

# Adsorption of Zirconium–Phosphonate Multilayers onto Phosphate-Derivatized Glassy Carbon Substrates

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Two methods were developed to modify glassy carbon surfaces with phosphoric acid groups. In the first method, phosphoryl chloride was reacted directly with oxides on the glassy carbon surface. Oxidative and reductive pretreatment of the polished surface improved the phosphate site density, as determined by X-ray photoelectron spectroscopy. In the second method, the carbon surface was modified with an  $\omega$ -aminoalcohol by electrochemical oxidation, prior to phosphorylation, yielding similar phosphate site densities. Zirconium 1,10-decanediylbis(phosphonic acid) (Zr-DBP) multilayers were deposited upon these modified glassy carbon substrates. Variable takeoff angle XPS studies and the steady increase of zirconium and of phosphorus with each metal–phosphonate deposition indicate regular adsorption of each multilayer. Higher than ideal zirconium-to-phosphorus ratios are attributed to deposition kinetics, signal attenuation, and the random character of the glassy carbon surface. Zr–DBP layers exhibited ellipsometric thickness of 17 Å or higher, plausibly due to adsorption of excess ionic species into disordered regions or pockets of the film. Contact angle measurements concur with this picture of an imperfect film. The ability of the films to insulate the carbon interface from solution species was investigated by cyclic voltammetry of potassium ferricyanide; heterogeneous electron transfer was significantly hindered after one to two Zr–DBP adsorption steps.

## Introduction

Organic films<sup>1</sup> have been the subject of intensive research as model surfaces in fields as diverse as adhesion, tribology, biology, and electrochemistry. At the focus have been self-assembled monolayers of alkanethiols on gold, which combine well-ordered interfaces, and control over chemical and physical properties, with ease of preparation. Other well-studied systems include films formed from silane coupling agents at silicon or glass, Langmuir–Blodgett techniques, or deposition of carboxylic acids upon metals. The technique of self-assembly has been extended to development of multilayer systems; layer-by-layer deposition of transition-metal phosphonates, upon thiol or siloxane monolayers, has been one rather prominent approach.<sup>2</sup>

Our interest in the creation of sensor devices via the coupling of inorganic oxide films to various substrates

has led us to seek routes which permit chemical functionalization yet provide an interface that maintains its integrity under exposure to harsh environments. In particular, the growth of zeolite films under hydrothermal conditions is a promising avenue to the design of selective sensor interfaces,<sup>3</sup> but the typical hydrothermal conditions (high pH, high temperature) preclude the use of common monolayers such as thiols or silanes.

A substrate potentially attractive for application of molecular sieve films as selective electrochemical sensors is glassy carbon, a randomly structured, conductive form of carbon resistant to chemical attack.<sup>4</sup> Activation of carbon by plasma,<sup>5</sup> chemical,<sup>6</sup> or electrochemical<sup>7</sup> treatment can generate a higher density of oxidic functional groups at the surface. Covalent bonding to the glassy carbon surface, or similarly to carbon fibers, has typically proceeded through amidization<sup>8</sup> or esterification<sup>9</sup> of surface carboxylic acids, or reaction of

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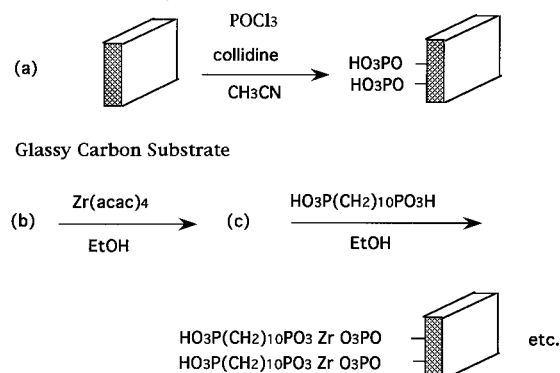
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**Scheme 1. Metal–Phosphonate Multilayer Film Deposition: (a) Formation of Primer Layer on Glassy Carbon, followed by Layer-by-Layer Deposition of (b) Zr(acac)<sub>4</sub> and (c) Alkylbis(phosphonic acid)**



surface alcohols with organosilanes<sup>10</sup> or transition-metal compounds such as TiCl<sub>4</sub>.<sup>11</sup> For these modes of attachment, however, hydrolysis in aqueous environments is a concern.

