size.³² Nuclei form in both the grain boundaries and on the facet surfaces. This indicates that both regions are electrochemically active and support the flow of current.

Secondary diamond growth.-In general, electrodeposited Pt metal particles weakly adhere to the hydrogen-terminated diamond surface without a secondary diamond growth, as the particles can easily be dislodged during hydrogen and oxygen gas evolution.² Figure 4A-D shows $5 \times 5 \,\mu\text{m}$ AFM images (force mode, air) of Pt-coated films after 3 h of additional diamond growth. The images are of the same Pt-coated films shown in Fig. 3. Numerous particles are randomly distributed over the surface on both the microcrystallites and in the grain boundaries, particularly for 200, 300, and 400 s electrodeposition times. The nominal particle size is slightly increased by the secondary diamond growth, ranging from 50 to 400 nm, but the distribution is lower, $\sim 10^8$ cm⁻². The process of entrapping the particles with diamond slightly reduces the total active Pt exposed. This is seen by comparing the hydrogen desorption charge in Table I. There is a 30-37% loss in Pt activity, as measured in the hydrogen desorption voltammetric charge between 0 and



Figure 5. SEM images of a Pt metal particle on the diamond surface (A) and the corresponding energy dispersive X-ray analysis spectrum for the particle (B).

-300 mV. This is consistent with the secondary diamond growth around the base of the metal deposits. The loss is further discussed below.

SEM and semiquantitative X-ray fluorescence measurements confirmed the deposits are Pt. Figure 5A shows an SEM image of several diamond microcrystallites decorated with metal deposits. The deposits occupy sites on both the facet surfaces and in the grain boundaries, as is the case in the AFM images. The corresponding energy dispersive X-ray analysis spectrum taken from one of the deposits is shown in Fig. 5B. The C K α (0.277 keV), O K α (0.525 keV), and Pt M α (2.05 keV), L α (9.44 keV) emissions are observed. The estimated atomic percentage of each element is 94.8, 1.7, and 3.5, respectively, yielding Pt/C and O/C atomic ratios of 0.037 and 0.018.

Basic electrochemical properties.-Figure 6 shows cyclic voltammetric *i-E* curves for the Pt/diamond composite electrode before (solid line) and after (dashed line) the secondary diamond growth. The curve shapes were unchanging with cycling and were obtained in nitrogen-purged 0.1 M HClO₄ at a scan rate of 50 mV/s. The potential sweep was initiated at 200 mV and scanned in the positive direction. All the characteristic current features of polycrystalline Pt are present. Two reversible hydrogen adsorption/desorption peaks are evident in the potential region from 0 to -300 mV. Integration of the area under these peaks was used to estimate the electrochemically active surface area of the Pt particles.³⁴ The roughness factor $(RF = voltammetric charge density/210 \,\mu C/cm^2)$ of the Pt/ diamond composite electrode can be calculated assuming a coulombic charge of 210 μ C/cm² for hydrogen adsorption on an atomically flat Pt(111) surface.²² The results are presented in Table I. Both the hydrogen desorption charge and the roughness factor increase with



Figure 6. Cyclic voltammetric *i*-*E* curves for a Pt-coated diamond thin film in 0.1 M HClO₄, before (solid line) and after (dashed line) a 3 h secondary diamond growth. The Pt deposition time is 200 s. Scan rate = 50 mV/s.

the deposition time (*i.e.*, Pt loading), as the progressive nucleation and growth leads to particles of varying size. Assuming a 100% current efficiency, the mass of Pt deposited is calculated to be 25.2, 50.3, 75.8, and 100.1 μ g/cm² for the 100, 200, 300 and 400 s deposition times, respectively. Thus, the hydrogen-desorption charge per mass of Pt, after the secondary diamond growth, is calculated to be 12.6, 11.1, 10.7, and 9.2 μ C/ μ g, respectively. The ratio decreases with increasing deposition time because of the increase in the nominal metal particle size. The mass loadings given above would certainly be upper limits, as the coulometric efficiency is probably less than 100% due to competing hydrogen evolution.

