

# Laser activation of carbon microdisk electrodes: surface oxide effects on $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ kinetics

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## Abstract

Cyclic voltammetric experiments triggered by a laser pulse permitted rapid-scan ( $1000\text{--}3000\text{ V s}^{-1}$ ) voltammograms to be obtained at various times (0.01 s to 30 min) after laser activation of carbon fiber electrodes. A heterogeneous electron transfer rate constant  $k^\circ$  of  $0.90 \pm 0.05\text{ cm s}^{-1}$  was observed for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  at a laser-activated carbon fiber disk electrode of diameter  $60\text{ }\mu\text{m}$ . This value was constant with time after laser activation for about 10 s but decayed by approximately 70% over a 20–30 min period. Laser exposure did not cause activation in  $\text{O}_2$ -saturated electrolyte, and brief electrochemical oxidation rapidly decreased the observed rate constant. The results indicate inhibition of  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  electron transfer by a neutral surface oxide layer. A model for the decay of  $k^\circ$  after laser activation based on first-order formation of a neutral oxide layer is proposed.

## 1. Introduction

Surface preparation of carbon electrodes has been an active area of research [1], and the laser activation approach has been emphasized in our laboratory [2–8]. In contrast with carbon activation procedures based on polishing [9,10] or vacuum heat treatment [11–13], laser activation can be carried out rapidly in situ. Furthermore, it does not involve intentional oxidation, as do the electrochemical activation procedures [14–22]. The mechanism of laser activation varies for different carbon materials and redox systems, but usually involves desorption of impurities and modification of the carbon microstructure [1]. In many cases, laser activation yields heterogeneous electron transfer rate constants  $k^\circ$  significantly larger than those obtained with other activation methods. Several reviews of laser activation and carbon electrode activation in general are available [1,9,10].

The nature of laser activation provides a special advantage which is useful for understanding kinetic effects at carbon electrodes. Unlike vacuum heat treat-

ment or polishing, it is possible to monitor events at a laser-activated electrode very quickly after activation, without exposure to anything other than the electrolyte solution. Since activation pulses are typically 7–15 ns long, it is possible in principle to measure electrode kinetics within milliseconds or less after the laser pulse. An analogous experiment is fracturing of the carbon electrode in situ [5,23,24], but laser activation provides a convenient means of triggering an electrochemical experiment and the resulting surface is geometrically well defined. In the work reported here the time resolution of laser activation was exploited by acquiring voltammograms at short intervals following activation.

The time course of  $k^\circ$  for  $\text{Fe}(\text{CN})_6^{3-/4-}$  on polished glassy carbon (GC) has been examined by Kamau et al [10], who concluded that surface oxides affect  $k^\circ$ . Deakin et al [25] noted that protonation of surface carboxylates can affect  $k^\circ$  via a Frumkin effect, with an increase in pH causing a decrease in  $k^\circ$  for anionic redox systems. Conversely, cation systems were accelerated at  $\text{pH} > 6$  owing to attraction of the redox system to the anionic surface carboxylate. Hsueh and Brajter-Toth [26] recently studied  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ ,  $\text{Fe}(\text{CN})_6^{3-/4-}$  and uric acid kinetics at freshly cut carbon fiber electrodes. Repeated potential cycling (1000–1500 scans) caused a decrease in  $k^\circ$  for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ ,

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and this effect was attributed to formation of an inhibiting surface oxide. By using a  $7\ \mu\text{m}$  diameter carbon fiber and active IR compensation, scan rates of up to  $11000\ \text{V s}^{-1}$  were possible and  $k^\circ$  values of  $1.22 \pm 0.07\ \text{cm s}^{-1}$  and  $0.13 \pm 0.02\ \text{cm s}^{-1}$  were reported for  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  and  $\text{Fe}(\text{CN})_6^{3-/4-}$  respectively. We recently reported the behavior of transient currents during laser activation in a laser-induced chronoamperometry experiment [27]. The current transients were attributed to thermal disruption of the double layer which was strongly dependent on surface oxidation. Finally, an early report from our laboratory on laser activation noted a slow decay of  $k^\circ$  for  $\text{Fe}(\text{CN})_6^{3-/4-}$  with time after activation [2].

