

Voltammetric measurements with solid electrodes

Introduction

The voltammetric measurements are important experimental methods of electrochemistry and electroanalytical chemistry. In voltammetric measurements the electrode potential of an appropriate working electrode (usually it is marked as W) is controlled by a preset electrode potential – time program. The electrode surface is in contact with the electrolyte solution content of the measuring cell. The current passing through the cell reflects the processes taking place at the electrode surface. Therefore during the measurements the current is recorded, or information is collected about its instantaneous value using a data collecting unit. From the data collected voltammograms are made. The voltammogram shows the dependence of the current on the electrode potential. The conditions applied in the cell during measurements, the properties of electrode potential – time program as well as the way of collecting, and processing the current influence the shape, size and information content of the voltammograms. Accordingly, high a variety of voltammetric measuring techniques has been worked out and has been used.

DC voltammetry means direct current voltammetry. SWV or SWP means square wave voltammetry or square wave polarography. Further more often used PV pulse voltammetry DPV differential pulse voltammetry, or alternative current voltammetry –ACV.

The different inverse voltammetric techniques, -they often called stripping voltammetry- are among the analytic methods providing very low detection limits.

The word “polarography” is used when the voltammetric methods are made with mercury electrode. Dropping mercury electrodes or hanging mercury electrodes were the favorite working electrodes in the early times of voltammetry. In our days the use of the mercury electrodes are very much limited because of the environmental hazard nature of the mercury. In our days most often solid electrodes are used in practice of voltammetry.

Use of dropping mercury electrode (DME) has two important advantages. On one hand it renews itself drop by drop. Its surface does not get fouled by the product of the electrode reaction. The other advantage is the very high over potential of the hydrogen gas evolution. Owing to this, the mercury electrode can be used for reduction of different metal ions dissolved in aqueous solutions. The mercury is not a noble metal. Polarizing it to the anodic direction (positive) would result in dissolution of the metal. Therefore mercury electrodes are not used as working electrode in analyzing electroactive organic species through their electrochemical oxidation.

In positive potential range solid electrodes made of platinum or gold are used as working electrode. For the analysis of electroactive organic molecules, among them several drugs, carbon electrodes are used. Very well performing working electrodes can be made using the mixture of carbon powder and nujol (paraffin oil) as it has been invented by Ralph Adams. The measuring surface of the commercial carbon electrodes are made of Glassy Carbon. Miniaturized carbon electrodes use carbon fiber as active ingredient.

Recently the so-called chemically modified electrodes are gaining broad scale application. Their measuring surface is coated with special layers that improve property of the electrode. Higher sensitivity, selectivity, improved lifetime, electrocatalytic action etc. can be obtained resulted by the special modifying layers.

Two additional, other kinds of electrodes are needed for carrying out voltammetric measurements. One is the reference electrode (Usually marked R). This is an electrode that keeps its potential constant. It does not get polarized during measurements. The potential of the working electrode relates to the potential of the reference. Most often calomel electrodes ($\text{Hg}/\text{Hg}_2\text{Cl}_2$, Saturated Calomel Electrode, SCE) or silver/silver chloride electrodes (Ag/AgCl) are used as reference. Often the reference electrode is connected to the cell through a current bridge. The other additional electrode needed is named counter (C) or auxiliary (A) electrode. The counter electrode process

takes place at the surface of this electrode. Usually electrodes with high surface area and made of noble metals are used as counter electrode.

During voltammetric measurements the three electrodes are in contact with the liquid content of the cell. It can be melted salt or electrolyte solution of appropriate conductivity.

The solution called back ground electrolyte. It contains solvent, ionic components giving high conductivity, buffer and other additives. Often the oxygen content of the solution would disturb the measurements. Therefore the oxygen needed to be taken out of the solution. It most often is done by bubbling clean nitrogen or argon gas through the cell before voltammograms taken.

Different kinds of instruments are used in making voltammetric experiments. In early times mechanic voltage divider (Kohlrausch drum) gave simple DC voltage - time program and mechanic current recording units, like XY recorders were used. The modern instruments use computer controlled current programing, data collecting handling and evaluating program. In the laboratory practice an advanced computerized electrochemical workstation is used. It is recommended to take along a flash drive, or other data storage tool, so the collected data can be analyzed after the measurements for finalization of the notebook. Word Excel, Origin or any kind of evaluating, drawing programs can be used.

The description of the measurements.