Other covalent derivatizations, which may promise much greater robustness than SAMs of thiolates and silanes, rely upon direct carbon–carbon coupling of alkenes to oxide-free carbon<sup>12</sup> or upon ether formation<sup>13</sup> at graphite. Several approaches toward carbon–nitrogen bonding include attachment of amines,<sup>12b,14</sup> electrochemical reduction of diazonium salts,<sup>15</sup> or reaction with hydrazine.<sup>16</sup>

We approached our goal of developing thermally, hydrolytically stable metal–phosphonate multilayer films on glassy carbon substrates by first functionalizing the surface with pendant phosphoric acid species and then carrying out the deposition procedure developed by Mallouk, as outlined in Scheme 1. We selected two routes toward initial derivatization of the substrate: (i) creation of phosphate groups directly at the surface; and (ii) electrochemical oxidation of an  $\omega$ -functional alkylamine at the glassy carbon, followed by modification of the terminal functionality to phosphate. Advantages of both paths i and ii include simplicity in terms of reagent handling and chemistry as well as safety, in comparison to the use of diazonium salts. We describe our results obtained from cyclic voltammetry, XPS, ellipsometry, and contact angle characterization and discuss a plausible model for the multilayer films.

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## Experimental Section

**Materials.** Analytical reagent grade lithium perchlorate, butylamine, decylamine, 6-aminohexanol, octadecylamine, phosphoryl chloride, 2,4,6-collidine, acetonitrile, hexadecane, and zirconium acetylacetonate [Zr(acac)<sub>4</sub>] were purchased from Aldrich, and potassium ferricyanide was from Fisher. Absolute ethanol was from McCormick Industries. Chemicals were used as received.

Sigradur G grade (treated to 3000 °C) glassy carbon plates were obtained from EMC Industries.

**Electrochemistry.** Cyclic voltammetry was performed with a Bioanalytical Systems (BAS) CV-27 voltammograph and recorded on a Soltec X-Y recorder, at glassy carbon working electrodes (gce), 3 mm in diameter, obtained from BAS. Pt wire or foil was used as the counter electrode; all potentials are cited relative to a BAS Ag/AgCl/KCl reference electrode (−45 mV vs. SCE). Carbon electrodes were initially polished successively with 15, 3, and 1  $\mu$ m diamond polishes on nylon (Buehler), and thereafter with 1 and 0.05  $\mu$ m aluminas on felt (Buehler). Polished electrodes were sonicated in DI water for 3 min, then rinsed and dried under a nitrogen stream. The electrodes were typically scanned in 1 mM solutions of amine with 0.1 M LiClO<sub>4</sub> in absolute ethanol at 10 mV/s between 0.0 and 1.40 or 1.45 V vs our reference electrode. The electrode was then rinsed with ethanol and water and dried under nitrogen before other measurements were performed. K<sub>3</sub>Fe(CN)<sub>6</sub> was prepared 0.1 M in 0.1 M KCl(aq); the electrode was scanned between −0.2 and 0.8 V, beginning at 0.0 V.

**XPS.** Glassy carbon plates, typically cut to 12 × 15 × 2 mm, were polished and treated electrochemically in the same manner as the glassy carbon electrodes, and for electrochemistry they were connected to a stainless steel wire which was isolated from solution with Teflon tape and parafilm. XPS spectra were taken on a Perkin-Elmer 5300 spectrometer equipped with a hemispherical analyzer, using Perkin-Elmer's PHI acquisition program. Samples were mounted with copper clips over a gold-covered stainless steel holder. Data were collected at 15 kV and 300 W with the Mg anode (K $\alpha$  radiation at 1253.6 eV) under a main chamber pressure at or below 5 × 10<sup>−9</sup> Torr. Survey spectra were acquired for 10 min at a pass energy of 44.75 eV. High-resolution scans of regions no larger than 20 eV were obtained for C 1s, N 1s, O 1s, Zr, and P 2p at a bandpass of 8.95 eV with acquisition time for the three to four regions collected on each sample typically totaling 2–3 h. Survey scans did not typically reveal chlorine after chemical or electrochemical treatments. Takeoff angles, measured from the parallel to the substrate, were either 45°, or 10° where noted. Relative concentrations and elemental ratios were calculated from integrated areas obtained from the high resolution scans, and from atomic sensitivity factors supplied for this particular instrument by Perkin-Elmer. Peak areas (A norm) are normalized to the sum of all peak areas, corrected for atomic sensitivity.

