Exercise: Electroplating of bronze (total of 8pts / capped at 6pts)

Copper and tin can be codeposited in alkaline or acidic aqueous electrolytes, from $CuSO_4$ and $SnSO_4$ salts, to yield bronze electrodeposits.

1) On the following Pourbaix diagrams, and for $[CuSO_4] = [SnSO_4] = 10^{-2}$ mol.L^{-1}, draw the E-pH regions where Cu and Sn can be electrodeposited individually (alkaline and/or acidic conditions):

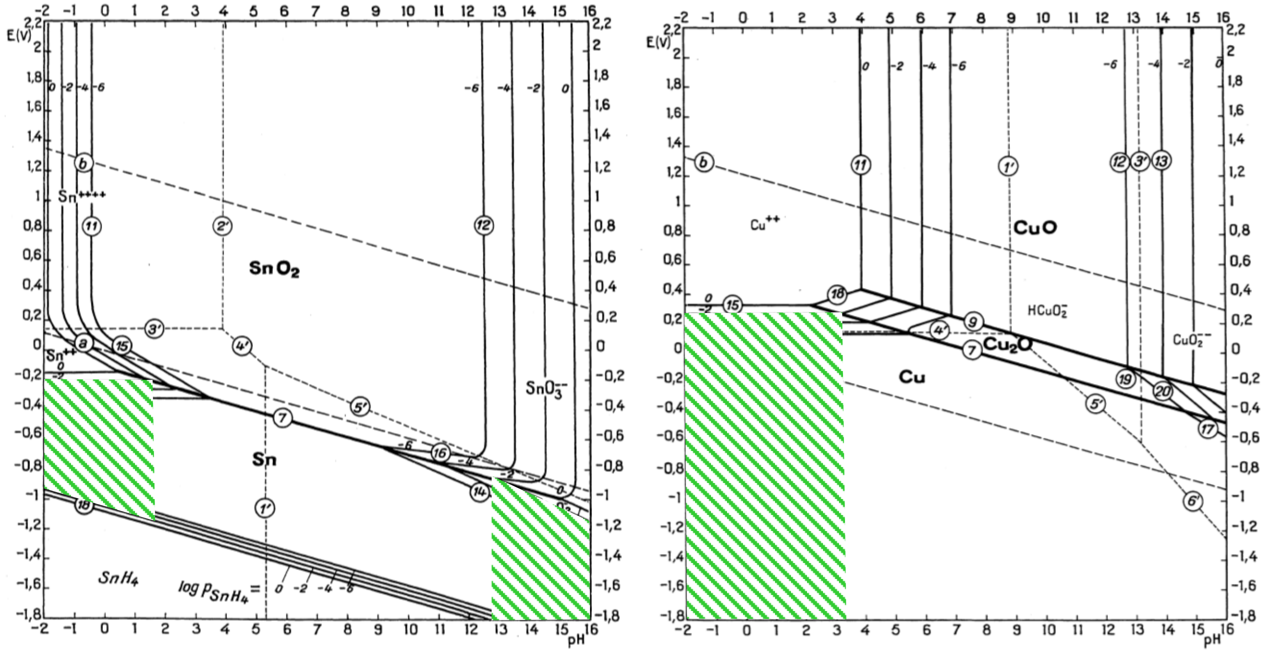

Figure 1: Potential-pH equilibrium diagrams for the systems tin-water (left) and copper-water (right) at 25°C.

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2) Alkaline electroplating of bronze involved the use of cyanide as a complexing agent in order to stabilize the electrolyte. Because of cyanide toxicity, cyanide-free acidic aqueous baths were developed. Indicate the role of each constituent of the following formulation:

Compound	Type	Role	
$CuSO_4$	Metal salt	Cu^{+II} initial supply	/0.25pt
$SnSO_4$	Metal salt	Sn^{+II} initial supply	/0.25pt
H_2SO_4	Acid	pH adjustment	/0.25pt
Sodium gluconate	Complexing agent	Stabilization of Cu^{+II} and Sn^{+II}	/0.25pt
Hydroquinone	Antioxidant Suppresses $Sn^{II} \rightharpoonup Sn^{IV}$	Prevents the precipitation of SnO_2 Improves the faradaic efficiency	/0.25pt
Na_2SO_4	Supporting electrolyte	Increase the ionic conductivity of the electrolyte	/0.25pt
2-Mercaptobenzothiazole	‘Leveler’	Achieves a more uniform current density even on complex substrate geometries	/0.25pt
Polydipropyl sulfonate	‘Brightener’	Decreases the crystallite size and roughness and improves the brightness and hardness of the deposit	/0.25pt

/2pts

3) Prior to each experiment, electrolytes were degassed with a pure argon stream for 30 minutes. What is the action of the argon stream and why is that important?

