Electrodeposition. Principles and Applications

Victoria A. Nikitina

Center for Energy Science and Technology
Skolkovo Institute of Science and Technology

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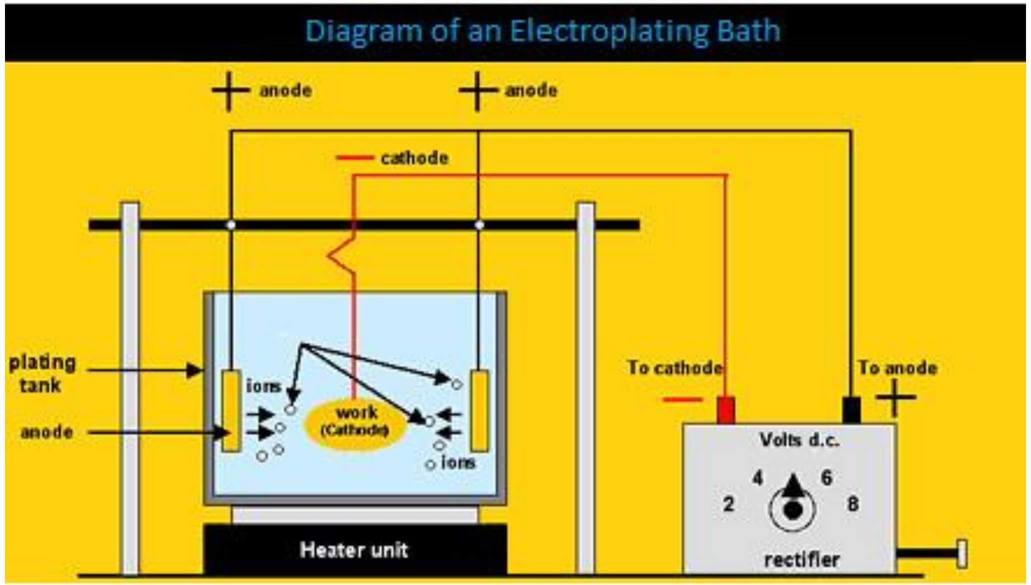
Electrodeposition

- Electroplating is the electrochemical deposition of metal precipitates (coatings) on objects

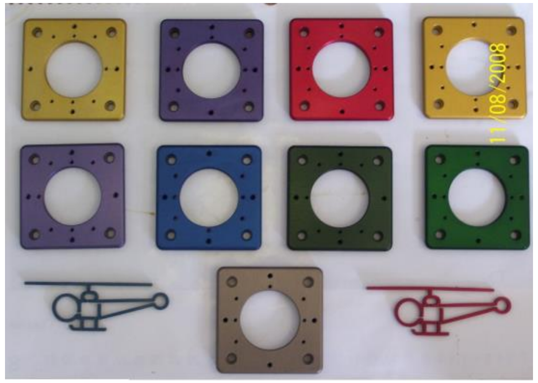


Decorative

Industrial

Protective

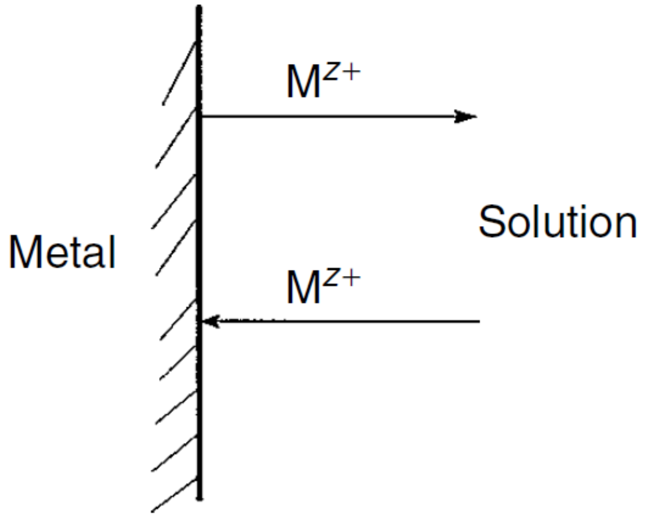
Aluminum anodizing



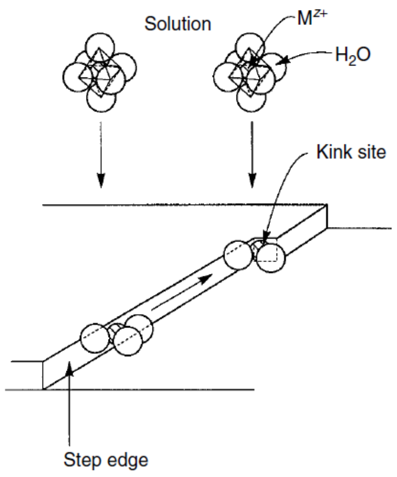
Metallization of plastic

Atomistic aspects

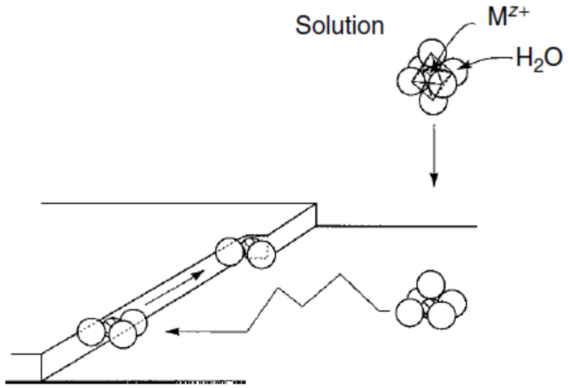
$$M^{z+} + ze \longleftrightarrow M$$



Step edge transfer

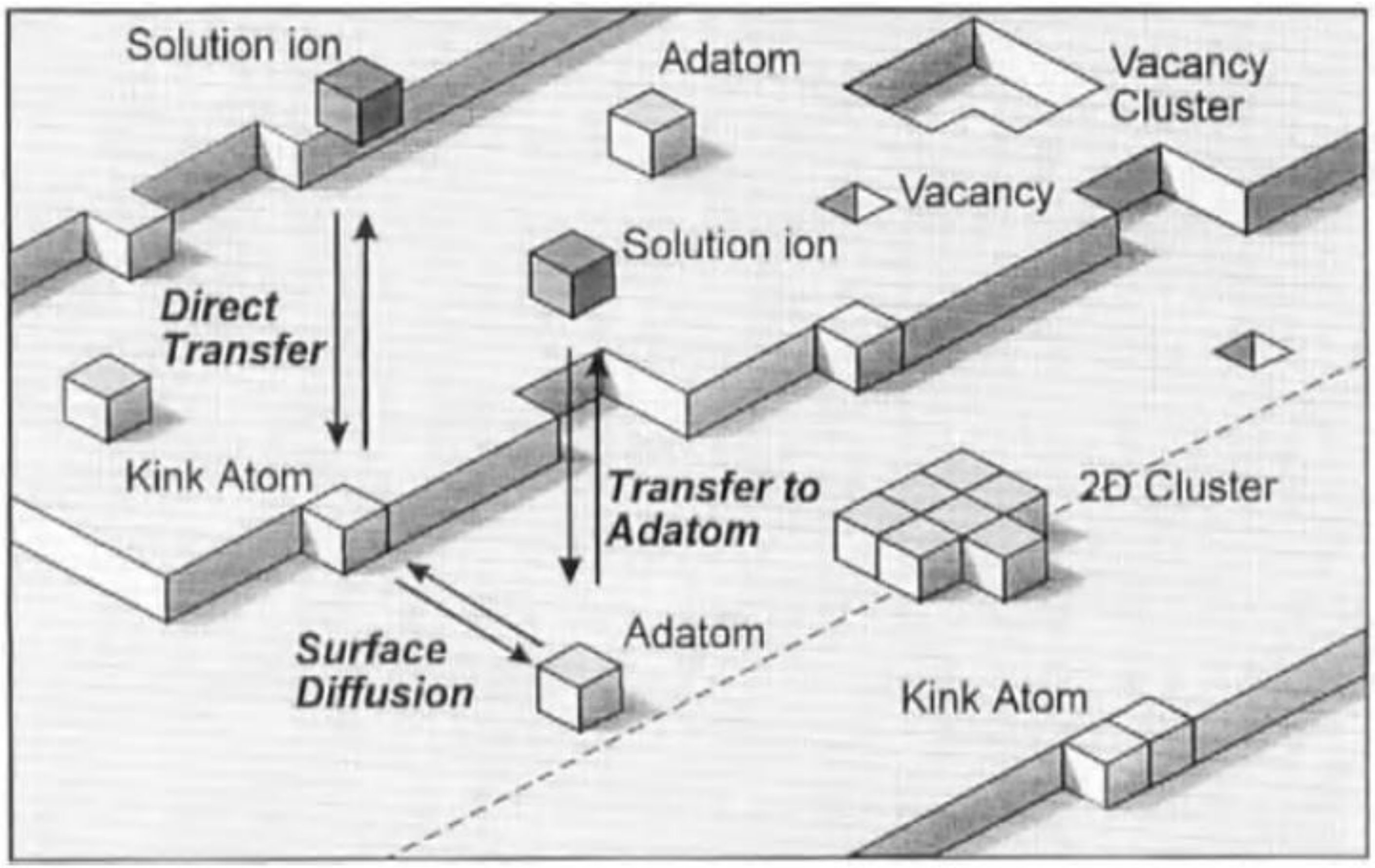


Terrace ion transfer



"Overpotential" deposition

$$[M(H_2O)_x]^{z+}(\text{solution}) \longrightarrow M^{z+}(\text{kink})$$



Atomistic aspects

9 nm x 9nm

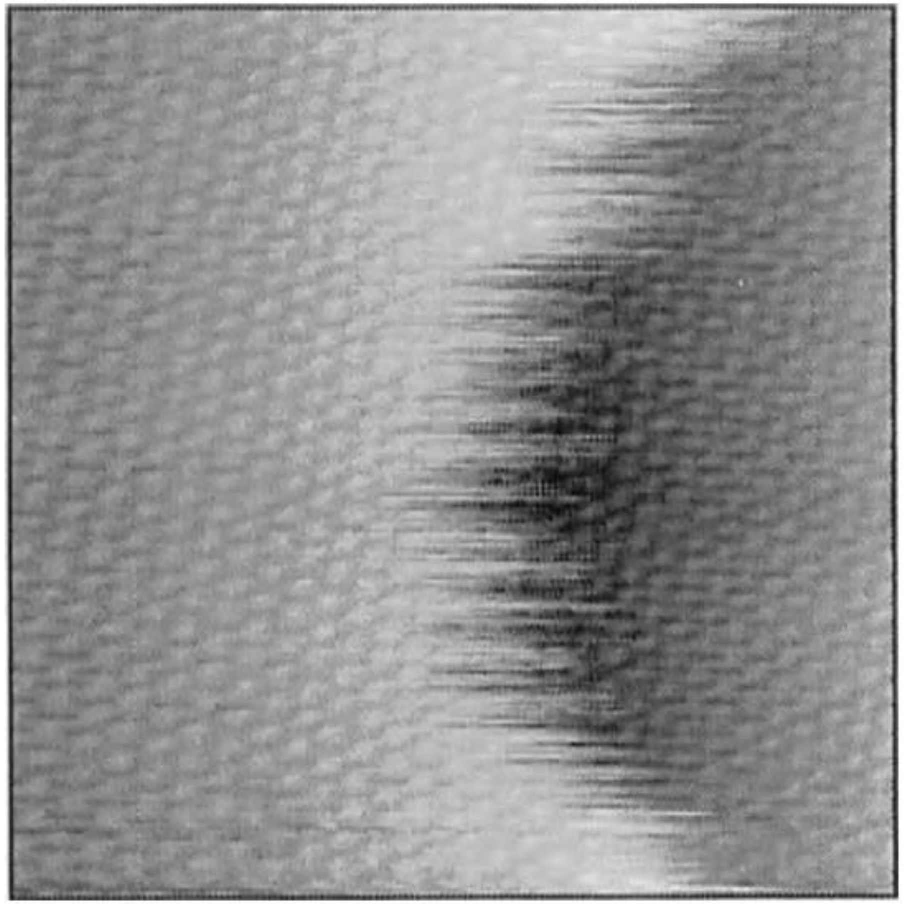
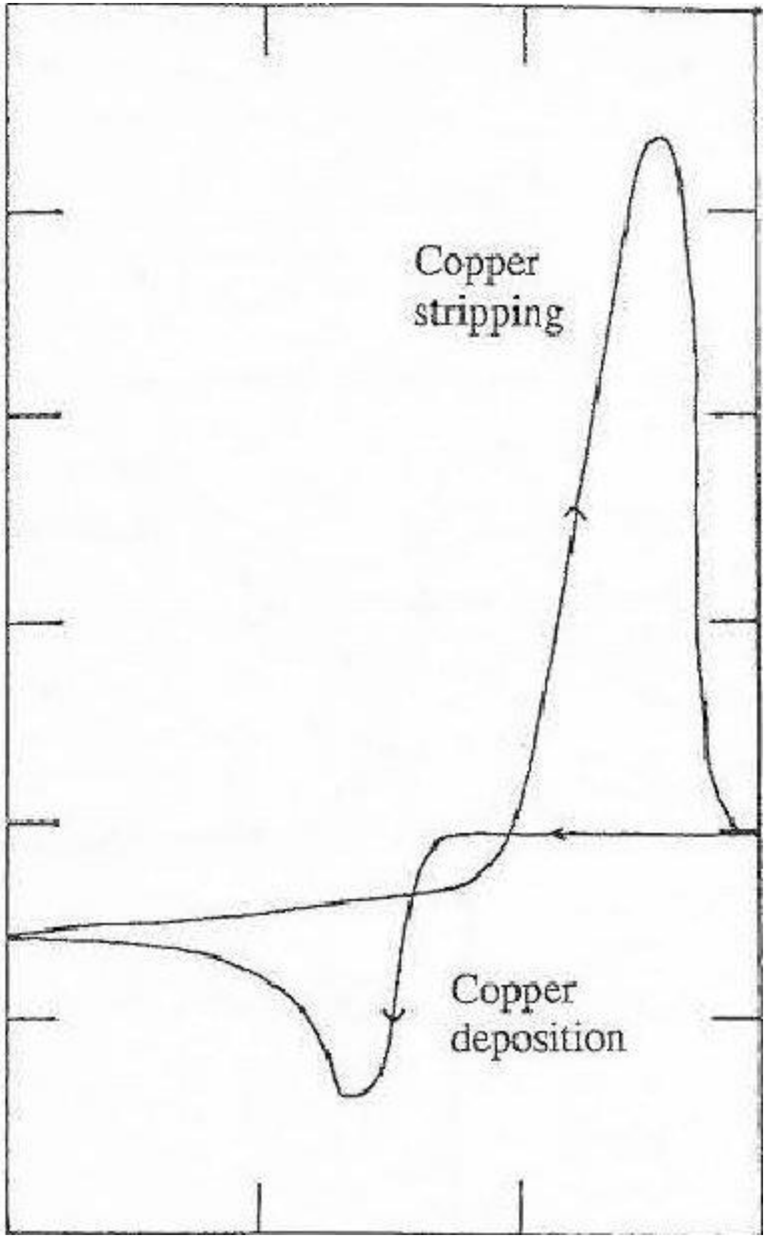