**Ellipsometry and Contact Angle Measurements.** Thickness measurements ( $d$ , Å) were taken on large glassy carbon plates with a Rudolph Research rotating analyzer ellipsometer (Model 43603-200E) equipped with a white light source and 633 nm filter, at 25° polarization and 70° angle of incidence. Plates, polished as described for the small electrodes for preparation with amines, were applied as working electrodes, with a 1 cm<sup>2</sup> geometric area defined by a viton O-ring, in a specially designed Teflon cell. Optical constants for the bare substrate were determined for each individual sample. All measurements were taken at a minimum of three locations on the plate and averaged, with the plate also being rotated by 45° or 90° about its axis during this data collection.  $\psi$ ,  $\delta$ ,  $n_s$ ,  $k_s$ , and  $d$  values were calculated from changes in the polarization and azimuth experienced upon reflection of the light, using Rudolph Research 2000FT software. A value of 1.54<sup>2a</sup> was assumed for the film refractive index for measurements of the metal–phosphonate multilayers.

Aqueous contact angles were read with a home-built device, under 100% humidity with drop size approximating 1  $\mu$ L. At least two angles obtained from each of three drops at different locations on the surface were averaged.

**Chemical Modification Procedure and Multilayer Deposition.** Polished or pretreated carbon surfaces were phosphorylated with phosphoryl chloride and 2,4,6-collidine (0.2 M each in  $\text{CH}_3\text{CN}$ ) following the procedure of Frey et al.<sup>2g</sup> In this context, "pretreated" surface implies either (i) a polished glassy carbon plate applied as an electrode for cyclic voltammetry in a 6-amino alcohol solution, or (ii) a polished glassy carbon plate heated in air at 70 °C overnight<sup>11</sup> and then suspended in a slurry of  $\text{LiAlH}_4$  in ether for 3 h.

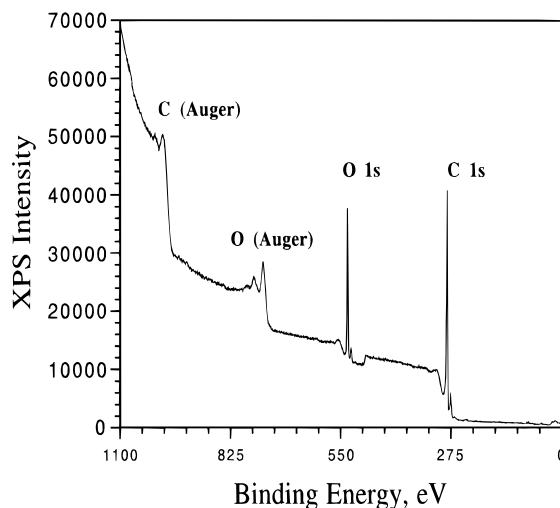
1,10-Decanediybis(phosphonic acid) (DBP) was prepared following the method of Lee et al.<sup>2a</sup> Carbon surfaces previously treated with the phosphoryl chloride solution were then sequentially immersed overnight, unless stated otherwise, in 5 mM ethanolic solutions of either  $\text{Zn}(\text{acetate})$  or  $\text{Zr}(\text{acac})_4$  and then 5 mM ethanolic DBP, and were rinsed in an ethanol bath for at least 0.5 h between each deposition step.  $\text{Zr}(\text{acac})_4$  was chosen because it exists as a monomeric species in ethanol;<sup>2j</sup> one drawback, however, is that its ligands may not easily dissociate.

## Results and Discussion

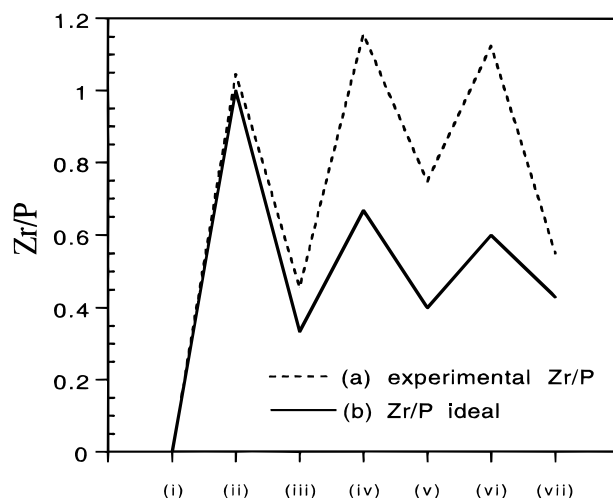
We have pursued the deposition of metal ion–bis(phosphonic) acid multilayers upon modified carbon substrates. This approach (Scheme 1), originally carried out at gold and silicon substrates by Mallouk,<sup>2a–d,l</sup> and then others,<sup>2e–k</sup> takes advantage of spontaneous adsorption from solutions of metal ions and bis(phosphonic acid), to form thermodynamically stable surfaces analogous to bulk layered metal phosphonate salts. Tetravalent or divalent metal ions and alkylphosphonate compounds are sequentially deposited at a substrate, previously derivatized with phosphoric acid groups, to form uniform multilayer films that are held together by ionic bonding within the inorganic metal-phosphonate network and van der Waals forces between the alkyl chains. Order within the alkyl regions is limited by the packing structure of the inorganic regions of the film.

