An Introduction to Electrochemistry for Undergraduates: Detection of Vitamin C (Ascorbic Acid) by Inexpensive Electrode Sensors

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Abstract: This paper describes an undergraduate laboratory for general chemistry that can be used to supplement the teaching of oxidation–reduction reactions. The laboratory experiment also introduces students to basic electrochemical techniques and instrumentation. Using inexpensive materials to make carbon-paste electrodes, ascorbic acid (vitamin C) is oxidized with the cyclic voltammetry technique. The students learn to operate the potentiostat, prepare electrodes from inexpensive materials, and oxidize the vitamin C in over the counter tablets.

Introduction

Oxidation–reduction reactions are introduced in general chemistry and studied in upper-level chemistry courses. These types of reactions are very important to the food, biological, and pharmaceutical industries. Many different chemicals used by these industries are detected and analyzed using oxidation–reduction reactions. One compound, ascorbic acid is routinely analyzed in foods, beverages, and drugs. Ascorbic acid is easily oxidized at a carbon electrode and can be detected by electrochemical techniques, such as cyclic voltammetry.

Cyclic voltammetry is a common electrochemical technique that is simple and versatile and can be used to study redox states of molecules [1–3]. In cyclic voltammetry the potential of a working electrode is cycled linearly between two potential values at which the oxidation and reduction of a solute occurs. The resulting current–potential curve is a cyclic voltammogram. The reducing or oxidizing strength of the electrode is controlled by the applied potential. When the potential is scanned in the negative direction, the electrode becomes a stronger reductant. If the potential is scanned in the positive direction the electrode becomes a stronger oxidant. This laboratory uses cyclic voltammetry to introduce students to various oxidation–reduction reactions. Students also create their own working electrodes from carbon paste [4, 5]. A carbon-paste electrode (CPE) is made from a mixture of conducting graphite powder and a pasting liquid. These electrodes are simple to make and offer an easily renewable surface for electron exchange.

The experiments can be completed in one or two laboratory periods. In the first experiment, the ferri/ferrocyanide couple is oxidized and reduced. In the second experiment ascorbic acid is oxidized. The difference between a reversible and irreversible electrochemical reaction is shown.

Experimental

Materials and Reagents. Potassium chloride (Aldrich), silicon oil (Fisher), graphite powder (Aesar), potassium ferrocyanide (Fisher), potassium phosphate monobasic (Fisher), potassium phosphate dibasic (Fisher), nitric acid (Fisher), vitamin C tablets (250 mg), copper wire, glass tube (70 mm long × 5 mm diameter), wax paper, 1-L and 250-mL volumetric flasks.

Instrumentation. The electrochemical experiments were controlled with a Pine Bi-potentiostat (AFCBP1). Voltammograms were recorded on a Linseis *xy* recorder (LY16100-11). Data was also collected using LabVIEW software (National Instruments) and an AT-MIO-16DH A/D board (National Instruments) on a 386 computer interfaced to the potentiostat. Collected data was saved as ASCII files and manipulated with either Origin 5.0 or Excel.

Solution Preparation. The test solutions consist of 250 mL of 10^{-3} M potassium ferrocyanide in 0.1 M potassium chloride and 250 mL of an ascorbic acid solution. The ascorbic acid solution was prepared by dropping a 250 mg vitamin C tablet in a beaker containing 250 mL of phosphate buffer, then stirred until mostly dissolved. Binding agents in the tablet will not dissolve. It is not necessary to filter out the binding agents.

Electrode Preparation. Weigh 5.66 g graphite powder and grind to a fine powder with a mortar and pestle. Add 3.00 mL of silicon oil and mix until a fine paste is obtained. Pack the end of a glass tube with the paste until approximately 20 mm of the tube is filled. Insert a spiraled copper wire from the opposite end of the tube into the paste for electrical contact. While pressing the front end of the paste against a flat surface, take and insert a small solid glass rod into the opposite end of the tube and tap the paste down. Then polish the front face of the paste to a smooth finish on wax paper or an index card.

