Materials and Methods Summary:
Boston College REU
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Electrode Making

FTO-Coated Glass for FTIR

1. The sheet of glass is cut using the linear glass cutter to dimensions of about 0.6 x 3.5 cm.
2. Two holes are drilled using a dremel with a ⅛ in diamond tip.
3. The electrodes are then cleaned by sonicating for 15 minutes in the following solvents:
    a. Acetone
    b. Isopropanol
    c. Ethanol
    d. Water
4. The electrodes should then be dried using compressed nitrogen and placed on top of a cloth into a petri dish.
5. A copper wire is then cut to about 4-5 inches, the ends are slightly shaved off using a razer blade to expose clean copper, then one end is bent around a pair of tweezers first in a 180 degree bend then is a 90 degree bend perpendicular to the original bend so that the end of the wire looks like a 'U'.
6. A silver epoxy is then made by mixing a 1:1 ratio of the A and B epoxy.
7. A small amount of epoxy is applied using a toothpick to the short edge of the electrode and a small amount is applied going onto the FTO side of the glass to make the side of the electrode conductive.
8. The electrode is then pressed FTO side down onto a petri dish to make a thin layer of the epoxy.
9. Some of the silver epoxy is applied to the "U" part of the copper wire, and the wire is then applied to the electrode.
10. Once finished, the electrodes need to go to the oven for an hour to solidify the silver epoxy.
11. Then the blue insulating epoxy is made using a 1:1 ratio of the blue and white epoxy.
12. This is then applied to the electrode to cover the silver epoxy and then pressed against the petri dish FTO side down to make the insulating epoxy as thin as possible.
13. The electrodes then go into the oven for another hour to solidify the blue epoxy.
14. The area is then calculated using a ruler.

FTO-Coated Glass for Water-in-Salt Experiments

1. The sheet of glass is cut using the linear glass cutter to dimensions of about 0.8 x 0.5 cm.
2. The electrodes are then cleaned by sonicating for 15 minutes in the following solvents:
    a. Acetone
    b. Isopropanol
    c. Ethanol
    d. Water
3. The electrodes should then be dried using compressed nitrogen and placed on top of a cloth into a petri dish.
4. A small insulated wire is cut to about 4 inches and both ends are stripped.
5. A silver epoxy is then made by mixing a 1:1 ratio of the A and B epoxy.
6. The epoxy is applied to the wire and is placed against the FTO side of the glass.
7. Once finished, the electrodes need to go to the oven for an hour to solidify the silver epoxy.
8. Then the blue insulating epoxy is made using a 1:1 ratio of the blue and white epoxy.
9. The blue epoxy is applied to the electrode to cover the silver epoxy and along all of the FTO edges to form a clear and distinguished edge.
10. The electrodes then go into the oven for another hour to solidify the blue epoxy.
11. The area of the electrode can then be calculated using the following instructions:
    a. Tape the electrodes FTO side down onto the scanner.
    b. Press the bottom button of the scanner and set the DPI to 600.
    c. Import the scan to the computer and open it in photoshop.
    d. Use the selector to select the portion of the electrode that is exposed FTO.
    e. Look at the number of pixels involved in the selection and divide that number by 55,800 to get the area in cm^2.

Solutions

CoOx Catalyst Deposition Solution - FTIR

1. 0.01 M $Co(NO_3)_2$
2. 0.1 M $NaCH_3CO_2$

CoOx Catalyst Deposition Solution - CV/Tafel

1. 0.5 mM $Co(NO_3)_2$
2. 0.1 M KH_2PO_4 / K_2HPO_4 - pH adjusted to 7
3. Note: can also do dilution from Chaochao's 0.1M $Co(NO_3)_2$ solution
4. Note: This was used previously, now use the FTIR solution for deposition

CoOx FTIR Electrolyte - D_2O *

1. Make about 1-2 mL of 6 M NaOH in D_2O
2. Make 2-4 mL of 0.1 M KH_2PO_4 and **0.4 M KCl in D_2O
3. Adjust the pH using the NaOH until the pH is <u>6.60</u>

* For H_2O^{18} solution, replace everything with H_2O^{18} instead of D_2O

** Didn't add this to original experiments, so current data doesn't include this

CoOx Electrolyte - Water-In-Salt Experiment

1. Make 100 mL of 0.1 M KH_2PO_4
2. Make 120 mL of 0.1 M K_2HPO_4
3. Starting with the 120 mL of the K_2HPO_4, add about 75 mL of the KH_2PO_4.
4. Measure the pH.
5. Slowly add more of the KH_2PO_4 until the pH reaches 7.
6. Using this solution, make the following concentrations of $NaNO_3$:
    a. 0 M
    b. 2 M
    c. 4 M
    d. 7 M

$Ni_{0.75}Fe_{0.25}OOH$ Catalyst Deposition Solution

1. Make 15 mL of 0.075 M $Ni(NO_3)_2$
2. Place parafilm over the vile and purge with nitrogen for ~20 minutes
3. Add $FeCl_2$ to a final concentration of 0.025 M
    a. If a precipitate forms, try purging in nitrogen again

Depositions

CoOx for FTIR

1. Record the area and resistance of the electrode (for FTO electrode only).
2. Tape together either the FTO(with holes) or Gold working electrode and a Pt wire counter electrode such that the FTO or Gold side is facing away from the counter electrode.
3. Place the taped together electrodes into the 0.01 M $Co(NO_3)_2$ solution and set the parameters of the deposition to the following:
    a. Galvanostatic deposition
    b. Current density: 0.05 mA / cm^2 (use the area for this)
    c. Time: 322 s
    d. Slight stirring

