Video Article

Reductive Electropolymerization of a Vinyl-containing Poly-pyridyl Complex on Glassy Carbon and Fluorine-doped Tin Oxide Electrodes

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Abstract

Controllable electrode surface modification is important in a number of fields, especially those with solar fuels applications. Electropolymerization is one surface modification technique that electrodeposits a polymeric film at the surface of an electrode by utilizing an applied potential to initiate the polymerization of substrates in the Helmholtz layer. This useful technique was first established by a Murray-Meyer collaboration at the University of North Carolina at Chapel Hill in the early 1980s and utilized to study numerous physical phenomena of films containing inorganic complexes as the monomeric substrate. Here, we highlight a procedure for coating electrodes with an inorganic complex by performing reductive electropolymerization of the vinyl-containing poly-pyridyl complex onto glassy carbon and fluorine doped tin oxide coated electrodes. Recommendations on electrochemical cell configurations and troubleshooting procedures are included. Although not explicitly described here, oxidative electropolymerization of pyrrole-containing compounds follows similar procedures to vinyl-based reductive electropolymerization but are far less sensitive to oxygen and water.

Video Link

The video component of this article can be found at http://www.jove.com/video/52035/

Introduction

Electropolymerization is a polymerization technique that utilizes an applied potential to initiate the polymerization of monomeric precursors directly at the surface of an electrode and has been exploited to produce thin electroactive and/or photochemically active polypyridyl films on electrode and semiconductor surfaces.[1-4] Electrocatalysis,[5-10] electron transfer,[11,12] photochemistry,[13-16] electrochromism,[17] and coordination chemistry[18] have been investigated in electropolymerized films. This technique was first developed at the University of North Carolina in a Meyer-Murray collaboration for the electropolymerization of vinyl[3,5,7,8,11-15,19,20] and pyrrole[6,9,21-24] derivatized metal complexes on a variety of conducting substrates. **Figure 1** presents a number of common pyridyl based ligands that, when coordinated to metal complexes, have produced electropolymers. In reductive electropolymerization, electropolymerization of vinyl containing compounds occurs upon the reduction of pyridyl ligands conjugated to vinyl groups, while with pyrrole-functionalized ligands, electropolymerization is initiated by oxidation of the pyrrole moieties, resulting in oxidative electropolymerization (**Figure 2**). Electropolymerization technology was developed with the goal of providing a generalized methodology for directly attaching virtually any transition metal complex to any electrode. The versatility of the method opens the door to numerous investigations of electropolymer modified electrodes.

In contrast to other attachment strategies, which involve direct bonding to the electrode, electropolymerization offers the advantage of not requiring electrode surface pre-modification. Therefore it can be applied to any number of conducting substrates, regardless of surface composition or morphology.[4,10,25,26] This versatility is a result of changing physical properties as the polymer length grows; the monomers are soluble in the electrolytic solution but as polymerization occurs and cross-linking rigidifies the film, precipitation and physical adsorption the electrode surface occurs (**Figure 3**).[27]

Compared to oxide surface-bound carboxylate, which are unstable on oxide surfaces in water, or phosphonate-derivatized complexes, which are unstable at elevated pH's, commonly used in solar fuels research, these interfacial electrode-polymer film structures offer the added benefit of stability in a variety of media including organic solvents and water over a large pH range (0-14).[28-30] Electropolymerization can also deposit films with large ranges of apparent surface coverages, from sub-monolayer to dozens or hundreds of equivalents monolayer, whereas carboxylate or phosphonate-derivatized complexes-interface structures are limited to monolayer surface coverages.

Although any number of vinyl or pyrrole containing pyridyl and polypyridyl compounds are capable of polymerization, $[Ru^{II}(PhTpy)(5,5'\text{-}dvbpy)(MeCN)](PF_6)_2$, (**1**; PhTpy is 4'-phenyl-2,2':6',2''-terpyridine; 5,5'-dvbpy is 5,5'-divinyl-2,2'-bipyridine; **Figure 4**) will be utilized as a model complex to demonstrate reductive electropolymerization on glassy carbon and fluorine-doped tin oxide, FTO, electrodes in this report. **1** is an example of a modern electropolymer precursor that has potential electrocatalytic applications and, due to its metal-to-ligand charge transfer, MLCT,

absorption spectrum lying in the visible region of the light spectrum, can be investigated with UV-Vis spectroscopy.[18,30] Please note that some results presented here for **1** have already been published in a slightly modified form.[18]

Protocol

1. Synthesize 1

Synthesize **1** (PhTpy is 4'-phenyl-2,2':6',2''-terpyridine; 5,5'-dvbpy is 5,5'-divinyl-2,2'-bipyridine; **Figure 4**) according to the procedure outlined previously.[18]

