

Electrochemistry and Detection of Organic and Biological Molecules Such as Catechol and Ascorbic Acid at Conducting Poly (2,2-bithiophene) Electrode

Suzanne K. Lunsford ^{a*}, Jelynn Stinson ^a, and Justyna Widera ^b,

^a *Department of Chemistry, Wright State University, 3640 Colonel Glenn Hwy., Dayton, OH 45435*

^b *Department of Chemistry, Adelphi University, Garden City New York 11530*

Abstract: This paper describes an undergraduate laboratory for an electroanalytical chemistry course that can be used to supplement the teaching of oxidation and reduction reactions. The laboratory also introduces basic electrochemical techniques, instrumentation, and preparation of a conducting polymer film, poly (2,2-bithiophene), as a chemical sensor for the detection of an organic molecule catechu in the presence of a common interferent, ascorbic acid.

Published as an Analytical Sciences Digital Library Online Article Using the Creative Commons Attribution-NonCommercial-ShareAlike 2.5 License

Introduction

The goal of this laboratory is to provide an application of oxidation and reduction reactions in the upper-level chemistry courses such as Analytical Chemistry. These reactions are very important in biological studies of neurotransmitters. Catecholamines are a class of neurotransmitters (1,2-dihydroxybenzenes), and their detection in the human body has been of great interest to neuroscientist. Catechol is secreted in the brain and altered levels have been associated with mental and such behavioral disorders as schizophrenia, attention deficient disorder, Alzheimer's disease, Parkinson's disease, eating disorders, epilepsy, amphetamine and cocaine addiction [1-6].

The presence of common interferents, such as ascorbic acid, may complicate catechol analysis. This experiment uses cyclic voltammetry to detect catechol in the presence of common interferents. Electrodes modified by the electrodeposition of the conducting poly (3-methylthiophene) film (P3MT) and the poly (2, 2-bithiophene) film (PBTP) electrode was studied as chemical sensors for catechol, which is of industrial and medicinal interest. The scope of the experiment involved optimizing the modified polymer poly (2, 2-bithiophene) electrode to detect catechol in the presence of ascorbic acid. Further studies can be expanded in this lab experiment by studying the modified surface with Scanning Electron Microscopy (SEM).

These modified poly (2,2-bithiophene) platinum electrodes are capable of decreasing the overpotential, and/or improving the reversibility of electrochemical processes for such compounds as catechol and the irreversible behavior of ascorbic acid. In addition, the development of electrochemical sensors using polymer coated electrode surfaces can improve the selectivity of such sensors for practical analysis of clinical and environmental samples. Modified electrode coatings offer the assurance of bringing higher selectivity and reduced fouling compared with the corresponding bare electrochemical sensor [7,8]. For example, Wang et al. [9] showed that a microelectrode array, each coated with a different polymer possessing a different analytical function

(based on differences in size, porosity charge or polarity, etc), could be employed for simultaneous multi-species analyses. In contrast, modified electrodes based on the immobilization of redox mediators onto the electrode surface are also commonly used.

In the present work this paper will illustrate results that students have generated in an Analytical Chemistry course.

Experimental

Reagents and materials

Tetrabutylammonium tetrafluoroborate (TBATFB), Sulfuric acid (A.C.S. Reagent), and catechol (certified) were obtained from Fischer Scientific. Acetonitrile (HPLC grade, Aldrich) was used as solvent for electrochemical polymerization and, 2,2-bithiophene monomers were obtained from Aldrich. The monomers were stored at 0°C, 0.1 M Sulfuric Acid, (ACS Reagent, Fisher), was used as electrolyte in cyclic voltammetric studies. Deionized water was from Barnsted. All solutions were freshly prepared before each polymerization.

Electropolymerization conditions and apparatus

The electropolymerization of the 0.05M 2,2-bithiophene monomer solution diluted with 0.1 M TBATFB in acetonitrile at a polished Pt electrode (1.6mm) were carried out in a one compartment cell containing three electrodes, (as illustrated in Figure 1): working, reference and auxiliary. Platinum wire was the auxiliary electrode and the reference electrode was Ag/AgCl/3M NaCl (MF-2074, BAS) used in the three-electrode compartment cell. Various constant potentials of +1.8V, +1.7V, +1.6V or +1.5V were applied for 10 seconds using a CH 650B potentiostat-galvanostat (CH Instruments Inc.). Surface and spectral examination was performed using a JEOL 35 scanning electron microscope.

