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Chapter

Electrochemical Preparation and Characterization of Chemically Modified Electrodes

Kenneth L. Brown

Abstract

This chapter will focus on the use of electropolymerization schemes and reactions to modify electrode surfaces with organo- and organometallic compounds such as metal(II)-4, 9, 16, 23-tetraminophthalocyanines and metal complexes of 5-amino-1, 10-phenanthroline. The chemical modification described herein focuses on the formation of polymer films on electrode surfaces. In addition, the characterization of such films using cyclic voltammetry, chronoamperometry, chronocoulometry, and electrochemical impedance spectroscopy will be a key emphasis within this chapter. A brief review of the literature concerning these techniques along with relevant compounds that have been used in studies related to these voltammetric techniques is presented.

Keywords: electropolymerization, cyclic voltammetry, polymer films

1. Introduction

Chemically modified electrodes (CMEs) over the last decade has continued to spark considerable interest in analytical chemistry with respect to electrocatalysis, development of new electrochemical and spectroelectrochemical sensors, and electrochromic displays, just to name a few. Since the novel work by Lane and Hubbard involving chemisorbed metals on platinum electrode surfaces, numerous methods have been developed to immobilize species onto a variety of electrode surfaces. These modification techniques include covalent attachment, spin coating, electropolymerization, and others.

2. Significance of electrode modification

The significance and role of chemically modified electrodes (CMEs) to catalyze or modify the rate of chemical reactions has been extensively surveyed for a number of applications [1–4] . The methodology for modifying an electrode surface has a significant impact on its short-term and long-term use in analytical applications. Many of these applications involve the detection of different types of analytes, including transition metal ions, peroxides, anions, and organic species [5–8]. Understanding the properties of a chemically modified electrode such as mechanisms of charge transfer, electrode stability in different chemical environments

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such as low and high pH certainly lays a foundation for developing methods based on certain types of reactions (e.g., chemiluminescence).

Immobilized species on electrode surfaces can be composed of several monolayers or several thousand monolayers, as in the case of electropolymerized thin films [1]. The electrode modification procedure is tailored to control charge transfer rates for specific applications such as (1) electrocatalysis, (2) solar energy conversion, (3) improving electrode stability, (4) development of sensors/biosensors, (5) directed and controlled mediated charge transfer, and (6) electrochromism for color displays which are potential dependent [9–13]. Such applications are usually based upon the charge-transfer properties of the compound immobilized on the electrode. Presently, many applications involve the use polymeric multilayered thin films, which may be loaded ionomers, redox polymers, or electronically conducting polymers. Some of the methods for modifying electrodes include chemisorption, covalent binding, vacuum deposition, electroplating, electropolymerization, and others [14–20].

One of the benefits of using electropolymerization reactions to modify electrode surfaces is the ability to change the properties of the polymer film by changing the experimental conditions (e.g., scan rate in cyclic voltammetry); the ability to chemically modify irregular shaped electrodes, and the ability to tailor an electrode surface for specific applications.

Electropolymerized thin films as selective reagents on various surfaces have been at the forefront in designing amperometric sensors. Two significant advantages of using electropolymerized thin films and coatings in electrochemical amperometric sensors and spectroelectrochemical sensors are the ability to (1) better control the chemical and physical nature of the reaction system, and (2) provide a much higher "effective concentration" per unit area for reactions to occur. The challenge in designing polymeric films is tailoring the molecular architecture to control and direct chemical reactivity with selected compounds [17, 18]. One of the most widely used methods in developing polymeric films on various electrode surfaces is electropolymerization via cyclic voltammetry [19, 20]. This technique, under consistent experimental conditions, produces a polymeric film consistent in molecular architecture and reactivity toward specific compounds.

The electrochemical reactivity of specific compounds toward polymeric films is influenced by a variety of factors such as polymer lattice orientations, film thickness, solvent content within the film, and counterion ingress and egress into and out of the polymeric film [19, 20]. A number of electrochemical and hyphenated electrochemical techniques have been used to characterize chemically modified electrodes and these include cyclic voltammetry, square wave voltammetry, spectro-electrochemistry, electrochemical quartz crystal microbalance, and electrochemical impedance spectroscopy, just to name a few.

3. Classification of polymer modified electrodes

3.1 Loaded ionomers

These polymer coatings are polycation or polyanion ion-exchange polymers, which contain electroactive species. The ion-exchange polymer is attached to an electrode via solvent evaporation or spin coating which is then dipped into a solution containing electroactive species. The electroactive species are essentially bound to the ion-exchange polymer through electrostatic forces. One of the most popular and extensively used ion-exchange polymers is Nafion, a perfluorosulfonate

ion-exchanger [9]. Other ion-exchange polymers which have been investigated are protonated forms of poly(vinylpyridine), and poly-N-methylpyrrole with immobilized poly(4-styrenesulfonate) ions as a cation-exchanger [9].

Anson and Oyama utilized protonated forms of poly(4-vinylpyridine) as cation exchange polymers to incorporate Ru^{3+}, hexacyanoferrate ($Fe(CN)_6^{3-/4-}$, and hexachloroiridate ($IrCl_6^{2-/3-}$) [10]. Maksymuk and Doblhofer used poly-N-methylpyrrole with immobilized poly(4-styrenesulfonate) ions as a cation-exchanger to incorporate $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/4+}$, Eu^{3+}/Eu^{2+}, $Co(en)_3^{3+/2+}$, and $Fe(C_2O_4)_3^{3-/4-}$ [11]. The electropolymerization of pyrrole, aniline, or N-methylpyrrole in the presence of polyanions such as poly(vinylsulfate), and poly-(stryrenesulfonate) forms an ion-exchanger, which is electroactive over a wide potential range [9]. Other workers have incorporated electroactive inorganic cations such as $Co(2,2'\text{-bipyridine})_3^{2+}$, and $Ru(2,2'\text{-bipyridine})_3^{2+}$ into polystyrene sulfonate [12]. The widely used Nafion has been utilized by Yagi and co-workers to investigate the charge transfer properties of tris(2,2'-bipyridine)Ru^{2+} [13]. The charge transport parameters are based upon two processes, namely, physical displacement of the electroactive center, and electron hopping or electron self-exchange between electroactive centers [9]. Although this method is useful in studying charge transport properties of redox active species within membranes, it suffers from a major disadvantage in that the electroactive species are not irreversibly bound to the ion-exchange matrix, and consequently leaches out into the solution.