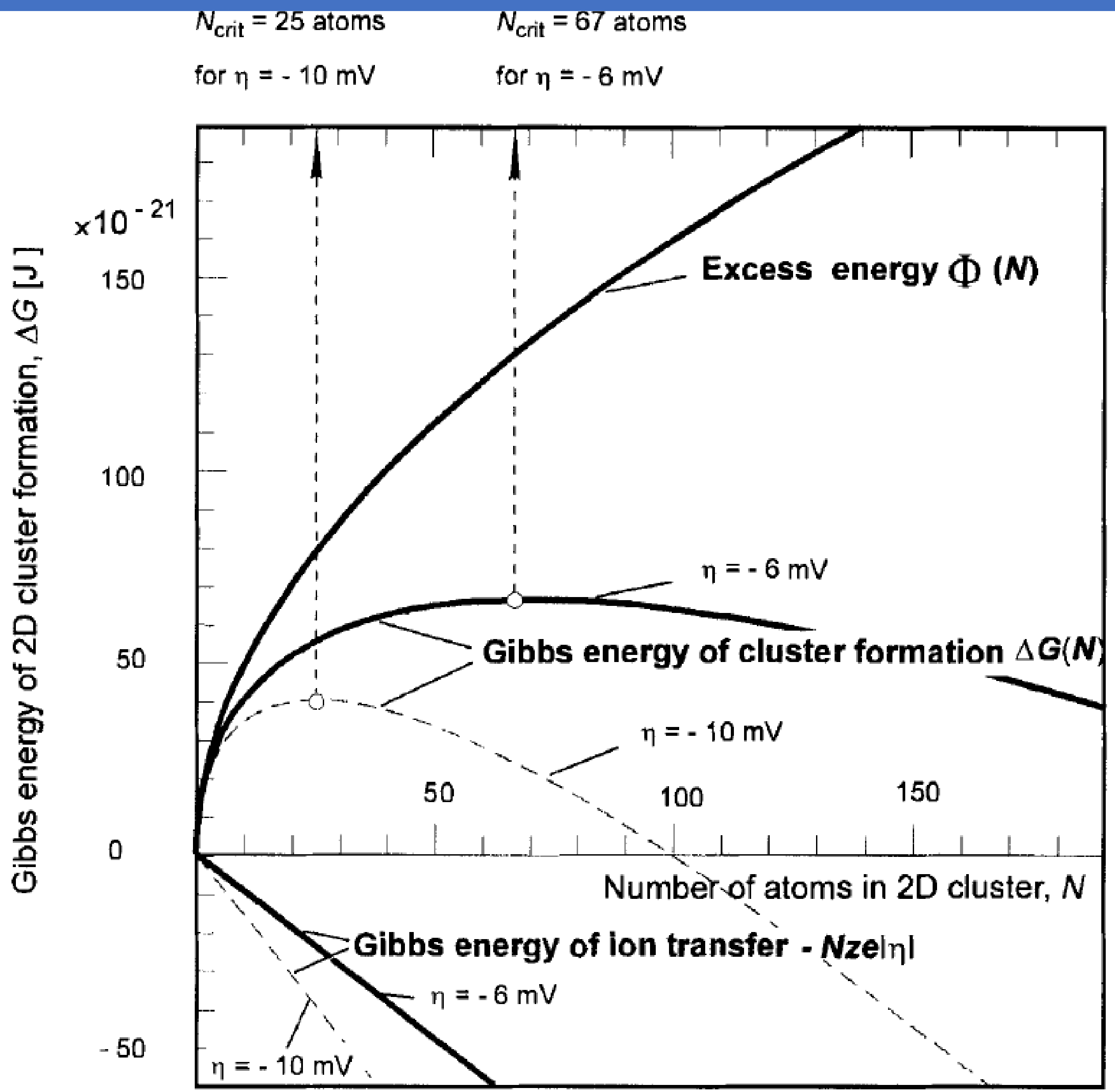
Figure 2.10 In situ STM image showing the frazzled appearance of a monatomic step on Ag(111) substrate [2.22]. System Ag(111)/10^{-4} M $CuSO_4$ + 5 x 10^{-2} M H_2SO_4 at E = 60 mV vs. SCE and T = 298 K. Reprinted from Surface Science Letters, Vol. 327, M. Dietterle, T. Will, D.M. Kolb, Step dynamics at the Ag(111)–electrolyte interface, p. L495, 1995, with kind permission of Elsevier Science.

CV in the course of Cu electrodepostion



- **Nucleation:** localized formation of a distinct thermodynamic phase
- Nucleation normally occurs at *nucleation sites* on surfaces contacting the liquid or vapor. Suspended particles or minute bubbles also provide nucleation sites. This is called ***heterogeneous nucleation***
- Nucleation without preferential nucleation sites is ***homogeneous nucleation***
- Nucleation occurs spontaneously and randomly, but it **requires superheating or supercooling** of the medium

Nucleation



Gibbs free energy to form a cluster of N atoms

Energy to form new phase boundaries

$$\Delta G(N) = -Nze|\eta| + \Phi(N)$$

- As the cluster grows, ΔG(N) increases (dominated by the increase in surface energy). Most of the clusters dissolve back to liquid phase
- Once some of the clusters reach the size of N_{crit} and pass the barrier of $\Delta G(N_{crit})$, further growth of clusters will lead to decrease in ΔG(N). The cluster will continue to grow
- For a 3D nucleus:

$$N_{\mathrm{crit}} = \frac{8BV_{\mathrm{m}}^2\sigma^3}{27(ze|\eta|)^3}$$

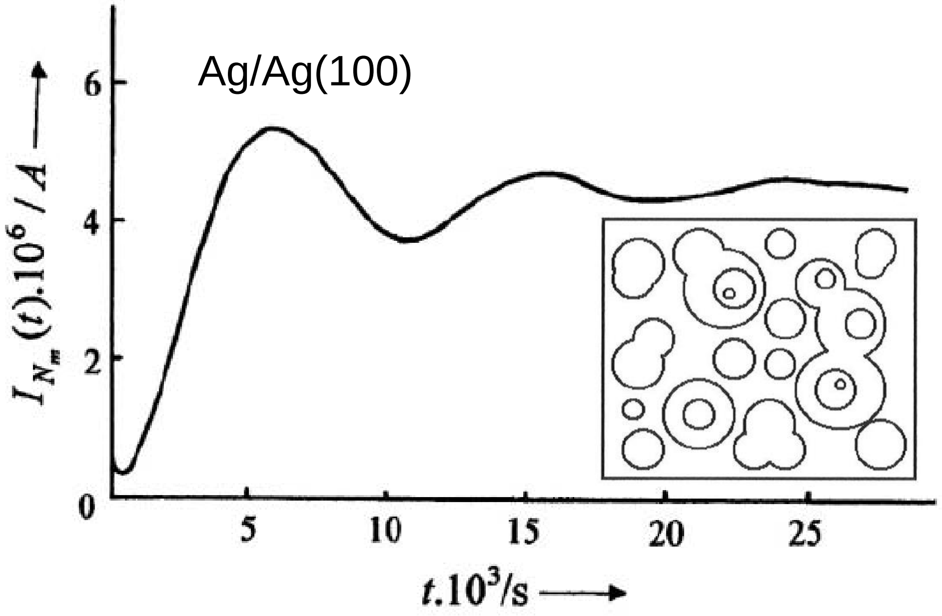
Nucleation rate

- Nucleation probability

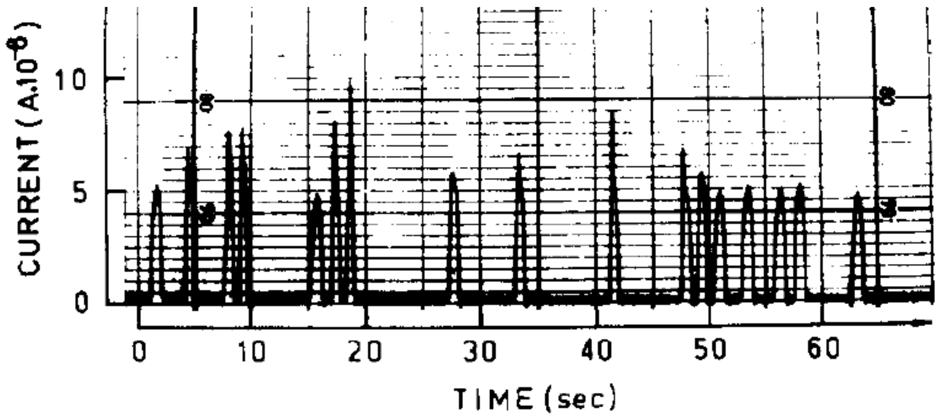
$$J = A \exp\left(-\frac{\Delta G_{\text{crit}}}{kT}\right)$$

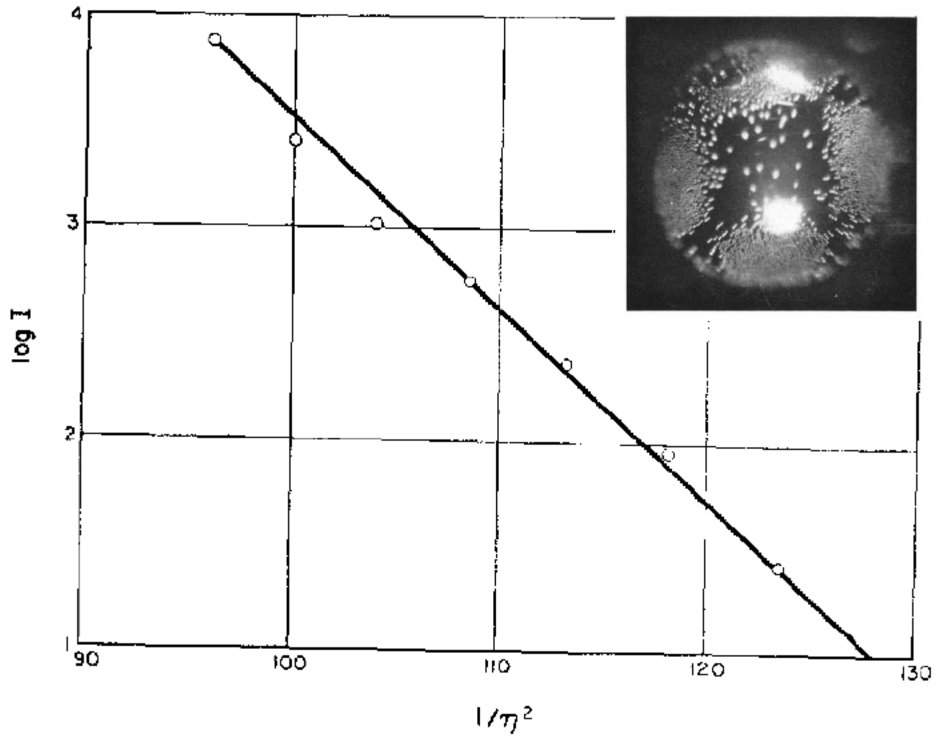
$$J = A_{3D} \exp\left(-\frac{4BV_m^2\sigma^3}{27(ze|\eta|)^2 kT}\right)$$

