

Cyclic Voltammetric Studies of Electropolymerized Films Based on Ruthenium(II/III) Bis(1,10 phenanthroline) (4-methyl-4'-vinyl-2,2'-bipyridine)

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Abstract

A ruthenium complex of bis(1,10-phenanthroline)(4-methyl-4'-vinyl-2,2'-bipyridine) was used to modify glassy carbon electrodes during cyclic voltammetry. The modification procedure is rapid and produces a polymer film on the glassy carbon electrode. Characterization cyclic voltammograms of the ruthenium-based polymer films in supporting electrolyte solutions are very similar to the electropolymerization cyclic voltammograms. The polymer thin films derived from the ruthenium complex exhibit Nernstian electron transfer with respect to the applied potential at low scan rates. This is shown by the small peak separation between the cathodic and anodic peaks during characterization. At scan rates greater than 1.00 V/sec, the films model the Randles-Sevcik equation for diffusion-controlled mass transfer processes. Surface coverage ranges from 9.42×10^{-11} mol/cm² to 4.76×10^{-10} mol/cm² and was calculated by integrating the area under the anodic peak of the characterization cyclic voltammograms.

Keywords: Electropolymerization, Cyclic voltammetry, Thin films

1. Introduction

Chemically modified electrodes (CMEs) over the past several decades have sparked considerable interest in analytical chemistry with respect to catalysis, electrochemical and chromo-electrochemical detection of organic compounds, and chemical sensor development. Since the pioneering work by Lane and Hubbard, over 20 years ago, involving chemisorbed metals on platinum electrode surfaces, numerous methods have been developed to immobilize compounds on electrode surfaces (Lane 1973). Several modification techniques of electrode surfaces include covalent attachment, spin coating, and electropolymerization. This research focuses on polymer films on glassy carbon electrode derived from electropolymerization.

Deliberate chemical alteration of the electrode surface may result in a more favorable interaction between an analyte and electrode surface by changing the thermodynamic and kinetic behavior of reactants, products, or intermediates involved in the redox transformation. These new electrodes possess properties which may be exploited to lay a foundation for new and interesting applications and devices such as electrochromic displays and sensors (Green et. al 1983, Hurrell et. al 1989, Li et. al 1991, Wang 1996, Allen et. al 1994, Bobacka et. al 1994). Electropolymerization offers a unique strategy of reproducibly immobilizing metal complexes with various degrees of electrochemical activity onto electrode surfaces (Brown et. al 1998, Brown et. al 2002). Research in the development of chemically modified electrodes by electrochemical polymerization using Ru(II) and Fe(II) vinylbipyridine complexes was performed by Calvert (Calvert et al. 1983). Others such as Guarr et al. have investigated the mechanism of electropolymerization for ruthenium bis(1,10-phenanthroline)(4-methyl-4'-vinyl-2,2'-bipyridine), Ru(II)-(phen)₂vbpy (where vbpy=vinyl bipyridine), complexes onto glassy carbon electrode surfaces (Guarr et. al 1987). The electrodes presented herein require approximately 30 minutes to modify depending upon the scan rate used for electropolymerization.

More recently, we investigated the use of electrodes chemically modified with Ru(II)-5-amino-1,10-phenanthroline-bis(bipyridine) complexes towards the electrochemical oxidation detection of hydrazine at significantly lowered overpotentials (Pinter et. al 2007). These films were based on the oxidation of the amine group of the organic moiety. Planning the incorporation of immobilized ruthenium complexes for the design of amperometric sensors for hydrazine, we have revisited the electropolymerization of a ruthenium compound containing mixed ligands of vinylbipyridine and phenanthroline. The films derived from these mixed ligands were electrochemically characterized using cyclic voltammetry. The characterization data would provide

useful information related to the design of sensors for hydrazine. This paper reports on some of the electrochemical characteristics of the ruthenium-based films on glassy carbon electrode surfaces.