3.2 Redox polymers

Polymer films with redox-active centers covalently bound to a redox inactive polymer organic moiety is a redox polymer. These polymers can be synthesized in large quantities, and then immobilized onto electrode surfaces by spin coating, or dip coating. One major obstacle associated with using preformed redox polymers is its low solubility in solvents. The solvent must evaporate when using spin coating, dip coating, or solvent evaporation methods in order to leave the preformed polymer on the electrode surface. The mechanism of charge transfer has been exclusively identified as electron hopping or electron self-exchange between neighboring redox centers. Such polymers only show conductivity over a limited potential range. Shgehara and co-workers incorporated $Fe(CN)_5^{3-}$ into poly(4-vinylpyridine) via coordination, and attached the polymer to graphite electrodes by solvent evaporation [21].

One of the most successful and appealing ways to form redox polymers on electrode surfaces is through electropolymerization using cyclic voltammetry. Electropolymerization is an attractive approach because it allows film thickness to be consistently reproduced, and monitored. In addition, electrode coverage is normally complete after many scans, and requires many layers because the polymer may not grow in regular layers. This gives rise to what is commonly called a multilayered polymeric thin film. As mentioned previously, these electrodes show a greater electrochemical response than monolayer coverages. Multilayered films have more electroactive sites in the form of layers and as many as 1000 layers can be formed on a single electrode surface [1, 22]. Iron and ruthenium complexes of 2,2'-bipyridine have been electropolymerized on platinum, glassy carbon, and metal oxide electrodes by Ellis and Meyer to selectively direct charge transfer to redox species in solution [23]. The same research group performed oxidative electropolymerization of ruthenium complexes of 4-aminopyridine, 3-aminopyridine, and 5-amino-1,10 phenanthroline [24]. Metalloporphyrins have been used in electropolymerization by several research groups. Derivatives of nickel(II) and

cobalt(II)-tetraphenylporphyrins with amino-, hydroxy-, and pyrrole-, substituents have been electropolymerized by Murray and co-workers [25]. Such compounds are used because of their rich chemistry in terms of electron transfer properties. These type of compounds can be used as possible catalysts since the central metal ion is capable of axially coordinating with extra ligands. The mechanism(s) for generating polymeric multilayered films are based upon similar principles of either forming radical cations or anions which couple together. This process is looked into further under the discussion of "electropolymerization reactions."

3.3 Electronically conducting polymers

Electronically conducting polymers are marked by extended π-electron systems which are delocalized. These are can be formed in a similar manner as redox polymers using electropolymerization schemes. One of the first compounds to be used in forming these polymers was pyrrole by Diaz and Kanazawa [26]. Later, other research groups explored aniline, furan, and other heterocyclic aromatic compounds for electropolymerization. The polymerization of these compounds proceeds by the mechanism(s) similar to derivatives of metalloporphyrins. For example, pyrrole forms polymeric films via radical cation intermediates. In all cases, electropolymerization is governed by Faraday's Law and hence it is easy to monitor film thickness.

Charge transport within the electropolymerized film is attributed to interchain electron hopping coupled the egress or ingress of counterions to maintain charge electroneutrality during electrochemical characterization or stimulation. The chain alignment plays a significant role in the kinetics of charge transfer, and the conductivity of these films. Film thickness can be an important factor in designing sensors because analytes may penetrate through the film to the electrode surface, partially through the film, or to the film solution interface in order to undergo a charge transfer electrocatalytic reaction [11].

4. Electropolymerization reactions

Electropolymerization can be performed using cyclic voltammetry (CV) wherein experimental CV conditions such as scan rate, number of cycles, and the potential window all affect the overall composition of the resultant polymeric thin films. Electropolymerization reactions are first preceded by a small of amount of adsorption onto the electrode surface. In order for a monomer to be electropolymerized on an electrode surface, it must possess functional groups which can be oxidized or reduced via a π* molecular orbital or non-bonding electrons on a heteroatom. The most common functional groups noted to facilitate electropolymerizations reactions are amino-, hydroxy-, and vinyl groups. In these instances, there is a lone pair of electrons or a π-electron system available. These organic moieties give rise to radical cations or anions depending upon whether oxidation or reduction is the initiation step. These radical species couple at the electrode surface, and undergo redox processes to generate the thin film. The conductivity of the developing film on the electrode surface serves to mediate charge transfer at the film-solution interface so that more monomers can be incorporated into the growing film. Statistically, increasing the number of aforementioned functional groups on a compound favors the formation of radical species and a heavily cross-linked polymer film. In addition, multiple functional groups on the monomer for initiating polymerization reactions promote the correct orientation for the incorporation of

monomer units into the growing polymer film. This is significant when one considers how the electrode surface can be fully covered with up to 1000 monolayers.

4.1 Oxidative electropolymerization

Oxidative electropolymerization can be performed when compounds have such substituents such as amino-, and hydroxy- groups. It has been well-established that with such functional groups electropolymerization proceeds by oxidation involving the lone pair of electrons on the heteroatom [27]. The electrooxidation of aniline (1) in **Figure 1**, via the lone pair of electrons of the nitrogen yields the radical cation (2). The radical cation (2), loses a proton (3), and then undergoes radical coupling to form (4). The dimers are oxidized to form N=N double bonds (5).