3D	2D
$\ln I = const - \frac{k_1}{\eta^2}$	$\ln I = const_1 - \frac{k_2}{\eta}$

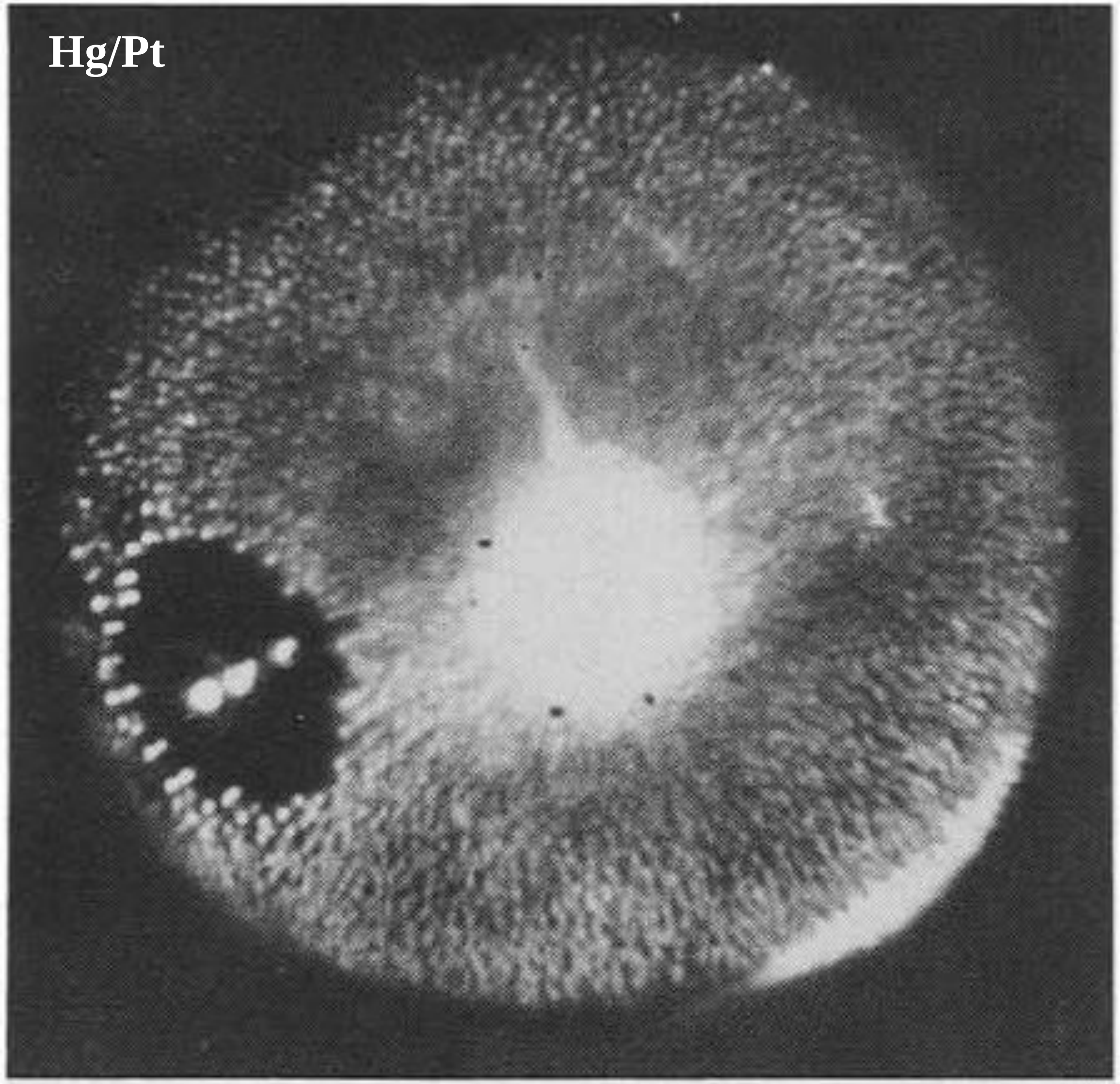


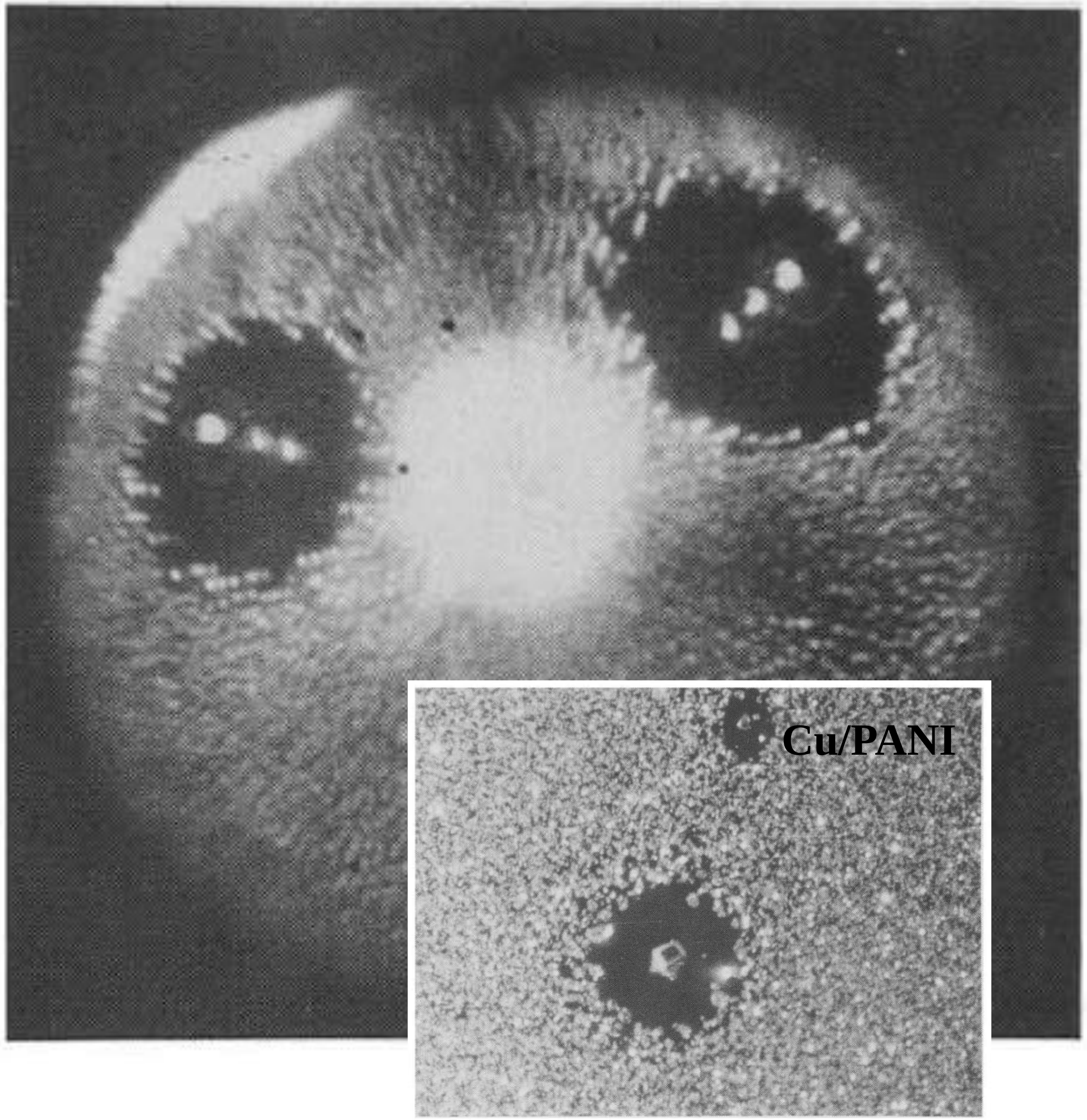
Nucleation – random process





Nucleation suppression

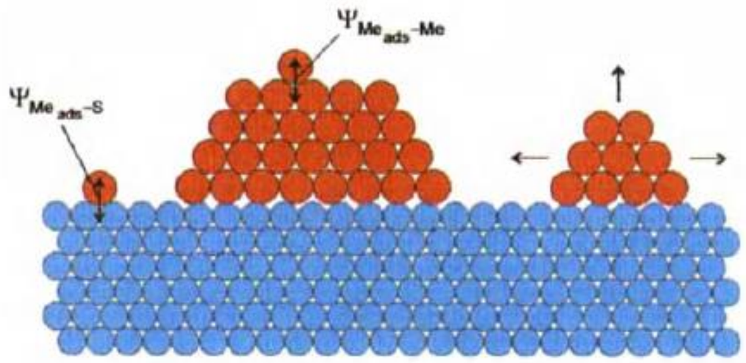




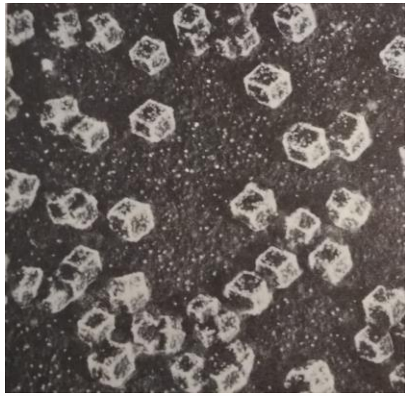
Electrodep. Surf. Treatment 3 (1975) 385

weak M-S interaction

3D metal island formation

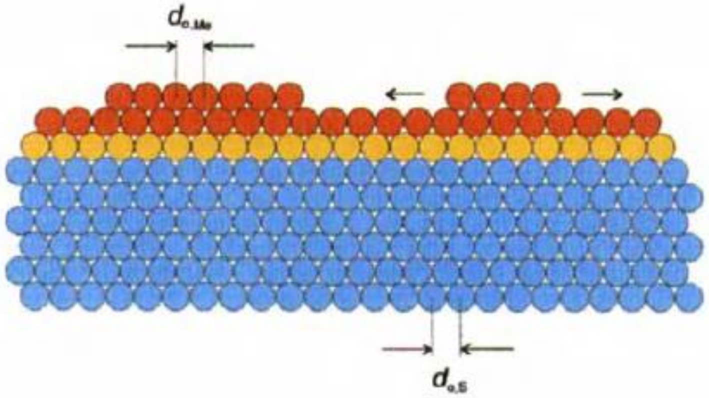


Ag_2O on Ag

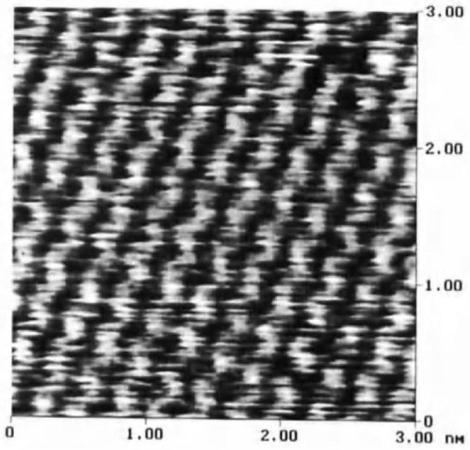


strong M-S interaction + zero misfit

layer-by-layer growth

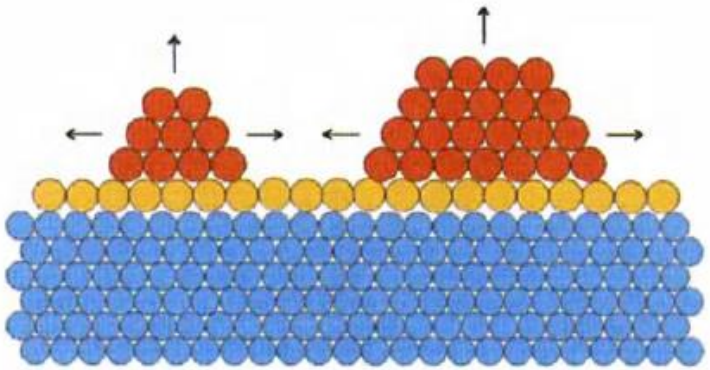


Ag on Au(100)

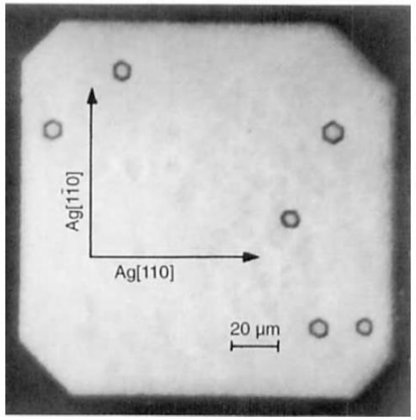


strong M-S interaction + misfit

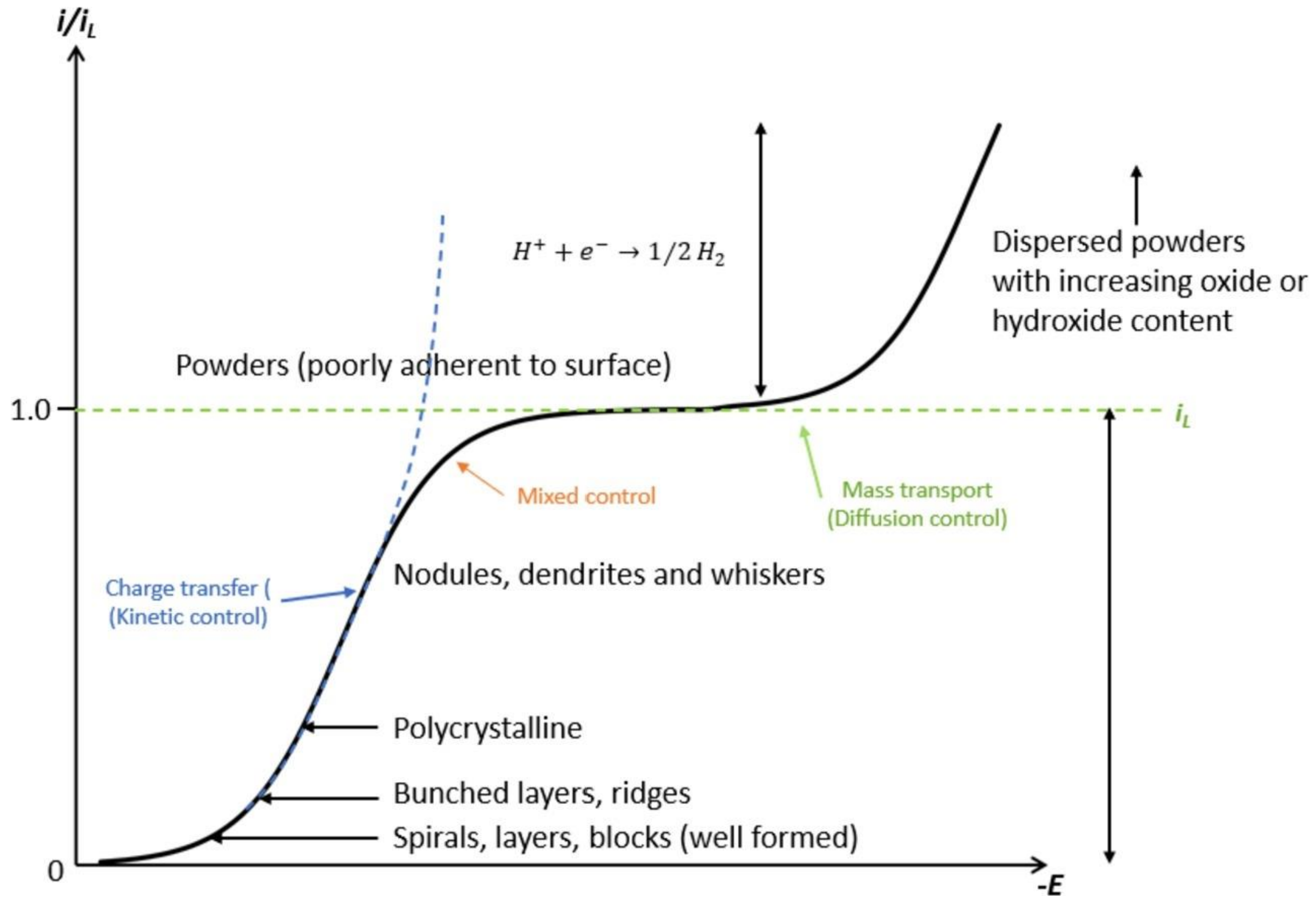
3D metal island formation on top of 2D layer



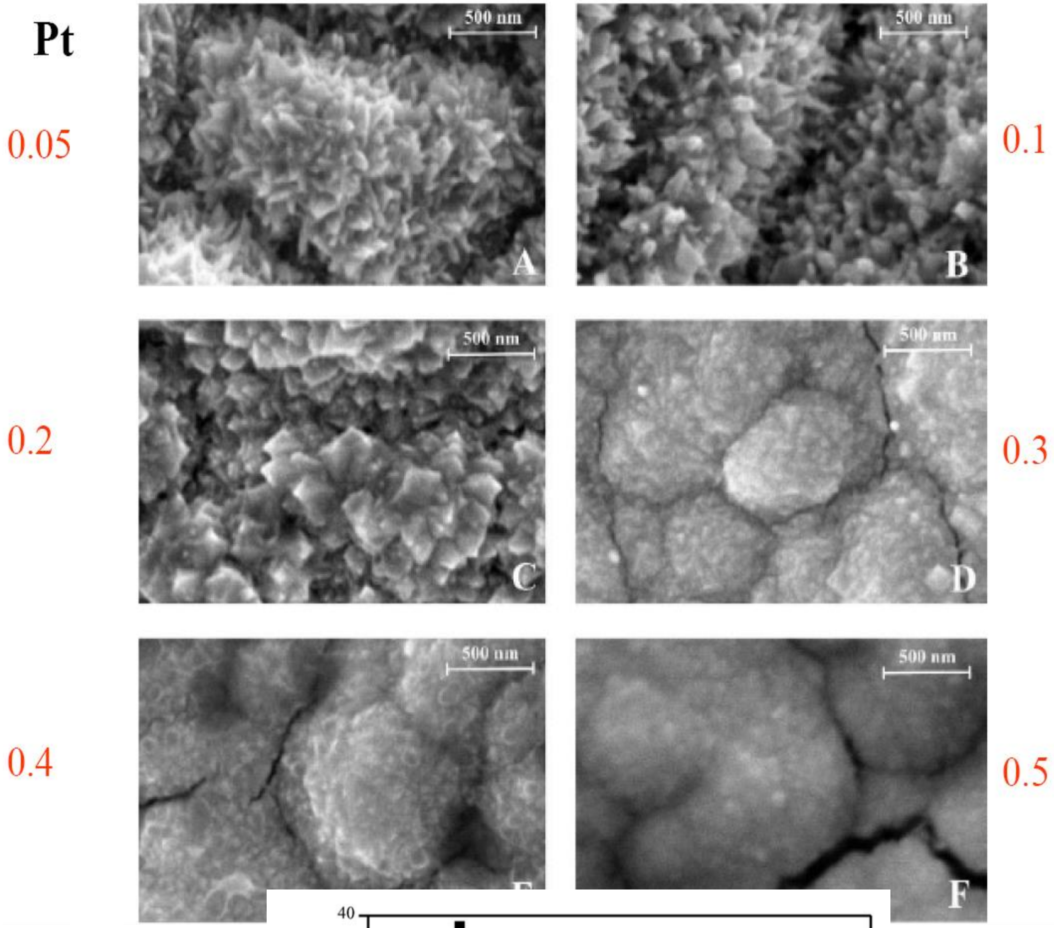
Pb on Ag(100)

