Electrochemical Protocols

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1. Platinum Electrodeposition
2. PEDOT:pTS Electrodeposition
3. Iridium Oxide Electrodeposition

Platinum Electrodeposition

Materials Needed:

- Deionized Water
    - *Any supplier*
- Hydrochloric acid - HCl (37%)
    - *HYDROCHLORIC ACID 37 % ANALAR NP REAG.PE - Analytical Grade*
- Ethanol (100%) or Isopropyl Alcohol
    - *Any supplier*
- Chloroplatinic Acid 8% in H_2O
    - *262587 - Chloroplatinic acid solution from Sigma*
- Platinum wire
    - *Any supplier*
- Potentiostat
    - *Can be any model! But the model used in for these protocols was the PalmSens4*

Making the plating solution:

- Simply mix **1:1 8% chloroplatinic acid with deionized water** to make a 4% solution for electroplating

- Store the chloroplatinic acid solution in a sealed container as it is highly toxic

Electrodeposition Protocol:

- Pour **~100 mL of deionized water** and **ethanol** into containers

- Pipette **~10 mL of HCl** into a small glass beaker

- Pipette **~25 mL of chloroplatinic acid** into the deposition area

- Submerge the electrodes into ethanol and then put directly into the HCl
    - Note: the ethanol significantly increases the wettability of the small electrodes and thus is necessary for the desired etching of the electrodes with HCl

- Hold the electrodes in **HCl for ~30 seconds**

- Transfer the electrodes from the HCl to deionized water and rinse

- Transfer the electrodes to the chloroplatinic acid in the plating bath

- Once submerged and held in place, attach the working electrode clip from the potentiostat to the electrodes that will be plated on

- Submerge an addition piece of solid platinum to the plating bath and connect to the counter electrode clip
    - Note: in order to prevent hydrogen formation on the counter electrode the surface area of this platinum wire/piece must be approximately equal to the surface area of the electrodes you are plating onto

- Finally submerge the tip of the silver/silver chloride reference electrode into the bath and connect that to the reference clip

- Set the potentiostat to run in mixed mode with **4 cycles of 60 seconds** each cycle

- The current should be set to alternating positive and negative currents equal to **0.215 nA/um^2** (multiply this value by the total area to be plated to get the final current to apply)

- After plating the electrodes should be disconnected from the potentiostat and rinsed in deionized water
    - Note: For ideal long-term coating stability it is necessary to store in deionized water for **24 hours** before drying completely

- If the deposition is successful, the electrodes should have significantly darkened in color to almost black grey color

PEDOT:pTS Electrodeposition

Materials Needed:

- Deionized Water
    - *Any supplier*
- Hydrochloric acid - HCl (37%)
    - *HYDROCHLORIC ACID 37 % ANALAR NP REAG.PE - Analytical Grade*
- Ethanol (100%) or Isopropyl Alcohol
    - *Any supplier*
- PEDOT:pTS electroplating solution
    - Acetonitrile
        - *ACETONITRILE EMPLURA*
    - p-Toluenesulfonic acid monohydrate
        - *402885 - p-Toluenesulfonic acid monohydrate from Sigma*
    - EDOT monomer (3,4-Ethylenedioxythiophene)
        - *483028 - 3,4-Ethylenedioxythiophene from Sigma*
- Platinum wire
    - *Any supplier*
- Potentiostat
    - *Can be any model! But the model used in for these protocols was the PalmSens4*

Making the plating solution:

- Mix **25 mL of deionized water** with **25 mL of acetonitrile** in a glass beaker

- Stir in **430.5 mg pTS** (can be purchased from Sigma)

- Once the pTS has dissolved into the water/acetonitrile solvent, pipette in **534 uL of EDOT** solution
    - Note: the EDOT will form many globules at first, this is normal because it is not highly miscible in aqueous solutions.