The glassy carbon structure has been portrayed as a network of interwoven graphitic ribbons,<sup>4b</sup> presenting randomly oriented basal and edge plane carbon at the surface—by scanning tunneling microscopy, the surface was found to be primarily amorphous but having crystalline domains of graphitic or diamond-like lattices.<sup>17</sup> XPS of a polished glassy carbon (Figure 1) exposed to ambient shows oxygen present, the intensity being sensitive to sample history and pretreatment procedures. These oxides, heterogeneously distributed within exposed regions of edge plane carbon, can include ether, carboxylic acid, and phenol among other species. By means of XPS, Tougas and Collier<sup>18</sup> were able to quantify surface phenols and carbonyls on glassy carbon using chemical labels selective to each of these species.

**Multilayers on Carbon Modified with Phosphate Groups.** We sought to create phosphoric acid groups directly at the glassy carbon, by reacting phosphoryl chloride with phenols present at the surface, in order to prepare a primer for multilayer deposition. Exposure of a polished glassy carbon substrate, after treatment with  $\text{POCl}_3$  for ca. 1 h, alternately to 5 mM ethanolic solutions at 1 h of  $\text{Zr}(\text{acac})_4$  and DBP produced Zr/P area ratios (Figure 2) following the trend predicted if ideal deposition of each layer occurred. The ratios of Zr/P calculated for the ideal case assume stoichiometric



**Figure 1.** XPS survey spectrum of a polished glassy carbon substrate. Carbon and oxygen peaks are labeled.



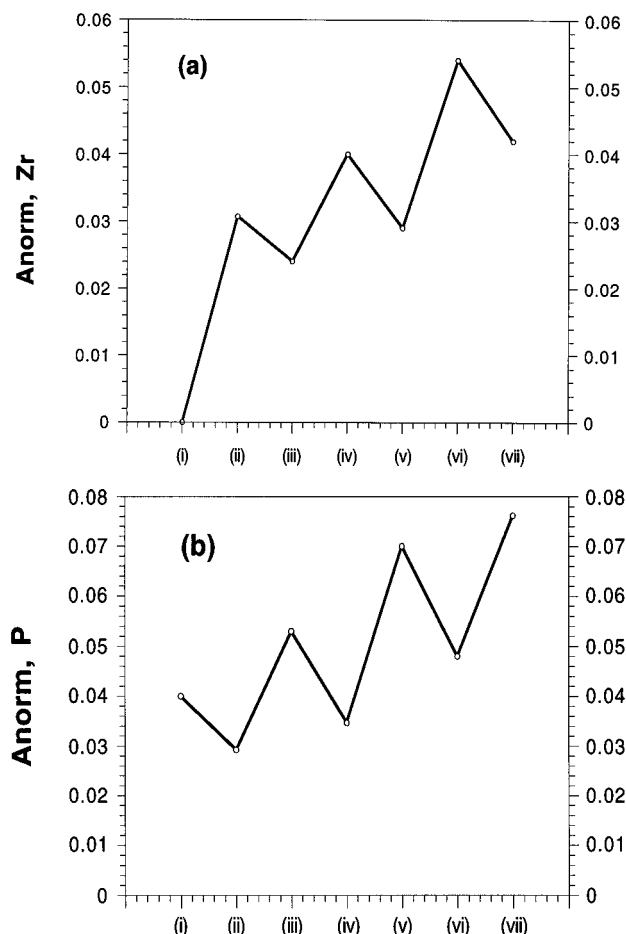
**Figure 2.** (a) Experimental and (b) ideal Zr to P ratios for a glassy carbon surface (i) exposed to  $\text{POCl}_3$ , followed by sequential/alternate deposition of  $\text{Zr}(\text{acac})_4$  (ii), (iv), (vi) and 1,10-decanediylbis(phosphonic acid) (DBP) (iii), (v) (vii).

