The Cottrell Experiment and Diffusion Limitation

PSAPP-003 Electrochemical Experiment

PalmSens
Compact Electrochemical Interfaces

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1 Instructions

The following instructions will guide you to perform the experiment. The theory on which these experiments are based, can easily be checked online at palmsens.com, then search for "Introduction of Detection of Hydrogen Peroxide". The material needed for the experiments can be ordered via https://www.palmsens.com/product/educational-kit/#contents.

2 Devices and Equipment

- EmStat / EmStat Blue
- sensor cable
- maybe a USB cable
- computing unit (PC, Laptop, notebook, tablet PC (android), smartphone (Android))
- potentiostat software (PStrace, PStouch)
- calculation and plotting software (Excel, Origin, MatLab, Mathematica)
- counter electrode
- reference electrode
- working electrode
- retort stand
- retort clamp
- cell top
- beaker (electrochemical cell)

3 Chemicals

- 0.1 M KCl solution (prepared from solid KCl and demineralized water)
- 1 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl solution (prepared from solid KCl, $K_3[Fe(CN)_6]$ and demineralized water)

4 Instructions

4.1 Capacitive Current

1. Set up the retort stand including the clamp. Insert the white cell top with holes into the clamp. Insert the counter electrode (platinum wire), the working electrode (platinum disc in Teflon) and the reference electrode, the silver / silver chloride electrode (the electrode with the liquid filled glass body), into the three holes of the cell top. Please be aware that the part with the diaphragm of the reference electrode always has to be in solution or otherwise protected from drying. During evaporation of solution little crystals form in the pores of the frit and the electrode will be blocked. This should be avoided.
2. Fill the beaker with 0.1 M KCl solution. Position the electrodes in a way that all three electrodes are immersed and fix the position with the help of the clamp. Connect the counter electrode to the black cable, the reference electrode to the blue cable, and the working electrode to the red cable.
3. Start PSTrace.
4. Choose the scientific mode in the upper left corner.
5. Select your potentiostat from the drop down menu. If it is not in the list, press the refresh button (green arrows). Maybe your computer takes a while to install the USB driver. Press the *Connect* button. Your device should be connected now.
6. Maybe your instructor already prepared a method file for you.

    a. YES: Go to the menu *Method – Load method* and choose the file that was prepared for you.

    b. NO: Choose *Multistep Amperometry* from the *Technique* list. In *Sample* and *Sensor* you can add comments for your own data organization. Choose the current ranges from 1 µA to 10 mA. Set *t condition* and *t deposition* to 0, because the electrode needs no treatment before the measurement. The *t equilibration* is the time during which the first potential of the measurement is already applied without recording the current. This is usually done to exclude capacitive current from the beginning of the graph. Set this time to 8 s. The *t interval* is the time between two measurement points. If it is very small, the amount of recorded data and thus the size of the file containing the data will be big. A longer *t interval* will allow collecting more values, averaging them and displaying the average as one point resulting in a less noisy graph, but the time resolution is reduced. A *t interval* of 0.01 s is suitable for this measurement. The numbers of *Cycles* is 1. The *Cycles* define how often the steps entered below will be repeated. For making a potential step, 2 *Levels* are needed. One potential level before and one after the jump. Although the Cottrell experiment is first conducted without an electrochemical species, we want to perform the same step as if we want to reduce an iron complex. The first level has to be higher that the formal potential of the latter used $[Fe(CN)_6]^{3-}$ complex. This potential can be found in literature with around 210 mV vs Ag/AgCl. The potential of level 1 (*E level 1*) is set to 0.35 V and to make sure a stable current is reached before the potential step is performed, the time this potential is applied (*t 1*) is set to 20 s. The second level potential should be below the formal potential. Set *E level 2* to +0.15 V. The time *t 2* is set to 100 s.

7. Start the measurement. And save the curve by choosing *Save curve…* from the *Curve* menu.
8. This curve only shows the capacitive current of the electrochemcial double layer.
9. The potassium chloride solution is harmless and can be disposed in the sink. The electrodes and cell should be cleaned with demineralized water. Otherwise the drying solution will leave salt stains.

4.2 The Cottrell Experiment

1. The setup is the same as in the previous experiment. Except for the solution in the beaker which is now 1 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl solution.
2. Use the same parameters for the *Multistep Amperometry* as before.
3. Before you start the measurement choose in the drop down menu next to the Run button the option *Overlay* instead of *New*. If the curve of the capacitive current you recorded before is no longer displayed load it. Start the measurement. The reaction at the electrode is:

$$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$$

4. Save the new curve as well.
5. The capacitive current as well as the sum of the capacitive and Faraday current can be compared with each other. They should meet the expectations set earlier.
6. The next step should be a better time resolution. Look at the maximum current that was measured during step 3. Choose the smallest current range which value doubled is bigger than the maximum current. The part of the curve before the step shows when a stable current is reached. For the equilibration time choose a time that is big enough to reach a constant current. Choose for the *t1* 5 s and *t2* 65 s. Reduce the *t interval* to 0.001 s.
7. Choose *New* in the drop down menu next to the start button and start the measurement.
8. Save the curve.
9. The potassium chloride solution is harmless and can be disposed in the sink. The electrodes and cell should be cleaned with demineralized water. Otherwise the drying solution will leave salt stains. Solution containing iron need to be collected in a container for liquid waste containing heavy metal. The pH of the collected heavy metal solution should be alkaline (pH > 9). The container should be disposed according to local laws.
10. To find the area of the electrode a plot of the absolute I vs $t^{-\frac{1}{2}}$ and a linear regression are needed. Export the data to software that can do this, for example Excel, Origin, etc. If you decide to use Excel or Origin, you can use the one-click-to-Excel-export or one-click-to-Origin-export in the toolbar at the left side of the graph.

11. Set the time of the potential step to 0 s by subtracting 5 s from the time. Afterwards calculate $t^{-\frac{1}{2}}$ and plot I vs $t^{-\frac{1}{2}}$. According to the [Cottrell equation](#) the resulting plot should be a line.
12. Make a linear fit of the linear part of the curve. Calculate from the slope the area of the electrode. Remember that the slope is described by equation 1.6 in [this article](#). Although D can be found in literature, it is not easy. We recommend to use D($[Fe(CN)_6]^{3-}$ in 0.1 M KCl) = (7.17 ± 0.18)·10^{-6} cm^2/s found in Baur, John E.; Wightman, R.Mark (1991): Diffusion coefficients determined with microelectrodes. In J. Electroanal. Chem. 305 (1), pp. 73–81. DOI: 10.1016/0022-0728(91)85203-2.
13. Discuss the difference between expectations and measured values. What could explain a deviation from the expected values?

In this experiment you discovered the influence of the diffusion limitation.

Please note that teachers can request the answers to the question in the instructions, using
https://www.palmsens.com/contact/