

ELECTRODEPOSITION OF MATERIALS USING POURBAIX DIAGRAMS AND EVALUATING CHARGE STORAGE

General Schedule and Comments *(this text is the same as was presented for Lab 2)*

In general, the format for this discussion session will be the same each week and is as follows:

1. Briefly review the experiments, their goals, and any updates to the hands-on activities
2. Break into groups of two or three, set-up each workspace, and make a connection between a laptop running Windows and the BioLogic potentiostat using the EC-Lab software
3. Perform experimental procedure(s), while being assisted by the Instructor
4. If time permits, as a class provide feedback on the activity and recommend future changes
5. Clean-up each workspace, return items used, and store electrodes for subsequent weeks
(You are not dismissed from the discussion session until this is complete)

It is recommended that you read through and save and/or print procedures and reference publications/files before you watch the experimental pre-lab video and attend the hands-on discussion sessions. This will help you to become acquainted with the experiment and formulate questions to ask during the discussion session. Being interactive with the videos (e.g. by actively asking yourself questions as to why the experiment is set up in a certain way, why data looks the way it does, etc.) will help to increase your knowledge and comfort with the techniques shown. This will then help you to successfully complete homework assignments and implement techniques in your own research.

Introduction

Last week you learned how to fabricate most of the electrodes that are needed throughout the course and (ideally) how they can be used to perform cyclic voltammetry experiments. This week, you will learn how to use another electrode consisting of a transparent conductive oxide (TCO), namely silica glass with a thin layer of conductive fluorine-doped tin oxide (FTO) on one side. This TCO makes it facile to visualize what you are depositing on the electrode surface, and to do transmission-mode spectroscopy on it, if desired (e.g. Ultraviolet–Visible Spectroscopy). Using FTO-coated glass and your knowledge of Pourbaix diagrams, you will learn how electrochemistry can be used to deposit weakly conductive cuprous oxide, $\text{Cu}^{\text{I}}_2\text{O}$, and electrically insulating silicon dioxide, $\text{Si}^{\text{IV}}\text{O}_2$.

Purpose

The purpose of this hands-on discussion activity is to learn how to use Pourbaix diagrams to control chemical syntheses. This will be achieved by performing a series of chemical transformations with copper and silicon species for various combinations of applied potential and solution pH. First, you will observe that a qualitative titration of the pH of an aqueous solution containing a soluble

copper species, from acidic to alkaline conditions and back to acidic conditions, results in changes in coloration and solubility as copper species transform into other copper species. When solid copper forms during these homogenous solution titrations it will become apparent that making an electrode by this process is unreasonable. Then, you will determine how to electrochemically deposit copper onto an electrode and quantitatively analyze the amount deposited, the faradaic efficiency (FE) of the electrodeposition, and the electrochemically-active surface area (ECSA) of the electrode. This electrodeposition process will then be compared to electrochemical deposition of an insulating material, i.e. silica (SiO_x). This will provide you with a better understanding of the utility of Pourbaix diagrams and will introduce you to straightforward procedures that you can use to quantify properties of electrodeposited materials.

Safety

For each hands-on discussion session, you must bring and wear personal protective equipment consisting of a lab coat and safety glasses/goggles. In addition, at a minimum you must wear closed-toe shoes, pants, and a shirt that covers your entire torso, or else you will not be allowed to enter the lab. While in the lab you will also need to wear gloves, which we will supply as nitrile gloves. In addition, to reduce the possibility of electric shock to you and your labmates be sure to control the correct channel of the potentiostat and that all persons are away from the experimental apparatus before starting an electrochemical experiment. **Caution:** All acidic and alkaline solutions should be prepared in a *fume hood*. Also, observe caution with dissolution of solid KOH since it is an exothermic process, thus giving off heat, and concentrated KOH is caustic. *Note that to facilitate safety and best-use of time the Instructor may prepare the solution indicated below before the hands-on discussion session. The Instructor will also bring extra PPE.*

Procedures

Part A: Validating regions of the Pourbaix diagram for copper

Portions of the following procedure were adapted from “Environmental Chemistry – Microscale Laboratory Experiments” by Ibanez, J. G., Hernandez-Esparza, M., Doria-Serrano, C., Fregoso-Infante, A., Singh, M. M., 2008, pp. 79 – 88.