amounts of Zr and P without signal attenuation effects taken into account. Our analysis does not include the influence of Zr and P photoelectron escape depths, because the structure of the multilayer is unknown. However, the concept of periodicity of the Zr/P ratios supports layer-by-layer buildup of the film, with the metal atoms situated in between DBP layers. Further evidence for buildup of the film comes from the normalized peak area of Zr (Figure 3a), which increases in an approximately linear fashion for each additional metal ion deposition step, as does the normalized peak area of P 2p (Figure 3b) with each alkylphosphonate deposition. However, the ratio of Zr to P, for the sample shown in Figure 2, implies that less than a complete layer forms at each step, particularly concerning the adsorption of phosphonate, because the zirconium content is unusually high for several of the steps represented. The possibility of the DBP exposure time being too short or zirconium depositing in clusters on the surface should be kept in mind.

Even for films on gold and silicon substrates, Chidsey et al.<sup>2i</sup> observed overestimates of film thickness obtained by ellipsometry for metal phosphonate multilayers and the inability of the layers to diminish the capacitance

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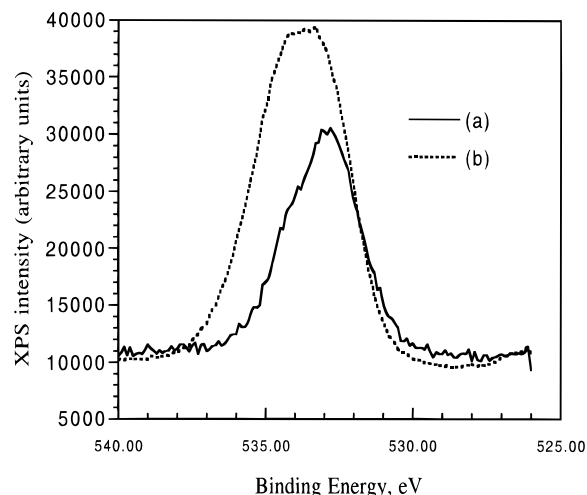


**Figure 3.** Normalized XPS peak area of (a) Zr and (b) P measured for steps i–vii of the previous figure.

measured by CV. The authors hypothesized that ionic solution may reside in pores created by disordered regions and contribute to the overall thickness; electrolyte may penetrate through these pores such that the insulating nature of the film does not improve. Similarly, a plausible model for the high zirconium content of our films could involve zirconium ions residing in pockets created by incomplete deposition of previous phosphonate layers.

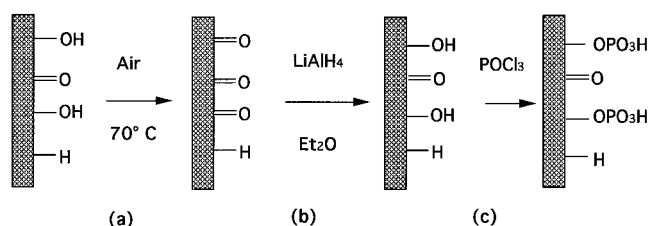
**Multilayers on Pretreated Carbon Modified with Phosphate Groups.** By exposing the substrate to an oxidative then a reductive environment, as outlined in Scheme 2, so as to promote the content of phenolic surface species prior to reaction, we were able to significantly increase the surface density of phosphorus detected by XPS-P/C, measured at grazing takeoff angle after exposure to  $\text{POCl}_3$ , increased from 0.057 at the polished glassy carbon surface to 0.155 at the surface treated as in Scheme 2. The simultaneous increase in oxygen content—O/C changed from 0.37 to 0.29 to 0.65 at  $10^\circ$  takeoff, after the oxidation, reduction and phosphorylation, respectively—is consistent with high yield for the last step of Scheme 2. Additionally, the broadening of the O 1s peak width (Figure 4) after phosphorylation may be attributed to the formation of phosphate species.

The substrate modification and layer growth were also followed by contact angle (Table 1). After oxidation, reduction, and then treatment of the glassy carbon with  $\text{POCl}_3$ , the contact angle decreased substantially from that of the polished carbon. The aqueous contact angle



**Figure 4.** High-resolution scans of the O 1s regions of (a) polished carbon heated in air at  $70^\circ\text{C}$  and then stirred in a slurry of  $\text{LiAlH}_4$ / ether and (b) the same, after exposure to  $\text{POCl}_3$ . Intensities are scaled to equivalent data collection time.