The voltammetric curve for the Pt-coated diamond film, prior to the secondary growth (solid line), was obtained after the first scan, and the shape remained unchanged during ten subsequent scans. However, the voltammetric curve for the Pt-coated diamond film, after the secondary diamond growth (Fig. 6, dashed line), had a poorly shaped first scan, especially in the hydrogen adsorption/ desorption region. In fact, multiple scans were required for the characteristic Pt features to develop. This observation is consistent with the removal of surface contamination formed during the diamond deposition. It is highly probable that the Pt surface is initially covered with adsorbed carbon and/or hydrocarbon moieties, and these contaminants block surface sites for the hydrogen adsorption. The contaminants are effectively removed by potential cycling between the oxygen and hydrogen evolution regimes.¹⁰ Hence, potential cycling is the normal protocol for cleaning and activating the Pt surface after the secondary diamond film growth. The potential cycling (50-100 cycles) is performed in 0.1 M HClO₄ at a scan rate of 50 mV/s between 1500 mV and -400 mV. The voltammogram shown for the Pt-diamond composite electrode is for the 100th cycle. The flat oxide-formation region at potentials between 700 and 1200 mV indicates the oxidation of adsorbed contaminants is not occurring to any appreciable extent.

There are, however, some notable differences between the two voltammograms. The hydrogen adsorption/desorption peaks, the Pt oxide formation/reduction waves, and the double-layer charging current between 0 and 250 mV are slightly reduced after the secondary diamond growth, indicating a reduction in the active Pt surface area. An average of 34% of the active surface atoms are lost, based on the reduction in the hydrogen desorption charge between -250 and 100 mV. This is summarized in Table I.

Several possible causes for the reduced Pt activity were systematically investigated. One possibility, actually confirmed in recent cross-sectional SEM measurements, is the complete coverage of some of the smaller particles by the secondary diamond layer. How



Figure 7. SEM images of Pt/diamond composite electrode (A) before and (B) after acid etching in aqua regia. The Pt deposition time is 200 s.

much active Pt is lost by this process is unknown at present. Another possibility is particle aggregation on the diamond surface at the deposition temperature of ca. 850°C. Still another possibility is gasification or sputtering of the Pt by the atomic hydrogen present in the plasma. To examine these latter two possibilities, an experiment was performed in which another set of Pt-coated diamond films, similar to those shown in Fig. 3, were placed into the CVD reactor. The electrodes were then exposed to the conditions used for the secondary diamond growth except that no CH4 was added. The absence of CH₄ did not significantly affect the substrate temperature, at least as determined by an optical pyrometer. Again, the morphology was examined by AFM and the active surface area was determined from the hydrogen adsorption/desorption voltammetric charge in 0.1 M HClO₄ before and after a 3 h hydrogen plasma treatment. No significant change in the particle size or voltammetric charge for hydrogen desorption was observed (AFM images are not shown here), at least for Pt particles with diameters from 20 to 300 nm. Therefore, the loss in active Pt is not due to particle aggregation, gasification, or sputtering. Voltammetric measurements indicated that only 2-4%, not 30-37%, of the active Pt was lost during the 3 h hydrogen plasma treatment. The melting and smoothing of small particles may contribute to the slight activity loss. Although the melting temperature of bulk Pt is 1772°C, nanometer-sized Pt particles have a much lower melting temperature, as indicated by the size-dependent melting temperature theory.35 As the size of the particle decreases, an increased proportion of atoms occupy surface or interfacial sites. These atoms are more loosely bound than bulk atoms, which facilitates the melting.³⁶ Pt particles with diameters of less than 2 nm have a melting point less than 850°C, based on the application of the theory. It should also be noted that segregated Pt particles, rather than a continuous film, can be formed on different substrates by high-temperature annealing in vacuum.^{37,38} The breakup of an initially continuous or quasi-continuous Pt film into individual Pt aggregates on a quartz substrate has been achieved by vacuum heat-treatment at 600 K.3

Confirmation that the secondary diamond growth causes much of the active Pt loss by covering the base of the metal deposits was next addressed. In the experiment, a Pt/diamond composite electrode was etched in hot aqua regia [3 HCl:1 HNO₃ (v/v)] to dissolve the Pt particles. The diamond lattice is quite stable in this solution and undergoes no morphological alteration. SEM images of the compos-



Figure 8. Cyclic voltammetric *i*-*E* curves for (A) a Pt/diamond composite electrode, (B) a clean Pt foil electrode, and (C) a bare, boron-doped diamond thin film electrode in oxygen-saturated 0.1 M HClO₄. The Pt deposition time for the composite electrode is 200 s. Apparent loading = $50.3 \,\mu$ g/cm². Scan rate = $50 \,$ mV/s.

ite electrode, before and after the acid etching, are presented in Fig. 7A and B. Pt particles with diameters of 50-300 nm are seen on the surface, prior to the chemical treatment (Fig. 7A). Numerous pits are observed in the diamond film after treatment. These pits are the voids left after dissolving the metal and have diameters of 50 to 300 nm. This observation confirms that the diamond film does surround the base of some of the metal particles, entrapping and anchoring them in the surface microstructure. The depth of the pits depends on the secondary diamond-growth time.