2. Experimental

2.1 Reagents and Solutions

The ruthenium complex, Ru(II)-(phen)₂vbpy, was provided by Guarr and co-workers. Propylene carbonate and tetraethylammonium perchlorate (TEAP), used as solvent and supporting electrolyte for electropolymerization of the monomer and characterization of the films were obtained from Sigma-Aldrich (St. Louis, MO). The TEAP was dried under vacuum prior to use. The concentration of monomer and TEAP were 1.00 x 10⁻³ M and 0.100 M respectively.

2.2 Instrumentation

Electropolymerizations and other cyclic voltammetric measurements were performed with a 601A Electrochemical Analyzer (CHI Instruments, Inc., Austin, TX). The three-electrode electrochemical cell used in this work consisted of a glassy carbon working electrode (diameter = 3 mm), a Ag/AgCl, 3 M NaCl reference electrode, and a platinum wire auxiliary electrode, all from CHI Instruments.

2.3 Electropolymerization and Characterization of Thin Films

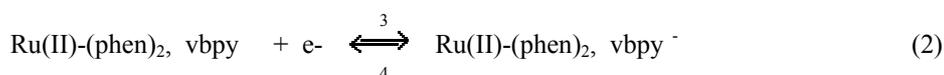
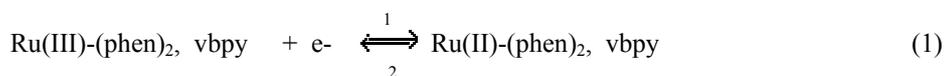
Before commencing with the electrode modification with the ruthenium complex, the glassy carbon working electrode was polished by placing several drops of polishing alumina suspension (0.05 μm particle size from Bioanalytical Systems) on a wetted polishing pad and moving the electrode in a circular motion across the surface of the polishing pad. Prior to all electropolymerizations, the solutions containing the ruthenium complex and the supporting electrolyte were deoxygenated with nitrogen gas for five minutes and a nitrogen blanket was maintained over the solutions for the duration of the experiments. The electropolymerization was accomplished by cycling the potential of the glassy carbon electrode between +1.600 V and -1.600 V. The dependence of peak current on the scan rate of electropolymerization was made using scan rates from 0.100 V/sec to 1.000 V/sec. The maximum number of electropolymerization cycles was 90.

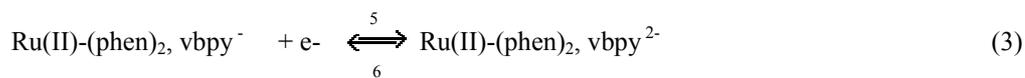
The films were characterized between +1.600 V and -1.600 V or -0.400 V vs. Ag/AgCl in the supporting electrolyte solution of propylene carbonate with TEAP. Scan rates for characterization ranged from 0.10 V/sec to 10 V/sec.

3. Results and Discussion

3.1 Electropolymerization of Ru(II)-(phen)₂vbpy on Glassy Carbon Electrodes

The deposition of the ruthenium complex onto glassy carbon electrodes by initiating reductive electrochemical polymerizations of the ruthenium complex was accomplished by cycling the potential applied to the glassy carbon electrode from 1.600 V to -1.600 V. This is an efficient way of producing a multi-layered polymer film and hence produce a three-dimensional network of ruthenium redox centers. Several researchers have reported values of 24-1560 monolayers based upon the packing density of the polymer films formed from Bis(vinylterpyridine)cobalt(II). These films were used in the electrochemical reduction of carbon dioxide and oxygen (Abruna et.al 1981, Hurrell et. al 1988). After completing 90 cycles of electropolymerization, three redox couples showing electrochemical reversibility persisted as shown in Figure 1. The first redox couple (Peaks 1 and 2) has a formal reduction potential, E⁰=(E_{pa}+E_{pc})/2, of 1.215 V and is related the electrochemical activity of Ru(III/II). Two other key redox couples with E⁰ values of -1.255 V (Peaks 3 and 4) and -1.413 V (Peaks 5 and 6) were identified. These peaks correspond to the electrochemical activity of the ligand, vinylbipyridine (Meyer et. al 2005, Guarr et. al 1987, Calvert et.al 1983). Several research groups also identified two ligand-based redox processes of the ruthenium vinylbipyridine complexes based upon potential scanning methods. Cathodic peak 7 (ca. -1.150 V) and anodic peak 8 (ca. 1.250 V) did not appear until cycle 5, and are associated with the processes of charge trapping as the polymeric thin film forms (Guarr et. al 1987). Equations 1-3 summarize the electrochemical reactions corresponding to the reversible electrochemical processes shown in Figure 1.





