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REFERENCES

1. K. W. Frese, Jr., and C. Chen, *This Journal*, **139**, 3234 (1992).
2. C. Chen and K. W. Frese, Jr., *ibid.*, **139**, 3243 (1992).
3. J. S. Escher, P. E. Gregory, and T. J. Maloney, *J. Vac. Sci. Technol.*, **16**, 1394 (1979); C. R. Crowell and S. M. Sze, in *Physics of Thin Films*, G. Hass and R. E. Thun, Editors, Academic Press, Inc., New York (1967).
4. K. W. Frese, Jr., M. J. Madou, and S. R. Morrison, *This Journal*, **128**, 1527 (1980). K. W. Frese, Jr., *J. Phys. Chem.*, **85**, 3911 (1981).
5. B. Pelle, J. Kispeter, and J. Peiszner, *Acta Phys. Chem.*, Nova Series, **30**, 39 (1984).
6. S. R. Morrison, *Electrochemistry of Semiconductor and Oxide Electrodes*, Plenum Press, New York (1980).
7. A. K. Vi Vih, *Electrochemistry of Metals and Semiconductors*, Marcel Dekker, Inc., New York (1973).
8. P. J. Boddy, *J. Electroanal. Chem.*, **10**, 199 (1965).
9. K. J. Vetter, *Electrochemical Kinetics*, p. 429, Academic Press, Inc., New York (1967).
10. S. M. Sze, *Physics of Semiconductor Devices*, p. 454, Wiley-Interscience, New York (1969).
11. E. H. Nicollian and J. R. Brews, *MOS Physics and Technology*, Chap. 8, pp. 297, 317, 369, John Wiley & Sons, Inc., New York (1981) and references therein.
12. S. R. Morrison, M. Madou, and K. W. Frese, Jr., Paper 11, ACS Symposium Series No. 146. A. J. Nozik, Editor, The American Chemical Society (1981).
13. J. M. Hale, in *Reactions of Molecules and Electrodes*, N. S. Hush, Editor, Wiley-Interscience, New York (1970).
14. M. Lax, *Phys. Rev.*, **119**, 1502 (1960).
15. D. H. Kittel, *Introduction to Solid State Physics*, 4th ed., John Wiley & Sons, Inc., New York (1971).
16. R. A. Marcus, *J. Phys. Chem.*, **43**, 679 (1965); *J. Chem. Phys.*, **43**, 3477 (1965).

Laser-Induced Transient Currents on Glassy Carbon Electrodes

Double Layer and Ion Adsorption Effects

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ABSTRACT

Intense laser pulses delivered to a glassy carbon (GC) surface *in situ* result in a transient current which depends both on electrode potential and the electrolyte solution. The transient decayed with a time constant of several hundred microseconds, much longer than the laser optical or thermal transient. The linear dependence of the transient charges on potential implies that the mechanism involves perturbation and restoration of the double layer and adsorbed ions. The charge contained in the current transient was a small (<10%) fraction of the total double layer charge indicating incomplete disruption of the double layer. In addition, the magnitude of the response is higher for surfaces with higher oxide coverage. The observations are consistent with adsorption of electrolyte cations with the strength of interaction decreasing in the order $H^+ > Li^+ > Na^+ > K^+ > Et_4N^+$. The cation interaction increases with increasing surface oxidation, probably because of interactions with surface functional groups.

Understanding the structure of the electrode/solution interface is of paramount importance in investigations of electrode kinetics at carbon electrodes. It is well-known that the rich surface chemistry of carbon materials contributes to the complexity and irreproducibility of kinetic measurements. Several electrode pretreatment procedures have been proposed to alleviate this problem and obtain more controllable surface structures and faster electrode kinetics, particularly for glassy carbon (GC). These include polishing,^{1,2} electrochemical activation,³⁻⁹ vacuum heating,¹⁰⁻¹³ fracturing,^{2,14-17} and laser activation.¹⁶⁻²⁴ Of relevance to the current report is the observation that intense laser pulses (ca. 25 MW/cm², 9 ns, 1064 nm) delivered to glassy carbon *in situ* results in a ca. 100-fold increase in the electron transfer rate for the $Fe(CN)_6^{3-/4-}$ couple.^{17,19} Roughness changes and gross microstructural changes have been ruled out as mechanisms for the observed activation, and the rate enhancement was attributed to effective surface cleaning for the case of GC.^{16,17} A unique feature of pulsed laser activation compared to conventional pretreatments is the ability to monitor an active surface very quickly after its creation, with microsecond time resolution if desired. The current effort was undertaken to investigate transient electrochemical phenomena initiated by laser activation, not only to learn about carbon surface properties, but also to investigate electrochemical events occurring very quickly after exposure of a reactive carbon surface to electrolyte solution. The overall objective of the work is an understanding of the factors affecting electrode kinetics on carbon electrodes and particularly the mechanism of laser activation.

Much lower energy pulses which cause only a slight transient increase of the electrode surface temperature were employed in studies of the electrical double layer on mercury electrodes²⁵⁻²⁸ and more recently to probe the electrode kinetics of fast reactions.^{29,30} It was shown that pulsed irradiation of the electrode in supporting electrolyte solution produced current transients when the electrode was held at constant potential.²⁵ Analysis of the total charge of the current transients at various potentials gives the charge *vs.* potential curve. This technique did not become widely accepted for routine analysis of double layer properties on mercury, mainly because the existing classical techniques³¹ were simpler, cheaper, and offered superb accuracy. Open-circuit potential measurements after laser pulses, however, were successfully employed to study thermal properties of the double layer.²⁶⁻²⁸ It should be emphasized that the laser pulses used for activation of carbon electrodes have much higher power density and should be much more disruptive to the interfacial region.

