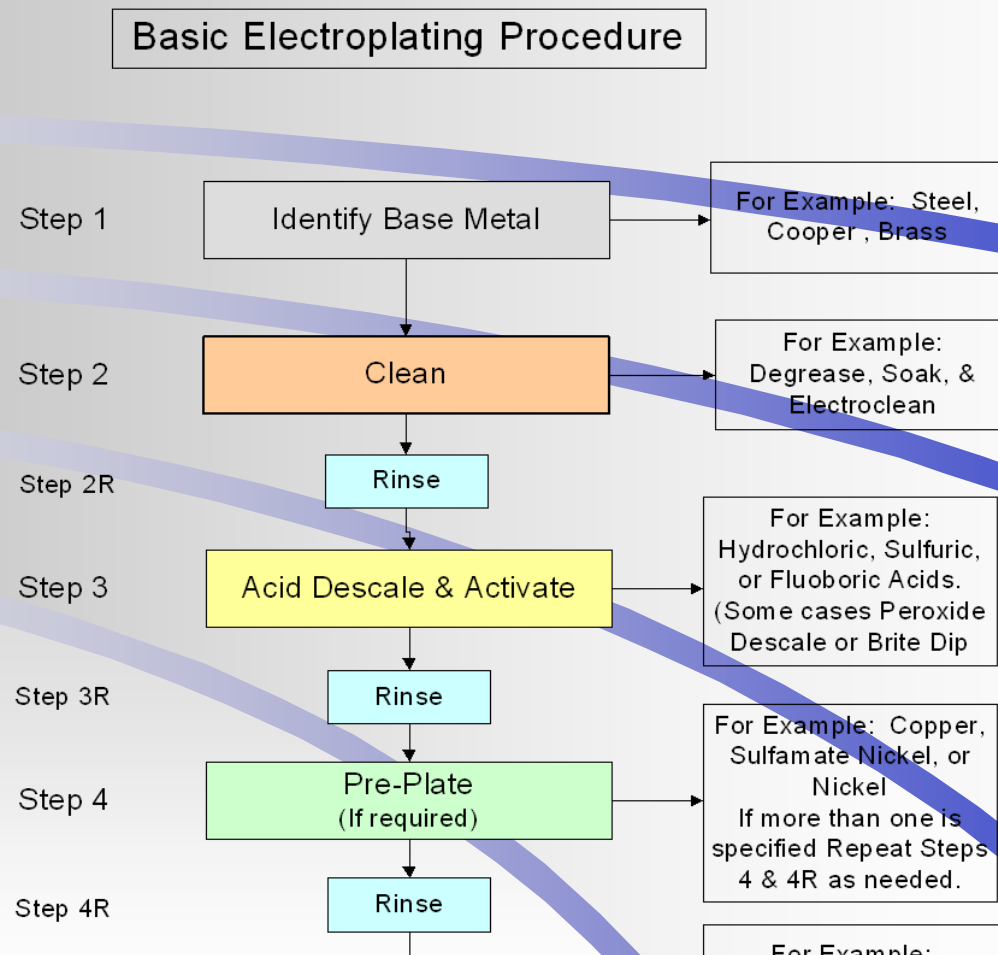


Electrochemistry

CHEM 5390

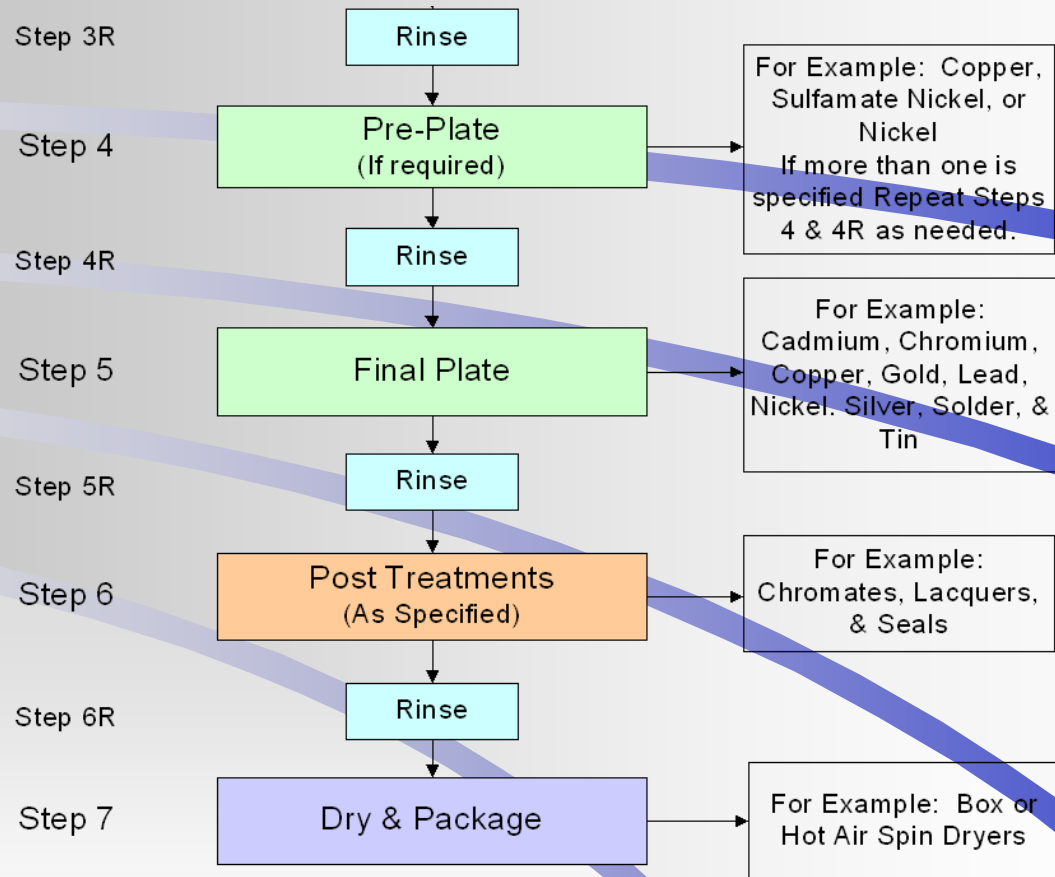
Electrodeposition and Electroplating

Basic Process



Electrodeposition and Electroplating

Basic Process



Electrodeposition and Electroplating

Electroplating is the deposition of a coating onto a surface by applying a current or potential to the object while immersing in a plating solution.

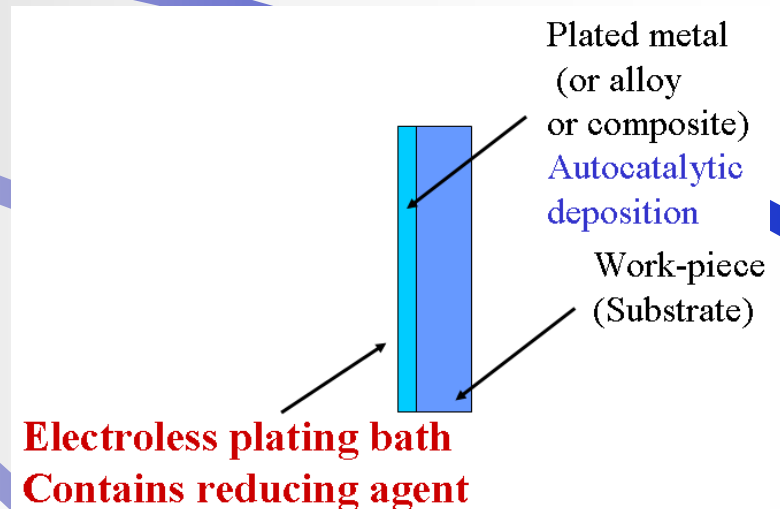
The coating can be metallic, metal oxide, conductive polymer, or composite.

There can also be an electroless plating process which uses oxidants and reductants to help apply the coating.

Electrodeposition and Electroplating

Electroless plating process

- Electroless deposition: this process uses only one electrode and no external source of electric current.
- Electroless deposition: the solution needs to contain a reducing agent so that the reaction can proceed:
- **Metal ion + Reduction solution**
→ Metal solid + oxidation solution



Electrodeposition and Electroplating

Advantages of Electroless Deposition

No electrical contact is needed.

Possible to plate both conductive and insulating surfaces.

Readily adaptable for three-dimensional coverage.

No field lines are present, and this enhances deposit uniformity.

Electrodeposition and Electroplating

Electroless plating process

Example: Ni and Ni(OH)₂ nanopowders

- Nickel nanoparticles were synthesized from a nickel hydrazine mixture in NaOH
- At high pH (~ 12.5)

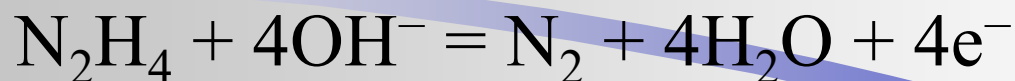
(J.Tientong, S.Garcia, C.R.Thurber, T.D.Golden, <http://dx.doi.org/10.1155/2014/193162>)

Electrodeposition and Electroplating

Electroless plating process

Example: Ni and Ni(OH)₂ nanopowders

- Hydrazine (N₂H₄) has a standard reduction potential of -1.16 V in an alkaline solution.



- Nickel, which has a standard reduction potential of -0.25 V

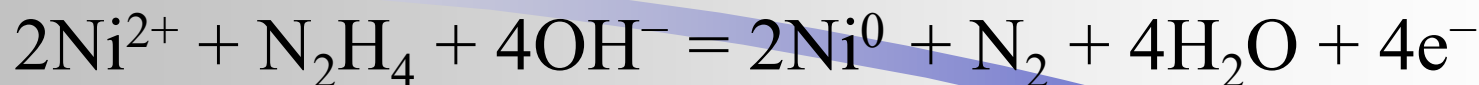


Electrodeposition and Electroplating

Electroless plating process

Example: Ni and Ni(OH)₂ nanopowders

- Chemical reduction of nickel ion with hydrazine:



By controlling pH and Temperature and complexing or stabilizing Nickel ion in solution can get Ni or Ni Hydroxide nanoparticles.

Electrodeposition and Electroplating

Electroless plating process

Example Ni and Ni(OH)₂ nanopowders

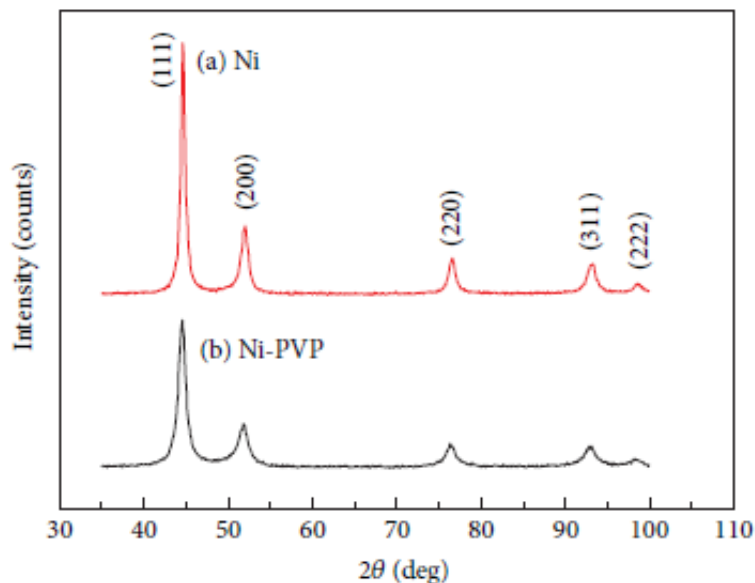


FIGURE 1: XRD pattern of (a) nickel and (b) nickel powders stabilized by PVP, precipitated by a chemical reduction method and sonication at temperature 55–65°C.

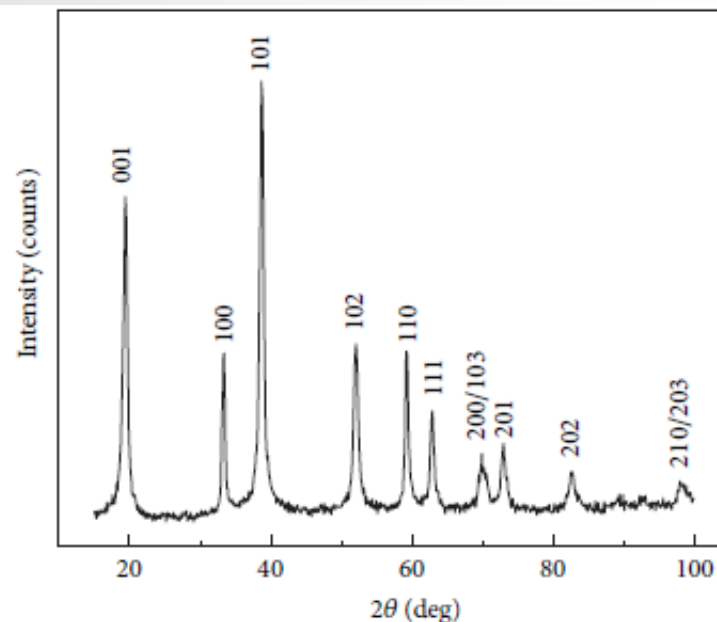
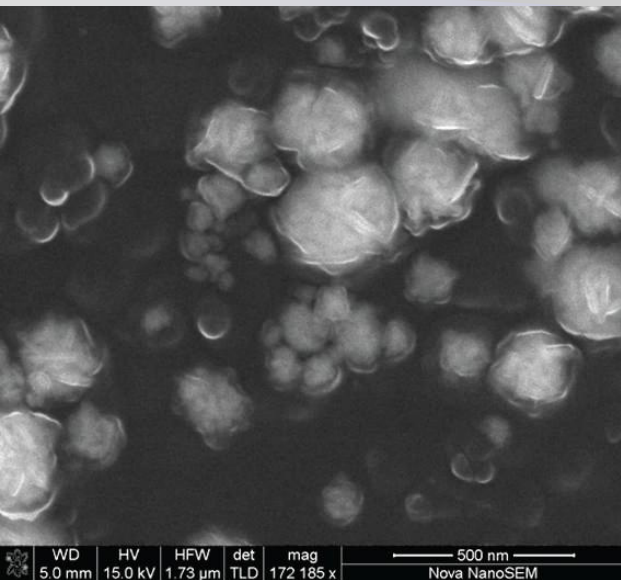


FIGURE 3: XRD pattern of precipitated nickel hydroxide powder produced by titrating nickel chloride with hydrazine-sodium hydroxide solution at pH ~10.

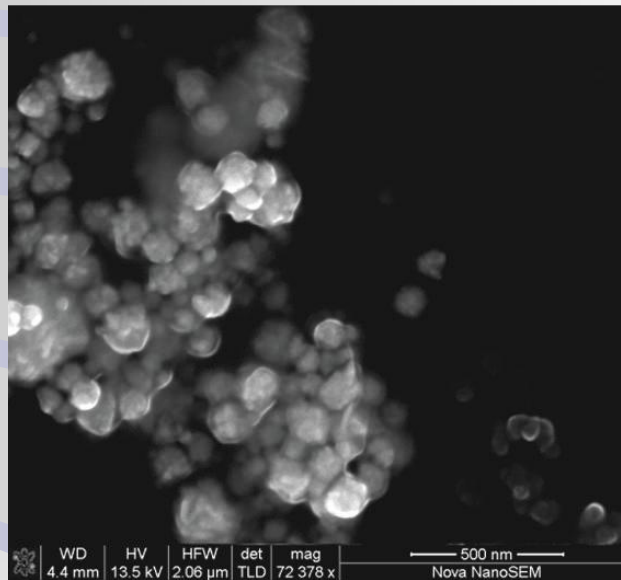
Electrodeposition and Electroplating

Electroless plating process

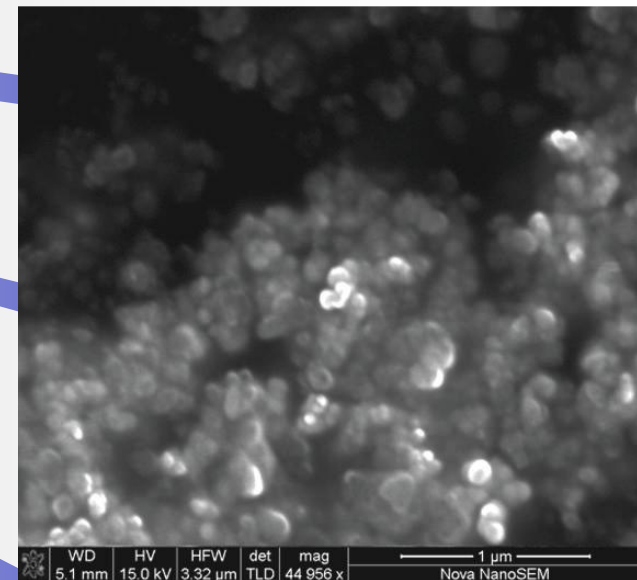
Example Ni and Ni(OH)₂ nanopowders



Ni



Ni-PVP



Ni(OH)₂

Electrodeposition and Electroplating

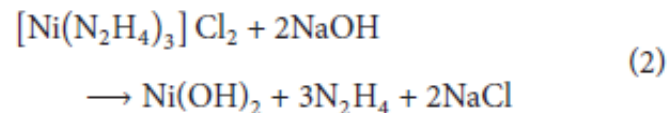
Electroless plating process

Example Ni and Ni(OH)₂ nanopowders

TABLE 1: Particle size of the nanopowders measured using the Williamson-Hall analysis from the X-ray diffraction data and the dynamic light scattering method.

Nanopowders	Measured particle size (nm)	
	Williamson-Hall plot	Dynamic light scattering ($n = 40$)
Nickel	12	101.7 ± 25.6
Nickel-PVP	7	25.9 ± 4.4
Nickel hydroxide	14	63.1 ± 16.2

$$\begin{aligned} E &= E^{\circ} - \frac{RT}{4F} \ln \frac{1}{[\text{OH}^{-}]^4 [\text{Ni}^{2+}]^2} \\ &= E^{\circ} - \frac{2.303}{4F} \log \{ [\text{OH}^{-}]^4 [\text{Ni}^{2+}]^2 \}. \end{aligned} \quad (1)$$



Electrodeposition and Electroplating

Electrodeposition and Electroplating can seem simple but as previous example shows, it is much more complicated because many factors affect the outcome:

pH

Temperature

Anion effect

Ligands/Complexing

Additives

Potential/Current

Stir rate

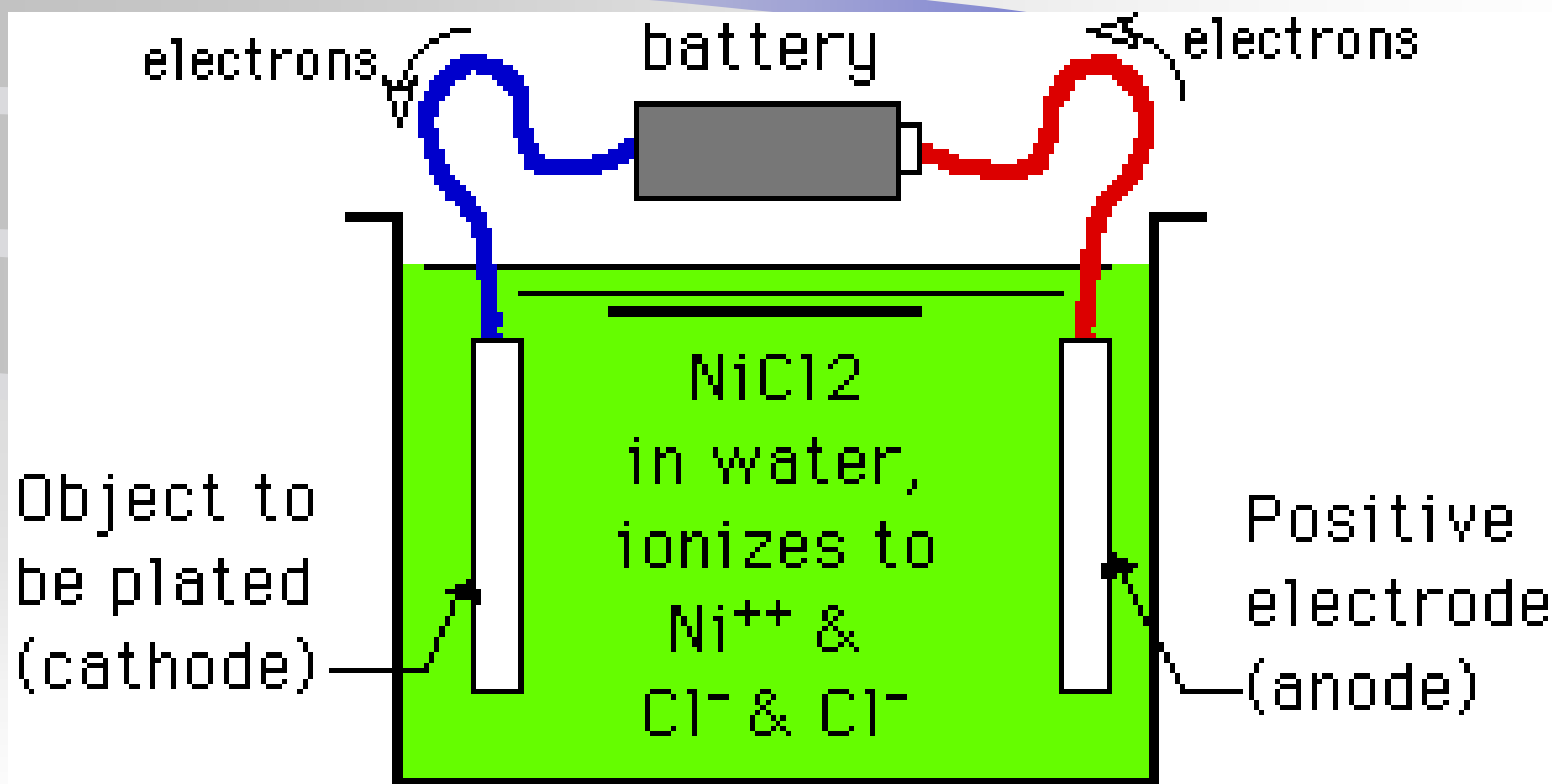
Co-deposition

Induced deposition

etc.....

