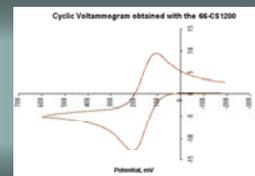


Experiments in Analytical Electrochemistry



2. Cyclic Voltammetry With A Microelectrode

PURPOSE: To determine the characteristics of a disk microelectrode by cyclic voltammetry.

BACKGROUND: The experiment titled *Cyclic Voltammetry at Solid Electrodes* is a precursor to this experiment with microelectrodes. Please review the Background and Theory sections of that experiment to prepare for this one. Two online articles of interest are:

http://www.utdallas.edu/~tres/microelectrode/microelectrodes_ch01.pdf. This article describes how to make microelectrodes, their properties, and illustrates uses and applications.

http://www.iupac.org/publications/pac/2000/7208/7208pdfs/7208stulik_1483.pdf. This article is part of the International Union of Pure and Applied Chemistry (IUPAC) commission's report discussing definition, characterization and applications of microelectrodes.

What is the dimension of a microelectrode and how does it behave electrochemically in comparison to macro-sized electrodes? There are several different geometries and configurations of microelectrodes (e.g., spherical micro-ball, thin cylindrical shaped fiber, tapered microtip, etc.). For the current discussion, the microelectrode will be a flat disk configuration with diameter of tens of micrometers or less. For example, a popular size is a 10 μm diameter glassy carbon, Pt or Au disk. At the extreme of smallness, a microelectrode made from a carbon multi-wall nanotube of 100 nm in diameter has been reported [ref. 1].

THEORY: The cyclic voltammetry (CV) wave is shaped differently at a microelectrode, as illustrated in Figure 1, for the oxidation of ferrocene in acetonitrile. Not only is the magnitude of the current much less due to the smaller electrode area, but also the current goes to a steady-state value and is not peak-shaped. This steady-state current is explained by envisioning the microelectrode as a "dot" with the diffusion layer being hemispherical in shape and extending out into the solution. The amount of electroactive species diffusing to the electrode surface is defined by the volume enclosed by this expanding hemisphere, rather than a plane projecting into the solution as for a planar electrode. Only at very short times when the diffusion layer, δ , is still much smaller than the radius, r_0 , of the microelectrode, will the current be approximated by what is given by the Cottrell relationship [ref. 2] if the applied potential is a step function. At times when $\delta \gg r_0$, diffusion to the edge of the electrode becomes significant; i.e., the diffusion profile approximating a hemispherical shape. Under such a condition, the current goes to a steady-state value as given by [ref. 3]

$$i_{ss} = 4nFD C^b r_0 \quad (1)$$

where i_{ss} is the steady-state current in ampere, n is the number of electrons in the reaction, D is the diffusion coefficient of the electroactive species in cm^2/s , C^b is the bulk concentration of the electroactive species in mole/cm^3 , and r_0 is the radius of the disk microelectrode in cm.

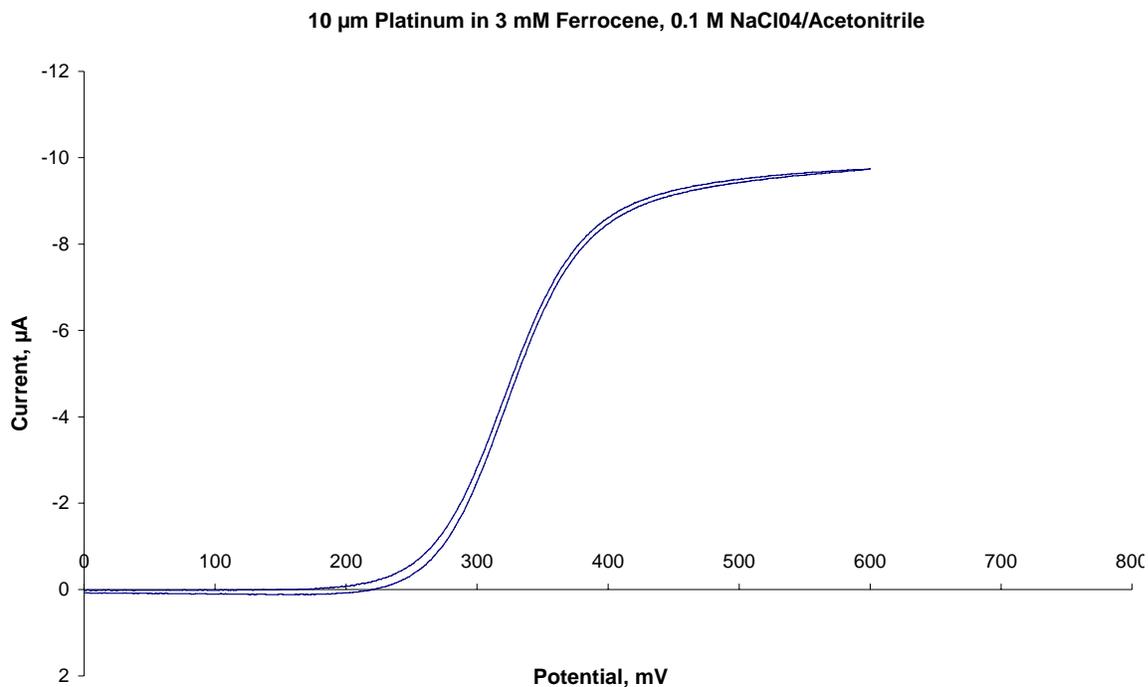


Figure 1. Oxidation of 3 mM ferrocene in 0.1 M NaClO_4 with acetonitrile as the solvent. 10 μm Pt microelectrode with a gel-filled Ag/AgCl reference electrode. The scan rate is 100 mV/s.