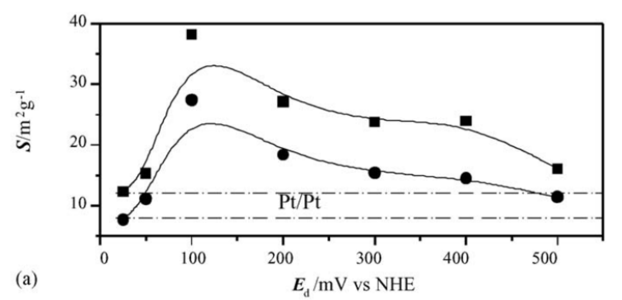


Growth morphologies



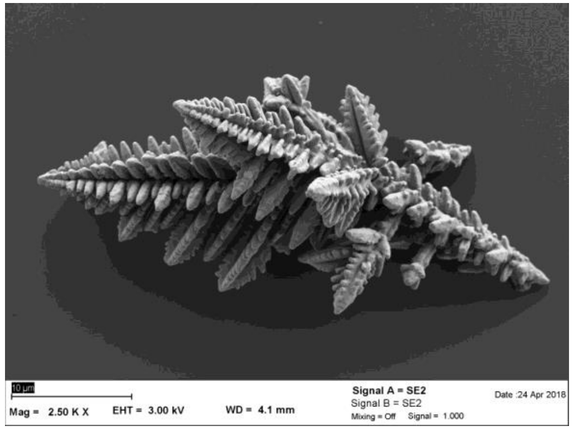
D. Pletcher, F.C. Walsh, Industrial Electrochemistry

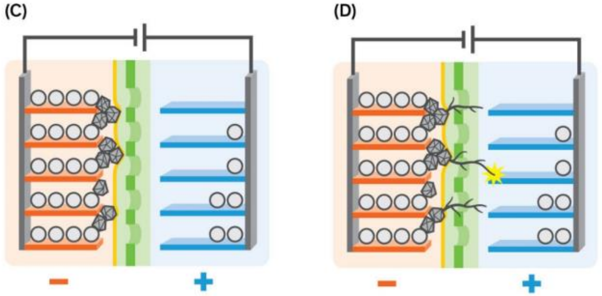


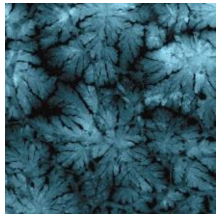


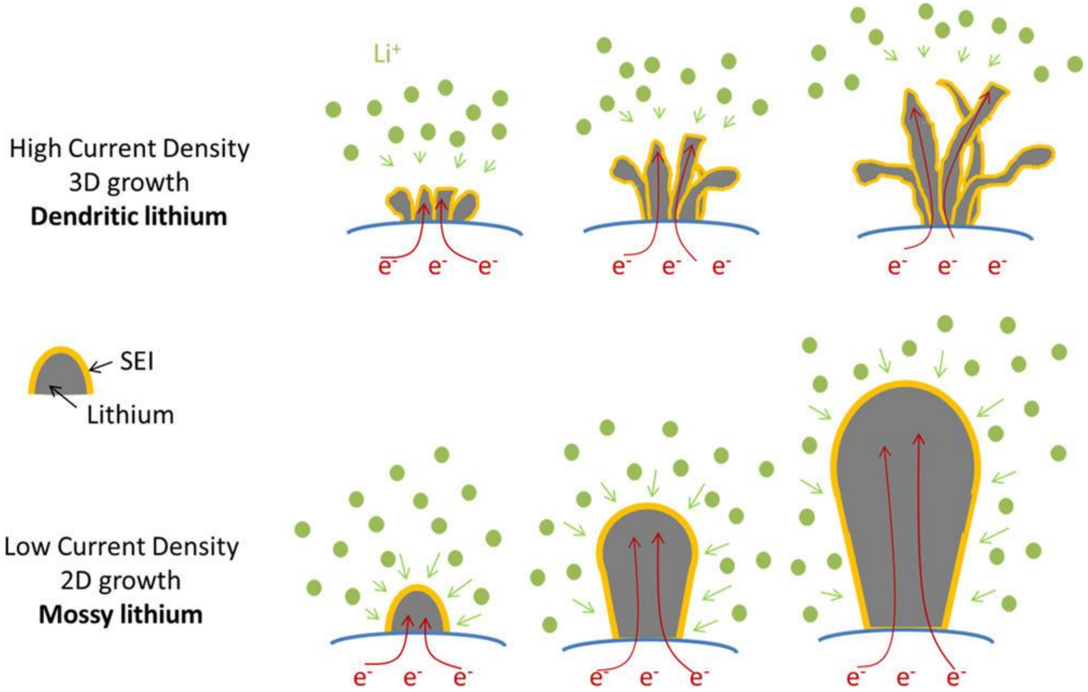
Electrochimica Acta 51 (2006) 4477–4488

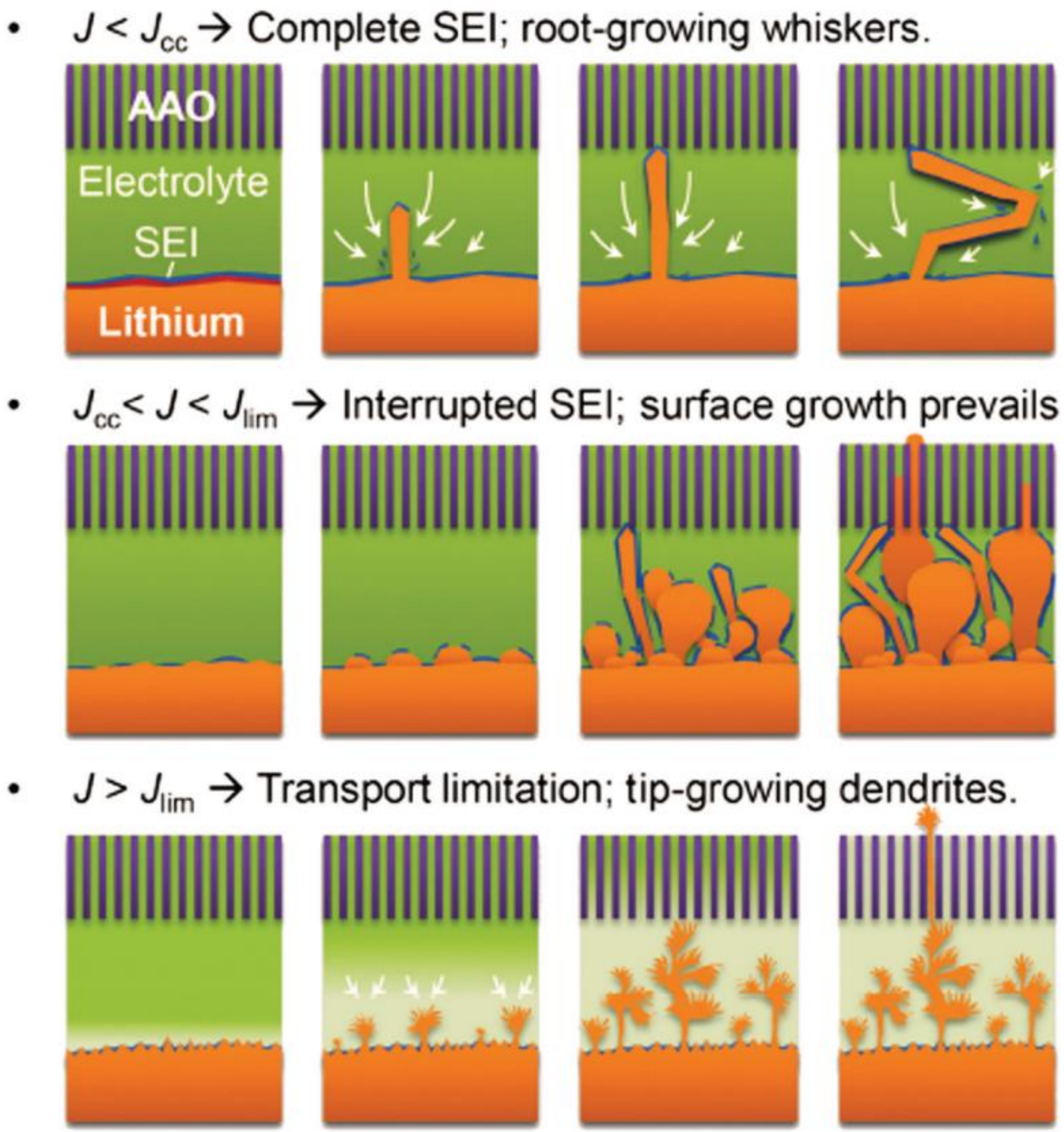
Morphology control











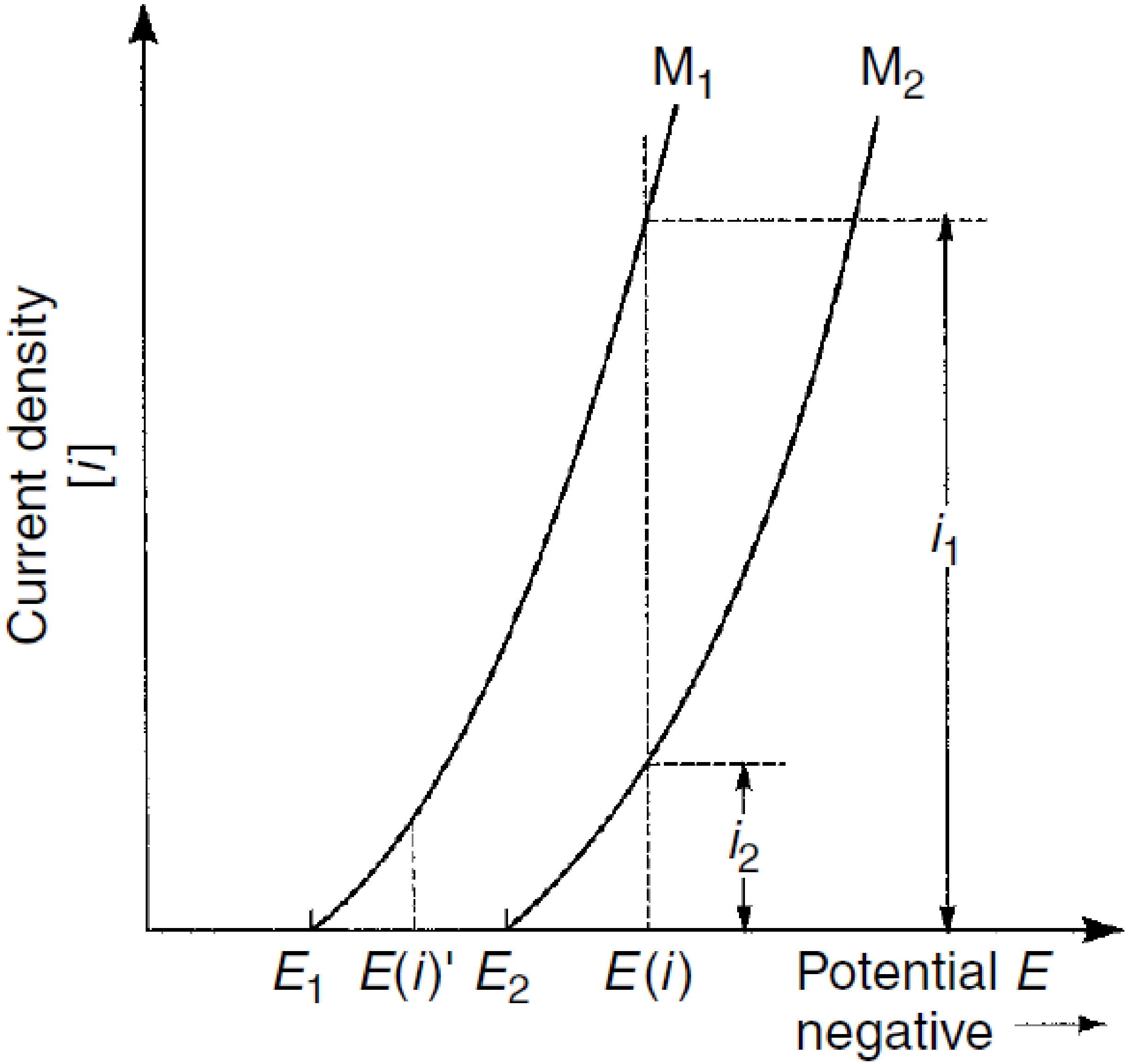
Joule, 11 (2018) 2201

Electrodeposition of metals and alloys

- If we deposit at **E(i)’** only M1 will be plated
- If we deposit at **E(i)** both M1 and M2 will be plated
- Alloy composition will be determined by the ratio of the values of current densities of deposition of individual metals at that potential

$$\frac{M_1}{M_2} = \frac{i_1}{i_2}$$

$$\frac{i_1}{i_2} = \left(\frac{i_{o,1}}{i_{o,2}}\right) \exp[af(E_{eq,1} - E_{eq,2})]$$



Electrodeposition of metals and alloys

- Even when the difference in equilibrium potentials is large, it is still possible to deposit an alloy with desired composition