A significant difference between mercury and solid electrodes (including carbon) lies in the fact that the surface of a solid electrode is not easily renewable. This problem significantly complicates double layer studies on carbon electrodes using classical methods.³²⁻³⁶ Differential capacity and surface tension on carbon materials were studied by Soffer and co-workers³⁷⁻⁴⁴ using differential cyclic voltammetry and spatial measurements of the electrodes.

In this paper we present a different approach for studying double layer properties on carbon electrodes. It is based on the application of laser pulses to probe the properties of the carbon electrode/solution interface and takes advantage of *in situ* surface cleaning by the laser pulse. The temperature transients generated by laser pulses with power

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densities of 10 and 20 MW cm⁻² are too low to cause major structural changes on GC and highly oriented pyrolytic graphite (HOPG) electrodes, but high enough to cause transient disturbance of the interfacial region and induce current transients. Short laser pulses also renew the surface by impurity desorption, thus activating the surface toward electron transfer. Therefore, the laser pulse provides not only a way of probing the properties of the interface but also *in situ* renewal of the electrode surface. Of particular note is the time resolution of the method compared to other pretreatment procedures. Since the laser pulse and resulting temperature transient occur on a nanosecond and microsecond time scale, respectively, the electrode may be monitored within microseconds after perturbation by the laser. A variety of electrochemical effects, including double layer relaxation, adsorption, and electron transfer may thus be examined within microseconds of the laser perturbation. In the case of laser activation of kinetics, the time resolution is many orders of magnitude faster than heat-treatments, polishing, or chemical pretreatments. In this study, we examined laser-induced perturbation of the double layer, with particular attention to the effects of electrolyte composition.

Experimental

The experimental apparatus is shown in Fig. 1. The Nd:YAG beam (Quantel 580-10) operating at 1064 nm (9 ns pulse length) was used to illuminate the electrode surface. Before entering the electrochemical cell through a quartz window, the laser beam passed near a photodiode (Sciencetech) which generated a trigger for the LeCroy 9400 digital oscilloscope. A conventional three-electrode potentiostat with a 0.1 μ s time constant was used to monitor laser-induced current transients. The time constant of the cell was measured with a 5 mV square wave potential applied to a polished electrode in 0.1M KCl, and equaled 120 μ s. In all cases, the charge resulting from a laser pulse, Q , was determined by numerically integrating the current *vs.* time transient. The Nd:YAG beam was aligned with a 632.8 nm HeNe pilot beam to allow positioning of the Nd:YAG beam on the electrode. The beam passed through approximately 5 mm of solution before striking the electrode, and totally illuminated the GC surface exposed to electrolyte. The measurements with GC were performed by applying a given electrode potential for 1 s before irradiating the electrode surface with the laser pulse. The measurements were performed in series of ten laser pulses separated by 1 min intervals. The working electrode was at open circuit between the measurements. Each series was carried out with a freshly polished and, where noted, further pretreated electrode (see below).

Commercial GC-20 electrodes (Bioanalytical Systems), GC-20 disks (Tokai), and HOPG (a gift from Arthur Moore of Union Carbide) were used. Standard procedure for the GC electrode surface preparation consisted of polishing with silicon carbide paper (600 grit) and then with 1.0, 0.3,

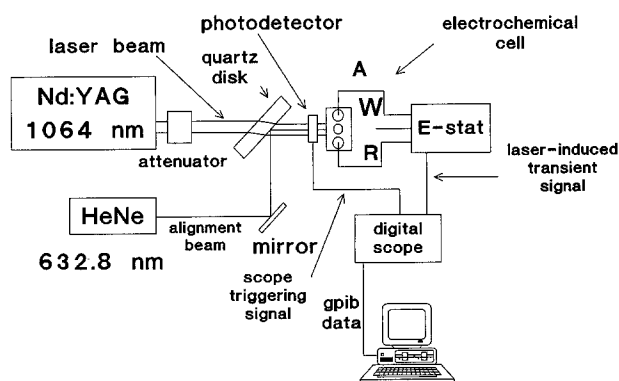


Fig. 1. Experimental apparatus for recording laser-induced current transients. A, W, and R stand for auxiliary, working, and reference electrodes, respectively.

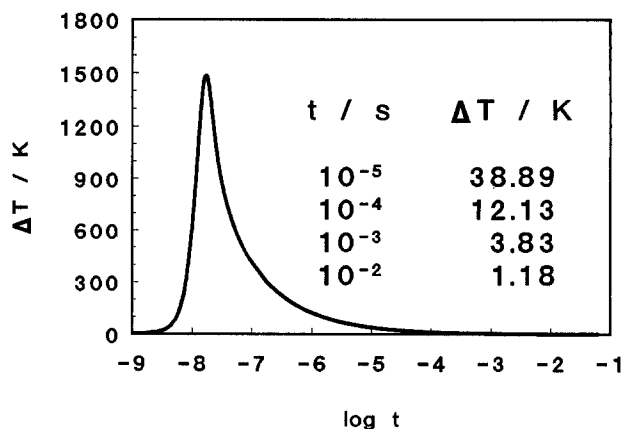


Fig. 2. The simulated temperature profile of a GC electrode surface in water during and after a 9 ns laser pulse with power density of 10 MW cm⁻². The temperature values after selected times are indicated, and the peak laser intensity occurs at log (t) = -8.3.

and 0.05 μ m alumina. Electrodes were sonicated for 5 min between the polishing steps. Where noted, electrodes were further pretreated by anodic oxidation in 0.1M NaNO₃ at 1.8 V for 3 min, oxidation in a saturated solution of (NH₄)₂Ce(NO₃)₆ for 5 min, or ultrahigh vacuum heating at 600°C and 2 × 10⁻⁹ Torr for 2 h. Basal plane HOPG electrodes were prepared by cleaving superficial layers with adhesive tape. All working electrodes used in this work had surface areas equal to 0.071 cm². Platinum wire served as the auxiliary electrode. All potentials were measured and reported *vs.* Ag/AgCl reference electrode (BAS). Cathodic currents and charges are reported as positive values in tables and figures.