Our research group has applied this mechanism to the electropolymerization of metal(II)-tetraaminophthalocyanine [M(II)TAPc] to prepare polymer thin films. For compounds such as M(II)TAPc multiple amine sites allow polymerization to continue, and film thickness to increase with greater crosslinking; the initiation step for generating poly-M(II)TAPc begins with an electrochemical oxidation of the amino- substituent that produces a radical cation. In the electropolymerization of zinc, and cobalt-tetraaminophthalo-cyanine shown in **Figure 2** using cyclic voltammetry, three reversible redox couples were identified [28, 29]. All electrochemical transformations within the zinc complex occur on the ligand system whereas CoTAPc has redox reactions on the ligand and central metal. The nonzero current of these polymer films at the negative switching potential is the result of the capacitance of the polymer films due to extensive crosslinking facilitated by the multiple amine sites on the compound. Metal complexes of ruthenium and iron involving the 5-amino-1-10-phenanthroline ligand shown in **Figure 3** have been electropolymerized onto glassy carbon, platinum, and ITO electrode surfaces.

These films on indium tin oxide surfaces demonstrate reversible electrochromism when the applied potential changed from 0 to 1.50 V (vs Ag/AgCl in 3 M KCl). Several research groups have shown that the electropolymerization of these complexes
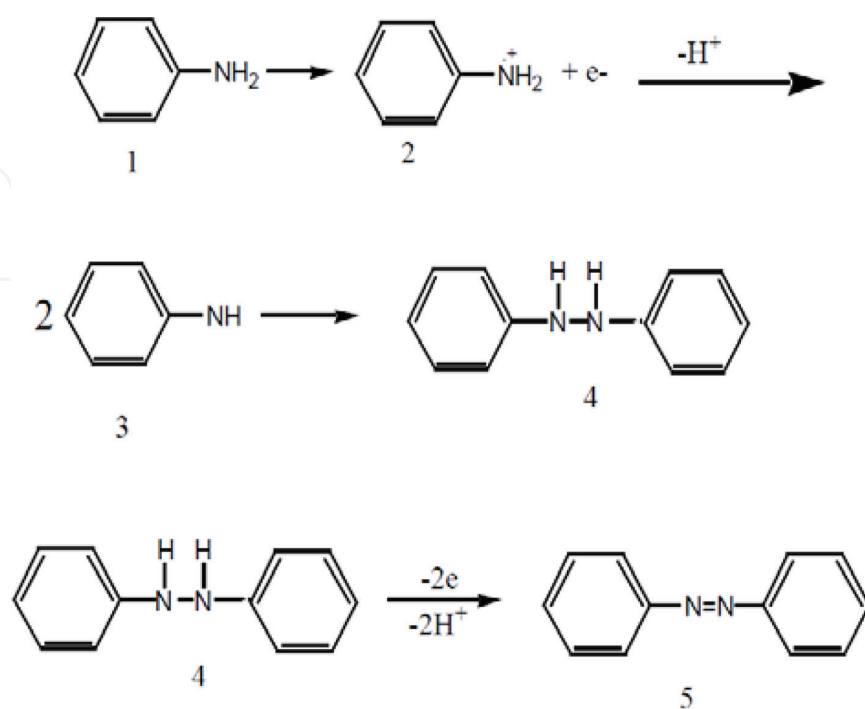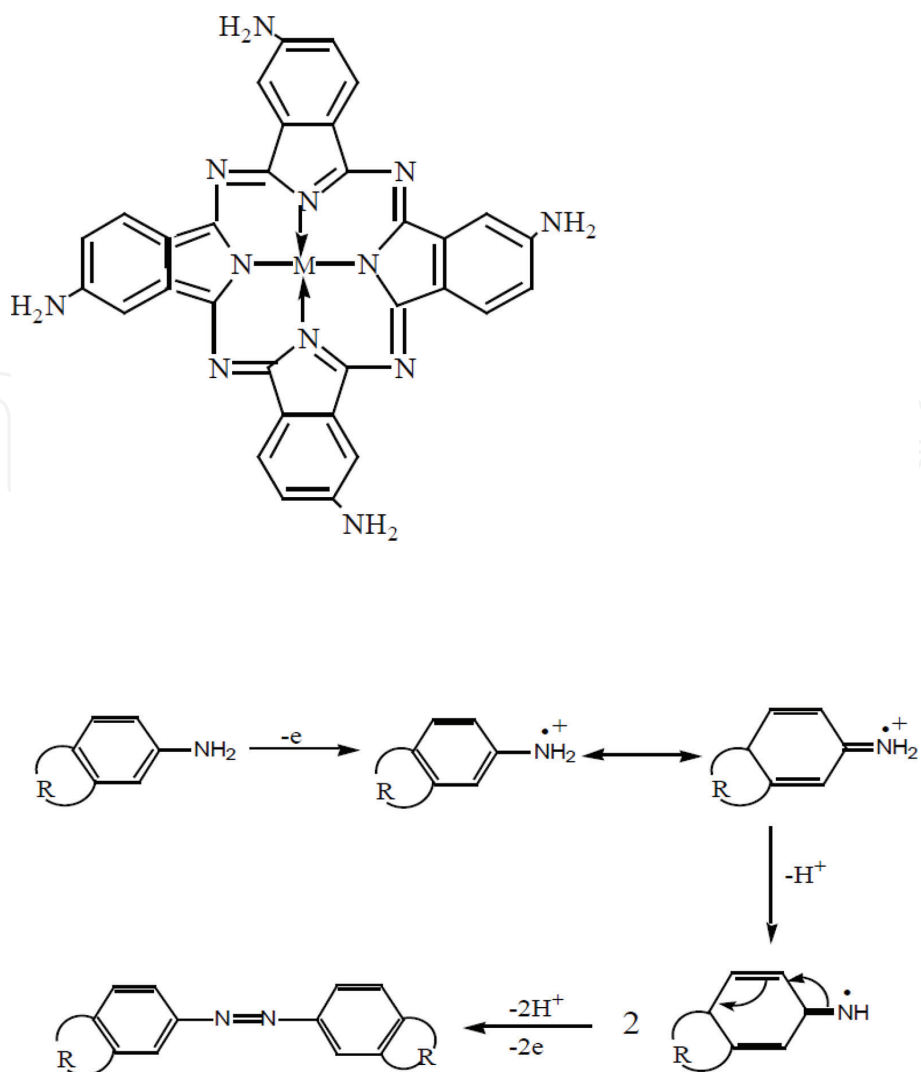
Figure 1.
Electropolymerization reactions of aniline.