Tools/materials needed: ~10 mL beakers, cleaned 25 mL scintillation vial, FTO-coated glass (~1 cm x 4 cm), stir bar, stir plate, 1 mL disposable plastic pipettes, pH paper, aqueous 0.1 M CuSO_4 , aqueous 1 M KOH, aqueous 8 M KOH, aqueous 1 M HCl, aqueous 10 mM HCl, aqueous 50% HNO_3 , sodium bicarbonate for neutralizing solutions and possible spills

(I) Cu^{2+} to $\text{Cu}(\text{OH})_2$: Place 2 mL of aqueous 0.1 M CuSO_4 into a small beaker and add aqueous 1 M KOH dropwise, with mixing if necessary. When the pH reaches ~4.5 a pale sky-blue precipitate of $\text{Cu}(\text{OH})_2$ forms. (Some Pourbaix diagrams indicate that this may then convert into CuO , since $\text{Cu}(\text{OH})_2$ is metastable, but CuO should be darker brown-to-black in color.) At this point, stop adding KOH and record the pH of the solution using pH paper.

(II) $\text{Cu}(\text{OH})_2$ to CuO_2^{2-} : To the previous reaction mixture, add a few drops of a highly concentrated aqueous 8 M KOH and mix. A deep royal-blue color indicates the production of cuprite ion, CuO_2^{2-} , or other charged species of copper.

(III) CuO_2^{2-} to $\text{Cu}(\text{OH})_2$: Remove half of the contents from the beaker and carefully discard them in a waste container. To the mixture remaining in the beaker, add aqueous 1 M HCl dropwise, with mixing if necessary. This should result in a pale sky-blue color indicating the formation of $\text{Cu}(\text{OH})_2$ precipitate, again.

(IV) $\text{Cu}(\text{OH})_2$ to Cu^{2+} : Upon further addition of aqueous 1 M HCl, with mixing, the $\text{Cu}(\text{OH})_2$ precipitate starts dissolving and another color appears, indicating that copper is back to its initial form, i.e. Cu^{2+} .

(V) Electrodepositing cuprous oxide (Cu_2O) onto FTO from cupric ions (Cu^{2+}) (*quick-and-dirty*)

- (1) Place ~3 mL of aqueous 0.1 M CuSO_4 in a new small beaker and carefully adjust the pH to more alkaline with dilute aqueous KOH (and aqueous HCl, if needed), stopping at a pH value that is just before a $\text{Cu}(\text{OH})_2$ precipitate forms.
- (2) Set-up a three-electrode electrochemical cell using a pre-rinsed vial or small beaker half-filled with the solution from the previous step as the electrolyte, an FTO WE, an Ag/AgCl RE, and one of the other electrodes (Pt wire, carbon button, or carbon cloth) as the CE. Using a Pourbaix diagram (*there are many good examples available from the Internet*), determine the potential to apply to plate Cu_2O onto FTO. With stirring, try to deposit Cu_2O onto FTO. When the FTO becomes noticeably colored, stop applying the potential bias. (*Notably, you could have predicted that the now-colored side of the glass has the thin FTO coating on it by first measuring its resistance using a multimeter, because FTO is electrically conductive.*)
- (3) Because both *desired* Cu_2O and *undesired* Cu are reddish-brown-to-orange in color, to evaluate whether any of the deposit is mistakenly Cu^0 metal, take the FTO-coated glass **over to the hood** and **carefully** dip the colored portion into a few milliliters of dilute aqueous 10 mM HCl. In this case, copper oxides and hydroxides should dissolve, while copper metal should not. (*Notably, you may have been able to predict the outcome of this test because Cu may exhibit a significantly shinier metallic luster compared to the expected dull matte appearance of Cu_2O .*)
- (4) If you electrodeposited Cu_2O then your quick-and-dirty experiment worked, and so record the pH value you used and move on to Part B below. If, instead, you mistakenly electrodeposited mostly Cu, or mistakenly just precipitated $\text{Cu}(\text{OH})_2$ or CuO via a pH swing (which are colored differently), repeat the procedure above, or explore other routes, until you deposit Cu_2O .