All chemicals were of reagent grade and were used without further purification. Solutions and rinses employed house distilled water, further purified using a Barnstead "NanoPure" System.

Results

The major effect of a short, intense, 1064 nm laser pulse on the electrode surface is a transient temperature excursion. With the significant assumption of no phase changes in electrode or solution, the surface temperature may be simulated, as noted previously by us and others.⁴⁵⁻⁵⁰ The transient in Fig. 2 should be considered the maximum excursion of surface temperature for a 10 MW/cm², 9 ns, 1064 nm laser pulse on GC, and it provides an estimate of the duration of the transient. Even when solvent vaporization is ignored, ΔT decreases to 100 K in about 1 μ s, and to 12 K in 100 μ s.

The current transient resulting from a 10 mW/cm² laser pulse delivered to a GC electrode at a fixed potential of -0.2 V *vs.* Ag/AgCl is shown in Fig. 3A (points). The current represents a response to the laser perturbation in the absence of any intentional electroactive species and is presumably due to restoration of the surface and double layer after thermal disturbance. The integrated charge under the current transient is 0.59 μ C/cm² in this case. For comparison, a GC electrode with a typical capacitance of 30 μ F/cm² held at a potential 280 mV away from the PZC has a double layer charge of 8.4 μ C/cm². Thus the laser perturbation is small relative to the total charge present. Although the current transient follows a roughly exponential decay, a plot of log *i vs.* *t* is nonlinear. Figure 3b shows three exponential decays which are summed to yield the smooth curve of Fig. 3A. The three time constants indicated in Fig. 3B vary only slightly with potential and remain approximately an order of magnitude apart.

Figure 4 indicates the reproducibility of the integrated charge following the laser pulse (Q) for different surfaces. Figure 4A is a Q *vs.* laser pulse number for three physically different freshly polished electrodes, and Fig. 4B is a similar plot for a single electrode polished a total of four times.

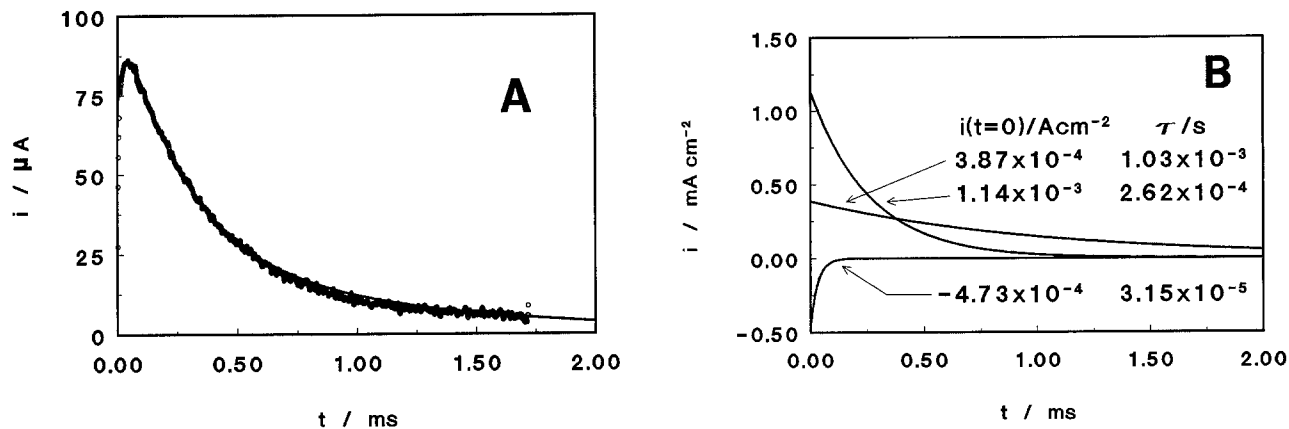


Fig. 3. Laser-induced current transient recorded at GC electrode in 0.1M KCl solution at -0.2 V. Laser power density was 10 MW cm^{-2} . Plot A shows the experimental transient (points) and the sum of the three component exponentials (smooth curve). Plot B shows the three exponential components and associated parameters.

In both cases, several laser pulses (3 to 5) were required to reach a constant value of Q for subsequent pulses, probably due to removal of surface debris or oxides by the laser. After this induction period, fairly constant Q values were observed for pulses 6–10. The relative standard deviation for the 6th to the 10th pulse on the same electrode polished four times was 13% ($N = 18$), while that for four different electrodes polished once each was 20% ($N = 19$). In subsequent measurements and plots, the Q of pulses 6 to 10 was averaged for a given surface unless noted otherwise.