Investigation of the cyclic voltammetric behavior (CV) of the $K_4Fe(CN)_6/K_3Fe(CN)_6$ redox couples

Using platinum disc working electrode and sulfuric acid back ground electrolyte we can get close to reversible cyclic voltammograms of the $K_4Fe(CN)_6/K_3Fe(CN)_6$ redox couples. We make 50 cm³ solution that contains both the oxidized and reduced species in 0.5 mM concentration and 0.5 M sulfuric acid as back ground electrolyte. We pour about 25 cm³ of this solution into a beaker of 50 cm³ and insert the three electrodes. The electrodes should be connected to the workstation carefully finding the W, R and C inputs. We use platinum disc working electrode, platinum wire auxiliary electrode and calomel reference one. A magnetic stirring bar is introduced.

Finding a broad potential windows like:

Initial potential: -0.2 V, Final potential: -0.2 V

Turning potential: 0.8V

Polarization rate: 0.1V/s

We make CV-s, and we select the right potential window. (It is narrower than the first broad window). Using the selected potential windows we make at least 7 CV-s with different polarization rates. We collect the following data v , i_{p_a} , E_{p_a} , i_{p_c} , E_{p_c} , ΔE in a nice table:

v (V/s)	i_{p_a}	E_{p_a}	i_{p_c}	E_{p_c}	ΔE

From the data we make the $v^{1/2} - i_{p_a}$; $v^{1/2} - i_{p_c}$; $v - \Delta E$ graphs

It is known that in case of an electrochemically reversible couples $E_{p_a} - E_{p_c} = \Delta E = 58.8$ mV and $i_{p_a} = i_{p_c}$

Randles-Sevcik equation:

$$i_p = kAn^{3/2}cD^{1/2}v^{1/2}$$

where n is the number of electrons taking part in the process, k is constant, A is the surface area, c is the concentration D is the diffusion coefficient, v is the scanning rate. Therefore the $v^{1/2} - ip_a$; $v^{1/2} - ip_c$ dependences should be linear.

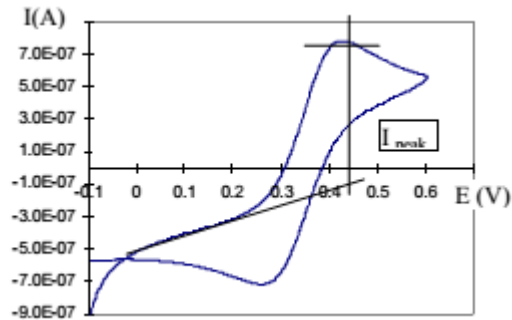


Fig.1a Cyclic voltammogram. The way of getting the ip_a value is indicated

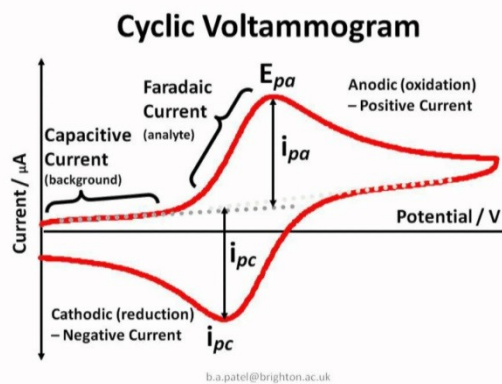


Fig.1b Cyclic voltammogram. The way of getting the ip_a value is indicated

Experimental study of the Tafel dependence

As it is well known, linear dependence exists between the logarithm of current (i) or current density ($j = i/A$) and the overpotential (η , $\eta = E - E_0$). It is true in conditions when the rate determination step of electrode process is the electron exchange step. The Tafel equation shows the function.

$$\eta = (E - E_{eq})$$

$$\ln j = \ln j_0 - \alpha \eta F / (RT)$$

Where j_0 is the exchange current density, A is the surface area, α is the so-called "charge transfer coefficient", the value of which must be between 0 and 1. R is the universal gas constant, F is the Faraday constant, T is temperature.

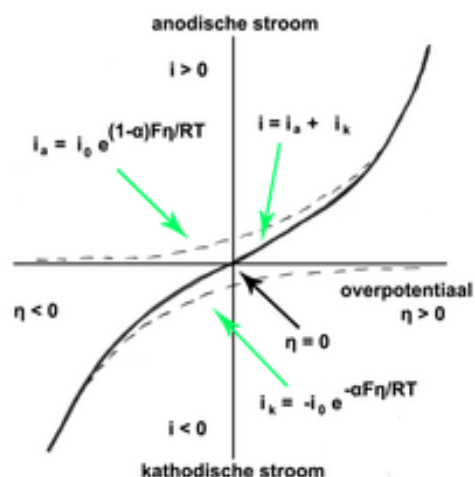


Fig. 2 Dependence of the current on overpotential $\eta = E - E_{eq}$. The anodic and cathodic current are shown as i_a and i_k , respectively. The total current $i = i_a + i_k$.