In this paper we discuss the results of time-resolved voltammetry applied to  $60\ \mu\text{m}$  diameter carbon fiber microdisk electrodes at times ranging from less than 1 ms to 30 min after laser activation. Variation of the solution pH and  $\text{O}_2$  concentration was used to assess the importance of surface oxidation to the kinetics observed for the  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  system.

## 2. Experimental

### 2.1 Instrumentation

The experimental apparatus shown in Fig 1 was modified from that described previously [27] by the addition of a digital delay/pulse generator (Stanford Research Inc) and a function generator (Tektronix). An Nd YAG beam (Quantel 580-10), operating at 1064 nm (9 ns pulse), was employed to illuminate the working electrode and was positioned using a 632.8 nm HeNe pilot beam. Before reaching the electrode, the

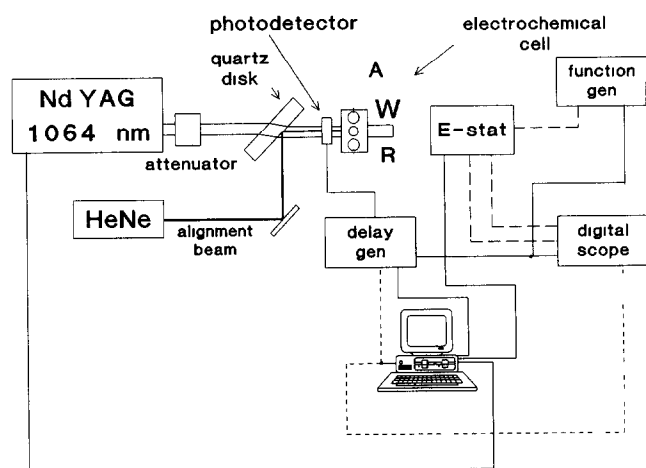


Fig 1 Experimental apparatus. A, auxiliary electrode, working electrode, R, reference electrode, — TTL signal lines (pulse or continuous), - - - GPIB data transfer lines, . . . electrochemical signals (potential and current) transferred between the potentiostat, the function generator and the oscilloscope, ●● electrode leads

laser beam passed through a photodetector (Scientech) which generated a trigger signal for the delay/pulse generator. The delay/pulse generator then triggered the function generator and a digital oscilloscope (LeCroy 9400A). The triggering of the function generator and the oscilloscope can be delayed for a controlled period of time after the laser pulse. A conventional three-electrode potentiostat (Advanced Idea Mechanics, Columbus, OH) with a time constant of  $10^{-7}\ \text{s}$  and an all-glass electrochemical cell was used. The apparatus is able to perform cyclic voltammetry, chronoamperometry and potentiometric experiments triggered by a laser beam reaching the electrode surface or by a computer transistor-transistor logic (TTL) pulse. The recording of the voltammogram was delayed with respect to the laser pulse for periods ranging from a few microseconds up to 10 s, and longer delays were achieved manually. The system is computer controlled and uses the GPIB protocol to communicate with the digital oscilloscope and the delay/pulse generator. The potentiostat and the function generator were controlled using TTL signals generated by a Lab Master interface (Scientific Solutions Inc). The computer program for experimental control was written in Borland C.

Voltammograms were acquired at relatively long times after laser activation ( $> 10\ \text{s}$ ) by activating the electrode with three  $25\ \text{MW cm}^{-2}$  Nd YAG pulses and recording a series of voltammograms of the  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  redox couple at various times after the three pulses. The electrode was on open circuit between the voltammograms and during laser activation. Scan rates of  $490\text{--}5750\ \text{V s}^{-1}$  were used, but most kinetic measurements were conducted at  $1000\text{--}1500\ \text{V s}^{-1}$ . Rate constant values were obtained from the difference between the anodic and cathodic peak potentials [28]. The accuracy of this method was tested by simulating several voltammograms [5] using rate constants obtained from the peak potential difference.

Voltammograms at short times (from 0 to 10 s) after the laser pulse were acquired in a different way. Because of the time constraints, only a single voltammogram could be recorded after the laser pulse on this time-scale. Therefore the experiment was repeated several times with different delay times after activation. The potential (ca.  $0.25\ \text{V}$ ) was applied to the electrode during the activation and while waiting for the specified delay time to elapse. A single laser pulse ( $25\ \text{MW cm}^{-2}$ ) was used to activate the electrode and trigger the experiment.

