Adsorption of Catechols on Fractured Glassy Carbon Electrode Surfaces

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Glassy carbon surfaces exposed by fracturing a glassy carbon rod in the electrolyte solution exhibit fast electron transfer kinetics compared to conventionally polished surfaces, implying that glassy carbon is inherently active toward electron transfer before any intentional surface modification. The adsorption of dopamine and related compounds was examined on fractured glassy carbon surfaces and compared to polished or electrochemically pretreated (ECP) surfaces. While the catechols and ascorbic acid had the anticipated fast electron transfer on fractured glassy carbon, their adsorption behavior differed substantially from that reported for polished, ECP, or vapor-deposited carbon. Dopamine, 4-methylcatechol (4-MC), and dihydroxyphenylacetic acid (DOPAC) adsorbed to similar degrees on fractured glassy carbon, with no apparent discrimination on the basis of adsorbate charge. If the surface was partially oxidized, however, cationic dopamine was preferentially adsorbed over anionic DOPAC or neutral 4-MC. The results support an adsorption mechanism on fractured glassy carbon which is not charge specific and probably involves the catechol ring rather than the side chain. The implications of this finding to the analytical utility of carbon electrodes are discussed.

INTRODUCTION

Pretreatment of glassy carbon (GC) surfaces is a necessary practice for producing electrodes with reproducible characteristics. Although pretreatment provides improved electron transfer capabilities or selectivity for certain sample components, it can also modify the electrode surface in essentially unknown ways. Electrode activity is affected by factors such as chemi- and physisorbed species, microscopic surface area, polishing debris, and active sites such as graphitic edge plane or oxygen-containing functional groups. The changes in these variables with pretreatment along with the assortment of pretreatment procedures utilized make it difficult to define the electrode surface structure for a given experiment. If the goal is a better understanding of the relationship between the GC surface structure and its electrochemical reactivity, it is important to reproduce and characterize the surface structure as much as possible.

Pretreatment procedures generally involve polishing under a variety of conditions, in many cases followed by activation by heat treatment under vacuum or inert atmosphere, laser irradiation, or electrochemical pretreatment procedures (ECP).[1] By comparison of polished surfaces with activated surfaces, several requirements for rapid electron transfer have been proposed. A concern about this approach, however, is that the polished surface which serves as a starting point is not well-defined. Polished surfaces are characterized by polishing debris, loose carbon particles, and various levels of impurities and surface oxides.[2-5] Activation by heat treatment and laser ablation of polished GC surfaces is believed to occur through a cleaning mechanism which exposes or creates active sites on the bulk carbon.[5-11] Activation by electrochemical pretreatment also cleans the surface, but with oxidation of the carbon to an extent depending on the strength of the electrochemical treatment.[12-16] Functional groups generated at the carbon surface during ECP may promote electron transfer by participating in a proton-exchange mechanism, causing electrostatic interactions with redox centers, acting as catalytic sites for adsorption or electron transfer, or decreasing the hydrophobicity of the carbon surface.[17-21] The most pronounced effects of ECP seem to be on complex, multistep redox systems which involve proton transfer or adsorption effects.

The objective of the research discussed here is to clarify the effects of activation procedures and to define better the characteristics of an active carbon surface. For this purpose, the practice of fracturing a glassy carbon rod in solution has been adopted. In this procedure, the surface utilized has had no exposure to polishing abrasives and limited exposure to environmental factors such as oxygen or impurities. Because of its relatively short history, this surface provides a unique starting point where the GC substrate has been modified as little as possible. In this report, catechol voltammetry and adsorption on the fractured surface are discussed. The fractured carbon surface exhibits electron transfer and adsorption behavior significantly different from that which has been observed on polished or pretreated carbon surfaces.