You have made several CV of the $\text{K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$ redox couples. You have the data in digital form. Select the exponential section of the CV data and plot it against the electrode potential. The $\log i - E$ plot should be linear. (It is known that in early section of the CV the rate determining step is the electron exchange). *One graph is needed in your note book.*

Investigation of the Cottrell experiment

The Cottrell experiment shows how the current depends on the time if the rate determining step of the electrode process is planar diffusion of the electroactive species toward the electrode surface. In this experiment we use conventional size platinum disc working electrode, platinum wire auxiliary electrode and SCE reference one. We pour into the measurement cell (it can be a small beaker of 25 or 50 cm^3 volume) 10-20 cm^3 5mM $\text{K}_4\text{Fe}(\text{CN})_6$ or $\text{K}_3\text{Fe}(\text{CN})_6$ solution in 0.5M sulfuric acid. We introduce into the cell and connect to the potentiostat the electrodes. Looking the CV we find an electrode potential (E_0) where no reaction takes place at the electrode surface and another where the electron exchange reaction is very fast (E_t) (this potential should be over the E_{p_a} or E_{p_c}).

After obtaining steady current for E_0 at instant $t = 0$ we switch to E_t and collect the current – time data pairs. The collecting period can be between 10 and 20 seconds. The collecting frequency is 0.01-0.1 data pairs/s.

Plotting the current against the time we obtain a monotone decreasing curve as the Cottrell equation predicts. (Current – time plots recorded at constant electrode potential called chronoamperometric curves)

$$i = \frac{n F A D^{1/2} C}{(\pi t)^{1/2}}$$

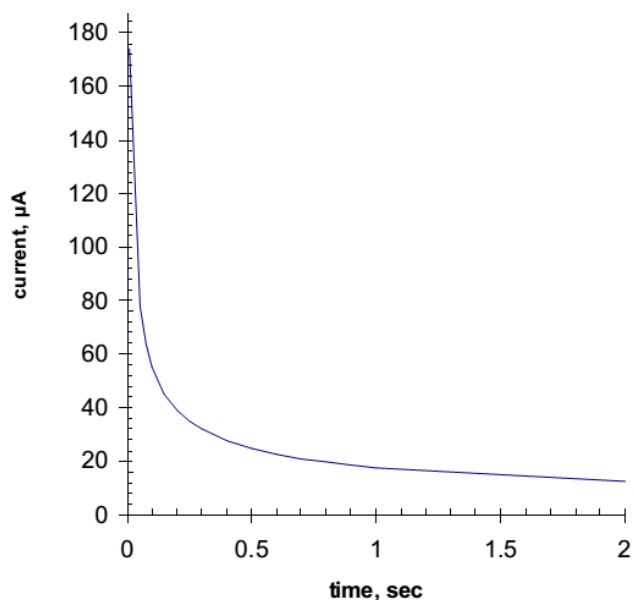


Fig. 3 Chronoamperometric curve in case of Cottrell experiment

If we multiply both sides of the Cottrell equation by $t^{1/2}$ then only constants stay in the right side. Therefore plotting the $i_t \cdot t^{1/2}$ against t we should obtain a horizontal line indicating that the rate determining step of electrode reaction is the planar diffusion. The note book must contain both ($i_t \cdot t^{1/2} - t$ and $i_t - t$) diagrams.

Investigation of voltammetric behavior of N-acetyl p-aminophenol (paracetamol)

Acetaminophen (paracetamol) (*N*-acetyl-*p*-aminophenol) is a popular, antipyretic and non-steroidal anti-inflammatory drug. It is the preferred alternative to aspirin, particularly for patients who cannot tolerate aspirin. The paracetamol can be electrochemically oxidized using different working electrodes. As usual in case of organic molecules- the pH, the property of the solvent and the nature of the working electrode can have substantial influence on the mechanism and kinetics of the electrode process. (see Fig. 4.)

In this experiment we investigate the voltammetric behavior of paracetamol in 0.1 M HCl solution using platinum and Glassy Carbon disc working electrodes.