Part B: Analytically depositing Cu_2O onto FTO and determining the faradaic efficiency and the roughness factor of the electrode

Tools/materials needed: ~10 mL beaker, cleaned 25 mL scintillation vial, FTO-coated glass (~1 cm x 4 cm), stir bar, stir plate, 1 mL disposable plastic pipettes, pH paper, aqueous 0.1 M CuSO₄, aqueous 1 M KOH, aqueous 1 M HCl, sodium bicarbonate for neutralizing solutions and possible spills

- (1) Place ~3 mL of fresh aqueous 0.1 M CuSO₄ into a small beaker and carefully adjust the pH to the pH value that you determined in Part A above. If you desire, transfer this solution to a pre-rinsed vial in order to perform electrochemistry.
- (2) *Mass a new clean piece of FTO glass, and record this value.*
- (3) Set-up and perform the following experiments, in the order indicated:
 - a. OCV (for 1 min; measure every 1 s) – this is good to include because it could tell you valuable information when troubleshooting
 - b. 3 CVs (measure over a ~300 mV region where only non-faradaic current will flow at 20 mV/s, then 100 mV/s, and then 500 mV/s) – this will be used to determine the capacitance of the baseline (i.e. “flat”) electrode, which is a decent way to quantify its electrochemically surface area
 - c. CA (Chronoamperometry) (apply an appropriate potential bias for at least 30 min; measure every 1 sec) – this will deposit your material; you can either deposit for a set amount of time at a given applied potential or pass an appropriate amount of charge for the experiment.
 - d. OCV (for 1 min, measure every 1s)
 - e. 3 CVs (measure over a ~300 mV region where only non-faradaic current will flow at 20 mV/s, then 100 mV/s, and then 500 mV/s)
- (4) **Gently** wash the film with deionized water and dry it under a stream of air.
- (5) *Mass the FTO glass with the deposit, and record this value.*

Part C: Depositing Silica (SiO_x) onto FTO and determining the faradaic efficiency and the roughness factor of the electrode

Tools/materials needed: scintillation vial, FTO-coated glass (~1 cm x 4 cm), stir bar, stir plate, 1 mL disposable plastic pipettes, pH paper, aqueous 0.1 M NaNO₃, aqueous 0.1 M HCl, ethanol, sodium bicarbonate for neutralizing solutions and possible spills

- (1) *If not already prepared by the Instructor, as a class prepare a ~100 mL aqueous silica precursor solution according to “Silica Nanowire Arrays for Diffraction-Based Bioaffinity Sensing” by Loget, D. & Corn, R. M., Chemistry – A European Journal, 2014, 20(34), 10802 – 10810, DOI: 10.1002/chem.201304800.*
- (2) Place ~3 mL of fresh aqueous silica precursor solution into a small beaker or pre-rinsed vial.
- (3) *Mass a new clean piece of FTO glass, and record this value.*
- (4) Perform the same series of experiments as above for electrodeposition of cuprous oxide but instead apply a potential bias sufficient to evolve H₂ (e.g. -1.2 V vs. Ag/AgCl).
- (5) **Gently** wash film with deionized water and dry under a stream of air.

(6) Mass the FTO glass with the deposit, and record this value.

Assignment 2 – Lab 3 (combined with last week's activity; due on Wednesday, October 21, 2026 at noon) (You must show your work for credit on all problems.)

1. Either using the data provided to you for Lab 3, or your own data if your laboratory experiments were successful, do the following.
 - a. Calculate the faradaic efficiency (FE) of the CA experiment where cupric ions were converted to cuprous oxide by analyzing the amount of charge passed.
 - b. Calculate the relative electrochemically-active surface area (ECSA) of the final cuprous oxide electrode compared to the bare FTO electrode to estimate its roughness factor (by assuming the FTO electrode is nearly flat).
 - c. Do you hypothesize that the cuprous oxide electrode is porous or not? Provide evidence in support of your hypothesis based on the data and/or your data analysis.
 - d. Repeat parts a-c but for deposition of SiO_x (i.e. calculate the faradaic efficiency, calculate the roughness factor of the SiO_x electrode, and hypothesize about the SiO_x porosity).
 - e. What was difference between the overall electrodeposition of cuprous oxide and the electrodeposition of silica? In your explanation, include balanced chemical equations and reduction potentials for the reactions that occurred. Also make sure to explain differences in the mechanisms of electrodeposition and any differences that you observed in the CA data and/or faradaic efficiency.