2. Prepare 1.3 mM Monomer Solution of 1 in an Electrolyte Solution

1. Prepare a 0.1 M stock electrolyte solution of tetra-*n*-butylammonium hexafluorophosphate, TBAPF$_6$, in acetonitrile, MeCN.
   1. Place MeCN over activated 3 Å molecular sieves, or K$_2$CO$_3$, for 24 hr to remove adventitious H$_2$O.
   2. Place TBAPF$_6$ (0.969 g, 2.50 mmol) in a 25.00 ml flame dried volumetric flask.
   3. Filter the molecular sieve or K$_2$CO$_3$ particulates from the dried MeCN and bring the 25.00 ml volumetric flask containing TBAPF$_6$ to volume.
2. Place **1** (0.0049 g, 5.2 x 10^{-6} mol) in and dry 4 dram vial or a 10 ml round bottom flask and add 4.00 ml of the stock solution of 0.1 M TBAPF$_6$ in MeCN.
3. Transfer 3.5-4.0 ml of the red-orange colored electrolytic solution of **1** into the central compartment of a 3-compartment cell, with each compartment separated by a medium porosity glass frit.
4. Quickly fill the outer compartments of the 3-compartment cell to an equal height as the central compartment stock solution, with some of the remaining dry 0.1 M TBAPF$_6$ in MeCN to prevent leakage to the outer compartments. Note: Time is an important factor because solutions in the different compartments will slowly mix and significantly change the concentration of the main compartment if the solvent heights are not the same.

3. Electropolymerize 1 on a 3 mm Diameter Glassy Carbon Electrode or a 1.0 cm^2 FTO Electrode

1. Prepare septa for nitrogen/argon degassing tubes and for electrodes.
   1. Cut a slit into each of the 3 rubber septa and guide a thin polytetrafluoroethylene, PTFE, tube through the slit.
   2. Slide the Ag/AgNO$_3$ reference electrode through one of the septa, place the reference electrode/PTFE tube/septum in one of the outer compartments, and seal the compartment with the septum.
   3. Guide the platinum wire/gauze counter electrode through a different septum place the platinum wire/PTFE tube/septum in one of the outer compartments, and seal the compartment with the septum. If the slit is not sufficiently large or wire sufficiently stiff to prevent bending the wire, use a wide bore needle to guide the platinum wire counter electrode through the septum.
   4. Guide a freshly polished 3 mm glassy carbon electrode through the remaining septum and place it such that the electrode is suspended in the solution or, for an FTO slide, guide a wire connected to an alligator clip through the septum, then clamp the FTO slide with the alligator clip and make sure that the conductive side of the slide is perpendicular to the counter electrode when submerged.
      1. Prior to inserting the glassy carbon electrode: polish the glassy carbon by placing alumina (0.5 µm) on a wetted polishing pad, then, move the electrode in a figure-8 motion for 30 sec while holding the electrode perpendicular to the pad — to polish all sides of the electrode evenly — and rinse any remaining alumina off with a H$_2$O water squirt bottle followed by an MeCN squirt bottle rinse.
      2. Prior to clamping the FTO slide: wrap several layers of non-conductive Kapton tape around the center part of a 30 x 10 mm FTO slide such that a 10 x 10 mm portion of the slide is exposed.
      3. Collect a UV-Vis spectrum of the FTO slide by placing/holding the FTO slide in a position in the beam path of the spectrometer that has been predetermined to ensure consistency.

2. De-aerate the solutions in the 3-compartment electrochemical cell.
   1. Connect one end of Tygon tubing to the nitrogen/argon supply and connect the other end to a gas washer containing MeCN.
   2. Cut another piece of Tygon tubing, connect one end to the outflowing MeCN washed nitrogen/argon, and connect the other end to a 4 way splitter.
   3. Connect the PTFE tubes to the 3 remaining connections of the 4 way splitter.
   4. Submerge the PTFE tubes into the solutions in each of the compartments and turn on the flow of nitrogen/argon such that a rapid bubbling of the solution commences.
   5. Continue de-aerating the solution for 5-10 min, then pull the PTFE tubes just above the surface of the solution, leaving the flow of nitrogen/argon on in order to keep a positive pressure of inert gas on the system and to prevent solution convection caused by bubbling.

3. Perform electrochemical experiments.
   1. Connect electrodes from the potentiostat to the appropriate electrodes in the 3#compartment cell.
   2. Perform a cyclic voltammetry, CV, experiment with the following parameters: switching potentials = 0 V and -1.81 V; scan/sweep rate = 100 mV/sec; number of cycles = 5.

3. When the CV experiment is complete, remove the working (glassy carbon or FTO) electrode from the polymerization solution and gently rinse the surface of the electrode with MeCN from a pipette or a squirt bottle to remove any remaining monomer solution.

4. Surface Coverage Determination

1. Place the rinsed working electrode in a freshly prepared solution of 0.1 M TBAPF$_6$/MeCN in an electrochemical cell containing a counter electrode and a reference electrode (preferably the same reference electrode used in the electropolymerization).
2. Perform a cyclic voltammetry, CV, experiment with the following parameters: switching potentials = 0 and +1.5 V; scan/sweep rate = 100 mV/sec; number of cycles = 15.
3. Integrate the charge under the anodic and cathodic peaks for the adsorbed electropolymer Ru(III/II) couple, average the charge under the anodic and cathodic peaks, and using Equation 1 determine the surface coverage.
4. For the FTO slide: place/hold the FTO slide in the predetermined position in front of the UV-Vis sample holder such that the beam-path passes through the colored film. The FTO slide can be wet or dry but make comparisons under the same conditions as the blank spectra was collected under.
5. Subtract the spectrum obtained for the FTO spectrum that was collected for that particular slide prior to electropolymerization from the spectrum of the film-on-FTO in order to produce an absorption spectrum for the film itself.