Electrodeposition and Electroplating

Can be as simple as depositing a metal coating onto a conducting object.



Electrodeposition and Electroplating

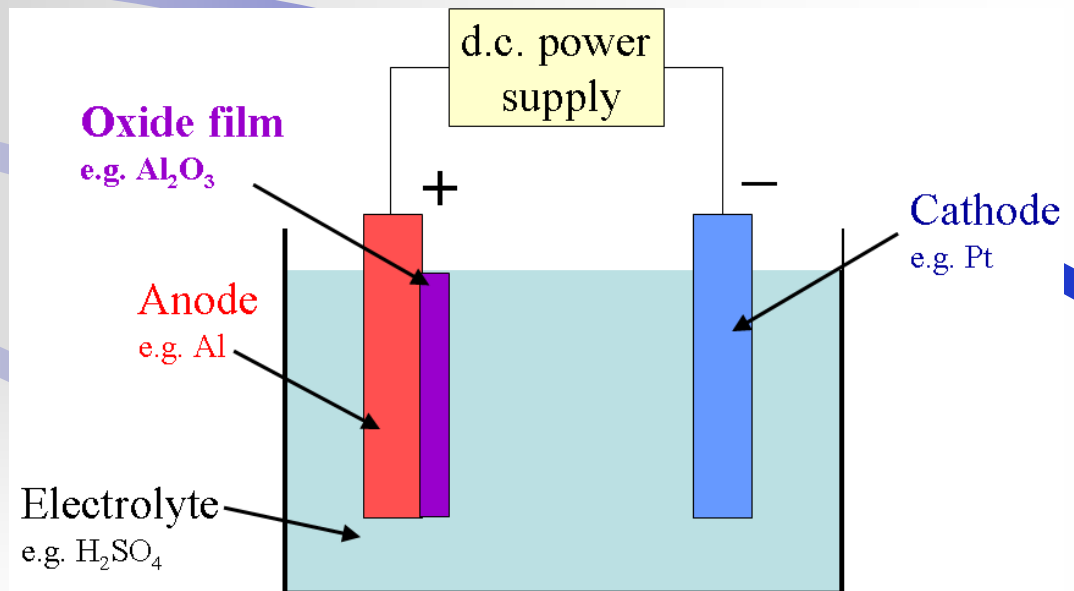
Anodization

Process where a metal is connected to a voltage source and placed in anodizing solution made up of sulfuric acid or some other oxidant. The metal is oxidized forming a metal oxide coating on the surface.

Electrodeposition and Electroplating

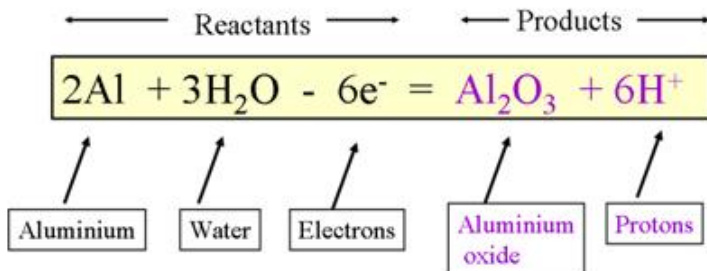
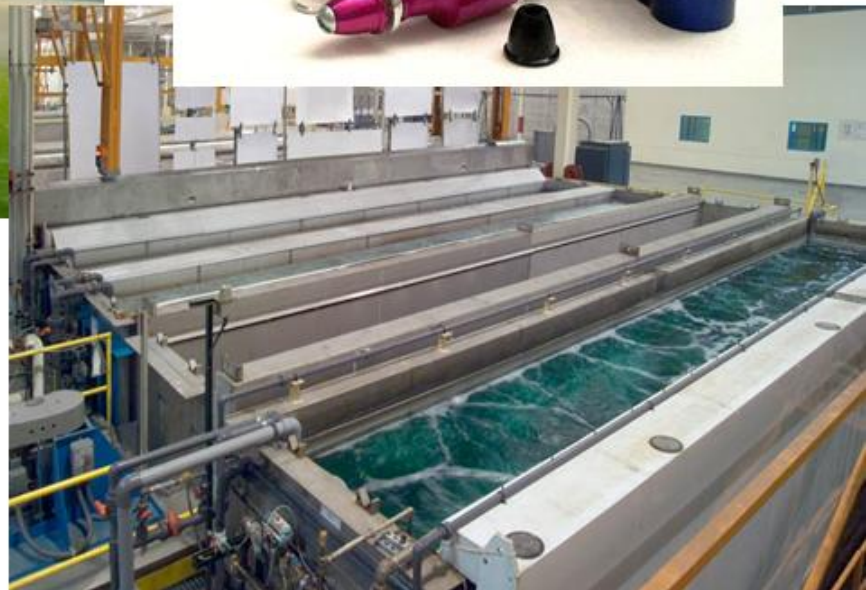
Anodization can include these for metals:

- Chromating,
- Phosphating,
- Metal coloring,
- Passivating



Electrodeposition and Electroplating

Industrial scale anodizing of Aluminium



Electrodeposition and Electroplating

Passivation

An electrolytic passivation process.

An anodic oxidation of metal at the anode, e.g. Al, Ti, Mg and is usually accompanied by hydrogen evolution at an inert electrode (the cathode), e.g. Ti, stainless steel.

Typical cell voltage 5 to 100 V.

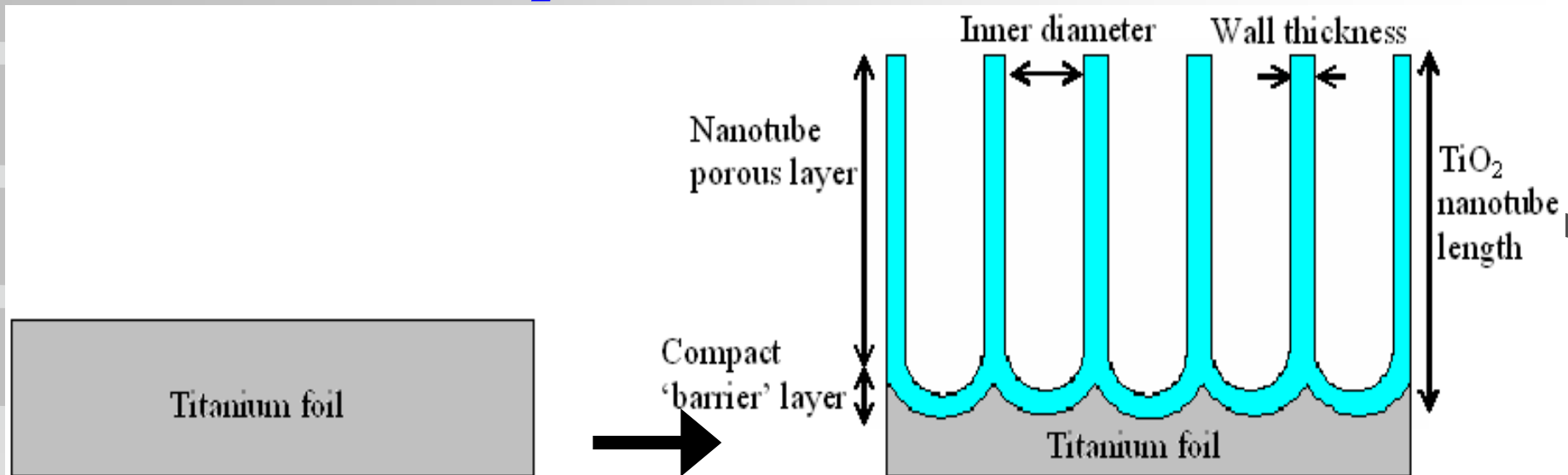
Electrodeposition and Electroplating

Passivation

- Deliberately producing a stable oxide coating
 - by anodic treatment of a metal surface
- Coating is usually non-conducting
 - thermally and electrically insulating
- Oxide is usually protective
 - against corrosion or wear or heat
- Anodized film can be post-treated
 - with dye, polymer, lubricant...

Electrodeposition and Electroplating

Electrochemical anodizing Transformation of Ti foil to TiO₂ nanotubes:



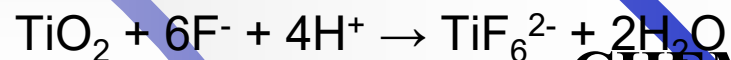
Anodizing e.g. 10-100 V

Competing reactions for the formation of TiO₂ nanotubes

Electrochemical formation of oxide



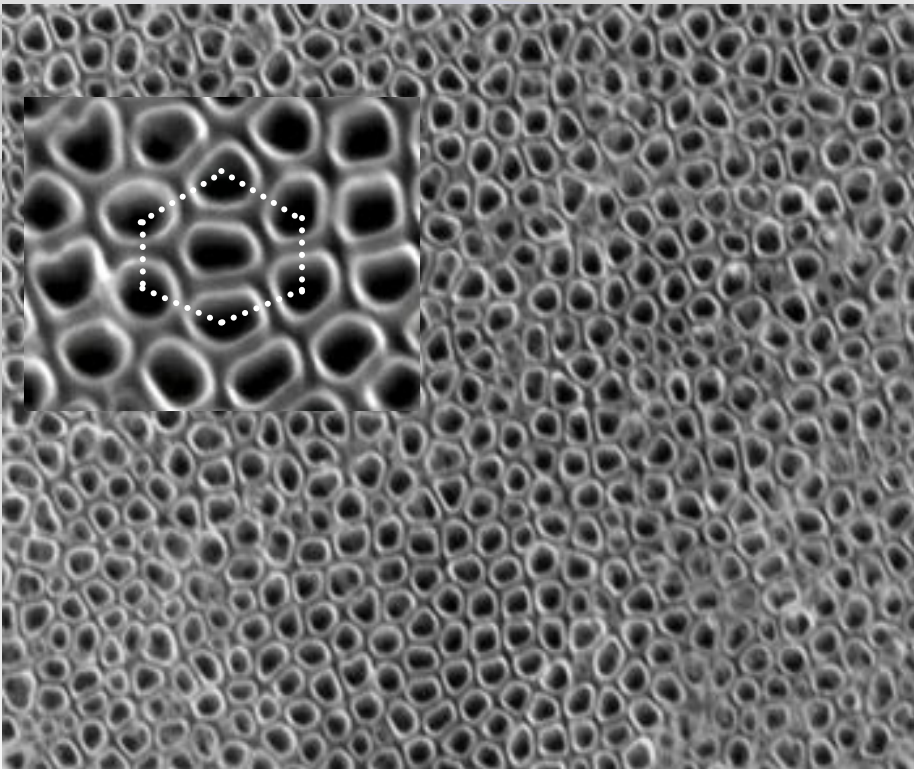
Chemical dissolution of oxide



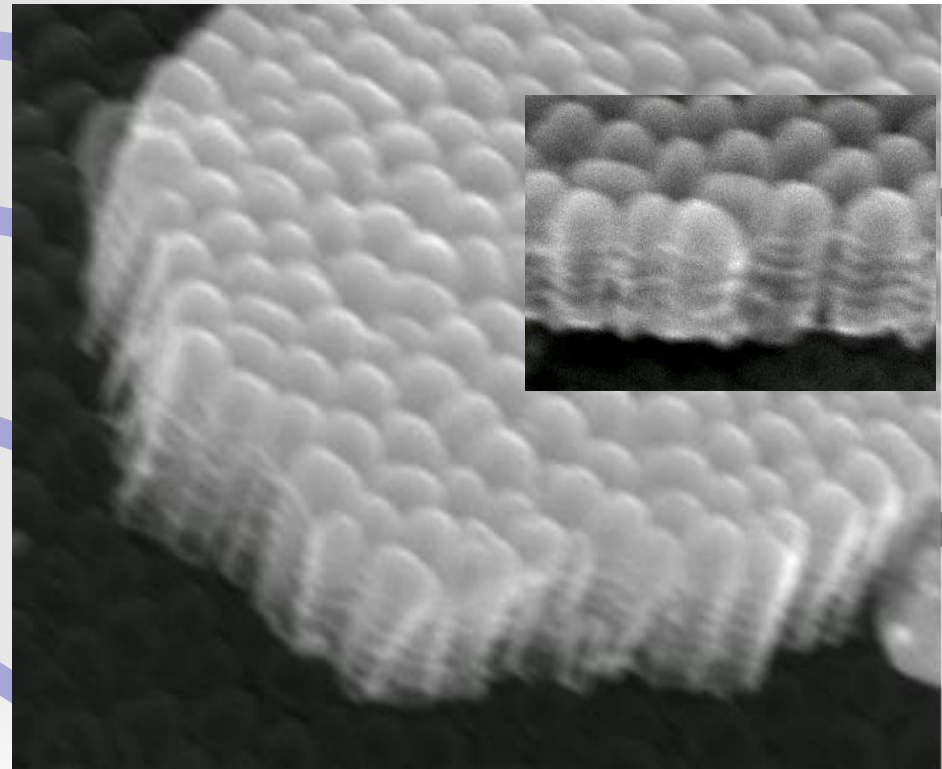
Electrodeposition and Electroplating

Green electrolyte, $\text{CH}_3\text{SO}_3\text{H}$

Anodizing of TiO_2 nanotubes from Ti foil



200 nm



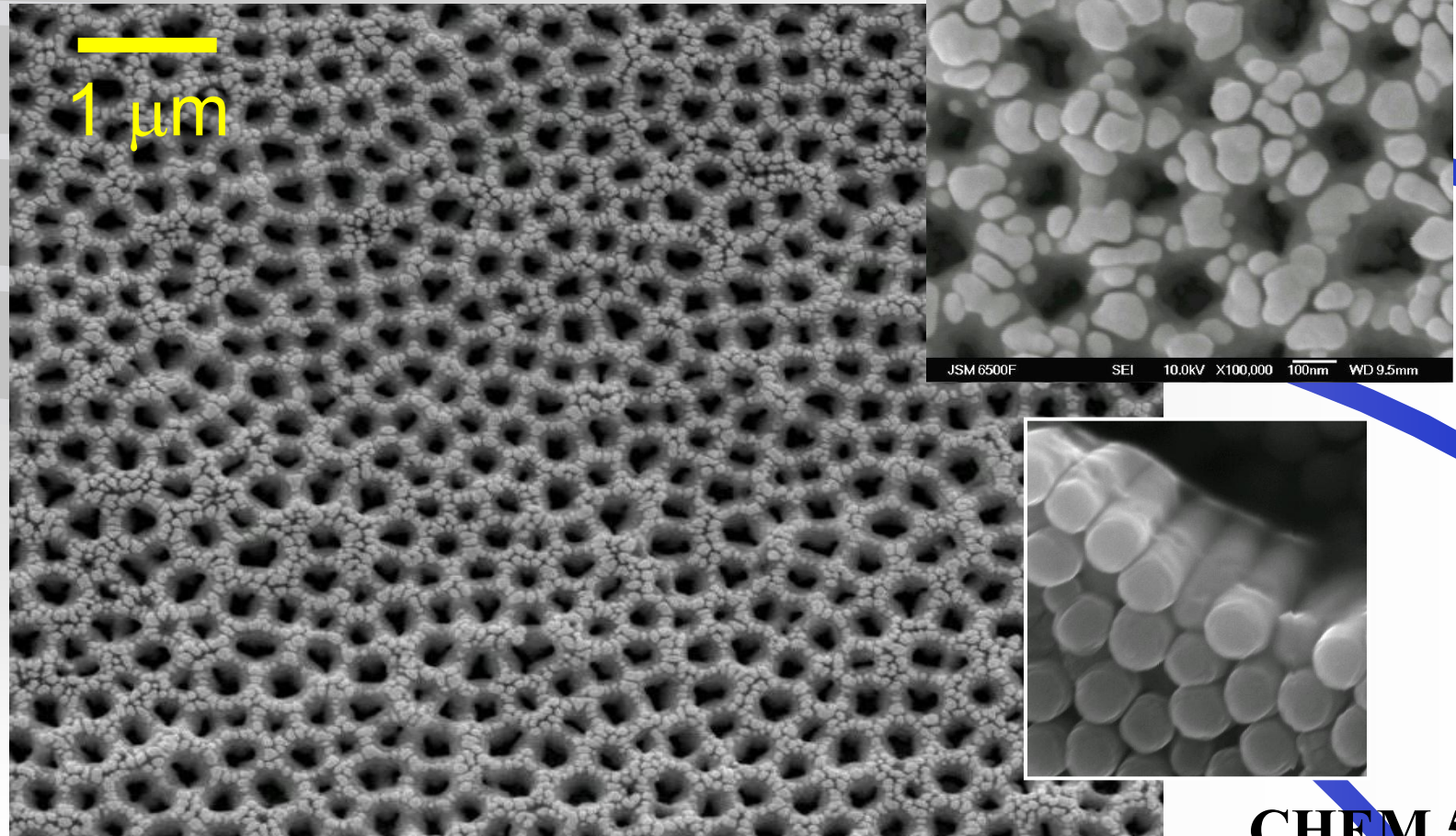
200 nm

CHEM 5390

Electrodeposition and Electroplating

Surface microstructure

Nanotubes Au-TiO₂ vertically aligned array



Electrodeposition and Electroplating

Electrochemical Deposition of nanotubes/wires/whiskers/etc:

InSb Nanowires Grown in Flexible Polycarbonate Membranes

The electrolyte solution:

0.15 M indium chloride (InCl_3),

0.1 M antimony chloride (SbCl_3),

0.36 M citric acid ($\text{C}_6\text{H}_8\text{O}_7\text{H}_2\text{O}$),

0.17 M potassium citrate ($\text{C}_6\text{H}_5\text{K}_3\text{O}_7$)

pH value 1.8.

constant potential (between -1.0 and -1.5 V) vs (Ag/AgCl) 15 min.

(A.P. Singh, ..., T.D.Golden, U.Philipose, Nanomaterials 2019, 9, 1260; doi:10.3390/nano9091260)

Electrodeposition and Electroplating

InSb Nanowires Grown in Flexible Polycarbonate Membranes

- $\text{In}^{+3} + 3\text{e}^- \rightarrow \text{In}$ ($E^0 = -0.46\text{V}$)
- $\text{SbO}^+ + 2\text{H}^+ + 3\text{e}^- \rightarrow \text{Sb} + \text{H}_2\text{O}$ ($E^0 = +0.39\text{V}$)

Example of anomalous co-deposition

where the nucleation of one species affects the deposition of another species in solution. (common in iron based alloys).

Electrodeposition and Electroplating

InSb Nanowires Grown in Flexible Polycarbonate Membranes

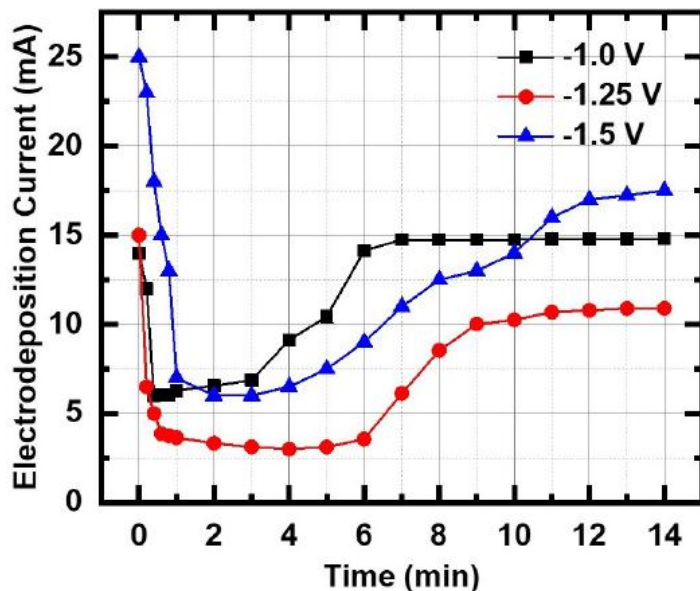


Figure 2. Current transient of room temperature InSb nanowire growth in Au-coated polycarbonate membrane at three different deposition potentials: -1.0 V, -1.25 and -1.50 V.

