by electron exchange between the adjacent redox centers. Whichever explanation is correct, the new design of electrode should allow electrochemical ESR to be used first to study shorter lived intermediates and second to study intermediates and products in the kinetics of modified electrodes.

Experimental Section

The ESR spectrometer used was a Bruker ER 200 tt. The spectrometer has a dual cavity. In the second cavity a solid solution of Mn^{2+} in MgO serves as a permanent standard to calibrate the sensitivity of the spectrometer. The flow system and the method of construction of the tube electrode have been described previously.[6] The nonelectroactive part of the semiannular or the missing sector electrodes was made of Teflon and assembled in the same way as a complete annular electrode. Except where stated, all chemicals and reagents were of AnalaR grade. Dimethylsulfoxide (BDH) was purified and dried as described previously.[16] Acetonitrile (Fison's dried distilled) was refluxed with 1% (w/v) CaH_2 for 2 h and then fractionally distilled. TEAP (Fluka, purum) was recrystallized once from water. TBAT (Fluka, purum) was recrystallized once from a mixture of ethanol and petroleum ether. TMPD (BDH, L. R. grade) was recrystallized as described by Michaelis.[17] Poly(nitrostyrene) was synthesized by the method of Wiley and Smith.[18] It was coated on to the platinum tube electrode by using the method of Miller.[13]

Vinylanthraquinone was synthesized by the method of Manecke and Storck.[19] The monomer was polymerized by using benzoyl peroxide initiator in tolulene solution at 100 °C for 240 h. The modified electrode was made by dip coating the platinum electrode in a 1% (w/v) solution of polymer in CH_2Cl_2.

All electrochemical experiments were controlled by a purpose built potentiostat of modular construction.

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Registry No. Pt, 7440-06-4; TMPD, 100-22-1; TMPD radical cation, 34527-55-4; poly(*p*-nitrostyrene), 24936-54-7; poly(*p*-nitrostyrene) radical anion, 87842-91-9; poly(2-vinylanthraquinone), 73546-39-1; poly(2-vinylanthraquinone) radical anion, 87842-93-1.

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Electrocatalysis by Electrodeposited Spherical Pt Microparticles Dispersed in a Polymeric Film Electrode

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Abstract: Electrochemical methods for the dispersion of Pt microparticles at microgram levels in polymeric matrices of poly(vinylacetic acid) glassy carbon electrodes, Pt-PVAA/GC, are described. The PVAA film was formed on a GC surface by refluxing *neat* VAA monomer under nitrogen. Cyclic voltammetry and single and double potential step electrolysis were applied to form the Pt^0 particles on PVAA/GC from an acidic hexachloroplatinate solution. The Pt particles were randomly dispersed in the polymer and were spherically shaped. This Pt-PVAA/GC electrode exhibited high activity toward the electrochemical generation of hydrogen and reduction of oxygen. Preliminary results indicate that the other catalytic electrodes based on a combination of substrates, polymers and electrochemically dispersed metals, mixed metals and metal/metal oxide particles can be generated by the same method.

Recently polymers have been used for the immobilization of redox mediators.[1,2] They have also been used as supports for platinum catalysts which are in the form of thin films[3] or dispersed colloids.[4] Wrighton[5] has used an ion exchange type polymer to disperse Pt^0 in the polymeric matrices via photoreduction or electrochemical reduction methods. This kind of modification improves the efficiency of hydrogen evolution at p-type silicon semiconductor photocathodes.

Doblhofer and Durr[6] have discussed two charge-transfer mechanisms for small particles dispersed in a polymer film on an electrode surface. One mechanism considers charge transfer to occur only at particles in contact with the electrode surface. The other is an electron-hopping mechanism.

Polymeric PVAA films have been formed on a GC surface at a monolayer coverage[7] by a mechanical abrasion method[8] or for thicker films by plasma polymerization.[7] It has been discovered in this laboratory that a film can also be produced by refluxing the glassy carbon electrodes in the monomer.

The preparation and characteristics of a poly(vinylacetic acid) coated glassy carbon electrode with dispersed spherical platinum microparticles (Pt–PVAA/GC) are described. The application

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and properties of such an electrode for electrocatalytic generation of hydrogen and reduction of oxygen are also discussed.