Representative Results

Electropolymer growth is most easily recognized when observing the progress of the prescribed CV experiment (Protocol Text STEP 3.3.2). **Figure 5** exemplifies electropolymer growth on a 0.071 cm^2 (3 mm diameter) glassy carbon electrode with **1**. The first cycle of the experiment produces a voltammogram roughly resembling that which is expected for a ruthenium solution of similar concentration (**Figure 5**, black trace) but upon successive cycles, through the 1st and 2nd ligand centered reduction waves, increasingly enhanced currents are observed (**Figure 5**, red, blue, green, and pink traces). This phenomenon is observed due to the summation of the current for the monomer in solution and that of the electropolymer film that is deposited from the previous cycle past the ligand centered reduction waves. There is a reduction before the two ligand-centered reductions that moves to more negative potentials on each successive scan. This has been associated with isolated sites of damaged, charge-trapped portions of the polymer.[25,31] Also, one referee pointed out that the two ligand-centered reductions do not grow at the same rates in **Figure 5**; the first ligand-centered reduction seems to only grow between the first and second scans, while the oxidation associated with the first oxidation does not appear to grow at all. We do not understand this phenomenon but are investigating further.

After the electropolymerization experiment on the glassy carbon electrode is complete, cyclic voltammetry is performed in a fresh solution of 0.1 M TBAPF$_6$/MeCN for a number of reasons. First, most electropolymers need to be equilibrated by cycling either oxidatively or reductively for varying amounts of time, in order to allow the films to accommodate ion channels necessary to produce an electrically conductive film; as electrons migrate through the redox polymers via self-exchange reactions between reduced and oxidized neighbors, a flow of counterions is needed to compensate for the charges of the fixed redox sites — a phenomenon dubbed electrochemical charge transport.[25] **Figure 6** shows an example of the electropolymer of **1** equilibrating with oxidative scans between 0 and +1.5 V. Equilibration occurs after a number of cycles, which varies depending upon the thickness of the electropolymer film. The pink trace in **Figure 6** is the first cycle after reductive electropolymerization, while the blue trace is the second cycle, and the remaining 3rd-15th cycles are in black. The red arrows indicate decreasing current while the green arrows indicate an increase. The redox couple at $E_{1/2}$ = +0.998 V corresponds to that of the Ru(III/II) couple of the electropolymer of [Ru^{II}(PhTpy)(5,5'-dvbpy)(MeCN)](PF$_6$)$_2$.[18] Passing through the large couple near +0.25 V begins to initiate the flow of counterions ejected by the reductive cycling and equilibration to that representative of *poly*-**1**.[25] We are currently investigating the origin of the couple near +0.75 V but that too decreases with successive scans.

Second, insight into the electropolymer stability is gained following the equilibration routine. For example, the electropolymer film in **Figure 6** equilibrates after about 11 cycles, where it remains constant thereafter. The constant current throughout the remaining cycles indicates that this particular electropolymer is stable to these conditions and likely to remain on the surface of the electrode under these CV conditions for decades, hundreds, or even thousands of cycles.

Third, since the surface area of the electrode is known, the surface coverage — the amount of electropolymer on the electrode per unit area, in mol/cm^2 — can be easily and quantitatively determined by integrating the anodic and cathodic waves, taking their average (Equation 2) and using Equation 1.[1] is apparent surface coverage, n is the number of electrons passed per redox couple (moles e$^-$), F is Faraday's constant (96,485 C/mol), A is the area of the electrode (cm^2), and Q is the accumulated charge.

$$\Gamma = \frac{Q}{nFA} \quad \text{(Equation 1)}$$

$$Q = \frac{Q_{Ep,a} + Q_{Ep,c}}{2} \quad \text{(Equation 2)}$$

Fourth, to confirm surface adsorption by measuring the peak-to-peak separation, ΔE_p, between anodic peak potentials, $E_{p,a}$, and cathodic peak potentials, $E_{p,c}$. One of the first indicators that a species is directly attached to the electrode is the absolute value of the difference between their peak potentials, $\Delta E_p = |E_{p,a} - E_{p,c}|$. For a freely diffusing species in solution that undergoes rapid electron transfer with the electrode surface, the theoretical ΔE_p minimum is 59 mV.[4] Because surface adsorbed species are held directly at the electrode interface, and thus solution diffusion is not a factor, ΔE_p can be <59 mV. For surface adsorbed species, the ΔE_p depends upon the kinetic parameters of the system (electron transfer rate, ion transfer through film, *etc.*)[1] and is scan rate dependent. Laviron has developed an analytical procedure to analyze the electron transfer

dynamics of systems adsorbed to electrode interfaces.[32,33] By measuring the change in ΔE_p as a function of sweep rate, information about kinetic parameters such as rates of electron transfer, rate of diffusion of ions throughout the electropolymer film, etc. can be determined.