Figure 2.
Structure of metal(II)-4, 9, 16, 23-tetraaminophthalo-cyanine [M(II)TAPc] and corresponding electropolymerization reactions.
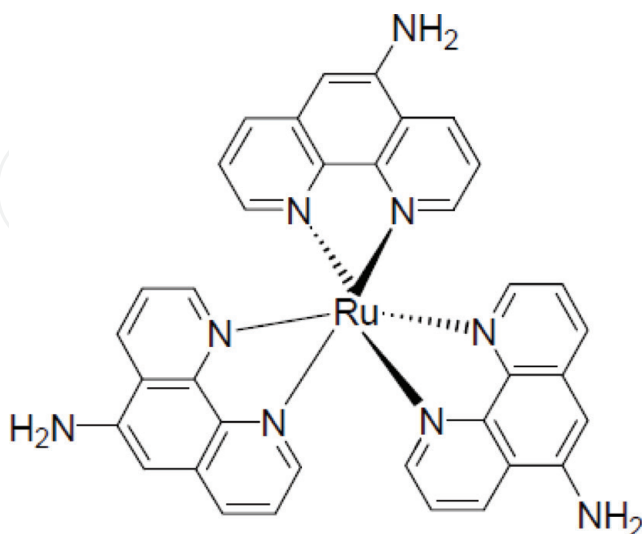

Figure 3.
Structure of 5-amino-1, 10-phenanthroline ruthenium(II).

proceeds in a similar manner as the TAPc metal complexes (**Figures 4** and **5**) but the electrochemical reversibility is more noted with the 5-amino-1-10-phenanthroline ligand.
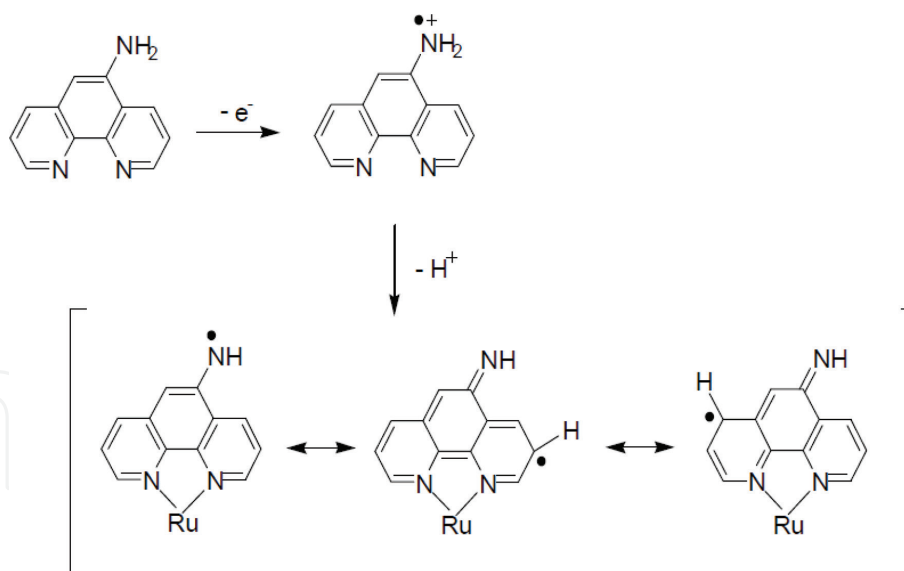
Figure 4.
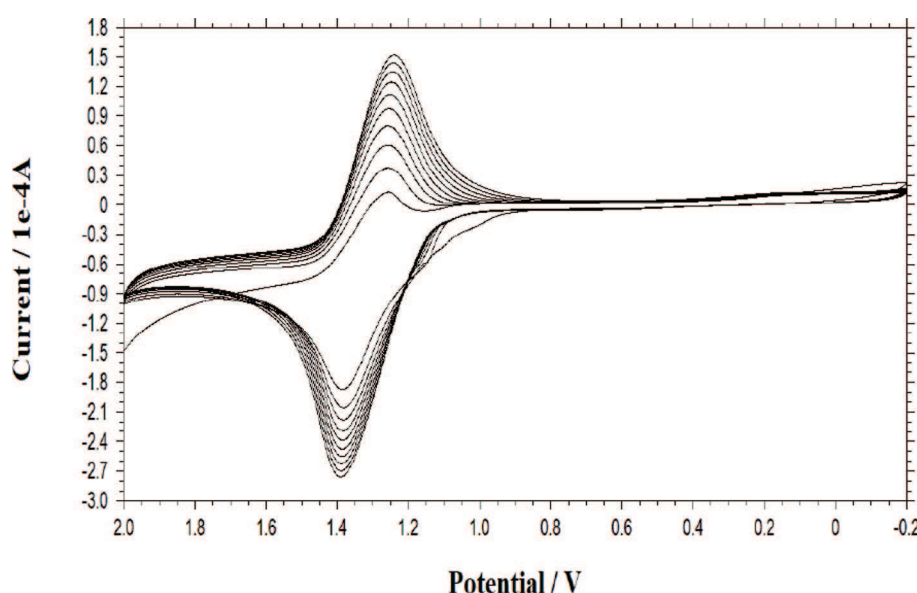*Electrochemical initiation step involving the 5-amino-1, 10-phenanthroline ligand.*

Figure 5.
Cyclic voltammogram of the electropolymerization of 5-amino-1, 10-phenanthroline iron(II).