### 2.2 Electrodes

Cyclic voltammetry was carried out using carbon fibers (Avco, Special Materials Division, Lowell, MA)

sealed in glass under vacuum. A piece of soft glass tubing (3 mm outside diameter) was sealed at one end and a 60  $\mu\text{m}$  diameter carbon fiber was positioned inside it. The other end of the tubing was then connected to a mechanical vacuum pump and it was evacuated to ca.  $10^{-3}$  Torr. The part of the evacuated tubing containing the fiber was slowly heated until the glass collapsed and sealed the carbon fiber. One end of the carbon fiber was glued to a brass wire with silver epoxy to provide electrical contact. The other end of the tubing was polished off until the end of the sealed carbon fiber was exposed. Every new electrode was checked for the quality of the seal under an optical microscope. The electrical connections were tested by immersing the polished electrode into a mercury pool and checking the resistance. In all cases the electrodes were polished with SiC paper (600 grit) and then with 1.0, 0.3 and 0.05  $\mu\text{m}$  alumina in Nanopure water on a polishing cloth (Buehler). The final test of each electrode involved recording a cyclic voltammogram for the  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  redox system. Values of rate constants in the range 0.4–0.6 were considered acceptable for the polished surface. A platinum flag was used as auxiliary electrode, and potentials were measured and reported versus a  $\text{Ag}/\text{AgCl}$   $\text{KCl}(\text{sat})$  electrode (Bioanalytical Systems Inc). Cathodic currents are reported as positive values.

### 2.3 Solutions

Fresh solutions were prepared daily using reagent grade chemicals that were not further purified. The supporting electrolyte was 1 M  $\text{KCl}$  except when electrochemical pretreatment was involved in which case 1 M  $\text{KNO}_3$  was used. All voltammetric experiments were carried out using 5 mM  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ . Nanopure (Barnstead) water was used for all solutions and rinses.

Before each experiment the solution was purged for 20 min with either prepurified argon or oxygen. Argon was further purified by passing through a Supelco Carrier Gas Purifier. In cyclic voltammetry experiments the solution was slowly purged with the gas (argon or oxygen) during the measurements. Because of the very short time-scale of the voltammetric experiment (millisecond or less), there was no difference in the voltammogram shape whether the solution was purged or not.

## 3. Results and discussion

The results will be discussed in three sections: kinetic behavior of  $\text{Fe}(\text{CN})_6^{3-/4-}$  and  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  on 60  $\mu\text{m}$  carbon electrodes, the time dependence of  $k^0$  for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  following laser activation and the effect of surface oxidation on  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  kinetics.

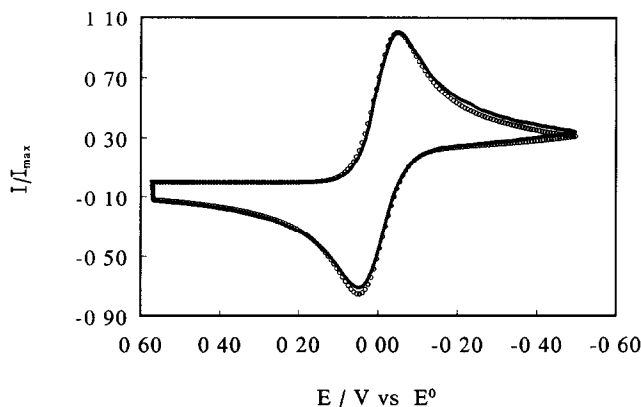


Fig. 2. Experimental (solid curve) and simulated voltammograms for 6 mM  $\text{Ru}(\text{NH}_3)_6^{3+}$  in 1 M  $\text{KCl}$ . The experimental curve is the average of five runs at a scan rate of  $971 \text{ V s}^{-1}$ . For simulation,  $k^0 = 0.47 \text{ cm s}^{-1}$  and  $\alpha = 0.55$ .

Following these results, a mechanism of oxidation-induced electrode deactivation will be proposed.

