

# Suppression of Cathodic Reactions on Aluminum Alloy 2024-T3 Using Polyaniline Coating Systems

A Summary Report to The Electrochemical Society for the 2004 Edward G. Weston Summer Research Fellowship

by Jesse C. Seegmiller

The mechanism by which poly(aniline)-poly(methylmethacrylate) (PANI/PMMA) blends inhibit cathodic reactions on aluminum alloy AA2024-T3 has been explored. PANI-containing coatings have been used for several metal substrates as a corrosion protection measure. Figure 1 shows three mechanisms by which PANI coatings may act as a corrosion inhibition system. In case A, the open-circuit potential (OCP) of the metal substrate is raised to a level at which the formation of a protective oxide on the surface occurs.<sup>1,2</sup> Another possible mechanism is case B, where once the PANI component of the blend is reduced, it releases its counteranion which complexes with metal ions released from the metal surface, forming an insoluble salt.<sup>3</sup> In a third mechanism, the PANI component of the coating raises the OCP of the interface to values where cathodic reactions are kinetically hindered. For example, O<sub>2</sub> reduction occurs on this alloy surface at potentials more negative than -0.4 V.<sup>4</sup> Thus, at potentials positive of this value, dioxygen reduction will not be important. The use of scanning electrochemical microscopy (SECM), has afforded a way to probe the electrochemical activity on aluminum<sup>5</sup> and aluminum alloy<sup>6,7</sup> surfaces in a more localized fashion, allowing a differentiation between these mechanisms.

AA2024-T3 samples were coated with PANI-CSA (20%)/PMMA blends, along with PMMA blanks, where both coatings are dissolved in *m*-cresol. The films were 10 μm thick. The PANI/PMMA blend raises the OCP of the alloy to -0.12 V vs. Ag/AgCl in a 10 mM H<sub>2</sub>SO<sub>4</sub> (pH 2) solution. If the PANI component is excluded, the OCP is -0.75 V, identical with the value at an uncoated substrate. The coated samples were then scribed with a razor and the scribed region was imaged with SECM using 1.25 mM (dimethylaminomethyl)ferrocene as a mediator species, 10 mM H<sub>2</sub>SO<sub>4</sub> (pH 2) electrolyte and a 10 μm Pt probe held at +0.4 V. Figure 2 shows SECM line scans of damaged regions on three different AA2024 samples. Scan A is for a PANI/PMMA blend coated, scribed surface. Scan B is for a scribed PMMA coated surface, and scan C is for a

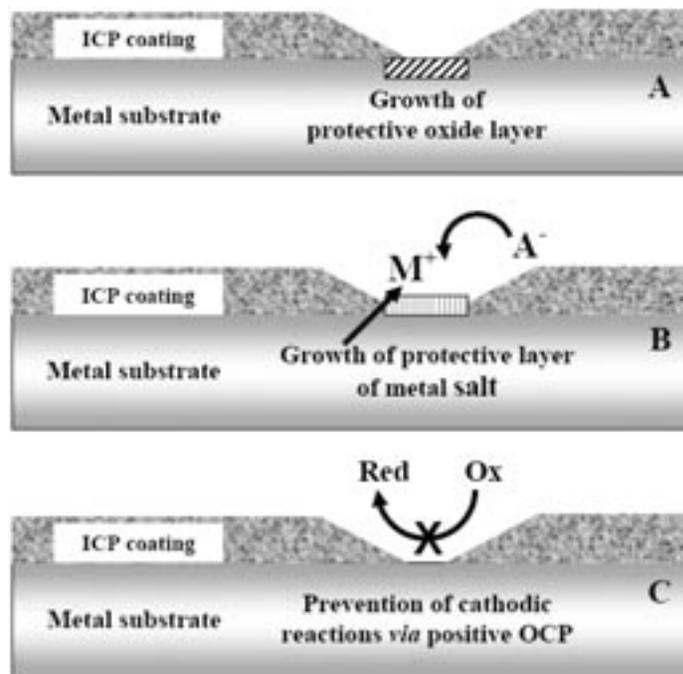


Fig. 1. Schematic depictions of three different mechanisms by which conductive polymers can provide corrosion protection.