The argon stream removes dissolved O_2 from the aqueous media. It improves the cathodic efficiency by suppressing the parasitic reactions that involve O_2.

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4) A rotating disk electrode (RDE) was used as working electrode and the cathodic behavior of three electrolytes (individual cations Cu (curve 2, solution B) and Sn (curve 3, solution C) and mixed cations (curve 1, solution A)) was investigated by linear scan voltammetry.

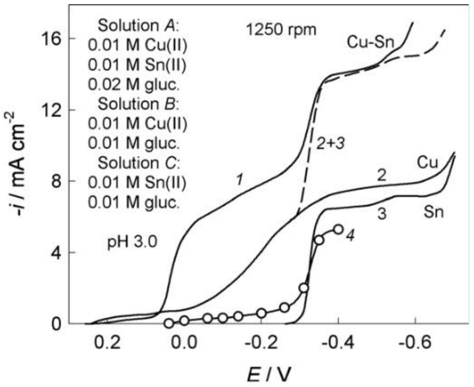

Figure 2: Experimental voltammograms obtained at 1250 rpm for solution A (curve 1), solution B (curve 2) and solution C (curve 3). The dashed line represents the sum of individual voltammograms 2 and 3.

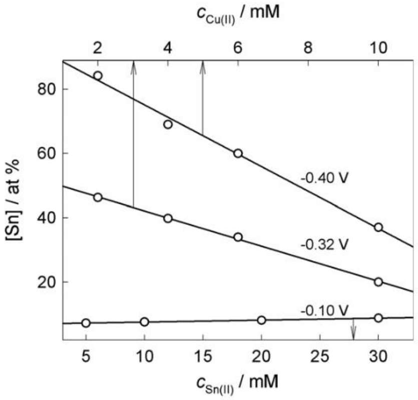

Figure 3: Amount of tin in Cu–Sn coatings (XPS data). Yellow bronze was deposited at −0.10 V in the solutions containing 0.01 M of Cu(II) and different [Sn^{+II}] and white bronze was obtained at −0.32 and −0.4 V for solutions containing 0.01 M of Sn(II) and different [Cu^{+II}].

4.1. Write the Cu plating reaction:

$Cu^{2+} + 2e^- \rightarrow Cu^0$ or $CuL_x{}^{(2-x)+} + 2e^- \rightarrow Cu^0 + xL^-$ (both answers are counted as valid)

/0.25pt

4.2. Write the Sn plating reaction:

$Sn^{2+} + 2e^- \rightarrow Sn^0$ or $SnL_x{}^{(2-x)+} + 2e^- \rightarrow Sn^0 + xL^-$ (both answers are counted as valid)

/0.25pt

4.3. What can you say from the difference in shape of the cathodic curves (2) and (3):

The cathodic curve for copper shows a slower kinetic/smaller exchange current density than that of tin. In addition, the Cu^{2+} reduction wave is preceded by a small shoulder (0.2 to 0 V vs Ag/AgCl) which could be interpreted as the formation of a Cu^+ intermediate state or the surface limited underpotential deposition of copper. More experimental data are needed to identify this mechanism.

/0.25pt

4.4. Identify the main difference between the summed curve (2+3) and measured curve (1) for Cu-Sn codeposition. How would you explain it? Support your answer with the composition analyses (Figure 3).

The main difference between the summed curve (2+3) and the measured curve (1) for mixed Cu and Sn reduction is in the first cathodic wave (0 to -0.26 V vs Ag/AgCl). The codeposition of Cu and Sn starts at a lower overpotential than individual compounds which may be linked to either a direct codeposition mechanism or the underpotential deposition of Sn on Cu. Composition analyses show that deposits are always Cu-rich in this region even when Sn^{+II} was largely in excess in the plating bath. This supports that the current onset is due to the contribution of the underpotential deposition of Sn on electrodeposited Cu.