CoOx for Tafel and CV

1. Using the small FTO electrodes (with no holes), tape together the working electrode, a SCE reference electrode, and a Pt wire counter electrode in that order using tape such that the FTO side of the working electrode is facing away from the reference electrode.
2. Place the taped together electrodes into the 0.01M $Co(NO_3)_2$ solution and set the parameters of the deposition to the following:
    a. Potentiostatic deposition
    b. Voltage: 0.86 V
    c. Charge Density: 20 mC / cm^2 (use the area for this)
    d. Time: set for about an hour
    e. Slight stirring

CoOx for EQCM

1. Clean the side of the EQCM crystal in 1M H_2SO_4 using the following methods:
    a. Cyclic voltammetry:
        i. Range: (-2.5) - (2.5) V
        ii. Counter Electrode: Glassy carbon
        iii. 200 mV/sec
        iv. 2 cycles
2. Check that the crystal is clean using the following methods:
    a. Cyclic voltammetry:
        i. Range: 0 - 0.7 V
        ii. Counter Electrode: Glassy carbon
        iii. 10 mV/sec
        iv. 2 cycles

3. Deposition:
    a. Galvanostatic:
        i. 322 seconds
        ii. 0.015 mA
        iii. Stirring
        iv. Cobalt Nitrate Solution (0.01M)
        v. CE: Pt wire

Gold-Deposited ATR Crystal

1. Solution Making
    a. Deposition Solution
        i. Add the following amounts of chemicals into 4 mL of water
            1. $NaAuCl_4 \cdot 2H_2O$ 0.0217g
            2. Na_2SO_3 0.0756g
            3. $Na_2S_2O_3 \cdot 5H_2O$ 0.0496g
            4. NH_4Cl 0.0107g
        ii. Fully dissolve the previous chemical in water then add
    b. HF Solution ~2 mL
        i. 87 µL in 2 mL of water
    c. Place both solutions into the water bath (63 C) for at least 10 minutes before the deposition
2. Polishing (hand polish)
    a. 6 µm diamond paste for 5 minutes
    b. 1 µm diamond paste for 5 minutes
    c. 1 µm alumina paste for 5 min (polish on dry part for 30s to remove alumina on the crystal at the end)
    d. Rinse under water with chemwipe for 1 minute
3. Sonication
    a. 10 min water, 5 min acetone, 5 min water, 5 min acetone, 5 min water
4. Deposition
    a. Mix the two solutions in a blue centrifugation tube cap
    b. Etch the crystal in NH_4F for 1 min 50 s, rinse with water
    c. 1st deposition: Dip crystal in deposition solution mixture for 2 min 30 sec
    d. Wash the Au film off with Aqua Regia, and rinse with copious amounts of water
    e. 2nd deposition: Dip the crystal in deposition solution mixture for 2 min 30 sec
    f. Potential 3rd deposition if the film doesn't look ideal
    g. Rinse with water
    h. Usual resistance: 10Ω

Data Collection

Tafel Data

1. After deposition of the catalyst onto the electrode, place the taped together electrodes into each of the following solutions and run the method mentioned after:
    a. 0 M $NaNO_3$
    b. 2 M $NaNO_3$
    c. 4 M $NaNO_3$
    d. 7 M $NaNO_3$
2. Perform a CV with the electrodes using the following parameters:
    a. 1.2 - 0.5 V (vs SCE)
    b. Scan rate: 20 mV/s
    c. # of Cycles: 1
3. Use the following parameters for the data collection:
    a. Staircase Linear Sweep
    b. Voltage Range: 0.843 - 1.143 V (vs SCE)
    c. Scan rate 0.0666 mV/s
    d. Step: 20 mV
    e. Time: 1 Hr 15 Min
4. Repeat for each concentration of $NaNO_3$

FTIR Methods

1. Set up one of the electrochemical cells (for gold or FTO)
2. Once the cell is setup and contains all of the electrodes and electrolyte, follow the following procedure:
    a. Determine IR impedance
    b. Run a CV that ranges from 1.0 - 1.6, and do it twice to remove the initial hump
    c. Leave the cell alone and measure the open circuit potential (~800mV)
    d. Begin the FTIR data collection and linear sweep potentiostatic data collection:
        i. Begin at 1.6 and decrease to 1.0 in 100 mV steps after holding each step for 300 seconds.
        ii. To decrease between steps, a 20 mV/s rate was used
        iii. Once at 1.0 V, increase in 200 mV steps until back at 1.6 V
        iv. For the FTIR, data collection happens every 4.611 seconds
    e. After the FTIR data collection is complete, another CV is ran to test the stability of the film and to determine if any film degradation occurred during the trial.

EQCM Data Collection

1. Set up the EQCM cell by placing the EQCM crystal into the cell bottom with the deposited gold surface facing up
2. Screw in the bottom part of the cell into the middle part using the four screw holes
3. Fill the middle part of the cell with the 0.1 M potassium phosphate electrolyte
4. Cover the cell with the lid of the cell
5. Place the counter electrode and reference electrode into the cell and connect the red and white wires, respectively, to each electrode
6. Attach the EQCM wires (green and black) to the leads of the EQCM crystal through the opening in the cell
7. Perform either Linear Sweep Voltammetry or Cyclic Voltammetry and click the button to collect QCM data simultaneously with the electrochemical data