Zn-Cu alloy

Standard potentials:

$$E^0_{\mathrm{Cu^{2+}/Cu}} = 0.3419\ \mathrm{V\ (SHE)}$$

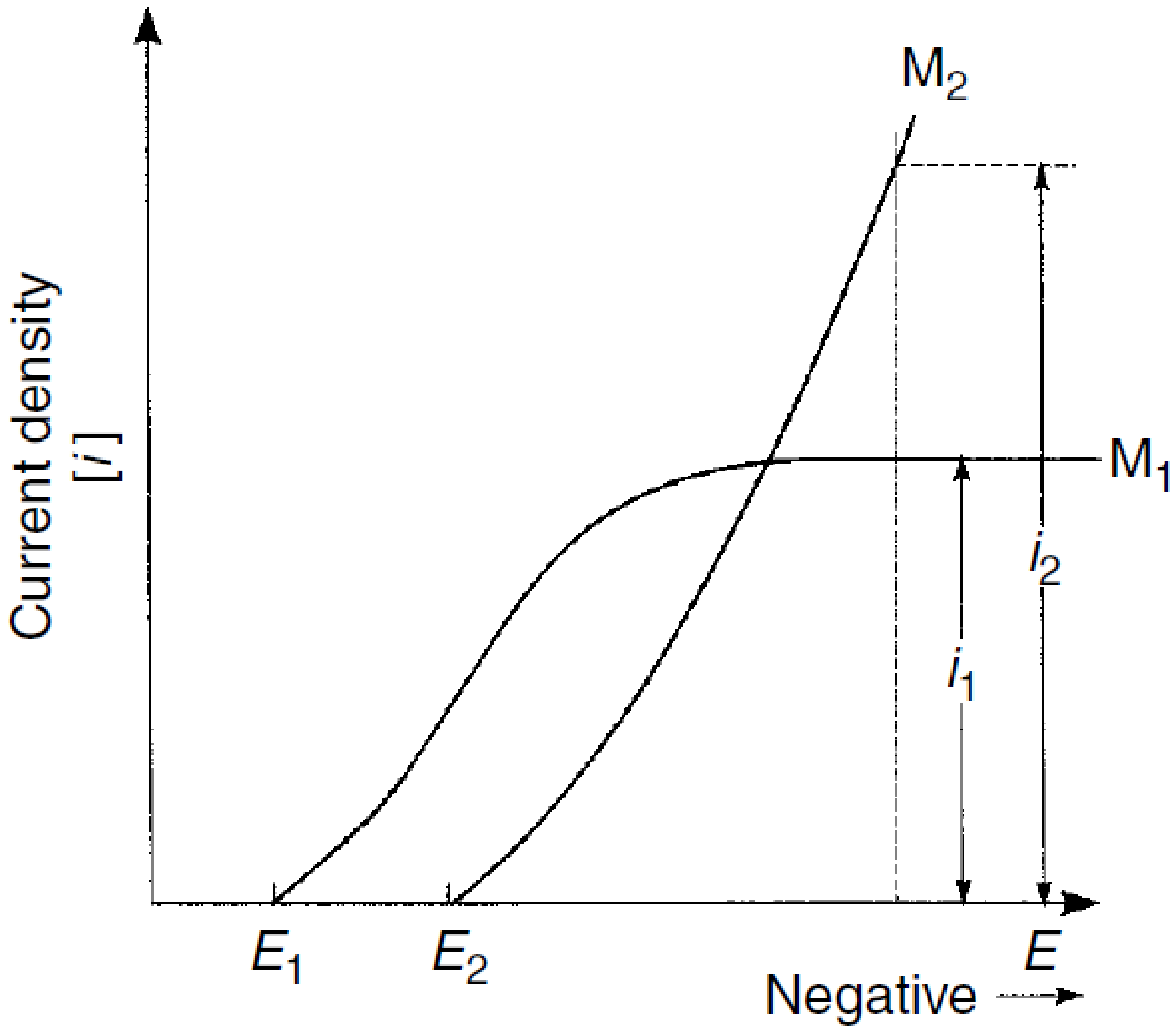
$$E^0_{\mathrm{Zn^{2+}/Zn}} = -0.7618\ \mathrm{V\ (SHE)}$$

Difference:

$$\Delta E = 1.1037\ \mathrm{V}$$

- **Deposition of M_1 is limited by diffusion**

- **Deposition of M_2 is limited by ET rate**



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$$E^0_{Zn^{2+}/Zn} = -0.7618 \text{ V (SHE)}$$

Difference:

$$\Delta E = 1.1037 \text{ V}$$

- The difference in potentials can be reduced by complexing Cu^+ and Zn^{2+} ions in solution

$$\frac{(Cu^+)(CN^-)^3}{([CuCN)_3]^{2-})} = 5.6 \times 10^{-28}$$

$$\frac{(Zn^{2+})(CN^-)^4}{[Zn(CN)_4]^{2-}} = 1.3 \times 10^{-17}$$

0.05 M $[Cu(CN)_3]^{2-}$
0.0001 M CN^-
$C(Cu^+) = 2.8*10^{-17}$ M

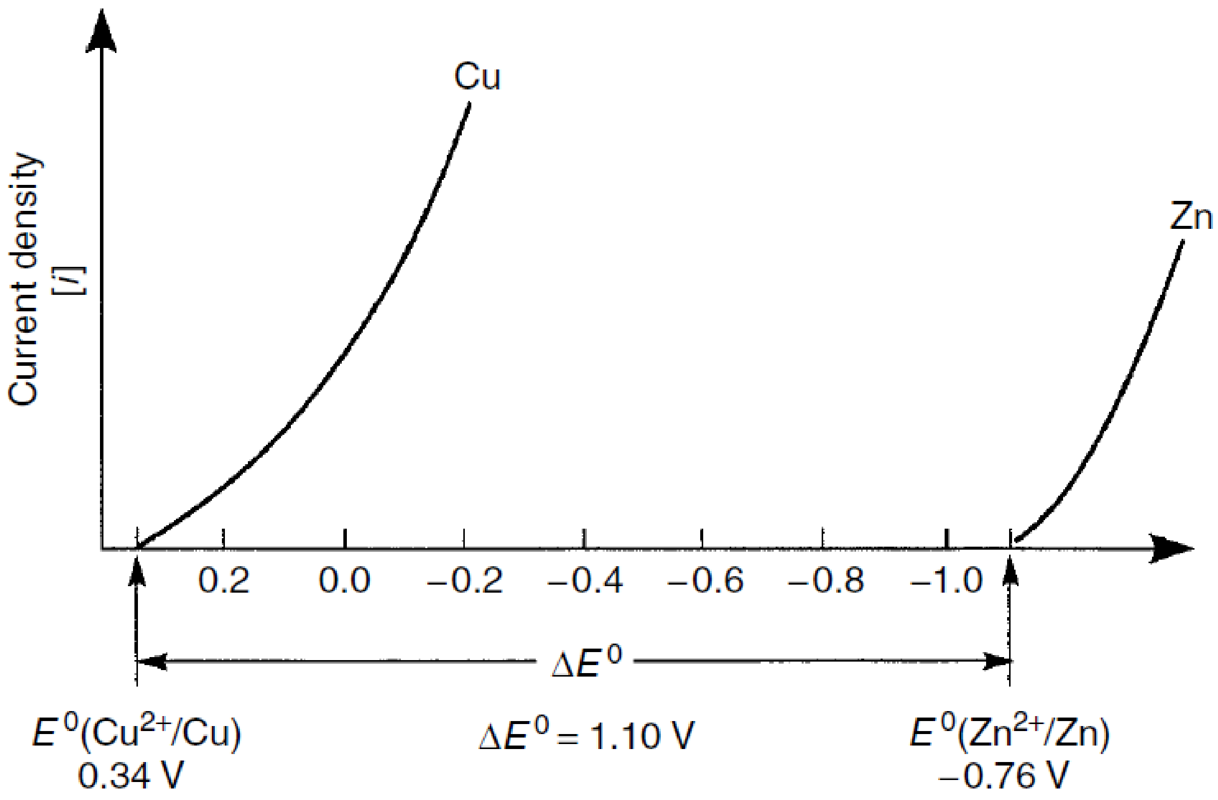
$E_{rev}(Cu^+/Cu) = -0.43$ V

0.025 M $[Zn(CN)_4]^{2-}$
0.0001 M CN^-
$C(Zn^{2+}) = 6.62*10^{-5}$ M

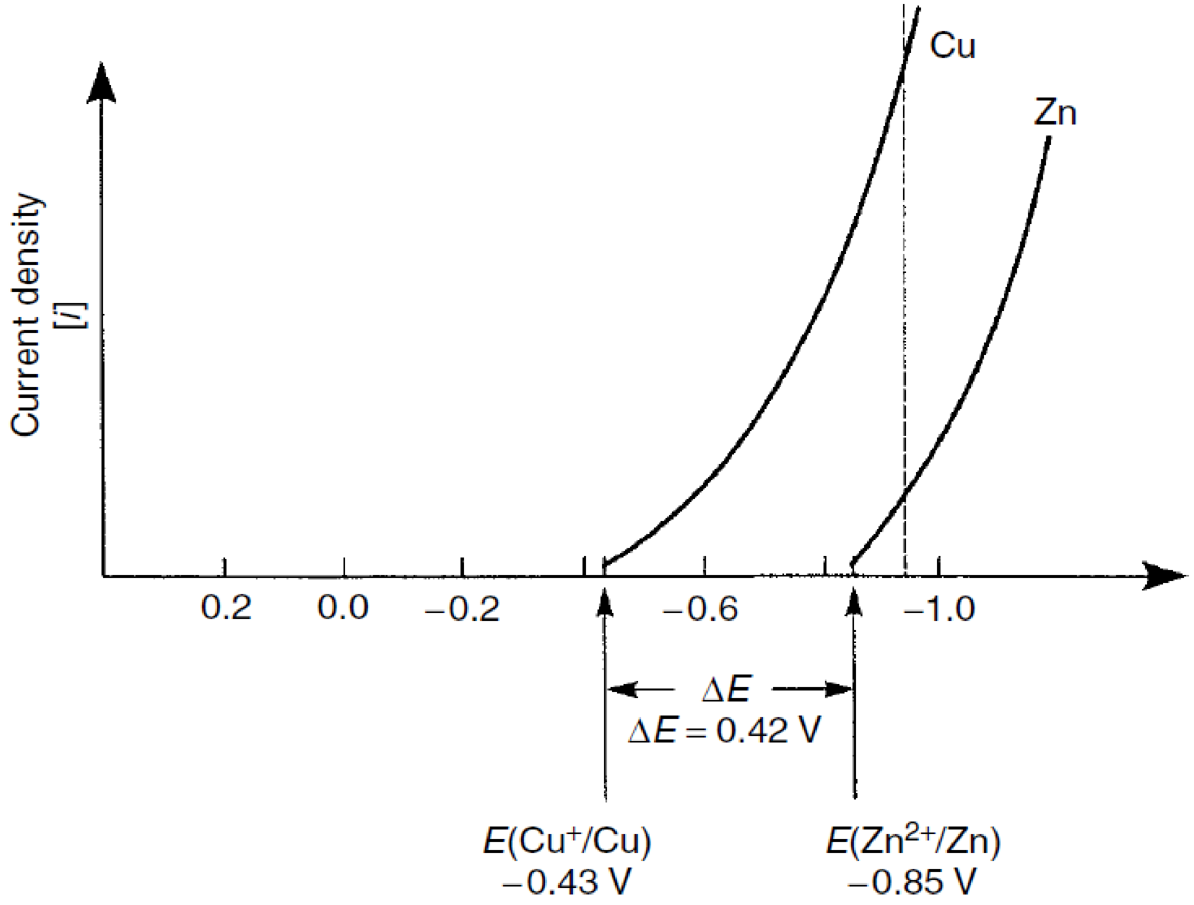
$E_{rev}(Zn^{2+}/Zn) = -0.85$ V

Alloy formation

Without complexing



With complexing



Eutectic alloys

- Many elements do not mix in the solid phase - they crystallize as pure metal crystals
- Characteristic of a eutectic are extremely fine crystal grains, so that the alloy appears microscopically homogeneous. Even laboratory X-ray techniques cannot discern the phase structure

Sn/Pb
Cd/Zn
Sn/Zn
Ag/Cu

Tin-Lead (Sn-Pb) Solder

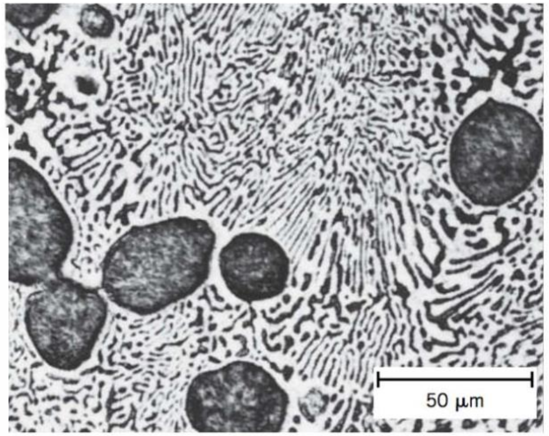
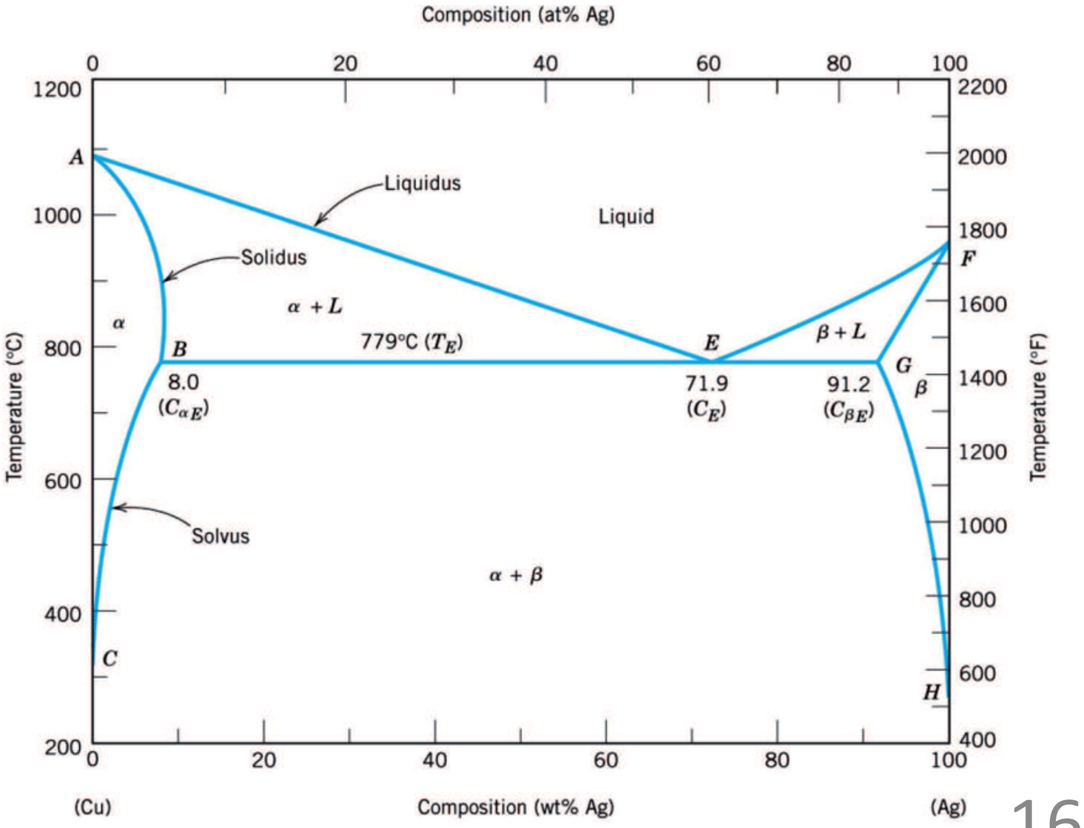