/0.5pt

5) In a mixed Cu^{II}-Sn^{II} electrolyte of equimolar concentrations, the effect of convection on the cathodic voltametric behavior was analyzed by varying the rotation speed of the RDE.
For a RDE, the limiting current density is given by the Levich equation:

$$j_{lim} = 0.620\ zFC°D^{\frac{2}{3}}\nu^{-\frac{1}{6}}\sqrt{\omega}$$

Where z is the number of exchanged electrons, F = 96485 $C.mol^{-1}$ is the Faraday constant, C° ***(mol.cm^{-3})*** is the bulk concentration of the cation, D ($cm^2.s^{-1}$) is the diffusion coefficient of the cation, ν ($cm^2.s^{-1}$) is the kinematic viscosity of the medium, and ω is the RDE rotation speed in $rad.s^{-1}$.

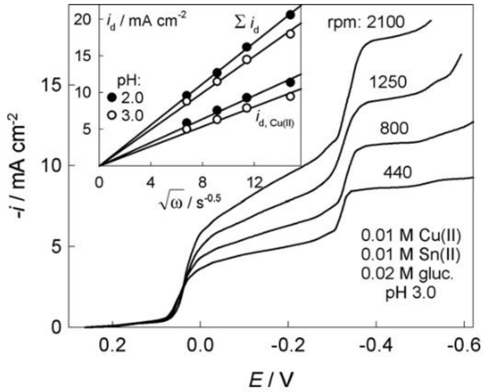

Figure 4: Effect of the intensity of forced convection on cathodic voltammograms. RDE rotating velocity (revper min) is indicated at the curves. Levich plots are shown in the inset. Limiting currents were determined at −0.2 and −0.5 V.

Table 1: Levich slope values at -0.2 and -0.5 V vs Ag/AgCl

	Levich slopes ($mA.s^{1/2}.cm^{-2}$)	
E (V vs Ag/AgCl)	**pH = 3**	**pH = 2**
-0.2	0.673	0.802
-0.5	1.246	1.397

5.1. From the Levich plots (inset), you notice that the current densities recorded at -0.2 V and -0.5 V are proportional to the square root of the RDE rotation speed. What can you conclude?

The electrodeposition of Cu and Sn is limited by mass transfer at both potentials.

/0.25pt

5.2. Explain why the Levich slopes cannot be used directly to determine the diffusion coefficients. What are the 2 corrections that are needed?

The Levich slopes, as calculated from the experimental data, contain the contributions of both cation reductions and parasitic current. In order to calculate the diffusion coefficients, one must take into account the faradaic efficiency and separate the partial currents of Cu and Sn reduction.

/0.5pt

5.3. In order to correct the Levich slope, electrodepositions were performed at -0.2 V vs Ag/AgCl for 10 min. At 2100 rpm and pH = 3, the integration of the current gave a total charge of 6.3 C. The corresponding coating had a total mass of 2.19 mg and a composition of 93 at.% Cu and 7 at.% Sn.

5.3.1. With $M_{Cu} = 63.546\ g.mol^{-1}$ and $M_{Sn} = 118.71\ g.mol^{-1}$, calculate the Faradaic efficiency knowing that the charge is related to the number of moles of product n by the Faraday law $Q = \sum z_i n_i F = \int i.dt$. (Demonstrate your calculation)

$$\eta_F = \frac{2F(n_{Cu}+n_{Sn})}{\int i.dt} \qquad m = m_{Cu} + m_{Sn} = (0.93M_{Cu} + 0.07M_{Sn})(n_{Cu} + n_{Sn})$$

$$\eta_F = \frac{2F}{\int i.dt} x \frac{m}{0.93M_{Cu} + 0.07M_{Sn}} = \frac{2 * 96485 * 2.19x10^{-3}}{6.3 * (0.93 * 63.546 + 0.07 * 118.71)} \approx 0.99514$$