5. Characterization of chemically modified electrodes

Chemically modified electrodes have been characterized using a variety of electro-
chemical, spectroscopic, mechanical, and hyphenated electrochemical-spectroscopic
techniques. The most notably electrochemical characterization tools are cyclic voltam-
metry, chronocoulometry, quartz crystal microbalance, electrochemical impedance
spectroscopy, and spectroelectrochemistry. Using a dynamic potential scanning
method such as cyclic voltammetry provides both quantitative and qualitative data on
the nature of electropolymerized films. For example, when characterizing polymer
films using cyclic voltammetry, it has been well-established that the peak width
at half-height for cathodic and anodic peaks is 90.4 mV/n, where n represents the
number of electrons involved the redox transformation. However, many electropo-
lymerized films have peak widths at half height that exceeds 90.4 mV/n (**Figure 6**).
This is indicative of repulsive or attractive forces in the film or the presence of non-
equivalent redox sites within the film. The electrochemical response of these films is
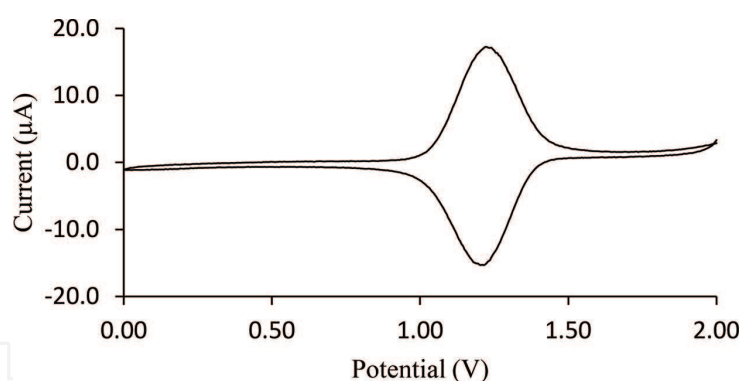
Figure 6.
Characterization of 5-amino-1, 10-phenanthroline iron(II) polymer film on a glassy carbon electrode.

the result of electron self-exchange reactions, or "electron-hopping" within the film. Concomitantly, egress or ingress of counterions from the polymer film or supporting electrolyte solution, respectively occurs when the film is oxidized or reduced using cyclic potentiodynamic conditions.

Electrochemical quartz crystal microbalance (EQCM) during CV studies have been used to determine the number of ions and associated solvent molecules entering or leaving polymer film as the films become oxidized or reduced. This provides a better understanding of the composition of polymer films real-time when they undergo a redox transformation. Cyclic voltammetry coupled with chronocoulometry has been used to determine the apparent charge transfer coefficient for electron hopping-self-exchange reactions for polymer films. Electrochemical impedance spectroscopy is widely used to study thin dynamics, corrosion of surfaces, to guide the development of sensors and biosensors, and a host of other applications.

5.1 Electrochemical quartz crystal microbalance studies

Quartz crystal microbalance (QCM) studies are based upon a deviation of the oscillation resonant frequency of a quartz crystal when the mass of the crystal changes. Oscillation frequency decreases as mass of the crystal increases. The instrumentation is sensitive enough to monitor the adsorption of gases onto the surface of the quartz crystal. When electrochemistry is combined with QCM as a hyphenated technique (EQCM), simultaneous *in situ* electrochemical and mass measurements at electrode surfaces are possible which allows electropolymerization mechanisms to be studied [30, 31]. Using EQCM it would be possible to determine the potential that causes the initiation step for electropolymerization and to determine the amount of material deposited on the electrode surface. It has been shown that reduction or oxidation processes occurring within a polymer film require that charge electroneutrality be maintained within the film. This necessitates the egress or ingress of solvated counterions with respect to the film, which can cause the film to swell.

$$\Delta f = \frac{-2f_0^2 \Delta m}{A(\mu \rho)^{\frac{1}{2}}} \tag{1}$$

$$\Delta f = \frac{(MW)(C_f)(Q)}{nF} \tag{2}$$

This impacts charge transfer within the films and may reduce the mechanical stability of the polymer film and adhesion of the polymer film to the electrode.

Research groups have used EQCM, an *in situ* mass measurement-electrochemical method, to monitor ion transport, solvent transport, and charge transfer properties within the films. The goal for these studies is oftentimes to discriminate between solvent movement and ionic movement within the films that should provide insight into whether or not charge transfer and charge electroneutrality within the films is limited by counterion movement within the films. The relationship between the change in frequency (Δf) and the change in mass (Δm) of a coated quartz crystal is given by the Sauerbrey equation (Eq. (1)) [32], where μ and ρ are the shear modulus and density of the quartz crystal, respectively. Eq. (2) is used to determine the apparent molar mass of the species causing the mass change where C_f is the mass sensitivity constant for the crystal. The applicability of this equation for solutions requires a uniform distribution of material across the surface of the crystal. In addition, the film must be rigid enough at all oxidation states to avoid dampening the shear wave that is applied to the crystal (i.e., the coating does represent a viscous medium) [30, 31]. First, in order to validate the Sauerbrey equation, films of various thicknesses based on the monomers are prepared. It is beneficial to use Atomic Force Microscopy (AFM) to verify that the material is uniformly distributed on the surface. Establishing a linear correlation between film thickness and Δf allow researchers to determine the rigidity of the film, and validate the applicability of the Sauerbrey Equation [32]. Based upon Eqs. (1), (2), it is possible to determine the molar mass, and hence, the species causing the change in mass of the film. For each cyclic voltammetric characterization of polymer film, peak separation values of the redox couples, with respect to scan rate and number of electropolymerization cycles can be evaluated to determine polymer film dynamics and characteristics. At low scan rates of cyclic voltammetric characterization, peak separation values should be near 0 V for facile charge transfer of materials immobilized onto electrode surfaces, which indicates Nernstian equilibrium with a applied potential. However, a constant low scan rate of characterization, with increasing film thickness may increase the peak separation due to limitations of charge transfer, ionic mobility, or polymer lattice motions necessary to accommodate charge transfer. Atomic force microscopy and SEM measurements provides information on changes in polymer structure after cyclic voltammetric characterization of the films and can be compared to EQCM measurements.