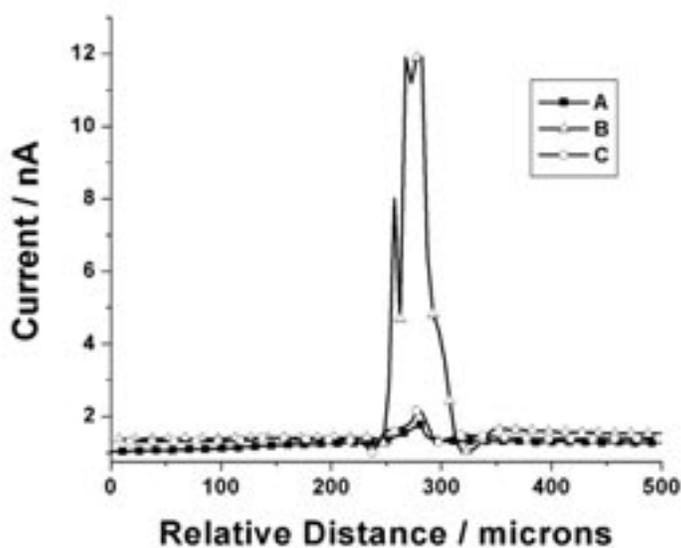


Fig. 2. Plots of tip current vs. relative distance across the surface for SECM line scans from left to right across a scratch on coated AA2024 substrates. For all cases, the supporting electrolyte was 1.25 mM (dimethylaminomethyl)ferrocene + 10 mM H<sub>2</sub>SO<sub>4</sub>, and the scratch is located at ca. 260 μm on the x axis. (A) (—■—) AA2024/PANI-CSA (20%)/PMMA surface at an OCP value of -0.12 V, (B) (—△—) AA2024/PMMA surface at an OCP value of -0.74 V, (C) (—○—) AA2024/PMMA surface held potentiostatically at -0.12 V.

scribed PMMA coated surface where the potential of the substrate was held at -0.12 V. The PMMA coated surface at open-circuit displays a very high cur-

rent response (12 nA), which is attributed to H<sub>2</sub> evolution on this surface in a type of a substrate-generation, tip-col-

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# DNA Damage Inhibition by Dietary Antioxidants: Voltammetric Detection of Inhibition Using Metallopolymer Catalysts

A Summary Report to The Electrochemical Society for the 2004 Colin Garfield Fink Summer Research Fellowship

by Amos Mugweru

Reactive oxygen species (ROS) derived from biochemical utilization of oxygen initiate pero-oxidation of unsaturated lipids especially those that constitute bio-membranes and are responsible for health problems such as aging, cancer,<sup>1</sup>therosclerosis, and ischemia-reperfusion disturbances in the brain and heart.<sup>2</sup> Diet may have a profound effect on carcinogenesis, and it is often suggested that cancer deaths may be decreased by ingestion of dietary antioxidants.<sup>3</sup> Epidemiological and experimental results suggest protective effects of dietary antioxidants from vegetables and vitamin supplements.<sup>4</sup> It is often unclear whether ROS are involved in the formation/inhibition of deoxyribonucleic acid (DNA) lesions, or how they may be promoted by xenobiotic chemicals. In this work we investigated inhibition of DNA damage by dietary antioxidant, vitamin C (ascorbic acid) using metallopolymer films.