Nucleation and growth kinetics seen here

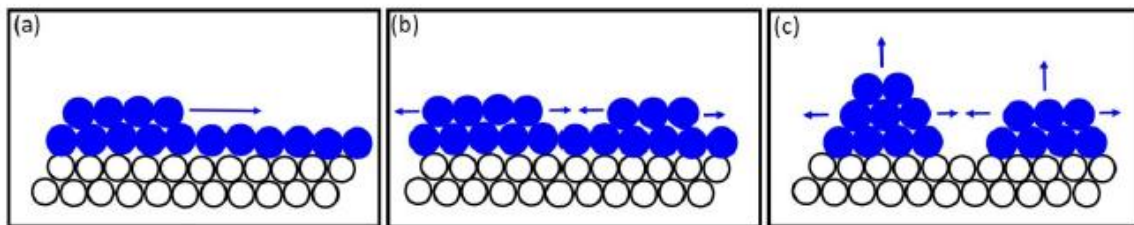
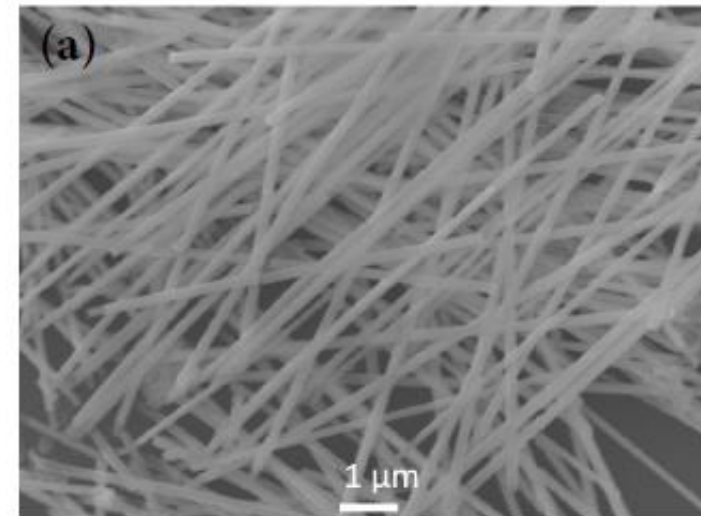
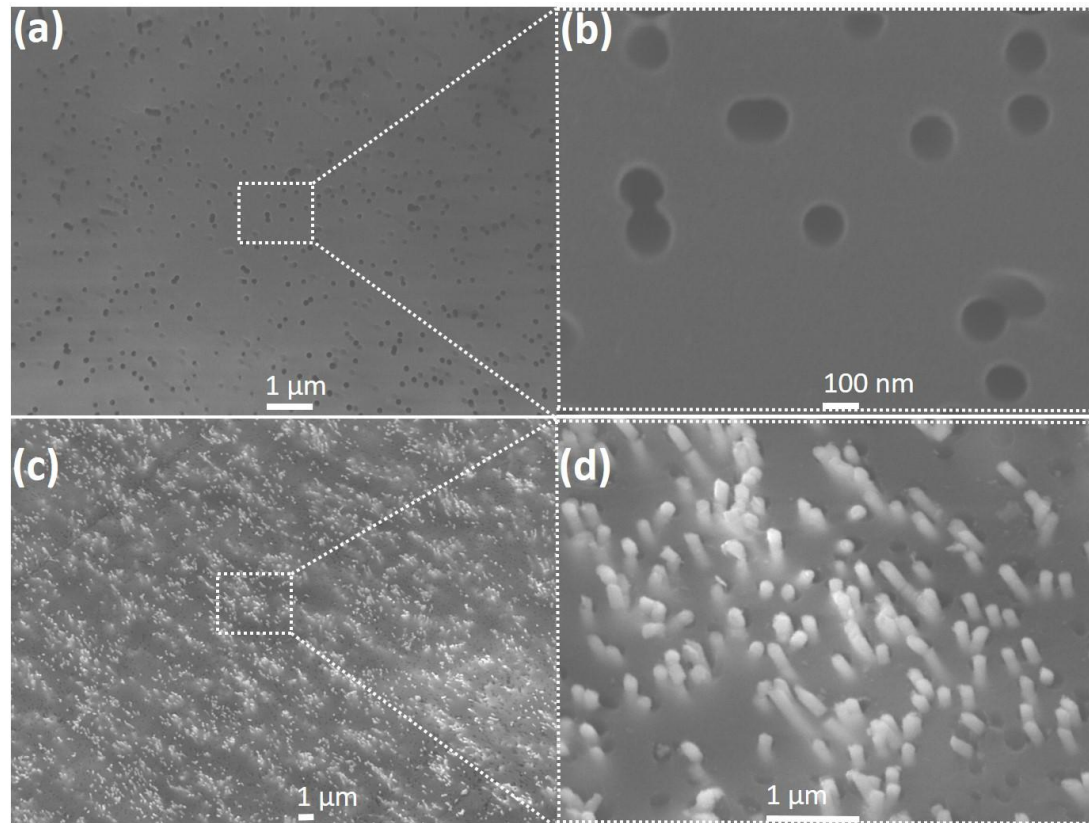


Figure 9. A schematic of the 'nucleation-coalescence' growth mechanism, where: (a) a few monolayers of InSb grow on the Au electrode; (b) islands form over the monolayer; (c) coalescence of the islands to form individual crystals/grains.

Electrodeposition and Electroplating

InSb Nanowires Grown in Flexible Polycarbonate Membranes



Electrodeposition and Electroplating

InSb Nanowires Grown in Flexible Polycarbonate Membranes

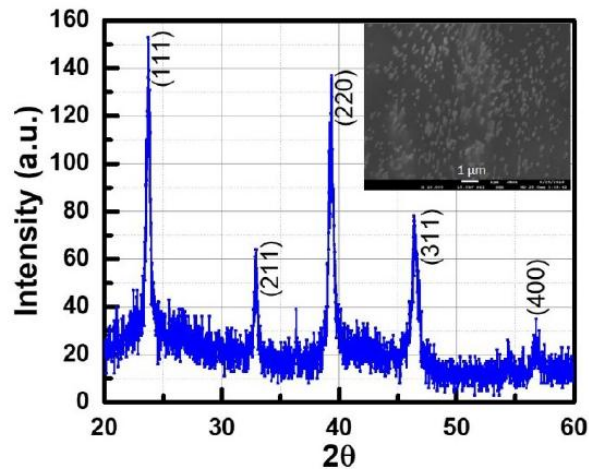


Figure 6. X-ray diffraction (XRD) spectrum of as grown InSb nanowire in polycarbonate template.

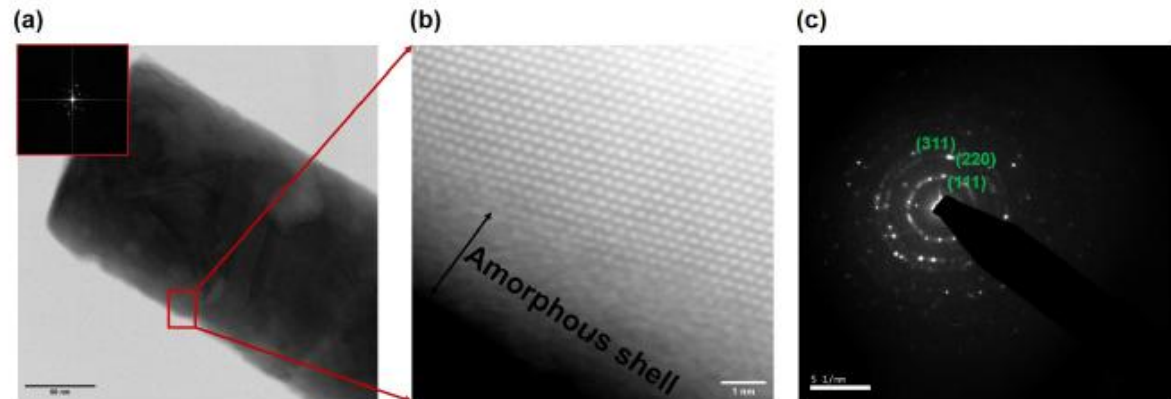


Figure 7. A scanning transmission electron microscope (STEM) images is taken along a single InSb nanowire clearly showing the presence of an amorphous oxide shell: (a) Annular bright-field (ABF)-STEM image of a relatively smooth nanowire that shows several crystal grains; the inset shows a fast Fourier transform (FFT) of the image indicating multiple crystallographic orientations; (b) magnified high-angle annular dark-field (HAADF)-STEM image of outlined region in (a), looking down the (111) direction of one of the larger grains, with a measured distance of 0.25 nm; (c) selected area diffraction pattern (SAED) shows indexed rings with discrete spots confirming polycrystalline nature of the nanowire.

Electrodeposition and Electroplating

Anomalous co-deposition

Example: Ni-Mo

Electrodeposition of only Mo metal onto substrates has proved elusive. An early attempt to deposit metallic Mo from aqueous solutions had a maximum current efficiency of only ~2%. A more productive route was discovered in which the codeposition of Mo occurred with iron-based alloys. This pathway came to be known as an induced codeposition mechanism described by Brenner. For the induced codeposition of nickel-molybdenum, the role of each component in the plating solution and the deposition mechanism is not clear and still under debate.

Electrodeposition and Electroplating

Anomalous co-deposition

Example: Ni-Mo

A little known pathway uses citrate or pyrophosphate solutions containing nickel sulfate, sodium molybdate dihydrate, and sodium citrate. The pH of the solution is adjusted to higher pH using ammonia.

The initial Ni species for the citrate and ammonia bath at pH 8 were 50% $\text{NiH}_2\text{Cit}_2^{4-}$, 20% $\text{Ni}_2\text{Cit}_2^{4-}$, 22% NiHCit^- , and 7% NiOH^+ ; and for pH 11 : 1% $\text{NiH}_2\text{Cit}_2^{4-}$, 7% $\text{Ni}_2\text{Cit}_2^{4-}$, trace% NiOH^+ , and 92% $\text{Ni}(\text{NH}_3)_n^{2+}$.

Electrodeposition and Electroplating

Anomalous co-deposition

Example: Ni-Mo

However, adding borate with the citrate gave deposits that had hardness values 100X than steel.

- $\text{NiCit}^- + 2\text{e}^- \rightarrow \text{Ni(s)} + \text{Cit}^{3-}$ Eq. (1)
- $\text{MoO}_4^{2-} + \text{NiCit}^- + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow [\text{NiCitMoO}_2]_{\text{ads}}^- + 4\text{OH}^-$ Eq. (2)
- $[\text{NiCitMoO}_2]_{\text{ads}}^- + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{Mo(s)} + \text{NiCit}^- + 4\text{OH}^-$ Eq. (3)
- $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ Eq. (4)

Electrodeposition and Electroplating

Anomalous co-deposition

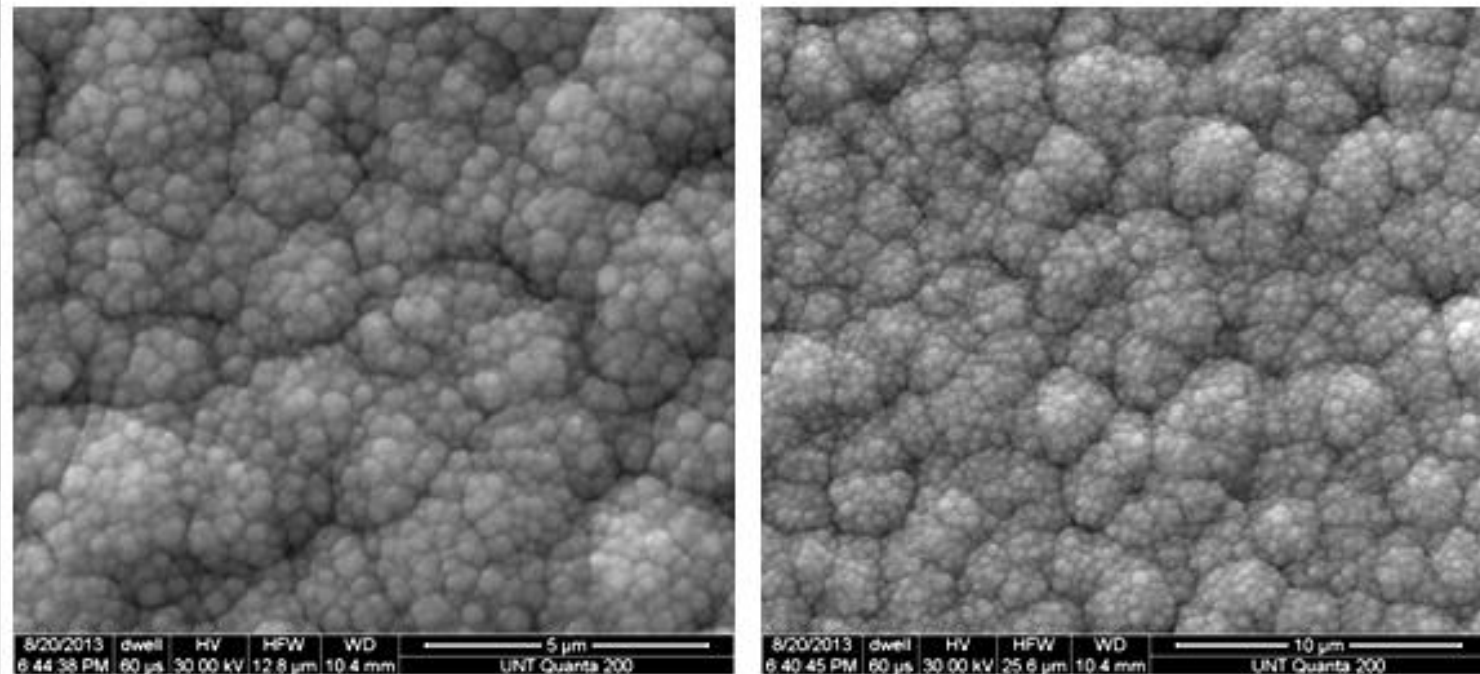


Figure 4. SEM images of nickel-molybdenum alloys at different magnifications (5 and 10 µm) deposited from citrate-borate electrolyte (pH 9.5) plating solution of the $[\text{MoO}_4^{2-}]/[\text{Ni}^{2+}]$ molar ratio of 0.1

Electrodeposition and Electroplating

Anomalous co-deposition

Ni-Mo alloy was prepared by an electrochemical deposition technique using pulsed potential modification.

The cycle of the pulsed potential deposition was started with a cathodic potential at E1: -1.35 V and held for 10 seconds then pulsed to an anodic potential at E2: -0.7 V, held for 3 seconds then pulsed back to the initial potential at E1: -1.35 V.

Pulse Deposition – another technique that influences final outcome of the deposit.

Electrodeposition and Electroplating

Anomalous co-deposition

Corrosion resistance also increased 1000 fold.

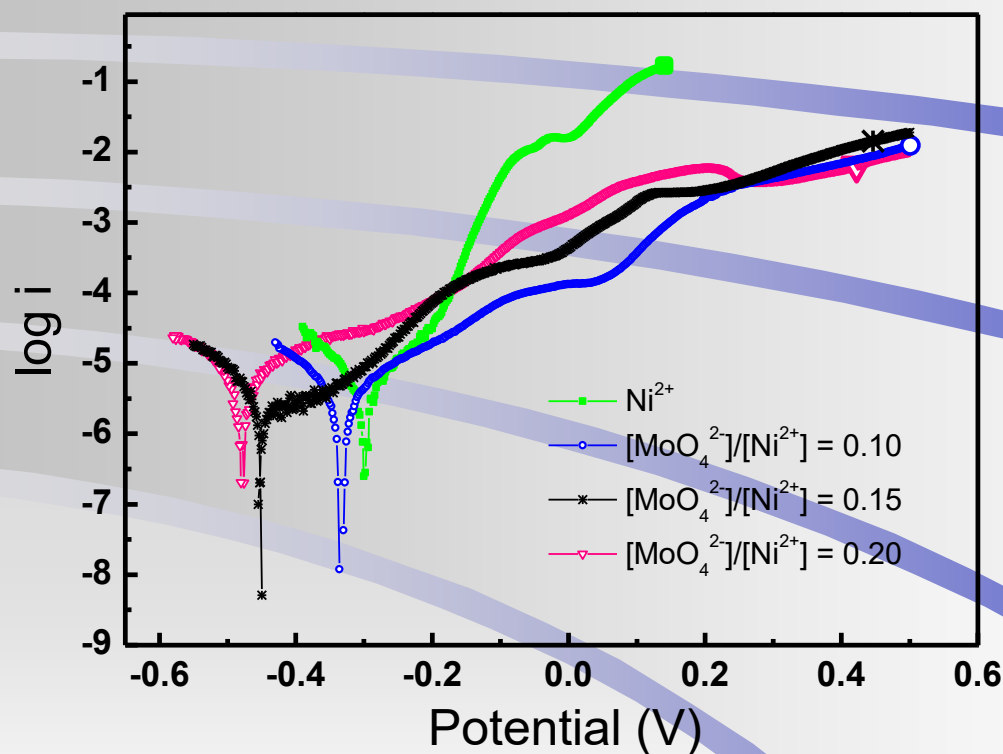


Figure 5.13: Tafel plot and anodic polarization of nickel-molybdenum alloy in 3.5% NaCl solution. The alloys were electrodeposited from citrate-borate plating solutions at different $[\text{MoO}_4^{2-}]/[\text{Ni}^{2+}]$ molar ratios of 0.1, 0.15, and 0.2 compared to pure nickel deposit.

Electrodeposition and Electroplating

Pulse or Step Plating

In dc-plating, constant current or potential is used, and the rate of arrival of metal ions depends on their diffusion coefficient or convection.

In pulse plating and pulse reverse, a modulated current waveforms is used to get a better leveling of the deposit, and to minimize the porosity, contamination, etc.

The morphology of some metal and alloy deposits were found to be superior to the dc-plated deposits. Complex current wave forms can be generated by using pulse generator.

Electrodeposition and Electroplating

Pulse deposition

To characterize a set of current or potential pulses, parameters need to be known:

- The cathodic (anodic) peak pulse current or potential.
- The cathodic (anodic) pulse length (t)
- The opposite or step to new pulse current or potential.
- The cathodic (anodic) pulse length (t)
- The interval between pulses (t_p)

The duty cycle (T) represents the portion of the time in each cycle when the current or potential is ON.

Electrodeposition and Electroplating

Pulse or Step Deposition

Pulse deposition affects the mechanism of electro-crystallization, which controls the physical and mechanical properties of the deposit.

Nucleation rate of the deposit $\propto$ current density.

Use of high J pulses can produce deposits with reduced porosity, and finer grains through the desorption of impurities and renucleation of deposits with the formation of new, smaller crystal grains.

Grain size depends on the duty cycle and the bath.

Electrodeposition and Electroplating

Pulse Deposition

The crystalline structure formed as a result of electrodeposition depends on a competition between rates of new crystalline formation and existing crystal growth.

Hydrogen evolution is important to control.

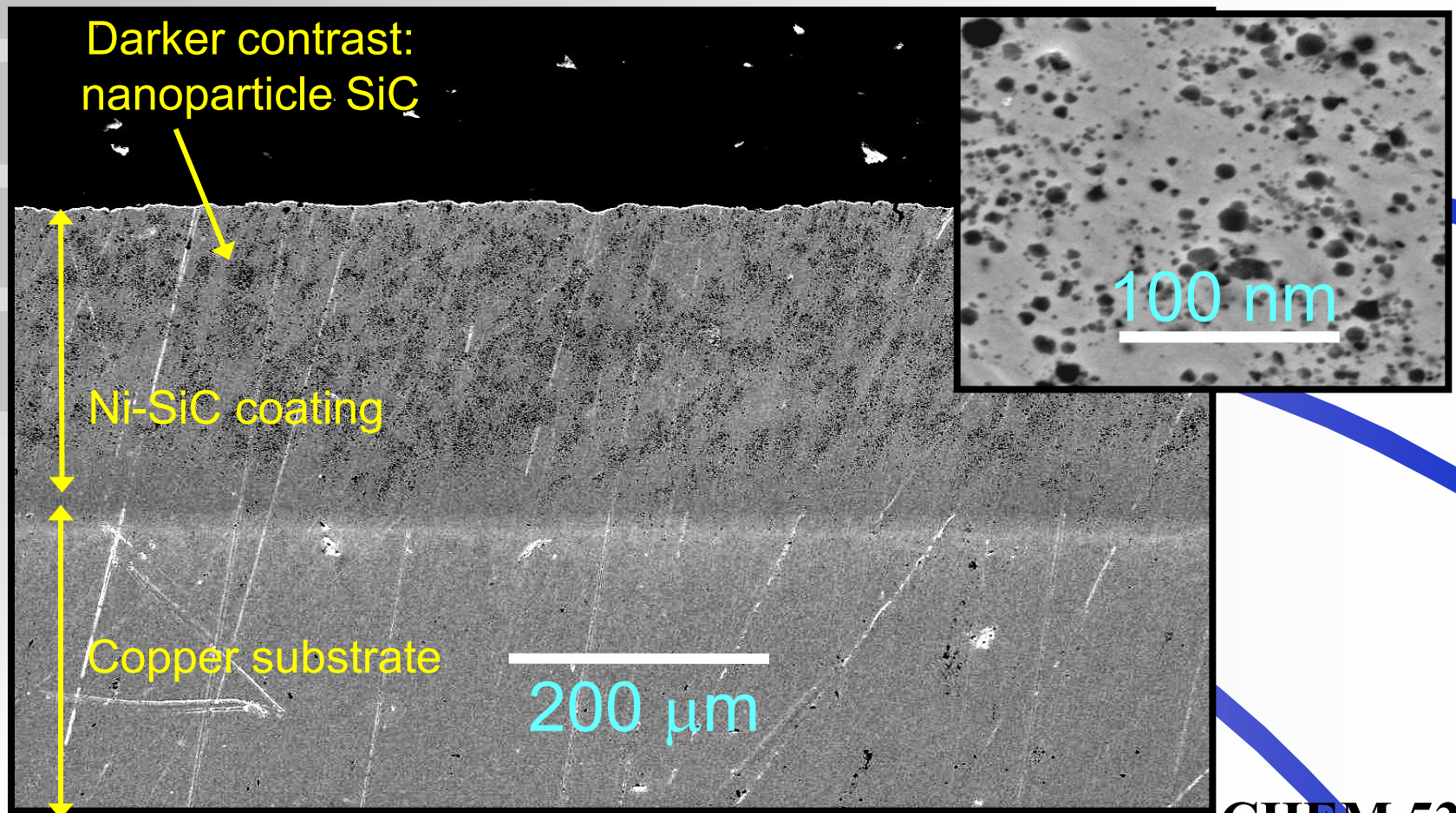
Electrodeposition and Electroplating

Imbedding Nanoparticles into a metal matrix is a huge area of research to produce unique electronic, optical, and physical properties.

To do this electrochemically can be difficult, since usually the researcher is trying to combine a non-electroactive species with an electroactive one.