The electrolyte solutions of 0.1 M TBATFB dissolved in acetonitrile were deaerated with argon for ten minutes. After the electropolymerization, the PBTP electrode was rinsed with deionized water. A scan rate of 50mV s⁻¹ was used through out the studies.

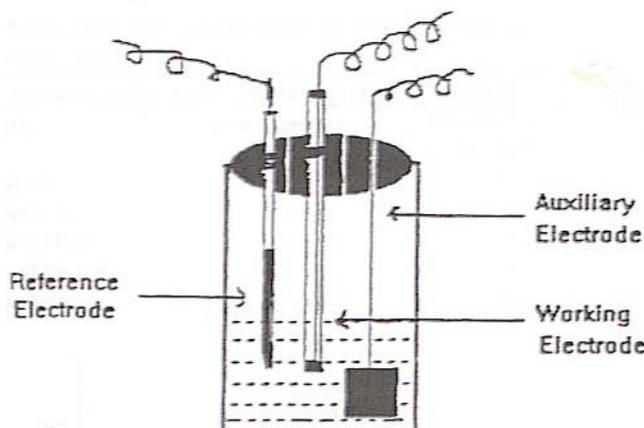


Figure 1. Schematic diagram of three-electrode compartment single compartment cell.

Hazards

All solution preparations are carried out under a fume hood. In this laboratory, the use of acetonitrile and hydrochloric acid required precaution. Acetonitrile is toxic or fatal by inhalation, ingestion or skin absorption. Upon mixing concentrated acid with water heat evolves and precaution was taken in this mixing step. All waste was disposed of in the proper waste container with labels. Protective garment and gloves should be worn at all times.

Results and Discussion

The anodic peak potentials obtained for catechol and ascorbic acid on a PBTP electrode were found to be dependant on the electropolymerization potentials. In this study the polymer film was grown electrochemically on a platinum substrate at four different potentials; +1.5V, +1.6V, +1.7V, +1.8V. The results obtained from the cyclic voltammograms carried out utilizing these PBTP electrodes showed that the ΔE_p values for the catechol, decreased from +1.5V to +1.8V and the peak separation became smaller. Table 1 and 2 lists the E_{p_a} values obtained for catechol and ascorbic acid, which displays that the bare platinum electrode the anodic peaks to be closer together for catechol at 625 mV and ascorbic acid at 699 mV. The modified PBTP polymer film there is a greater separation between the catechol and ascorbic acid anodic peaks. These values were obtained from the positive scan of the first voltammetric cycle at a scan rate of 50mVs⁻¹. Therefore, the electrocatalytic activity of the PBTP polymer film can be seen from the fact that these E_{p_a} values were consistently more negative than those obtained from the bare platinum. These results suggest that there is less problem of overlap between the anodic peaks for the modified PBTP platinum electrode between catechol and ascorbic acid.

Table 1. Comparison of oxidation potentials of bare platinum and modified platinum PBTP in the detection of catechol

Catechol	E_{p_a} / mV	E_{p_c} /mV	ΔE mV
Bare Platinum	625	404	221
Platinum PBTP (1.8V)	573	450	123

Table 2. Comparison of oxidation potentials of bare platinum and modified platinum PBTP in the detection of ascorbic acid

Ascorbic Acid	E_{p_a} /mV
Bare Platinum	699
Platinum PBTP (1.8V)	460

Table 3. Electrochemistry of catechol and ascorbic acid at platinum electrode modified by 2,2-bithiophene synthesized at different potentials, AA=Ascorbic Acid

Catechol (Pt)	Ep_a /mV	Ep_c /mV	? E mV
1.5V	601	414	187
1.6V	590	427	163
1.7V	579	448	131
1.8V	573	450	123
AA			
1.5V	470	--	--
1.6V	437	--	--
1.7V	407	--	--
1.8V	402	--	--

Table 4. Electrochemistry of catechol in the presence of ascorbic acid (AA) at a platinum electrode by 2,2-bithiophene synthesized at different potentials

Catechol	Ep_a/mV (AA)	Ep_a/mV	Ep_c/mV	? E mV
1.5V	450	582	458	124
1.6V	421	577	458	116
1.7V	402	575	464	108
1.8V	402	575	464	108

Table 3, and 4 presents the data illustrating the consistent decrease in the peak separation as the electropolymerization potentials increased. The data strongly suggests electrodes modified with polymer films electrochemically grown at +1.8V exhibits a greater sensitivity, selectivity and effectiveness in detecting catechol and ascorbic acid separately and catechol in the presence of AA with data from Figures 2 and 4.