Electrochemical Cell Setup. The electrochemical cell was a 400-mL beaker cleaned with dilute nitric acid and rinsed with deionized water. The cell consists of a carbon-paste working electrode (CPE) (made as described in the previous section), a reference electrode (Ag/AgCl or saturated calomel electrode (SCE)), and a Pt wire or Pt gauze as a counter electrode. Reference electrodes can be prepared in the laboratory according to procedures described in literature [6, 7] or can be purchased from a chemical supplier.

Procedure. Fill the beaker with 250 mL of the analyte solution. Place the end of the three electrodes into the solution and hold into place with clamps. Connect the copper wire of the CPE to the working electrode lead of the potentiostat, the saturated calomel electrode (SCE) to the reference lead of the potentiostat, and the Pt wire to the counter lead of the potentiostat. Turn on the potentiostat and the *xy* recorder. Run a cyclic voltammogram at a sweep rate of 50 mV s^{-1}.

Results and Discussion

A diagram of the electrochemical set-up is shown in Figure 1. The cell consists of three electrodes immersed in a solution. The three electrodes are connected to the potentiostat by leads. The potentiostat controls the potential of the working electrode with respect to the reference electrode while also measuring the current flow between the working electrode and counter electrode. To perform a cyclic voltammogram experiment, the potential is scanned starting at a negative potential to a

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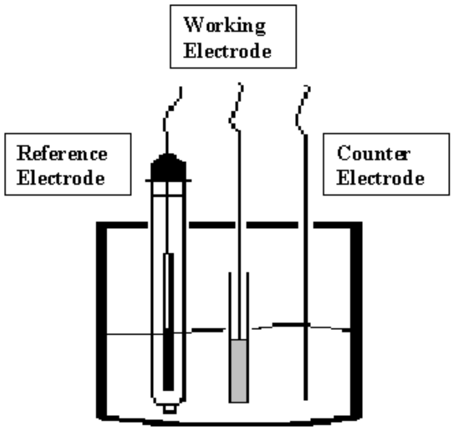


Figure 1. Schematic of the electrochemical cell.

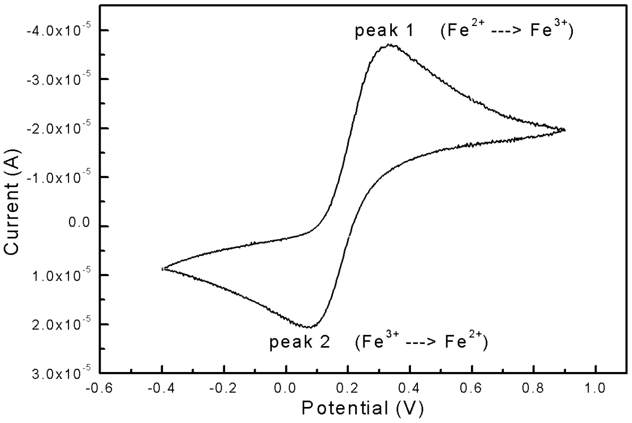


Figure 2. Cyclic voltammogram of ferrocyanide.

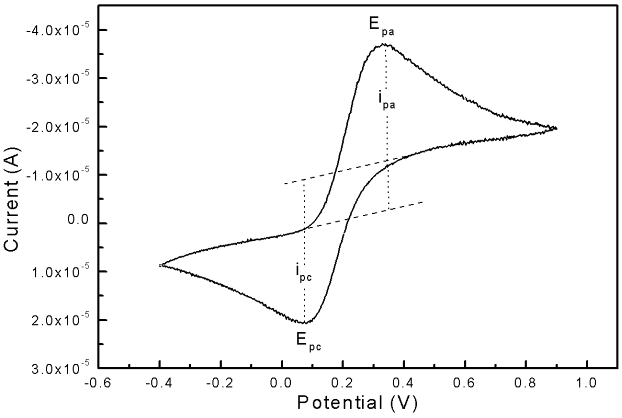


Figure 3. Cyclic Voltammogram of Ferrocyanide.

positive potential and back. Figure 2 shows the resulting current–potential (cyclic voltammogram) curve for potassium ferrocyanide in solution using a carbon-paste electrode made from graphite and silicon oil. From the starting potential of –0.400 V, the potential is scanned to more oxidizing (positive) potentials to the right, until the potential is sufficient to oxidize $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ (peak 1). The *y* axis depicts the oxidizing (anodic) current as up and reducing (cathodic) current as down. The potential is then reversed at +0.900 V and scanned towards more reducing (negative) potentials, where $Fe(CN)_6^{3-}$ is then reduced to $Fe(CN)_6^{4-}$ (peak 2).

