Introduction to Electrochemistry

Aim

To investigate core concepts of electrochemical techniques using a copper solution.

Introduction

Southampton has an established world-class reputation in electrochemistry research. Electrochemistry is a broad subject covering all areas of charge transfer reactions at interfaces and impacts on daily life in many immediate ways from corrosion and energy storage, through water treatment and purification, clean energy generation and environmental monitoring to medical diagnostics and electrodeposition.

This practical uses basic concepts of electrochemistry to investigate copper redox couples. An electrochemical cell will be set up and experimental data will be obtained via a voltametric technique. The data will then be analysed using the Randles-Sevcik equation to explain the observed results.

Learning outcomes

At the end of this practical students will be able to:

- Utilise PSTrace software to run voltammetric experiments

- Understand and process useful information from cyclic voltammetry experiments

- Determine the diffusion coefficient from the data obtained.

Underlying Theory

The cell that will be studied in this experiment essentially acts as a reverse of a battery. In regular batteries a reaction occurs, which drives the electron transfer and therefore generates electric charge. In this case it is the electric potential passed through the solution in the cell that causes a reaction to occur. Depending on the potential applied two different reactions may be observed, i.e. in the case of this practical $Cu^{2+} + e^- \rightarrow Cu^+$ and $Cu^+ + e^- \rightarrow Cu$.

The difference between this cell and a battery is that the cell is constructed from three electrodes instead of two. In this practical the first electrode is a carbon disc working electrode, it makes contact with the analyte (copper species). The second is a platinum gauze reference electrode, which is a half cell with a known reduction potential. The reference electrode does not take part in the reaction (no current is passed through it), it just measures the potential difference between itself and the working electrode. The last electrode is a carbon rod; it passes all the current needed to balance the current observed at the working electrode and is referred to as the counter electrode.

In the experiment redox couples will be investigated with the use of **cyclic voltommetry**. In cyclic voltammetry, the electrode potential ramps linearly versus time (as shown in the diagram to the right). The ramping is known as the **scan rate** (V/s). That means that the voltage applied cycles throughout the whole duration of the measurement and hence the name of the technique. The data obtained from these readings is presented in the form of a graph of current (at the electrode) versus the potential applied known as a **cyclic voltammogram** (CV).

Cyclic Voltammetry Potential Waveform
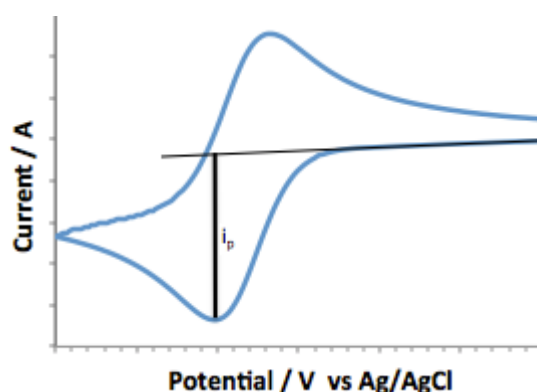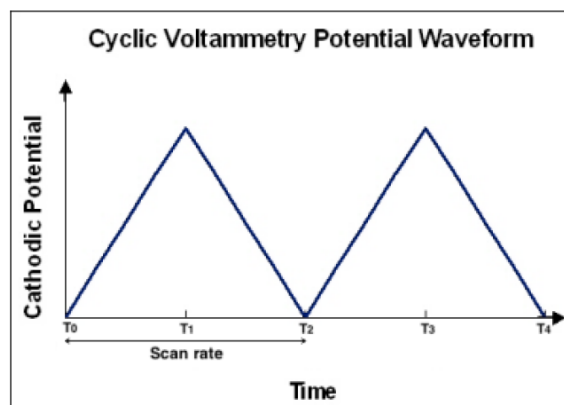
An example of a CV for a redox couple is presented on the diagram to the left. Note the "tailing off" shape at the right end - a characteristic feature that arises because the reaction is diffusion limited i.e. at this stage the reagent at the electrode has been depleted so the rate of the reaction now depends on how fast new reactants can reach the electrode. These graphs can be very useful in obtaining data, inter alia the **diffusion coefficient**, a proportionality constant specific for each reactant. It can be found using the **Randles-Sevcik equation** (eq.1).