Figure 9.17 Photomicrograph showing the microstructure of a lead–tin alloy of composition 50 wt% Sn–50 wt% Pb. This microstructure is composed of a primary lead-rich α phase (large dark regions) within a lamellar eutectic structure consisting of a tin-rich β phase (light layers) and a lead-rich α phase (dark layers). 400×.
(From *Metals Handbook*, Vol. 9, 9th edition, *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)



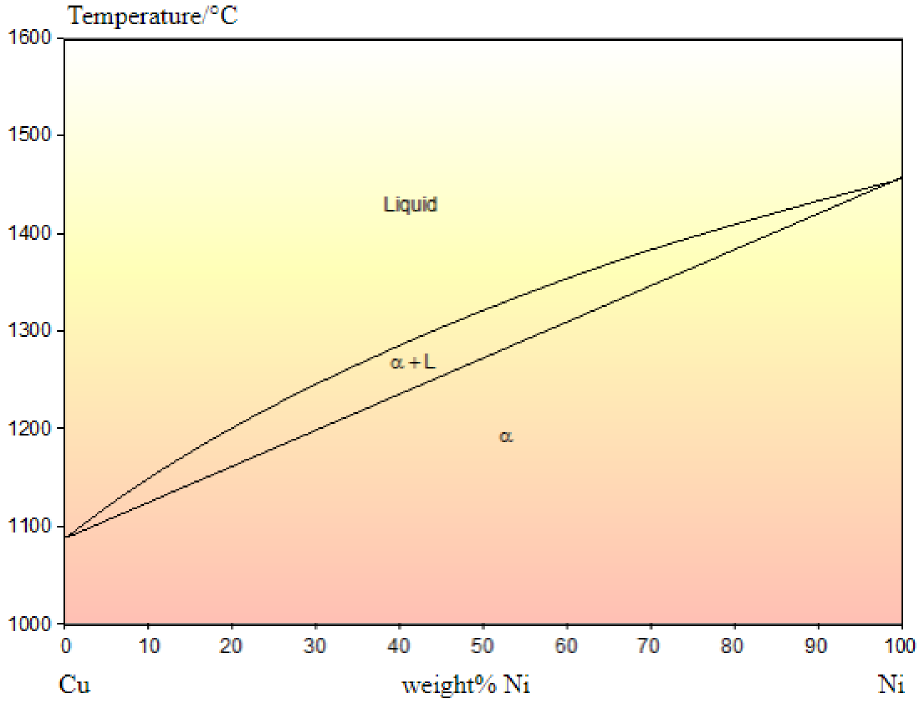
Solid solutions

Solid solutions

Ni/Co
Cu/Ni
Fe/Co
Fe/Ni

- Components are miscible in the solid at the atomic level over the entire range of compositions
- For an ideal solid solution, the enthalpy of mixing is zero and only the entropic term is important (9 mV for *p*, *q* = 2 (virtual additivity of $E^0_{\mathrm{A^{p+}/A}}$ and $E^0_{\mathrm{B^{q+}/B}}$)

$$E_{AB} = \frac{1}{2}\left[E^0_{\mathrm{A^{p+}/A}} + E^0_{\mathrm{B^{q+}/B}}\right] - \frac{\mu^0_{\mathrm{A_{0.5}B_{0.5}}}}{2F}$$



- Copper-nickel (also known as cupronickel) alloys are widely used for marine applications due to their excellent resistance to seawater corrosion, low macrofouling rates, and good fabricability

Heat exchanger

TIG welding

Splash zone sheathing

Intermediate phases and intermetallics

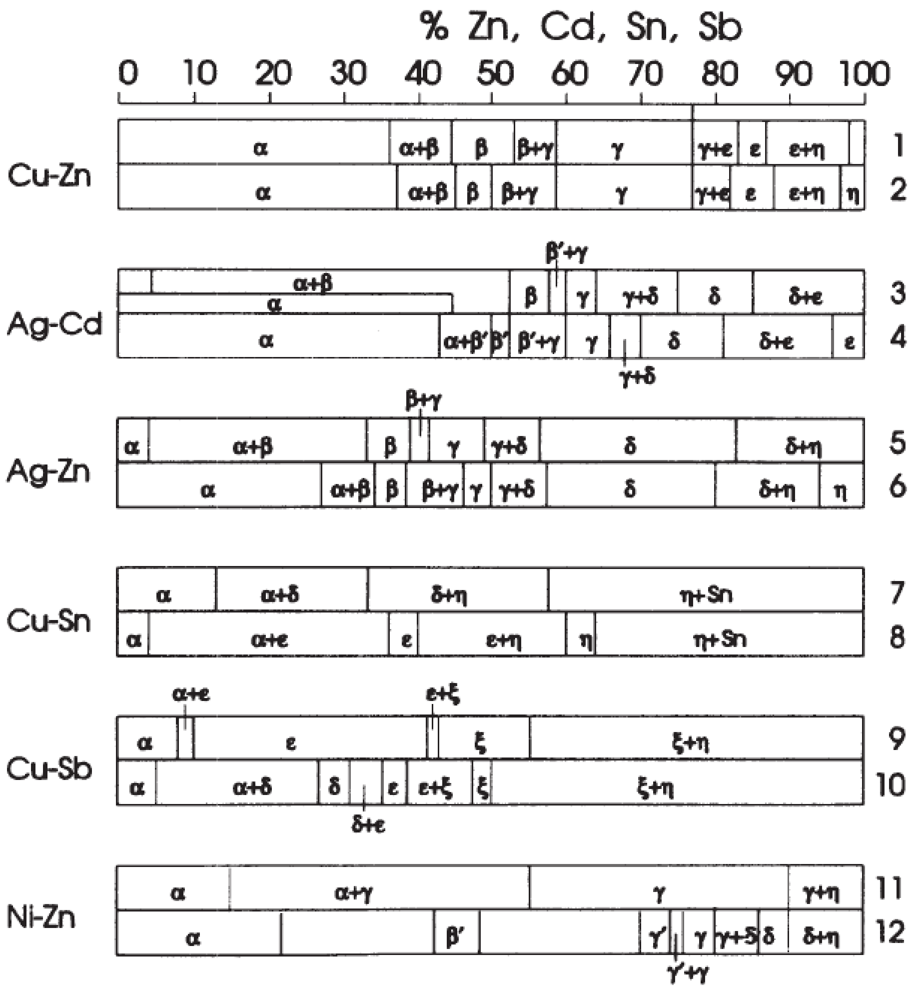
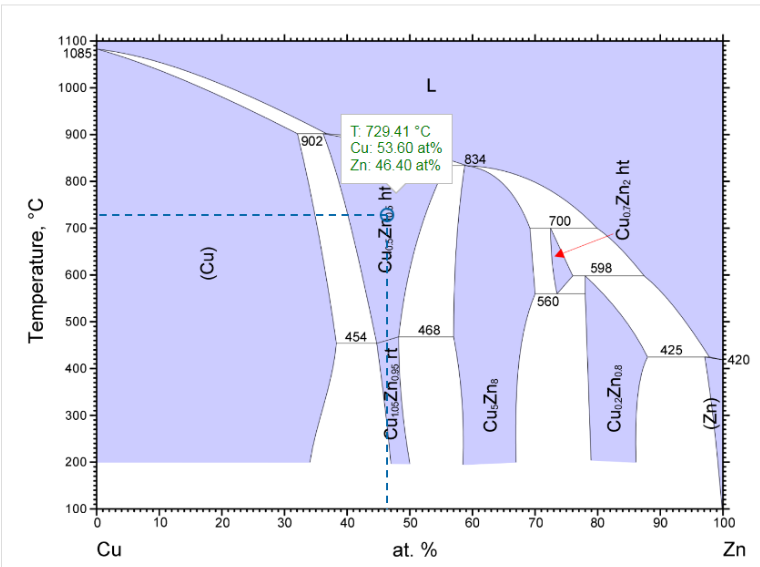


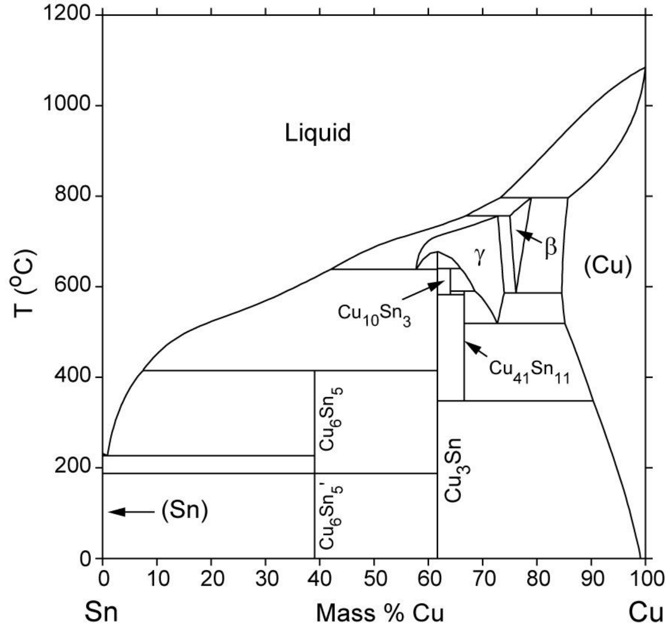
Figure 4. Distribution of phases in electrodeposited and recrystallized alloys. 1, 3, 5, 7, 9, and 11, Electrodeposited alloys; 2, 10, and 12, after recrystallization at 400°C; 4, after recrystallization at 200°C; 6, after recrystallization at 280°C; 8, distribution of phases according to the phase diagram of the alloy at 200°C.