Electropolymerization on FTO follows roughly the same trends as with glassy carbon but with the added benefit of 1) larger surface areas and 2) transparency. Large surface area electrodes are optimal for those desiring to perform bulk electrolysis experiments with electropolymer absorbed electrocatalysts due to more rapid product synthesis as compared to smaller area electrodes. UV-Vis spectral analysis can be performed on the films until the point where the films become so thick that no light is transmitted through the film-FTO slide. **Figure 7** shows the UV-Vis spectrum for the FTO slide subtracted electropolymer-coated-FTO to give the spectrum of the film alone. The UV-Vis spectrum of **1** is overlaid for comparison.
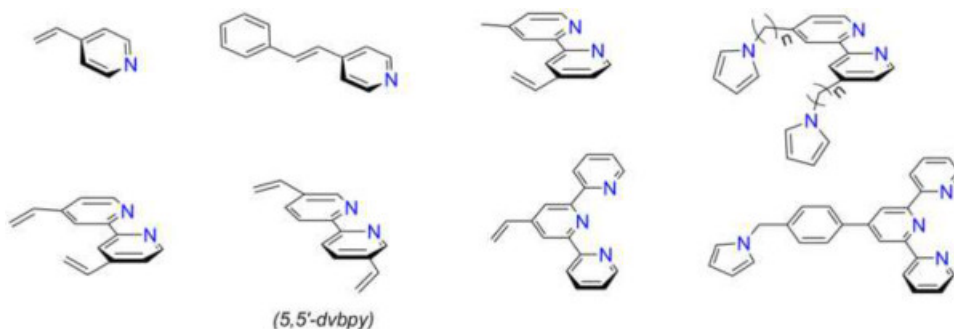

(5,5'-dvbpy)

Figure 1. Common vinyl- and pyrrole-based pyridyl ligands used for electropolymerizing inorganic species.
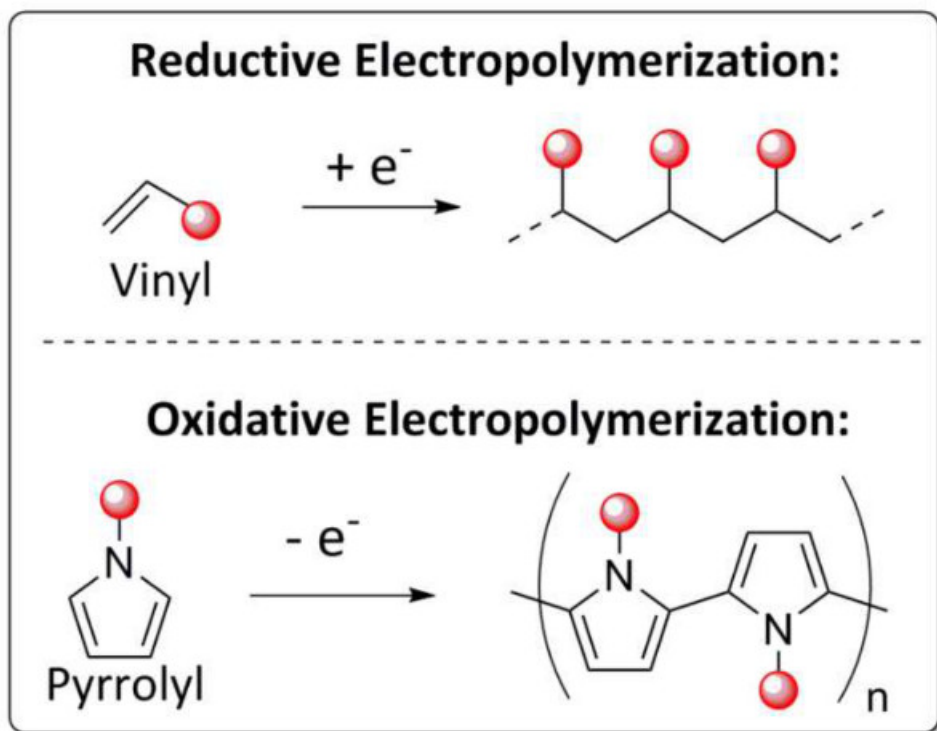

Figure 2. Initiation of electropolymerization for vinyl (reductive) and pyrrolyl (oxidative) groups. The red balls can be any number of poly-pyridyl inorganic complex fragments.
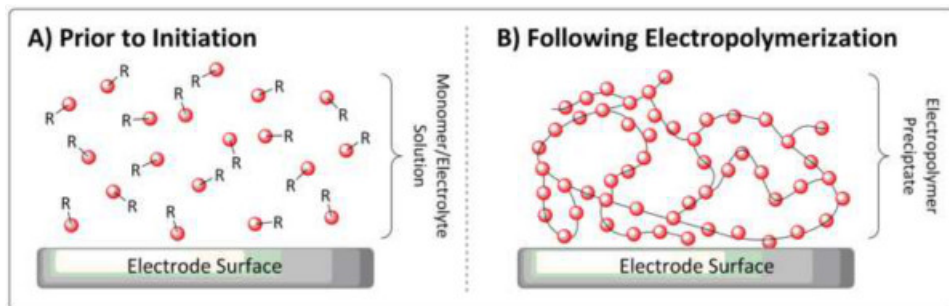
Figure 3. Depiction of solution-electrode interface A) prior to electropolymerization initiation by an applied potential from a potentiostat and B) following electropolymerization. R = vinyl for reductive electropolymerization and pyrrole for oxidative electropolymerization. As the electropolymer chain-length grows the electropolymer precipitates on the surface of the electrode. Note that there is no direct covalent linkage between the two as the primary attachment mechanism. Please click here to view a larger version of this figure.
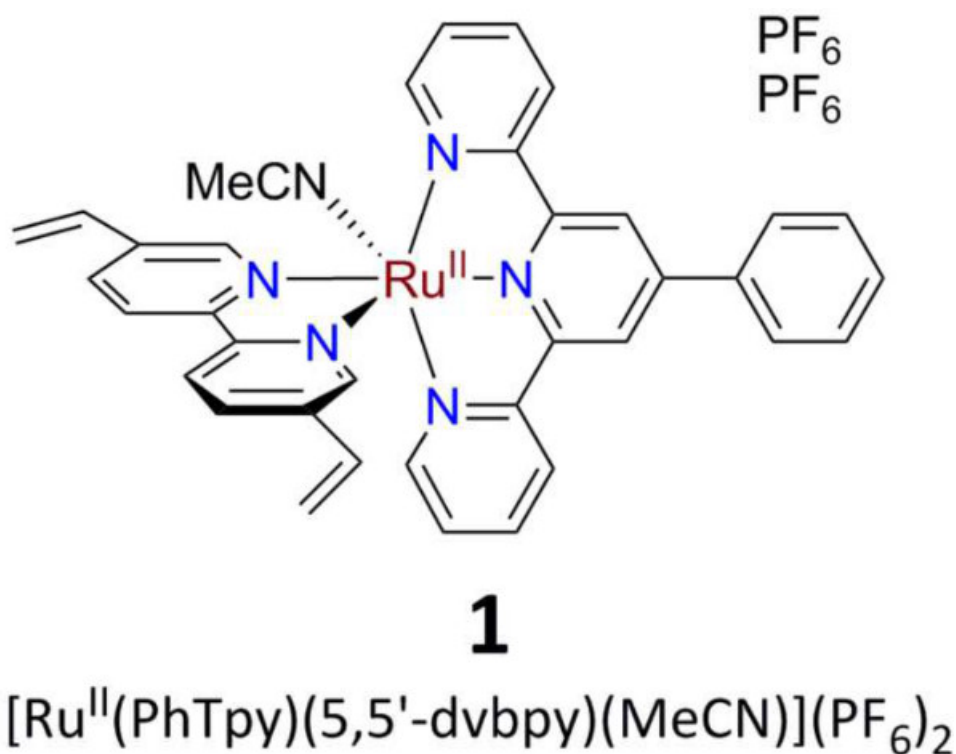