5.2 Determination of the apparent charge transfer diffusion coefficient

For the electrochemical characterization of the polymer films, the apparent charge transfer diffusion coefficient for a polymer thin film of a given thickness can be determined through chronoamperometric-coulometric methods, using the Cottrell equation (Eq. (3)) [28].

$$I = \frac{nFAD_{ct}^{\frac{1}{2}}C\pi^{\frac{1}{2}}}{\sqrt{t}} \tag{3}$$

The current response for an electroactive compound is given by the Cottrell equation where C and D_{ct} are the concentration (mol cm^{-3}) of redox species and apparent charge transfer diffusion coefficient (cm^2 s^{-1}), respectively. The other symbols have their normal electrochemical convention. The slope of the linear plot, I versus $t^{-1/2}$, allows the product $D_{ct}^{1/2}C$ to be calculated. Recently, we have shown that AFM can be used to determine film thicknesses and surface roughness factors for both redox polymer films and organic conducting polymer films and these

properties change as the number of electropolymerization cycles change. Using the film thickness, the concentration of redox species and hence D_{ct} can be determined. The product of $D_{ct}^{1/2}C$ can also be evaluated from CV characterization data. If the mechanism proposed by Engler and Kaufman is followed for these systems, the redox sites in metal containing films that are near the outer boundary at the solution-film interface are reduced and oxidized via electron transfer between neighboring redox centers [19, 33]. The value of D_{ct} is then translated to the rate of electron transfer which may be influenced by counterion ingress and egress from film, solvent content within the film, and polymer lattice orientations, any of which could be rate determining for the electron transfer. Interpretation of D_{ct} values for the polymer films provides information on the maximum limits for electron transfer rates with an electroactive analyte in solution.

5.3 Rotating disk electrode voltammetry

Several possibilities exist for electron transfer between the analyte in solution and the polymer film and will affect the reaction between the redox mediator and the respective analyte. The analyte may penetrate to the electrode-film interface, several monolayers into the film, or interact with the film-solution interface. Koutecky-Levich plots [34] can be obtained from the polymer films on rotating disk electrodes at various rotational velocities (ω), and concentrations (C_h) of analyte (i.e., glucose, hydrazine, and metal ions). Analyzing variable film thicknesses helps determine if electron self-exchange in the polymer film or diffusion of analyte through the polymer film is rate limiting. This helps elucidate the kinetics of analyte reduction or oxidation. The overall current in the RDE method is composed of a catalytic current (I_{cat}), kinetic current (I_k), and Levich current (I_{lev}), as shown in Eqs. (4)–(6). The catalytic current is derived from the mediated charge transfer reaction, the kinetic current from the cross exchange reaction between the polymer film and analyte, and the Levich current from the mass transfer of analyte in solution [34].

$$\frac{1}{I_{cat}} = \frac{1}{I_{lev}} + \frac{1}{I_k} \tag{4}$$

$$I_{lev} = 0.620nFAD^{\frac{2}{3}}\omega^{\frac{1}{2}}v^{\frac{-1}{6}}C_h \tag{5}$$

$$I_k = nFAk_hC_h \tag{6}$$

Extrapolation of the linear plot of $1/I_{cat}$ with respect to $1/\omega^{1/2}$ should give an intercept of $1/I_k$ when extrapolated to $\omega^{-1/2} = 0$ to determine the rate constant, k_h, for the cross reaction between the analyte and polymer film. For these experiments, films of different thicknesses prepared on electrode surfaces and the currents from the RDE measurements helps determine if the current response is diffusion limited for the analyte.

5.4 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) has been used by a variety of researchers to study charge transfer processes at electrode/solution interfaces, ionic transport within films, and diffusion mass transport processes [35]. Corrosion is
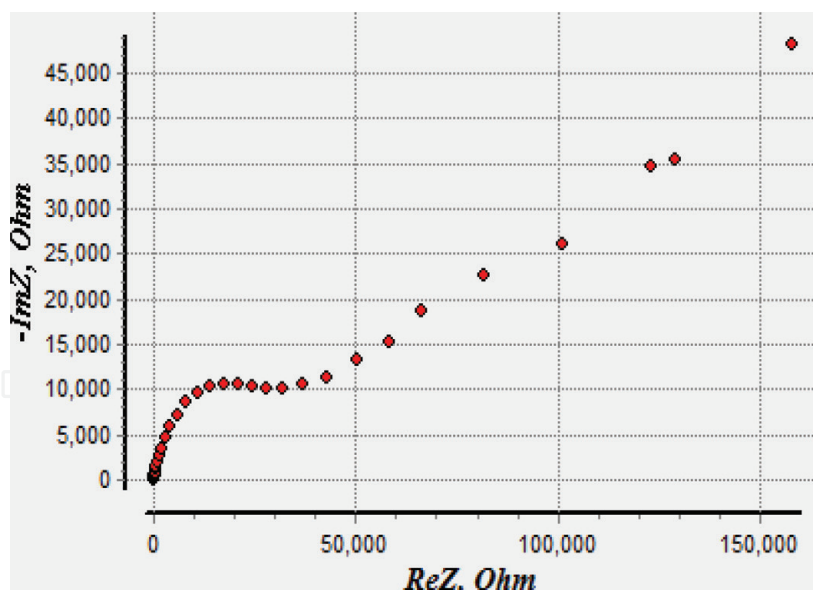
Figure 7.
Electrochemical impedance spectroscopy of electropolymerized film of 5-amino-1, 10-phenathroline-iron(II) on a glassy carbon electrode.