The Randles-Sevcik equation relates the peak current, i_p, (measured as the distance from the baseline to the peak of the graph) to the scan rate, allowing determination of the diffusion coefficient. The equation is written as:

$$i_p = 2.69 \times 10^5 n^{1.5} A c D^{0.5} v^{0.5} \qquad (eq. 1)$$

where n is the number of electrons transferred in the reaction, A is the area of the electrode (in m^2), c is the concentration of the solution used (in mol m^{-3}), D is the diffusion coefficient (in m^2 s^{-1}), v is the scan rate (in V s^{-1}) and the constant (2.69×10^5) has units of C mol^{-1} $V^{-0.5}$.

The graph can also be used to determine the number of moles (of copper in the case of this practical) that are reduced at the electrode during the reaction. By finding the area under the curve of the CV and dividing it by the scan rate it is possible to obtain the charge, Q (in C), that is associated with the electron transfer in a reaction. The charge is then directly related to the number of moles by the equation:

$$Q = mnF \qquad (eq. 2)$$

where n is the number of electrons transferred in the reaction, m is the number of moles and F is the Faraday constant (96485 C mol^{-1})

SI-2

Understanding hazard, minimising risk

Reagent	Amount	Hazards	Minimising Hazards	Spillage & Disposal
Copper Sulfate Pentahydrate	<1 g	Harmful if swallowed (H302). Causes skin irritation (H315). Causes serious eye irritation (H319). Very toxic to aquatic life with long lasting effects (H410).	Avoid release to the environment (P273). Wear gloves/eye protection (P280).	Dispose of (made) solutions in supplied waste container. Collect solid spills for disposal in toxic solids waste container.
Sodium Chloride	<25 g	Repeated or prolonged exposure is not known to aggravate medical conditions.	GLP	Dispose of down the sink with copious amounts of water.
Polishing Alumina	<10 g	Excessive exposure may cause cough, mucus production. May cause eye irritation.	GLP	Sweep up and collect for disposal.

Procedure

Organisation

The experiment must be performed in the assigned groups - It is not permitted for groups to share data. The analysis must be performed on an individual basis.

Apparatus

- Chemicals: Copper Sulfate Pentahydrate, Sodium Chloride, Alumina.

- Equipment: Carbon Working Electrode, (Platinum Gauze) Reference Electrode, (Carbon Rod) Counter Electrode, Potentiostat & Laptop, Electrochemical Cell, Polishing Dish/Cloth, 1 x 250ml Stoppered Volumetric Flask, 1 x 100ml Stoppered Volumetric Flask, 2 x 50ml Beaker, 1 x Measuring Cylinder (50 or 100ml), 2 x Spatula, 1 x Glass funnel.

Important: Do not touch the wires while the electrochemistry experiments are running - Otherwise the results may be unreliable.

Part A - Preparation of the Stock Solution

- Weigh out sufficient NaCl to make 250 ml of a 1.5 M solution. Add this to a 250 ml volumetric flask and partially fill with deionised water. Agitate until the NaCl completely dissolves, then fill to the line with deionised water. *This will be your electrolyte solution*.

- Next weigh out enough $CuSO_4.5H_2O$ to make up 100 ml of a 5 mM solution. Add this to a 100 ml volumetric flask and partially fill with the <u>electrolyte solution</u>. Agitate until the copper sulphate has completely dissolved, then fill to the line with the <u>electrolyte solution</u>. *This will be your working solution*.

Part B - Equipment Setup

1. Use a measuring cylinder to add 50 mL of the working solution to the cell clamped to the retort stand.

2. Using the N_2 gas tubing, bubble nitrogen through the solution for 5 minutes, moving the tube around the cell for the last minute. Whilst bubbling, polish the (carbon disc) working electrode using the alumina and the polishing cloth provided. Rub the electrode in a figure of 8 and rotate it 90° regularly to prevent grooves forming on the surface of the electrode. After 5 minutes of polishing and N_2 bubbling, remove and turn off the nitrogen supply.

   > **IMPORTANT**: IF AT ANY TIME DURING THE PRACTICAL YOU NOTICE THAT THE QUALITY OF YOUR RESULTS IS DECLINING - THE BUBBLING AND POLISHING ROUTINE WILL NEED TO BE REPEATED BEFORE CONTINUING WITH THE PRACTICAL.

3. Rinse all three electrodes with deionised water. Position the (carbon disc) working electrode in the provided electrode holder so that the tip is in solution.

