

## POLYMER FILMS ON ELECTRODES

### PART XV. THE INCORPORATION OF $\text{Ru}(\text{bpy})_3^{2+}$ INTO POLYMERIC FILMS GENERATED BY ELECTROCHEMICAL POLYMERIZATION OF 2,2'-BIPYRAZINE ( $\text{bpz}$ ) AND $\text{Ru}(\text{bpz})_3^{2+}$

PUSHPITO K. GHOSH and ALLEN J. BARD

*Department of Chemistry, The University of Texas at Austin, Austin, TX 78712 (U.S.A.)*

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#### ABSTRACT

Modified glassy carbon electrodes have been prepared by anodic oxidation of solutions of  $\text{Ru}(\text{bpz})_3^{2+}$  ( $\text{bpz} = 2,2'$ -bipyrazine) or  $\text{bpz}$ . A measurement of film resistance indicates  $\rho = -10^6 \Omega$  for the 'bpz' film. These electrodes readily incorporate  $\text{Ru}(\text{bpy})_3^{2+}$  ( $\text{bpy} = 2,2'$ -bipyridine) and cyclic voltammetry in pure supporting electrolyte solution yields reversible redox waves corresponding to the  $\text{Ru}(\text{bpy})_3^{2+/3+}$  couple. The thickness of films deposited by the above technique can be systematically varied by altering the duration of electropolymerization, and the surface concentration of incorporated  $\text{Ru}(\text{bpy})_3^{2+}$  varies accordingly. The cyclic voltammograms exhibit surface film behavior for the thin films while the behavior for thick films is diffusional in nature (apparent diffusion coefficient,  $D_{\text{app}} = 2.2 \times 10^{-9} \text{ cm}^2/\text{s}$  for films  $\sim 1.6 \mu\text{m}$  thick). The concentration of surface-confined polypyridyl complex can be as high as  $3.5 \times 10^{-8} \text{ mol/cm}^2$  of electrode area (i.e., an effective bulk concentration of  $0.22 \text{ M}$  for a  $1.6 \mu\text{m}$  film) but gradual loss of electroactive material is observed upon cycling the potential between the redox waves. The loss of material does not occur, however, in  $5 \times 10^{-5} \text{ M}$   $\text{Ru}(\text{bpy})_3^{2+}$ . Incorporation of  $\text{Ru}(\text{bpy})_3^{2+}$  from solutions at pH 10.5 led to voltammograms with an additional reversible couple ( $E_{1/2} = 0.69 \text{ V}$  vs. SSCE), believed to arise from the decomposition of  $\text{Ru}(\text{bpy})_3^{2+}$  at high pH. Electrogenerated  $\text{Ru}(\text{bpy})_3^{2+}$  in the film reacts with oxalate ions in solution to produce chemiluminescence. The films are completely porous to hydroquinone dissolved in the supporting electrolyte ( $0.05 \text{ M}$  phosphate buffer;  $0.1 \text{ M}$   $\text{Na}_2\text{SO}_4$ ; pH 4.8) and the hydroquinone-quinone couple is considerably more reversible at these modified electrodes; however, a similar increase in reversibility is observed at the bare electrode following anodization in  $7 \text{ M}$   $\text{H}_2\text{SO}_4$ .

#### INTRODUCTION

Electrode modification has become an important area of investigation in recent years, especially because electrode stabilization and electrocatalysis are possible [1-4]. There is also interest in the nature of the various processes which govern charge (electronic and ionic) transport at modified electrodes [5-9]. While several different modified electrodes have already been reported in the literature, electroactive coatings containing  $\text{Ru}(\text{bpy})_3^{2+}$  continue to be of interest, because of the fast

kinetics of electron exchange and the very favorable excited and ground state properties of the redox couple [10]. Moreover, several systems involving this couple, including polymeric films, have been shown to produce electrogenerated chemiluminescence (ECL) [11,12]. Another important reaction which may be useful in the design of efficient photoanodes is the Co(II) catalyzed oxidation of water by  $\text{Ru}(\text{bpy})_3^{3+}$  [13]. For these reasons we have been interested in electrodes modified with  $\text{Ru}(\text{bpy})_3^{2+}$ . Several techniques for the immobilization of  $\text{Ru}(\text{bpy})_3^{2+}$  on an electrode surface have been reported. Thick coatings of  $\text{Ru}(\text{bpy})_3^{2+}$  have been obtained via silanization [14] and via electropolymerization [15]. In addition, the incorporation of  $\text{Ru}(\text{bpy})_3^{2+}$  into Nafion coatings on electrode surfaces has also been introduced as a simple modification technique [16]. Unfortunately, with the exception of electroactive Nafion films, all of the other modified electrodes exhibit poor voltammetric response in aqueous electrolytes. In this paper we describe the synthesis and report some of the characteristics of electrodes prepared by a new modification method which takes place in aqueous media, namely, the incorporation of  $\text{Ru}(\text{bpy})_3^{2+}$  into stable, polymeric films resulting from the apparent electropolymerization of 2,2'-bipyrazine (bpz) and  $\text{Ru}(\text{bpz})_3^{2+}$ . We might also note recent work where catalysts have been incorporated into films on electrode surfaces by the electropolymerization of polypyrrole in the presence of a solution species [17].

## EXPERIMENTAL

### *Measurements*

Electrochemical measurements were performed in a single compartment cell with a Pt flag counter electrode and aqueous saturated sodium chloride calomel electrode (SSCE). The ECL experiments employed an Ag quasi-reference electrode. The working electrode was a Teflon shrouded glassy carbon (Tokai Carbon Co., Japan) disk ( $0.17 \text{ cm}^2$ ). The instrumentation for electrochemistry comprised a PAR Model 173 Potentiostat, a Model 175 Universal Programmer and a Model 179 Digital Coulometer. Relative ECL intensity measurements were made with a Hamamatsu R928 photomultiplier tube. Photoelectron spectra were obtained using a VG Scientific Ltd. ESCALAB. A Mg anode at 15 kV and 20 mA of current was used and the base pressure was  $1 \times 10^{-9}$  Torr.