Figure 4. Molecular structure of 1, [Ru^{II}(PhTpy)(5,5'-dvbpy)(MeCN)](PF$_6$)$_2$.
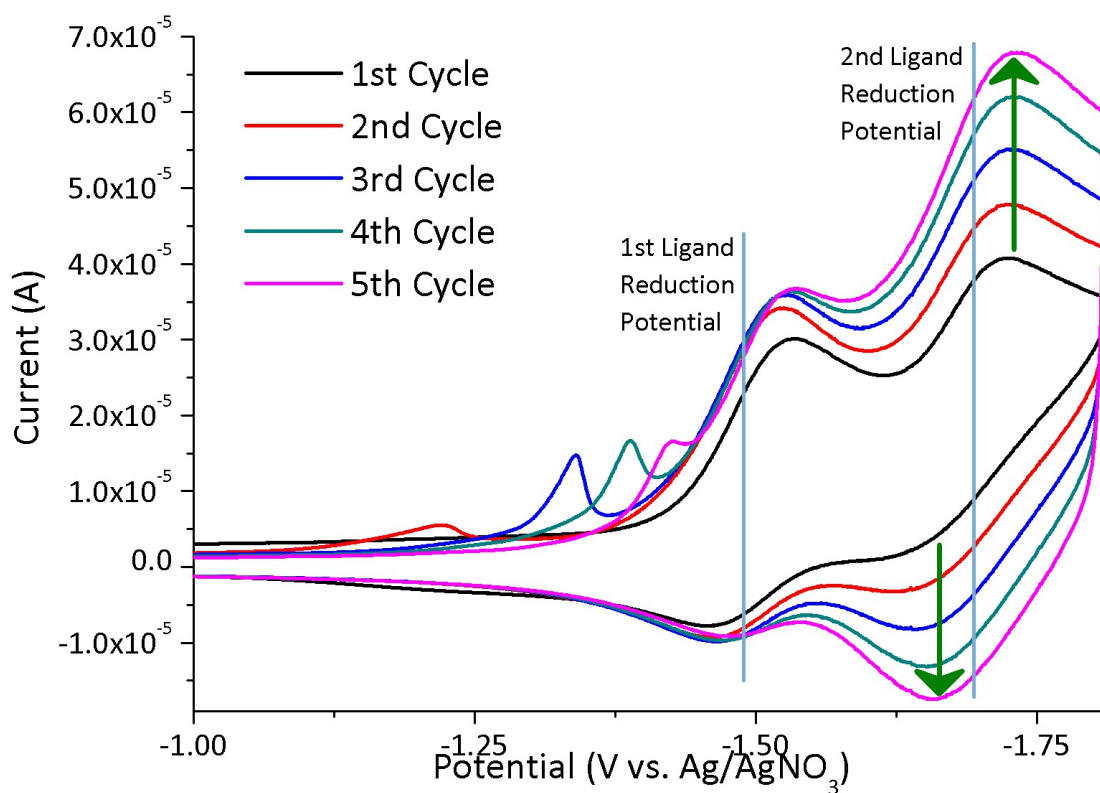
Figure 5. Reductive electropolymerization of a 1.3 mM solution of 1 in 0.1 M TBAPF$_6$ under a N$_2$(g) atmosphere using a 0.071 cm^2 glassy carbon electrode. Green arrows highlight the increase in current between successive reductive scan cycles, indicating polymer growth.
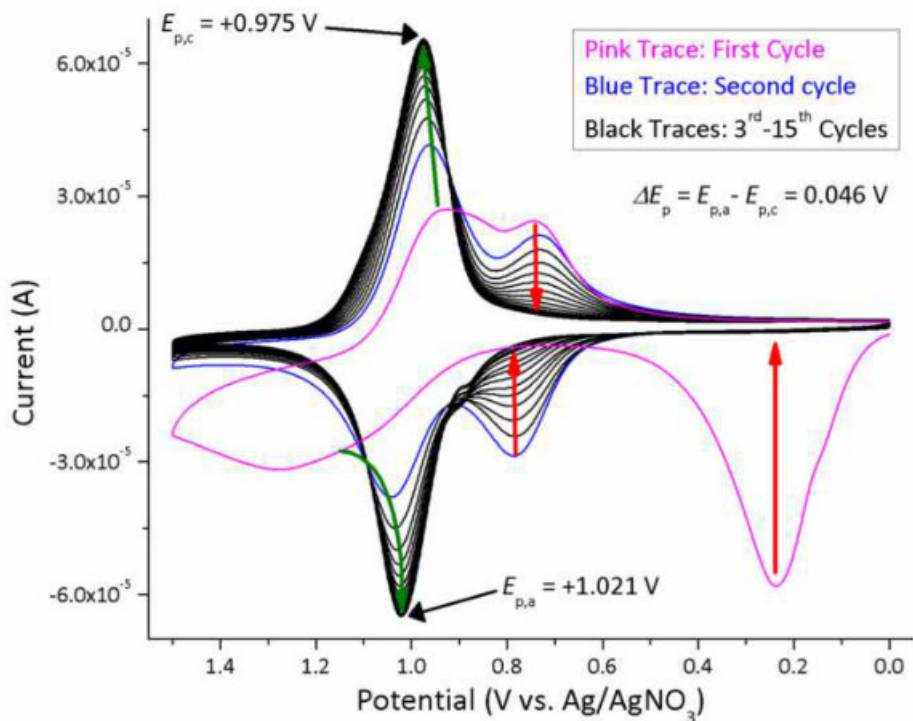
Figure 6. Oxidative equilibration of the electropolymer film produced in Figure 5. The polymer glassy carbon electrode (0.071 