Experimental Section

Pretreatment of GC Electrodes. The GC electrodes used were either GC-10, GC-20, or GC--30 Tokai glassy carbon (Tokai Carbon Co., Tokyo, Japan) or V-25 glassy carbon (Atomergic Chemetals Corp., New York, NY). Before polymer coating, the GC electrodes were first polished with 1.0, 0.3, and 0.05 μm alumina (Buehler Co., Chicago, Ill.) on an optical flat (Harrick Scientific Corp., Ossining, NY) to a mirro-like finish followed by ultrasonic cleaning with doubly distilled water for at least 15 min to remove any residual alumina on the surface.[9] The electrode was then washed with a stream of doubly distilled water and dried in an oven at 105 °C.

Polymer Coating. The films employed were formed on GC surfaces by refluxing in *neat* vinylacetic acid (3-butenoic acid) (Aldrich Chemical Co., Milwaukee, WI) monomer at 165 °C under nitrogen for at least 16 h.[10] The electrodes were then subjected to a Soxhlet extraction with acetone for ca. 24 h. The monomer was used as received.

Electrochemistry. A conventional two-compartment glass cell was used. Electrochemistry was performed with an in-house constructed potentiostat or a Bioanalytical System CV-1A potentiostat. An Omnigraphic 2000 X–Y (Houston Instrument Co., Austin, TX) or a Linear strip chart recorder (Linear Instrument Co., Irvine, CA) was used for data acquisition. Potentials are reported with respect to a Ag/AgCl (saturated KCl) reference electrode. Chemicals were analytical grade and were used without further purification. Solutions were prepared with doubly distilled water.

Dispersion of Pt Spherical Particles. Three electrochemical methods, cyclic voltammetry (CV), and single and double potential step electrolysis (SPSE and DPSE), were applied to disperse Pt particles into the polymeric film from an acidic bath containing sodium or potassium hexachloroplatinate(IV) and 1 M H_2SO_4 or 1 M $HClO_4$. The typical potential limits for CV were +0.80 and −0.40 V. For SPSE the potential was stepped from +0.80 to 0.00 V. A square wave (+0.80 to −0.40 V) at a frequency of 0.05 Hz was applied for DPSE. The amount of Pt deposited was quantitated from the electrochemcial charge consumed during electrolysis for SPSE, assuming a 100% current efficiency and a four-electron process for the reduction of Pt(IV) to Pt^0. For CV and DPSE the quantity of Pt dispersed was controlled by the exhaustive electrolysis of a known amount of hexachloroplatinate contained in a stirred 1-mL cell. The quantitation of Pt from the electrochemical charge consumed was not applicable for CV or DPSE because of the difficulty in correcting for the charge due to platinum oxide formation and possible dissolution of Pt. The loading levels of Pt on the electrodes were between 0.2 and 50 μg/cm² (geometric area of GC). The electrodes employed for hydrogen generation and oxygen reduction studies and those examined by the scanning Auger microprobe (SAM) were prepared by using the CV method at scan rates of 10 or 40 mV/s.

Surface Analysis of Modified Electrodes. Electrode surfaces were examined by using either an ISI Model SX-30 scanning electron microscope (SEM) (International Scientific Instruments, Inc., Santa Clara, CA) or a Cambridge Stereoscan Model S4-10 SEM (Cambridge Instruments, Cambridge, England) equipped with an Ortec Model 6200 Multichannel Energy Dispersive X-ray Analyzer (EDX) (EG and G, Oakridge, TN). The elemental identity of the particles was determined with EDX and with a PHI (Physical Electronics Instruments, Inc., Eden Prarie, MN) Model 595 Scanning Auger Microprobe (SAM). Prior to surface analysis, Pt-PVAA/GC electrodes were washed with a stream of doubly distilled water and air dried.

Particle Size. Particle-size distribution was determined by a computer-imaging system (Videoplan by Carl Zeiss, Inc., West Germany) using enlarged SEM photographs. The distribution function of the particle diameters was determined as well as the average and the standard deviation of the diameters, the apparent surface areas, and the particle volumes. The smallest particle diameter that could be imaged was 50 Å.

Results and Discussion

a. Characterization of PVAA/GC.

Examination of the PVAA/GC surface by SEM revealed a smooth, uniform film of PVAA on the GC. Films that were formed by refluxing more than 16 h were also found to be pinhole free. The film thickness was estimated to be on the order of 400–1000 Å from SEM photomicrographs of boundaries of the film and GC. These boundaries were edges of ruptures in the film after extensive hydrogen generation.