### *Materials*

$\text{Ru}(\text{bpz})_3\text{Cl}_2$  (bpz = 2,2'-bipyrazine) and bpz were provided by Professor A.B.P. Lever.  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  was purchased from G.F. Smith Chemical Co. and used without further purification. All other chemicals were reagent grade and were used as received. Triply distilled water was used throughout.

### *Film formation*

A glassy carbon (GC) disk electrode was polished with  $1 \mu\text{m}$  diamond paste and then rinsed thoroughly with ethanol and water, respectively. The electrode was

subsequently placed in an ultrasonic bath for 10 min and finally rinsed with water. Film formation occurred when the electrode was placed in a cell containing an aged solution (at least 7 days old) of 1 mM  $\text{Ru}(\text{bpz})_3\text{Cl}_2$  in 7.5–8.0 M  $\text{H}_2\text{SO}_4$  and the potential cycled between 2.4 and 0.6 V vs. SSCE for 2 to 30 min at 5 V/s. Film formation also occurred in a 1 mM bpz solution in  $\sim 6$  M  $\text{H}_2\text{SO}_4$  (scan range 2.1 V to 1.5 V, scan rate,  $v$ , 500 mV/s).

#### *Incorporation of $\text{Ru}(\text{bpy})_3^{2+}$*

The electrode treated as above was rinsed with water and then placed in a cell containing an aq. solution of  $1.4 \times 10^{-4}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  (0.05 M  $\text{KNO}_3$ , pH 2.5–6.5). In a few experiments the solution pH was 10.5. Upon cycling the electrode repeatedly between 1.5 and 0.6 V at 100 mV/s, the voltammetric waves corresponding to the  $\text{Ru}(\text{bpy})_3^{3+/2+}$  couple grew progressively until steady state behavior was attained.

## RESULTS AND DISCUSSION

### *Film formation*

As described in the experimental section, a film was formed on the surface of a glassy carbon (GC) disk electrode when it was cycled repeatedly between 2.4 and 0.6 V in an acidic solution containing  $\text{Ru}(\text{bpz})_3^{2+}$ . Film formation was also observed in acidic solutions of bpz. The formation of a film is evident from the change in appearance of the GC surface following such electrochemical treatment; the electrode displays a rich assortment of colors, from its initial shiny black to metallic blue to purple to green to yellow, depending upon the duration over which the potential is scanned repeatedly. Such colors are largely attributed to interference effects, with different colors observed at different film thicknesses. Similar effects have been reported for the electropolymerization of polypyrrole films. X-ray photoelectron spectra (XPS) recorded for a polished electrode and for an electrode covered with a relatively thin film generated in the presence of  $\text{Ru}(\text{bpz})_3^{2+}$  are shown in Figs. 1a and 1b, respectively. In Fig. 1b the attenuation of the 285 eV signal of C in GC is accompanied by growth of a large signal at 290 eV which is attributed to the film carbon. Sputtering the electrode restored its clean surface and a spectrum similar to Fig. 1a was obtained. Thus, the XPS data confirm the presence of a film. Similar results have been obtained for electrodes modified in the presence of bpz. Unfortunately, signals due to N and Ru could not be detected, so that XPS did not distinguish between films formed from  $\text{Ru}(\text{bpz})_3^{2+}$  and those from bpz solution. We might note that XPS also failed to detect Ru in Nafion films containing incorporated  $\text{Ru}(\text{bpy})_3^{2+}$ , whose presence was otherwise evident from the strong coloration of the films. The cyclic voltammograms of these modified electrodes in supporting electrolyte were also quite featureless. Somewhat larger background currents are observed for the 'bpz'-modified electrode. This can be ascribed to capacitive

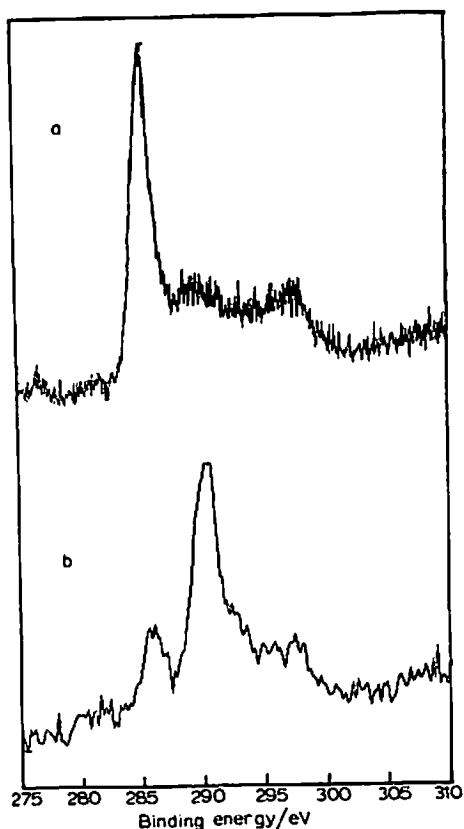


Fig. 1. XPS spectra for: (a) polished glassy carbon electrode and (b) glassy carbon electrode coated with film formed from  $\text{Ru}(\text{bpz})_3^{2+}$  solution via electropolymerization.

charging of the film, but such charging effects are very small in comparison to polypyrrole films [17]. It therefore appears that the 'bpz' films are not very conducting. The resistivity,  $\rho$ , obtained for a dry 'bpz' film was  $\sim 10^6 \Omega\text{-cm}$ . No redox activity was found in the accessible anodic range, but, for electrodes modified in the presence of bpz, there was a large reduction wave at  $-1.34 \text{ V}$  (aqueous solution, pH 7), while films formed from  $\text{Ru}(\text{bpz})_3^{2+}$  solution display a very broad cathodic wave, beginning at  $-0.4 \text{ V}$ .