cm^2) was transferred to a fresh 0.1 M TBAPF$_6$/MeCN solution and oxidatively cycled between 0 V and +1.5 V at 100 mV/sec sweep rate. The film equilibrates after ~11 CV cycles. Fifteen cycles are shown. The pink trace is the first cycle after electropolymerization, the blue trace indicates the second cycle, and the black traces are the remaining 3-15 cycles. Red arrows indicate the decrease in current as the cycle number increases while green indicate an increase in current. Note: the ΔE_p indicates a surface adsorbed species.
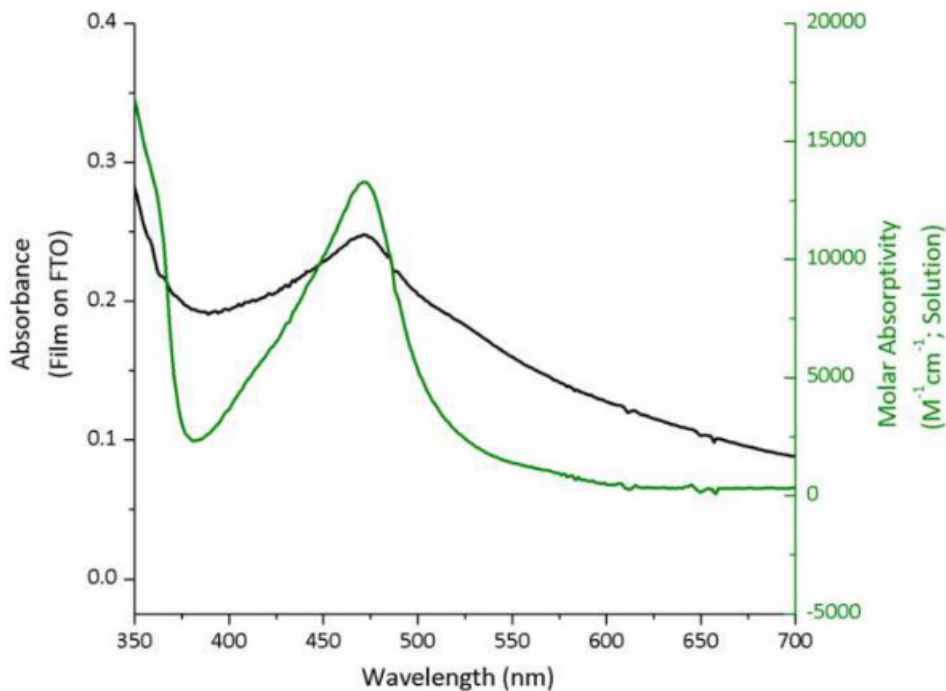