4. Position the (platinum gauze) reference and (carbon rod) counter electrodes in the electrode holder, so that they are in the solution and **none** of the electrodes touch each other or the cell wall.

5. Clip: The green (Earth) wire to the metal clamp securing the cell; the red wire to the (carbon disc) working carbon electrode; the blue wire to the (platinum gauze) reference electrode; the black wire to the (carbon rod) counter electrode.

6. Once the cell has been assembled, open the **PSTrace** software from "Your School Software".

7. The "Settings" dialogue box may appear. If it does, ensure "Scientific" mode is selected and deselect "Bluetooth present" before clicking **OK**.
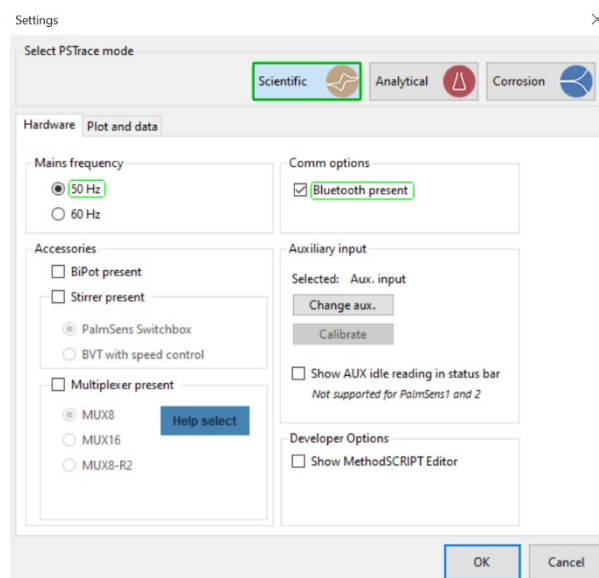
8. Close any "Help" screen that appears and connect the potentiostat by clicking the **Connect** button in top left corner of the screen. The dialog box should say "EMStat4 LR [1]" or something similar. If it says "VirtualEmStatPico", try to hit the refresh button. If this does not change, then the USB port on your machine is likely faulty. Disconnect the cable and plug into the different USB port, then repeat the step to connect to the potentiostat. You may need to hit refresh after changing USB port to see a difference.
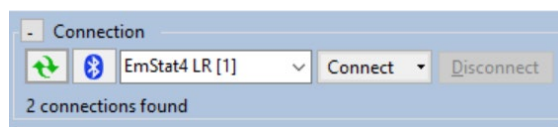
## Part C - Investigating the Cu(II)/Cu(I) Couple

1. From the drop-down menu labelled **Technique** select Cyclic Voltammetry.

2. Select the current range as 10 µA, 100 µA, and 1 mA.

3. Use the values shown opposite as the CV settings.

4. Under "Advanced" (i.e. click on the three dots) below the **Cyclic Voltammetry** settings there is the option to **measure vs OCP** - make sure this **is not selected.**

5. Select Overlay from the drop down menu.
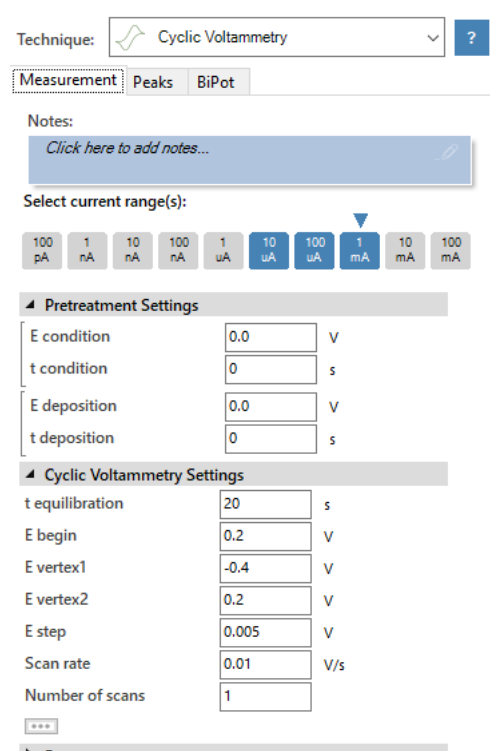
6. Click the (green) play button next to the drop down menu.