The exact nature of these films and the mechanism by which they are formed have not yet been elucidated. The large positive potential (2.1–2.4 V) needed to derivatize the electrode suggests that the film is formed as a result of oxidative polymerization of an electroactive constituent in solution. Solutions of bpz and  $\text{Ru}(\text{bpz})_3^{2+}$  exist predominantly as  $\text{bpzH}_2^{2+}$  and  $\text{Ru}(\text{bpz})_2(\text{bpzH})^{3+}$  respectively in strongly acidic solutions (7.5–8.0 M  $\text{H}_2\text{SO}_4$ ) [18]. The solution species were reported to be very rugged and the protonation–deprotonation steps, completely reversible.

Thus  $\text{bpzH}_2^{2+}$  and  $\text{Ru}(\text{bpz})_2(\text{bpzH})^{3+}$  are good candidates for the electroactive species involved in the oxidative polymerization process. On the other hand, such species should be extremely resistant to oxidation. In our experiments oxidation leading to film formation occurs at the solvent limit and the process is irreversible, since no reverse cathodic peak could be observed. It is unclear if the anodic limit employed (2.1 V vs. SSCE for bpz solutions and 2.4 V for  $\text{Ru}(\text{bpz})_3^{2+}$  solutions) is adequate to oxidize the protonated species or whether some other solution species are involved in the polymerization process. It is conceivable that hydroxyl radicals generated at the electrode surface could play a role in initiating polymerization.

#### *Incorporation of $\text{Ru}(\text{bpy})_3^{2+}$*

Modified electrodes prepared by the procedure described above incorporated  $\text{Ru}(\text{bpy})_3^{2+}$  readily into the film matrix. Most of the results described here concern films prepared from  $\text{Ru}(\text{bpz})_3^{2+}$  solutions. Figure 2 typifies the effect of repetitive potential sweeps on the voltammograms obtained in an aqueous electrolyte containing 0.14 mM  $\text{Ru}(\text{bpy})_3^{2+}$ . The voltammetric waves grow larger on successive scans and continue to do so until the film is saturated with the electroactive ion. Beyond this point the voltammograms remain essentially constant even for scan durations as

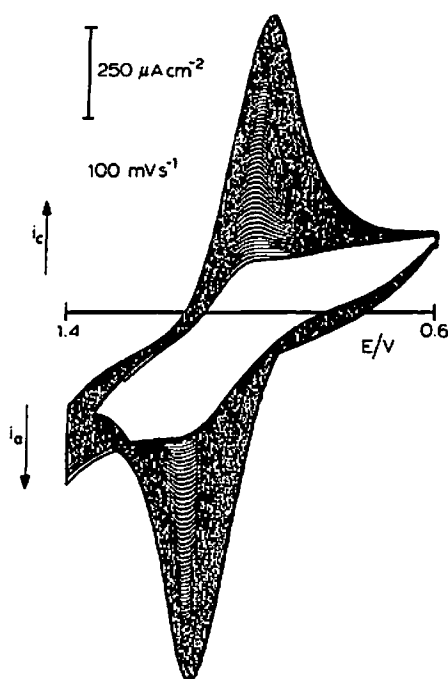


Fig. 2. Voltammetric growth curves showing the incorporation of  $\text{Ru}(\text{bpy})_3^{2+}$  at a coated glassy carbon electrode.  $\nu = 100 \text{ mV/s}$ , cycles 1 to 50.

long as 2 to 3 h. The rate of incorporation of  $\text{Ru}(\text{bpy})_3^{2+}$  varies considerably with the thickness of the film (relative film thicknesses can be determined quite accurately and will be discussed below). Qualitatively, ion uptake from a  $10^{-4} M \text{Ru}(\text{bpy})_3^{2+}$  solution is quite rapid for thin films while the process is slower for thicker films. A noticeable enhancement of the uptake rate occurs upon stirring, suggesting depletion of  $\text{Ru}(\text{bpy})_3^{2+}$  at the film solution interface is a factor. Thicker films show a distinct orangish hue following uptake of  $\text{Ru}(\text{bpy})_3^{2+}$ .

When an electrode containing  $\text{Ru}(\text{bpy})_3^{2+}$  is placed in pure supporting electrolyte ( $0.05 M \text{KNO}_3$ ) the peak heights for this couple decrease on scanning and are smaller than the waves obtained in  $0.14 mM \text{Ru}(\text{bpy})_3^{2+}$  (compare the solid and dashed curves in Fig. 3). Electroactive material is apparently lost from the electrode on sweeping the potential over the redox waves and the dotted curve corresponds to the 325th scan in pure electrolyte. The loss rate is illustrated more quantitatively in Fig. 4B (for a different electrode prepared in an analogous fashion) and seems to