### 3.1 Kinetics at 60 $\mu\text{m}$ carbon fibers

The rate constant for  $\text{Fe}(\text{CN})_6^{3-/4-}$  observed a few seconds after three laser activation pulses ( $25 \text{ MW cm}^{-2}$ ) was  $0.37 \pm 0.01 \text{ cm s}^{-1}$  ( $N = 3$ ). This value is larger than the value of  $0.13 \text{ cm s}^{-1}$  reported for a freshly cut carbon fiber [26], but smaller than the values for laser-activated GC ( $> 0.5 \text{ cm s}^{-1}$ ) or fractured GC ( $0.5 \text{ cm s}^{-1}$ ) [1,5]. The ratio of the intensities of the  $1360 \text{ cm}^{-1}$  and  $1580 \text{ cm}^{-1}$  Raman bands obtained on the side of the Avco fibers was 0.75 compared with 1.1 for fractured GC-20 [6,24]. The Raman peaks were somewhat broader than those of GC-20, and indicated a degree of disorder intermediate between GC-10 and GC-20. The Raman results imply a fiber microstructure similar to but not identical with that of GC-20. Since the roughness factor of a GC surface can vary from ca. 1.5 to ca. 3.5 [6], the  $k^0$  range observed for  $\text{Fe}(\text{CN})_6^{3-/4-}$  on fibers and GC-20 is within the range attributable to surface roughness and will not be considered further. Simulated and experimental voltammograms for  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  on the 60  $\mu\text{m}$  diameter fibers are shown in Fig. 2. The  $k^0$  for  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  observed within 2 s of three laser activation pulses was  $0.90 \pm 0.05 \text{ cm s}^{-1}$  ( $N = 5$ ). This value is lower than the  $1.22 \text{ cm s}^{-1}$  reported for 7  $\mu\text{m}$  fibers by Hsueh and Brajter-Toth [26], but again it is within the range anticipated for surface roughness variations. Since  $iR$  compensation was not employed here, we verified that  $k^0$  was independent of scan rate for a polished electrode (Table 1).

The constancy of  $k^0$  with scan rate up to  $2900 \text{ V s}^{-1}$  supports the accuracy of the observed value of  $0.9 \text{ cm}$

$s^{-1}$ , but it is still possible that the true value is higher owing to instrumental limitations. Variations in  $k^\circ$  with pH, time and oxidation noted below would not be observable if the  $k^\circ$  value were limited solely by ohmic error or other instrumental factors. Overall, the results with 60  $\mu\text{m}$  carbon fiber microdisk electrodes indicate that voltammetry with scan rates of 1000–3000  $\text{V s}^{-1}$  yields reproducible  $k^\circ$  values which are comparable with those observed on activated but otherwise conventional GC. An advantage of the relatively “large” 60  $\mu\text{m}$  fiber diameter is the higher signal-to-noise ratio, permitting useful voltammograms to be obtained by averaging one to five potential cycles.

### 3.2 Time course of $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ kinetics

The changes in  $k^\circ$  on a time-scale of several minutes after laser activation was determined by fast voltammetry after three activation pulses, with the results shown in Fig. 3 (dotted lines). Each activation resulted in an approximately three-fold increase in  $k^\circ$ , which decayed in about 30 min. The decay did not depend upon the number of voltammograms acquired during the decay, indicating that potential scans during  $k^\circ$  measurement were not themselves causing the observed deactivation.

TABLE 1 Values of  $k^\circ$  for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  in 1 M KCl at a 60  $\mu\text{m}$  diameter carbon fiber

Electrode	Solution	Delay time/s	$\nu/\text{V s}^{-1}$	$k^\circ/\text{cm s}^{-1}$
Polished	Ar saturated	NA	490	$0.51 \pm 0.03^a$
		NA	970	$0.46 \pm 0.04$
		NA	1470	$0.50 \pm 0.06$
		NA	2990	$0.52 \pm 0.03$
		NA	5750	$0.35 \pm 0.02$
$3 \times 25 \text{ MW cm}^{-2}$	Ar saturated	~ 2	1100	$0.90 \pm 0.05$
		60	1100	$0.96 \pm 0.07$
		120	1100	$0.81 \pm 0.05$
		300	1100	$0.73 \pm 0.02$
		600	1100	$0.58 \pm 0.04$
		1200	1100	$0.43 \pm 0.43$
		1800	1100	$0.37 \pm 0.01$
$1 \times 25 \text{ MW cm}^{-2}$	Ar saturated	0.25	1500	$0.85 \pm 0.04$
$3 \times 25 \text{ MW cm}^{-2}$	$\text{O}_2$ saturated	~ 2	1100	$0.56 \pm 0.09$
		60	1100	$0.56 \pm 0.05$
		120	1100	$0.54 \pm 0.05$
		300	1100	$0.53 \pm 0.03$
		600	1100	$0.51 \pm 0.02$
		1200	1100	$0.47 \pm 0.05$
		1800	1100	$0.43 \pm 0.01$
$1 \times 25 \text{ MW cm}^{-2}$	$\text{O}_2$ saturated	~ 0.0	1010	$0.77 \pm 0.04$
		0.02	1010	$0.79 \pm 0.08$
		0.25	1010	$0.72 \pm 0.02$
		1.0	1010	$0.9 \pm 0.1$
		2.0	1010	$0.77 \pm 0.04$
		10.0	1010	$0.74 \pm 0.03$

