

ELECTRODEPOSITION OF MATERIALS USING POURBAIX DIAGRAMS AND EVALUATING CHARGE STORAGE

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

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

1. Present brief outline of experiments, goals, and updates
2. Break into groups of two or three, set-up work space, and connect to the BioLogic potentiostat using the EC-Lab software on a PC laptop
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 other activities
5. Clean-up work space, return items, 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 the procedures and reference publications/files before you watch the experiment 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 (i.e. by actively asking yourself questions as to why the experiment is set up in a certain way and why data looks the way it does, etc.) will increase your knowledge and comfort with the techniques shown. This will help with completion of homework assignments and allow you to 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 learned how they could 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. Using FTO and your knowledge of Pourbaix diagrams, you will learn how electrochemistry can be used to deposit weakly conductive cuprous oxide, Cu_2O , and electrically insulating silicon dioxide, $\text{Si}^{\text{IV}}\text{O}_2$.

Purpose

The purpose of this hands-on e-discussion activity is to become more familiar with Pourbaix diagrams, by learning how to perform activities with copper and silicon at various combinations of reduction potential and solution pH. First, you will observe that a qualitative titration of the pH of a 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 solution titrations it will become

apparent that making an electrode by this process is unreasonable. Then, you will see how to electrochemically deposit copper onto an electrode and quantitatively analyze the amount deposited, the faradaic efficiency of the electrodeposition, and the electrochemically active surface area (ECSA) of your electrode. This electrodeposition process will then be compared to electrochemical deposition of an insulating material, silica (SiO_x). This will provide you with a better understanding of the purpose of Pourbaix diagrams and will introduce you to simple procedures you can use to analyze 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 tee-shirt that covers your entire torso. While in 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 KOH dissolution as it is an exothermic process, thus giving off heat, and concentrated KOH is caustic. Also, NO_x fumes are toxic and HNO_3 is highly corrosive to tissue.

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, scintillation vial, FTO (~1 cm x 4 cm), stir bar, aqueous 0.1 M CuSO_4 , aqueous 1 M KOH, aqueous 8 M KOH, aqueous 1 M HCl, aqueous 10 mM HCl or 50% HNO_3 , pH paper, sodium bicarbonate for neutralizing solutions and spills

(I) Cu^{2+} to $\text{Cu}(\text{OH})_2$

Place 2 mL of aqueous 0.1 M CuSO_4 in a small beaker and add aqueous 1 M KOH dropwise. When the pH reaches ~4.5 a sky-blue precipitate of $\text{Cu}(\text{OH})_2$ forms. At this point, stop adding KOH and record the pH of the solution.

(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-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 add aqueous 1 M HCl dropwise (with mixing) to the mixture remaining in the beaker, which should result in a 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 1 M HCl (with mixing) to the mixture remaining in the beaker, 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) Electroplating Cu^{2+} onto FTO as Cu_2O (*quick-and-dirty*)

- (1) Place ~3 mL of 0.1 M CuSO_4 in a new small beaker and adjust the pH to alkaline with dilute aqueous KOH (and aqueous HCl, if needed), but not so alkaline that a precipitate forms.
- (2) Set-up a three-electrode electrochemical cell in the vial using the solution from the previous step, 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, determine the potential to apply to plate Cu_2O onto FTO. With stirring, try to deposit Cu_2O onto FTO until it becomes colored. Stop applying a potential bias.
- (3) To make sure that the deposit is not Cu metal, take the WE **over to the hood** and **carefully** dip the colored portion into a few milliliters of highly concentrated aqueous 50% HNO_3 . Brownish fumes of NO_2 indicate that Cu^0 metal was electrodeposited and not Cu_2O . An alternative test can be performed in the same way, but using dilute aqueous HCl (for example, 10 mM) instead of 50% HNO_3 . In this case the Cu_2O deposit dissolves, whereas Cu^0 metal does not.
- (4) If you deposited Cu_2O , then record the pH you used. If you deposited some Cu^0 , repeat this procedure until you deposit cuprous oxide.

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, scintillation vial, FTO (~1 cm x 4 cm), stir bar, aqueous 0.1 M CuSO_4 , aqueous 1 M KOH, aqueous 1 M HCl, pH paper, sodium bicarbonate for neutralizing solutions and spills

- (1) Mass a new clean piece of FTO glass, and record this value.
- (2) Place ~3 mL of fresh aqueous 0.1 M CuSO_4 in a small beaker and carefully adjust the pH to the pH value you determined above. If you desire, transfer this solution to a scintillation vial in order to perform electrochemistry.
- (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 pass 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
 - c. CA (Chronoamperometry) (apply an appropriate bias for at least 30 min; measure every 1 sec) – This will deposit your material; you can either deposit for a set time at a given bias 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 pass at 20 mV/s, then 100 mV/s, and then 500 mV/s)
- (4) **Gently** wash film with deionized water and dry 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

Tools/materials needed: scintillation vial, FTO (~1 cm x 4 cm), stir bar, aqueous silica precursor solution

- (1) Mass a new clean piece of FTO glass, and record this value.
- (2) Place ~3 mL of fresh aqueous silica precursor solution in a small beaker or scintillation vial. The silica precursor solution was prepared 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.
- (3) Perform the same series of experiments as above for electrodeposition of cuprous oxide but instead apply a bias sufficient to evolve H₂ (i.e. -1.2 V vs. Ag/AgCl).
- (4) **Gently** wash film with deionized water and dry under a stream of air.
- (5) Mass the FTO glass with the deposit, and record this value.

Assignment 2 – Lab 3 (combined with last week’s activity; due on Monday, October 23, 2023 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. Determine the relative surface area (roughness factor) of the final cuprous oxide electrode versus the bare FTO electrode.
 - b. Determine the faradaic efficiency of the first CA experiment in which Cu²⁺ was converted to Cu.
 - 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 a roughness factor for the SiO_x electrode, calculate a faradaic efficiency, and hypothesize about the SiO_x porosity).
 - e. What was different 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.