EXPERIMENTAL SECTION

Electrodes used for fracturing were constructured by diamond sawing pieces of GC-20 from a plate (Tokai). These pieces were sanded to yield a post with a cross-sectional area of approximately 0.003–0.008 cm^2. The use of small electrodes for fracturing has been addressed in a previous publication,[10] and it was concluded that small electrode areas are necessary to avoid microcracking during the fracturing process. After sanding, the carbon piece was sonicated in acetone to remove cutting oils and excess carbon particles, then embedded in an epoxy (Eccobond 55, Emerson and Cuming, Inc.), which was cured at 60 °C for 24 h. The epoxy provided mechanical stability and a good seal but also minimized electrode surface contamination compared to other encapsulation materials. The issue of surface fouling is addressed in more detail below. Chronoamperometry was performed after fracturing to obtain the electrode area. To perform chronoamperometry the rod was sanded to a smooth surface, polished conventionally (1.0-, 0.3-, 0.05-μm alumina on polishing cloth), and then placed in a cell with 1 mM $K_4Fe(CN)_6$ in 1 M KCl. The potential was stepped to 0.6 V vs Ag/AgCl and held for 10 s. Chronoamperometry was also performed in 1 M KCl so that curves used for area calculations were always background subtracted. Chronoamperometric areas obtained on polished and fractured surfaces showed good agreement. The fracturing procedure involved filing away the epoxy to expose a protruding tip of approximately 2–3 mm. The GC was scored with a glass-cutting file at the epoxy/GC junction to define a preferential plane for fracturing. The electrode was inserted into the electrochemical cell using Teflon tape as a seal. This cell was flushed a number of times and filled with the analyte solution, and the electrode was fractured by impact from the side, exposing the GC surface. Electrochemical experiments were performed immediately after fracturing and monitored over time. The cell was completed with a Ag/AgCl (3 M NaCl) reference electrode and a platinum auxiliary electrode. For experiments on polished surfaces, Eccobond mounted GC-20 electrodes were sanded with 600-grit silicon carbide paper, polished successively

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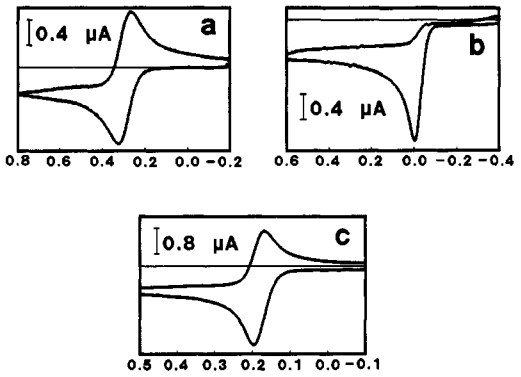

Figure 1. Voltammetry of systems on fractured GC-20. Ferrocyanide in 1 M KCl, ΔE_p = 59 mV, background subtracted (a), ascorbic acid in phosphate buffer pH 7.0, E_p = 0.0 V (b), dopamine in phosphate buffer pH 7.0, ΔE_p = 28 mV (c). Concentrations are approximately 1 mM; ν = 0.1 V/s; potentials vs Ag/AgCl.

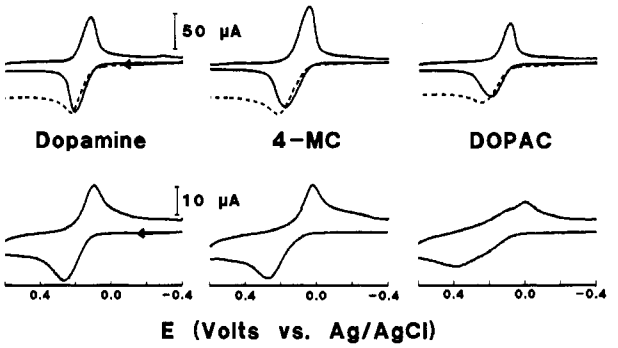

Figure 2. Top: Voltammetry of catechols on fractured GC-20 with associated semiintegrals, not background subtracted; ΔE_p values are DA = 90 mV, 4-MC = 136 mV, DOPAC = 109 mV. Dashed lines are semiintegrals of oxidation scan. Bottom: Catechols on polished GC-20; ΔE_p values are DA = 178 mV, 4-MC = 255 mV, DOPAC = 412 mV. Concentrations are approximately 1 mM; ν = 10 V/s; electrode area for all trials is approximately 0.003 cm^2; supporting electrolyte is phosphate buffer pH 7.0.