Bulk PVAA (16–24 h) is soluble in acetone. Since a film remained on the electrode after a 24- Soxhlet extraction with

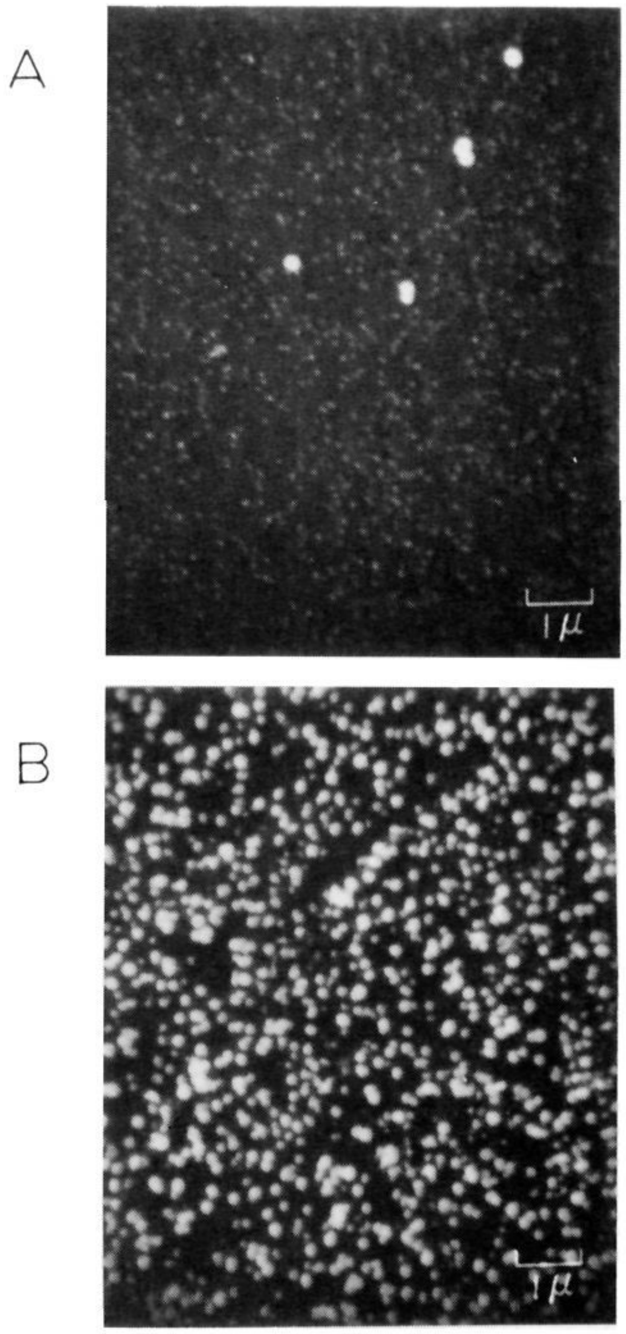

Figure 1. Scanning electron micrographs of Pt microparticle dispersed PVAA/GC electrodes. The electrodes were prepared by the CV method using a 16-h polymer film with Pt weights, of (A) 9.3 and (B) 50 μg/cm².

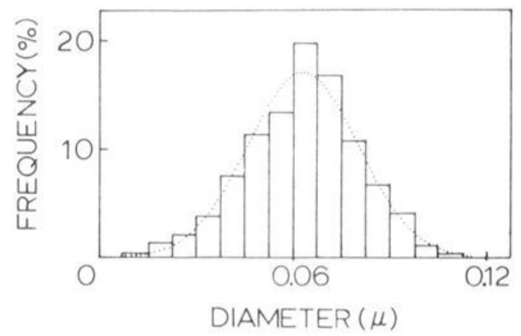

Figure 2. Histogram of the particle diameter distribution measured from Figure 1A.

Table I. The Size Distribution, Average Diameter, and Population Density of Particles at Various Loading Levels Prepared by the Three Electrochemical Methods

method of preparation	loading, μg/cm²	diameter, Å	density, counts/μm²	distribution function
CV, 40 mV/s	9.3	647 ± 233	14.7	Gaussian
CV, 40 mV/s	50.0	1755 ± 474	12.2	Gaussian
CV, 10 mV/s	5.5	452 ± 177	35.2	Gaussian
CV, 10 mV/s	11.9	378 ± 230	57.9	Gaussian
SPSE	7.9	2931 ± 800	0.80	neg. skewness
SPSE	19.2	3221 ± 674	1.40	neg. skewness
DPSE	14.6	532 ± 91	74.7	Gaussian