As shown in Fig. 5, the laser-induced current transient is strongly dependent on the applied potential. For $E_{\text{app}} = 0.1$ V, the transient is quite small, while Q was positive or negative at potentials away from 0.1 V. As shown in Fig. 6, Q vs. E_{app} is linear, with an x -intercept of 0.18 V in this case. The slope of this plot is $2.8 \mu\text{F/cm}^2$, much less than the differential capacitance of ca. $30 \mu\text{F/cm}^2$. Note also from Fig. 6 that a higher laser power density changes both the slope and x -intercept of the Q vs. E_{app} plot. Figure 6 was based on the average of 6th to 10th laser pulses after polishing, where Q was weakly dependent on pulse number.

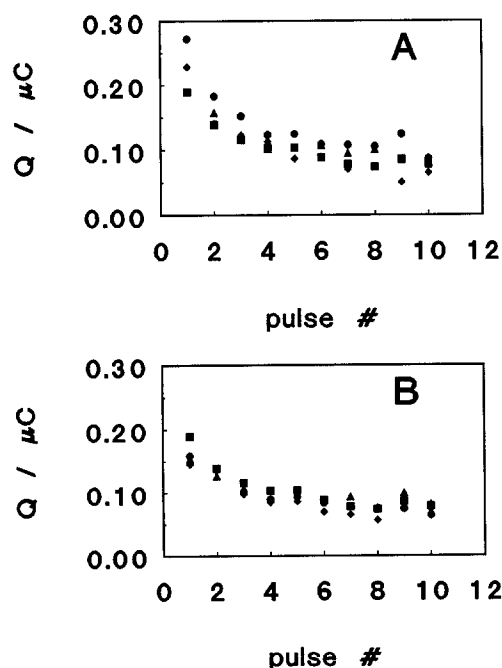


Fig. 4. The effect of the polishing procedure on the reproducibility of Q on GC in 0.1M HCl at -0.1 V with laser power density of 20 MW cm^{-2} . (A) Physically different electrodes polished before pulse no. 1. (B) A single GC electrode, repolished before each pulse series.

When the first pulse after polishing was used to construct Q vs. E , the plot was linear but with a higher slope. The x -intercept did not depend on laser pulse number, showing no trend with repeated pulses, and a mean and standard deviation of 0.19 ± 0.02 V ($N = 10$). The potential of zero response (PZR, where Q total = 0), is listed in Table I for several electrolytes.

The effect of electrolyte concentration on the transient response was examined briefly for KCl electrolytes, but the available range of concentrations was limited. For a range of concentrations from 1.0 to 0.01M KCl, the observed time constant increased greatly with decreasing concentration, as expected due to increasing solution resistance, and therefore RC . For example, the time constant increased by a factor of eight when the KCl concentration was decreased from 0.10 to 0.01M. Concentrations other than 0.1M were not studied in detail due to the poor signal to noise ratio for lower concentrations and potentiostat saturation for high concentrations.

Finally, several modifications to the carbon electrode surface were considered to explore their effects on the laser-induced current transient. Figure 7 shows transients for $E_{\text{app}} = -0.1$ V for polished GC (b); heat-treated GC (c, heated for 2 h at 600°C , at 2×10^{-8} Torr); HOPG freshly cleaved (d), and anodized GC (a, 1.8 V, 3 min, in 0.1M NaNO_3). Note that Q for HOPG is much smaller than for polished GC, and heat-treatment reduces Q for GC significantly. Anodized GC has a much larger Q than any other surface considered. The charge, PZR, and $\Delta Q/\Delta E$ for these surfaces are listed in Table II.

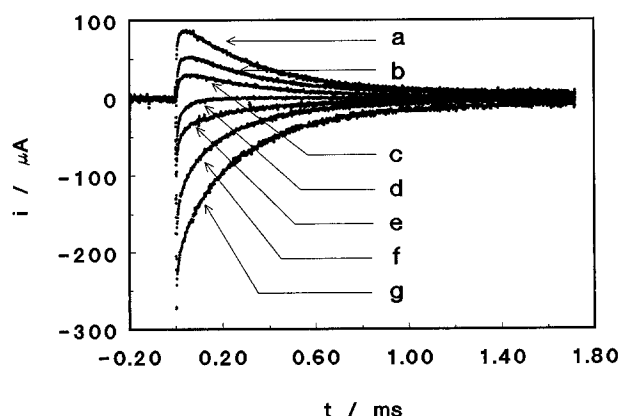


Fig. 5. The effect of the electrode potential on the laser-induced current transients on GC electrode in 0.1M KCl at power density of 10 MW cm^{-2} . The electrode potential was: a, -0.2 V; b, -0.1 ; c, 0.0; d, 0.1; e, 0.2; f, 0.3; and g, 0.4 V. Electrode was repolished before each transient.

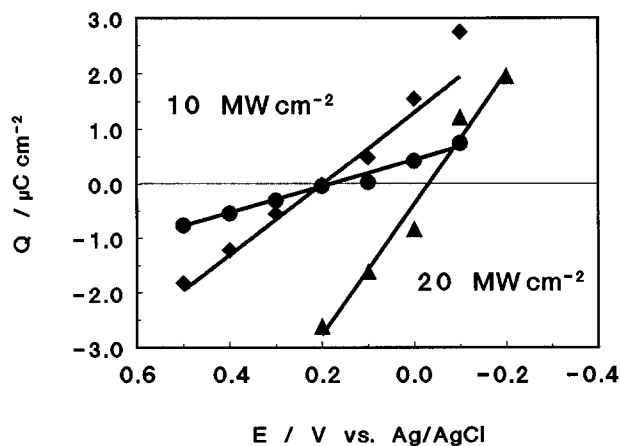


Fig. 6. The effect of the laser power density on Q in 0.1M HCl. Circles: 10 MW/cm², average 6th to 10th laser pulse after polishing; diamonds, 10 MW/cm², first pulse after polishing; triangles, 20 MW/cm², 6th to 10th pulse after polishing.

