Copper and Nickel Deposition

PSAPP-004 Electrochemical Experiment

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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 Glucose with a Self-Made Biosensor”. 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 / PalmSens
- sensor cable
- maybe a USB cable
- computing unit (PC, Laptop, notebook, tablet PC (android), smartphone (Android))
- potentiostat software (PStrace, PStouch)
- counter electrode
- reference electrode
- a few metal paper clips or a metal wire
- retort stand
- retort clamp
- beaker (electrochemical cell)
- stirrer and magnetic stirring bar

3 Chemicals

- 18 mM $CuSO_4$ in 0.5 M H_2SO_4 solution (prepared from solid $CuSO_4$)
- 18 mM CuSO4 and 18 mM $ZnSO_4$ in 0.5 M H_2SO_4 solution (prepared from solid $CuSO_4$ and $ZnSO_4$)
- 18 mM $ZnSO_4$ in 0.1 M NaOH solution (prepared from solid $ZnSO_4$, NaOH and demineralized water)
- concentrated NaOH or solid NaOH

4 Instructions

4.1 Deposition of Copper from a Copper Sulfate Solution

1. Set up the retort stand including the clamp. Insert the white cell top with holes into the clamp. Put the stirrer under the clamp and 50 mL beaker with a magnetic stirring bar between them. Bend the paper clip into a straight piece of wire. Most paper clips have an insulating coating. Use some emery paper to remove it. The actual shape of the paper clip wire is not important for the experiment, but a straight wire is easy to handle. Insert the counter electrode (platinum wire) and the reference electrode, the silver / silver chloride electrode (the electrode with the liquid filled glass body), into two of the cell top’s holes. Connect the paper clip to the working electrode cable (red) with the crocodile clip. Connect the counter electrode to the black cable and the reference electrode to the blue cable. Please be aware that the part of the reference electrode containing the diaphragm always needs to be in the 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 the copper salt solution. Position the electrodes in such a way that all three electrodes are in the solution. The paper clip wire should not be immersed deeper than the platinum wire.
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 *Amperometric Detection* from the *Technique* list. In *Sample* and *Sensor* you can add comments for your own data organization. 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, but since we are only interested in the deposited metal and not in the measurement set this time to 0 s. The potential applied during the measurement (*E dc*) has to be low enough to reduce copper but high enough to avoid zinc deposition. The electrochemical series contain the standard potentials for copper and nickel. They are $E^0(Cu^{2+}/Cu)$ = 0.345 V and $E^0(Zn^{2+}/Zn)$ = -0.760 V. These values are the standard potential, which is relative to the potential of the standard hydrogen electrode (SHE) that is by convention 0 V. The reference electrode supplied with this kit is an Ag/AgCl electrode. It has a potential of $E^0(AgCl/Ag)$ = 0.205 V. So a potential of 0 V vs the SHE is a potential of -0.205 V for the Ag/AgCl electrode. The other values can be treated analogously:

$E^0(Cu^{2+}/Cu)$ vs Ag/AgCl	0.140 V
E^0(SHE) vs Ag/AgCl	-0.205 V
$E^0(Zn^{2+}/Zn)$ vs Ag/AgCl	-0.965 V

    So to deposit copper the potential has to be lower than 0.140 V but higher than -0.965 V. Two other species might interfere with our experiment. Potentials below -0.205 V might lead to hydrogen evolution depending on the overpotential of hydrogen at your paper clip surface. Since experience tells that the large overpotentials for hydrogen evolution lead to an active evolution at around -1.2 V vs Ag/AgCl, hydrogen should be no issue. Most paper clips contain iron and E^0(Fe2+/Fe) is -0.41 V (SHE) or -0.605 V vs Ag/AgCl. A potential above this value may lead to corrosion of the paper clip itself. Assuming that no other species in our solution will react, an *E dc* of -0.5 V vs Ag/AgCl should suffice and avoid gas bubbles from hydrogen. The *t interval* is the time between two measurement points. Set it to 1 s. The parameter *t run* is the time the experiment lasts or in this particular case how long the potential is applied. Set it to 60 s.
7. Switch on the stirrer, adjust the speed to a gentle stir and start the measurement. Observe the paper clip.
8. After the measurement is finished you can take out the paper clip and rinse it with demineralized water to observe it more closely.
9. The solution can be reused for multiple paper clips. You can vary the deposition time and observe the influence on the result. Or try to immerse an uncoated part of the paper clip without applying a potential.
10. If you have to dispose the solution keep the following in mind: Solutions containing copper or zinc 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. The electrodes and cell should be cleaned with demineralized water. Otherwise the drying solution will leave salt stains.