Electrodeposition and Electroplating

Example: Nanoparticles SiC in a nickel matrix Wear resistance coating



Electrodeposition and Electroplating

Nanocomposites

Can use:

Special cells

Modified electrolytes

Charges on non-electroactive species

Electrodeposition and Electroplating

Nanocomposites

Special cells

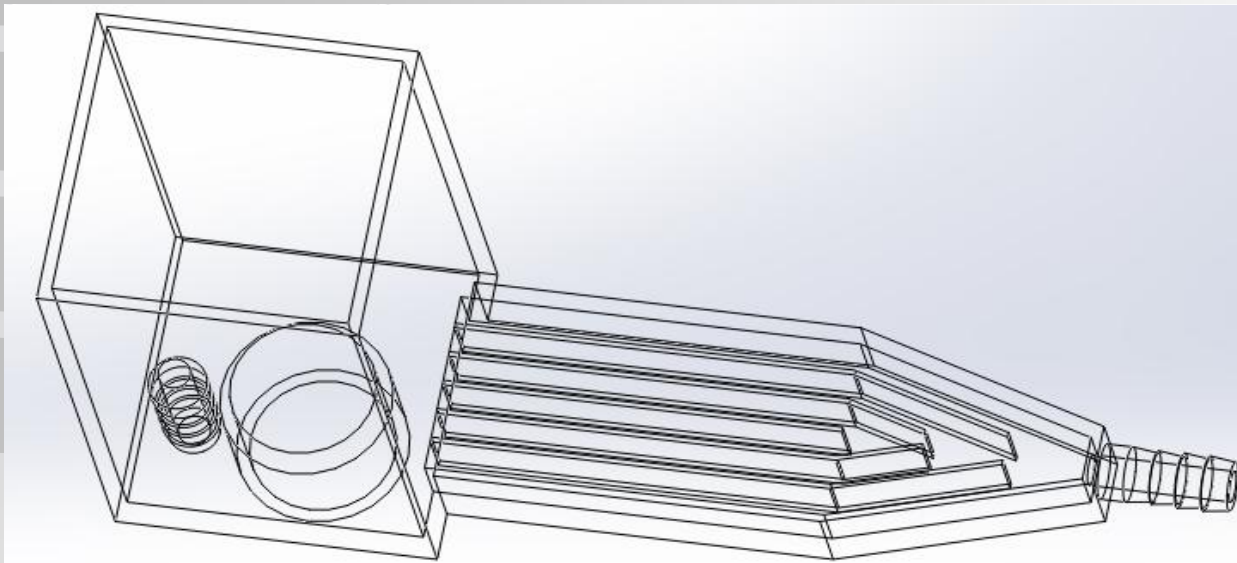


Figure 2: Diagrams of the flow cell I designed for use in deposition of nickel-layered silicates.

Electrodeposition and Electroplating

Nanocomposites

Special cells

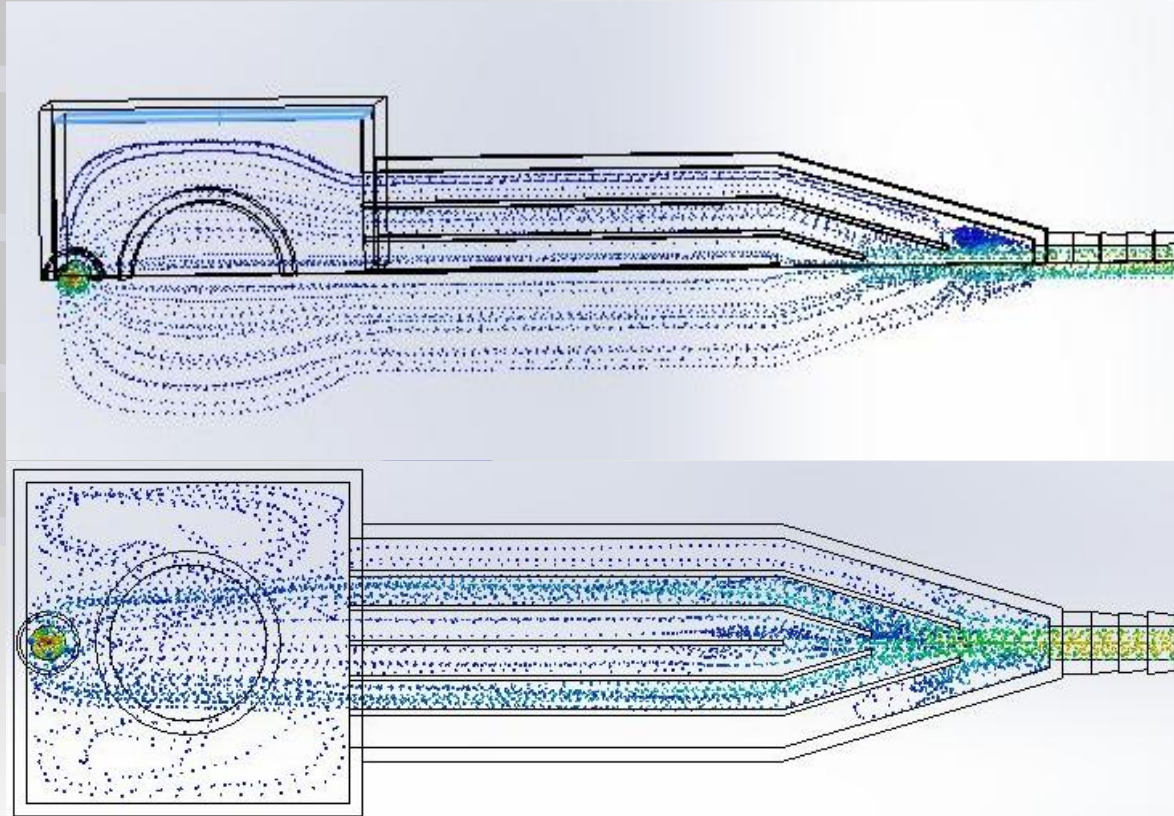


Figure 1: Flow patterns for (a) the finished cell at optimal flow rate and (b) the finished cell under high flow rate and thus turbulent flow, which disrupts the orientation of platelets. The electrolyte flows from the inflow valve, on the right, to the outflow valve on the left. Velocity follows the visual spectrum, from blue (slow) to red (fast).

Electrodeposition and Electroplating

Nanocomposites

Special cells

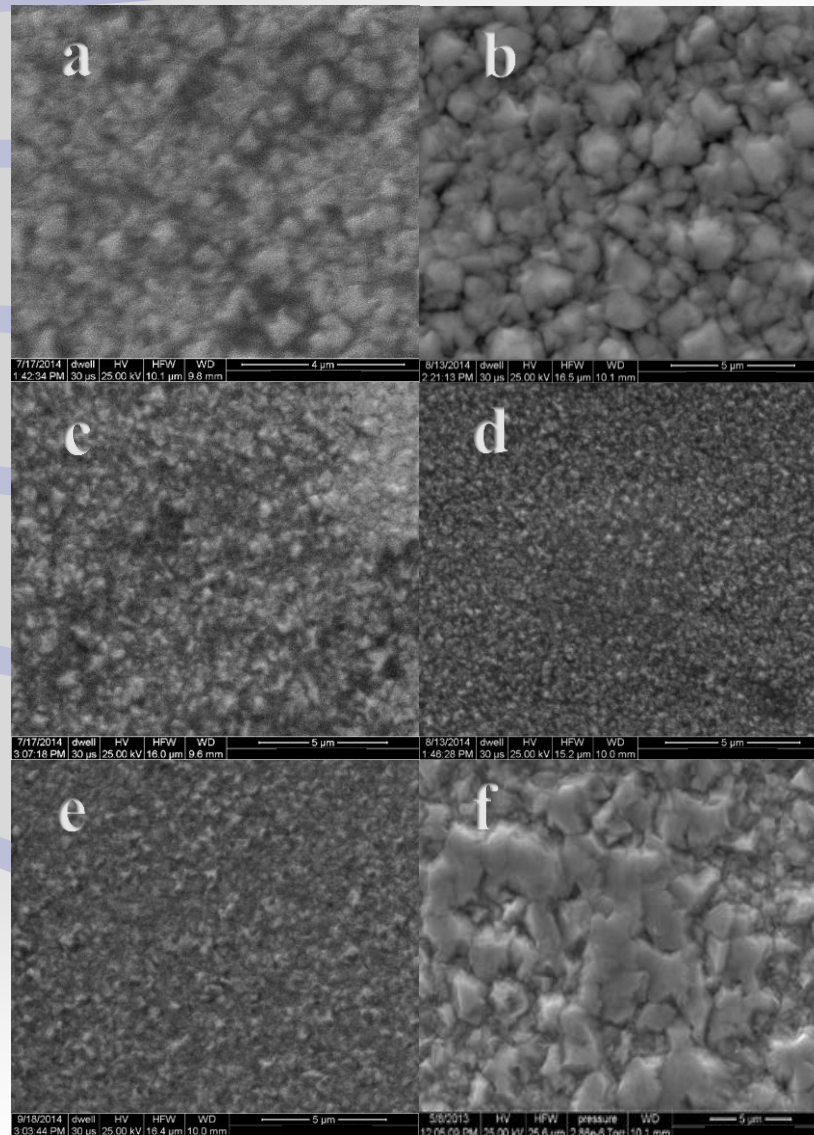
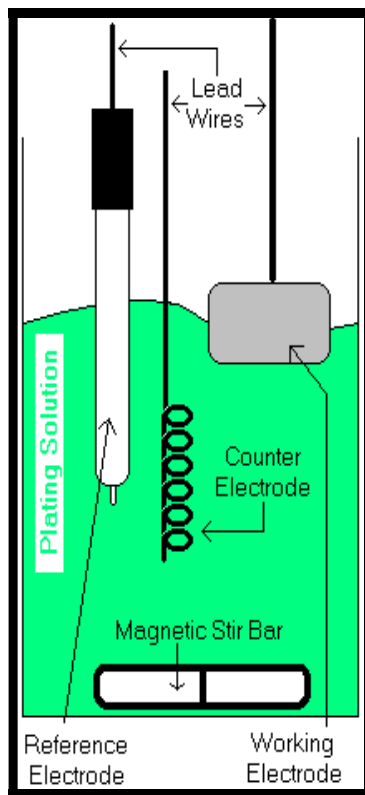


Figure 3: SEM pictures of samples run under flow rates of a) 40, b) 60, c) 80, d) 100, and e) 120 ml/min. Picture f) shows a non-flowed sample run under the same parameters.⁹

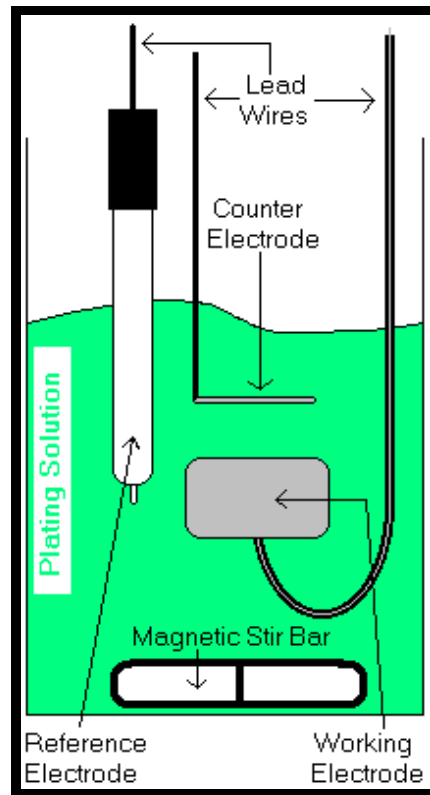
Electrodeposition and Electroplating

Nanocomposites

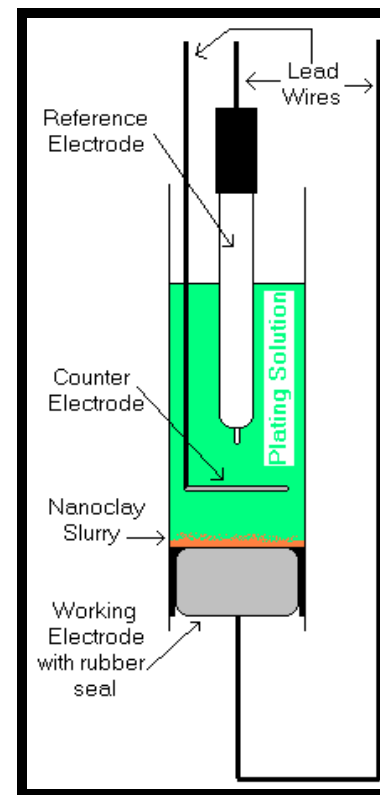
Cell Design



Cell 1



Cell 2

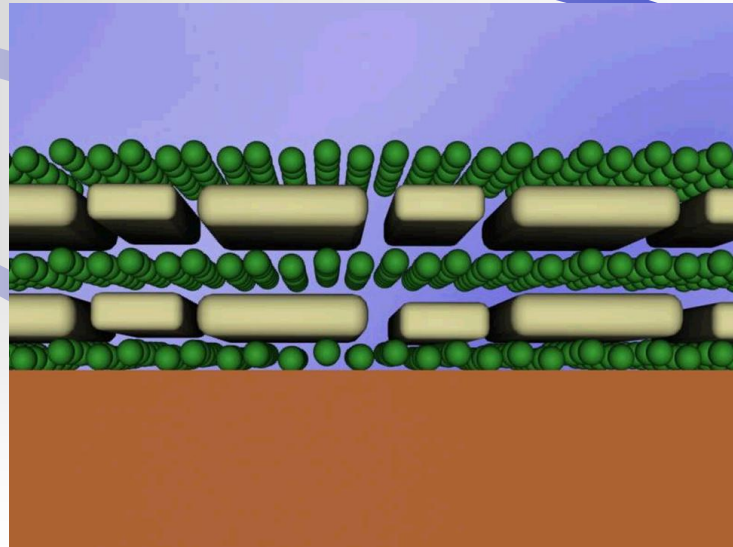
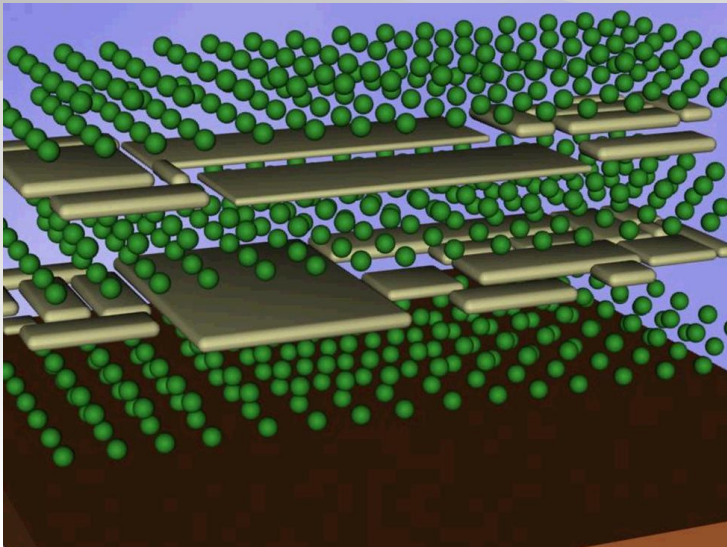
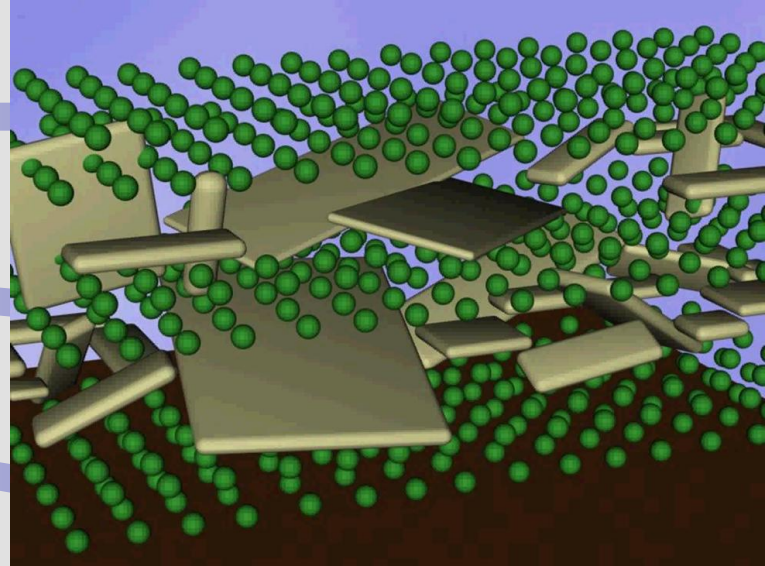


Cell 3

Electrodeposition and Electroplating

Nanocomposites

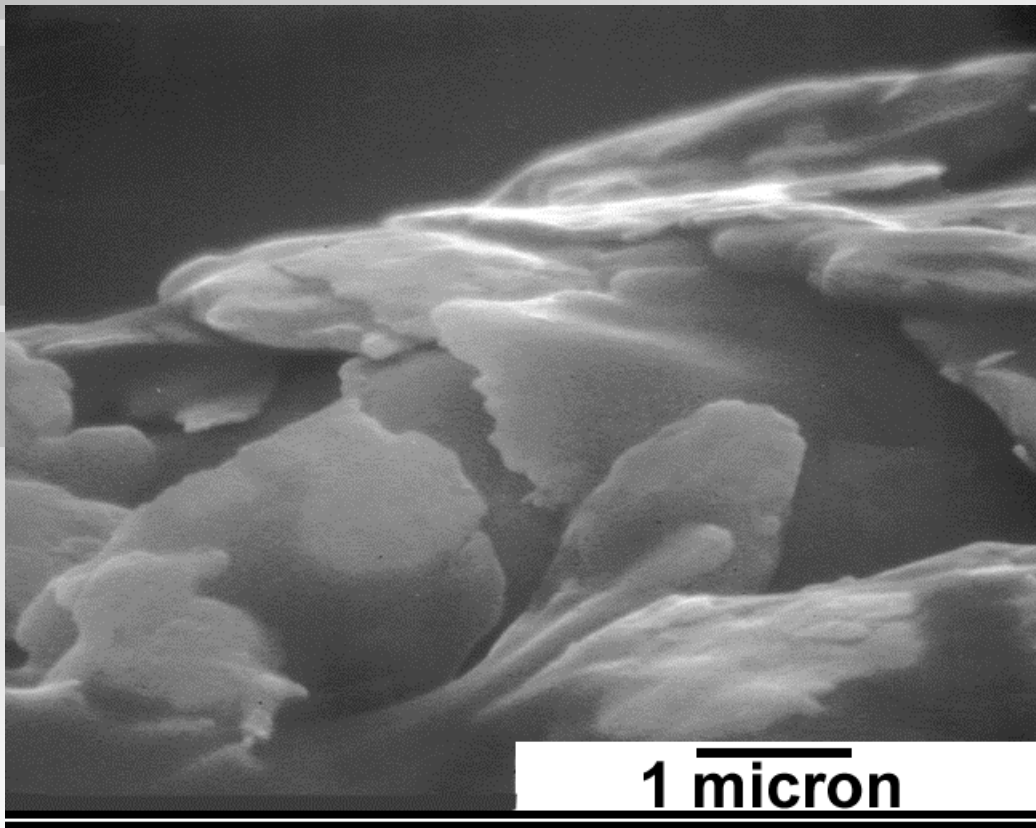
Nanoclays in Ni coatings



Electrodeposition and Electroplating

Nanocomposites

Nanoclays in Ni coatings



Electrodeposition and Electroplating

Nanocomposites

Can use:

Special cells

Modified electrolytes

Charges on non-electroactive species

Electrodeposition and Electroplating

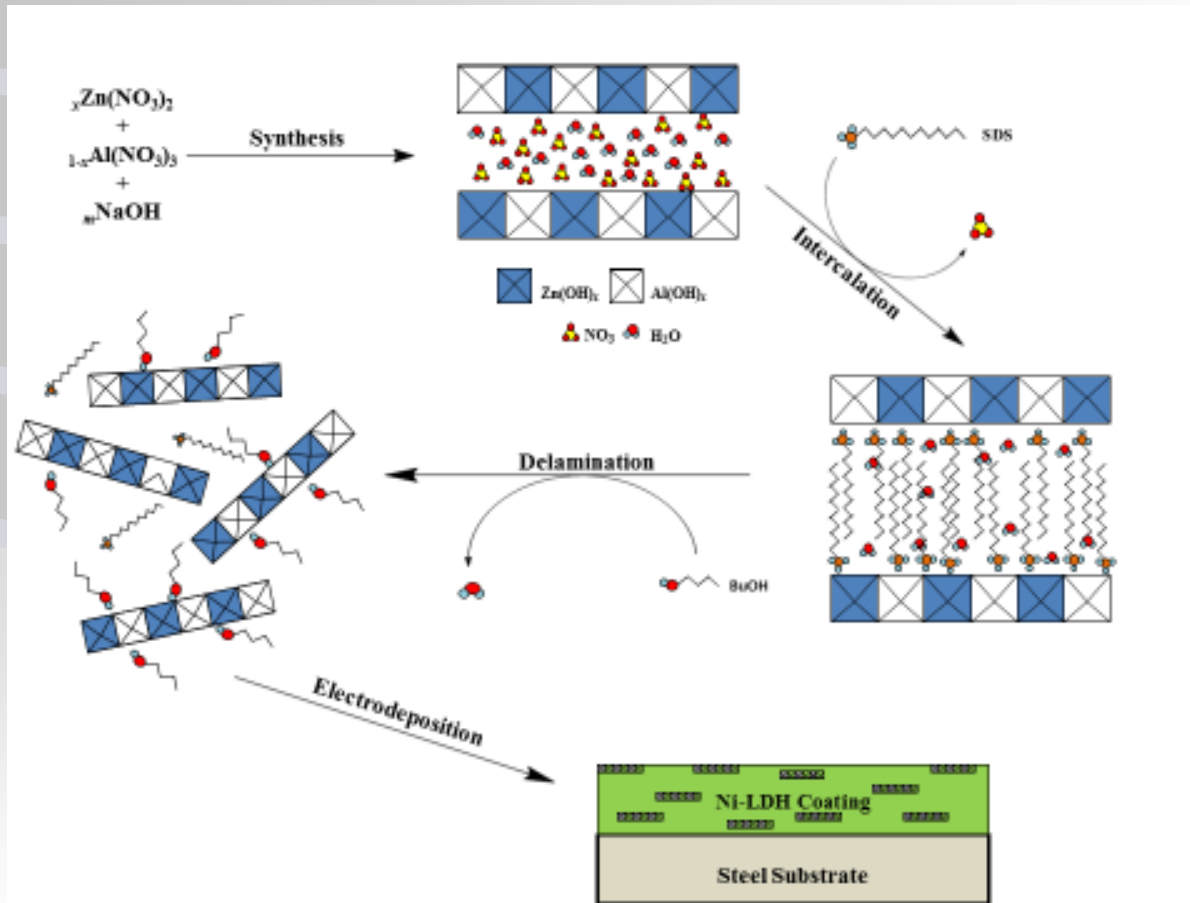
Nanocomposites

Aqueous-organic bath systems can help stabilize nanoparticles of very low solubility during electrodeposition of metal-matrix nanocomposite coatings.