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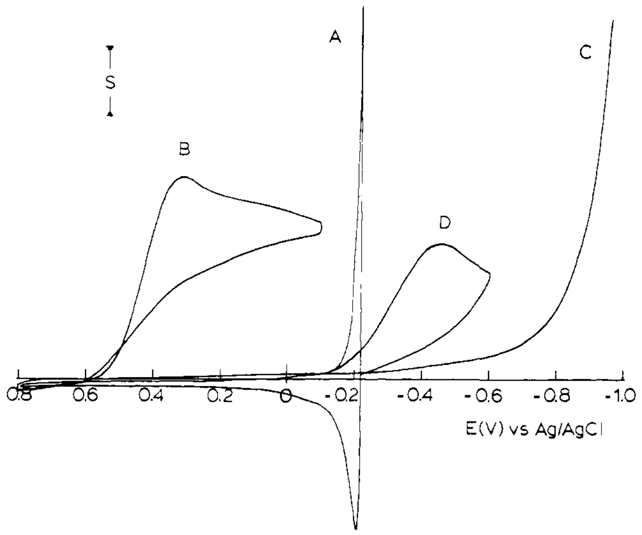

Figure 3. Cyclic voltammograms for hydrogen evolution and oxygen reduction at the Pt-PVAA/GC electrode (A, B) and bare GC (C, D) in 1 M sulfuric acid: S = 200 μA for A, C and 50 μA for B, D; 16-h refluxed film; geometric electrode area 0.55 cm^2; Pt loading 25 μg/cm^2; scan rate 10 mV/s.

acetone, the film must be "bound" to the surface in some way. Grafting of acrylate polymers to carbon fibers has been postulated to involve interaction of carboxyl groups on the polymer and the carbon[11] (Grafted polymer was defined as polymer that remained on the carbon after a 24-h Soxhlet extraction with acetone).

b. Characterization of Pt. Examination of the Pt-PVAA/GC surfaces by SEM indicated that the Pt particles were spherical and randomly distributed throughout the polymeric film (Figure 1). The distribution function, the average diameter at various loading levels, and the density of particles on electrodes prepared by the three different methods are listed in Table I. A histogram for the particle-diameter distribution obtained from the SEM in Figure 1A is shown in Figure 2. All the particles studied had diameters in the range of 50–3000 Å, but the size distribution for a given electrode depended on the preparation method. The distribution for the particles produced by CV and DPSE matched a normal Gaussian distribution function with a confidence level greater than 95%. SPSE produced particles with a distribution curve skewed toward the smaller diameters. CV and DPSE produced distributions with a smaller average diameter, a smaller standard deviation, and a higher particle population density than SPSE. Slower CV scan rates, e.g., 10 mV/s, produced smaller diameter particles with a higher density than higher scan rates, e.g., 40 mV/s. An increase in the concentration of hexachloroplatinate for a given SPSE deposition time resulted only in an increase in particle size, whereas for CV and DPSE the particle size and density both increased (e.g., Figure 1). A more detailed study of the nucleation/growth mechanisms of Pt deposition in the PVAA film is currently in progress in an effort to better control the size, density, and distribution of particles in the film. The weight of the dispersed Pt metal calculated from the average diameter and particle density, assuming solid spheres and bulk Pt properties, and the amount of Pt electrodeposited agreed within ±20%.

A variation in the brightness of the SEM particle images was observed within a given micrograph. This brightness variation was independent of the particle size. The brighter images are believed to be particles nearer the surface were poor electrical contact with the GC substrate may promote charging and the signal is not attenuated by the film. Thus, this difference in intensity is an indication that the particles are dispersed three-dimensionally throughout the polymer film rather than only two-dimensionally at the electrode/polymer interface. At low loading levels, occasionally, a few large particles were observed (e.g., Figure 1A). Since these particles were always brighter than the others, they were speculated to be due to the preferential growth of the nuclei near or at the polymer surface.

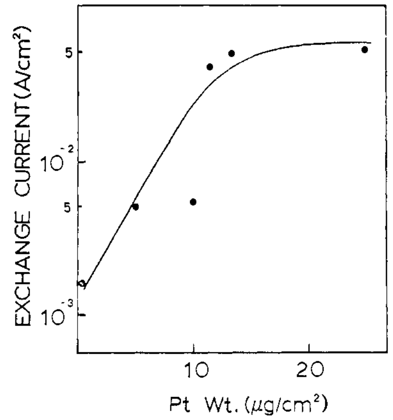

Figure 4. Plot of the exchange current density Gaussianized to the apparent Pt surface area vs. Pt loading. The Pt-PVAA/GC electrodes with a mean particle diameter between 300 and 600 Å were used.