Figure 7. The UV-Vis spectrum of the electropolymer film derived from 1 (black) after subtraction of the FTO slide and the UV-Vis spectrum of 1 (green).

Number of Cycles	Surface Coverage (mol/cm^2)	Equivalent Monolayers
1	1.43E-09	14.28845
2	3.18E-09	31.78795
3	4.72E-09	47.20541
4	6.25E-09	62.52022
5	8.23E-09	82.33637

Table 1. Surface coverage and equivalent monolayers of the electropolymer on a 0.071 cm^2 glassy carbon electrode as a function of the number of cycles through the reduction waves of 1 (1.3 mM, 0.1 M TBAPF$_6$, dry MeCN).

Discussion

Electropolymerization offers a large range of controllable variables that are not common to other techniques. In addition to standard reaction variables like reagent (monomer) concentration, temperature, solvent, *etc.*, electropolymerization can be additionally controlled by electrochemical experiment parameters common to electrochemical methods. CV scan rates, switching potentials, and number of cycles affect the deposition of electropolymers. For example, as the number of cycles through the ligand reduction waves is increased, so too is the surface coverage. In the range presented here, is linear with respect to the number of cycles performed (**Table 1**).

Many vinyl containing compounds undergo reductive electropolymerization but at varying rates of growth. For compounds that rapidly undergo electropolymer growth, faster CV scan rates and lower concentration monomer electrolytic stock solutions will afford greater control over apparent surface coverage as well as a more consistently structured electropolymer network. Conversely, extending reaction times will assist with growing electropolymers with sluggish rates of polymerization.

Another electrochemical technique that can be utilized for electropolymerization is controlled potential electrolysis, or bulk electrolysis, as it may offer an additional degree of control.[18] Much like the microelectronics industry, underpotential deposition, UPD, or overpotential deposition, OPD, should allow for the production of electropolymer films of varying structure and stability.

Experimental setup is crucial to producing optimal conditions for reproducibility. One of the most important experimental details to consider is the electrochemical cell that is being used for the experiment. For a standard 3 electrode configuration, using a cell that holds each of the three electrodes in the same solution can be disastrous for the experiment over moderate periods of time (minutes to hours). Byproducts produced at the counter electrode are free to diffuse to and interfere with the electrochemical processes taking place at the working electrode, while the reference electrode solution (in this case Ag/AgNO$_3$) is free to do the same. Arguably these two processes are slow but essentially limits a particular monomer solution to a handful of electropolymerization experiments. For a 3-compartment cell — one that separates each of the compartments with semi-porous frits — the reference, working, and counter electrode solutions are physically separated and dramatically increases the time that it takes for Ag/AgNO$_3$ or unknown counter electrode byproducts to contaminate the working electrode (monomer) solution. Caution should still be observed because dilution of the monomer does occur, as evidenced by the gradual coloration of the reference and counter electrode compartments, and will eventually lead to reproducibility problems. The timescale of this dilution is dependent upon the experimental setup (*i.e.,* the porosity of frits in the 3-compartment cell) but should be slow enough to lead to reproducible results for at least a number of hours. This process can be monitored by UV-vis spectra of the outside cells. Monomer solutions should be prepared every couple of hours, and probably more frequently, due to dilution and the gradual uptake of water by the acetonitrile.

Additionally, placing a gas washer — filled with the solvent that electrochemistry is being performed on — in line with the inert gas flow dramatically slows the rate of solvent evaporation from the solutions in the cell; a gas washer usually has a fritted tip that forces the gas to bubble through a solvent and saturates the gas with that solvent, which then flows through the main electrochemical solution. Thus, the gas washer helps to maintain a constant concentration of the monomer solution for long periods of time and enhances the reproducibility of electropolymerization between different experiments. Because the gas washer helps maintain a constant volume of solvent, it is often possible to use the same solution for electropolymerizations on electrode surfaces over long periods of time; some solutions can be used for hours under this configuration depending upon how sensitive to air and water the monomers are (and depending on the rate of monomer solution dilution as described above). Pressure differences may arise in the individual compartments of the 3-compartment cells due to differences in pressure from the degassing tubes. These pressure differences may cause the solvent heights to change. This can be averted by the use of a pressure equilibrated 3-compartment cell.

It is also important to note that the stability of the electropolymer films on electrodes to reductive and oxidative cycling can be affected by a number of things. In some cases, individual films can be incredibly sensitive to the operating window of cyclic voltammetry. On one hand, electropolymer growth may not be achieved if the complex is not sufficiently reduced. A single electron reduction of the complex may not lead to a complex activated enough to induce polymerization but rather may require a second reduction into the ligand centered orbital. In the case of **1**, the electropolymerization primarily takes place at the second reduction (**Figure 5**). Alternatively, windows that are too negative (or too positive) may degrade or damage the electropolymer film, leading to a film that rapidly desorbs from the electrode upon submersion in a fresh solution of electrolyte. In other cases, the relative humidity of the environment can dramatically affect electropolymerization depending upon the sensitivity of the polymerization process to water, which varies between monomer precursors.

A procedure detailing the modification of electrode surfaces with electropolymers produced by reductive cyclic voltammetry has been presented here. Although this procedure addresses reductive electropolymerization, the same principles and similar procedures apply to oxidative electropolymerization of pyrrole, thiophene (not discussed here), and aniline (not discussed here) containing organic and inorganic moieties.[4,21,23,24,34] Oxidative electropolymerization is convenient in that oxygen does not significantly interfere with polymerization as it does with reductively electropolymerized compounds. Also, stringently drying the monomer electrolytic solutions may be detrimental to the oxidative

electropolymerization, at least in the case of pyrrole containing compounds, as it has been found that small amounts of water accelerate and stabilize the electropolymer films of pyrrole.[24]

Electropolymerization is an extremely useful technique for the attachment of inorganic complexes to any number of electrode surfaces, with a large degree of experimental control. In addition to glassy carbon and FTO,[18] platinum,[25] silcon,[2] mesoporous TiO_2,[10] and vitreous carbon electrodes[26] have proven to be suitable electrode substrates. The control afforded by a potentiostat translates into control over the speed with which the electropolymers are grown and surface coverages, which, depending upon the desired application, may be critical for tuning the properties of the system under investigation.