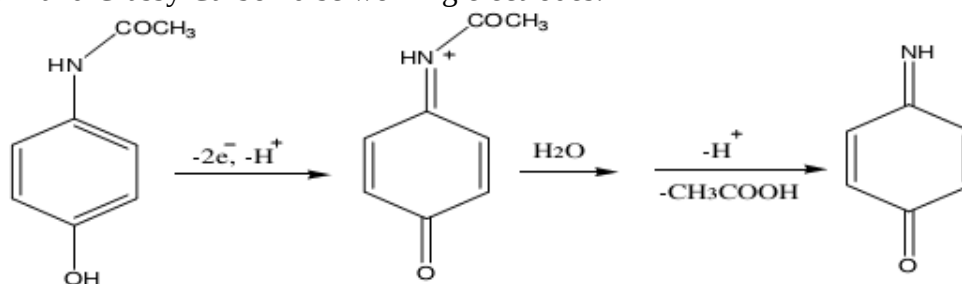


Fig. 4 Scheme of electrooxidation of paracetamol

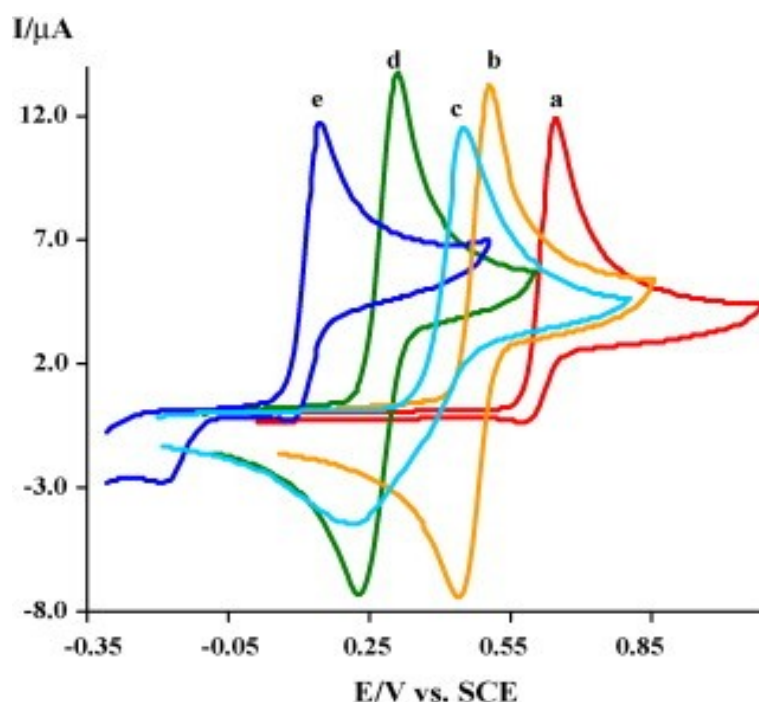


Fig. 5 CV-s of 1mM paracetamol at glassy carbon electrode in in buffer solution of different pH, pH from *a* to *e* are: 1.2, 5.0, 7.0, 9.0 and 13.0. Scan rate: 50 mV s^{-1} . $t = 25 \pm 1 \text{ }^\circ\text{C}$.

First we make a stock solution of paracetamol in a 25 cm^3 volumetric flask using 0.1 M aqueous HCl solution as solvent. ($M_w = 151.169 \text{ g/mol}$). After we select two 25 cm^3 beakers, we use them as measuring cell. We add 10 cm^3 0.1 M HCl background electrolyte into both cells and into one of them 0.5 cm^3 paracetamol stock solution. We make CV-s with platinum and Glassy Carbon working electrodes in both cells. (We use platinum auxiliary electrode and SCE reference). A broad potential window and 0.1 V/s scanning rate should be adjusted together with the right sensitivity. The voltammograms are recorded in quiescent solution but between each scan intensive stirring with magnetic stirrer must be employed. Comparing the obtained CV-s we see the sensitivity, the potential range and the reversibility of the voltammetric measurement. We can select the right potential window and sensitivity for the next experiment (preparation of calibration curve). The surface of the solid electrodes can get fouled when the product of the electrolysis stays adsorbed. Therefore it is a good practice if before measurements we renew the measuring surface of the working electrodes. It can be done by wet polishing the surface with polishing powder spread on a piece of fine fabric tissue.

For making the calibration curve we pipette 10 cm^3 HCl solution into a well cleaned, dry 25 cm^3 beaker (measurement cell). Inserting the electrodes and the stirring bar we record voltammograms in quiescent solution. One after the other we add 0.1 cm^3 doses of the paracetamol solution stock to increase the paracetamol concentration. Between measurements we employ intensive stirring. Several parallel measurements should be made at each every paracetamol concentration. Then we calculate the concentration and measure the i_{p_a} values. For making a reliable calibration curve we need to get at least 5-7 different data pairs. From the data pairs we make a table and prepare the calibration curve plotting the i_{p_a} values against the concentration

Table showing the data pairs for calibration curve preparation:

C (mM)	i_{p_a} (μA)

It worth mentioning, that the voltammetry is not sample destructive method. The amount of material oxidized at the electrode surface is very small. Electrode reaction does not effect the sample concentration in the measuring cell.

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