7. Allow the sweep to run to completion, your graph should be drawn automatically.
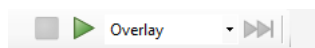
8. Use the software to determine the peak current (i_p) of the cathodic (negative) peak and record this value in your lab-book. The peaks should be autodetected by the software, but if this does not work you can detect the peaks by clicking on the peak finder icon (graph icon with a green cog, circled right). For your report – make sure you know which reaction this peak corresponds to (refer to Blackboard resources as needed).

9. Click the **Export to Excel** icon on the left of the graph. This will automatically paste your data into Excel and plot the graph for you.

10. Acquire, determine the peak current (i_p) and save additional voltammograms at *Scan Rates* (aka "Sweep Rates") of **0.025, 0.05, 0.075** and **0.1 V/s**.
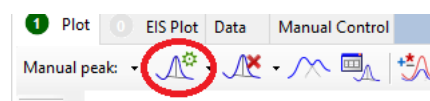
Important – PSTrace will automatically background correct the i_p values. When you export the CVs to Excel, this background subtraction is lost. You must separately record the i_p values along with the corresponding scan rate in a lab book or Excel table.

11. Save the files.

Part D - Investigating the Cu(I)/Cu(0) Couple

1. Click **Clear Plot**, found in the **Plot** menu (located on topbar).

2. Keep the current range as 10 µA, 100 µA, and 1 mA.

3. Use the values shown opposite as the settings.

4. Click the green play button.

5. Allow the sweep to run to completion, your graph should be drawn automatically.

− Pretreatment settings		
E condition	0.0	V
t condition	0	s
E deposition	0.0	V
t deposition	0	s

− Cyclic Voltammetry settings		
t equilibration	20	s
E start	-0.4	V
E vertex1	-1.4	V
E vertex2	-0.4	V
E step	0.005	V
Scan rate	0.01	V/s
Number of scans	1	

6. Repeat the reading but, using the orange pause button, pause the scan when the voltage first passes -1.3V. After it has paused for 45-60 s, click the button again to continue with the remainder of the reading. Note: The pause button stops scanning the potential, but the potential is still being applied. So, during the 45 – 60 s pause, the potential is being held at -1.3 V, and all reactions at -1.3 V are continuing.

7. Click the **Export to Excel** icon on the left of the graph, make sure this has pasted the data (i.e. the two CVs) into a new Excel document and save this.

Part E - Electrochemistry of Copper

1. Click **Clear Plot** under the **Plot** tab.

2. Keep the current range as 10 µA, 100 µA, and 1 mA.

3. Use the values shown opposite as the settings.

4. Click the green play button and allow the sweep to run to completion.

5. Click the **Export to Excel** icon on the left of the graph, make sure this has pasted the data into a new Excel document and save this.

− Pretreatment settings		
E condition	0.0	V
t condition	0	s
E deposition	0.0	V
t deposition	0	s
− Cyclic Voltammetry settings		
t equilibration	20	s
E start	0.4	V
E vertex1	-1.4	V
E vertex2	0.4	V
E step	0.005	V
Scan rate	0.01	V/s
Number of scans	1	

Deadlines, assessment and feedback on performance

Pre-lab

Pre-lab requirements are as specified in the folder for this practical in the "CHEM1056 - Introduction to Practical Chemistry II" Blackboard course.

In-Lab Assessment

The assessment for this practical is in the form of a smart worksheet. The worksheet itself will guide you through the assessment process, asking you to perform a series of analysis steps and calculations on your data. When prompted, submit your answer to each question in the worksheet. If you are correct, you will be awarded a full mark. Otherwise, you will receive some feedback and a chance to resubmit a new answer for a slightly reduced mark. There is therefore an incentive to get the correct answer first time, although it is worth remembering that the point reduction is not severe, and it is still possible to score very well overall, even if some questions take a couple of attempts.

Please actually read the feedback! The smart worksheet is coded, where possible, to guess where you may have made a mistake. It is able to guess if you have made a rounding error, a unit error, a common misconception or used the wrong parameter in a calculation. Similarly...

Please actually read the instructions on the smart worksheet! There are guides to help analyse data correctly on the worksheet. One important is that i_p values should be given as absolute values in amps, not negative values in microamps, yet this is often ignored. Following the instructions on the worksheet is the simplest way to high marks!

The worksheet works by performing the same analysis on the same data in the background, and will then compare your submitted answer to its calculated answer. **It is very important that you use the highest precision value in your calculations.** The worksheet will use high precision numbers in all calculations, so if you round numbers in the middle of your calculation steps, you may be marked as incorrect.