We have used metallopolymer films containing DNA and monitored DNA damage after incubation with ROS in the presence and absence of antioxidants. Fenton reagent was used to generate free radicals under standard conditions developed earlier.<sup>5</sup> Films containing  $[\text{Os}(\text{bpy})_2(\text{PVP})_{10}\text{Cl}]^+$  and  $[\text{Ru}(\text{bpy})_2(\text{PVP})_{10}\text{Cl}]^+$  metallopolymers were first assembled layer-by-layer<sup>6</sup> on pyrolytic graphite electrodes to make sensors that selectively detected oxidized DNA.<sup>5</sup> These films showed reversible, independent electrochemistry for electroactive  $\text{Os}^{3+}/\text{Os}^{2+}$  and  $\text{Ru}^{3+}/\text{Ru}^{2+}$  centers, with formal potentials of 0.34 and 0.76 V vs. a saturated calomel electrode (SCE), respectively. The combination of ruthenium and osmium metallopolymers in the films provided a catalytic Os square wave voltammetry (SWV) peak that is mainly selective for 8-oxoguanine, and the detection of other oxidized nucleobases from the Ru peak. Alternate adsorption cycles of Salmon testes DNA (2 mg/mL) and PDDA (2mg/mL) were repeated until the desired numbers of layers were made. Final films are denoted by order of layer assembly as CIRu-PVP/PSS/CIOs-PVP/DNA/PDDA/DNA.

Earlier results<sup>7</sup> showed that 8-oxoguanine (8-oxoG) was generated

FIG. 1. Difference SWV of films at pH 7.0 buffer of PSS/CIRu-PVP/PSS/CIOs-PVP/DNA/PDDA/DNA film before and after 3 min incubation in Fenton reagent (4 mM  $\text{H}_2\text{O}_2$  + 1 mM  $\text{FeSO}_4$ ).

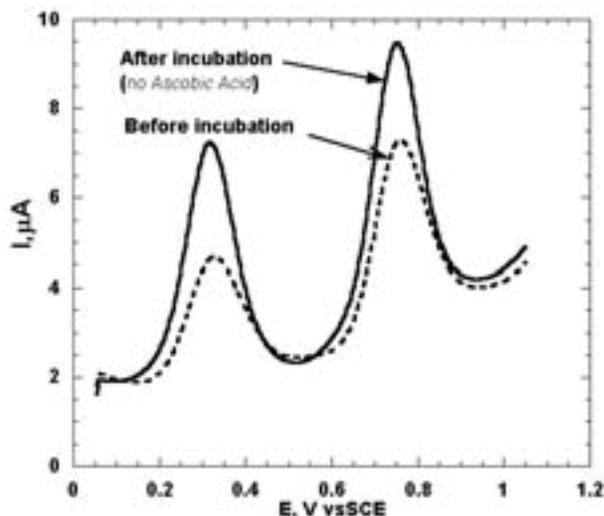
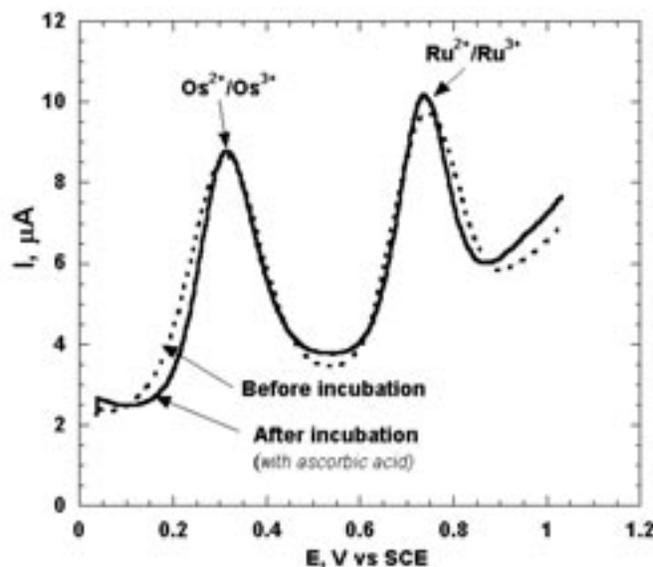


FIG. 2. Difference of SWV of PSS/CIRu-PVP/PSS/CIOs-PVP/DNA/PDDA/DNA film at pH 7.0 buffer before and after 3 min incubation in Fenton reagent (4mM  $\text{H}_2\text{O}_2$  + 1 mM  $\text{FeSO}_4$ ) in presence of excess ascorbic acid.