**Scheme 2. Process To Increase Phenol Density on Glassy Carbon Surface:** (a) Air Oxidation at  $70^\circ\text{C}$ , (b) Reduction of Surface Oxides with  $\text{LiAlH}_4$ , and (c) Treatment of Surface with  $\text{POCl}_3$  To Create Phosphoric Acid Groups



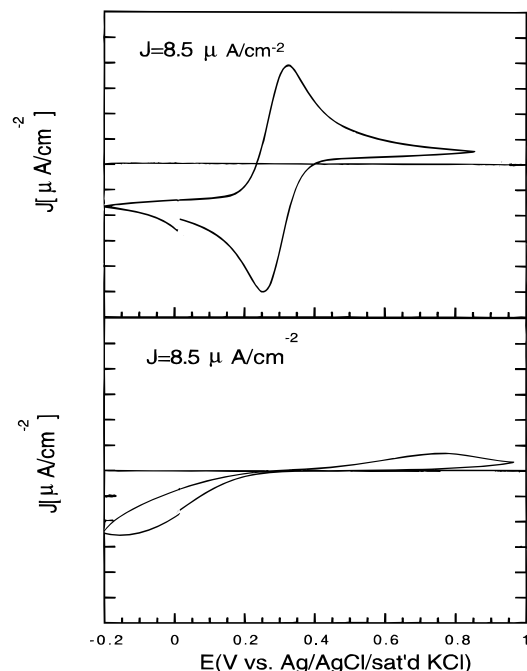
**Table 1. Water Contact Angles on Modified Glassy Carbon Plates**

Treatment	degrees
as received	72
polished	45
air $70^\circ\text{C}$	47
$\text{LiAlH}_4$	55
$\text{POCl}_3$	26
$\text{Zr}(\text{acac})_4$	70
DBP	70
electrooxidized amines	
butylamine	60
decylamine	64
octadecylamine	64
6-aminohexanol	53

rose to approximately  $70^\circ$  after deposition of the first Zr–DBP layer and remained unchanged as additional layers were adsorbed. This contact angle is higher than that for a well-ordered interface, on a gold surface, terminated by phosphonic acid.<sup>19</sup> Taken together with the fact that hexadecane wets the multilayer surfaces well ( $<10^\circ$ ), aqueous contact angle data support the existence of disorder or imperfect packing within the methylene regions of the film.

Initial ellipsometric studies showed a  $5\text{--}10\text{ \AA}$  increase in thickness (d) after polished carbon surfaces had been subjected to the three step process of Scheme 2. Immersion in 5 mM ethanolic solutions of  $\text{Zr}(\text{acac})_4$  and DBP for 1 h each yielded a minimum  $16\text{--}19\text{ \AA}$  increase.

(19) We have determined a contact angle of  $49^\circ$  for 100% DBP on gold: Feng, S.; Bein, T., to be published.

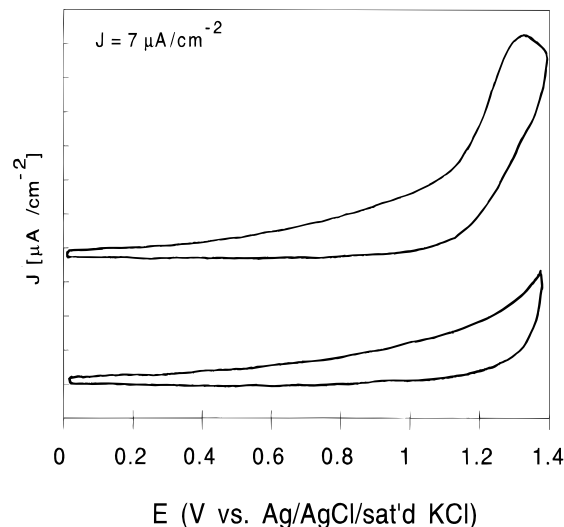


**Figure 5.** Cyclic voltammogram of 0.1 M  $\text{K}_3\text{Fe}(\text{CN})_6$  (aq) at 20 mV/s for a polished glassy carbon electrode (upper), and following deposition of one layer Zr-DBP on a carbon surface phosphorylated as in Scheme 2 (lower). Anodic current is up from the zero baseline; spacing between tickmarks on the current scale represents  $8.5 \mu\text{A}/\text{cm}^2$ .

Films on silicon or gold prepared from DBP have displayed an interlayer distance of  $17 \text{ \AA}$ .<sup>2b</sup> Thus, we might expect each Zr-DBP layer deposited upon the carbon substrate to exhibit thickness similar to this, or less if the films are disordered, barring excess adsorption of either reagent.

