Cyclic Voltammetry – A Simulation Experiment

Purpose: To demonstrate the use of cyclic voltammetry to characterize electrochemical systems. We will explore the effect of the following on the appearance of CVs: scan rate, analyte concentrations, ionic strength of solution, electrode charging capacity, kinetics of the electrochemical reaction, diffusion constant, and the coupled reversible chemical reactions to electrochemical process.

References: Bard & Faulkner: Electrochemical Methods, Fundamentals and Applications (2nd ed.): Chap 6 & 12
DigiSim online tutorial: http://www.epsilon-web.net/Ec/digisim/tutorials/index.html

Procedure:
Familiarize yourself with the operation of DigiSim
- Generate simple electrochemical mechanism: O + e = R
- Set the CV parameters as shown. Assume \( E_0 = 0.00 \) V for this reaction.
- Run simulation, and watch “CV-the movie!” to correlate concentration profile at the electrode/electrolyte interface and the shape of CV.
- Find \( i_p \) and \( E_p \) values from the program.
- Determine from your observation if the reaction simulated is Nerstian.

Task 1: Investigate \( i_p \) and scan rate (v) relationship
- Using the simple mechanism generated above, simulate CVs at various scan rates (at least 5 values).
- Record \( i_p \) value (either anodic or cathodic) at each scan rate.
- Plot your data to justify the Randles-Sevick equation.

Task 2: Investigate the effect of supporting electrolyte
- Evaluate the adjustable parameters in DigiSim under the “CV parameter” tab, and decide which parameter can demonstrate the effect of supporting electrolyte.
- Adjust the parameter (choose 3 values), and observe the changes.
- Rationalize your observation.

Task 3: Investigate the effect of double layer charging (for ideally polarized electrodes)
- Evaluate the adjustable parameters in DigiSim under the “CV parameter” tab, and decide which parameter can demonstrate the effect of double layer charging.
- Adjust the parameter (choose 3 values – make sure they are REASONABLE), and observe the changes.
- Rationalize your observation.

Task 4: Investigate the effect of return sweep potential (E_{rev})
- This task demonstrates the effect of how close after the voltammetric peak the scan is reversed on the readability of the CV.
- Change \( E_{star} \), \( E_{rev} \), and \( E_{end} \), and note the changes to the shape of the CV.
- What is a safe value of potential reversal?

Task 5: Investigate the effect of the kinetics of a preceding reaction (CE reaction)
- Build new coupled reaction mechanisms, including a preceding chemical reaction.
- Adjust the “homogeneous reaction” equilibrium constants (\( K_{eq} \) and \( k_1 \)), and find conditions under which the effect of the chemical reaction will be apparent.
- Adjust scan rate, and find condition where the CV appears diffusion limited.
- Rationalize your observations.

Task 6: Investigate the effect of the kinetics of a following reaction (EC reaction)
- Build new coupled reaction mechanisms, including a following chemical reaction.
- Repeat steps 2~4 in “Task 5” for this mechanism.

Task 7: Investigate a multiple electron transfer process (EE reaction)
- Build new mechanism that demonstrates two step electron-transfer reactions.
- The appearance of the voltammogram depends upon the location of the std. potentials, \( E_1^{eq} \) and \( E_2^{eq} \), and the spacing between them, \( \Delta E^0 = E_2^{eq} - E_1^{eq} \). Fix \( E_1^{eq} \) value, and vary \( E_2^{eq} \) value. Note the minimal difference in std. potentials when two separate peaks can be distinguished in CV.
**Data Treatment:** Record all observations in your lab notebook. Explain your observations, and answer the questions at the end of each task. For the summary, focus on how cyclic voltammetry provides chemical and kinetic information of the electrochemical systems we created (do not focus on the operation of DigiSim).

**Background:** Cyclic voltammetry (CV) is a very useful tool in modern analytical chemistry. Applications of CV have been extended to almost every aspect of chemistry. A few examples are given here to give you a glimpse of its versatile utility for the study of electroactive species: these include investigation of biosynthetic reaction pathways (organic chemistry), ligand effect on metal complex potential (inorganic chemistry), enzymatic catalysis (biochemistry), solar energy conversion (materials chemistry), etc. Cyclic voltammetry is often the first experiment performed in an electrochemical study of a compound or an electrode surface. The effectiveness of CV results from its capability for rapidly observing the redox behavior over a wide potential range. The resulting voltammogram is analogous to a conventional spectrum in that it conveys information as a function of an energy scan.

Voltammetry is an electroanalytical method in which information about the analyte is obtained from the measurement of current as a function of applied potential. For the 3-electrode configuration, the potential is applied to the working electrode with respect to a reference electrode, and an auxiliary electrode is used to complete the electrical circuit. A working electrode is typically made of noble metals (platinum or gold) or carbon (i.e., glassy carbon). The auxiliary electrode usually uses a Pt wire. Two commonly used reference electrodes are Ag/AgCl electrode (E° = 0.20 V vs. SHE) and saturated calomel electrode (SCE, E° = 0.25 V vs. SHE). The excitation wave in CV is a linear potential scan with a triangular waveform as shown in the figure. The potential is linearly scanned from an initial value, (“B”) to a predetermined limit (“E”), where the direction of the scan is reversed (to “H”). A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan.

A redox couple in which both species rapidly exchange electrons with the working electrode is termed an electrochemically reversible couple. The formal potential (E°) for a reversible couple is centered between Epa and Epc.

$$E° = \frac{E_{pa} + E_{pc}}{2}$$

The peak separation, \(\Delta E_p\), for a reversible couple is related to the number of electrons transferred in the electrode reaction (n)

$$\Delta E_p = E_{pa} - E_{pc} \geq \frac{0.059}{n}$$

The peak current for a reversible system is described by the Randles-Sevick equation:

$$i_p = (2.69 \times 10^5 \frac{1}{n^2}) \frac{1}{D} \frac{1}{C} \frac{1}{V}$$

where \(i_p\) is peak current (A), n is electron stoichiometry, A is electrode area (cm²), D is diffusion coefficient (cm²/s), C is concentration (mol/cm³), and V is scan rate (V/s). Accordingly, \(i_p\) increases with \(V^{1/2}\) and is directly proportional to concentration.

The exact form of the voltammogram can be rationalized by considering the potential and mass transport effects. As the potential is initially swept from "B", the equilibrium at the surface begins to alter and the current begins to flow: The current rises as the potential is swept further from its initial value and the equilibrium position is shifted further towards products, thus converting more reactants. The peak occurs because at some point the
diffusion layer has grown sufficiently above the electrode so that the flux of reactant to the electrode is not fast enough to satisfy that required by the Nernst equation. In this situation the current begins to drop just as it did in the potential step measurements. In fact the drop in current follows the same behavior as that predicted by the Cottrell equation.

**Effect of coupled chemical reactions:**

Many electrochemical reactions involve an electron transfer step that leads to a species that rapidly reacts with components of the medium via so-called coupled chemical reactions. CV provides the capability of generating a species during the forward scan, and then probing its characteristics with the reverse scan and subsequent cycles, all in a matter of seconds or less. In addition, the time scale of the experiment is adjustable over several orders of magnitude by changing the potential scan rate. Depending on the kinetics of the coupled chemical process, the shape of the CV could appear dramatically different.

On topics regarding coupled chemical reactions, please read B&F Chap 12 (Preceding reaction – pg 488~491; Following reaction – pg 496~497; multi-electron transfer reaction – pg 505~507)