Discussion

The first question which arises about the laser-induced current transient at a given potential is its origin. Superficially, the transient behaves as expected for reestablishment of the double layer after thermal perturbation by the laser pulse. The charge involved is only about 7% of that stored in the double layer, implying that the double layer structure is only partially disrupted. The time required for recharging is roughly a millisecond or so, much longer than the microsecond scale of the surface temperature transient, implying that most of the double layer restoration occurs at the ambient solution temperature.

Upon closer inspection, the transient is not simply an exponential decay expected for double layer charging, but rather consists of at least three exponentials with different time constants. The shortest (<40 μs time constant) involves very little charge (<10% of total), is weakly potential dependent, and may reflect a thermal or even electronic effect. It will not be considered further, except to say that it accounts for the initial rise during the first 50 μs of the observed transients. The remainder of the current decay is empirically accounted for by two exponentials with roughly equal contributions to the total charge, but time constants which differ by about a factor of ten. The time constants do not depend on the applied potential, but the charge attributable to each exponential does, approximately linearly. The faster of the two has a time constant of about 300 μs, close to the cell time constant observed for a small potential step (120 μs). It would be premature to associate these exponential decays with particular or even distinct chemical phenomena, but it appears unlikely that the observed decay is related to a Faradaic process. One

Table I. The effect of supporting electrolyte ions on the laser-induced current transients recorded with polished GC electrode at 10 MW cm⁻².

Solution ^a	Q at -0.1 V (C cm ⁻²)	Q at 0.3 V (C cm ⁻²)	PZR (V)	$\Delta Q/\Delta E$ (F cm ⁻²)
HCl	7.6×10^{-7}	-3.2×10^{-7}	0.18	2.8×10^{-6}
LiCl	4.5×10^{-7}	-3.5×10^{-7}	0.12	2.0×10^{-6}
NaCl	4.6×10^{-7}	-4.5×10^{-7}	0.10	2.3×10^{-6}
KCl	3.5×10^{-7}	-4.4×10^{-7}	0.08	2.0×10^{-6}
(Et) ₄ NBr	2.4×10^{-7}	-3.9×10^{-7}	0.05	2.2×10^{-6}
NaF	1.3×10^{-7}	-2.1×10^{-6}	-0.08	5.5×10^{-6}
NaClO ₄	2.7×10^{-7}	-9.6×10^{-7}	-0.01	3.1×10^{-6}
NaNO ₃	4.5×10^{-7}	-5.8×10^{-7}	0.08	2.6×10^{-6}
NaCl	4.6×10^{-7}	-4.5×10^{-7}	0.10	2.3×10^{-6}
NaBr	4.9×10^{-7}	-6.3×10^{-7}	0.08	2.8×10^{-6}
NaI	5.6×10^{-7}	-4.2×10^{-6}	0.13	2.5×10^{-6}

^a 0.1M concentrations.

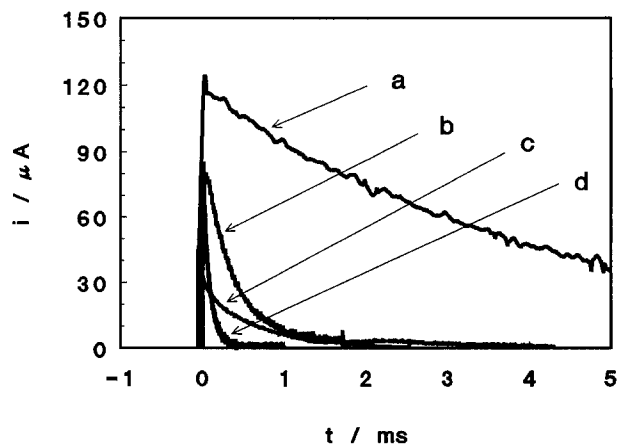


Fig. 7. The effect of electrode surface preparation on the current transient in 0.1M NaNO₃ at -0.1 V. Laser power density 10 MW cm⁻². Surfaces: a, GC after electro-oxidation in 0.1M NaNO₃ at 1.8 V for 3 min; b, polished GC; c, polished GC heated for 2 h at 600°C and 2×10^{-9} Torr; d, HOPG. The transient at HOPG was recorded in 0.1M NaCl solution.

would expect a redox process (surface or otherwise) to be strongly potential dependent, and not to show a linear progression through $Q = 0$ as the potential is varied around the PZR (Fig. 6). The potential dependence will be discussed in more detail below, but suffice it to say for now that Q vs. E_{app} has the behavior expected for a capacitor, without involving any Faradaic processes. Whatever the origin of the nonidealities in the exponential decay of the transient, the results are consistent with an origin based on thermally induced disruption of the double layer. There is no evidence for Faradaic processes, but the transient may involve both classical double layer effects and adsorption.

Surface reproducibility is a well-known problem with solid electrodes and was tested here by repetitive trials on several electrodes. Figure 4 demonstrates that the variation in Q is smaller for repetitive polishing than for physically different GC pieces. Previous experiments demonstrated that laser pulses of 25 MW/cm² and less have minimal effects on microscopic area.¹⁶ The variability observed here for repetitive experiments is much smaller than the effects of potential, electrolyte, and carbon type on the current transients.