with 1-, 0.3-, and 0.05-μm alumina, and finally sonicated. All electrochemical experiments were interfaced to a PC and controlled by a locally written program. Linear cyclic voltammetry wave forms were provided by a function generator (Tektronix) which was triggered with a pulse provided by a Labmaster A/D board (Scientific Solutions). A conventional three-electrode potentiostat (Advanced Idea Mechanics, Columbus, OH) was utilized with the RC filter value dictated by $RC\nu < 4$ mV.[22]

Determination of surface coverage Γ (mol/cm^2) of catechols was performed by integrating the peak area of cyclic voltammograms plotted on a time axis to obtain charge (Q), and taking $\Gamma = Q/nFA$ where $n = 2$ and A is the chronoamperometric area of the fractured region. Semiintegrals were calculated with the G1 algorithm of Oldham as in previous publications.[23] Capacitance measurements were performed with a 20-mV amplitude input triangular wave, centered on 0.0 V vs Ag/AgCl. The square wave output peak to peak current is proportional to the observed capacitance ($C°(\mu F/cm^2) = i_{p-p}/2\nu A$) where A = chronoamperometric area.[24,25] Dopamine, 4-methylcatechol, 3,4-dihydroxyphenylacetic acid (DOPAC), and ascorbic acid were obtained from Aldrich. $K_4Fe(CN)_6$ was obtained from Mallinckrodt. The various stock solutions were prepared with 70% $HClO_4$ from GFS Chemicals and mono- and dibasic potassium phosphate from Fisher Scientific and Mallinckrodt. All solutions were prepared daily with Nanopure water, with those at pH 7 prepared immediately before use. Solutions were degassed with argon or nitrogen for approximately 15 min before use.

RESULTS

The hypothesis driving this investigation is that the electrochemical behavior of the fractured surface reflects the bulk GC structure more accurately than polished or otherwise pretreated GC. Previous reports on electrochemistry at fractured GC-30 involved an investigation of electron-transfer rates and capacitance.[10,26] Figure 1 contains representative voltammograms of the benchmark systems $Fe(CN)_6^{3-/4-}$, dopamine (DA) and ascorbic acid (AA) on fractured GC-20. The ΔE_p values and E_p values obtained here are characteristic of fast electron transfer and confirm the results shown in previous publications. It is significant that these three redox systems exhibit fast electron transfer on the fractured surface without any pretreatment, implying that the bulk GC structure is inherently active for charge transfer. A subsequent investigation of adsorption on the fractured surface was performed, and these results constitute the bulk of the observations discussed here.

Dopamine adsorption has been observed frequently at surfaces which have been electrochemically pretreated.[27-33] Adsorption is believed to occur through electrostatic attraction and/or ion exchange between the negatively charged surface oxide layer and the positively charged DA amine group.[27,30,32] This interaction greatly enhances the sensitivity of DA relative to anions such as ascorbate and dihydroxyphenylacetic acid (DOPAC) and is the basis of several in vivo analyses. Because the fractured surface is presumably initially free of oxide functionalities, its adsorption properties may differ substantially from those of pretreated surfaces. The scan rate used here was 10 V/s to enhance current due to adsorbed species. The results are shown in Figure 2, contrasted with those obtained at a polished surface. The voltammetry obtained at the fractured surface exhibited a sharper peak characteristic of adsorbed species, and semiintegration also showed nonsigmoidal behavior indicative of adsorption.[23] The voltammogram on the fractured surface persisted even after replacement of the dopamine solution with background electrolyte. All indications showed that dopamine adsorption occurred on the fractured surface immediately after the fracturing process. These results were unexpected based on an electrostatic mechanism. In order to investigate this discrepancy further, 4-methylcatechol (4-MC) and DOPAC were also examined. These systems were chosen because of their similarity to dopamine in all aspects except side-chain structure and charge. 4-MC and DOPAC possess neutral and negative charges respectively at pH 7, while dopamine is a monocation. Voltammetry of these systems at the fractured surface is shown in Figure 2 with voltammetry at polished surfaces for comparison. Cyclic voltammetry and semiintegration at the fractured surface for 4-MC and DOPAC both indicate that significant amounts of adsorption occurred for these compounds as well as for dopamine. Adsorption through electrostatic interactions with surface oxides on the fractured surface (if present) is not likely since there is no obvious discrimination based on side-chain charge. In addition, the ΔE_p values obtained at the fractured surface for the three compounds are approximately equal while those at the polished surface show a definite trend based on charge (DA < 4-MC < DOPAC). The voltammetry obtained at the fractured surface is therefore significantly different from that at the polished surface and is distinct from other reported activated surfaces as well.