Figure 2. Cyclic voltammogram for 5mM catechol diluted with 0.1 M H₂SO₄ at PBTP modified Pt electrode

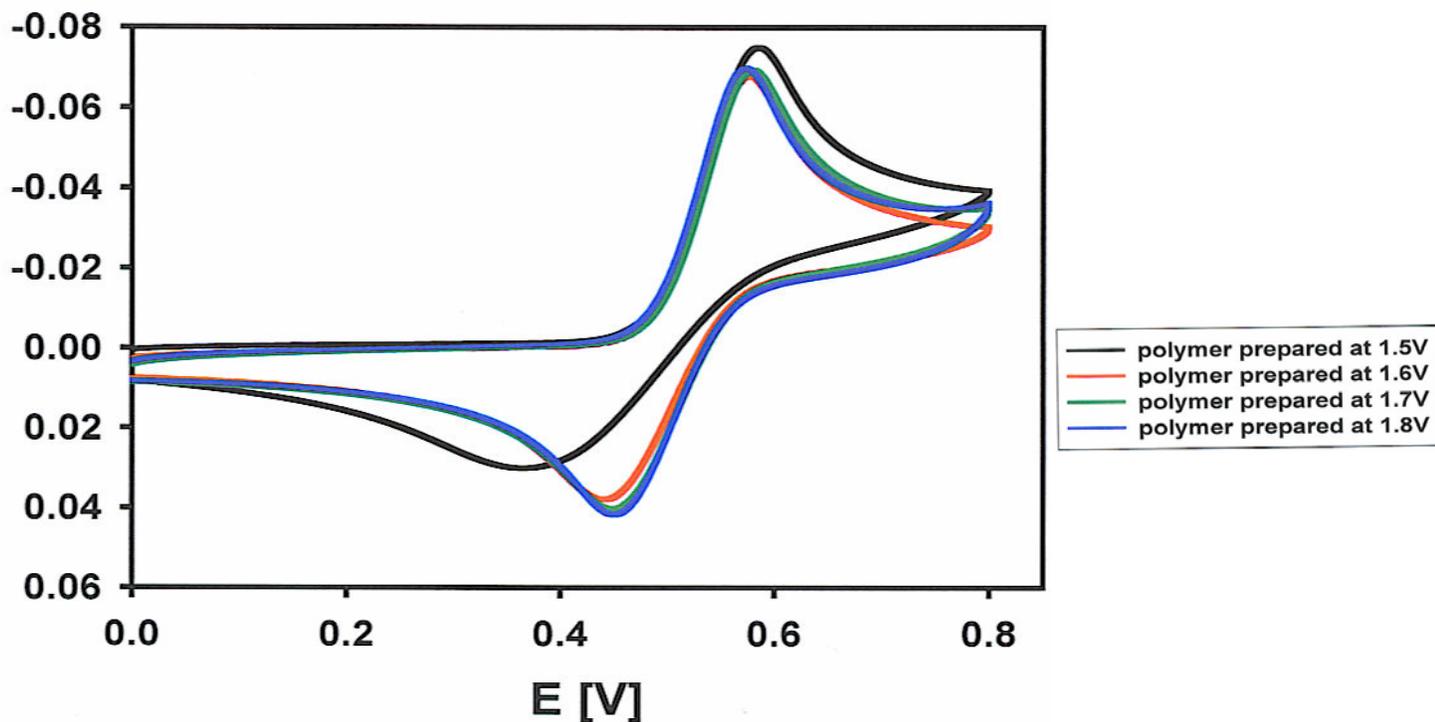


Figure 3. Cyclic voltammogram of 5mM ascorbic acid diluted with 0.1 M H₂SO₄ at a PBTP modified Pt electrode; Black= 1.5V, Red= 1.6V, Green= 1.7V and Blue= 1.8V