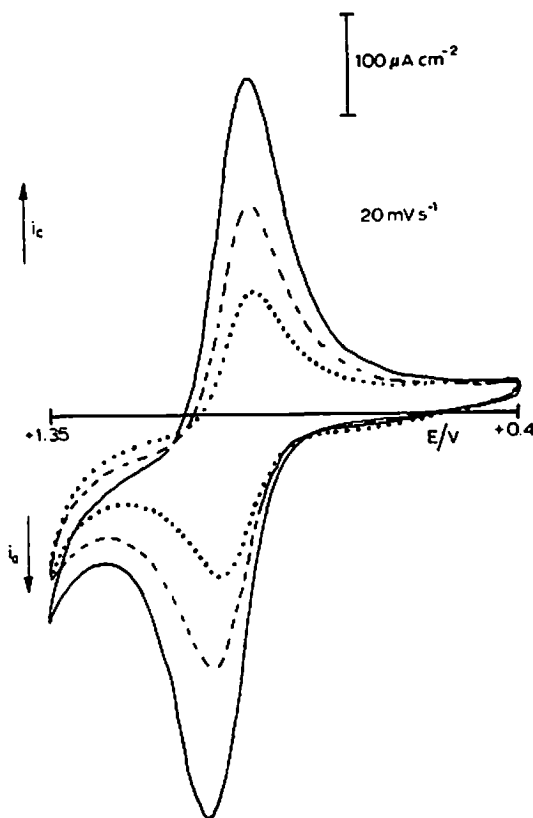


Fig. 3. Cyclic voltammograms of: (—) coated electrode in  $0.14 mM \text{Ru}(\text{bpy})_3^{2+}$  solution, following incorporation of  $\text{Ru}(\text{bpy})_3^{2+}$  into the film; (---) 4th scan in pure electrolyte and (.....) 325th scan in pure electrolyte.

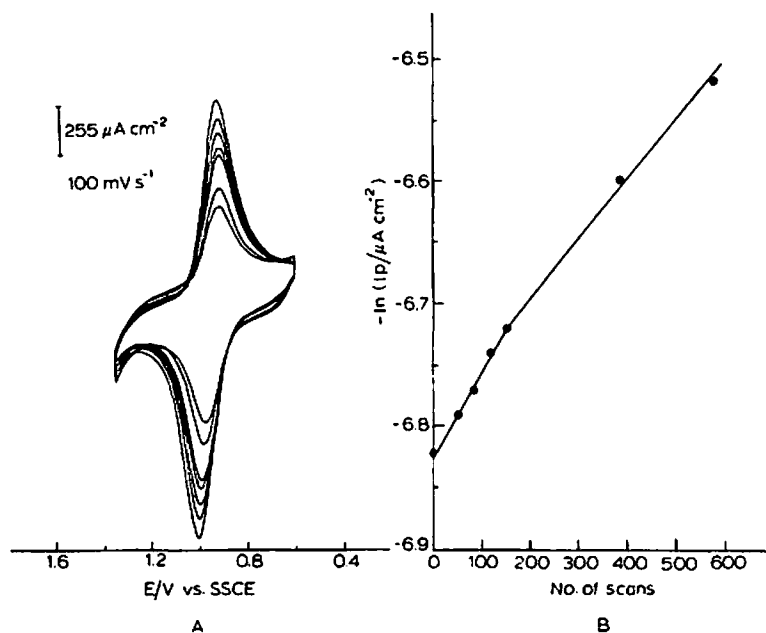


Fig. 4. (A) Cyclic voltammograms of modified glassy carbon electrode containing incorporated  $\text{Ru}(\text{bpy})_3^{2+}$ . The voltammograms were obtained in pure electrolyte ( $0.04 \text{ M KNO}_3$ ) and show the gradual loss of electroactive material upon cycling between the redox waves. (B) Plot of  $-\ln(i_p)$  ( $i_p$  = peak current) vs. the number of cyclic scans.

obey first order kinetics. If an electrode is placed back in a dilute solution of  $\text{Ru}(\text{bpy})_3^{2+}$  ( $0.05\text{--}0.15 \text{ mM}$ ) following electrochemical losses, the lost material can be replenished as indicated by an increase in the voltammetric peak heights. These results show that there is some degree of dynamic equilibrium (on the voltammetric time scale) between  $\text{Ru}(\text{bpy})_3^{2+}$  in solution and  $\text{Ru}(\text{bpy})_3^{2+}$  bound within the film. The more facile loss of material in pure electrolyte, as compared to that found for  $\text{Ru}(\text{bpy})_3^{2+}$  in Nafion [19], for example, indicates that fairly weak attractive forces are involved in holding this ion within the film. The nature of these forces is not known, but one likely possibility is a weak  $\pi\text{--}\pi$  interaction between film bipyrazyl and the bipyridine rings of  $\text{Ru}(\text{bpy})_3^{2+}$ . That the  $\text{Ru}(\text{bpy})_3^{2+}$  ions have a high affinity for the film is amply clear from an evaluation of the extraction coefficient,  $K$ :  $2000 < K < 6000$  (based on a bulk concentration of  $0.1\text{--}0.3 \text{ M Ru}(\text{bpy})_3^{2+}$  within the film for a solution concentration of  $0.05 \text{ mM}$ ).

#### *Voltammetric behavior as a function of film thickness*

Polymeric films of different thicknesses were prepared by controlling the duration of electropolymerization in a  $1 \text{ mM Ru}(\text{bpz})_3^{2+}$  solution. Voltammograms were then obtained for  $\text{Ru}(\text{bpy})_3^{2+}$  incorporated into these films. The peak current vs. scan rate