The potential dependence of the current transient shown in Fig. 5 and 6 demonstrates a linear dependence of Q on E . Both the overall Q and the charge attributed to both "slow" exponential decays show the same linear potential dependence. It is useful to define a potential of zero response (PZR) as the applied potential where Q is zero. Figure 6 shows that the PZR is about 0.18 V for 10 MW/cm² in 0.1M HCl. The PZR depends weakly on pulse number, with no trend observed in PZR for ten successive pulses. The PZR does vary with power density, as does the slope of Q vs. E . Like the total charge, the slope of the Q vs. E_{app} plot decreases

Table II. The effect of electrode surface preparation on the observed current transients on GC and HOPG in 0.1M NaNO₃ at 10 MW cm⁻².

Surface ^a	Q at -0.1 V (C cm ⁻²)	Q at 0.3 V (C cm ⁻²)	PZR (V)	$\Delta Q/\Delta E$ (F cm ⁻²)
GC oxidized ^b	7.5×10^{-6}	-1.2×10^{-6}	0.24	2.2×10^{-5}
GC oxidized ^c	3.8×10^{-6}	-2.3×10^{-6}	0.15	1.4×10^{-5}
GC polished	4.5×10^{-7}	-5.8×10^{-7}	0.08	2.6×10^{-6}
GC vacuum heated	2.5×10^{-7}	-3.2×10^{-7}	0.08	1.4×10^{-6}
HOPG ^d	9.7×10^{-8}	-1.2×10^{-7}	0.09	5.3×10^{-7}

^a See text for the details of surface preparation.

^b Anodic oxidation for 3 min at 1.8 V.

^c Oxidation in saturated solution of (NH₄)₂Ce(NO₃)₆ for 5 min.

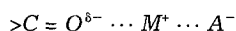
^d In 0.1M KCl.

with pulse number, reaching a steady value after ca. five pulses.

Although the PZR does not necessarily equal the PZC, it is analogous in several ways. At potentials positive of the PZR, the transient resulting from the laser pulse is in the anodic direction, indicating electron flow away from the interface, and a buildup of excess anionic charge in the double layer. Similarly, a positive charge excess occurs when the potential is negative of the PZR. The linear change of Q with E_{app} is expected for an ideal capacitor, but the slope is less than the full double-layer capacitance because the double layer is not completely destroyed by the pulse. If such experiments were possible, complete destruction of the layer should yield a Q vs. E_{app} slope equal to that observed if an electrode were suddenly exposed to the solution and the double layer is formed.

In order to evaluate the ability of the current technique to study the properties of the electrode/solution interface, a series of experiments with various supporting electrolytes was performed. The results (Table I) are divided into two groups. The first one contains solutions of alkali metal chlorides, tetraethylammonium bromide, and hydrochloric acid to test the effect of cations on the transients and PZR. Sodium halides, nitrate, and perchlorate solutions constitute the second group, selected to test the effect of anions on the PZR. It is reasonable to assume after Barker and Cloke²⁵ that the PZR is related to the potential of zero charge (PZC), and that the direction of PZR shifts is the same as that of PZC. Therefore, the shifts of the PZR value can be used as a test of adsorption of ions on the electrode surface. It is well known (see, for example Ref. 31), that adsorption of cations will shift the PZC in a positive direction and adsorption of anions will shift it in negative direction. The variation in the PZR with cation (Table II) is consistent with adsorption of cations on the GC surface, with the strength of the interaction decreasing in the order $H^+ > Li^+ > Na^+ > K^+ > Et_4N^+$. In studies of ion uptake on electrochemically pretreated GC, Nagaoka *et al.*⁵¹⁻⁵⁵ reported a similar sequence $Li^+ > Na^+ \approx K^+ > Ba^{+2}$. At this point we cannot completely explain the nature of interactions leading to apparent adsorption of cations on the carbon electrode surface. However, it is not unreasonable to assume that the functional groups present on the surface of GC⁵⁶ are at least partially responsible for the observed behavior. Carboxylate or semiquinoid groups on carbon are either anionic or can exchange cations, and the strength of the surface interaction should vary with the cation size and charge density. Oxides are also known to affect the polarizability of the carbon surface, thus enhancing interactions with polar or ionic species. Such a mechanism could also enhance ion adsorption for cations with high charge density such as H^+ and Li^+ .

Variation of the electrolyte anion does not produce a trend similar to the cations. Except for fluoride, the sodium halides show no trend in the PZR with anion size. The PZR for NaF is substantially more negative, implying a stronger anion interaction for F^- than for Cl^- , Br^- , or I^- . This observation is opposite to that observed for Pt, where larger halides chemisorb more strongly. In addition, fluoride would not be expected to interact more strongly with carbon via dispersion interactions, since it is less polarizable than iodide. However, these observations are consistent with ion adsorption mediated by surface oxides. The results in Table I imply that the cation is the major determinant of the PZR, probably due to cation interactions with anionic surface groups. Variation of the anion has a small effect for the sodium salts due to the relatively stronger interaction of Na^+ with the surface. In the case of fluoride, a bridging mechanism may be possible



In such a case the stability of the structure is expected to be greater for F^- than for large anions, due to the stronger interaction of the F^- anion with metal ions compared to Cl^- , Br^- , or I^- .