another area of intense research and makes extensive use of EIS measurements [36]. Using EIS it is possible to detect flaws in coatings on metals and to determine when a coating on a metal and alloy surface fails. Electrochemical impedance measurements are used to better understand how sensors operate theoretically by building equivalent circuits for charge transfer processes, mass transport processes, and ionic migration. Some films within electrochemical sensors become porous due to analyte diffusion and/or migration effects after extended use and EIS can be used to evaluate changes in morphology of the films that in turn affect sensor and biosensor performance. Electrochemical impedance spectroscopy employs alternating circuit (AC) theory to electrochemical cells [37, 38]. That is, an electrochemical cell can be modeled with electrical components consisting of resistors, capacitors, and inductors in a series or parallel arrangement. However, in complex systems, the arrangement of the equivalent circuit design is generally a series–parallel combination arrangement. Electron flow in an electrochemical sensor can be hindered via slow heterogeneous or homogeneous kinetics, slow diffusional or migration processes, or morphological changes in the films used. This total impedance is the combination of resistors, capacitors, and inductors. In EIS, an AC signal of approximately 5–20 mV is superimposed on a DC component of the electrochemical system that provides a pseudo-linear response over a wide frequency range. Films characterized with EIS ideally show charge transfer resistance (Rct), which is given by a semicircle and the semicircle intersects the real-Z' axis at high frequencies. At lower frequencies, when time is allowed for diffusion effects to be realized, a Warburg impedance dominates the charge transfer process as shown in **Figure 7**. Impedance measurements will also provide information about the porosity of films before and after use by determining the pore impedance (Z_{pore}). A time profile of Z_{pore} will indicate: (1) formation of pores, (2) collapsing of pores, or (3) constant pore structure [37].

6. Conclusion

An effective method of altering the properties of an electrode surface to prepare chemically modified electrodes is through the use of electropolymerization reactions. Electropolymerization by cyclic voltammetry as opposed to constant

potential or constant current depositions is more advantageous because there are certain energy requirements associated with propagating the electropolymerization that can be better achieved if a potential window is scanned. In addition, much information can be gained through cyclic voltammetry such as electropolymerization mechanistic pathways that cannot be attained using other deposition methods. Furthermore, these schemes allows irregular-shaped electrodes to be effectively covered with polymer thin films for placement in flow systems using chemically modified systems as part of the detection system and for the development of sensors and biosensors.

A number of electrochemical hyphenated techniques have been used to characterize chemically modified electrodes. Oftentimes, several electrochemical experiments using different methods must be used to fully understand the dynamics of charge transfer for these electrodes when they are used in the development of amperometric sensors and biosensors. For examples, quartz crystal microbalance when combined with cyclic voltammetry (EQCM) can provide real-time information about mass changes during electrochemical stimulation of chemically modified electrodes. One goal of electrochemical characterization of thin films is to correlate the properties of the polymer films to the processes occurring during the electropolymerization when the polymer film is prepared. One technique, electrochemical impedance spectroscopy, which is typically used to understand corrosion has been used to provide a clearer picture of the factors limiting charge transfer processes at the chemical modified electrode surfaces. Using this method, one experiment has the capability to give information equivalent to several experiments in cyclic voltammetry and chronocoulometry. However, no one electrochemical technique can provide all the information necessary to understand the dynamics of electron transfer phenomena within or at chemically modified electrode surfaces.

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References

[1] Murray R. Chemically modified electrodes. Accounts of Chemical Research. 1980;**13**:135-141

[2] Hillman AR. Electrochemical Science and Technology of Polymers. Elsevier: Amsterdam; 1987

[3] Hart JP, Wring SA. Chemically modified, carbon-based electrodes and their application as electrochemical sensors for the analysis of biologically important compounds. A review. Analyst. 1992;**117**:1215

[4] Kaneko M, Wohrle O. Polymer-coated electrodes: New materials for science and industry. Advances in Polymer Science. 1988;**84**:140

[5] Tse Y-H, Janda P, Lever ABP. Electrode with electrochemically deposited N,N',N'',N'''-tetramethyltetra-3,4-pyridinoporphyrazinocobalt(I) for detection of sulfide ion. Analytical Chemistry. 1992;**66**:384-390

[6] Wang J. Electrocatalytic reduction and flow injection analysis of organic peroxides at polymeric tetra-amino iron phthalocyanine modified electrode. Analytical Letters. 1996;**29**:1575-1587

[7] Schachl L, Alemu H, Klacher K, Jezkova J. Flow injection determination of hydrogen peroxide using a carbon paste electrode modified with a manganese dioxide film. Analytical Letters. 1997;**30**:2655-2673

[8] Collins G, Rose-Pehrsson SL. Chemiluminescent chemical sensors for oxygen and nitrogen dioxide. Analytical Chemistry. 1995;**67**:2224-2230

[9] Lane RF, Hubbard AT. Electrochemistry of chemisorbed molecules. I. Reactants connected to electrodes through olefinic substituents.