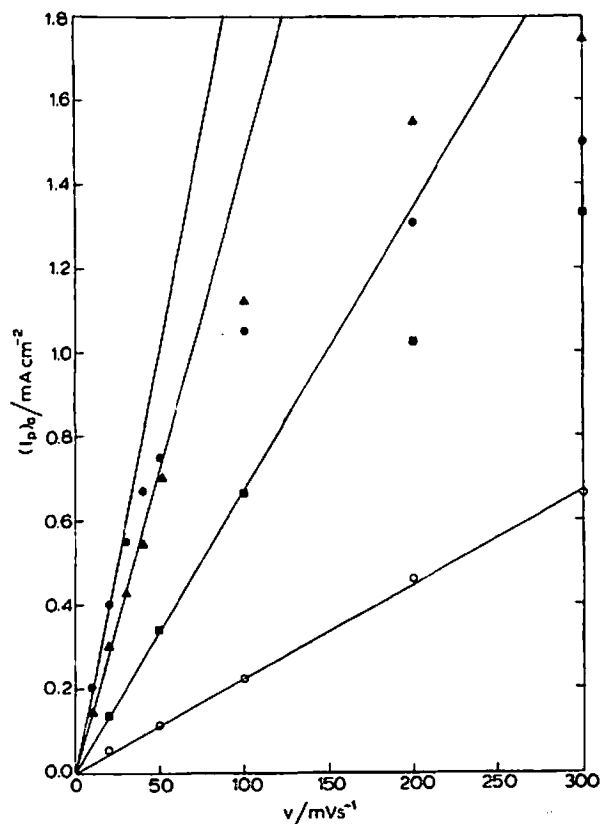


Fig. 5. Anodic peak current ( $i_{pa}$ ) vs. scan rate ( $\nu$ ) for coated glassy carbon electrodes with different film thicknesses; voltammograms were recorded in  $0.05 \text{ M Ru}(\text{bpy})_3^{2+}$  solution, following complete incorporation of  $\text{Ru}(\text{bpy})_3^{2+}$  into film. Film thickness was varied by controlling the duration of electropolymerization. (O) 2 min, (■) 5 min, (▲) 10 min and (●) 15 min.

TABLE 1

Voltammetric parameters for coated electrodes prepared from a solution of  $1 \text{ mM Ru}(\text{bpy})_3^{2+}$  in  $7.65 \text{ M H}_2\text{SO}_4$ <sup>a</sup>

Duration of electropolymerization/min	Concentration of incorporated $\text{Ru}(\text{bpy})_3^{2+}$ / $\text{mol cm}^{-2}$ <sup>b</sup>	Relative surface concentration of $\text{Ru}(\text{bpy})_3^{2+}$ in the various films	$\Delta E_p$ / $\text{mV}$ <sup>c</sup>	FWHH (anodic) / $\text{mV}$ <sup>c</sup>
2	$2 \times 10^{-9}$	2	15	130
5	$7 \times 10^{-9}$	7	40	120
10	$1.4 \times 10^{-8}$	14	72	170
15	$2.1 \times 10^{-8}$	21	96	250

<sup>a</sup> Electrode was cycled repetitively between  $+2.4$  and  $+0.6$  at  $5 \text{ V/s}$ .

<sup>b</sup> The concentrations were obtained from the linear portions of the slopes shown in Fig. 5.  $\text{Ru}(\text{bpy})_3^{2+}$  was incorporated from an aqueous solution of  $0.14 \text{ M Ru}(\text{bpy})_3^{2+}$  in  $0.03 \text{ M KNO}_3$ .

<sup>c</sup> For voltammograms recorded at  $100 \text{ mV/s}$ .



plots for four such films are shown in Fig. 5. Very thin films yielded linear plots up to a scan rate of 300 mV/s while deviations from linearity became progressively larger for thicker films. However, the slow scan rate plots, i.e., for  $v < 40$  mV/s, allow accurate estimates of the total amount of electroactive  $\text{Ru}(\text{bpy})_3^{2+}$  (i.e., the surface concentration of electroactive ions), since all the electrodes exhibit strictly thin film behavior in this region. Some of the relevant data, including the concentration of  $\text{Ru}(\text{bpy})_3^{2+}$ , are found in Table 1. Note that there is an almost 1:1 correlation between the surface concentration of  $\text{Ru}(\text{bpy})_3^{2+}$  in the film and the duration of electropolymerization involved in producing the film. Thus in the thickness domain under consideration, the film thickness increases linearly (and uniformly) with time. Preliminary results employing in situ ellipsometry also suggest that the thickness of bipyrazyl films grows linearly with the duration of electropolymerization; details of these experiments will be given elsewhere. Moreover, the

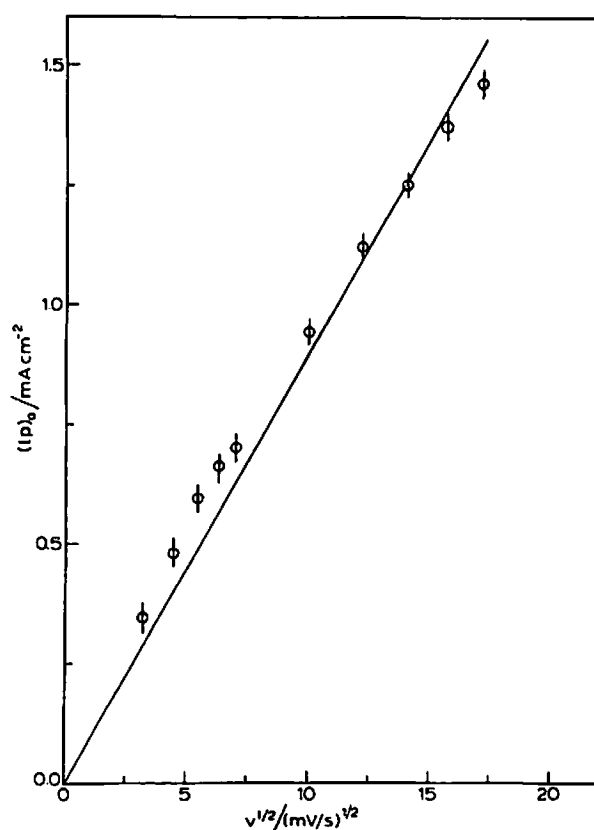


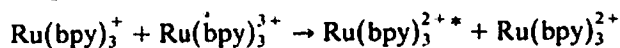
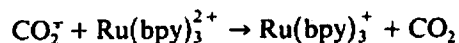
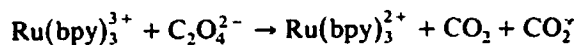
Fig. 6. Anodic peak current ( $i_{pa}$ ) vs.  $v^{1/2}$  ( $v$  = scan rate) for a thick film. Voltammograms were recorded in a 0.05 mM  $\text{Ru}(\text{bpy})_3^{2+}$  solution, following saturation of the film with  $\text{Ru}(\text{bpy})_3^{2+}$ . The film was prepared by electropolymerization in a solution of 1 mM  $\text{Ru}(\text{bpz})_3^{2+}$  in 7.65 M  $\text{H}_2\text{SO}_4$  for 30 min, at a scan rate of 5 V/s, and scan range +0.6–+2.4 V vs. SSCE.