An additional advantage of this type of surface attachment is the ability to rapidly study the electropolymer under a number of experimental conditions. For example, once a stable electropolymer has been deposited on an electrode, that electrode can be rapidly exchanged between different solution conditions to determine the effect that those conditions have on the electropolymer. This is particularly important when investigating the pH dependence of the metal centers in the electropolymer. Not only does this strategy allow for studies at high pH's, but a complete Pourbiax diagram can be produced with a single electropolymer film.[9]

Troubleshooting Procedures

While this protocol is relatively straight forward and the deposition of electropolymers on electrode surfaces is more often than not easily achievable, obtaining consistent and reproducible deposition results (*i.e.,* surface coverage, stability, equilibration times, *etc.*) with electropolymerization can be finicky, and is highly dependent on the particular compound that is being electropolymerized.

To enhance the reproducibility of the experiments, try 1) ensuring that the solvents have been sufficiently dried, 2) flame-drying all glassware, 3) making sure that the glassy carbon electrode is polished between each electropolymerization experiment, 4) making sure that the glassy carbon electrode is completely dry after polishing with water and MeCN, 5) ensuring that the glassy carbon electrode is suspended in the electropolymer solution 2-4 mm above the bottom of the cell, 6) making sure that all potentiostat leads are properly connected to the cell electrodes, and 7) making sure that the cell resistance (IR drop) is reasonable. The resistance should be as low as possible, but a practical value should be near 100-200 ohms). One possible solution here might be to sonicate the frits separating the compartments in a basic solution to make them more porous. Also, try 8) making sure the solution is properly de-oxygenated, 9) make sure to not to touch the glassy carbon electrode surface after polishing the electrode, and 10) utilizing a reference electrode with a reproducible potential by replacing daily the Ag wire reference electrode solution with a stock solution of 10 mM $AgNO_3$ in 0.1 M $TBAPF_6$/MeCN and measuring the potential with 1.0 mM $FeCp_2$ in 0.1 M $TBAPF_6$/MeCN, prior to performing electrochemical experiments. This will keep the potential window consistent between electropolymerization experiments that are performed days or weeks apart. The $E_{1/2}$ of 1.0 mM $FeCp_2$ in 0.1 M $TBAPF_6$/MeCN with this reference electrode is +0.094 V (ΔE_p = 75 mV); thus, subtract 94 mV of the reported potentials to reference vs. $FeCp_2$.

If problems should arise when working with FTO electrodes, try 1) to ensure that the conductive side of the FTO electrode is perpendicular to the counter electrode, 2) using a platinum gauze as the counter electrode to accommodate the larger surface area working electrode and for a more diffuse and consistent electric field between the working and counter electrode, 3) ensuring that the alligator clip holding the FTO electrode is (a) not submerged in the electrolyte solution and (b) that it is not touched by the bubbles from the electrolyte solution as it is being degassed, as the alligator clip may contaminate the electrolyte solution, and 4) cleaning or re-cleaning FTO slides by sonicating in isopropanol (*i*PrOH) for 20 min, discarding the *i*PrOH, sonicating again in *i*PrOH for 20 min, discarding this solution, then sonicating in ultrapure H_2O for 20 min, discarding the H_2O solution, sonicating in fresh ultrapure H_2O for an additional 20 min, discarding the H_2O solution, then air drying.

Regarding UV-Vis spectral data collection: If negative absorbances are observed in the subtracted spectra, re-collect the data to ensure that the slide is held/placed in exactly the same point and angle perpendicular-to-beam path. If possible, hold the FTO slide perfectly vertical. Positioning the FTO electrode such that the UV-Vis beam passes through the same area on the FTO electrode and at the same angle is crucial for optimal spectrum subtraction; placing the slide at a slight angle from perpendicular-to-beam path is enough to artificially change the absorbance between bare-FTO and film covered-FTO. Collect multiple scans of the same slide to increase your confidence.

If the cell setup is acceptable but electropolymerization is not occurring try: 1) increasing the reaction time by slowing the scan rate during electropolymerization CVs and/or increasing the number of cycles for the CV, 2) increasing the concentration of the monomer in solution, 3) changing the solvent of the monomer solution, 4) try changing the electrolyte to perchlorate salts such as tetra-*n*-butylammonium perchlorate or tetra-*n*-ethylammonium to help any electropolymers that form to precipitate on the electrode, and 5) try performing controlled potential electrolysis where the applied potential is set near, on, or past the ligand based reduction potentials for varying amounts of time as this may offer an additional degree of controlled deposition.[18]

If after exhausting all of the above troubleshooting procedures, polymerization does not occur, the ligand or ligand combinations are probably at fault. Try synthesizing new inorganic complexes with additional vinyl groups and try changing the position of the vinyl groups on the molecule. Certain configurations may not be favorable for long chain polymer growth or cross-linking between polymer chains, which will produce low molecular weight polymers that either (a) do not precipitate on the electrode or (b) precipitate but then rapidly disperse from the electrode.

Disclosures

No conflicts of interest declared.

Acknowledgements

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