Stability of the Pt/diamond composite electrodes.—The shortterm dimensional stability and catalytic activity of the Pt/diamond composite electrodes were investigated before and after anodic polarization in 85% phosphoric acid at 170°C and 0.1A/cm.^{11,12} Electrochemical and AFM measurements revealed no loss in Pt activity and no degradation of the diamond microstructure after 2 h of electrolysis. There was no pitting or grain roughening of the diamond support and no evidence for catalyst detachment due to any form of carbon corrosion. It should be noted that sp² carbon electrodes (*e.g.*, HOPG, glassy carbon, Grafoil, activated carbon) corrode and degrade catastrophically during exposure to these or even milder anodization conditions.^{3,12}

Electrocatalytic activity for oxygen reduction.—Figure 8A shows a cyclic voltammetric *i*-*E* curve for an electrode in oxygen-saturated 0.1 M HClO₄. For comparison, the voltammetric responses for a clean polycrystalline Pt foil and a bare diamond electrode are shown in Fig. 8B and C, respectively. The potential sweep was initiated at 600 mV and scanned in the positive direction at a scan rate of 50



Figure 9. Slow scan, linear sweep voltammograms for a Pt/diamond composite electrode in oxygen saturated 0.1 M (A) $HClO_4$, (B) H_2SO_4 , and (C) H_3PO_4 . The Pt deposition time is 300 s. Apparent loading=75.8 μ g/cm². Scan rate = 1 mV/s. The inset shows the corresponding Tafel plots constructed from the rising portion of the *i*-*E* curves.

mV/s. The response for the Pt/diamond composite electrode resembles that for the clean Pt foil. Oxygen is reduced to water by the Pt catalyst according to the reaction³⁹

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

The cathodic current commences at 400 mV and reaches a maximum of 215 μ A or 1.1 mA/cm² at *ca.* 250 mV. It should be noted that the cathodic current is a sum of the oxygen reduction current, the current due to Pt oxide reduction, and the double-layer charging current. Clearly, the oxygen reduction current at 250 mV is due solely to the activity of the Pt catalyst. This is evident by comparing the cyclic voltammetric *i*-*E* curve for the bare diamond electrode. This response is featureless from 1700 to -1000 mV with no reduction current at 250 mV. Diamond is known to have a large overpotential for oxygen reduction in both acidic⁴⁰ and basic media.⁴¹

Figure 9A-C shows slow scan linear sweep voltametric i-Ecurves (1 mV/s) for a Pt/diamond composite electrode in oxygensaturated 0.1 M HClO₄, H₂SO₄, and H₃PO₄, respectively. The polarization curves have been corrected for the background current, which was measured in nitrogen-purged solution. Peak-shaped curves are seen with E_p^{red} varying with acid type. Values of 460, 390, and 335 mV are seen for $HClO_4$, H_2SO_4 , and H_3PO_4 , respectively. The peak current, i_p^{red} , is -31.5, -29.5, and -28.0 A $(\sim 0.15 \text{ mA/cm}^2 \text{ or } \sim 2.0 \text{ mA/mg Pt})$, respectively. The decrease in the oxygen reduction current in the kinetically controlled region and the negative shift of $E_{\rm p}^{\rm red}$ can be explained by an anion adsorption effect.^{42,43} $H_2PO_4^-$ has been reported to strongly adsorb on the Pt surface in the potential region of the oxygen-reduction current onset. $H_2PO_4^-$ adsorption can slow down the electrode reaction kinetics by blocking sites for the initial oxygen chemsorption.⁴⁴ Changes in the double-layer structure, as a result of the adsorption, could also be influential.⁴⁴ The i_p^{red} in all the acids increases linearly with the square root of scan rate (50 to 200 mV/s), indicating the reaction rate is limited by semi-infinite linear diffusion of oxygen to the electrode surface.