The porosity of the films to solution species was checked by permeability of redox species such as  $\text{K}_3\text{Fe}(\text{CN})_6$ .<sup>20</sup> At scan rates as slow as 20 mV/s, little inhibition of electron transfer was seen at the carbon surface treated according to Scheme 2; significant reduction of current did occur after one to two layers of  $\text{Zr}(\text{acac})_4$  and DBP had been applied (Figure 5). In reports of metal phosphonates at thiolated gold,<sup>2a</sup> for comparison, one layer of Zr-DBP led to dramatic reduction of current density, and  $i$ - $E$  behavior characteristic of an ultramicroelectrode array. Similarly, one layer of Zr-1,2-ethanediylbis(phosphonate) on gold strongly hindered electron transfer; two layers fully insulated the interface.<sup>21</sup> Our cyclic voltammetry data concur with the model of the films discussed above; it is conceivable that the film is porous but the alkyl chains fold over to cover regions otherwise accessible to the redox couple.

**Multilayers on Carbon Modified with Functional Amines.** Our next approach toward creating a thermally stable interface at the glassy carbon as a base for multilayer deposition involved attachment of a primary  $\omega$ -amino alcohol following the method of Porter et al.<sup>14d</sup> and Pinson et al.<sup>14c</sup> Electrooxidation of 6-aminohexanol, 1 mM in ethanol, at a glassy carbon electrode



**Figure 6.** Electrochemical oxidation at 10 mV/s of 6-aminohexanol, 1 mM in 0.1 M  $\text{LiClO}_4$ /ethanol (top), at a glassy carbon electrode, as compared to electrolyte alone (bottom).

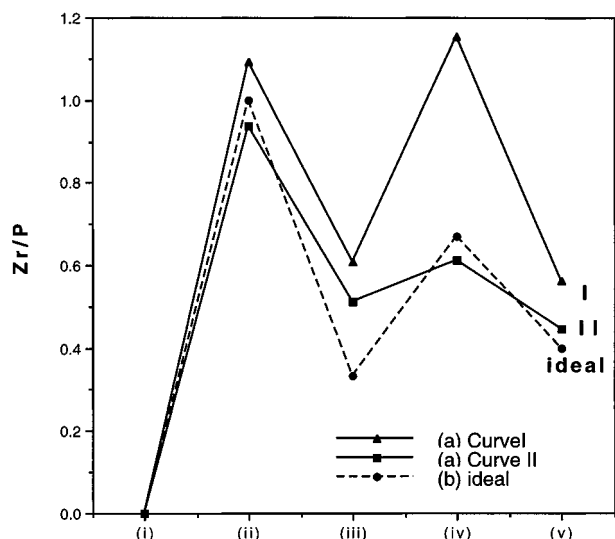
**Table 2. Nitrogen Content at Carbon Surface, As Detected by XPS at  $10^\circ$  Takeoff Angle**

treatment	% N/C	electrooxidation conditions
polished carbon	1.0	
electrolyte without amine	0.6	0.1 M $\text{LiClO}_4$ , 1 cycle
butylamine	4.5	1 mM, 1 cycle
	3.7	Porter: 1 mM, 1 cycle <sup>14d</sup>
6-aminohexanol	1.7	1 mM, 1 cycle
	1.8	1 mM, 90 cycles
decylamine	2.8	1 mM, 13 cycles
	2.2	5 mM, 1 cycle
	2.5	10 mM, 1 cycle
	3.3	0.1 M, 1 cycle
octadecylamine	2.4	5 mM, 1 cycle
	2.7	1 mM, 6 cycles

exhibited an irreversible wave (Figure 6) with an anodic peak at 1.3 V vs. Ag/AgCl/ saturated KCl. The oxidation wave agrees well with those of primary amines oxidized by Porter or Pinson, although the current density and the area ratio of N 1s/ C 1s XPS peaks are less than, for instance, that of butylamine, even at longer total oxidation time. For comparison, we thus examined several simple primary alkylamines differing only in the length of their methylene spacer (Table 2). Electrooxidation in butylamine produced a N/C ratio comparable to Porter's value; coverage of decylamine and octadecylamine was in the range of that attained with amino-hexanol. Conformational disorder within the alkyl chains may hinder access of the amine functionality to the carbon surface; combined with the fact that the C 1s content includes contribution from the organic carbon, this may explain the lower ratios obtained for the longer amines.