Electrodeposition and Electroplating

Nanocomposites

Nanoclays in Ni coatings



Electrodeposition and Electroplating

Nanocomposites

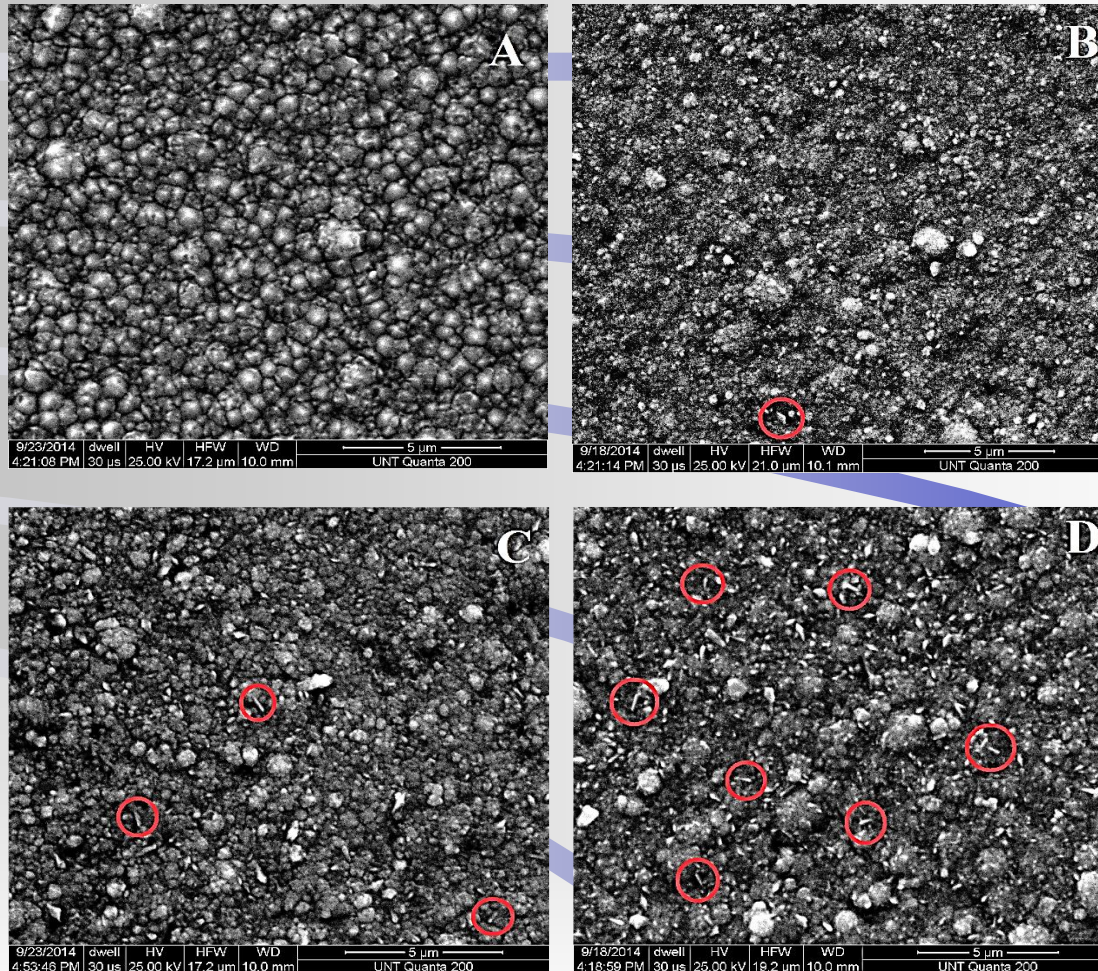
Can use:

Special cells

Modified electrolytes

Charges on non-electroactive species

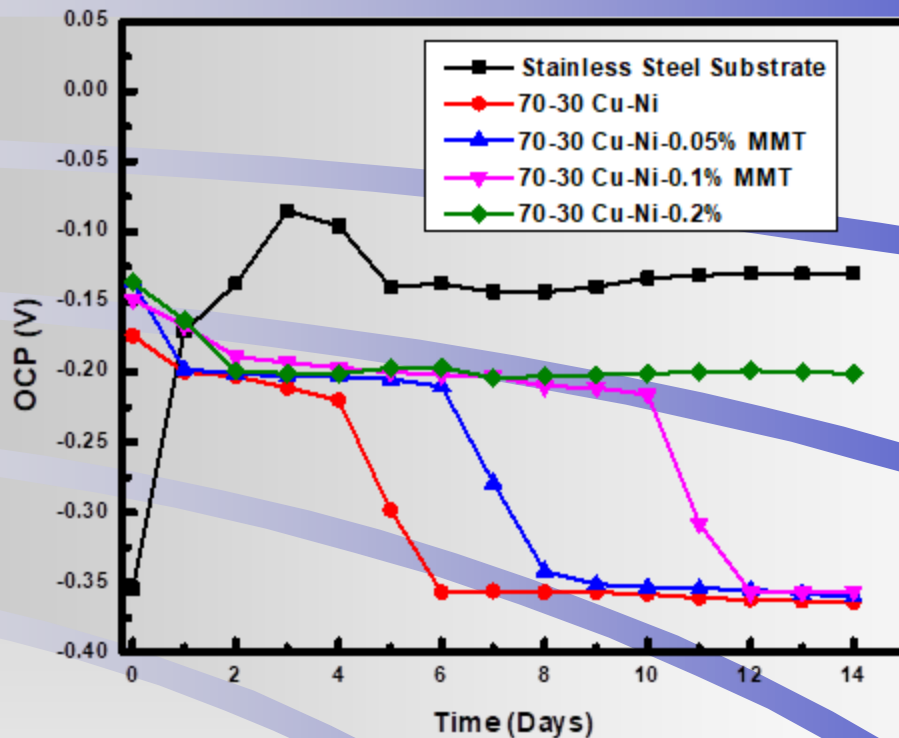
Electrodeposition and Electroplating Nanocomposites



SEM micrographs of: A) 70-30 Cu-Ni, B) 70-30 Cu-Ni-0.05 % MMT, C) 70-30 Cu-Ni-0.1 % MMT, and D) 70-30 Cu-Ni-0.2 % MMT. Red circles indicate MMT platelets

Electrodeposition and Electroplating

Nanocomposites

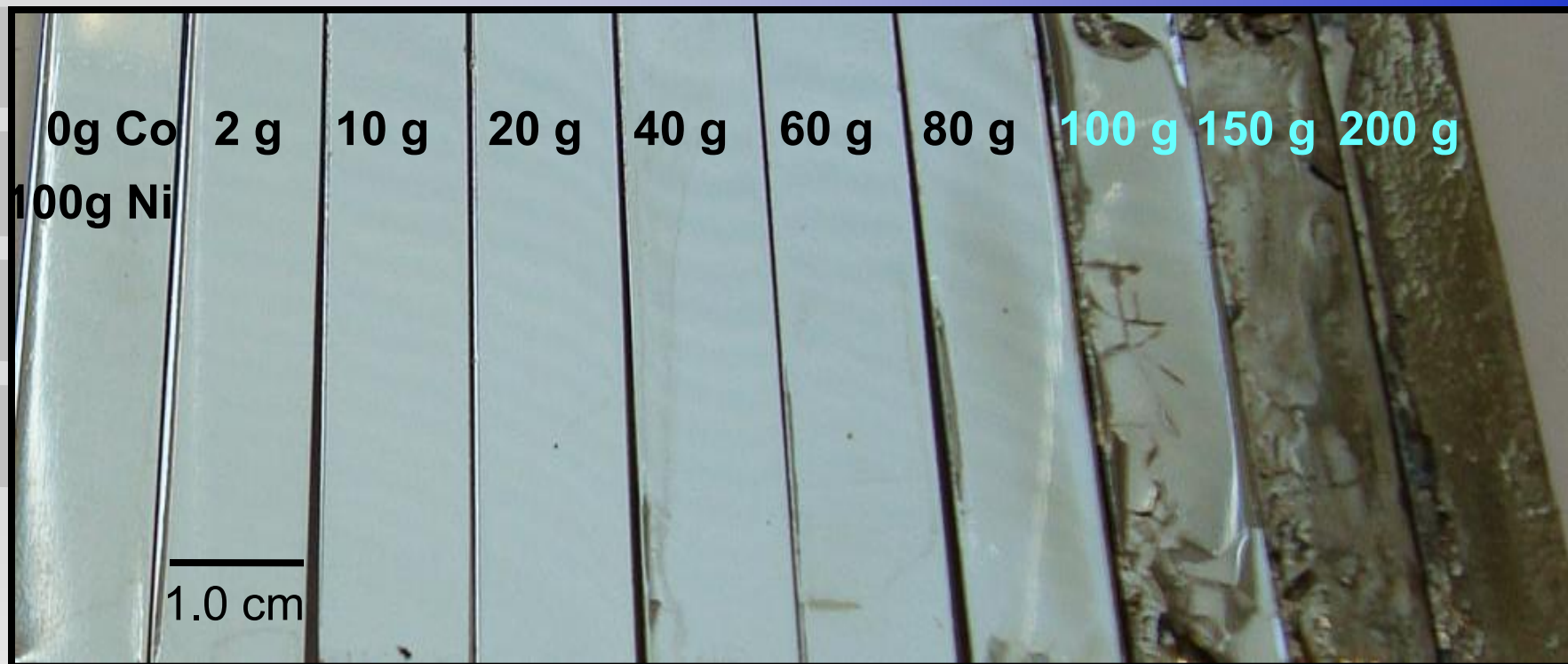


Plot of the immersion test for the 70-30 Cu-Ni coatings with and without MMT measured by OCP vs. time for 2 weeks in a 3.5% NaCl solution

Electrodeposition and Electroplating

Electrocatalysts for H_2O electrolysis

Nanocrystalline and amorphous Ni-Co alloys



→ Co content in alloyed electrocatalyst increases

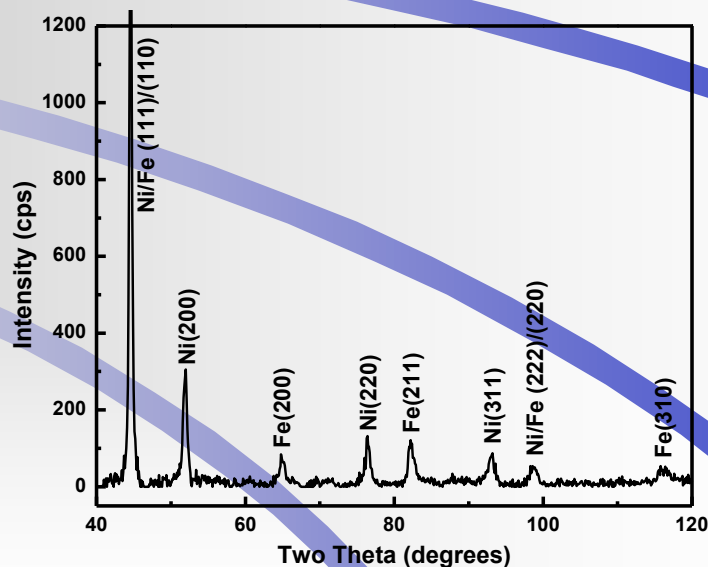
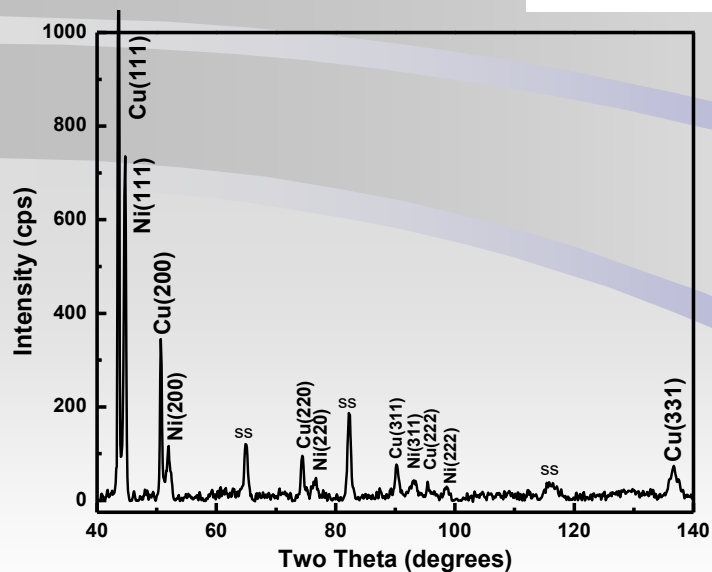
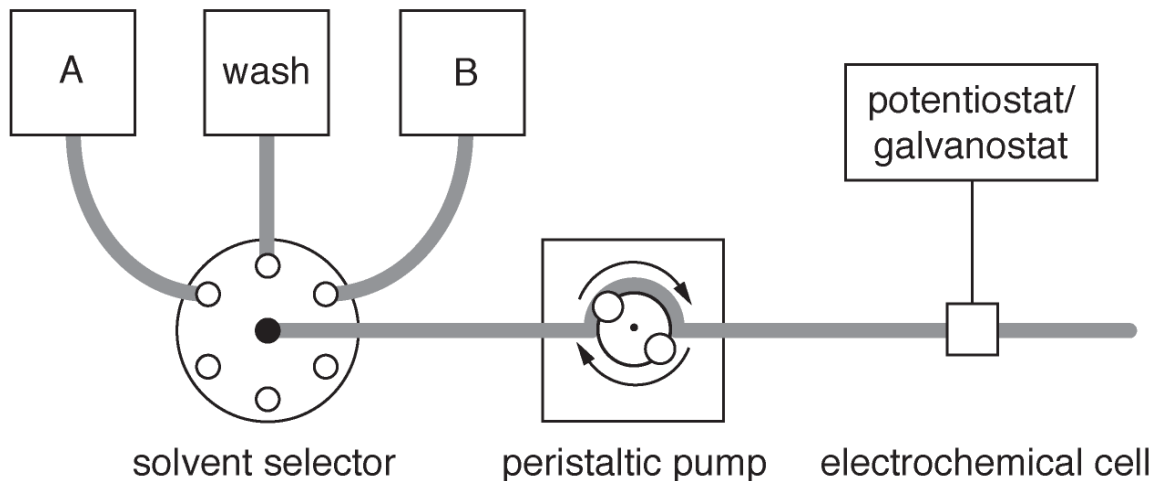
→ More effective electrocatalyst to evolution oxygen

Electrodeposition and Electroplating

Alloys

Multilayers

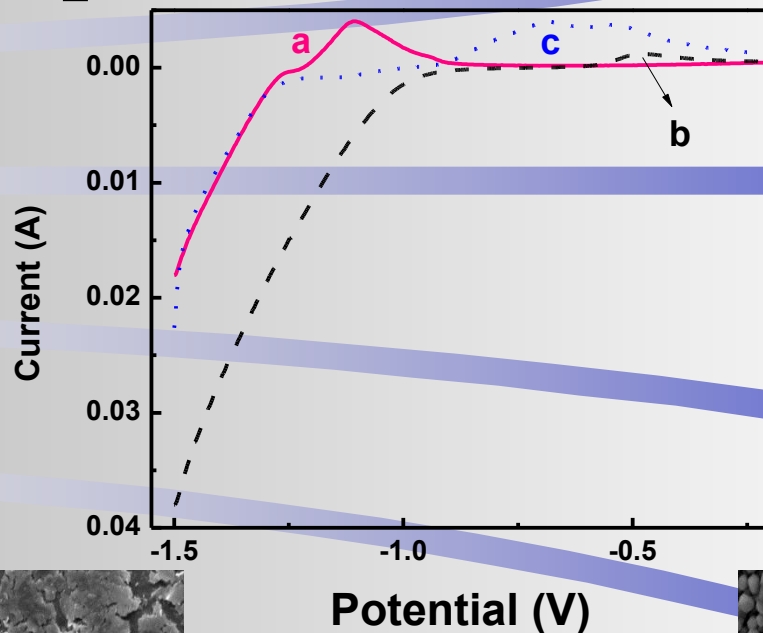
solution reservoirs purged with gas



Electrodeposition and Electroplating

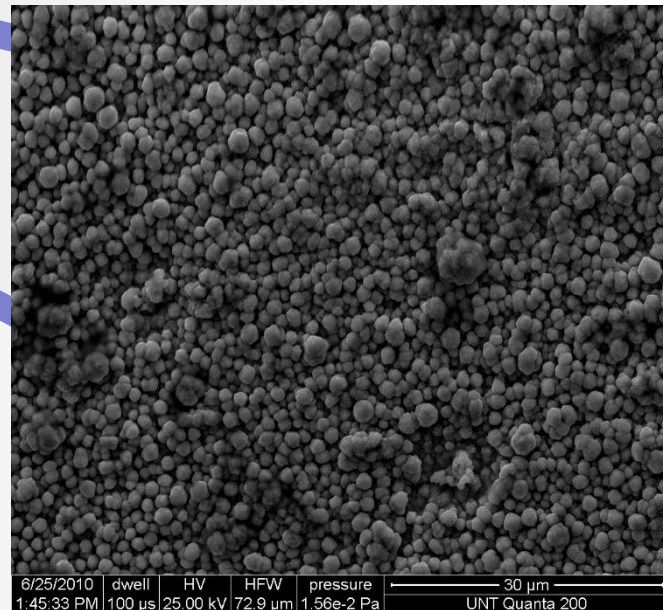
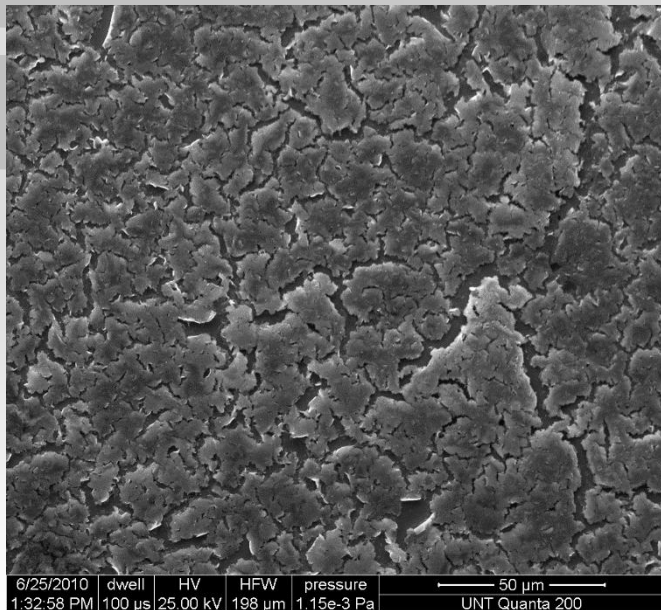
Alloys