The rising portion of the i-E curves in the kinetically controlled region was analyzed and Tafel plots were constructed, based on the equation

Plots of η vs. log *i* for the composite electrode are shown as an inset in Fig. 9. No correction for any mass-transfer effects was made in the analysis of these data. The Tafel plots for all three electrolytes are linear at low overpotentials, most likely being influenced at higher overpotentials by mass transfer effects. The slopes are -63, -69, and -80 mV/dec, respectively, for HClO₄, H₂SO₄, and H₃PO₄. These results are similar to those reported by Kita et al.⁴² and Damjanovic et al.^{45,46} Mass-transfer corrected Tafel plots for oxygen reduction at Pt in acid normally yields two slopes, ca. -60 mV/dec at low overpotentials and -120 mV/dec at high overpotentials.46 The low Tafel slope region corresponds to a potential regime where the oxygen reduction occurs on an oxide-covered surface. Adsorbed -O and -OH species affect the adsorption of O₂ and other reaction intermediates (Temkin conditions). The high Tafel slope region (-120 mV/dec) corresponds to a potential region where the reaction proceeds on an oxide-free surface (Langmuir conditions). Due to the influence of mass-transfer effects, this higher slope region is not observed in the present data. The slightly higher Tafel slopes observed in H₂SO₄ and H₃PO₄ are likely attributable to anion adsorption influencing the O_2 chemsorption on the surface.⁴² The exchange currents can be determined by extrapolating the linear Tafel region back to $\eta = 0$. Normalizing these currents to the electrochemically active surface area of the Pt (0.78 cm², as estimated from the roughness factor), yields exchange current densities, i_0 , of $1.9 \times 10^{-10} \text{ A cm}^{-2}$ in HClO₄, $4.6 \times 10^{-11} \text{ A cm}^{-2}$ in H₂SO₄, and $7.1 \times 10^{-12} \text{ A cm}^{-2}$ in H₃PO₄. Thus, the reaction rate increases in order of $H_3PO_4 < H_2SO_4 < HClO_4$. This is a wellknown phenomenon for smooth Pt surfaces and can be explained by the different degrees of adsorption of phosphate/biphosphate, sulfate/bisulfate, and perchlorate anions.⁴²

These preliminary results indicate that the kinetic parameters for the oxygen-reduction reaction at Pt/diamond composite electrodes are similar to the parameters for clean polycrystalline Pt.⁴² In addition, the diamond matrix exerts little influence on the oxygen-reduction response.

Conclusions

We report on a new, dimensionally stable Pt/diamond composite electrode that is fabricated by using a sequential procedure of diamond deposition, Pt electrochemical deposition, and diamond deposition. Dispersed Pt particles are galvanostatically deposited onto a boron-doped polycrystalline diamond thin-film surface and entrapped within the dimensionally stable microstructure by a subsequent diamond deposition. The second, short deposition serves to anchor many of the metal particles into the diamond microstructure by surrounding their base. The number of exposed particles, particle size, and distribution can be controlled by adjusting the galvanostatic deposition time and secondary diamond-growth conditions. Particle sizes are in the range of 10-300 nm with a distribution of $\sim 10^9$ cm⁻². This nominal particle size is still too large for a true catalytic electrode, and work is ongoing to reduce the particle size to the 10 nm range. About 33% of the active Pt surface is lost after the secondary diamond deposition due to a combination of complete coverage of some of the smaller particles and partial coverage of the base of the larger particles. The catalytic activity of the composite electrodes is extremely stable, as no microstructural alterations or activity losses are observed during the 2 h of anodic polarization in 85% H_3PO_4 at 0.1 A/cm² and 170°C.

The kinetic parameters for the oxygen-reduction reaction at the composite electrode are similar to those for clean polycrystalline Pt. Room-temperature Tafel slopes of -63 to -80 mV/dec are observed at low overpotentials in 0.1 M HClO₄, H₂SO₄, and H₃PO₄, with the lowest slope in HClO₄ and the highest in H₃PO₄. The exchange current density (10^{-12} to 10^{-10} A/cm² active Pt) increases in order of H₃PO₄ < H₂SO₄ < HClO₄. The maximum current density for oxygen reduction is observed in 0.1 M HClO₄, during slow

$\log i = \log i_0 + (\alpha_c n F/2.303 \ RT)\eta$

scan cyclic voltammetry measurement. The estimated Pt loading for this electrode is $75.8 \ \mu g/cm^2$.

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