from DNA incubated with Fenton reagent. The  $\text{Os}^{3+}/\text{Os}^{2+}$  redox couple in the metallopolymer film catalytically oxidized 8-oxoG formed after incubation. Figure 1 shows difference SWV of CIRu-PVP/PSS/CIOs-PVP/DNA/PDDA/DNA film before and after incubation with Fenton reagent. Catalytic current increase for the Os peak suggested Fenton-oxidized oligonucleotides containing guanine predominantly due

to the oxidation of 8-oxoG. Films incubated with a similar concentration of Fenton reagent but in the presence of excess ascorbic acid yielded no catalytic current at Os center (Fig. 2). Ascorbic acid is a known strong antioxidant that is capable of scavenging a wide variety of reactive oxygen and nitrogen species.<sup>8</sup> Absence of a catalytic peak at the  $\text{Os}^{2+}/\text{Os}^{3+}$  redox center (Fig. 2) suggests

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# Redox-Modulated Molecular Recognition: From Solution to the Solid State

A Summary Report to The Electrochemical Society for the 2004 Joseph W. Richards Summer Research Fellowship

by Joseph B. Carroll

The ability to control non-covalent interactions by modulating the redox properties between host and guest molecules is a concept that has great impact in different areas from biology to materials science. These electrochemical relationships have been studied extensively in solution, culminating in the development of model systems with interesting redox behaviors; however, these systems are not directly applicable to solid-state devices. My current research interests include the integration of electrochemistry and redox-modulated molecular recognition in the solid state, specifically surface modification using polymers. This fellowship has been extremely helpful in furthering my efforts from solution-based, model systems to the development of more complex, solid-state, redox controllable materials.

The study of redox-modulated molecular recognition in urea-quinone and analogous systems has been well established. What I hoped to accomplish during my tenure at the University of Massachusetts (UMASS-Amherst) is the development of more complex macromolecular systems eventually culminating in responsive materials based on urea-quinone interactions. Hydrogen bonding interactions between phenanthrenequinone and thiourea can be electrochemically tuned from strongly associating in the reduced species of the quinone to non-associating in the oxidized form, acting as a redox-triggered switch. The transition of these concepts to more complex polymeric and inorganic systems gives rise to very different electrochemical behaviors. Phenanthrenequinone underwent highly efficient proton transfer processes in the presence of thiourea-functionalized polystyrene copolymers and higher generation DAB-Am dendrimers whereas interactions with a similar benzyl-thiourea monomer reveal strong redox modulation of the quinone without proton transfer (Fig. 1). These highly efficient proton transfer processes are analogous to substrate-enzyme interactions in biology.

Similar to urea-quinone interactions, flavoenzyme models have demonstrated that three-point hydro-

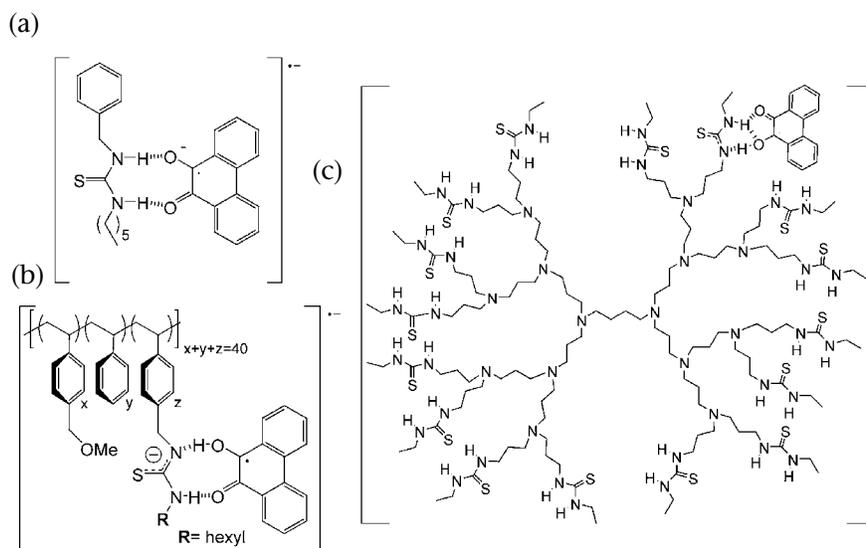


Fig. 1. Phenanthrenequinone undergoes highly efficient proton transfer processes in the presence of (b) thiourea functionalized polystyrene copolymers and (c) higher generation DAB-Am dendrimers; whereas interactions with a similar benzyl-thiourea monomer (a) reveal strong redox modulation.