4.2 Deposition of Zinc on Copper from a Zinc Sulfate Solution

1. Set the experiment up as in point 1 to 5 of the previous experiment (chapter 4.1) or use the same setup, but use the zinc sulfate solution instead. Instead of a new paper clip use a copper covered one. We recommend to only immerse 1/2 of the paper clip wire's copper covered part.
2. The *E dc* has to be more cathodic (negative) as seen in chapter 4.1. Due to the fact that the potential of the zinc reduction is close to the hydrogen evolution, the zinc reduction competes with proton reduction. This would lead to a bad deposition or no deposition of zinc. The potential of the hydrogen evolution depends on the concentration of H^+ and thus on the pH value. This can be verified by the Nernst equation. To avoid hydrogen evolution the concentration of H^+ is

reduced by using an alkaline solution. Please note that alkaline solutions are more aggressive and dangerous than acids. You need to work carefully. A side effect of the high pH value is the formation of zinc hydroxide, which precipitates and leads to an opaque solution. Taking these considerations into account a potential of -1.8 V for 120 s is suitable for a zinc deposition.

3. Switch on the stirrer, adjust the speed to a gentle stir and start the measurement. Observe the paper clip.
4. After the measurement is finished you can take out the paper clip and rinse it with demineralized water to observe it more closely. You should have three visible layers now. The blank paper clip, the copper layer and the nickel layer.
5. The solution can be reused for multiple paper clips. You can vary the deposition time and observe the influence on the result. Or try to immerse an uncoated part of the paper clip without applying a potential.
6. If you have to dispose the solution keep the following in mind: Solutions containing copper or zinc 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. The electrodes and cell should be cleaned with demineralized water. Otherwise the drying solution will leave salt stains.

4.3 Deposition of Copper and Nickel Separately from a Mixed Salt Solution

1. Set the experiment up as in point 1 to 5 of the previous experiment (chapter 4.1) or use the same setup, but use the mixed copper and zinc sulfate solution instead. Use a new paper clip.
2. The parameters are the same as for a copper deposition from a pure copper sulfate solution (*E dc* = -0.5 V, t run = 60 s).
3. Switch on the stirrer, adjust the speed to a gentle stir and start the measurement. Observe the paper clip.
4. After the measurement is finished you can take out the paper clip and rinse it with demineralized water to observe it more closely. Although there was zinc sulfate in the solution no zinc was deposited. Can you explain why?
5. As learned from the previous experiment (chapter 4.2) zinc is deposited in an alkaline solution. Use concentrated NaOH to increase the pH value to >12. This will be visible by a color change from transparent blue to opaque teal.
   It is very tempting to add solid NaOH directly to the salt solution to increase the pH. This might lead to a violent reaction of the sulfuric acid. We recommend first dissolving the hydroxide in water. Beware that dissolving of NaOH as well as the neutralizing of the sulfuric acid are exothermic.
6. Switch the stirrer off and immerse half of the paper clip's copper covered part.
7. The potential is the same as for zinc deposition from a pure zinc sulfate solution, but due to the lack of stirring the time has to be increased. (*E dc* = -1.8 V, t run = 240 s).
8. Start the measurement. Observe the paper clip.
9. After the measurement is finished you can take out the paper clip and rinse it with demineralized water to observe it more closely.
10. A mixture of zinc and copper forms a golden colored alloy known as brass, but this did not happen here. Do you know why?

In this experiment you deposited both copper and nickel on a metal wire.

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