<sup>a</sup> Mean  $\pm$  standard deviation ( $N=5$  for polished and  $1 \times 25 \text{ MW cm}^{-2}$  cases,  $N=4$  for others)

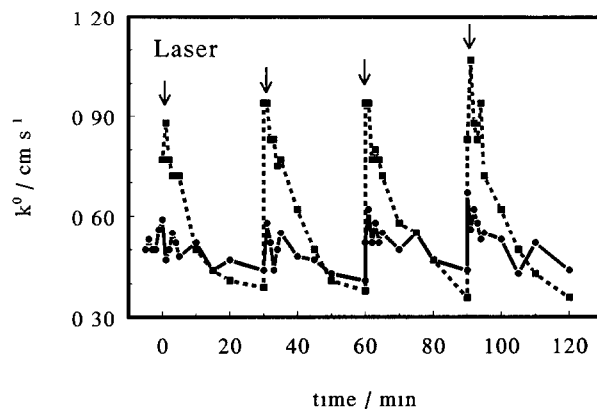


Fig. 3 Repeated laser activation of the carbon fiber surface. The electrode was activated at 0, 30, 60, and 90 min from the start of the experiment. The solution was 5 mM  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$  + 1 M KCl and was saturated with argon (■) or oxygen (●).

To acquire  $k^\circ$  values at shorter times, the voltammetric scan was triggered by the laser pulse after a variable delay with the results shown in Table 1. It should be noted that  $k^\circ$  does not appear to decay at times less than 1 s after activation. The results indicate a fairly slow decay of  $k^\circ$  for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  after laser activation, with no significant changes with time during the first second. Since the observed  $k^\circ$  is near the instrumental limit, it is possible that the rate exceeds  $1.0 \text{ cm s}^{-1}$  immediately after activation.

### 3.3 Effect of oxidation on $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ kinetics

Figure 3 shows the time course of  $k^\circ$  for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  after laser activation in otherwise identical solutions which were saturated with either Ar or  $\text{O}_2$ . In the presence of  $\text{O}_2$ ,  $k^\circ$  does not increase as much with laser activation. The high rate constants following activation could be restored after saturating with argon, indicating that the difference is not caused by impurities. To obtain further support for the hypothesis that  $\text{O}_2$  reduces  $k^\circ$  by surface oxidation, the carbon electrode was pre-oxidized as shown in Fig. 4. The electrode was first laser activated in Ar-saturated electrolyte. Following a delay of 0.25 s after the laser pulse, the potential was scanned to a preselected positive value, and then the scan was reversed and the  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  voltammogram was recorded. Thus the electrode surface was given electrochemical pretreatment (ECP) at various potentials, but for less than a millisecond owing to the high scan rate ( $1500 \text{ V s}^{-1}$ ). The effect of ECP on  $k^\circ$  is shown in Table 2. For ECP potentials of 0–0.25 V vs Ag/AgCl, there is little effect on  $k^\circ$ , but more positive potentials decrease  $k^\circ$  significantly.

Deakin et al. [25] observed a two-fold increase in  $k^\circ$  for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  on polished GC when the pH was

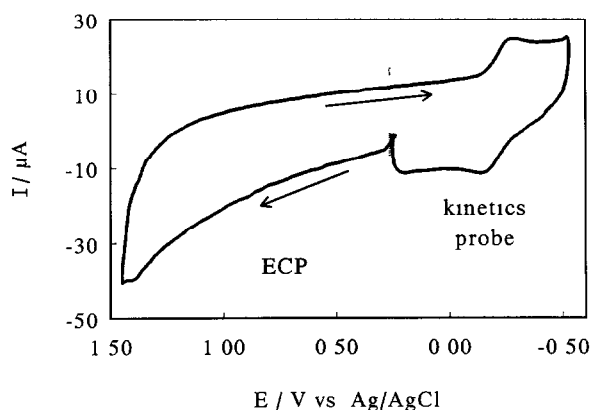


Fig 4 Voltammogram obtained in combined laser activation+ECP+kinetic analysis experiment in 5 mM  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ +1 M  $\text{KNO}_3$ . The starting potential is 0.25 V and the arrows indicate the direction of the potential scan. The laser activation consisted of a single pulse at  $25 \text{ MW cm}^{-2}$ . The solution was saturated with argon and the scan rate was  $1500 \text{ V s}^{-1}$ .

