Electrochemistry

Introduction to Cyclic Voltammetry

In this experiment, you will measure the current response of a ferricyanide solution exposed to different potential sweep parameters, to determine the formal potential of the ferricyanide/ferrocyanide redox couple and the diffusion coefficient of these ions in aqueous solution. Refer to the reference material for an introduction to the Cyclic Voltammetry (CV) technique.

1. Solutions: Prepare the following solutions:
   a. Electrolyte: 250 mL of 1 M potassium nitrate (KNO₃) in ddH₂O. 100 mL of 1 M sodium sulfate (Na₂SO₄) in ddH₂O.
   b. Potassium Ferricyanide K₃Fe(CN)₆ Solutions: Use the 1 M KNO₃ solution to make 25 ml of each of the following K₃Fe(CN)₆ concentrations: 0.002, 0.004, 0.006, 0.008 and 0.01 M
   c. Prepare 25 ml of 0.004 M K₃Fe(CN)₆ using the 1M Na₂SO₄ solution.

2. Setting up the Computer and the Cell
   a. Set up Electrochemical Cell - Position the electrodes in the cell and connect the cables as follows:
      | Green  | Working Electrode (will only fit in the largest holder positions) |
      | Red    | Auxiliary Electrode                                               |
      | White  | Reference Electrode (This electrode will only fit in the central position) |

   The glassy carbon working electrode will need to be polished mechanically between runs; otherwise a thin deposit of Prussian blue will build up at the surface of the electrode, that will result in a quasireversible electrochemical behavior of ferricyanide redox reaction. The TA will show you how to do this.

   The Ag/AgCl reference electrode is stored in a KCl solution. Rinse it with ddH₂O. When you complete your experiment, rinse with water and return to the vial containing the storage buffer. Wrap the top with Parafilm. WARNING: The Ag/AgCl electrode must NOT be allowed to dry out.

   Fix appropriate nitrogen flow and stirring rate.

   b. Experimental Parameters - Find the Power Suite icon on the desktop and double click it. Open the C114 experiment. Then open Experiment Properties. A window will pop up.

      Cell Definition: Check that the type of working electrode is solid and the type of reference electrode is Ag, AgCl / KCl (3.5M) (0.205V)

      Scan Definition: Select Initial Potential: 1.0V, Vertex Potential E₁: -1.0V, Final Potential: 1.0V. The Scan Rate will be changed between 20 and 500 mV/sec.

      PreScan Definition: Purge for 120 sec. and Equilibrate for 15 sec. These conditions will allow you to purge the solution for 2 minutes with the nitrogen bubbling through the solution. Then you will turn off the stirrer and turn the three way nitrogen valve to flow nitrogen over the solution and allow the solution to get unperturbed during the 15 second equilibration time.
3. **Data Collection**

   i. Examine the effect of oxygen: Run CV scans of the electrolyte and the 0.004 M ferricyanide solution before and after bubbling nitrogen through the solution.

   ii. Examine the effect of scan rate by running CVs from 10 to 200 mV/sec rates.

   iii. Examine the effect of concentration at a fixed scan rate.

   iv. Examine the effect of stirring *during* the run for two different scan rates: 20 and 200 mV/sec.

   v. Examine the effect of scanning direction: Reverse the initial, vertex and final potential sign for one particular run.

   vi. Verify the diffusion-limited character of the current: Polish the working electrode thoroughly.

      Set up the following run: initial: -1 V vertex and final potentials: 1V; scan rate: 1 mV/sec.

      Purge time: 2 min. Equil. Time: 0. Run for only 3 minutes.

   vii. Determine the formal potential of the Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ couple in the two different supporting electrolytes.

To save the data, after each scan right click on the graph and export the data as a text file, then erase the data using the little eraser and change the experiment properties, or the solution, in preparation for the next run.

**Shut Nitrogen off** after you are done with your experiments and turn potentiostat off!!

**Discard your solutions in the appropriate waste containers and clean the glassware!!**

4. **Data Analysis**

   Explain the oxygen data.

   Fit your data from ii and iii to the Randles-Sevcik equation: Both anodic and cathodic currents vs. concentration and versus square root of the scan speed. Check for consistency on the slopes:

   Calculate the diffusion constant. The area of the working electrode is: 0.068 ± 0.003 cm$^2$. Is this reaction reversible?

   Express your data from (vi) as current vs time (the scan rate relates potential and time) and fit the time decay to the Cottrell equation to obtain a diffusion constant. Compare this constant to literature values and to the one obtained from the Randles-Sevcik equation.

   Explain the data collected while stirring the solution (iv), why does it look so different to the solution-at-rest data? Can you estimate the re-dox potential from this data?

   Explain the data while scanning backwards (v): Why is the initial current positive and the first peak negative?

5. **References**