/0.5pt

5.3.2. The Faradaic efficiency was approximated to 99.5%. Correct the Levich slope to calculate the diffusion coefficient of Cu^{II} knowing that the kinematic viscosity of the electrolyte is $1.048 \times 10^{-2}\ cm^2.s^{-1}$. (Demonstrate your calculation)

$$L_{Cu^{+II}}^{pH3} = L^{pH3,-0.2V} * \eta_F * x_{Cu} = 0.673 * 0.995 * 0.93 \approx 0.62276\ mA.s^{\frac{1}{2}}.cm^{-2}$$

$$D_{Cu^{+II}} = \left\{\frac{L_{Cu^{+II}}}{0.620\ zFC^{\circ}\nu^{-\frac{1}{6}}}\right\}^{\frac{3}{2}} = \left\{\frac{0.62276 * 10^{-3}}{0.620 * 2 * 96485 * 10^{-5} * 0.01048^{-\frac{1}{6}}}\right\}^{\frac{3}{2}} \approx 3.8 * 10^{-6}\ cm^2.s^{-1}$$

/0.5pt

5.4. The effective diffusion coefficient for Cu^{II} was 3.8×10^{-6} and $5 \times 10^{-6}\ cm^2.s^{-1}$ at pH 3 and pH 2, respectively. Electroplating at -0.5 V operated at 99.1 % and 98.9 % efficiency at pH 3 and pH 2, respectively. Correct the Levich slopes to calculate the diffusion coefficient of Sn^{II} at both pH values. (Demonstrate your calculation)

Here is the fast way of doing it but one can also first substract the contribution of Cu^{II} to the Levich coefficient.

$$L * \eta_F = 0.620\ F\nu^{-\frac{1}{6}} * \left(2[Cu^{II}]D_{Cu}^{\frac{2}{3}} + 2[Sn^{II}]D_{Sn}^{\frac{2}{3}}\right) = 0.620 * 96485 * \ 0.01048^{-\frac{1}{6}} * 2 * 10^{-5}\left(D_{Cu}^{\frac{2}{3}} + D_{Sn}^{\frac{2}{3}}\right)$$

$$D_{Sn} = \left\{\frac{L * \eta_F}{0.620 * 96485 * \ 0.01048^{-\frac{1}{6}} * 2 * 10^{-5}} - D_{Cu}^{\frac{2}{3}}\right\}^{\frac{3}{2}}$$

$$D_{Sn}^{pH3} = \left\{\frac{1.246 * 10^{-3} * 0.991}{0.620 * 96485 * \ 0.01048^{-\frac{1}{6}} * 2 * 10^{-5}} - (3.8 * 10^{-6})^{\frac{2}{3}}\right\}^{\frac{3}{2}} \approx 3.7016 * 10^{-6}\ cm^2.s^{-1}$$

$$D_{Sn}^{pH2} = \left\{\frac{1.397 * 10^{-3} * 0.989}{0.620 * 96485 * \ 0.01048^{-\frac{1}{6}} * 2 * 10^{-5}} - (5 * 10^{-6})^{\frac{2}{3}}\right\}^{\frac{3}{2}} \approx 3.9012 * 10^{-6}\ cm^2.s^{-1}$$

/1pt

5.5. Keeping the Cu^{+II} concentration at 0.01 mol.L^{-1}, calculate the Sn^{+II} concentration that would produce coatings with 60 at.% Cu at pH 2, -0.5 V, and 1250 rpm (for a diffusion coefficient of Sn^{+II} of 3.9x10^{-6} cm^2.s^{-1}). (Demonstrate your calculation)

$$\frac{n_{Cu}}{n_{Sn}} = \frac{60}{40} = \frac{j_{lim}^{Cu}}{j_{lim}^{Sn}} = \frac{0.620\, z_{Cu} F [Cu^{II}] D_{Cu}^{\frac{2}{3}} \nu^{-\frac{1}{6}} \sqrt{\omega}}{0.620\, z_{Sn} F [Sn^{II}] D_{Sn}^{\frac{2}{3}} \nu^{-\frac{1}{6}} \sqrt{\omega}} = \frac{[Cu^{II}]}{[Sn^{II}]} \left(\frac{D_{Cu}}{D_{Sn}}\right)^{\frac{2}{3}}$$

$$[Sn^{II}] = \frac{n_{Sn}}{n_{Cu}} * [Cu^{II}] * \left(\frac{D_{Cu}}{D_{Sn}}\right)^{\frac{2}{3}} = \frac{40}{60} * 10^{-5} * \left(\frac{5 * 10^{-6}}{3.9 * 10^{-6}}\right)^{\frac{2}{3}} \approx 7.868 * 10^{-6}\, mol.cm^{-3} \equiv 7.868\, mM$$

/0.5pt

Total /8pts

Capped at 6 pts /6pts