high level of correlation observed with these data suggests that all of the incorporated  $\text{Ru}(\text{bpy})_3^{2+}$  is electroactive. Table 1 also provides data on the peak-to-peak separation ( $\Delta E_p$ ) and the peak width at half height, both of which increase with increasing film thickness.

Deviations from thin film behavior for the thicker films suggest that charge transport within the film is the rate-limiting step. For fairly thick films plots of  $i_p$  vs.  $v^{1/2}$  are approximately linear; one such plot is shown in Fig. 6. From the slope we have calculated an apparent diffusion coefficient ( $D_{\text{app}}$ ) of  $2.2 \times 10^{-9} \text{ cm}^2/\text{s}$ , based on a bulk concentration of  $0.22 \text{ M}$  for  $\text{Ru}(\text{bpy})_3^{2+}$ . The latter number was obtained from the known surface concentration,  $\Gamma$ , of  $3.5 \times 10^{-8} \text{ mol/cm}^2$  and a film thickness value estimated to be  $1.6 \mu\text{m}$ . The film thickness estimate is based on the observation that a  $0.2 \mu\text{m}$  'bpz' film contains eight times less  $\text{Ru}(\text{bpy})_3^{2+}$  ( $\Gamma = \sim 4 \times 10^{-9} \text{ mol/cm}^2$ ) than this film, and as concluded earlier, there is a good correlation between film thickness and the amount of  $\text{Ru}(\text{bpy})_3^{2+}$  incorporated into the film. For a bulk concentration of  $0.22 \text{ M}$  the metal-metal distance between adjacent  $\text{Ru}(\text{bpy})_3^{2+}$  ions is  $1.96 \text{ nm}$ , while the separation between bipyridyl rings of adjacent ions is  $0.6 \text{ nm}$  (assuming a hard sphere radius of  $0.68 \text{ nm}$  for  $\text{Ru}(\text{bpy})_3^{2+}$ ) [20]. The  $0.6 \text{ nm}$  separation is somewhat large for electron exchange between adjacent ions. However, if some degree of film reorganization can bring the ions into closer proximity, then electron hopping could be a reasonable mechanism for charge transfer within these films. On the other hand, the relative ease with which  $\text{Ru}(\text{bpy})_3^{3+/2+}$  moves in and out of these films suggests that physical diffusion of these ions to and from the electrode surface is also a possibility. For a film which is  $1.6 \mu\text{m}$  thick and for a  $D$  value of  $2.2 \times 10^{-9} \text{ cm}^2/\text{s}$ , the diffusion time,  $\tau$  ( $\tau = l^2/2D$ ) [13], is  $5.6 \text{ s}$ , which falls within the voltammetric time scale employed.

#### *Electrogenerated chemiluminescence*

Previous reports from this laboratory described ECL studies for the  $\text{Ru}(\text{bpy})_3^{2+}$ /oxalate system in purely aqueous solutions. Such studies have been carried out on dissolved  $\text{Ru}(\text{bpy})_3^{2+}$  as well as  $\text{Ru}(\text{bpy})_3^{2+}$  bound in Nafion membranes. As described above modified electrodes prepared by the present method show good voltammetric response and moderate stability in water and are therefore well-suited for ECL studies of this kind. Figure 7B illustrates the ECL behavior observed in a degassed solution containing  $1 \text{ mM}$  oxalate (pH 6); as can be seen, the ECL intensity tracks the voltammogram shown in Fig. 7A. The reaction sequence for ECL production has been proposed as [12b]:



The emission intensity, however, is very low for the filmed electrode, possibly

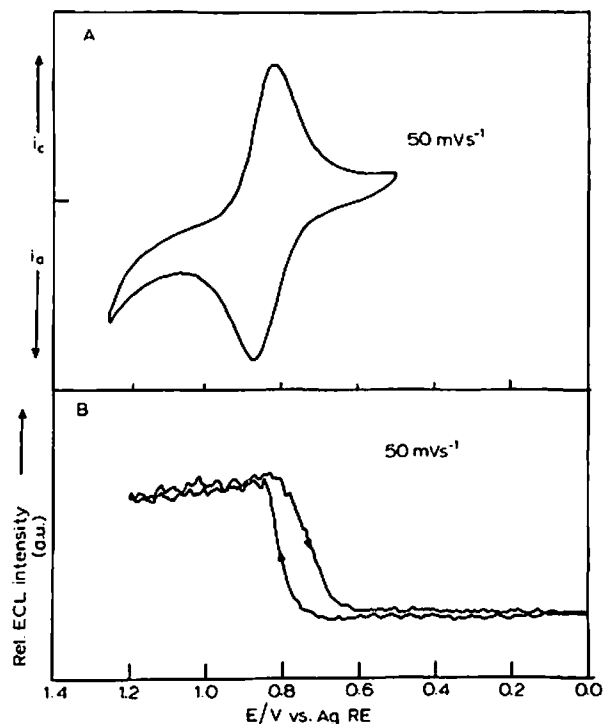


Fig. 7. (A) Cyclic voltammogram of surface-confined  $\text{Ru}(\text{bpy})_3^{2+}$  in  $0.04 \text{ M KNO}_3$  and (B) its relative ECL intensity as a function of potential, in the presence of oxalate ions ( $1 \text{ mM}$ ; pH 6).

because of quenching of the excited state by  $\text{Ru}(\text{bpy})_3^{3+}$  which is present in high concentration within the film. However, the existence of ECL with this system clearly indicates that  $\text{Ru}(\text{bpy})_3^{2+}$  is incorporated in the film and undergoes similar redox chemistry and reactions as that in Nafion-coated electrodes.