Journal of Physical Chemistry. 1973;**77**:1401

[10] Oyama N, Anson FC. Factors affecting the electrochemical responses of metal complexes at pyrolytic graphite electrodes coated with films of poly(4-Vinylpyridine). Journal of Electroanalytical Chemistry. 1980;**127**:640-647

[11] Maksymiuk L, Doblhofer K. Kinetics and mechanism of charge-transfer reactions between conducting polymers and redox ions in electrolytes. Electrochimica Acta. 1994;**39**:217-227

[12] Shaw BR, Haight GP, Faulkner LR. Electrochemical preparation of electrodes coated with crosslinked poly(styrenesulfonate). Journal of Electroanalytical Chemistry. 1982;**140**:147-153

[13] Yagi M, Mitsumoto T, Kaneko M. Potential-step chronocoulospectrometry of a polymer membrane incorporating tris(2,2'-bipyridine) ruthenium (II) complex. Journal of Electroanalytical Chemistry. 1997;**437**:219-223

[14] Calvert JM, Schmehl RH, Sullivan PB, Facci JS, Meyer TJ, Murray RW. Synthetic and mechanistic investigations of the reductive electrochemical polymerization of vinyl-containing complexes of iron(II), ruthenium(II), and osmium(II), Inorganic Chemistry. 1983;**22**:2151-2162

[15] Kobayashi T, Yoneyama H, Tamura H. Polyaniline film-coated electrodes as electrochromic display devices. Journal of Electroanalytical Chemistry. 1984:419-423

[16] Lyons MG. Electroactive Polymer Electrochemistry. New York, NY: Plenum Press; 1994

[17] Feldberg SW. Reinterpretation of polypyrrole electrochemistry. Consideration of capactive currents in redox switching of conducing polymers. Journal of the American Chemical Society. 1984;**106**:4671-4674

[18] Walczak RM, Cowart JS, Reynolds JR. Tethered PProDOTs: Conformationally restricted 3,4-propylenedioxythiophene based electroactive polymers. Journal of Materials Chemistry. 2007;**17**:254-260

[19] Sotzing GA, Reynolds JR. Electrochromic conducting polymers via electrochemical polymerization of bis(2-(3,4-ethylenedioxy)thienyl) monomers. Chemistry of Materials. 1996;**8**:882-889

[20] Paulson SC, Sapp SA, Elliott CM. Electrochemical and spectroelectrochemical investigations into the nature of charge-trapping in electrochemically generated homopolymer films of tris(4-vinyl-4'-methyl-2,2'-bipyridine)ruthenium(II). The Journal of Physical Chemistry B. 2001;**105**:8718-8724

[21] Shgehara L, Oyama N, Anson FC. Electrochemical responses of electrodes coated with redox polymers. Evidence for control of charge-transfer rates across polymeric layers by electron exchange between incorporated redox sites. Journal of the American Chemical Society. 1981;**103**:2552-2558

[22] Nyasulu FWW, Mottola HA. Electrochemical behavior of 5-amino-1,10-phenanthroline and oxidative electropolymerization of tris[5-amino-1,10-phenanthroline]iron(II). Journal of Electroanalytical Chemistry. 1988;**239**:175-186

[23] Ellis CD, Murphy WR, Meyer TJ. Selectivity and directed charge transfer through an electroactive metallopolymer film. Journal of the American Chemical Society. 1981;**103**:8480-7483

[24] Ellis CD, Murray RW, Meyer TJ, Margerur LD. Oxidative electropolymerization of polypyridyl complexes of ruthenium. Inorganic Chemistry. 1983;**22**:1283-1291

[25] Bettelheim A, White BA, Raybuck SA, Murray RW. Electrochemical polymerization of amino-, pyrrole-, and hydroxy-substituted tetraphenylporphyrins. Inorganic Chemistry. 1987;**26**:1009-1017

[26] Diaz AF, Kanazawa KK, Gardini GP. Electrochemical polymerization of pyrrole. Journal of the Chemical Society, Chemical Communications. 1979:635

[27] Genies AF, Kanazawa KK, Gardini GP. Spectroelectrochemical study of polypyrrole films. Journal of Electroanalytical Chemistry. 1983;**149**:101-113

[28] Brown KL, Mottola HA. Voltammetric, Chronocoulometric, and spectroelectrochemical Studies of Electropolymerized Films Based on Cu(II/I)- 4, 9,16, 23-Tetraaminophthalocyanine. Langmuir. 1998;**14**:3411-3417

[29] Brown KL, Shaw J, Ambrose M, Mottola HA. Voltammetric, Chronocoulometric and Spectroelectrochemical Studies of Electropolymerized Films Based on Co(III/II)-and Zn(II)-4, 9, 16, 23-Tetraaminophthalocyanine: Effect of High pH. Microchemical Journal. 2002;**72**:285-298

[30] Tjarnhage T, Sharp M. The use of a quartz crystal microbalance combined with ellipsometry and cyclic voltammetry for determining some basic characteristics of an electroactive

polymer film. Electrochimica Acta. 1994;**39**(5):623-628

[31] Cui S, Park S. Electrochemistry of conductive polymers XXIII: Polyaniline growth studied by electrochemical quartz crystal microbalance measurements. Synthetic Metals. 1999;**105**:91-98

[32] French HM, Henderson MJ, Hillman AR, Vieil E. Ion and solvent transfer discrimination at a nickel hydroxide film exposed to LiOH by combined electrochemical quartz crystal microbalance (EQCM) and probe beam deflection (PBD) techniques. Journal of Electroanalytical Chemistry. 2001;**500**:192-207

[33] Kaufman FB, Schroeder AH, Engler EM, Kramer SR, Chambers JQ. Ion and electron transport in stable, electroactive tetrathiafulvalene polymer coated electrodes. Journal of the American Chemical Society. 1980;**102**(2):483-488

[34] Maksymuk K, Doblhofer K. Kinetics and mechanism of charge-transfer reactions between conducting polymers and redox ions in electrolytes. Electrochemica Acta. 1994;**39**(2):217-227

[35] Mansfeld F. Use of electrochemical impedance spectroscopy for the study of corrosion protection by polymer coating. Journal of Applied Electrochemistry. 1995;**25**:187-202

[36] Zelinka SL, Stone DS, Rammer DR. Electrochemical corrosion testing of fasteners in extracts of treated wood. Corrosion Science. 2008;**50**(5):1251-1257

[37] Lvovich VF. Impedance Spectroscopy: Applications to Electrochemical and Dielectric Phenomena. Hoboken, New Jersey: John Wiley and Sons: 2012

[38] Krause S. Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry. Vol. 3. Wiley-VCH; 2001