Brass

Cu-Zn Binary Phase Diagram 0-100 at.% Zn



Bronze



Electrocrystallization of compounds

Cathodic electrocrystallization

$Cd^{2+} + SeO_3^{2-} + 6H^+ + 6e^- = CdSe + 3H_2O$

$Cu^{2+} + Cl^- + e^- = CuCl$

$2CuL_2^{2-} + 2e^- + 2OH^- = Cu_2O + 4L^{2-} + H_2O$

Anodic electrocrystallization

$Mn^{2+} + 2H_2O – 2e^- = MnO_2 + 4H^+$

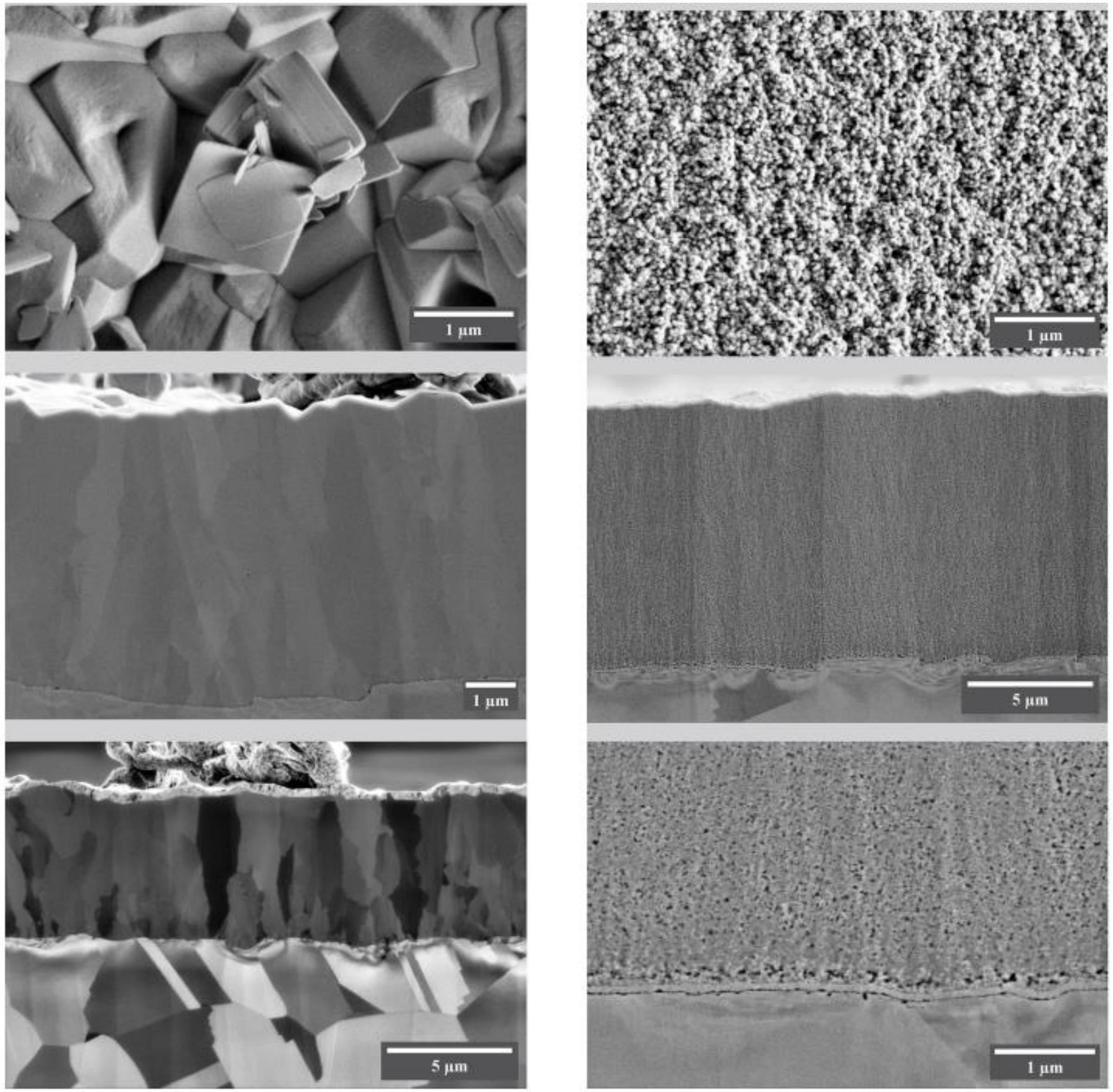
$Tl^+ + F^- + H_2O – 2e^- = TlOF + 2H$

Anodizing

$2Al + 3H_2O – 6e^- = Al_2O_3 + 6H^+$

$Si + 2H_2O – 4 e^- = SiO_2 + 4H^+$

Acetate solution | Lactate solution



Nanomaterials 2023, 13, 3064

Local pH shift

Anodic acidization

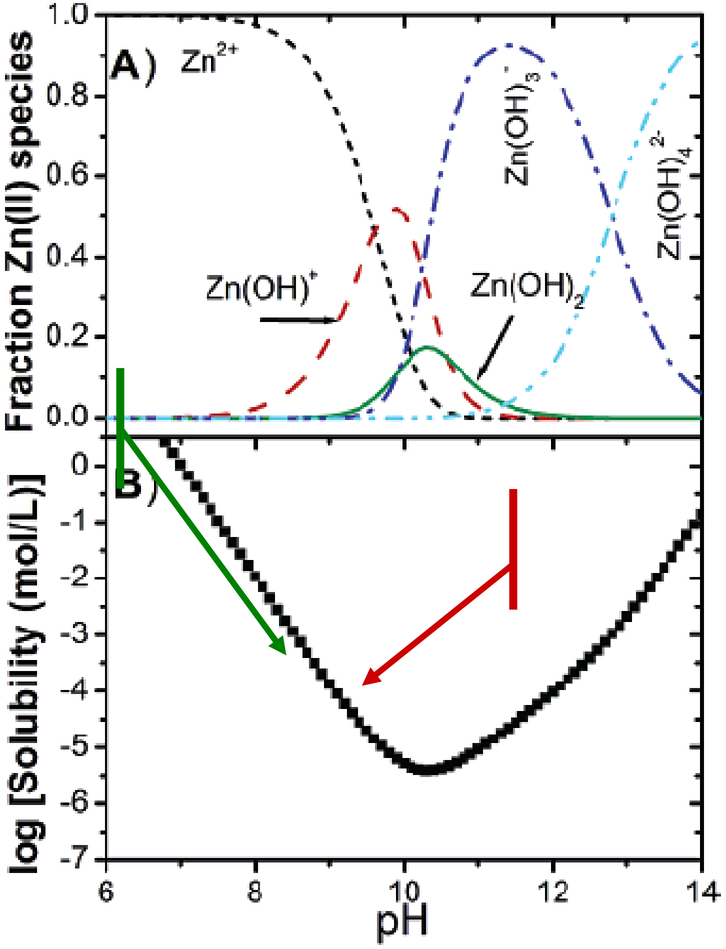
Ascorbic acid oxidation

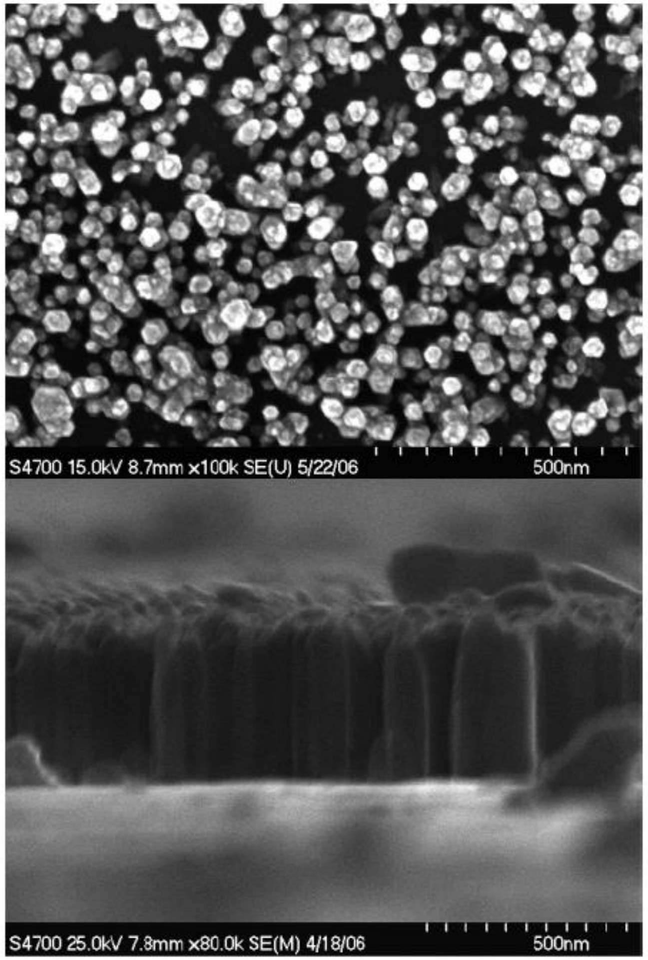
$$Zn(OH)_4^{2-} + 2H^+ \rightarrow ZnO + 3H_2O$$

Cathodic alkalinization

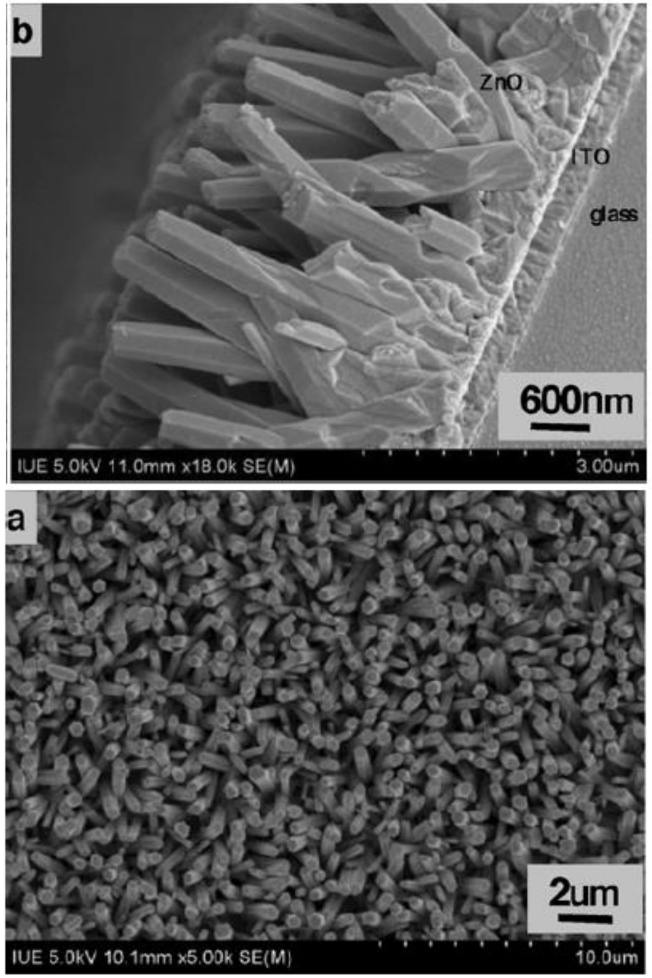
Hydrogen evolution

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O$$





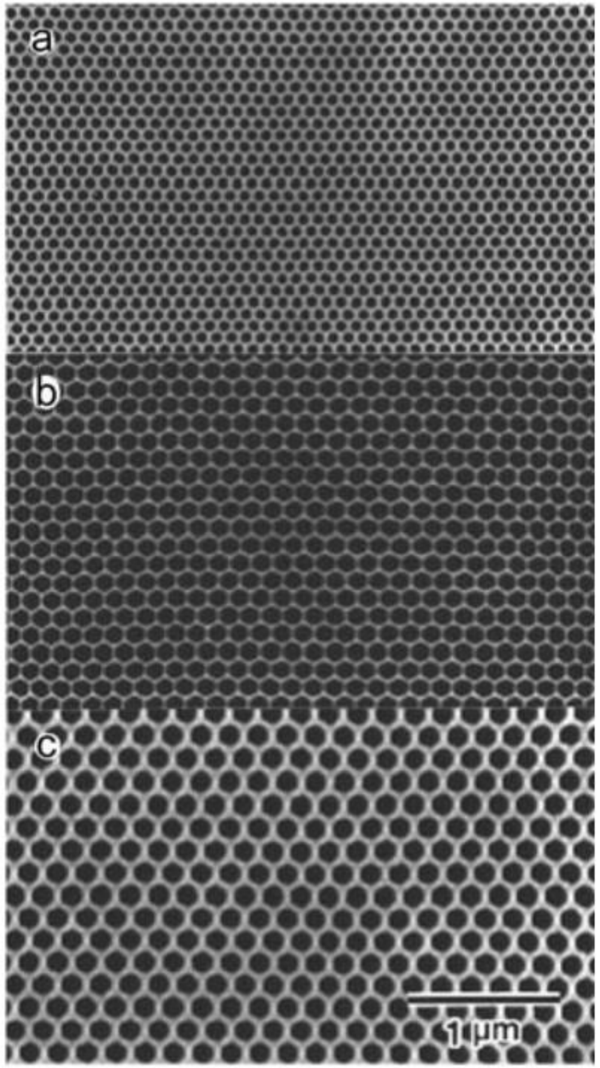
Langmuir 2006, 22, 10535-10539



Appl. Surf. Sci. (2011)

