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 laser pulses

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Understanding the structure of the electrode/solution interface is of paramount importance in investigations of electrochemical phenomena on 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, electrochemical activation, vacuum heating, fracturing, and laser activation. 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 an increase in the electron transfer rate for the Fe(CN)₅⁻/⁵⁺ couple. Roughness changes and rough 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. 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 understand the implications 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 increase of the electrode surface temperature were employed in studies of the electrical double layer on mercury electrodes and more recently to probe the electrochemical kinetics of fast reactions. It was shown that pulsed irradiation of the electrode in supporting electrolyte solution produced current transients when the electrode was held at constant potential. Analysis of the total charge of the current transients at various potentials gives the potential dependence of the double layer. This technique did not become widely accepted for routine analysis of double layer properties on mercury, mainly because the existing classical techniques 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. It should be emphasized that the laser pulses used for activation of carbon electrodes have much higher power density and should be 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. Differential capacity and surface tension on carbon materials were studied by Soffer and co-workers using differential cyclic voltammetry and spatial measurements of the double layer.

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 reductions. 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 (Scientech) which generated a trigger for the LeCroy 9400 digital oscilloscope. A conventional three-electrode potentiostat with a 0.1 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 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. 4 The transient in Fig. 2 should be considered the maximum excursion of surface temperature for a 10 MW/cm\(^2\), 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, \(\Delta T\) decreases to 100 K in about 1 ms, and to 12 K in 100 \(\mu s\).

The current transient resulting from a 10 mW/cm\(^2\) 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 \(\mu C/cm^2\) in this case. For comparison, a GC electrode with a typical capacitance of 30 \(\mu F/cm^2\) held at a potential 280 mV away from the PZC has a double layer charge of 8.4 \(\mu C/cm^2\). 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 \(t\) 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. 1. Experimental apparatus for recording laser-induced current transients. A, W, and R stand for auxiliary, working, and reference electrodes, respectively.](image)

![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.](image)
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 $E_{app} = 0.1$ 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 $\mu$F/cm$^2$, much less than the differential capacitance of ca. 30 $\mu$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.

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 $\pm$ 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 $E_{app} = -0.1$ V for polished GC (b); heat-treated GC (c, heated for 2 h at 600°C, at $2 \times 10^{-9}$ 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.

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**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.

**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.

**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 potentials were: $a$, $-0.2$ 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 0.1 M HCl. Circles: 10 MW/cm$^2$, average 6th to 10th pulse after polishing; diamonds, 10 MW/cm$^2$, first pulse after polishing; triangles, 20 MW/cm$^2$, 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. A 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 such exponential decays show the same linear potential dependence. It is useful to define a potential of zero response (PZR) for each electrode. The PZR is about 0.18 V for 10 MW/cm$^2$ in 0.1 M HCl. The PZR depends weakly on pulse number, with no trend observable here for repetitive experiments is much smaller than the effects on microscopic area. The variability observed here 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/cm$^2$ and less have minimal effects on microscopic area. 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 Figs. 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/cm$^2$ in 0.1 M 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. $E_{np}$ plot decreases 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. $E_{np}$ has the behavior expected for a capacitor, without involving any Faradaic processes. Whatever the origin of the nonideality 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/cm$^2$ and less have minimal effects on microscopic area.
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 with \( E_{\text{app}} \) 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. \( E_{\text{app}} \) 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 Cloke 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 shift 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 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. reported a similar sequence \( Li^+ > Na^+ > K^+ > Ba^{2+} \). 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 GC 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 anionic surface interaction for F- than for Cl-, Br-, or I-. This observation is opposite to that observed for Pt, where larger 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 role 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,\(^{57,58}\) while vacuum heat-treatment reduces the surface O/C ratio.\(^{55,56}\) 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,\(^{56}\) 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 graphitic 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.\(^{55,56}\) 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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An Impedance Study of Stainless Steel Electropolishing

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