#### *Chemical reduction of $\text{Ru}(\text{bpy})_3^{3+}$ at high pH*

As described above the incorporation of  $\text{Ru}(\text{bpy})_3^{2+}$  in the pH range 2–7 gives rise to a well-characterized voltammogram typical of the  $\text{Ru}(\text{bpy})_3^{3+/2+}$  couple. On the other hand a more complicated voltammogram emerges when  $\text{Ru}(\text{bpy})_3^{2+}$  is incorporated from a basic solution (pH 10.5). As can be seen from Figs. 8A and 8B, build up of  $\text{Ru}(\text{bpy})_3^{2+}$  is accompanied by the growth of an additional reversible couple ( $E_{1/2} = 0.69 \text{ V}$ ) within the film. Both redox waves are persistent when the electrode is placed in pure supporting electrolyte (Fig. 8C). The origin of the second couple is well understood in light of recent work on the mechanistic pathway for spontaneous reduction of  $\text{Ru}(\text{bpy})_3^{3+}$  in basic solution [21]. In that work the reduction process is rapid and is accompanied by degradation of ~ 5–10% of the

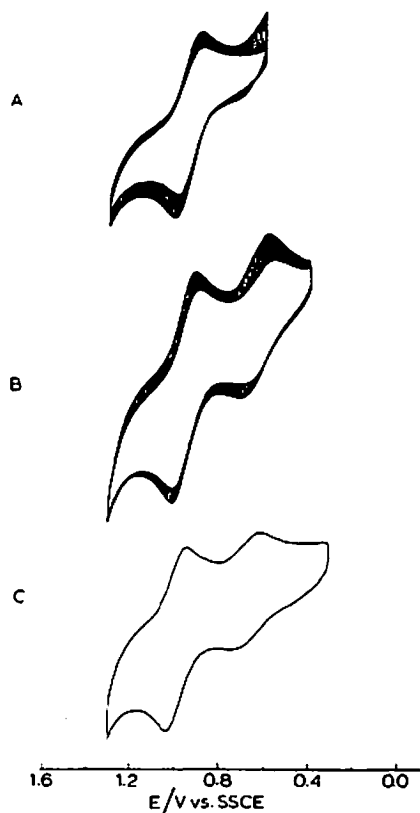


Fig. 8. (A) Voltammograms for a coated electrode in a  $\text{Ru}(\text{bpy})_3^{2+}$  solution (pH 10.5) showing the incorporation of  $\text{Ru}(\text{bpy})_3^{2+}$  into the film; (B) voltammograms showing that the incorporation of  $\text{Ru}(\text{bpy})_3^{2+}$  is accompanied by the growth of an additional reversible couple ( $E_{1/2} = 0.69$  V vs. SSCE); (C) Voltammogram for above modified electrode in pure electrolyte.

tris(bipyridine) complex and the primary degradation product, which was isolated by means of high pressure liquid chromatography (HPLC), had an  $E_{1/2}$  value of 0.67 V. This is virtually the same as that found for the additional reversible couple in Fig. 8. The large build up in the concentration of this couple is possible because of the large number of cycles over which  $\text{Ru}(\text{bpy})_3^{2+}$  is oxidized to the Ru(III) state.

#### *Electrocatalysis and mediated electron transfer*

Homogeneous solution studies have shown that  $\text{Ru}(\text{bpy})_3^{3+}$  can oxidize water to oxygen in the presence of a catalytic amount of Co(II) ions [13]. Such a reaction could be of importance in the design of photoelectrochemical systems involving the uphill splitting of water to oxygen and hydrogen. We have, therefore, investigated the possibility of Co(II) catalyzed oxygen evolution at our modified electrodes but

have failed to see any catalysis thus far. A possible reason for this failure lies in the stringent conditions required for this reaction. In solution studies, oxygen evolution is most efficient in the pH range 7–9 and a Co(II)/Ru(III) concentration of  $\sim 1:10$ . This would mean that for a bulk concentration of  $0.22\text{ M}$  for  $\text{Ru}(\text{bpy})_3^{2+}$  within the film the concentration of Co(II) would have to be  $\sim 2.2 \times 10^{-2}\text{ M}$ . Unfortunately, the solubility of Co(II) is only  $10^{-4}$ – $10^{-3}\text{ M}$  at pH 7 suggesting that Co(II) catalyzed oxygen evolution may be difficult to achieve at modified electrodes.