Further quantitation of the extent of catechol adsorption was achieved by reducing the analyte concentration to approximately 10 μM so that current due to diffusing species was reduced. These results are shown in Figure 3. Voltammograms were obtained as a function of time after fracturing, and those shown are for maximum adsorption of the species of interest. The time of maximum adsorption varied depending on the analyte but ranged from 3 to 7 min after fracturing. Almost no Faradaic current was observable at these low concentrations on a polished surface, nor was any of the current in Figure 3 attributable to diffusing species.

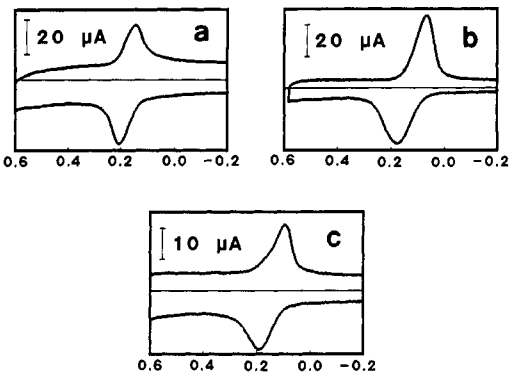

Figure 3. Voltammetry of catechols on fractured GC-20. Dopamine (a), 4-methylcatechol (b), DOPAC (c). Concentrations are 10 μM; ν = 10 V/s; supporting electrolyte is phosphate buffer pH 7.0; potential vs Ag/AgCl.

Table I. Adsorption on GC Surfaces (ν = 10 V/s, C^{bulk} = 10 μM)

	Γ,[a] pmol/cm²	
	pH 7.0	pH 0.8
fractured		
DA	156 ± 42[b] (N = 12)	312 ± 92 (N = 10)
4-MC	312 ± 64 (N = 8)	324 ± 66 (N = 5)
DOPAC	133 ± 44 (N = 10)	280 ± 40 (N = 5)
AA	<15 (N = 3)	42 ± 20 (N = 3)
fractured + ECP[d]		
DA	303 ± 30 (N = 3)	
4-MC	312 (N = 2)	
DOPAC	66 (N = 2)	
fractured + ECP[c]		
DA	493 ± 121 (N = 4)	447 (N = 2)
4-MC	296 (N = 2)	
DOPAC	59 ± 23 (N = 3)	
polished		
DA	9 ± 5 (N = 7)	29 ± 19 (N = 6)
polished + ECP[c]		
DA	503 ± 66 (N = 3)	352 (N = 2)

[a] Based on chronoamperometric area. [b] Standard deviation. [c] ECP conditions: 25 cyclic potential scans 0–1.8 V vs Ag/AgCl, in 0.1 M KNO_3. [d] ECP conditions: Same as c, but in pH 7.0 phosphate buffer.

Table I summarizes Γ (pmol/cm²) values obtained by integrating voltammograms for 10 μM solutions at acidic and neutral pH. At 10 μM concentration and pH 7.0, the largest amount of adsorption observed is for 4-MC, with less observed for DA and DOPAC. At pH 0.8, the differences are less significant, but all three compounds exhibited higher Γ. A specific mechanism of adsorption is not apparent from this data; however, some qualitative observations are evident. At GC surfaces prepared by polishing or ECP, electron transfer and adsorption activity have been observed to vary with the charge of the analyte.[27,30,31,32] At fractured surfaces, significant adsorption occurs for components regardless of their charge, with no preference for cations or anions. This behavior is not indicative of adsorption occurring through an electrostatic mechanism.