Diffusion controlled conditions dominate the mass transfer mechanism of the monomer to the electrode surface during electropolymerization as evidenced by linear diagnostic plots of the peak current versus the square root of the scan rate (Figure 2) provided during the third cycle of the electropolymerization (Brown et. al 2002). Peak separation for the Ru(III/II) redox couple ranges from 0.071 V-0.118 V using scan rates of 0.100 V/sec–1.00 V/sec, and follows the trend for electrochemical systems transitioning from reversible to quasireversible electrochemistry.

The semi-conducting film containing Ru(III/II) redox centers acts as a mediator at the film-solution interface to facilitate the electropolymerization process. Increases in the peak currents per cyclic voltammetric scan for electropolymerization indicates the formation and growth of the polymeric thin film on the glassy carbon electrode. After 90 cycles of electropolymerization, the peak currents approach a steady-state value. This is partly due to a reduced electrode surface area available for deposition as the number of electropolymerization cycles approaches 90, and a thicker film which causes a reduction in charge migration rate within the film. Furthermore, plots of the peak current versus the voltammetric cycle of electropolymerization are linear with a non-zero intercept which signifies a fast initial electropolymerization process that begins diffusion of the monomer to the electrode surface (Calvert et. al 1983). The mechanism for the electropolymerization of this complex and similar complexes with vinyl groups have been reported in detail and involves the formation of radical anions which react at the electrode surface and subsequent chemical reactions (Guarr et. al 1987).

3.2 Electrochemical Behavior of Ru(II)-(phen)₂, vbpy Polymer Films

After electrochemical deposition of the ruthenium complex, the glassy carbon electrode revealed a slight orange color. Figure 3 shows the subsequent electrochemical characterization of the electrode surface in 0.10 M TEAP in propylene carbonate at a scan rate of 0.100 V/sec which produced the same redox couples as shown in Figure 1. The peaks related to the charge trapping process were also observed when characterizing the thin films in the same supporting electrolyte solution. Observation of the peaks in the same proximity as the peaks in the solution phase electrochemistry provides further evidence for successful immobilization of the ruthenium complex onto the glassy carbon electrode. The electrochemical observations reflect charge transfer within the polymer film between neighboring redox centers through a proposed “electron-hopping” mechanism and are related to Equations 1-3.

Characterizing the film in the supporting electrolyte solution of 0.10 M TEAP in propylene carbonate with a circumscribed potential window from 1.600 V to 0.400 V (Figure 4) restricts the electrochemistry to involve the Ru(III/II) redox couple, corresponding to Equation 1. At scan rates higher than 1.000 V/sec, the voltammograms resemble solution phase diffusion mass transfer conditions. The ΔE_p values range from 0.0210 V to 0.485 V using scan rates between 0.100 V/sec to 10.0 V/sec. The increase in peak separation with higher scan rates is attributed to kinetic limitations of charge transfer between redox sites within the polymer film. Scan rates lower than 0.020 V sec⁻¹ produced $\Delta E_p \sim 0$ V. This peak separation indicates facile charge transfer within the film and Nernstian equilibrium conditions of charge transfer with the applied potential. The peak width at half-height is greater than 90.6 mV which indicates non-equivalent redox centers and/or repulsive or attractive forces within the film [Brown et. al 2002]. Worth mentioning is that when the film is in a fully reduced state, the film has a negative charge which must be compensated by a counterion entering the film, (i.e., N(CH₃CH₂)₄⁺), in order to maintain charge electroneutrality. Due to solvent-ion interactions, the entering counterion is accompanied by solvent sphere(s). This may result in possible polymeric film swelling. Diagnostic plots of the anodic and cathodic peak current versus the scan rate from 1.600 V to 0.400 V for the thin films were linear for scan rates < 1 V/sec. Using scan rates < 1 V/sec allowed for finite diffusion boundary conditions to dominate the electrochemical charge transfer process. However, plots of the peak current versus the square root of the scan rate were linear for scan rates > 1 V/sec, indicating semi-infinite diffusion conditions. Under the latter conditions, it is possible that not all the redox sites are reduced and oxidized during the voltammetric scan. In this case, the charge transfer models the Randles-Sevcik equation:

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C$$

where D represents the apparent charge transfer coefficient and C represents the concentration of oxidized or reduced ruthenium sites within the film. The other symbols have their normal electrochemical convention. In addition, at higher scan rates, the depletion layer above the surface of the electrode is thinner than the film thickness, and hence the system resembles semi-infinite diffusional boundary conditions (Collins 1996).

3.2.1 Surface Coverage

Surface coverage of the electrode was determined using the equation: $\Gamma = Q/nFA$, where Γ is the surface coverage in mol/cm², Q is the charge in coulombs, A is the area of the electrode surface in cm², and n is the number of electrons transferred during redox transformation. The value of Q was determined by integrating the area under the cathodic peak or anodic peak during the characterization of the electrode in the supporting electrolyte solution. The surface coverage was determined using anodic peak, corresponding to the $\text{Ru}^{2+} \rightarrow \text{Ru}^{3+} + e^-$ process. Figure 5 shows the surface coverage with respect to the number of cycles of electropolymerization. Surface coverage ranges from 9.42×10^{-11} mol/cm² to 4.76×10^{-10} mol/cm², corresponding to 30-90 cycles of electropolymerization. In addition, Figure 5 shows a leveling-effect corresponding to approximately 90 cycles of electropolymerization, correlating with the time needed to reach a steady-state peak current during the electropolymerization process.

4. Conclusion

Compared to other electrode modification procedures, the preparation of these films by electropolymerization using cyclic voltammetry is relatively simple in design, and is a one-step process. Building into the monomer an organic moiety such as a vinyl substituent allows for successful electropolymerization reactions to occur. The thin films exhibit facile electron transfer properties in propylene carbonate/TEAP supporting electrolyte solutions. For example, characterization scan rates near 1.000 V/sec produced peak separations under 0.100 V. At low scan rates, the peak separations are practically 0 mV. However, metal-based modified electrodes have peak separations of approximately 0.700 V at 1.000 V/sec (Razmi-Zerbin et. al 2002). The films presented herein require about 30 minutes to prepare and are now being investigated for long-term stability for potential use in flow injection analysis in the determination of hydrazine.

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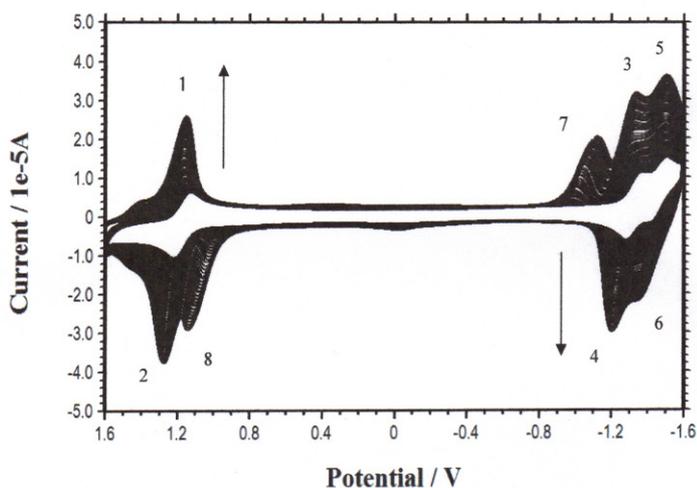