increased from 2 to 6. They concluded that surface carboxylates are deprotonated at neutral pH and cationic redox systems exhibit faster kinetics due to a Frumkin effect. Figure 5 shows changes in  $k^\circ$  with varying solution pH for the  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  system after laser activation. Decays are observed in all cases, but  $k^\circ$  is larger at higher pH.

The results permit several conclusions to be made about the kinetic behavior of the  $60 \mu\text{m}$  carbon fibers. First, the fibers support  $k^\circ$  values for  $\text{Fe}(\text{CN})_6^{3-/4-}$  and  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  comparable with those observed for active GC and freshly cut  $7 \mu\text{m}$  fibers. The similarity of the Raman spectra of GC and of the  $60 \mu\text{m}$  fibers indicates similar degrees of disorder, so that the similarity of rates is not surprising provided that the surfaces are clean. Second, ohmic errors in determining  $k^\circ$  were not apparent at scan rates up to  $3000 \text{ V s}^{-1}$ . Third, the presence of  $\text{O}_2$  or mild electrochemical oxidation reduced  $k^\circ$  significantly. Fourth,  $k^\circ$  decreased with time after laser activation on a time-scale of 0–20 min in Ar-saturated solution. Finally,  $k^\circ$  for

TABLE 2 Effect of rapid positive scanning on  $k^\circ$  for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  in 1 M  $\text{KNO}_3$  <sup>a</sup>

Positive limit	$k^\circ/\text{cm s}^{-1}$
0.25	$0.85 \pm 0.04$ <sup>b</sup>
0.50	$0.76 \pm 0.05$
0.98	$0.55 \pm 0.05$
1.45	$0.41 \pm 0.05$
1.78	$0.28 \pm 0.04$
Polished	$0.50 \pm 0.06$

<sup>a</sup> Scan rate,  $1500 \text{ V s}^{-1}$ , initial potential, 0.25 V (see Fig 4)

<sup>b</sup> Three trials in all cases

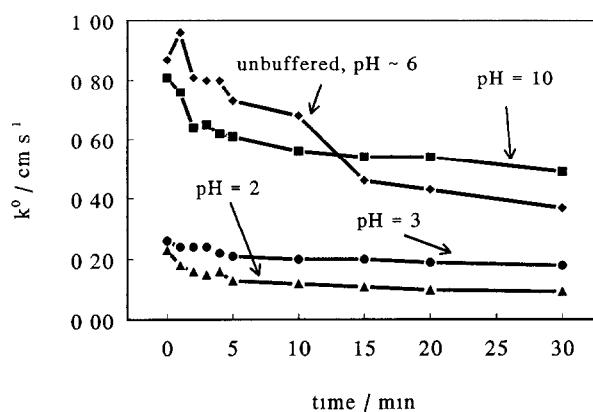


Fig 5 The pH dependence of the decay of  $k^\circ$  for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  after laser activation (three pulses at  $25 \text{ MW cm}^{-2}$ ) in argon-saturated 1 M KCl. Each decay is the average of four curves recorded in separate experiments. The electrode was at the open-circuit potential during the activation and between the acquisitions of the voltammograms.

$\text{Ru}(\text{NH}_3)_6^{2+/3+}$  is smaller for lower solution pHs, but decreases with time after the laser pulse at all pHs.

The conclusions are consistent with a mechanism involving oxide inhibition of the  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  charge transfer. The slow decay of  $k^\circ$  in Ar-saturated solution is unlikely to be caused by impurity adsorption since rigorous purification of the solution had no effect on the decay and because the decay could be greatly accelerated by oxidation. Furthermore, the inhibiting oxide is apparently not anionic at pH 10, since such a group (e.g. carboxylate) should increase the rate as it forms. A more likely possibility is a neutral functional group (e.g. phenolic OH) which increases the distance of closest approach and decreases  $k^\circ$ . The faster rates observed following activation at higher pH (Fig 5) are likely to be caused by anionic surface groups present at all times (before and after activation) on the polished GC surface.