Zn-Ni



← Low η

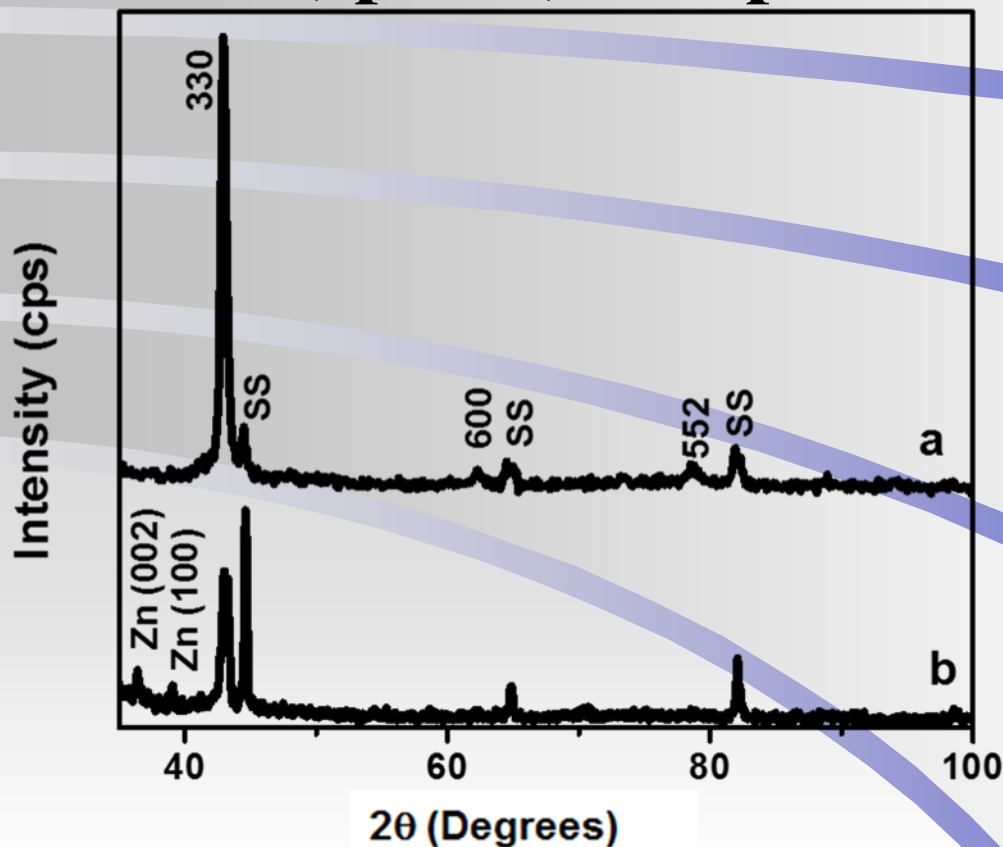
High η →



Electrodeposition and Electroplating

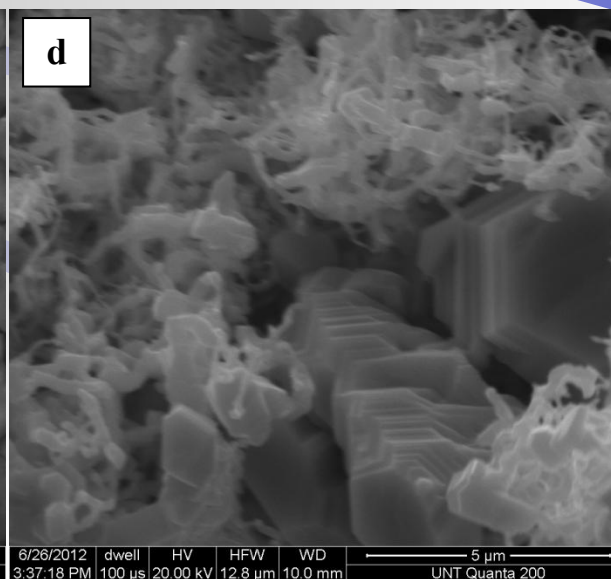
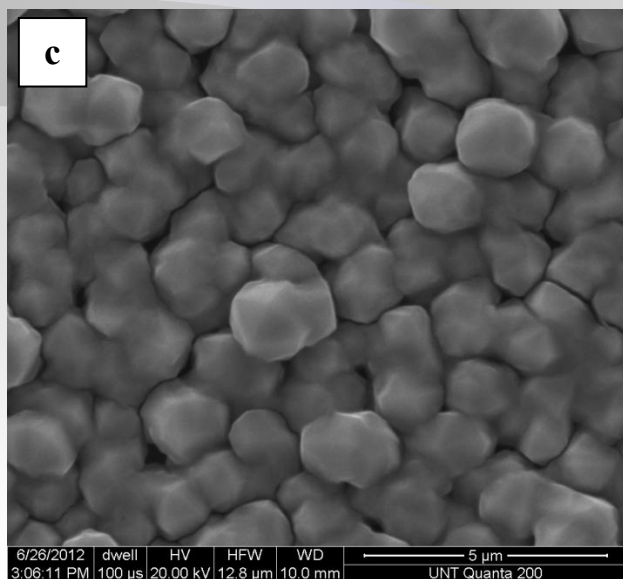
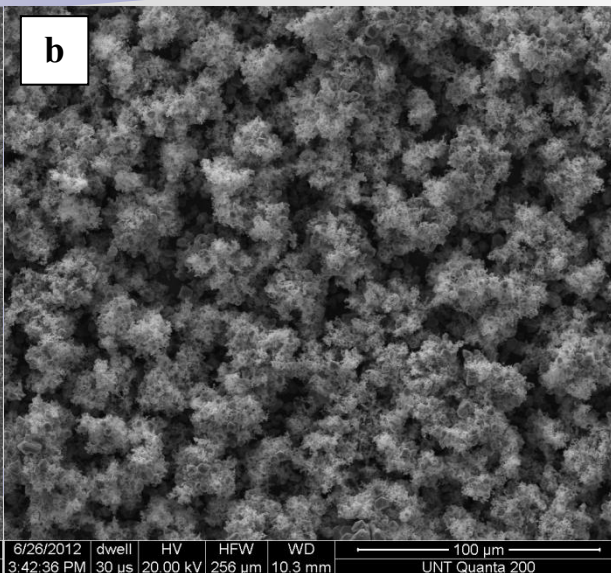
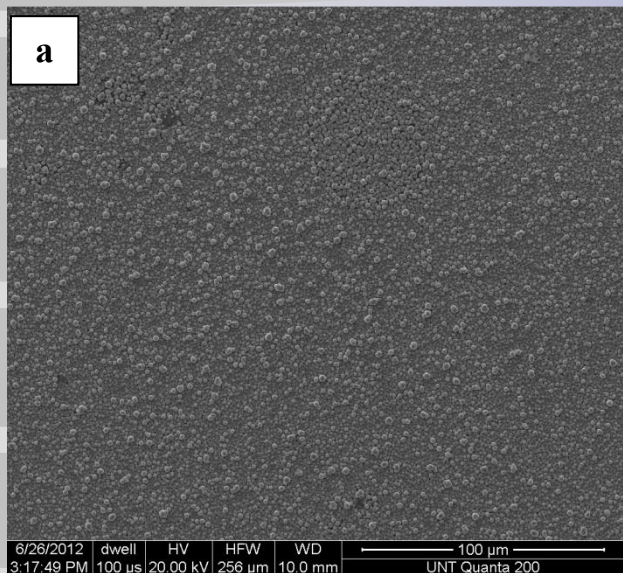
Metal Alloys

Anion, pulse, and pH Effect



XRD pattern of γ - phase zinc-nickel alloy deposited from 100mM borate solution onto stainless steel. (a) Coating obtained under modified pulse potential method; (b) coating obtained under direct potential method

Electrodeposition and Electroplating



(a,c) - 2:1
 $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$:
 $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
ratio deposit, pulse
potential deposition
method and (b,d) -
2:1 $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$:
 $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
ratio deposit, direct
potential deposition
method

Electrodeposition and Electroplating

Electrodeposition of polymers

Polymers can be difficult since most are not electroactive. So have several choices:

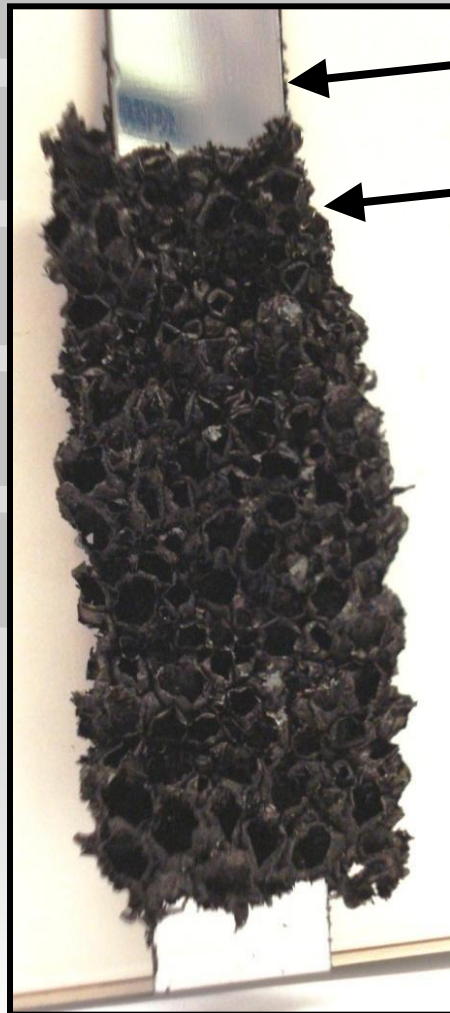
drop-casting or sol-gel

electrochemical

co-deposition

Electrodeposition and Electroplating

Electrodeposition of polypyrrole



Stainless steel substrate

Polypyrrole

1.0 cm



1.0 cm

CHEM 5390

Electrodeposition and Electroplating

Electrodeposition of polymers

Drop-casting or sol-gel easy but can suffer.

Eastman-AQ Polymer on electrode

Poly(ester sulfonic acid) cation exchanger

Electrodeposition and Electroplating

Electrodeposition of polymers

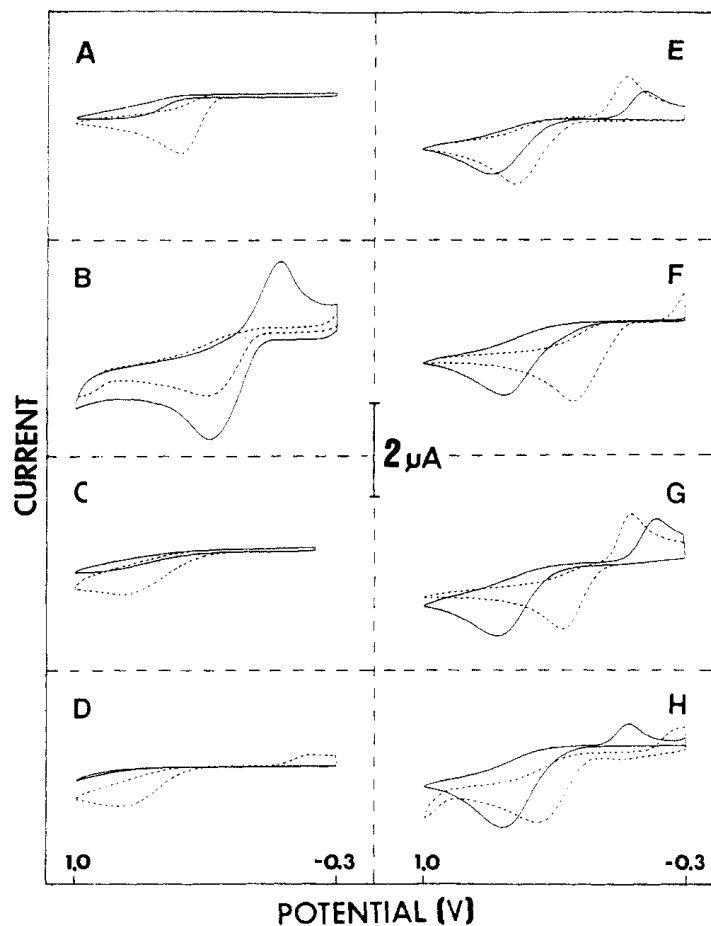


Figure 1. Cyclic voltammograms for 1×10^{-3} M uric acid (A), dopamine (B), ascorbic acid (C), DOPAC (D), catechol (E), epinephrine (F), 4-methylcatechol (G), and norepinephrine (H) at bare and coated glassy carbon electrodes (dotted and solid lines, respectively). Conditions:

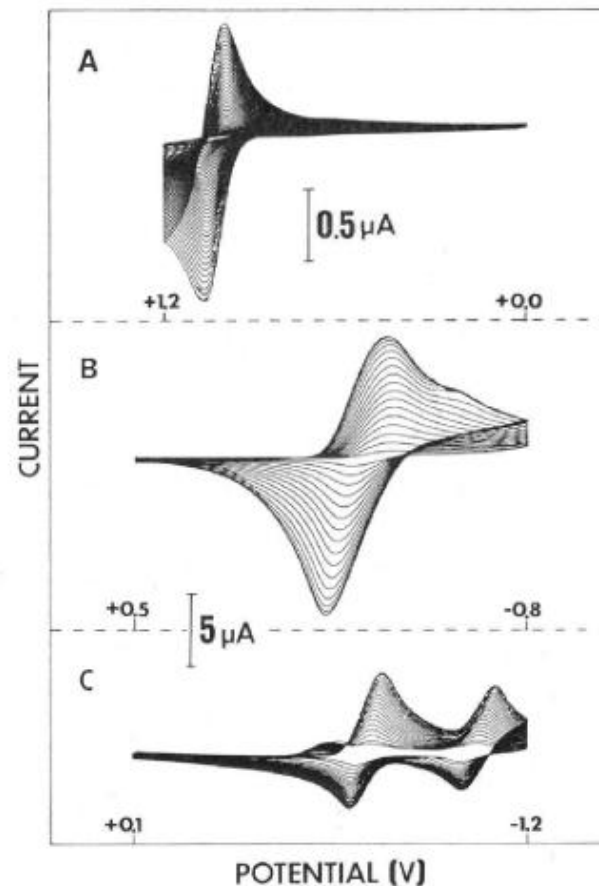


Figure 3. Cyclic voltammograms for 1×10^{-4} M $\text{Ru}(\text{bpy})_3^{2+}$ (A), $\text{Ru}(\text{NH}_3)_6^{3+}$ (B), and MV^{2+} (C) recorded continuously at a glassy carbon electrode coated with Eastman-AQ film. Scan rate is 20 mV/s; other conditions are as in Figure 1.

Electrodeposition and Electroplating

Electrodeposition of polymers

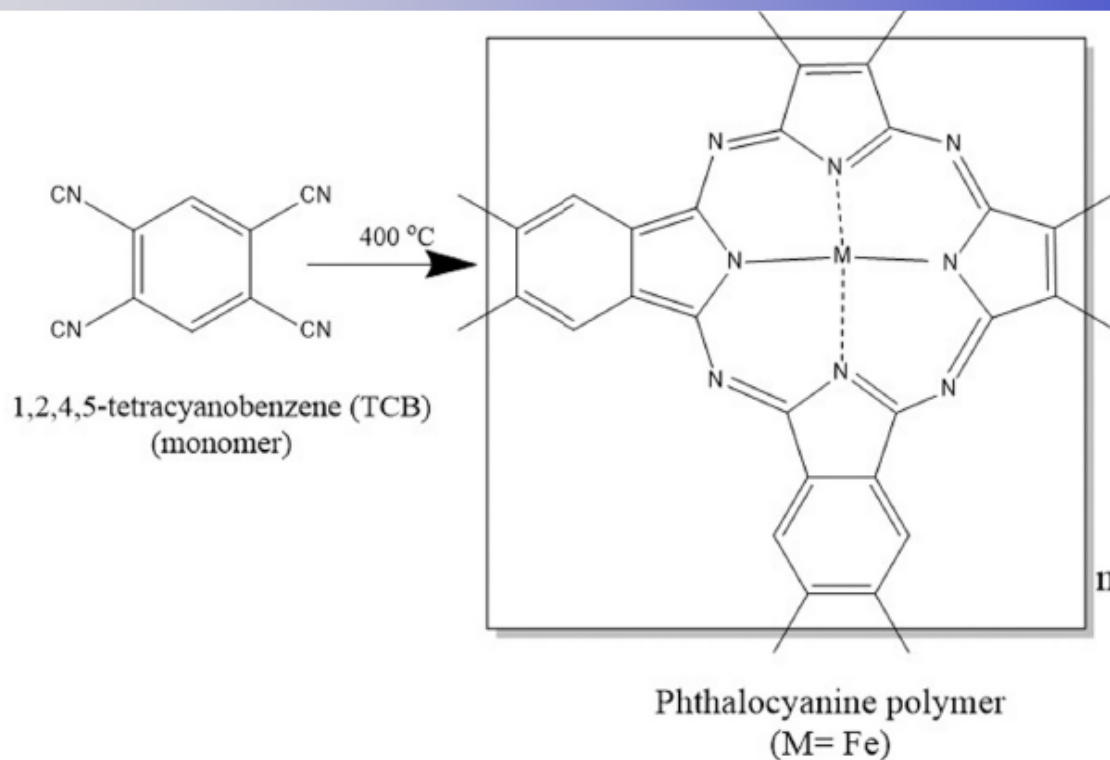


Fig. 1. Formation of polyphthalocyanine polymer film from heating at 400 °C for 30 min 1,2,4,5-tetracyanobenzene (TCB) on the metal surface. Metal center bond is iron.

Drop cast then heat to polymerize

Electrodeposition and Electroplating

Electrodeposition of polymers

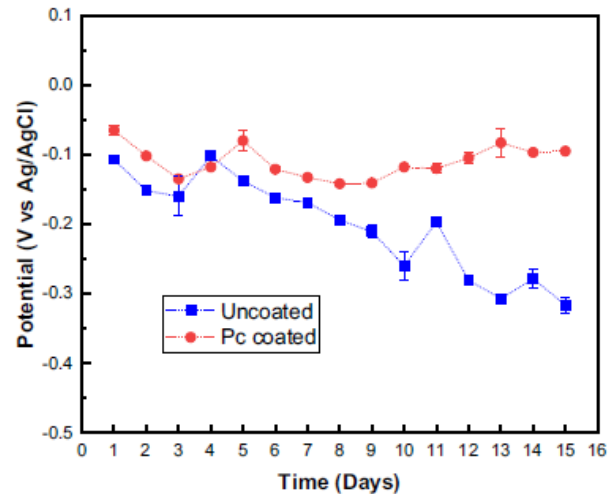
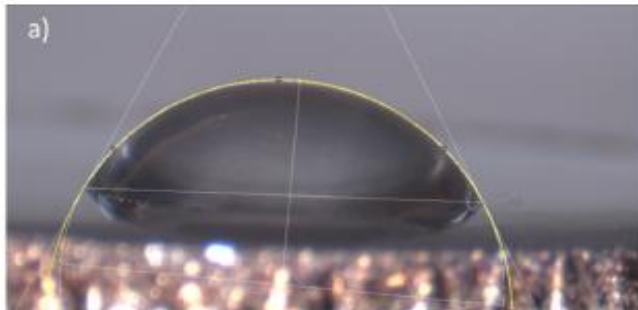
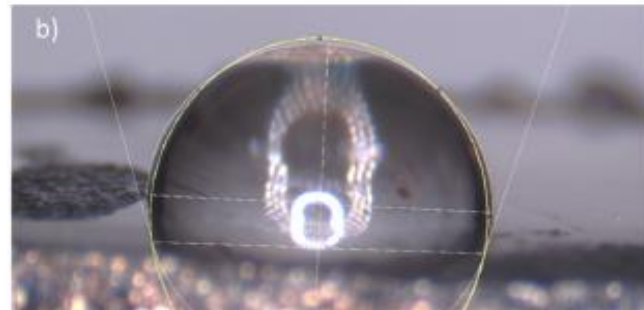


Fig. 8. Open circuit potential (OCP) versus time in 3.5 wt% NaCl solution of the uncoated (blue squares) and Pc coated (red circles) AM samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Contact angle for uncoated polished sample = $51 \pm 1^\circ$

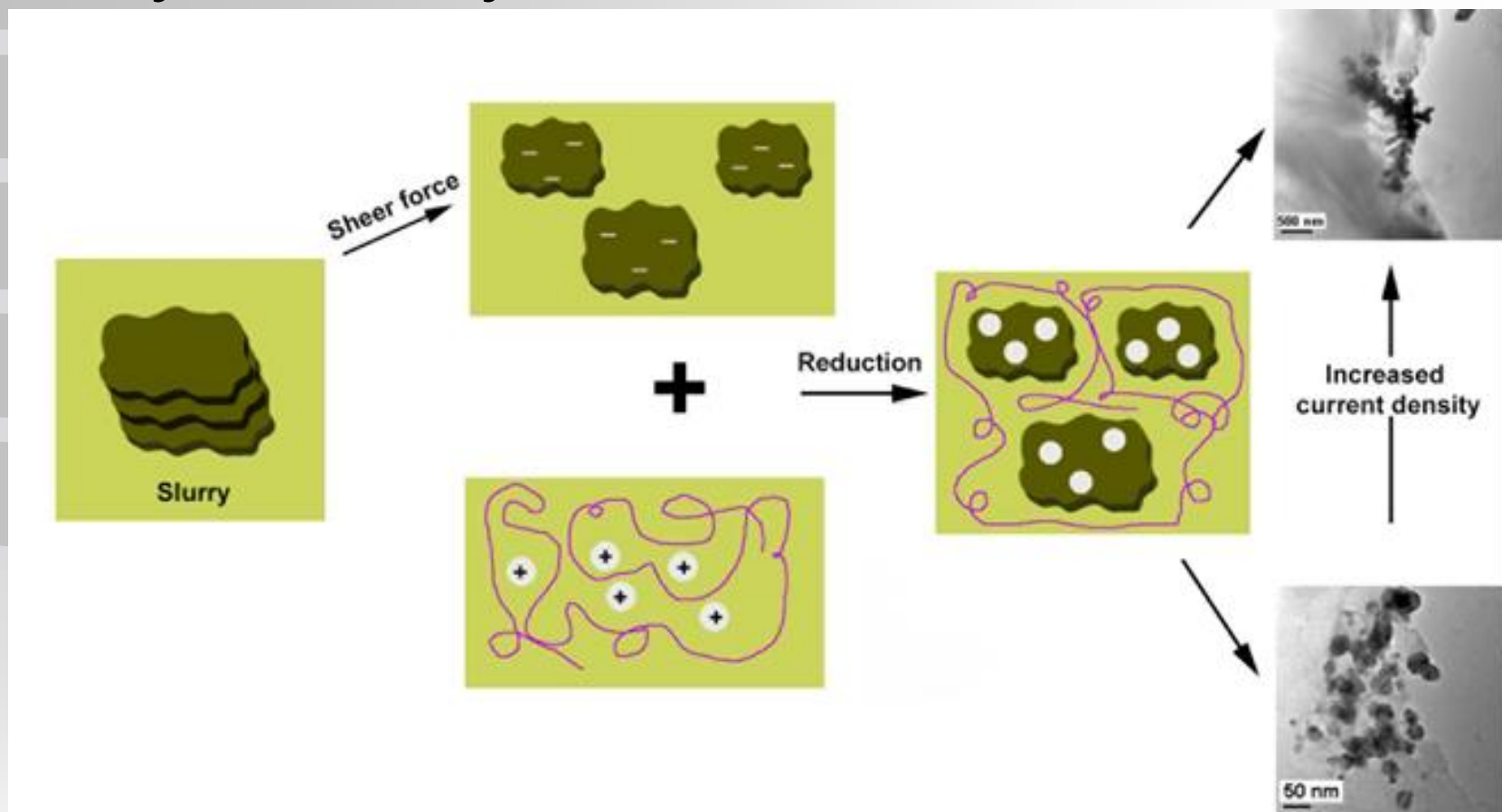


Contact angle for Pc coated sample = $120 \pm 1^\circ$

Fig. 7. Contact angle for (a) uncoated AM metal surface and contact angle (b) for Pc coated AM metal sample.