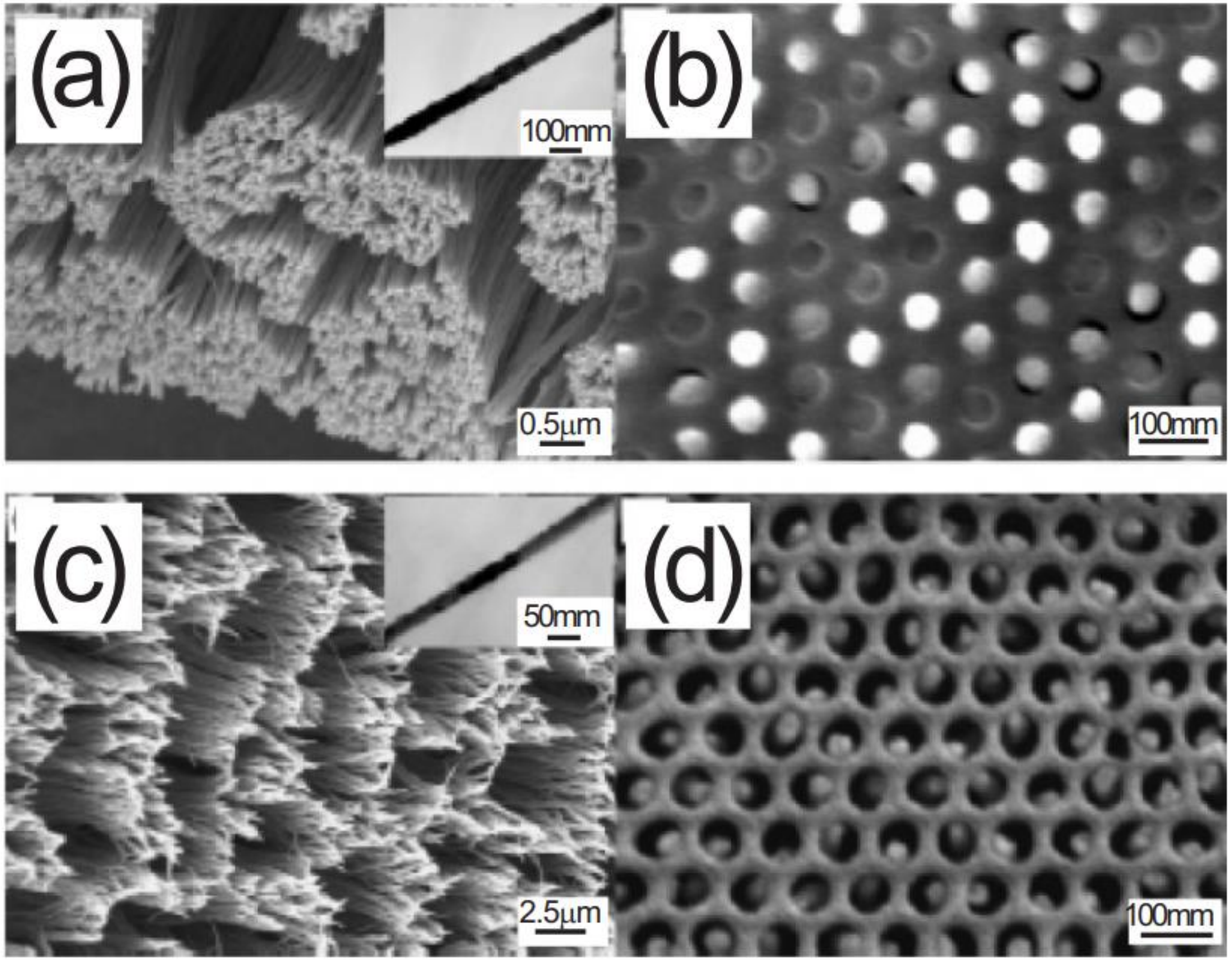
Template-assisted deposition

AAO membranes with different pore diameters



Appl. Phys. Lett., 1997, 71, 2770

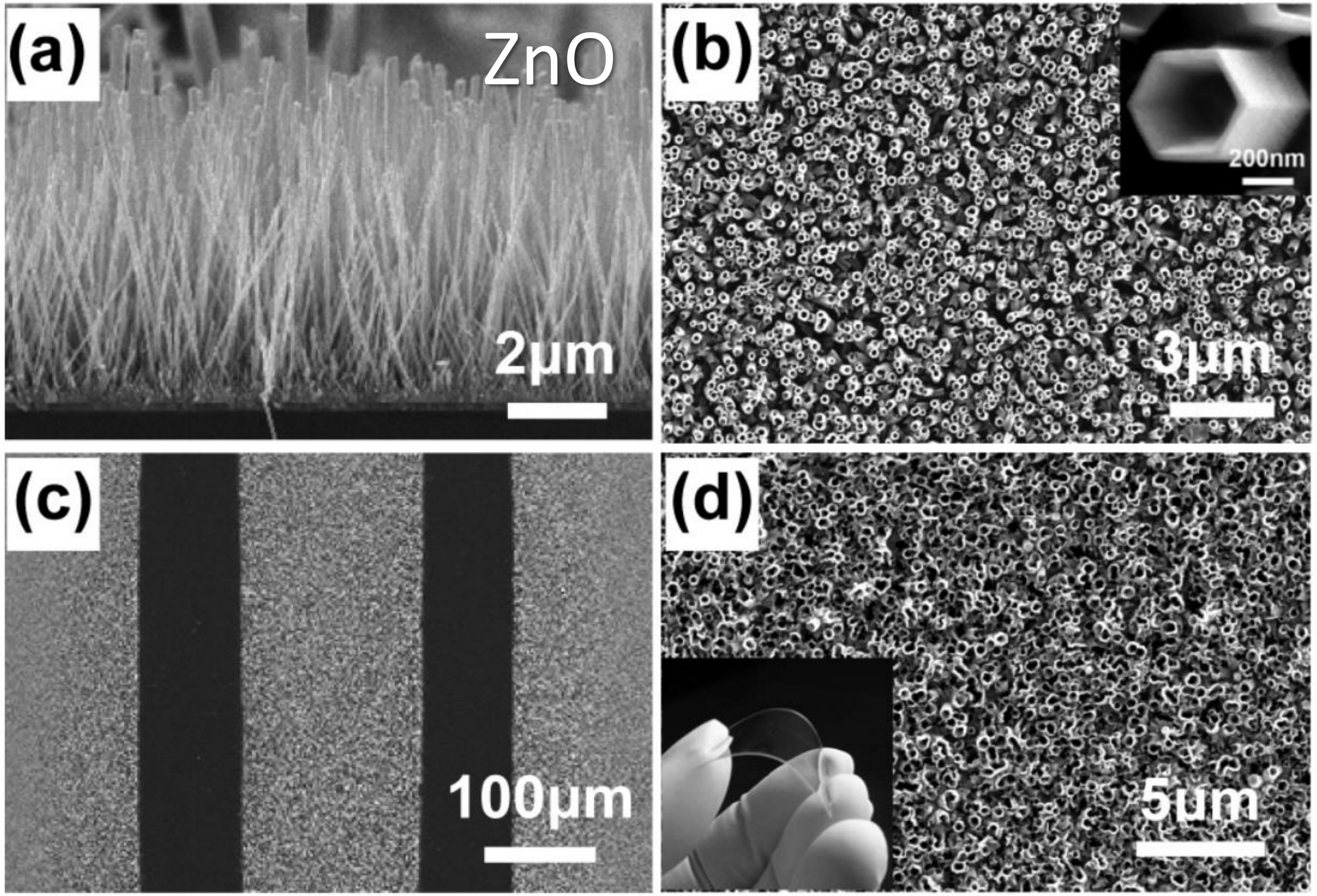
$Bi_{1-x}Sb_x$ alloy nanowires



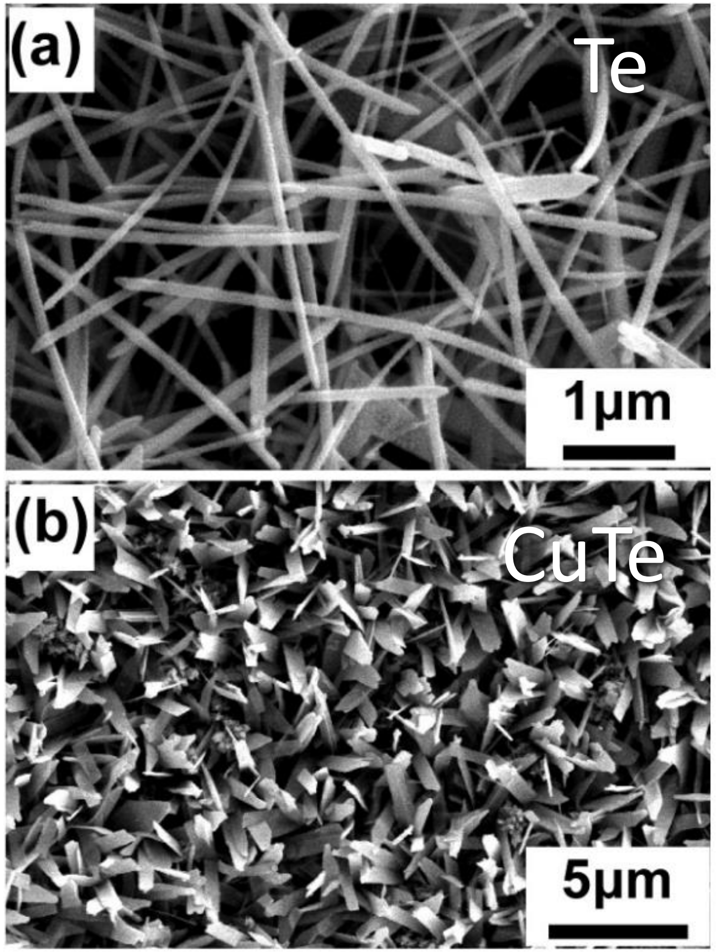
J. Phys. Chem. B, 2006, 110, 21572

Template-free deposition of nanostructures

- Some materials have the natural tendency towards 1D growth due to intrinsic highly anisotropic crystal structures
- Hexagonal ZnO nanorods or nanotubes, Te nanowires and CuTe nanoribbons



Appl. Phys. Lett., 2008, 92, 053111



Rec. Pat. Nanotechnol. 2009, 3, 182-191

Templating via H_2 bubbles during HER

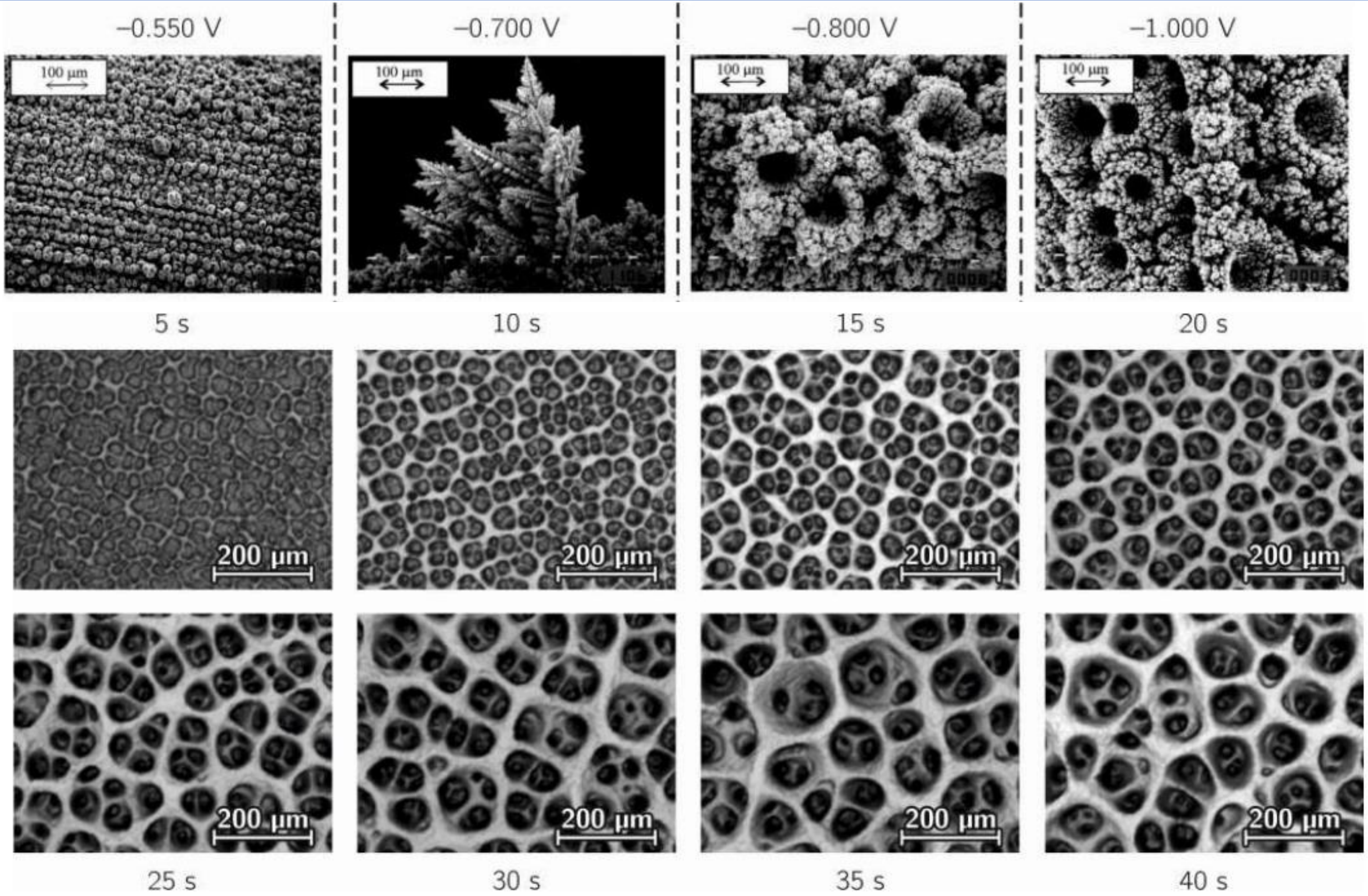
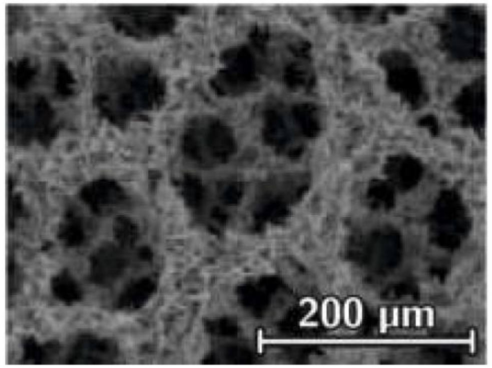
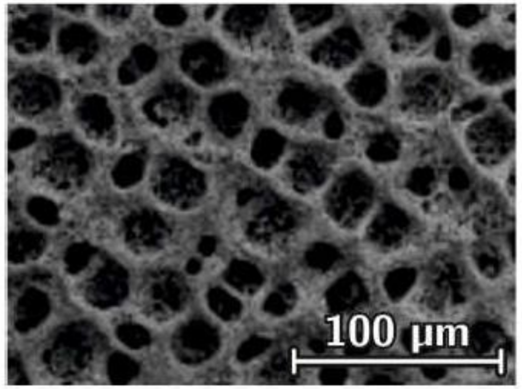


Figure 5. Morphologies of Cu deposits obtained after different times of galvanostatic electrolysis at –2.0 A cm^{-2}, from an aqueous solution containing 0.20 mol dm^{-3} $CuSO_4$ and 1.0 mol dm^{-3} H_2SO_4. Reproduced from Ref. 52 with permission of The Electrochemical Society.

Sn foam

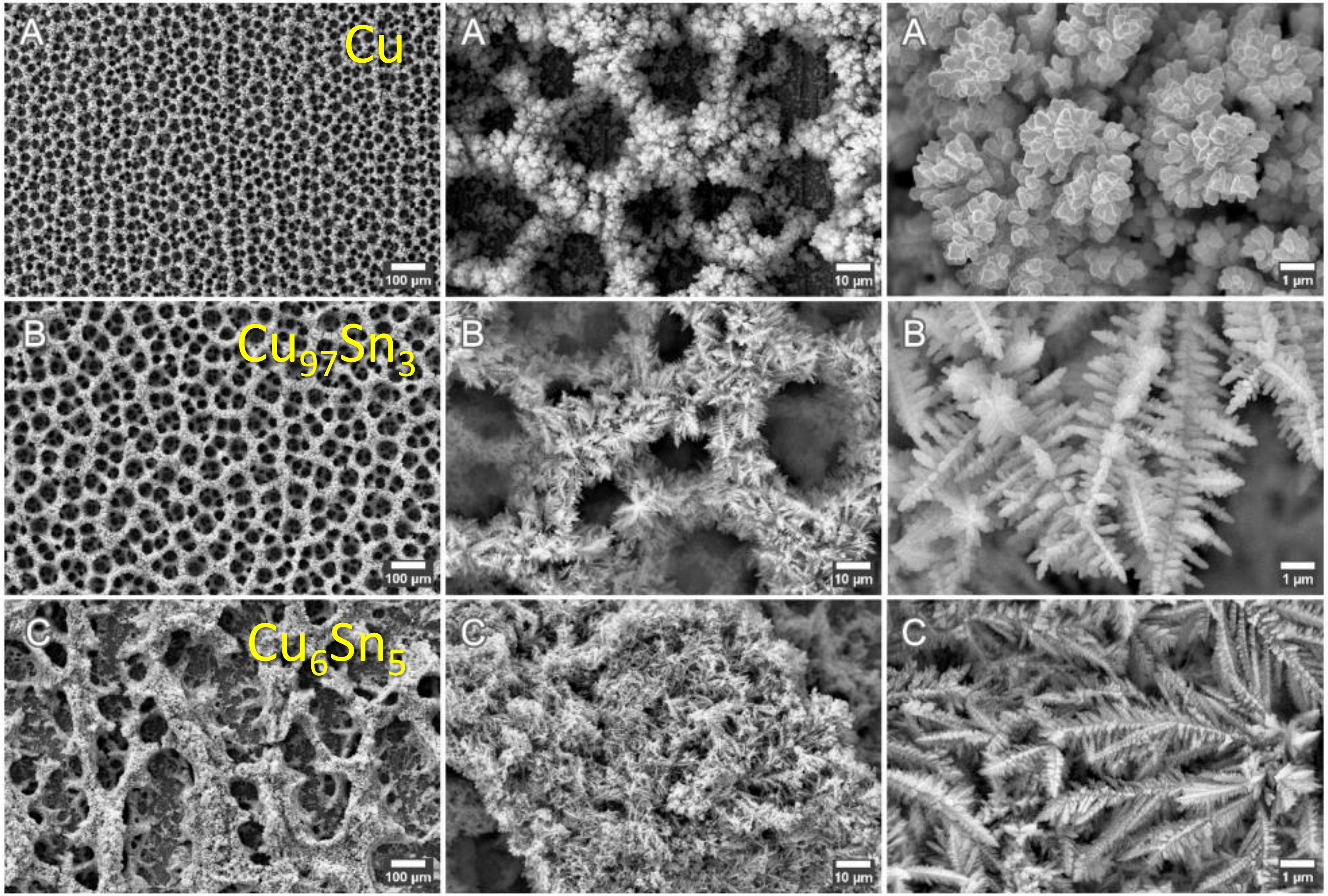


Ag foam

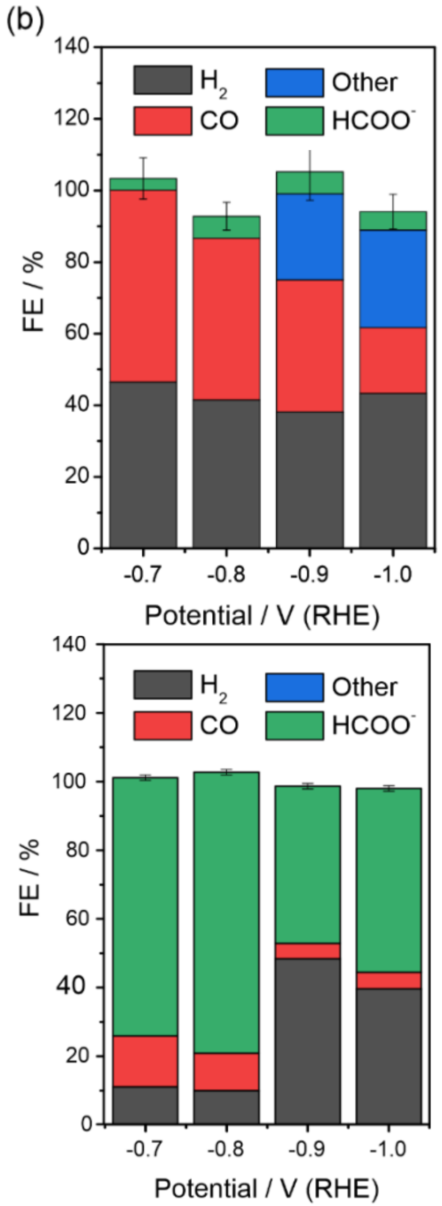


https://doi.org/10.1002/cctc.202001145

Templating via H_2 bubbles during HER



SEM images of Cu (A), $Cu_{97}Sn_3$ (B) and Cu_6Sn_5 (C) foams.



Спасибо за внимание!

Контакты: Виктория Андреевна Никитина
Старший преподаватель
Сколковский институт науки и технологий
Центр энергетических технологий
Моб. +7(926)3742677
e-mail: v.nikitina@skoltech.ru
Большой бульвар 30с1, 121205
Москва, Россия