An example of how adsorption differs for fractured, polished, and ECP surfaces is shown in Figure 4. Dopamine adsorption at 10 μM concentration is barely observable on polished surfaces, but is prominent for fractured and ECP surfaces. ECP of a fractured surface causes an increase in both dopamine adsorption and background current. Table I summarizes Γ values for ECP treatment.

A factor of some importance in determining the extent of adsorption at the fractured surface is variation of Γ with time after fracture. Peak areas for 10 μM concentrations increased

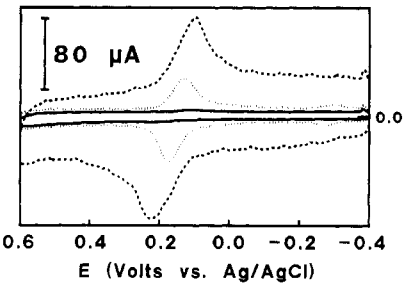

Figure 4. Dopamine voltammetry on polished (solid line), Γ = 11 pmol/cm²; fractured (dotted line), Γ = 178 pmol/cm²; and ECP (dashed line), Γ = 546 pmol/cm² surfaces. ECP procedure is 25 cyclic potential scans, 0–1.8 V vs Ag/AgCl in 0.1 M KNO_3. DA concentration is 10 μM; supporting electrolyte is phosphate buffer pH 7.0; ν = 10 V/s.

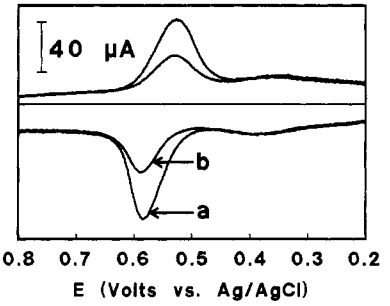

Figure 5. Voltammetry of dopamine on fractured GC-20, 10 μM in 0.1 M $HClO_4$, ν = 10 V/s, before addition of 1,4-dimethoxybenzene (a), immediately after addition of 10 μM 1,4-dimethoxybenzene (b).

for several minutes after the fracturing procedure, reached a constant value for some time, and then slowly decreased. The increase following fracture is at least partly attributable to finite diffusion time at low concentration. If only diffusion-controlled mass transport were operative, a monolayer would require about 6 min to adsorb for 10 μM bulk concentration.[1] The subsequent decrease in charge may be due to competition for adsorption sites by impurities which displace the adsorbed analyte. The effect of impurity competition is pronounced, perhaps due to the weak nature of the analyte adsorption. Initial experiments were performed on electrodes which had been encapsulated in Torr-seal (Varian) epoxy. Voltammetry of 1 mM solutions obtained at such electrodes immediately after fracturing was well-defined and displayed both low peak separations and peak shapes characteristic of adsorption. After a few minutes, however, a large decrease in peak height and a large increase in peak separation were observed. For 10 μM concentrations the adsorption was not even apparent at the Torr-seal electrodes because the time necessary to achieve sufficient analyte adsorption also allowed extensive competition by Torr-seal derived impurities. Obviously care must be taken to minimize impurities, and the epoxy used to fabricate the electrode appears to be a principle source of contamination. The Eccobond epoxy used in this study also contaminates the solution to some extent, though its effects are not as severe as those of Torr-seal. However, interpretation of quantitative results must be qualified accordingly. Modeling of the contamination process was attempted by introducing 1,4-dimethoxybenzene to the analyte solution, with the results shown in Figure 5. With the introduction of 1,4-dimethoxybenzene, the charge due to analyte adsorption did decrease significantly, indicating that the analyte species was displaced from the electrode surface. Although dimethoxybenzene is only a model for adventitious solution impurities, it does demonstrate that catechol adsorption is fairly weak and easily displaced by competitive adsorption of other solution species. Stated differently, catechol adsorption requires a quite clean surface.