Electrodeposition and Electroplating

Polymer, Clay, Metal

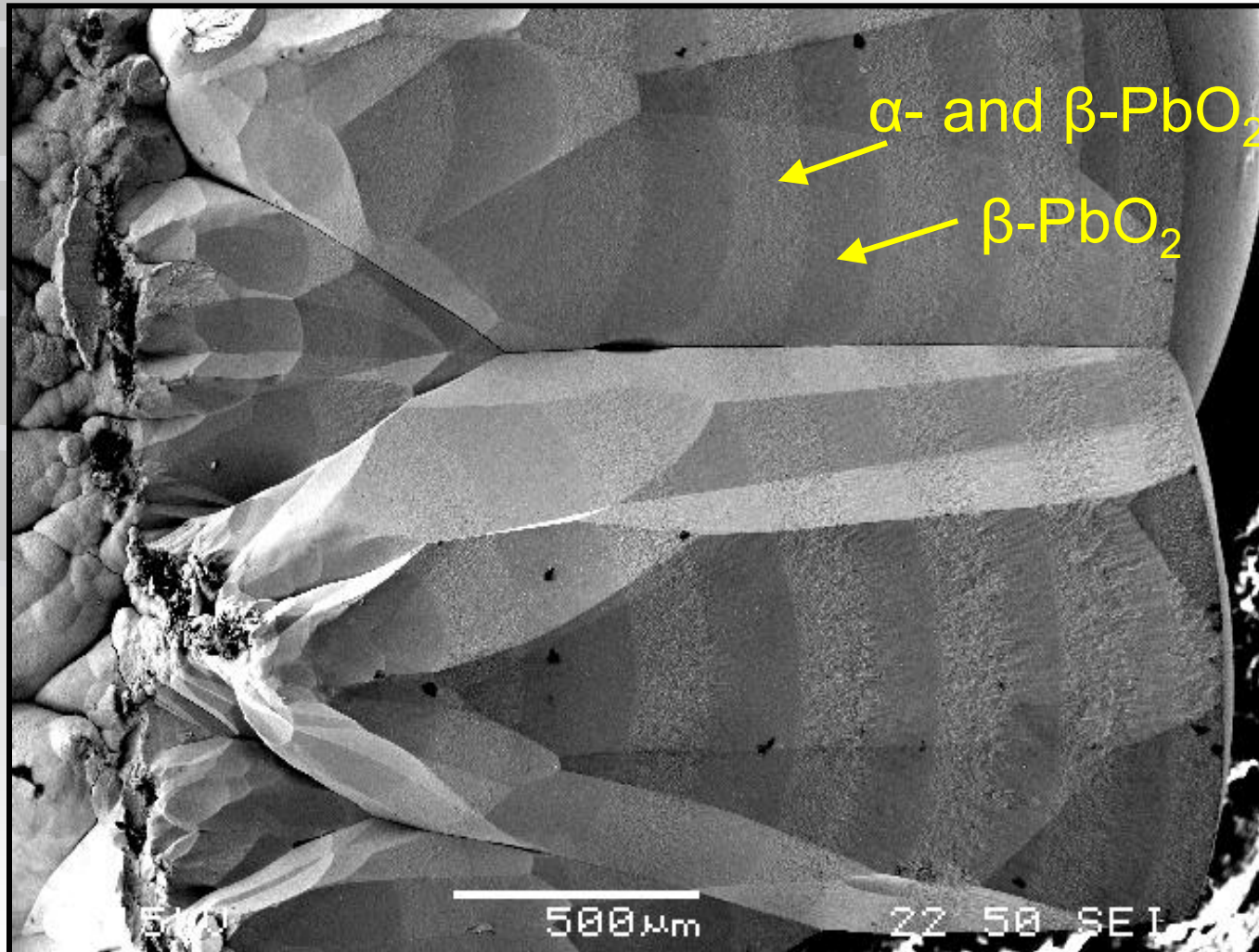


Schematic showing the overall electrochemical synthesis pathway to prepare Ag nanoparticles (white circles) stabilized jointly by the colloids of PVP (red strings) and exfoliated Na-MMT clay platelets (brown) in aqueous solution.

Yuan, Golden, 2020

Electrodeposition and Electroplating

Multilayered α - and β - PbO_2



Electrodeposition and Electroplating

Metal oxides also can be difficult:

Competing with the metal and various oxidation states of the metal oxide.

For example: Cu and CuO and CuO₂

All have very different properties.

Electrodeposition and Electroplating

Metal oxides also can be difficult:

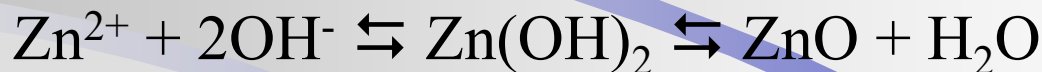
There are different electrochemical pathways to approach electrodeposition of metal oxides.

Deposition methods

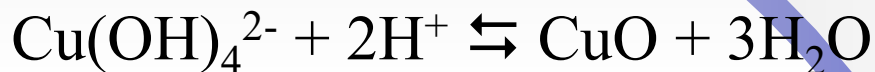
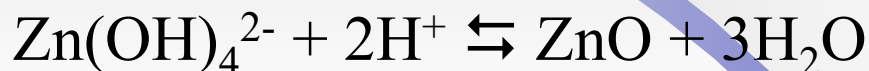
I. Redox Change



II. Base Generation: $2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$



III. Acid Generation: $2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$



Electrodeposition and Electroplating

CuO₂ coatings

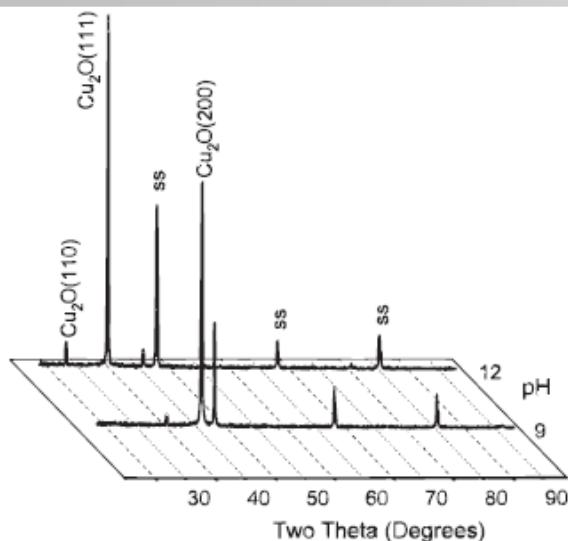


Figure 7. X-ray diffraction patterns of Cu₂O deposited from solutions of pH 9 and 12. The bath temperature is 65 °C and the applied current density is 0.8 mA/cm².

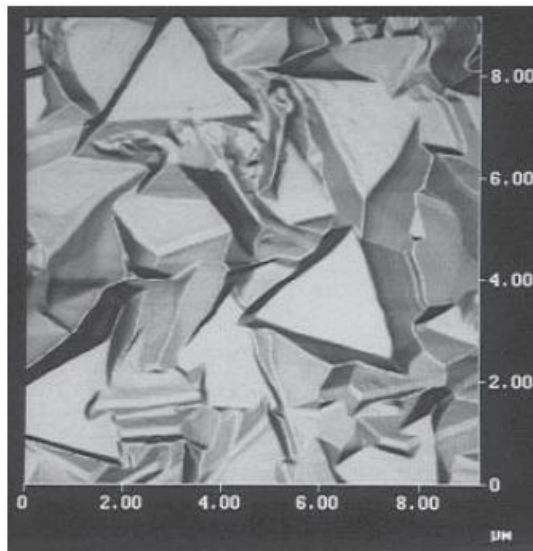


Figure 9. Top-view AFM image of a Cu₂O film deposited at pH 12, $E = -0.45$ V and 65 °C. AFM; z range = 4.2 μm, scan rate = 0.75 Hz.

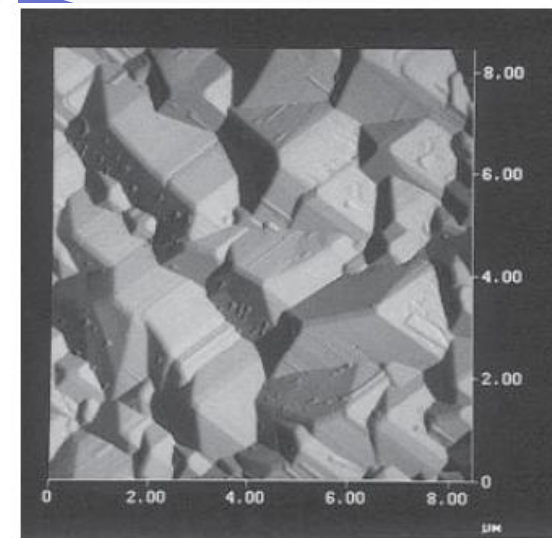


Figure 8. Top-view AFM image of a Cu₂O film deposited at pH 9, $E = -0.45$ V and 65 °C. AFM; z range = 2.5 μm, scan rate = 0.75 Hz.

Electrodeposition and Electroplating

Superlattices Pb-Tl-O

Oriented multilayers typically grown epitaxially

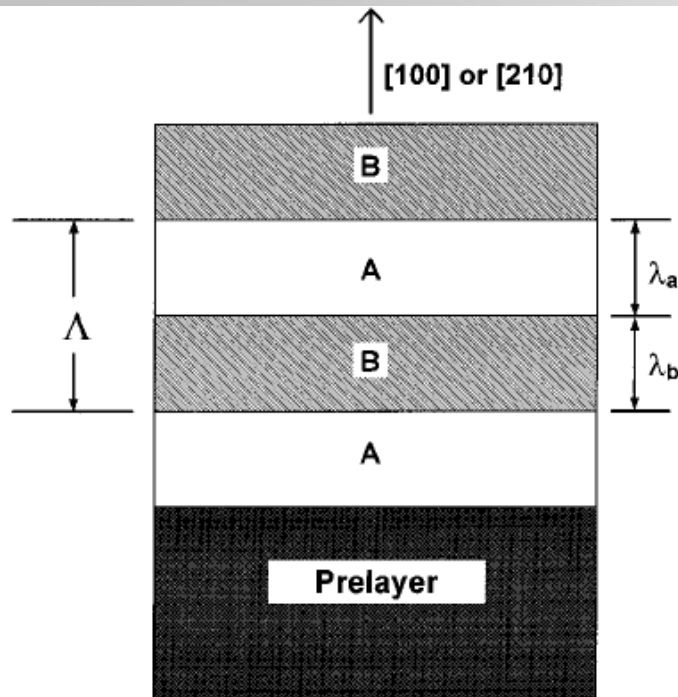


Figure 8. Idealized superlattice grown on an oriented prelayer. The orientation of the prelayer is maintained through the superlattice. The thickness of layer a is λ_a , and the thickness of layer b is λ_b .

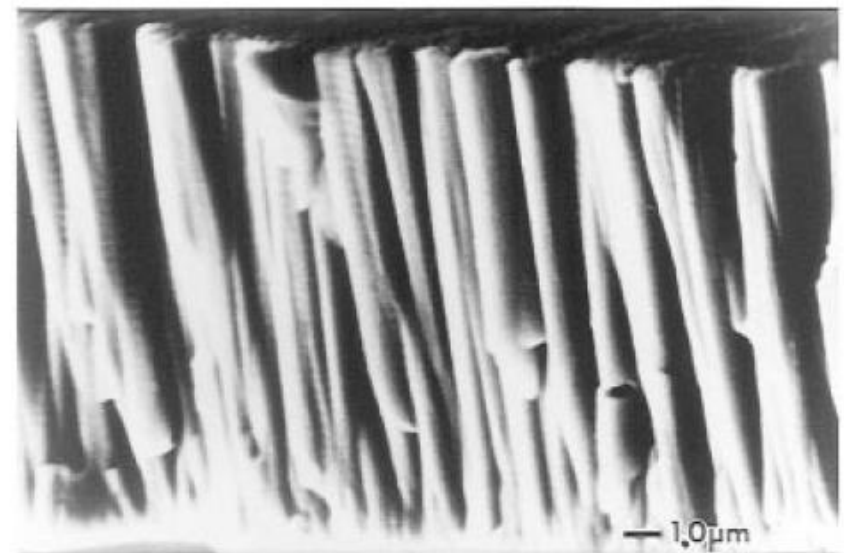
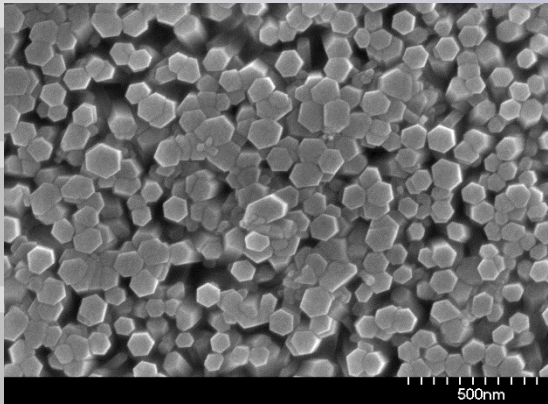


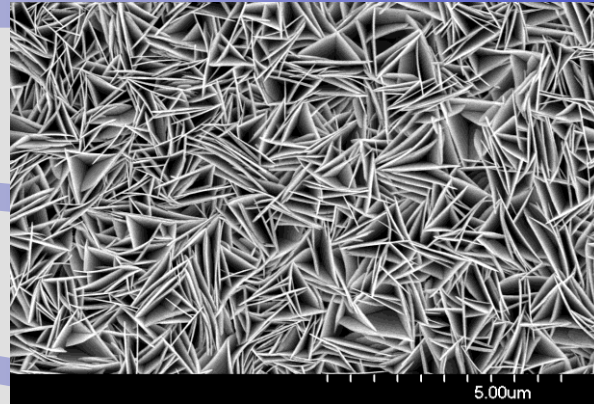
Figure 9. Scanning electron micrograph of an electrodeposited columnar superlattice structure. The individual layer thicknesses are approximately $0.5 \mu\text{m}$. The bar marker is $1.0 \mu\text{m}$.

Electrodeposition and Electroplating

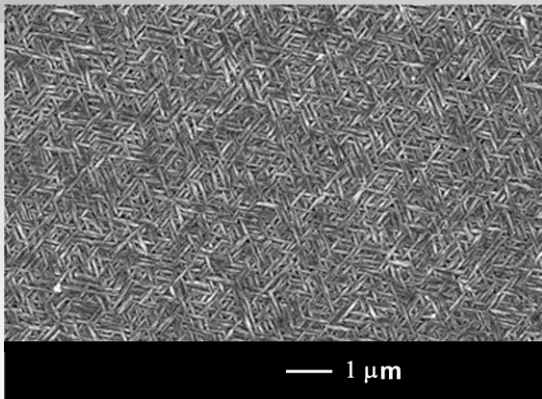
Electrodeposited Epitaxial Oxide Films



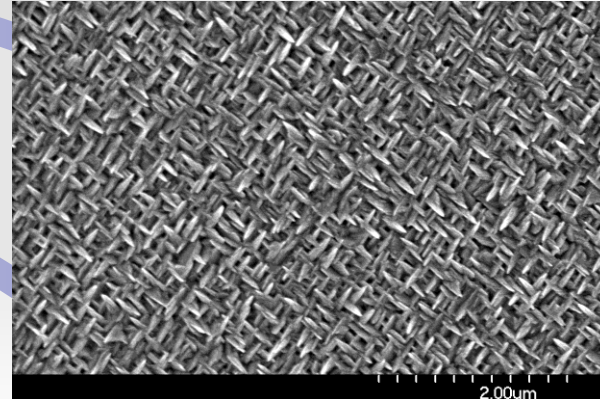
ZnO on Au(110)



AgO on Au(111)



Cu₂O on InP(111)



CuO on Au(100)

Electrodeposition and Electroplating

Metal oxides

Example: Cu/Cu₂O – even light can affect electrodeposition – How can that be?

Layered nanostructures such as superlattices and multilayers can be electrodeposited by pulsing the applied potential or current during growth. In the present work, the electrode potential spontaneously oscillates when a fixed current density is applied. Cuprous oxide is more resistive than Cu. The films are deposited at 30 °C in a stirred solution of 0.6 M CuSO₄ and 3.0 M lactate ion. Oscillations are observed if the pH is in the 8.5-10 range. In a stirred solution, the oscillations can persist for several days.

Electrodeposition and Electroplating

Metal oxides

Example: Cu/Cu₂O

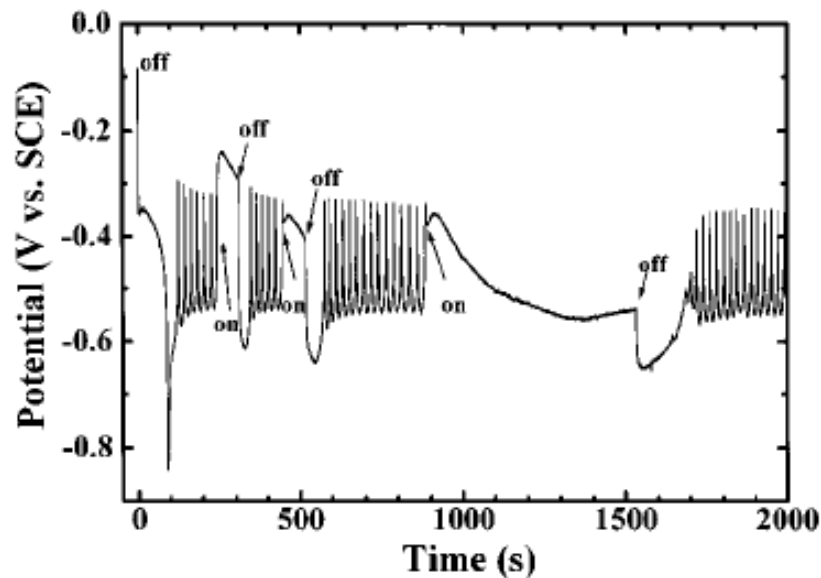
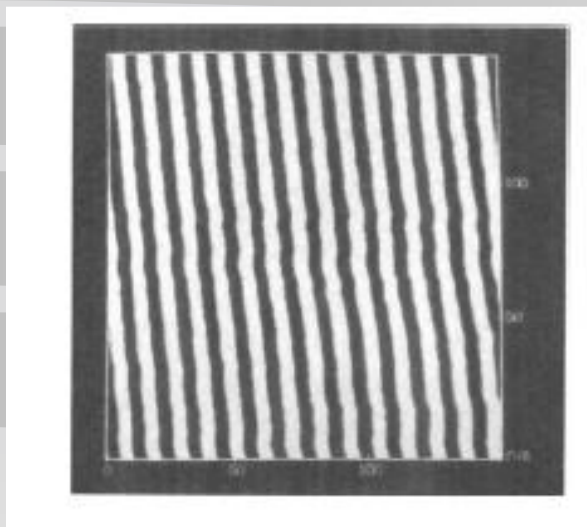


Figure 2. The effect of light on the potential oscillations for a film deposited at pH 9.0 and a current density of 0.2 mA/cm².

EQCM showed that Cu₂O was deposited during the positive-going spikes in potential, while Cu was deposited during the more negative swings in potential.

Electrodeposition and Electroplating

Metal oxides

Typically by cathodic base generation.

Direct method by anodic deposition.

Pathway?

CeO_2

PrO_2

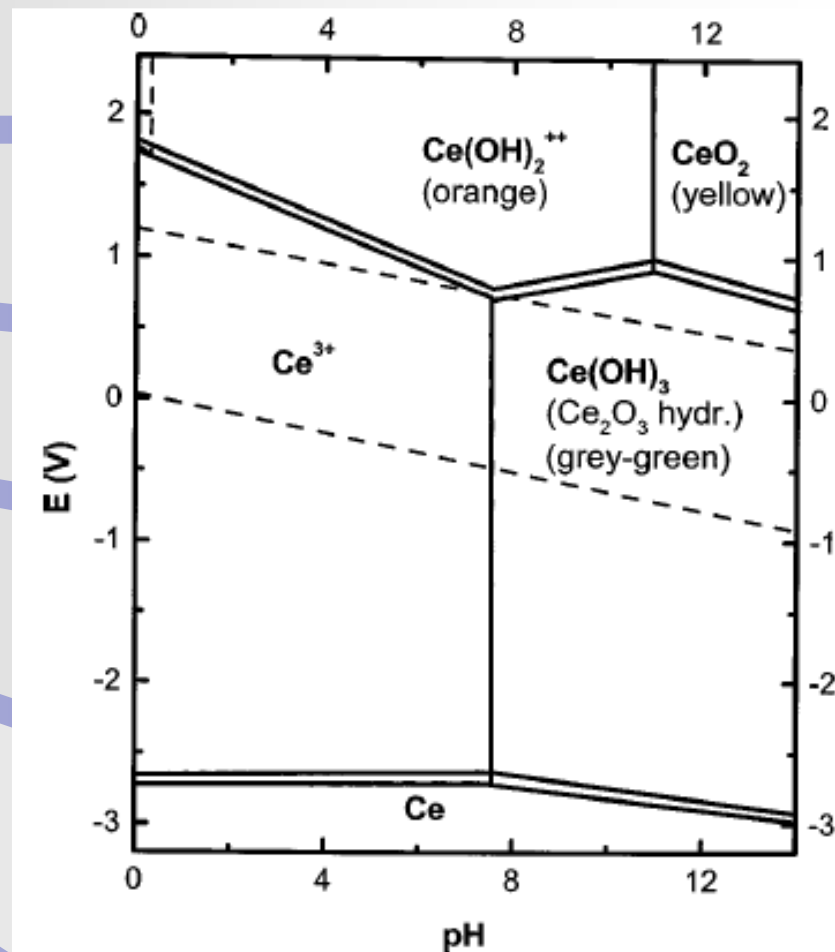


Figure 1. Simplified Pourbaix diagram of cerium species.