As noted earlier, Hsueh and Brajter-Toth [26] attributed a decrease in  $k^\circ$  for  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  with repeated potential cycling to surface oxidation. Several X-ray photoelectron spectroscopy studies concluded that  $\text{O}_2$  and  $\text{H}_2\text{O}$  react with clean carbon surfaces [29–32], with the  $\text{O}_2$  reaction being more rapid. Delannay et al [32] concluded that  $\text{O}_2$  chemisorbs rapidly on polycrystalline graphite in ultrahigh vacuum (UHV) while  $\text{H}_2\text{O}$  reacts slowly to form chemisorbed C–OH and C–H species. Combined with the current results, these observations lead to a hypothesis for the events following laser activation. The laser pulse thermally desorbs polishing debris and other impurities to yield a surface with both anionic (probably carboxylate) and radical sites. In the presence of  $\text{O}_2$  the radicals rapidly

react to bind it, probably as the peroxy radical. In the absence of intentional  $O_2$ , the decay could be caused either by trace  $O_2$  remaining after Ar saturation or by the slower reaction with  $H_2O$ . Additional purification of the Ar did not alter the decay, implying that  $H_2O$  is reacting slowly to form C-OH. Electrochemical oxidation apparently produces similar functional groups once the potential is above about 0.5 V vs Ag/AgCl.

A semiquantitative estimate of the effect of surface oxides on  $k^\circ$  can be made based on a simplified model. Suppose that the decay in rate depends primarily on the formation of neutral oxides such as phenolic OH (from  $H_2O$ ) and the peroxy radical (from  $O_2$ ). Assume that these oxides are formed on carbon radical sites which are formed by the laser pulse. Oxides will increase the distance of closest approach of the  $Ru(NH_3)_6^{2+/3+}$  and reduce  $k^\circ$  by a tunneling factor  $e^{-\beta\Delta r}$ , where  $\Delta r$  is the thickness of the oxide layer and  $\beta$  is a constant. For many outer-sphere processes  $\beta \approx 1.0 \text{ \AA}^{-1}$  [33] and  $\Delta r$  is in the range 1–3  $\text{\AA}$  where the oxides are present. The rate constant can then be estimated using

$$k_{\text{obs}}^\circ(t) = k_c^\circ[1 - \theta(t)] + k_{\text{ox}}^\circ\theta(t) \quad (1)$$

where  $k_c^\circ$  is the rate constant on unoxidized carbon,  $k_{\text{ox}}^\circ$  is the rate constant on a monolayer of neutral oxide and  $\theta(t)$  is the fractional coverage of oxide.

If  $\Delta r = 2 \text{ \AA}$  and  $\beta = 1 \text{ \AA}^{-1}$ ,  $k_{\text{ox}}^\circ = 0.14k_c^\circ$  if tunneling distance is the only factor involved. Now, if  $\theta(t)$  increases with time during the chemisorption of  $O_2$  or  $-OH$ ,  $k_{\text{obs}}^\circ$  will decrease from a maximum of  $k_c^\circ$  to a minimum of  $\theta(\infty)k_{\text{ox}}^\circ$ , with  $\theta(\infty)$  not necessarily equalling unity. While this model has several adjustable quantities which are only known approximately, it is based on reactions of  $O_2$  and  $H_2O$  with

surface radical sites as indicated by independent UHV [32] and electrochemical experiments [34].

If it is further assumed that the neutral oxides are formed from surface radicals by a reaction which is pseudo-first-order in surface radical concentration, then

$$\theta(t) = \theta^\infty[1 - \exp(-k_1t)] \quad (2)$$

where  $\theta^\infty$  is the oxide coverage at long times,  $t$  is the time after the laser pulse and  $k_1$  is the pseudo-first-order rate constant for oxide formation from surface radicals. A higher-order dependence on surface radical concentration is unlikely, since nearby radical pairs should couple rapidly. Substituting eqn (2) into eqn (1) and rearranging yields

$$k_{\text{obs}}^\circ = (k_c^\circ - k_c^\circ\theta^\infty + k_{\text{ox}}^\circ\theta^\infty) + (k_c^\circ\theta^\infty - k_{\text{ox}}^\circ\theta^\infty) \times \exp[(-k_1t)] \quad (3)$$