The low level of current makes iR losses negligible even at high scan rates. This allows the determination of kinetic rates of electron transfer that are very fast by scanning at high rates. Also, the small area means that the background or capacitive current is low in comparison to the Faradaic current so that the signal to noise (S/N) is enhanced, allowing measurements at lower concentrations. Of course, one important feature of microelectrodes, particularly carbon fibers, is being able to make measurements in small volumes such as applications in biological cells and nerve synapse [ref. 4]. A 3-electrode potentiostat with capability to measure small currents at a wide range of scan rates is recommended for working with microelectrodes. Some have been developed specifically for in-vivo and in-vitro studies of neurotransmitters, such as dopamine and norepinephrine [ref. 5].

Another difference between CV at microelectrodes compared to larger ones is that the reverse current is not due to the redox of the product formed during the forward scan, but is the continuation of the forward scan reaction. Thus, the forward and reverse waves track each other in an “ideal” reversible electrode reaction. In this experiment, the CV for the reduction of ferricyanide is used to characterize what happens at a microelectrode.

EXPERIMENT

Equipment

- A high sensitivity potentiostat with a wide range of scan rates is recommended. Please see your laboratory instructor for directions.
- Electrochemical cell and electrodes
 - 10 μm microelectrode, Pt or GC
 - Pt auxiliary electrode
 - Ag/AgCl reference electrode
 - Small volume electrochemical cell
 - Polishing kit

Chemical Solutions

- A. 100 ml stock solution of 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 0.1 M KNO_3
* An alternative is to use water-soluble ferrocene carboxylic acid (FCA) in pH 7 buffer.
- B. 100 ml of 1.0 M KNO_3
* Use high purity water throughout.

Procedure

1. Prepare 50 ml each of 1, 2, 5 and 10 mM ferricyanide in 0.1 M KNO_3 by appropriate dilution of solutions A and B.
2. Please see laboratory instructor for set-up and operational direction of the potentiostat.
3. Run scan rate (50, 100, 200 and 500 mV/s) dependence of i_{ss} with a 10 μm glassy carbon or Pt microelectrode. Scan from +600 mV to 0.0 mV and back to +600 mV with the 2 mM ferricyanide solution. The electrode surface may need to be cleaned by lightly polishing the tip on 0.05 μm alumina particles (slightly wet) on smooth glass surface. Use only light pressure and *polish carefully* since it is easy to crack or chip and destroy the tip of the electrode. Wash the tip with high purity water and touch the edges with Kimwipe™ or soft tissue paper to remove the excess water.

* There may be a small hysteresis between the forward and reverse CV wave. The waves should track each other within a few millivolts. If they are unsymmetrical with > 20 mV differences try polishing the tip with the directions given above and rescan. With larger electrodes, the polishing directions often end with an ultrasonication step. **Do not** ultrasonicate microelectrodes since the tip will be seriously damaged.

4. Run concentration dependence of i_{ss} with the 1, 2, 5 and 10 mM ferricyanide, scanning from +600 to 0.0 mV at a scan rate of 100 mV/s.

Record and save your data files.

REPORT (Data Analysis And Discussion):

Consult your laboratory instructor regarding the content and format of the report. The following are suggested items to consider and questions to answer.

1. Show example voltammograms for the reduction of ferricyanide (or the oxidation of FCA) and a short discussion on how experiments were conducted. Report any changes made to the procedure.
2. Equation 1 does not indicate a scan rate dependence for i_{ss} . Do your results agree with this? The i_{ss} can be corrected for the background charging current by extrapolating the linear portion of the background current and measuring i_{ss} from the background to the point at which you take the i_{ss} value.
3. Calculate a value for i_{ss} using equation 1 and compare it to what you get experimentally. The diffusion coefficient of ferricyanide is $0.65 \times 10^{-5} \text{ cm}^2/\text{s}$. If you used ferrocene carboxylic acid as the electroactive species, calculate a value of D from your experimentally determined i_{ss} .

REFERENCES

1. J.K. Campbell, Li Sun, R. M. Crooks, *Electrochemistry Using Single Carbon Nanotubes*, J. Am. Chem. Soc., 121 (1999) 3779.
2. This relationship was derived by F. G. Cottrell, a mathematician, over 100 years ago (*Z. Physik. Chem*, 42 (1902) 385). Its derivation by Laplace transform can be found in the classical monographs by a) P. Delahay, *New Instrumental Methods of Analysis*, Wiley Interscience, NY 1954 and b) A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd Ed. J. Wiley & Sons, NY (2001) ppg 161-163.
3. Refer to pages 170 – 175 of reference 2b.
4. The use of carbon microfibers for probing brain chemistry (i.e., dopamine) was pioneered by the late Professor Ralph N. Adams and his students at the University of Kansas. An article on the development of in-vivo microelectrodes for monitoring dopamine and norepinephrine in the brain is discussed in *Probing Brain Chemistry: Voltammetry Comes of Age* by J. A. Stamford and J. B. Justice, Jr., in *Analytical Chemistry*, Vol. 96 (1996) ppg. 359A – 366A. It is available online: <http://pubs.acs.org/hotartcl/ac/96/jun/jun.html>
5. R. Mark Wightman and Robert Ensman developed the EI-400. Wightman has been a leader in the development of electroanalytical methods involving fast scan voltammetry with microelectrodes for detecting and quantitating neurotransmitters. Please refer to: www.cypresssystems.com and click on “Mark Wightman/66-EI400” and <http://www.neuroscience.unc.edu/research/dopamine/dopamine.htm>.