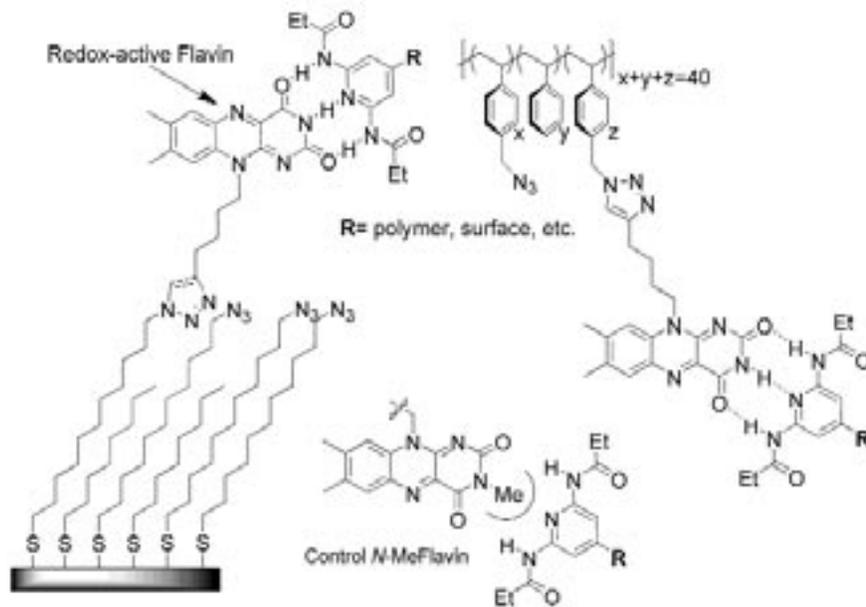


Fig. 2. Schematic illustration showing flavin-functionalized surfaces and polymers. Redox-modulated, three-point hydrogen bonding allows for electrochemically controlled interactions between flavin and diamidopyridine systems.

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# Gold Nanoparticle Multilayers: Rectification of Quantized Charging Even in the Presence of Hard Electrolyte Anions

A Summary Report to The Electrochemical Society for the 2004 F. M. Becket Summer Research Fellowship

by Fengjun Deng

Quantized capacitance charging of monolayer-protected gold nanoparticles (Au MPCs) can be rectified by hydrophobic electrolyte anions in aqueous solutions when the particles are immobilized on electrode surfaces forming monolayers.<sup>1</sup> These unique rectification behaviors are interpreted on the basis of a Randles equivalent circuit where the electrode interfacial capacitance consists of two components, one for the collective contribution of surface-immobilized MPC nanocapacitors and the other accounting for the interparticle void.<sup>2</sup> These interesting single electron-transfer characters demonstrate that these nanoscale entities can be used as building blocks for the fabrication of next-generation, nanoscale electronic devices.

In this work, we focus on the electrochemistry of self-assembled multilayers of gold nanoparticles in aqueous solutions which also exhibit rectified quantized capacitance charging characteristics, even in the absence of hydrophobic anions, in contrast to those with

nanoparticle monolayers. Gold nanoparticle multilayers were prepared by the following procedure. A polycrystalline gold disk (sealed in glass tubing; gold disk area 0.61 mm<sup>2</sup>) was used as the working electrode. Prior to use, the gold electrode was cleaned by a procedure described previously.<sup>2</sup> Briefly, the gold electrode was first polished with 0.05  $\mu\text{m}$  alumina slurries, followed successively by sonication in dilute nitric acid, sulfuric acid, and nanopure water. The electrode was then subjected to electrochemical etching by rapid potential sweep (10 V/s) in 0.10 M H<sub>2</sub>SO<sub>4</sub> within the potential range of +1.2 to -0.2 V for 5 min. After this, the electrode was rinsed with copious amounts of nanopure water and ethanol, and then dried in a gentle stream of ultrahigh-purity nitrogen. The resulting gold electrode was dipped into a dichloromethane solution containing *n*-hexanethiolate-protected gold particle (AuC6, core diameter *ca.* 1.6 nm) at a concentration of 1 mg/mL. The electrode was quickly pulled out and blow-dried by N<sub>2</sub>. The gold electrode, with multilay-