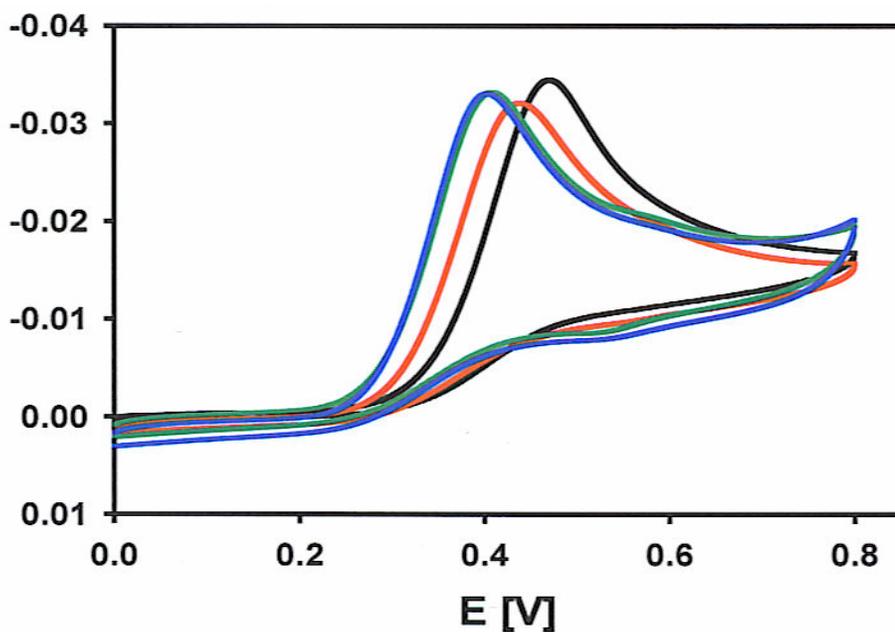


Figure 4. Cyclic voltammogram of an equimolar mixture of 5mM ascorbic acid and catechol diluted with 0.1 M H₂SO₄; Black= 1.5V, Red= 1.6V, Green= 1.7V and Blue = 1.8V