The cyclic voltammogram can then be labeled to show several important parameters (Figure 3): the cathodic peak potential (E_{pc}), the anodic peak potential (E_{pa}), the cathodic peak current (i_{pc}), and the anodic peak current (i_{pa}). A general representation of the oxidation–reduction reaction that occurs at the working electrode is as follows:

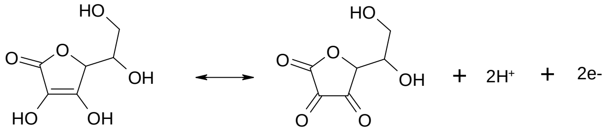
$$Ox_1 + ne^- \rightarrow Red_1 \qquad (1)$$

The potential between the two peak potentials is the formal reduction potential, $E^{o\prime}$:

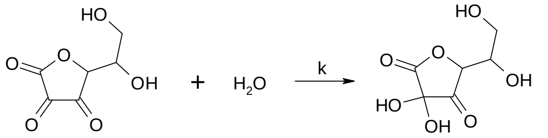
$$E^{o\prime} = (E_{pa} + E_{pc})/2 \qquad (2)$$

On the positive side of the formal potential the oxidized form of the couple is stable at the electrode, and on the negative side of the formal potential the reduced form of the couple is stable. Right around the formal potential region the oxidized and reduced species are in equilibrium. Ferri/ferrocyanide is a reversible redox couple in which both the oxidized species and reduced species exchange electrons easily with the working electrode.

The cyclic voltammogram of ascorbic acid measured with the carbon-paste electrode is shown in Figure 4. When the working potential is swept toward more oxidizing (positive) potentials, the oxidizing current (peak 1) for ascorbic acid is seen. However, when the potential is reversed and scanned towards reducing potentials, no peak occurs for the reduction of the oxidized ascorbic acid. There is no peak because the oxidized form of ascorbic acid is converted chemically to a species that is not reduced in the reverse sweep. The reaction pathway for ascorbic acid is shown below.



(3)



(4)

In eq 3, ascorbic acid is oxidized with the loss of two electrons. The oxidized form of ascorbic acid quickly undergoes a chemical reaction with the addition of water (eq 4). The resulting species formed in this reaction is not electroactive and will not be oxidized or reduced at the electrode. The above reactions show why the ascorbic acid exhibits irreversible electrochemical behavior, because the cyclic voltammogram shows only the oxidized (anodic) peak for the ascorbic acid.

Conclusion

Cyclic voltammetry of ferrocyanide and vitamin C (ascorbic acid) can be used to introduce oxidation–reduction reactions to general chemistry students. The oxidation and reduction of the two chemicals, ferrocyanide and ascorbic acid, also introduces

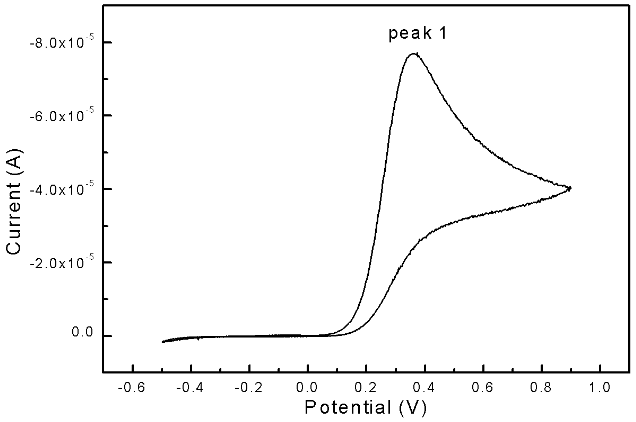


Figure 4. Cyclic Voltammogram of Ascorbic Acid.

the students to the difference between reversible and irreversible electrochemical reactions. In one or two laboratories, the students can complete electrochemical experiments to study oxidation–reduction reactions.

Supplemental Material

The student handout for laboratory experiment is available in the supporting documentation (520058tgs1.pdf).

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