Preliminary results of point analysis by SAM (resolution ca. 5–10 Å) confirmed the elemental identity of the particles. However, when the point analysis was performed on the "clean" areas where Pt particles were not observed by SEM, a finite Pt signal was detected. It is uncertain whether the platinum SAM signal from the clean areas arose from small amounts of trapped hexachloroplatinate in the polymeric film or from Pt particles that were not visible by SEM. Scanning transmission electron microscopy of thin film sections will be attempted in the near future to aid in resolving this uncertainty.

c. Electrochemical Generation of Hydrogen and Reduction of Oxygen. Figure 3 shows the cyclic voltammograms illustrating the catalytic generation of hydrogen (trace A) and oxygen reduction (trace B) at a Pt-PVAA/GC electrode with a Pt loading of 25 μg/cm^2, compared to H_2 (trace C) and O_2 (trace D) at an unmodified GC electrode in 1 M H_2SO_4. The overpotential for H_2 generation was decreased by ca. 600 mV (compare trace A to C), and the electrogenerated H_2 could be reoxidized during the reverse scan. The overpotential for O_2 was decreased by ca. 800 mV. The overpotentials for H_2 and O_2 observed on Pt-PVAA/GC were the same as those observed on a smooth Pt electrode.

The typical adsorption–desorption fine structure[12,13] of hydrogen at a smooth Pt surface was evident, although ill-defined, on Pt-PVAA/GC at higher scan rates, e.g., 500 mV/s, but it was indistinguishable from the background at lower scan rates, e.g., 40 mV/s. Determination of the "real" active Pt surface area from the electrochemical charge for the hydrogen adsorption was therefore not possible. The reason for this loss of fine structure is not known, but it does indicate that the film may have an effect on hydrogen adsorption.

The logarithm of the cathodic current for H_2 evolution was plotted vs. the potential (Tafel plot)[14] up to an overpotential, η, of ca. 150 mV. The current in this potential region was the same in both static and stirred solutions, indicating an absence of mass-transfer effects. The linear portion of each Tafel plot was extrapolated to the current axis ($\eta = 0$) to determine the exchange current. Since the particle–size distribution and population are known, the total surface area of Pt could be computed, assuming that all of the particles imaged were smooth spheres and active. When the exchange currents were normalized to their respective surface areas and plotted as a function of the Pt loading, the curve

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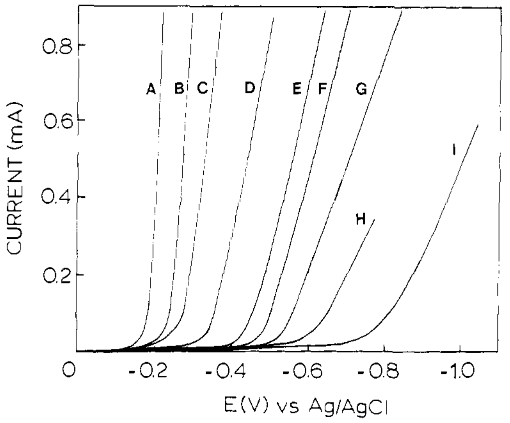

Figure 5. Cathodic *i–E* profile for H_2 generation at a Pt-PVAA/GC electrode in (A) 1 N $HClO_4$, (B) 0.1 N $HClO_4$ and 0.1 M phosphate buffer of pH (C) 2, (D) 3, (E) 4, (F) 5, (G) 6, (H) 7 and (I) 9. Pt loading 10.5 $\mu g/cm^2$, geometric electrode area 0.55 cm^2; scan rate 10 mV/sec.

shown in Figure 4 resulted. The exhange current density, I_0, increased dramatically with loading up to a level of approximately 12 $\mu g/cm^2$. Above this level, I_0 appeared to plateau and become independent of loading. The I_0 values obtained for H_2 of ca. 1 × 10^{-3} to 5 × 10^{-2} A/cm^2 for Pt loadings of 0.25 to 25 $\mu g/cm^2$ are of the same order of magnitude or larger than the literature values of 1 × 10^{-4} and 1 × 10^{-3} A/cm^2 for smooth Pt in sulfuric acid solutions.[15,16] This implies, within experimental uncertainty, that all the particles are active.