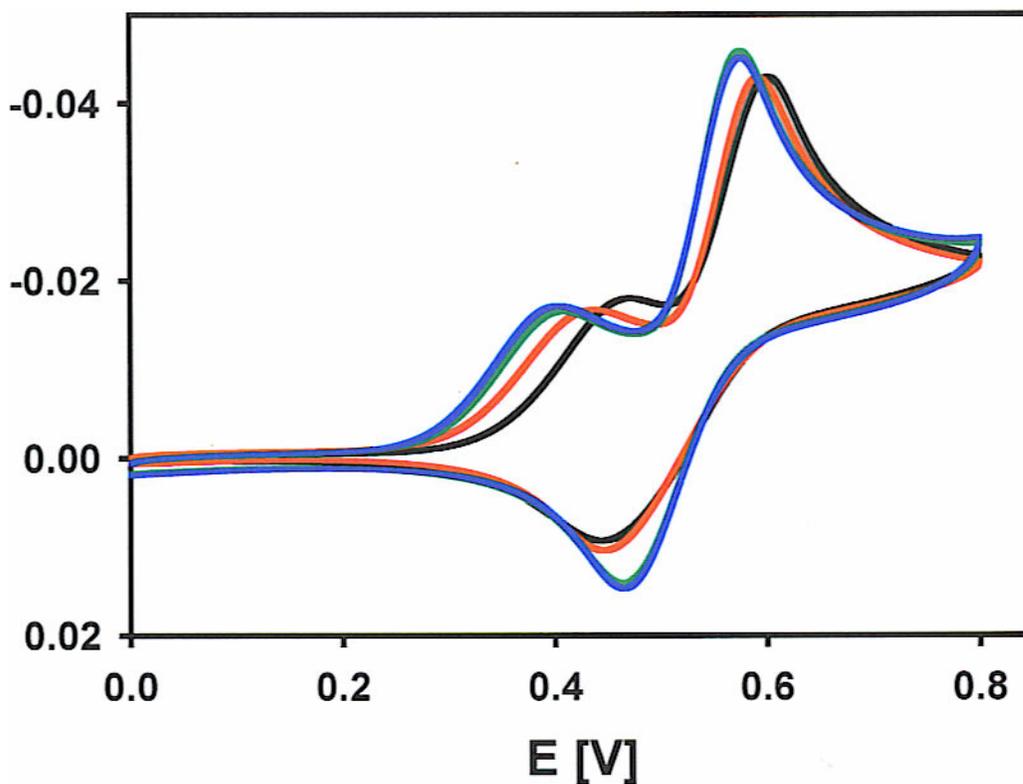


Figure 3 displays that the response of the PBTP electrode to ascorbic acid is irreversible and Figure 4 shows a mixture that catechol can be detected in the presence of common interferent ascorbic acid. Figure 4 demonstrates the selectivity principle in the electrochemical detection of catechol in the presence of ascorbic acid. We can conclude that PBTP modified electrodes have demonstrated that the reversibility of catechol is significantly improved compared to that of the bare platinum electrode. The PBTP modified electrodes are effective in detecting catechol and ascorbic acid simultaneously.

Polymers prepared at +1.8V has an improved catalytic activity compared to lower potentials. The SEM data in Figure 5 confirms that the PBTP polymerized at +1.8V has a more cross-linked/uniform film surface compared to +1.5 V. Thus the higher potential produces a more conductive matrix exhibiting a smaller and more reversible peak separation with higher peak current intensities as can be seen by cyclic voltammetry .

Conclusion

This experiment can be used to introduce electroanalytical chemistry skills to undergraduate students as well as the concept of electrochemical sensors. Modified chemical sensors are certainly one of the exciting developments of the last two decades. Modified electrodes can be utilized as chemical sensors for the detection of organic and biological molecules of industrial and medicinal interest. This laboratory can be carried out in approximately 10-12 hours of lab time. It allows the introduction and development of chemical sensors and modified electrodes, and it teaches the common interferences encountered, the use of the potentiostat-galvanostat, and the use of a cyclic voltammogram. This lab can be expanded into analyzing the modified surfaces with Scanning Electron Microscopy if time permits. The scope of this lab can be further expanded into the study of a) other common neurotransmitters and biological molecules, b) other common interferences in the detection of biological molecules and neurotransmitters, c) the use of other modified-polymer electrodes as sensors and d) improvements in the modified polymer electrode preparation.

Our students have found this laboratory to be both rewarding and challenging. It has required them to think the actual instrumental procedures and about the analysis of the results. This laboratory experiment can be tailored for more advanced students by using more than one interference and more than one neurotransmitter for these studies. Students could be required to learn additional instrumentation skills, such as amperometric detection/flow-injection detection of biological molecules of interest utilizing a modified polymer electrode. This type of study is really unlimited and relates well to students' interest in everyday biological molecules.

Acknowledgements

The authors would like to express gratitude to Research Experiences To Enhance Learning (REEL) project funded by the National Science Foundation and Ohio State University for their support as well. Also, gratitude goes to the College of Engineering at Wright State University for their generous help with the SEM work and helpful suggestions and comments to expand this lab experiment.

References

- [1] T.A. Skotheim (Ed.) Handbook of Conducting Polymers, Vols, 1&2, Marcel Dekker, New York, 1986.
- [2] H.D. Abruna in T.A. Skotheim (Ed.), Electroresonsive Molecular and Polymeric Systems, Vol 1, Marcel Dekker, New York, 1988.
- [3] A. Ivaska, *Electroanalysis*, **3** (1991) 247.
- [4] A.N.K. Lau, and L.L. Miller, *J. Am. Chem Soc.*, **105** (1983) 5271.
- [5] Bettelheim, B.A. White, S.A. Raybuck and R.W. Murray, *Inorg. Chem.*, **45** (1982) 1233.
- [6] A. Merz, and A.J. Bard, *J. Am. Chem. Soc.*, **100** (1987) 3222.
- [7] G. Strampalam and G.S. Wilson, *Anal. Chem.*, **55** (1983) 1608.
- [8] J. Wang, S.P. Chen and M.S. Lin, *J. Electroanal. Chem.*, **273** (1989) 231.
- [9] J. Wang, G. Rayson, Z. Lu, and H. Wu, *Anal. Chem.*, **62** (1990) 1924.