ers of AuC6 particles, was used as a working electrode in the electrochemical measurements. In a typical experiment, 10-20 layers of particles were deposited on the electrode surface as estimated by voltammetric measurements (*vide infra*).

The charge-transfer chemistry of these nanoparticle multilayers is drastically different from that of their monolayer counterparts. Figure 1 shows the cyclic (CV) and differential pulse voltammograms (DPV) of a AuC6 multilayer on a gold electrode surface in 0.1 M NH<sub>4</sub>NO<sub>3</sub>. From Fig. 1A and 1B, we see a series of well-defined voltammetric peaks within the potential regime of 0 to +0.8 V which are attributed to the quantized capacitance charging of the surface-bound gold particle multilayer; whereas in the negative potential regime, only featureless responses, the so-called rectified quantized charging can be seen. Figure 1C depicts the linear increase of the voltammetric peak current of the first charging peak with potential scan rate. From the slope, one can estimate the particle surface coverage to be *ca.*

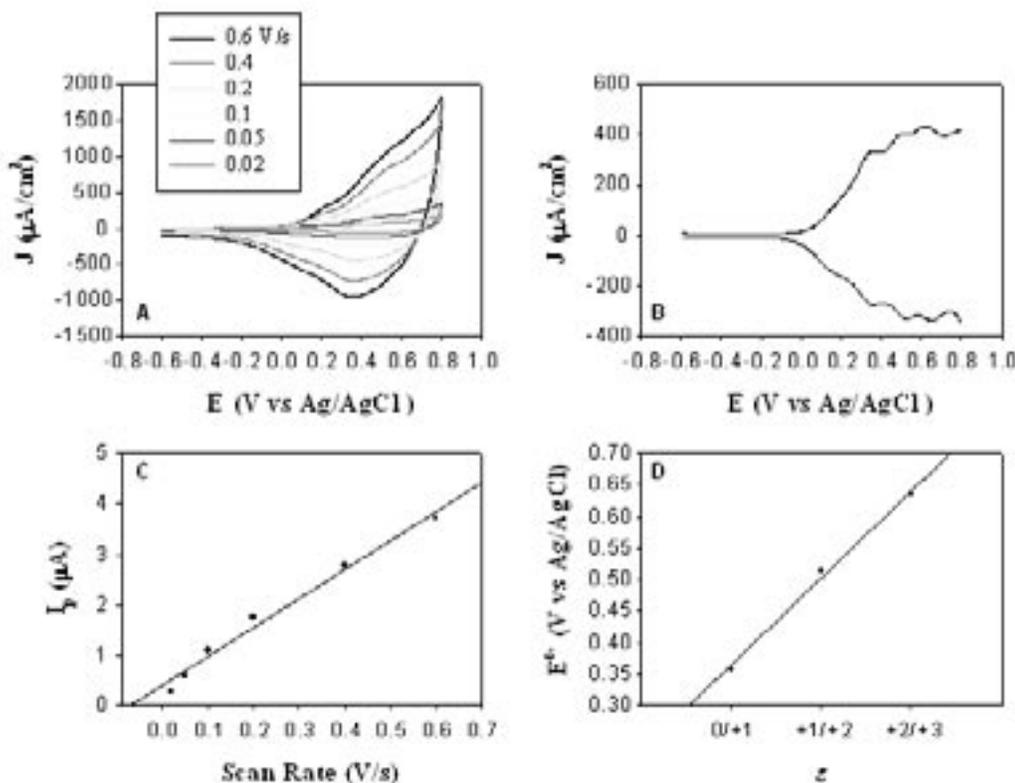


Fig. 1. Cyclic (A) and differential pulse voltammograms (B) of a AuC6 multilayer on a gold electrode surface (area 0.61 mm<sup>2</sup>) in 0.1 M NH<sub>4</sub>NO<sub>3</sub>. Ag/AgCl and Pt wires were used as reference and counter electrode, respectively. (C) Variation of voltammetric peak currents (first charging peak in A) with potential scan rate. (D) Variation of formal potentials of nanoparticle quantized capacitance charging (B) with particle charge state.