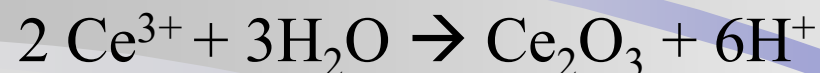
Electrodeposition and Electroplating

Metal oxides

pH<7



pH>7



Only get precipitates – however if can stabilize Ce^{3+}

Electrodeposition and Electroplating

Metal oxides

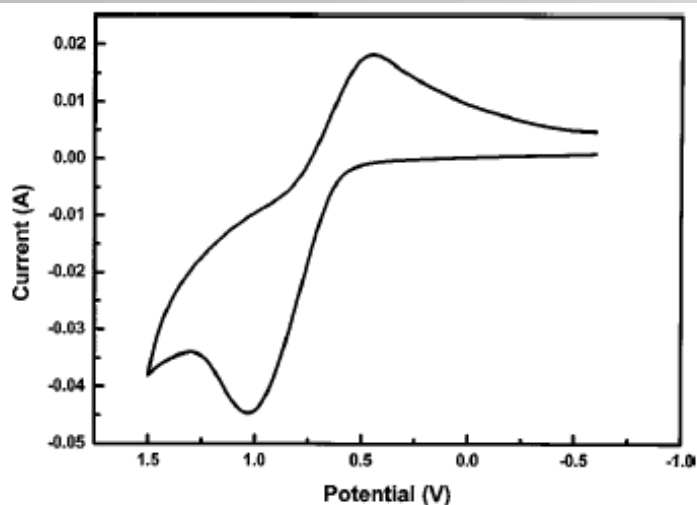


Figure 2. CV of cerium-EDTA complex in 0.1 M $\text{Ce}(\text{NO}_3)_3$ and 0.1 M EDTA, pH 8.0, $T = 25^\circ\text{C}$, and scan rate 50 mV/s.

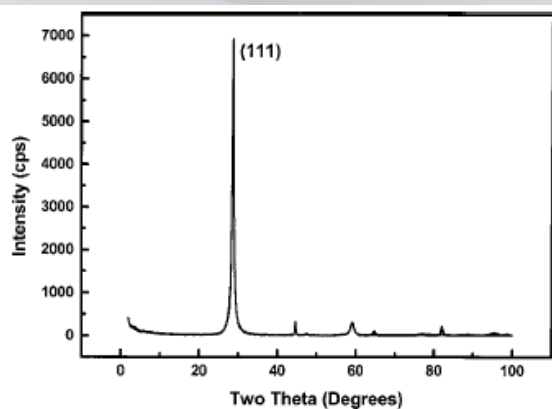


Figure 5. XRD of CeO_2 film deposited on stainless steel substrate from 0.1 M $\text{Ce}(\text{NO}_3)_3$ and 0.1 M acetic acid solution, pH 8.0, $T = 25^\circ\text{C}$.

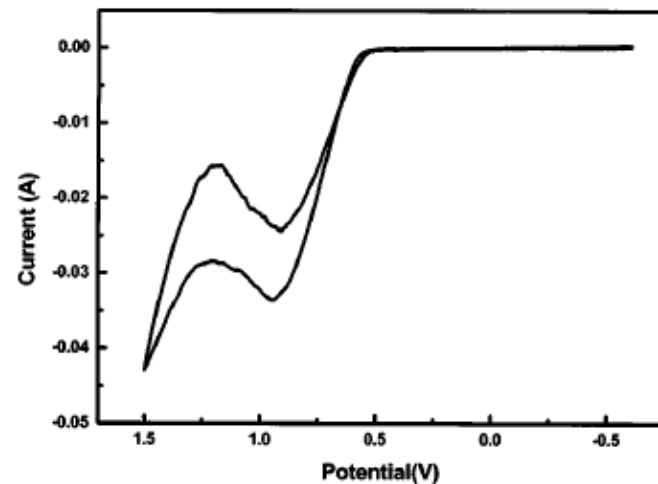


Figure 3. CV of cerium-acetic acid complex in 0.1 M $\text{Ce}(\text{NO}_3)_3$ and 0.1 M acetic acid, pH 12.0, $T = 25^\circ\text{C}$, and scan rate 50 mV/s.

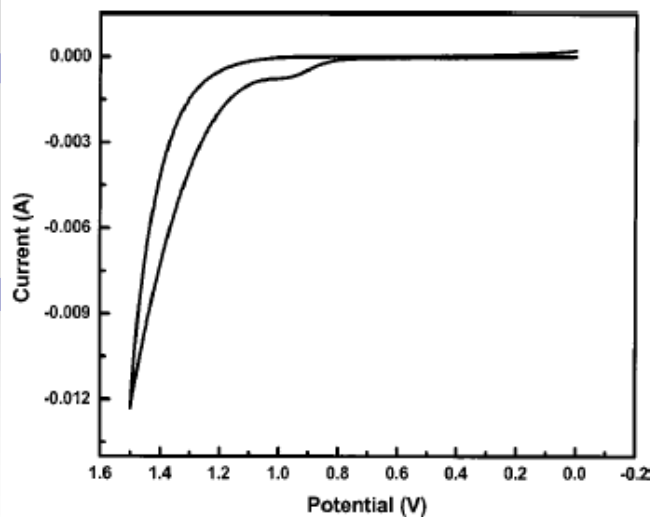


Figure 4. CV of cerium-acetic acid complex in 0.1 M $\text{Ce}(\text{NO}_3)_3$ and 0.1 M acetic acid, pH 8.0, $T = 25^\circ\text{C}$, and scan rate 50 mV/s.

Electrodeposition and Electroplating

Metal oxides

PrO₂

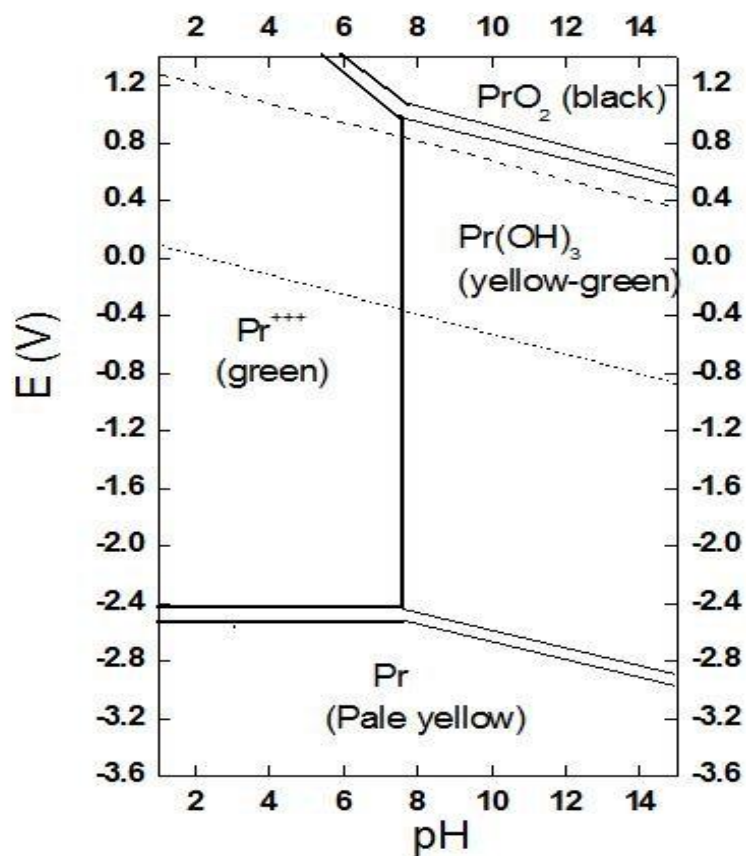


Table 3. Peak list of Pr 3d and calculation of Pr valence.

Peak #	Praseodymium contribution	Peak position (eV)	Area	% Area
m ₁	Pr(III)	927.408	171980	9.7440
m ₂	Pr(IV)	928.837	207250	11.74221
s ₂	Pr(IV)	932.384	423730	24.0079
s ₁	Pr(III)	934.128	261960	14.8424
m ₁ '	Pr(III)	947.820	132190	7.48986
m ₂ '	Pr(IV)	948.956	82829.93	4.69302
s ₂ '	Pr(IV)	953.220	363640	20.6030
s ₁ '	Pr(III)	956.640	121380	6.8773
Total			1764960	100
Pr(III)			687510	38.9537
Pr(IV)/Pr(III)				1.567
X in PrO _x				1.80
(Pr holds mixed valence of Pr ³⁺ and Pr ⁴⁺)				

Electrodeposition and Electroplating

Metal oxides PrO_2

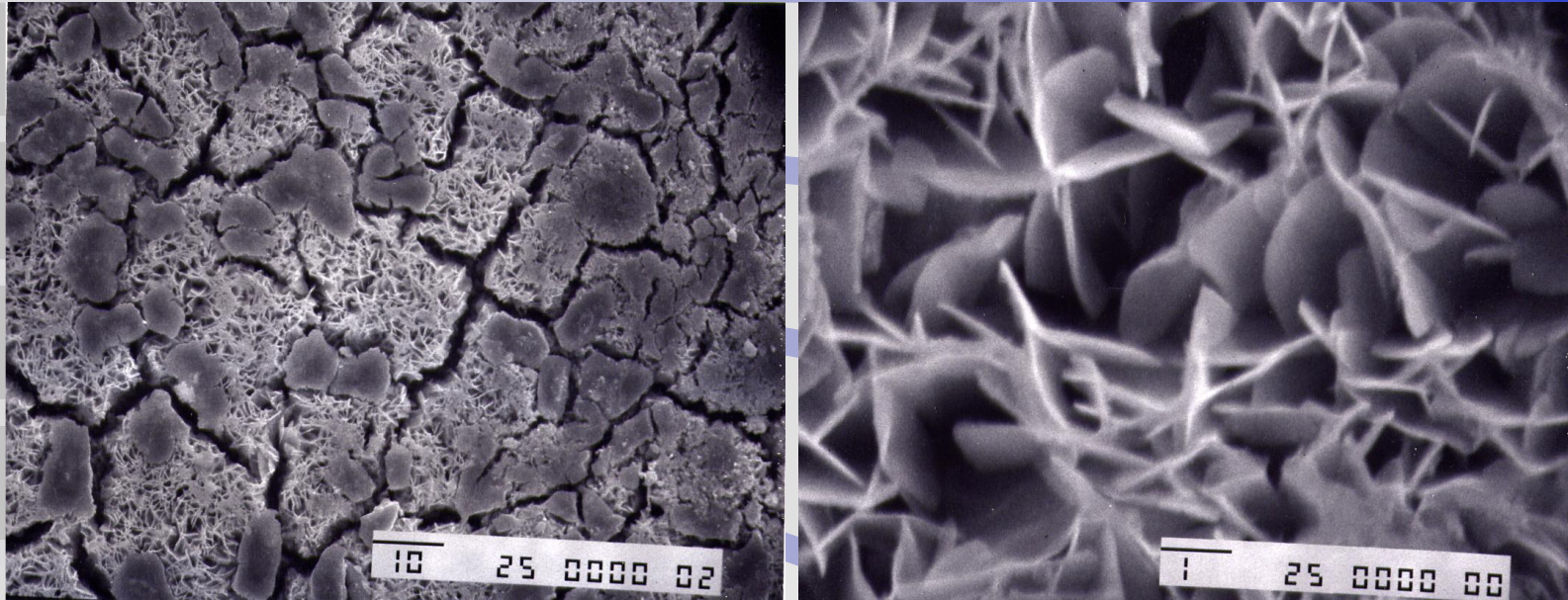
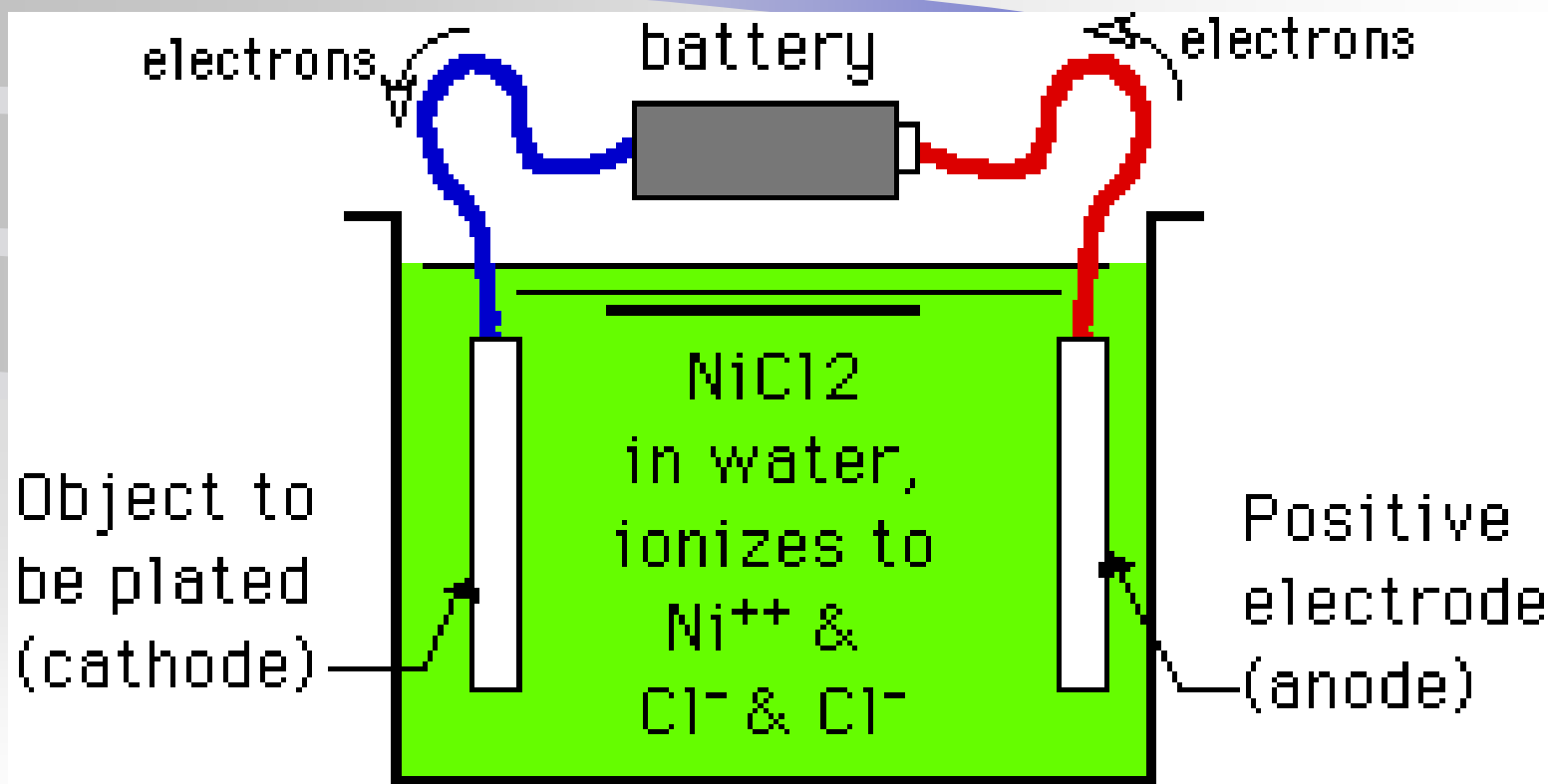


Figure. SEM images of Pr_6O_{11} film obtained by cathodic electrodeposition on stainless steel in an electrolyte system composed of 0.1M $\text{Pr}(\text{NO}_3)_3$ and 0.1M NH_4NO_3 solution, $j = 0.8 \text{ mA/cm}^2$, $T = 25 \text{ }^\circ\text{C}$, and after sintering at $600 \text{ }^\circ\text{C}$ for 1 hour; (left) magnification 1000; (right) magnification 10000.

Electrodeposition and Electroplating

Can be as simple as depositing a metal coating onto a conducting object.



Electrodeposition and Electroplating

Steps:

- read past literature
- study pourbaix diagrams
- pick possible plating solutions
- do solution studies (DLS, viscosity, etc...)
- run electrochemical test (LSV, CV, RDE, etc...)
- determine material properties (XRD, XPS, etc...)

Electrodeposition and Electroplating

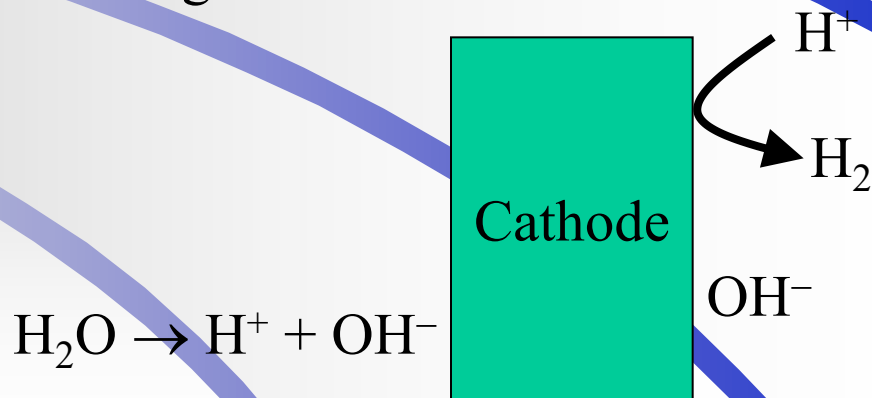
What is in a Bath (the electrolyte)?

Example: Watts Bath

- Ions of the metal to be plated, e.g.
 - **Ni^{2+} (nickel ions) added mostly as the sulphate**
- Conductive electrolyte
 - **NiSO_4 , boric acid, NiCl_2**
- Nickel anode dissolution promoter
 - **NiCl_2 provides chloride ions**
- pH buffer stops cathode getting too alkaline
 - **Boric acid (H_3BO_3)**
- **Additives**
 - **Wetters, levellers, brighteners, stress modifiers..**

Electrodeposition and Electroplating

- pH changes accompany electrode reactions wherever H^+ or OH^- ions are involved.
- In acid, hydrogen evolution occurs on the surface of cathode. This will result in a localised increase in pH near the surface of the electrode.
- In acid, oxygen evolution occurs on the surface of anode. This will result in a drop of pH near the surface of the electrode.
- pH buffer stops the cathode becoming too alkaline.
 - **Boric acid (H_3BO_3)**



Electrodeposition and Electroplating

- Plating (bath) additives

- Leveling agents

The ability of certain molecules to level out uneven topographies during metal electrodeposition. Occurs when less metal is deposited on the micropeaks than in the microvalleys. Levelling agent goes to peaks.

Ex. coumarin or thiourea for Ni; quaternary ammonium compounds for Cu

- Brighteners

Control the nucleation and growth of the deposit. Adjust the deposition layer stress, improve the surface smoothness, affect grain sizes.

Ex. saccharin, bis-3-sulfopropyl-disulfide for Cu; vanillin for Zn

Electrodeposition and Electroplating

- Plating (bath) additives

- Suppressants

Suppress formation of one form over another by affecting mass transport

Ex. Polymers, like polyethylene glycols (PEGs) for Cu; Pb in whisker formation in Sn

- Wetters

Change hydrophobic properties of surfaces, by combination of high surface roughness (micro and nanoscale) and low surface energy materials. Two approaches: 1) produce a high energy surface with high surface roughness and then modify the surface with a low surface energy material or 2) taking a hydrophobic material and creating high surface roughness.

Ex. Kahl and Golden; Zn-Al oxides w/ palmitic acid

Electrodeposition and Electroplating

- Plating (bath) additives

- Stress modifiers

Change the stress within the coating, affects hardness and young's modulus

Ex. P or Sc-CO₂ for Ni, pH, T for CeO₂ powders or Zn-Ni;

Electrodeposition and Electroplating

Current efficiency

Is the ratio between the actual amount of metal deposit, M_a to that calculated theoretically from Faradays Law, M_t .

$$\text{Current efficiency} = \frac{M_a}{M_t} \times 100\%$$

Electrodeposition and Electroplating

Faraday's Law of Electrolysis

Amount of material = amount of electrons or coulombs

$$n = \frac{q}{zF}$$

$$[\text{mol}] = \frac{[\text{C}]}{[\text{C mol}^{-1}]}$$

n = amount of material

q = electrical charge, Q

z = number of electrons

F = Faraday constant

Electrodeposition and Electroplating

Faraday's Law

$$\frac{w}{M} = \frac{It}{zF}$$

n = amount of material

w = mass of material

M = molar mass of material

I = current

t = time

z = number of electrons

F = Faraday constant

Electrodeposition and Electroplating

Current, Current density, Surface area

$$j = \frac{I}{A}$$

j = current density [mA cm^{-2}]

I = current [A]

A = surface area of the electrode [cm^2]

$j_{\text{electroplate}}$ = electroplating current density (metal electroplate)

$j_{\text{corrosion}}$ = corrosion current density (metal corrosion/dissolution)

Electrodeposition and Electroplating

Average thickness

$$w = \frac{M.I.t}{z.F}$$

$$x = \frac{M.I.t}{\rho.A.z.F}$$

w = weight (mass) of metal

M = molar mass of metal

I = current

t = time

z = number of electrons

F = Faraday constant

ρ = density of metal

A = Area

x = thickness of plating

Electrodeposition and Electroplating

Example

Nickel is plated from a Watts bath at a current density of 3 A dm^{-2} .

The current efficiency is 96%.

The molar mass of nickel is 58.71 g mol^{-1} .

The density of nickel is 8.90 g cm^{-3} .

The Faraday constant is $96\,485 \text{ C mol}^{-1}$.

What will be the averaged plating thickness in 1 hour?

Electrodeposition and Electroplating

Example

Assume that the reaction is:



So, two electrons are involved for every Ni atom, and $z = 2$

The current density used in plating nickel is 96% of the total current, i.e., $0.96 \times 3 \text{ A dm}^{-2}$.

Electrodeposition and Electroplating

Example

What will be the averaged plating thickness in 1 hour?

$$x = \frac{M \cdot I \cdot t}{\rho \cdot A \cdot z \cdot F}$$

$$x = \frac{(58.71 \text{ g mol}^{-1})(0.96 \times 3 \text{ A})(3600 \text{ s})}{(8.90 \text{ g cm}^{-3})(100 \text{ cm}^2)(2)(96485 \text{ C mol}^{-1})}$$

$$x = 3.54 \times 10^{-3} \text{ cm} = 35.4 \times 10^{-4} \text{ cm} = 35 \mu\text{m}$$

Class Assignment

- Research paper Due
- Final Dec 9th 8-10 am