Since the first term in parentheses in eqn (3) is the observed  $k^\circ$  at infinite time, we obtain

$$\ln[k_{\text{obs}}^\circ(t) - k_{\text{obs}}^\circ(\infty)] = \ln(k_c^\circ\theta^\infty - k_{\text{ox}}^\circ\theta^\infty) - k_1t \quad (4)$$

Thus a plot of the left-hand side of eqn (4) versus time should be linear with a slope equal to the pseudo-first-order rate constant for the formation of surface oxide. Equation (4) does not require that oxides retard electron transfer through a tunneling mechanism, but only that  $k_{\text{ox}}^\circ$  be different from  $k_c^\circ$  and that some oxide coverage  $\theta^\infty$  is reached by a first-order process after initiation by the laser pulse. If a tunneling mechanism were valid, then

$$k_{\text{ox}}^\circ = k_c^\circ e^{-\beta\Delta r} \quad (5)$$

and

$$\ln[k_{\text{obs}}^\circ(t) - k_{\text{obs}}^\circ(t = \infty)] = \ln(\theta^\infty k_c^\circ e^{-\beta\Delta r}) - kt \quad (6)$$

The appropriate plot to test eqn (4) is shown in Fig. 6. The plots are approximately linear with similar slopes at four different pH values. The slopes range from  $0.10 \pm 0.01$  (pH 3) to  $0.14 \pm 0.01$  (pH 2) decade  $\text{min}^{-1}$ , with correlation coefficients of 0.93 or greater. Based on eqn (4), the lack of a trend in the slope with pH implies that the rate of formation of oxides after the laser pulse is not pH dependent, as would be expected for  $O_2$  or  $H_2O$  chemisorption. The significance of the variation of the intercept with pH is not clear, but may be related to the relatively low concentration of ionizable oxides (a few percent according Deakin et al [25]). Another possibility is pulse-to-pulse variation in initial radical concentration.

#### 4. Summary

Although the quantitative aspects of this model must be considered speculative owing to the assumptions

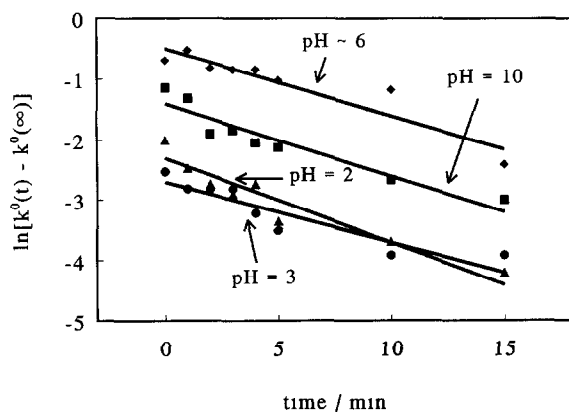


Fig. 6 Kinetic analysis of the surface deactivation process as a function of pH. The kinetic data were recorded in an Ar-saturated solution of 5 mM  $Ru(NH_3)_6^{3+}$  + 1 M KCl. Three Nd:YAG pulses at 25 MW  $\text{cm}^{-2}$  were used to activate the electrode.

involved, they are consistent with the qualitative conclusions based on electrochemical and UHV results. All the observations are consistent with formation of a neutral partial surface oxide layer following laser activation. This layer retards electron transfer between carbon and  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ , perhaps by increasing the tunneling distance. The process is much faster in  $\text{O}_2$ -saturated than in Ar-saturated electrolyte. Given the many reports of catalysis by surface oxides, it may be surprising that an oxide layer would reduce  $k^\circ$ . However,  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  is believed to be an outer-sphere system and should not require specific sites on the surface. In the present case, surface oxides appear either to reduce  $k^\circ$  by increasing the tunneling distance (for neutral oxides) or to modify  $k^\circ$  through a Frumkin effect (for ionized oxides). These observations are consistent with those of Hsueh and Brajter-Toth [26] for fractured carbon fibers, implying that slow oxidation of both the laser-activated and fractured surface inhibits  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  kinetics. Finally, it should be pointed out that  $\text{Ru}(\text{NH}_3)_6^{2+/3+}$  is used here as a representative probe of surface chemical changes, and both the technique and the current results can be applied to a variety of redox systems.

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