Figure 1. Electropolymerization of 1.00×10^{-3} M Ru(II)-(phen)₂vbpy. Supporting electrolyte is 0.100 M TEAP and solvent is propylene carbonate. Scan Rate = 0.100 V/sec. Seventy cycles of electropolymerization from 1.600 V to -1.600 V vs. Ag/AgCl

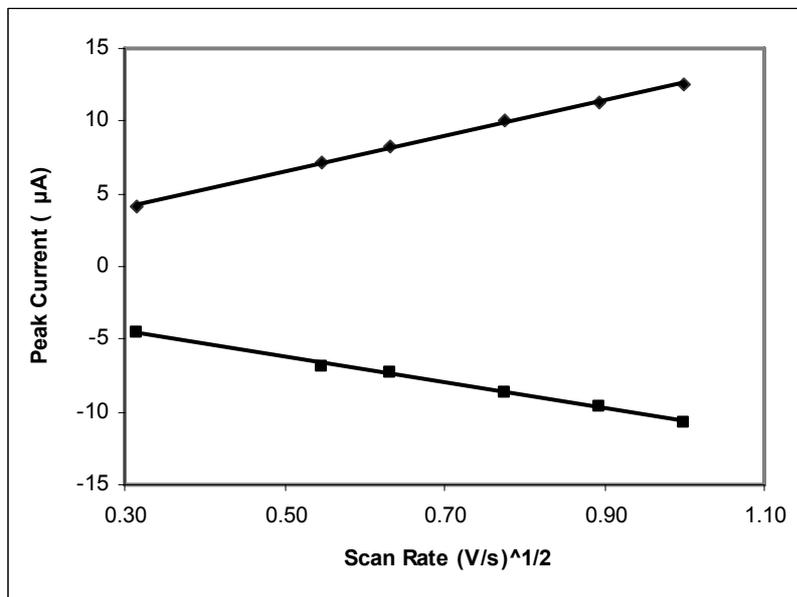


Figure 2. Plots of cathodic and anodic peak currents at various scan rates during electropolymerization of the ruthenium complex (1.00×10^{-3} M Ru(II)-(phen)₂v bpy in 0.10 M TEAP in propylene carbonate). Scan rates: 0.100 V/sec -1.00 V/sec. Peak currents taken during the third cycle of electropolymerization corresponding to the Ru(III/II) redox couple

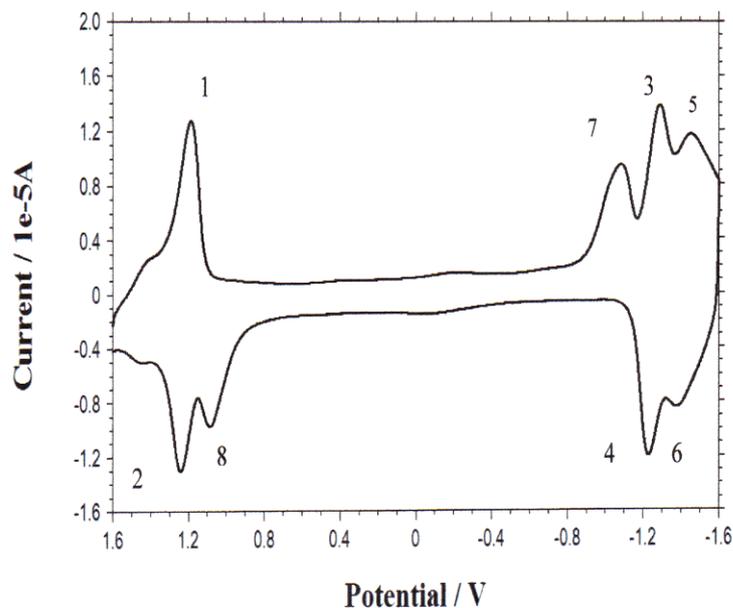


Figure 3. Characterization of ruthenium film in 0.100 M TEAP in propylene carbonate at 0.100 V/sec from 1.600 V to -1.600 V vs. Ag/AgCl