IMPORTANT: It is practically impossible to do this by hand – **this is what Excel is for! Use Excel for all of your calculations, and refer to cells in calculations rather than typing in a number**.

For example: current density is a parameter that involves dividing a current by the area of an electrode that passed it:

$$j = \frac{i}{A} \qquad (eq.\,3)$$

Say you wanted to do this for a peak current of 1.03 µA that you measured at a 1 cm diameter electrode. You would start by using πr^2 to calculate your area to be 0.784 cm^2, and then use this in calculations for current density. Consider two options. Option one, you use a calculator and enter the numbers for your peak current:

$$j = \frac{1.03 \times 10^{-6}\ \text{A}}{3.14 \times (0.5\ \text{cm})^2} = 1.31\ \mu\text{A cm}^{-2} \qquad (eq.\,4)$$

This might seem OK, but is actually incorrect, as low precision values were used in the calculation. Consider option two, where you do the calculations in Excel, and click on the relevant cells to carry the full precision values for current and for area:

$$cell\ A1 = current = 1.0346748573829596\ldots.\,10^{-6}\ \text{A} \qquad (eq.\,5)$$

$$cell\ A2 = area = PI() * (0.5\ \text{cm})^2 = 0.7853981633974\ldots.\,\text{cm}^2 \qquad (eq.\,6)$$

$$j = \frac{cell\ A1}{cell\ A2} = \frac{1.0346748573829596\ldots.\,10^{-6}\text{A}}{0.7853981633974\ldots.\,\text{cm}^2} = 1.32\ \mu\text{A cm}^{-2} \qquad (eq.\,7)$$

This may seem like a small difference, but this is only a basic example with a simple division. When you scale this up to multi-step calculations, especially involving powers, logs and exponentials. You will have to do this as part of your diffusion coefficient, where rounding errors, rather than using Excel, can lead to an error of up to 5% on the final value. This worksheet is designed to encourage you to use full precision values in all part of your calculations. This may be frustrating, but it's a vital skill to develop is science, so I'm afraid it's time to say goodbye to your calculators!

In order to see the full level of precision in Excel, highlight your data and then click on the **increase decimal** button in the top toolbar (red circle below).
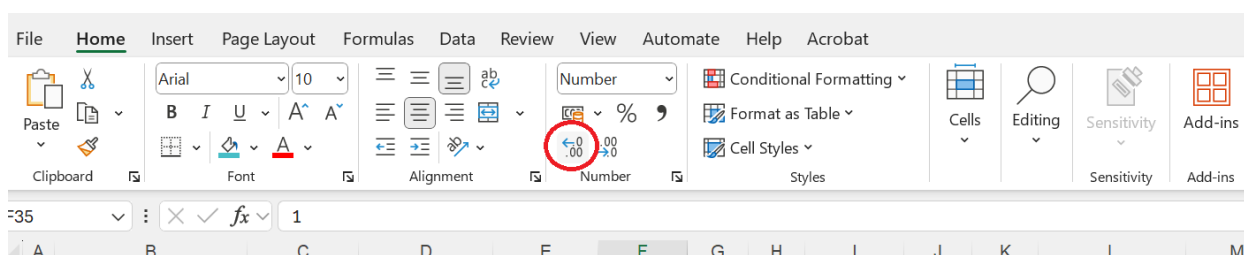
This button will increase the number of decimal places shown in your data. Keep clicking this button until your data doesn't gain any precision, i.e. the end of your number just shows extra

zeros at the end. Doing this before you copy your numbers into the spreadsheet will ensure that you are using the highest possible precision.

This worksheet is also able to plot data for you. Some questions will use your plotting knowledge to help the worksheet format its graph correctly. The worksheet contains a "Preview" button, that allows you to see the impact of your proposed solution on the graph before it is submitted. You can use the preview button as often as you like without point deduction.

Detailed guidance to content and formatting for your data is available on Blackboard in the "Scientific Writing and Data Presentation" guide, in the tutorials folder. The worksheet will assume that you have read and understood this document, and will mark your scientific writing accordingly.

<u>The smart worksheet must be completed by the end of the second session of your practical</u>.

Post-Lab Assessment

There is no post-lab assessment associated with this practical.

Feedback

Feedback is provided during the completion of the smart worksheet. If you would like to receive any more specific feedback during the practical, feel free to get in touch with a demonstrator or the lab manager at any point.