- Stir the solution until the EDOT is fully mixed
    - Note: the solution will appear clear

- Store the PEDOT:pTS solution in a sealed container as it is highly toxic

Electrodeposition Protocol:

- Pour **~100 mL of deionized water** and **ethanol** into containers

- Pipette **~10 mL of HCl** into a small glass beaker

- Pipette **~25 mL of PEDOT:pTS plating solution** into the deposition area

- Submerge the electrodes into ethanol and then put directly into the HCl
    - Note: the ethanol significantly increases the wettability of the small electrodes and thus is necessary for the desired etching of the electrodes with HCl

- Hold the electrodes in **HCl for ~30 seconds**

- Transfer the electrodes from the HCl to deionized water and rinse

- Transfer the electrodes to the PEDOT:pTS plating solution in the plating bath

- Once submerged and held in place, attach the working electrode clip from the potentiostat to the electrodes that will be plated on

- Submerge an addition piece of solid platinum to the plating bath and connect to the counter electrode clip
    - Note: in order to prevent hydrogen formation on the counter electrode the surface area of this platinum wire/piece must be approximately equal to the surface area of the electrodes you are plating onto

- Finally submerge the tip of the silver/silver chloride reference electrode into the bath and connect that to the reference clip

- Set the potentiostat to run in chronopotentiometry mode for **450 seconds at 2 mA/cm^2** (multiply this value by the total area to be plated to get the final current to apply)

- After plating the electrodes should be disconnected from the potentiostat and rinsed in deionized water

- If the deposition is successful, the electrodes should have significantly darkened in color to very deep blue/purple color

Iridium Oxide Electrodeposition

Materials Needed:

- Deionized Water
    - *Any supplier*
- Hydrochloric acid - HCl (37%)
    - *HYDROCHLORIC ACID 37 % ANALAR NP REAG.PE - Analytical Grade*
- Ethanol (100%) or Isopropyl Alcohol
    - *Any supplier*
- Iridium oxide electroplating solution
    - $IrCl_4$
        - *Iridium(IV) chloride hydrate – 500 mg from Insight Biotechnology*
    - 30% Aqueous Hydrogen Peroxide
        - *H1009 - Hydrogen peroxide solution from Sigma*
    - Oxalic Acid
        - *241172 - Oxalic acid from Sigma*
    - Potassium Bicarbonate
        - *P9144 - Potassium bicarbonate from Sigma*
    - Wide range litmus paper
        - *Any supplier*
- Platinum wire
    - *Any supplier*
- Potentiostat
    - *Can be any model! But the model used in for these protocols was the PalmSens4*

Making the plating solution:

- Mix **50 mL of deionized water** to a glass beaker

- Dissolve **70 mg of $IrCl_4$** into the water for **30 minutes**
    - Note: mild heat helps with the dissolving

- After the 30 minutes add **0.5 mL of 30% aqueous hydrogen peroxide (H_2O_2)** and stir for **10 additional minutes**

- Next add **250 mg of oxalic acid** to the solution and stir for another **10 minutes**

- Next ***slowly*** adjust the pH of the solution to **10.5** by stirring in **potassium bicarbonate** to the solution

- Confirm the pH with a test paper

    - Note: solution should be a yellowish-brown color

- Solution must be left covered at room temperature for **3 to 4 days to stabilize** at which time it will have changed to **deep purple** in color

- Store the iridium oxide solution in a sealed container as it is basic and will react explosively with acids

Protocol:

- Pour **~100 mL of deionized water** and **ethanol** into containers

- Pipette **~10 mL of HCl** into a small glass beaker

- Pipette **~25 mL of iridium oxide plating solution** into the deposition area

- Submerge the electrodes into ethanol and then put directly into the HCl
    - Note: the ethanol significantly increases the wettability of the small electrodes and thus is necessary for the desired etching of the electrodes with HCl

- Hold the electrodes in **HCl for ~30 seconds**

- Transfer the electrodes from the HCl to deionized water and rinse

- Transfer the electrodes to the iridium oxide plating solution in the plating bath

- Once submerged and held in place, attach the working electrode clip from the potentiostat to the electrodes that will be plated on

- Submerge an addition piece of solid platinum to the plating bath and connect to the counter electrode clip
    - Note: in order to prevent hydrogen formation on the counter electrode the surface area of this platinum wire/piece must be approximately equal to the surface area of the electrodes you are plating onto

- Finally submerge the tip of the silver/silver chloride reference electrode into the bath and connect that to the reference clip

- Set the potentiostat to run in cyclic voltammetry mode with a range from **-0.8 V to +0.7 V** and a **rate of 100 mV/s for 200 cycles**

- Repeat this step twice more for a total of **600 deposition cycles**

- After plating the electrodes should be disconnected from the potentiostat and rinsed in deionized water
    - Note: For ideal long-term coating stability it is necessary to store in deionized water for **24 hours** before drying completely

- If the deposition is successful, the electrodes should have significantly darkened in color to almost black blueish color