$1.01 \times 10^{-9}$  mol/cm<sup>2</sup>, corresponding to roughly 17 layers of closed-packed particle molecules. This observed rectified quantized charge transfer in nanoparticle multilayers is in great contrast with that in previous studies.<sup>1-3</sup> In previous studies with nanoparticle monolayers, quantized capacitance charging of gold particles could be observed only in the presence of hydrophobic (soft) anions, such as PF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, and BF<sub>4</sub><sup>-</sup>, whereas in solutions containing only hard anions, such as NO<sub>3</sub><sup>-</sup>, quantified capacitance charging features were not observable.<sup>1-4</sup> To our knowledge, this is the first time to observe that hard electrolyte ions such as NO<sub>3</sub><sup>-</sup> also may initiate particles quantized charging in aqueous solutions when the gold particles were in multilayer forms. However, the mechanism of NO<sub>3</sub><sup>-</sup>-induced rectification of gold particle quantized charging is not clear at the

moment. Figure 1D shows the variation of the formal potentials of quantized charging peaks with particle charge state, where one can calculate the effective AuC6 capacitance from the slope by linear regression,  $C_{MPC} = 1.15$  aF. This is somewhat larger than that with a particle monolayer (by a dithiol linkage) in the presence of PF<sub>6</sub><sup>-</sup> ( $C_{MPC} = 1.02$ - $1.05$  aF).<sup>1,4</sup>

Future work will focus on the effects of gold nanoparticle layer structures on their quantized capacitance charging especially in the presence of hard electrolyte ions using Langmuir-Blodgett and electrochemical quartz crystal microbalance techniques. ■

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## Suppression of Cathodic...

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lection experiment. In contrast, the PANI-PMMA coated surface at open circuit displays a very low anodic current (*i.e.*, little H<sub>2</sub> evolution). This behavior is mimicked by the PMMA control when it is held at a potential of -0.12 V, showing that the potential at which the interface is poised controls the evolution of H<sub>2</sub>, and therefore also the metal corrosion process. The data suggest that the mechanism by which the coating inhibits corrosion is by elevating the OCP to a level where cathodic reactions are suppressed.

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## DNA Damage...

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the absence of 8-oxoguanine in the DNA film.

The presence of ascorbic acid may have the effect of rapidly reacting with the hydroxyl radicals produced by Fenton's reagent such that none reacts with DNA. The next important step will be to assemble films as usual and incubate in increasing concentrations of the antioxidants. Plots of concentration of antioxidants at fixed concentration of Fenton reagent vs. catalytic peak current clearly point to the effects of the inhibitors. ■

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## Redox-Modulated...

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gen bonding recognition between flavin and diamidopyridine derivatives can be modulated by changing the electronic states of flavin. Ongoing research in our labs seeks the development of more complex macromolecular systems based on flavin-diamidopyridine binding (Fig. 2). Using click chemistry we have developed systems from surfaces to polymers, which are functionalized with flavin derivatives. During the summer, both of these systems have been characterized in detail using such techniques as IR, fluorescence microscopy, NMR, cyclic voltammetry (CV), quartz crystal microbalance (QCM), ellipsometry, water-contact angle measurements, and X-ray photoelectron spectroscopy (XPS).

In conclusion, multiple electrochemically controlled systems have been developed based on redox-modulated hydrogen bonding recognition. With the help of ECS we have been able to further our understanding of these complex redox behaviors and are closer to the development of well characterized, electrochemically controlled materials and surfaces. ■

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