When Pt particles were examined by SEM at the higher magnifications of 50 to 100 KX, the outer edge of the spheres appeared to have angular structures. These structures suggested that the particles might be formed as polycrystalline particles or as coalesced particle clusters. Since the I_0 values were normalized to an area that assumed a smooth surface, the I_0 values calculated could be high. It is reasonable to assume that such surface roughness will increase as the particle diameter increases up to some critical value, after which the roughness factor will remain essentially constant. Thus, the variation of I_0 with Pt loading can be explained. Nucleation/growth studies currently in progress will be extended to verify the above assumption.

The cathodic *i–E* curves for H_2 generation at a Pt-PVAA/GC (10.5 $\mu g/cm^2$) as a function of pH are reproduced in Figure 5. The cathodic current at each pH was observed to increase linearly with the applied potential beyond the Tafel region. If the linear region of each curve was extrapolated to the potential axis, this "intercept" potential plotted as a function of pH was linear with a slope of −56 mV/pH. Similar behavior was observed at a smooth Pt electrode.

For O_2 the CV peak current, i_p, increased linearly with the square root of the scan rate, indicating a mass transfer limited reaction in aqueous acidic solutions (H_2SO_4 or $HClO_4$). The i_p was also linearly dependent on the oxygen concentration at a given scan rate. The exchange current for O_2 reduction was determined from the Tafel plots by using the "foot" of the CV *i–E* curves. Both the pH dependence of the peak potential and the calculated exchange current density for O_2 reduction at Pt-PVAA/GC were similar to those determined at smooth Pt.[16,17] The loading effect on I_0 for O_2 reduction was not studied.

Stability. The platinum particles on Pt-PVAA/GC were not removed by ultrasonic cleaning for periods up to 15 min. Longer periods were not employed since it had been reported that 15 min was sufficient for removal of particles dispersed on bare GC.[9] Pt particles deposited on a bare GC electrode were rapidly lost from the surface in the ultrasonic bath (less than 1 min). The enhanced mechanical stability of the Pt against ultrasonic ablation was probably due to the physical entrapment of the particles in the polymeric film which adheres strongly to the GC surface, although the adsorption or adherence of the carboxylate groups of PVAA on the Pt particles may also have an effect.[18]

The stability of the Pt-PVAA/GC for H_2 generation was tested by controlled potential electrolysis in an aqueous H_2SO_4 solution at ambient temperatures. The current averaged 20 mA/cm^2 for more than 400 h. The I_0 was constant within experimental error over this time period. The mean geometric diameter of the Pt particles, as determined by SEM, before and after 400 h also did not change. Thus, there was no particle degradation due to sintering and recrystallization as had been observed at Pt fuel cell cathodes operating at higher temperatures.[19,20] At these ambient temperatures, the entrainment of the particles in the polymer apparently prevents particle aggregation.

The cyclic voltammetry of 1 × 10^{-3} M ferricyanide in 0.1 M KCl was determined at a Pt-PVAA/GC electrode. The peak separation in a CV of ferricyanide was less for Pt-PVAA/GC than for PVAA/GC, but both were greater than that at Pt or bare GC. This indicated that ferricyanide behavior at Pt-PVAA/GC was different from that of H_2 and O_2. The reason for this is not known, and an investigation is currently in progress to study this phenomenon.

Conclusions

The reasonably large surface area achieved with low loading levels, the high catalytic efficiency, and the excellent stability possible with dispersed microparticles in polymer film coated electrodes make them attractive for a variety of redox applications including photocatalysis.[5,21] Preliminary experiments have indicated that other metals such as Pd and Ni can be similarly deposited into PVAA/GC.[22] The method described herein should be applicable to dispersing other metals, multilayer metals, or alloys as particles into a variety of polymers on conducting or semiconducting substrates. By imbedding the metal particles in polymeric films, the loss of catalytic activity or efficiency due to physical or chemical loss of the catalyst can be suppressed. We are currently attempting to fabricate many new catalytic electrodes based on a combination of substrates, polymers, and electrochemically dispersed metals, mixed metals, or metal oxides.

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Registry No. Platinum, 7440-06-4; poly(vinylacetic acid) (homopolymer), 28391-17-5; carbon, 7440-44-0; hydrogen, 1333-74-0; oxygen, 7782-44-7; ferricyanide, 13408-62-3; vinylacetic acid, 625-38-7; hexachloroplatinate(IV), 16871-54-8.

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