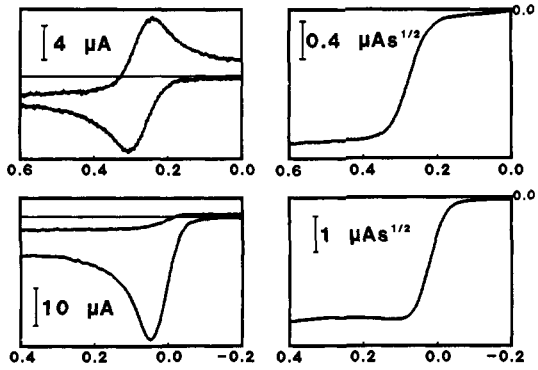

Figure 6. Voltammetry (upper left) of ferrocyanide (ΔE_p = 60 mV) on fractured GC-20 with associated semiintegral (upper right), 1 mM in 1 M KCl, ν = 10 V/s, ascorbic acid on fractured GC-20 (E_p = 0.05 V) (lower left) with associated semiintegral (lower right) 1 mM in phosphate buffer pH 7.0, ν = 10 V/s. CV's are background subtracted. Potentials vs Ag/AgCl.

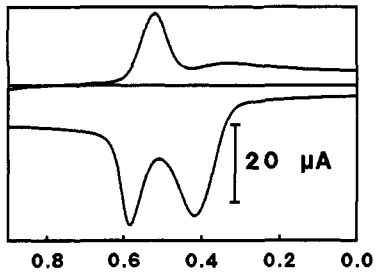

Figure 7. Voltammetry of 1 mM ascorbic acid + 10 μM dopamine on fractured GC-20 in 0.1 M $HClO_4$, ν = 10 V/s. Dopamine ΔE_p = 66 mV, ascorbic acid E_p = 416 mV; potential vs Ag/AgCl.

Since fracturing of glassy materials can lead to microcracking, there is a possibility that the apparent adsorption behavior is due to electrolysis of analyte in cracks. To test this possibility, ascorbate and $Fe(CN)_6^{3-/4-}$ were examined on fractured GC. Figure 6 contains voltammetry and corresponding semiintegrals for $K_4Fe(CN)_6$ and ascorbic acid at pH 7. No indication of adsorption in either the voltammetry or the semiintegrals was observed for $Fe(CN)_6^{3-/4-}$ under any of the conditions employed. For AA, no indication of adsorption on the fractured surface was apparent at pH 7, but weak adsorption was evident in 0.1 M $HClO_4$ for 1 mM AA. No voltammetric signal was observed for 10 μM AA under any conditions. These experiments were performed a number of times through the course of research, but at no time was adsorption at the level observed for the catechols ever observed for AA. A number of other factors also indicate that the voltammetric behavior of catechols is induced by adsorption and not microcracking. Figure 7 shows voltammetry at a fractured surface in a mixture of 1 mM ascorbic acid and 10 μM dopamine. The peak areas are similar for the two components even though the ascorbate is present at a much higher concentration. The behavior shown in Figure 7 persists for about 3–5 min, after which the AA peak broadens, ΔE_p for DA increases, and i_p for DA decreases, apparently due to impurity adsorption from solution. These results indicate preconcentration of the dopamine due to its adsorption at the electrode surface. In addition, capacitance measurements performed at the fractured surface result in almost model square wave behavior in response to an imposed triangle wave potential. If microcracking had occurred, some rounding of the square wave would be expected due to the presence of large RC components at the electrode surface microcracks.