Experiments have also been carried out to test the behavior of hydroquinone ( $\text{H}_2\text{Q}$ ) at these modified GC electrodes. The voltammogram shown in Fig. 9A was obtained at a polished GC electrode and is in good agreement with the data reported by Adams for the  $\text{H}_2\text{Q}/\text{Q}$  system at a carbon paste electrode [22]. The large irreversibility observed ( $\Delta E_p \sim 300\text{ mV}$ ) has been attributed to sluggish charge transfer kinetics for the overall  $2e/2\text{H}^+$  process [23]. The voltammograms obtained

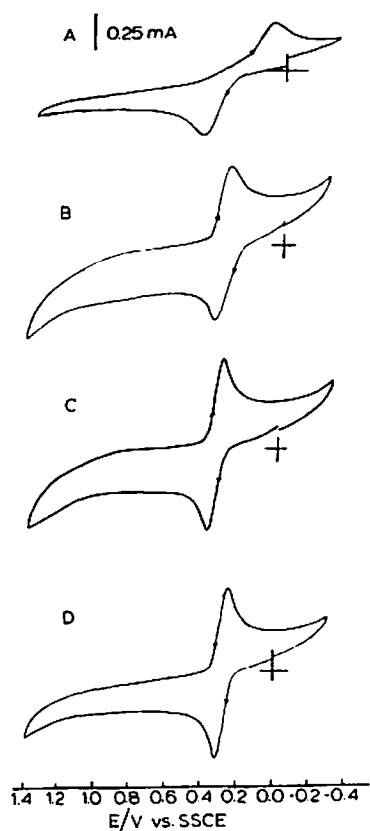


Fig. 9. Cyclic voltammetry in  $2\text{ mM}$  hydroquinone ( $0.05\text{ M}$  phosphate buffer; pH 4.8;  $0.1\text{ M}$   $\text{Na}_2\text{SO}_4$ ). (A) at polished GC electrode; (B) GC electrode modified in the presence of bpz; (C) GC electrode modified in the presence of  $\text{Ru}(\text{bpz})_3^+$ ; (D) GC electrode anodized in  $7\text{ M}$   $\text{H}_2\text{SO}_4$ . All voltammograms were recorded at  $20\text{ mV s}^{-1}$ .

for  $H_2Q$  at the modified electrodes prepared from bpz and  $Ru(bpz)_3^{2+}$  solutions are shown in Figs. 9B and 9C, respectively. Both electrodes behave identically with respect to the electrochemistry of the solution couple; there is a dramatic increase in reversibility of the overall charge-transfer process, with peak-to-peak separations of  $< 70$  mV and  $(i_p)_a/(i_p)_c \sim 1$ . The response was qualitatively similar for films of different thicknesses, and there was little change observed when  $Ru(bpy)_3^{2+}$  was incorporated into the films. The above result is of some interest in light of a recent report on the increasing reversibility of the  $H_2Q/Q$  system at a Pt electrode coated with a poly[2-(hydroxymethyl)-1,4-phenylene] oxide film [24]. However, in order to test whether the GC surface underwent any change during the film-forming process, a polished GC electrode was subjected to the same anodization process as used in preparing the film, but in the absence of dissolved bpz or  $Ru(bpz)_3^{2+}$ . The CV of  $H_2Q$  obtained at the anodized electrode (Fig. 9D) is very similar to those obtained at the filmed electrodes, but with an  $E_{1/2}$  value shifted  $\sim 60$  mV more negative. The above results suggest that in our case it is the anodized substrate, rather than the film, which plays a crucial role in enhancing the reversibility of the  $H_2Q/Q$  couple. A comparison of the traces in Figs. 9B, 9C and 9D also indicates that the films are quite porous, with  $H_2Q$  diffusing through them to the GC surface, since there is little difference in the relative peak heights for these voltammograms.

#### CONCLUSIONS

Bpz and  $Ru(bpz)_3^{2+}$  have been used for the preparation of two new types of films, both prepared via oxidative polymerization in acidic solutions. Based on the results described it appears that the films grow uniformly on the GC surface and the film thickness is proportional to the number of positive scans. The 'bpz' film is weakly conducting and preliminary experiments indicate a resistivity value of  $\sim 10^6 \Omega$  cm for this film.

The films incorporate  $Ru(bpy)_3^{2+}$  from aqueous solutions containing this ion and the concentration of electroactive material in the film is much greater than the solution concentration used to load the film. Hence, electrodes of this type may be useful in electroanalytical determinations of low concentration. The mechanism of retention of the electroactive ion is not well understood, but in light of the facile loss of material from the film, it appears that relatively weak attractive forces are involved. Perhaps hydrophobic interactions play an important role in retaining  $Ru(bpy)_3^{2+}$  within the film. Quite remarkably, loss of material from the surface is negligible when as little as 0.05 mM  $Ru(bpy)_3^{2+}$  is added to the supporting electrolyte. Since most modified electrodes are unstable upon cycling over a period of hours, modified electrodes of the present kind, i.e., those which are stable in the presence of minute quantities of the dissolved ion, are also interesting. We are uncertain about the mechanism of charge transport within the film. The inter-ionic separation of 0.6 nm does not rule out electron hopping within the film. At the same time, mass transfer of electroactive ions cannot be ruled out as a viable method of charge transport. Assuming that actual diffusion of  $Ru(bpy)_3^{2+}$  is the sole contributing

factor to  $D_{app}$ , it is estimated that the time required by the ions to diffuse across a 1.6  $\mu\text{m}$  film is  $\sim 5\text{--}6$  s, i.e., in the range of the voltammetric time scale. Moreover, the steady loss of material from the film upon electrochemical cycling in pure supporting electrolyte indicates that within the voltammetric time scale, electroactive ions are lost from the surface as well as the bulk of the film. Hence, physical diffusion of  $\text{Ru}(\text{bpy})_3^{2+}$  may indeed occur on the voltammetric time scale, and could, therefore, contribute to the charge transport process.

Upon oxidation the surface-confined  $\text{Ru}(\text{bpy})_3^{3+}$  reacts with hydroxide ions (pH 10.5) to give significant amounts of degraded product.  $\text{Ru}(\text{bpy})_3^{3+}$  also reacts with oxalate ions to give surface ECL. Thus oxalate ions appear to have rapid access to the film. The film is also very porous to  $\text{H}_2\text{Q}$ . The latter result contrasts the behavior of  $\text{H}_2\text{Q}$  at Nafion films, for which considerable attenuation of the voltammetric waves is observed.

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