To test the hypothesis that surface functional groups play a part in adsorption of ions on GC electrodes, the surface concentration of those groups was intentionally modified by either oxidation or vacuum heat-treatment of the electrode. Oxidation of a GC surface will increase the amount of surface functional groups,⁵⁷⁻⁶³ while vacuum heat-treatment reduces the surface O/C ratio.¹⁰⁻¹³ In addition to the specially treated GC electrodes, highly oriented pyrolytic graphite was employed as an electrode material. HOPG is known to have very low surface oxide concentration with the surface functional groups (if any) located on defects in the lattice structure. It should be emphasized that there are significant differences in structural and electronic properties between GC and HOPG which have to be taken into account when comparing these two materials.⁵⁶ However, these materials can be used to qualitatively correlate the charges observed in laser-induced current transients with a surface concentration of functional groups. The results for HOPG and GC after various pretreatments are shown in Table II. The Q for HOPG was much smaller than for GC, as would be expected for its smaller capacitance. More importantly, the substantial decrease in Q for vacuum heat-treated GC compared to polished GC supports the hypothesis that surface oxides play a role. Since heat-treatment does not affect surface morphology or roughness,⁶⁴ its main observable effect is reduction of surface oxygen. The much larger Q observed for anodized GC also indicates the strong dependence of surface charge on surface oxides.

Summary

The current vs. time and charge vs. potential responses to an *in situ* laser pulse on glassy carbon result in the following conclusions: first, the laser-induced temperature transient causes disruption of the double layer and adsorbed species, but the perturbation is small compared to the total double layer charge. Second, the potential dependence of the transient is consistent with double layer effects, but not a Faradaic process. Third, the potential dependence shows a trend with cation size, implying adsorption of cations in the order $H^+ > Li^+ > Na^+ > K^+ > Et_4N^+$, similar to that observed by Nagaoka *et al.* for anodized GC.⁵²⁻⁵⁵ Finally, the response increases greatly with surface oxidation, implying increased cation adsorption to oxygen containing functional groups. The importance of both cation adsorption and surface oxides to activation mechanisms is currently under study.

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REFERENCES

- G. N. Kamau, W. S. Willis, and J. F. Rusling, *Anal. Chem.*, **57**, 545 (1985).
- I. F. Hu, D. Karweik, and T. Kuwana, *J. Electroanal. Chem.*, **188**, 59 (1985).
- R. C. Engstrom, *Anal. Chem.*, **54**, 2310 (1982).
- T. Nagaoka and T. Yoshino, *ibid.*, **58**, 1037 (1986).
- L. J. Kepley and A. J. Bard, *ibid.*, **60**, 1459 (1988).
- G. M. Swain and T. Kuwana, *ibid.*, **63**, 517 (1991).
- M. S. Freund, A. Brajter-Toth, T. M. Cotton, and E. R. Henderson, *ibid.*, **63**, 1047 (1991).
- J. Wang, T. Martinez, D. R. Yaniv, and L. D. McCormick, *J. Electroanal. Chem.*, **278**, 379 (1990).
- R. C. Engstrom and V. A. Strasser, *Anal. Chem.*, **56**, 136 (1984).
- D. T. Fagan, I. F. Hu, and T. Kuwana, *ibid.*, **57**, 2759 (1985).
- G. W. Hance and T. Kuwana, *ibid.*, **59**, 131 (1987).
- K. J. Stutts, P. M. Kovach, W. G. Kuhr, and R. M. Wightman, *ibid.*, **55**, 1632 (1983).
- M. R. Deakin, K. J. Stutts, and R. M. Wightman, *J. Electroanal. Chem.*, **182**, 113 (1985).
- C. D. Allred and R. L. McCreery, *Anal. Chem.*, **64**, 444 (1992).