DISCUSSION

The results bear on two distinct questions about GC surface reactivity. First, does the fractured face of GC more greatly reflect the bulk GC properties than a polished or ECP surface? Second, does the adsorption behavior of the fractured surface differ from that of treated GC surfaces? Regarding the first question, current results confirm earlier observations that polishing or ECP substantially alter the GC structure. The Raman spectra and observed k° for a polished surface are quite different from the results for a fractured face, with the Raman spectrum indicating greater disorder on the polished surface.[10] For all systems studied, electron-transfer kinetics are faster on the fractured surface, an effect attributed to greater surface cleanliness. Furthermore, the k° value for the fractured face is as high or higher than the highest values for polished or laser activated surfaces, implying that fractured GC is inherently rich in active sites for electron transfer. Since a fractured surface must have initially unsatisfied valences, it cannot be identical to bulk GC. However, we conclude that the modification of the bulk structure is minimized for fracturing compared to polishing or laser activation. The agreement of theoretical and observed voltammograms and the lack of $Fe(CN)_6^{3-/4-}$ or ascorbate adsorption on the fractured surface indicate nearly ideal behavior with high electron transfer activity.

The adsorption behavior for DA, 4-MC, and DOPAC on GC varies dramatically depending on how the surface is prepared. This behavior is most easily considered for three cases: fractured, polished, and electrochemically pretreated GC. The fractured surface exhibits classical adsorption at low bulk concentration (10 μM) for DA, 4-MC, and DOPAC, but negligible adsorption for $Fe(CN)_6^{3-/4-}$ or ascorbic acid. Furthermore, the adsorption was independent of the charge of the adsorbate, although adsorption was significantly higher in acidic media. Soriaga and Hubbard[34] reported Γ for 4-MC on Pt electrodes to be 267 pmol/cm^2 for flat orientation and 525 pmol/cm^2 for edge orientation for monolayer adsorption. Roughness factors for fractured GC are approximately 2–3,[10,35] so the adsorption of catechols is somewhat less than a monolayer. When the analyte concentration was increased to 1 mM, diffusing material was observed on top of a strong response for adsorbed species.

On the polished surface, the electron-transfer kinetics decreased significantly and adsorption was not observable for 10 μM concentrations. Even at 1 mM, adsorption appeared weak, but was stronger for DA than for 4-MC or DOPAC. When a fractured surface underwent ECP in either nitrate or phosphate solution, adsorption for DA *increased* by 2 to 3 times, 4-MC changed little, and DOPAC *decreased*. Similarly, ECP of a polished surface greatly increased Γ for DA, by a factor of approximately 50 (Table I). Thus both the polished and ECP surfaces exhibited adsorption which discriminated for adsorbate charge, with the ECP surface being more pronounced in both magnitude and degree of discrimination. Thus the adsorption behaviors on polished and ECP surfaces are qualitatively similar but are clearly distinct from that on the fractured surface.

The observations are consistent with a qualitatively distinct adsorption mechanism for the fractured surface compared to polished or ECP surfaces. If adsorption to the fractured GC face occurred through the aromatic catechol ring, it would not be charge specific and would not occur for ascorbate or $Fe(CN)_6^{3-/4-}$. Furthermore, the clean, active fractured surface would yield fast electron transfer. When the surface is polished, both the adsorption and k°'s are decreased, apparently due to impurity adsorption. Upon ECP, adsorption strongly favors cations, implying an electrostatic mechanism. As noted by several other authors,[28–33] the preference for DA over ascorbate or DOPAC on the ECP surface is likely due to an ion exchange mechanism, probably at carboxylate groups in the oxide film. It should be noted that although DA yields a larger voltammetric response than AA for both fractured

and ECP surfaces due to selective adsorption, the adsorption mechanism for the two surfaces is fundamentally different. The current results are relevant to the area of voltammetric bioanalysis of catechols, particularly in small-animal tissue. In such experiments, a carbon fiber microelectrode is used to detect catechols in the presence of ascorbate after pretreatment by polishing[30-31] or ECP.[27,28,36,37] If the approach is to be successful, the electrode must discriminate heavily for DA over DOPAC or ascorbate, since DA is usually a minority component. The work reported here demonstrates that a fractured and presumably unmodified carbon surface will discriminate for catechols over ascorbate but not for DA over DOPAC. In contrast, a lightly polished carbon fiber microdisk does discriminate for DA over DOPAC,[31] implying that a charge-specific mechanism is operative. This observation implies that the surface of carbon fiber electrodes used thus far for in vivo analysis are partially oxidized, often unintentionally.

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