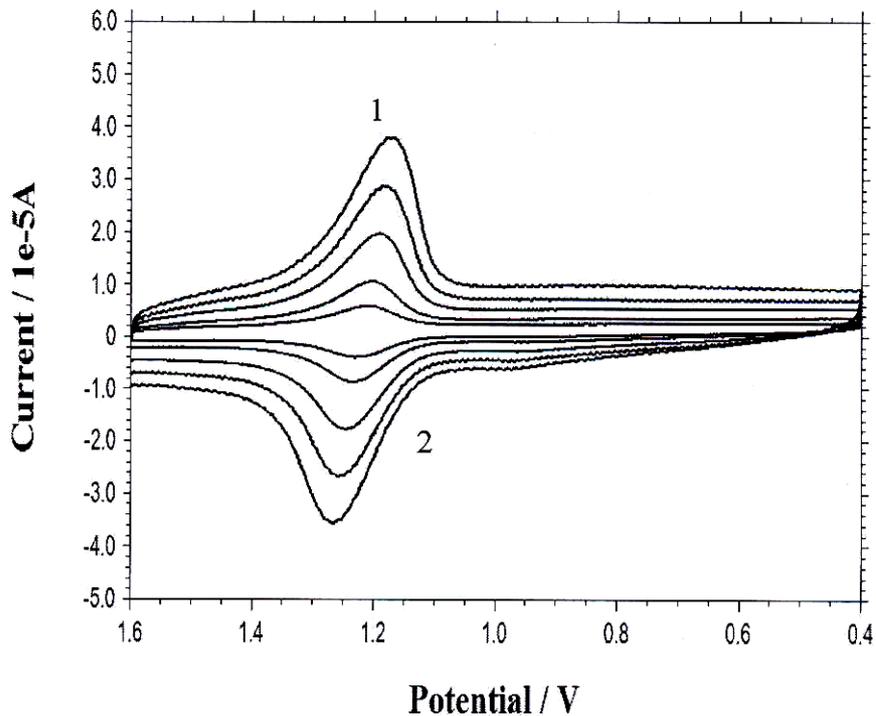


Figure 4. Characterization of ruthenium film in 0.100 M TEAP in propylene carbonate at 0.100 V/sec– 1.00 V/sec from 1.600 V to 0.400 V based on the Ru(III/II) redox couple

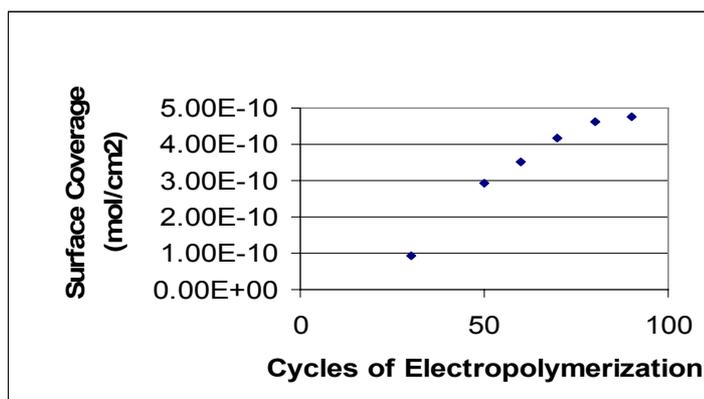


Figure 5. Profile of surface coverage with the number of electropolymerization cycles. Data taken from the characterization of the film corresponding to $\text{Ru}^{2+} \rightarrow \text{Ru}^{3+} + e^-$ anodic peak in 0.10 M TEAP in propylene carbonate