15. R. Rice, C. Allred, and R. McCreery, *J. Electroanal. Chem.*, **263**, 163 (1989).
16. N. M. Pontikos and R. L. McCreery, *ibid.*, **324**, 229 (1992).
17. R. J. Rice, N. M. Pontikos, and R. L. McCreery, *J. Am. Chem. Soc.*, **112**, 4617 (1990).
18. M. Poon and R. L. McCreery, *Anal. Chem.*, **60**, 1725 (1988).
19. M. Poon and R. L. McCreery, *ibid.*, **58**, 2745 (1986).
20. E. Hershenhart, R. L. McCreery, and R. D. Knight, *ibid.*, **56**, 2256 (1984).
21. M. Poon and R. L. McCreery, *ibid.*, **59**, 1615 (1987).
22. L. Bodalbai and A. Brajter-Toth, *ibid.*, **60**, 2557 (1988).
23. K. Stulik, D. Bradcova, and L. Kavan, *J. Electrochem.*, **250**, 173 (1988).
24. T. G. Strein and A. G. Ewing, *Anal. Chem.*, **63**, 194 (1991).
25. G. C. Barker and G. Cloke, *J. Electroanal. Chem.*, **52**, 468 (1970).
26. V. A. Benderskii, S. D. Babenko, and A. G. Krivenko, *ibid.*, **86**, 223 (1978).
27. V. A. Benderskii and G. I. Velichko, *ibid.*, **140**, 1 (1982).
28. V. A. Benderskii, G. I. Velichko, and I. V. Kreitus, *ibid.*, **181**, 1 (1984).
29. J. F. Smalley, C. V. Krishnan, M. Goldman, S. W. Feldberg, and I. Ruzic, *ibid.*, **248**, 255 (1988).
30. J. F. Smalley, R. A. MacFarquhar, and S. W. Feldberg, *ibid.*, **256**, 21 (1988).
31. A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, John Wiley & Sons, Inc., New York (1980).
32. J. P. Randin and E. Yeager, *This Journal*, **118**, 711 (1971).
33. J. P. Randin and E. Yeager, *J. Electroanal. Chem.*, **36**, 257 (1972).
34. J. P. Randin and E. Yeager, *ibid.*, **58**, 313 (1975).
35. H. Gerischer, *J. Phys. Chem.*, **89**, 4249 (1985).
36. H. Gerischer, R. McIntyre, D. Scherson, and W. Storck, *J. Phys. Chem.*, **91**, 1930 (1987).
37. Y. Oren, H. Tobias, and A. Soffer, *J. Electroanal. Chem.*, **162**, 87 (1984).
38. Y. Oren and A. Soffer, *ibid.*, **186**, 63 (1985).
39. Y. Oren and A. Soffer, *ibid.*, **206**, 101 (1986).
40. D. Golub, Y. Oren, and A. Soffer, *ibid.*, **227**, 41 (1987).
41. D. Golub, A. Soffer, and Y. Oren, *ibid.*, **260**, 383 (1989).
42. J. Koresh and A. Soffer, *This Journal*, **124**, 1379 (1977).
43. D. Golub, Y. Oren, and A. Soffer, *Carbon*, **25**, 109 (1987).
44. H. Tobias and A. Soffer, *J. Electroanal. Chem.*, **148**, 221 (1983).
45. R. J. Rice and R. L. McCreery, *ibid.*, **310**, 127 (1991).
46. V. A. Benderskii, I. O. Efimov, and A. G. Kirvenko, *ibid.*, **315** (1992).
47. J. Steinbeck, G. Braunstein, M. S. Dresselhaus, T. Venkatesan, and D. C. Jacobson, *J. Appl. Phys.*, **58**, 4374 (1985).
48. J. S. Speck, J. Steinbeck, and M. S. Dresselhaus, *J. Mater. Sci.*, **5**, 980 (1990).
49. J. Heremans, C. H. Olk, G. L. Esley, J. Steinbeck, and G. Dresselhaus, *Phys. Rev. Lett.*, **60**, 452 (1988).
50. A. M. Malvezzi, N. Bloembergen, and C. Y. Huang, *ibid.*, **57**, 146 (1986).
51. T. Nagaoka, Y. Uchida, and K. Ogura, *Anal. Chim. Acta*, **220**, 269 (1989).
52. H. Koshima and H. Onishi, *Talanta*, **33**, 391 (1986).
53. T. Nagaoka, T. Fukunaga, T. Yoshino, I. Watanabe, T. Nakayama, and S. Okazaki, *Anal. Chem.*, **60**, 2766 (1988).
54. T. Nagaoka, Y. Uchida, and K. Ogura, *J. Chem. Soc., Faraday Trans. 1*, **85**, 3757 (1989).
55. T. Nagaoka, T. Fukunaga, and T. Yoshino, *J. Electroanal. Chem.*, **217**, 453 (1987); **310**, 29 (1991).
56. R. L. McCreery, in *Electroanalytical Chemistry*, Vol. 17, A. J. Bard, Editor, pp. 221-374, Marcel Dekker, Inc., New York (1991).
57. J. F. Evans and T. Kuwana, *Anal. Chem.*, **49**, 1632 (1977).
58. C. Kozlowski and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 1*, **81**, 2745 (1985).
59. G. E. Cabaniss, A. A. Diamantis, W. R. Murphy, Jr., R. W. Linton, and T. J. Meyer, *J. Am. Chem. Soc.*, **107**, 1845 (1985).
60. K. F. Blurton, *Electrochim. Acta*, **18**, 869 (1973).
61. S. S. Barton, G. L. Boulton, and B. H. Harrison, *Carbon*, **10**, 395 (1972).
62. I. F. Hu, D. H. Karweik, and T. Kuwana, *J. Electroanal. Chem.*, **188**, 59 (1985).
63. D. R. Lowde, J. O. Williams, P. A. Attwood, R. J. Bird, and B. D. McNicol, *J. Chem. Soc., Faraday Trans. 1*, **75**, 2312 (1979).
64. M. T. McDermott, C. D. Allred, and R. L. McCreery, Submitted for publication.

An Impedance Study of Stainless Steel Electropolishing

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ABSTRACT

Electrochemical impedance diagrams have been measured under controlled mass-transport conditions for the transpassive anodic dissolution of Fe13Cr, a stainless-steel type alloy, in concentrated phosphoric-sulfuric acid electrolytes under both polishing and nonpolishing conditions. The impedance diagrams consist of four parts, each corresponding to a particular frequency range. At the highest frequencies the impedance results from a charge-transfer process, and at the lowest frequencies from a diffusion process for water or a water-related species which may be acting as an acceptor for dissolved metal ions. Changes in the shape of the impedance diagrams with temperature and water concentration are particularly visible in the lowest frequency range. The brightness of a polished surface depends on the importance of the diffusion process in the overall mechanism for metal dissolution, and it varies continuously as a function of temperature, potential, and water concentration. The results contain no evidence suggesting the presence either of a porous film behaving as an ohmic resistance or of a compact film through which ions migrate by high-field conduction.

Electropolishing, anodic dissolution of a metal workpiece resulting in a smooth, bright surface, is a widely used metal finishing technique. Since the pioneering studies of Jacquet,^{1,2} several workers have investigated the mechanisms of electropolishing, and a recent review of these works

can be found in Ref. 3. The electropolishing phenomenon has been classified into two processes: anodic leveling and anodic brightening. Anodic leveling results from a difference in the dissolution rate between peaks and valleys on a rough metal surface depending on the current distribution or mass-transport conditions.⁴⁻¹¹ Anodic brightening, on the other hand, is associated with the suppression of the influence of the metal microstructure on the dissolution rate. A smooth electropolished surface, which appears

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