Treatment of the amino alcohol-modified carbon surface with phosphoryl chloride leads to comparable attachment of phosphorus (XPS data:  $\text{P}/\text{C} = 0.056$ ), and O 1s and C 1s peak shapes similar to those observed for the surface directly reacted with  $\text{POCl}_3$ . These observations suggest that a similar surface concentration of edge plane sites was substituted in both this case and the direct phosphorylation. We do not exclude the possibility that the phosphorylating reagent may still access residual oxidic or edge plane sites located at the carbon surface.

(20) Active sites for electron transfer are on graphite edges: (a) Rice, R. J.; Pontikos, N. M.; McCreery, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 4617. Heterogeneous electron transfer between  $\text{Fe}(\text{CN})_6^{3-/4-}$  and glassy carbon appears to proceed via an inner-sphere route dependent upon specific surface interactions: (b) Cline, K. K.; McDermott, M. T.; McCreery, R. L. *J. Phys. Chem.* **1994**, *98*, 5314. (c) Chen, P.; Fryling, M. A.; McCreery, R. L. *Anal. Chem.* **1995**, *67*, 3115.



**Figure 7.** (a) Experimental and (b) ideal Zr to P ratios (i) at glassy carbon substrate treated with 6-aminohexanol then  $\text{POCl}_3$ , followed by sequential deposition of  $\text{Zr}(\text{acac})_4$  (ii), (iv), and DBP (iii), (v). Curve I represents 1 h exposure times, on the average, for each step; curve II, overnight exposure for each step.

We applied the same sequence toward multilayer deposition with these modified surfaces as with the previous approach. With phosphonate and zirconium deposition steps carried out for comparable times, we measured high zirconium contents (Figure 7a) as for our sample previously described. Extension of the time allowed for each adsorption step from 1 h to overnight in order to enable the layer to reach equilibrium, improved the zirconium ion deposition to near ideal, although the yield of phosphonate steps remained somewhat low. Signal attenuation due to increasing film thickness and limited yields of the deposition steps can lead to deviations on the low side in XPS signal intensities.<sup>21</sup> A picture of imperfect film formation is even more plausible at carbon substrates than on gold or silicon because the carbon surface itself presents an inhomogeneous foundation.

Electron transfer of the redox analyte  $\text{K}_3\text{Fe}(\text{CN})_6$  was studied at 6-aminohexanol- and model alkylamine-modified surfaces to assess the ability of this type of primer layer to inhibit access to solution species, in particular as a function of alkyl chain length, and to better understand the nature of defects in the organoamine film. The redox activity of  $\text{K}_3\text{Fe}(\text{CN})_6$  at the butylamine- and 6-aminohexanol-modified carbon was similar to the pseudoreversible wave at polished carbon.<sup>22</sup> The inability of short modifiers to block electron transfer is consistent with studies of alkanethiol mono-

layers deposited on gold, for which typically a minimum of 10 methylene units have been found necessary for the film to achieve crystalline packing and insulate the surface from heterogeneous electron transfer.<sup>23</sup> Accordingly, after electrooxidation of decylamine or octadecylamine, electron transfer across the interface is greatly reduced, exhibiting a large overpotential. The remaining cyclic voltammogram resembles that reported across basal plane HOPG.<sup>24</sup> A plausible model for the remaining access to the surface by the redox couple could involve slow electron transfer at basal plane carbon sites. From information provided by analogous experiments carried out at highly ordered graphite,<sup>14d</sup> amine radical cations have been proposed to react only at carbon edge plane sites. Also possible is that the presence of pinholes within the film leads to mixed radial/linear diffusion.<sup>25</sup>

## Conclusion

In this study, we have demonstrated that glassy carbon surfaces can be derivatized with phosphate terminal groups. The modification can be performed by either reacting hydroxyl-terminated carbon with  $\text{POCl}_3$ , or by phosphorylating amino alcohol layers that were previously deposited via electrooxidation. Metal-phosphonate multilayers could be deposited on the derivatized carbon.

XPS, contact angle, and voltammetry data for adsorption of metal-phosphonate multilayers via Scheme 1 upon either the 6-aminohexanol/ $\text{POCl}_3$  derivatized surface, or the surface prepared as in Scheme 2, best fits a model having some degree of disorder and porosity within the film even at extensive phosphonate exposure times. This disorder may stem from the amorphous nature and limited edge plane site density for reactivity of the glassy carbon substrate itself, as well as from the heterogeneous distribution of exposed edge plane regions and of oxidic sites therein.

We have already obtained initial results indicating growth of nonoriented zincophosphate molecular sieve crystals upon the carbon surface modified as in Scheme 2. Further studies are underway to determine the effect of multilayer deposition on glassy carbon upon crystal growth.

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