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University of Alabama | Chemical and Biological Engineering

THE UNIVERSITY OF ALABAMA RESEARCH

Chemistry Effects on the Electrodeposition of Superconducting Metals and Alloys

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http://eeml.ua.edu

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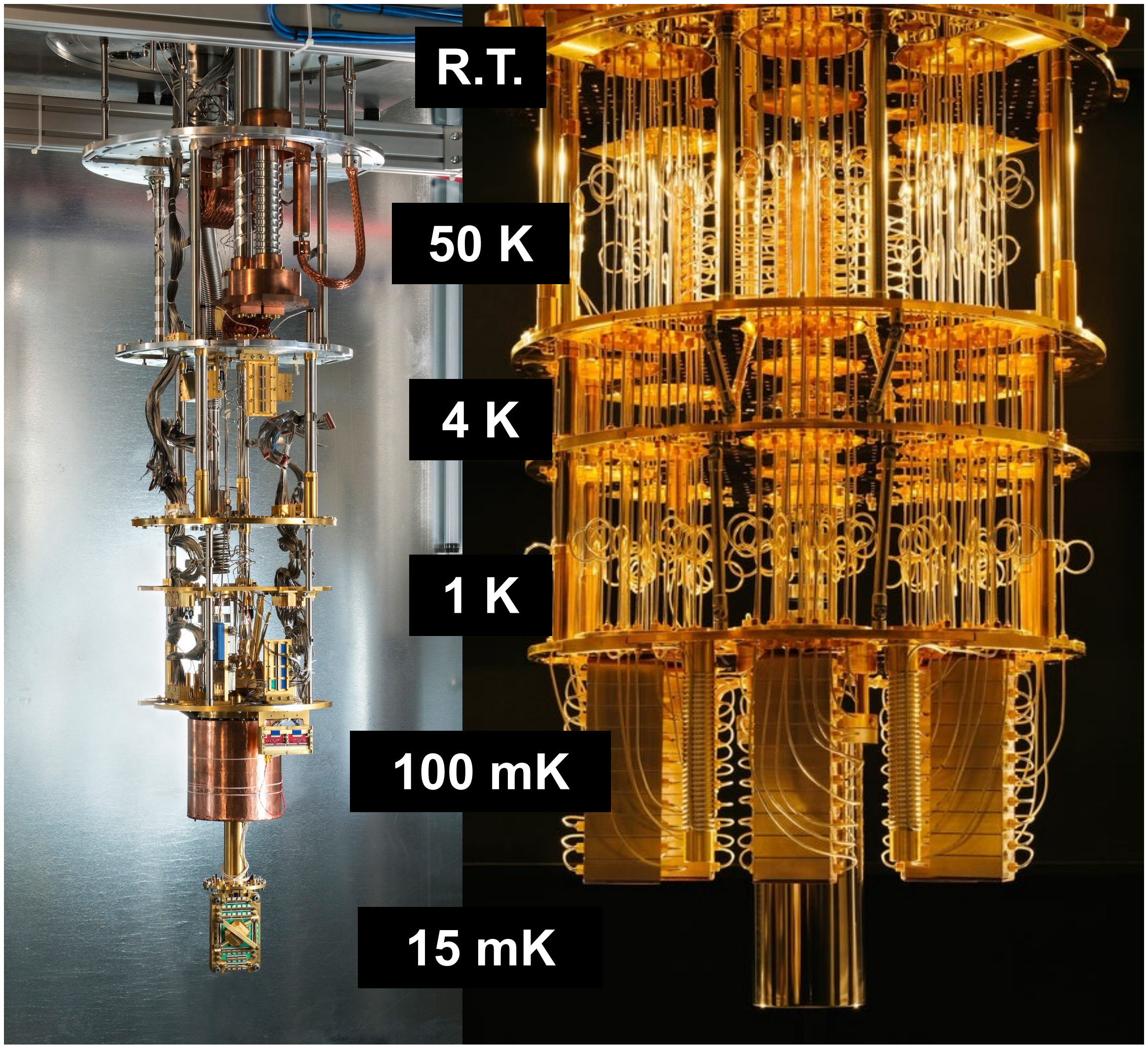
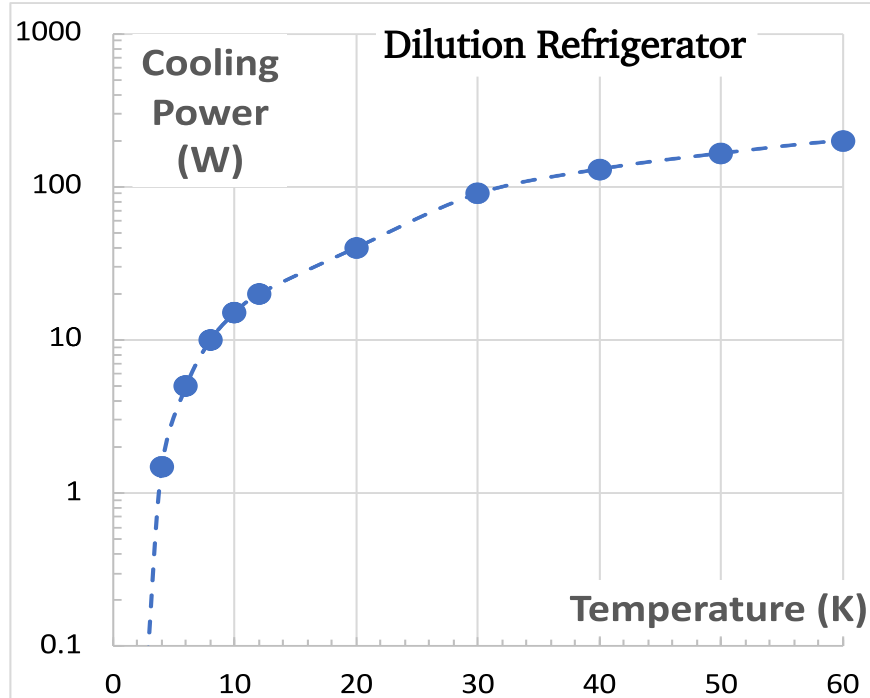
Superconductive Circuits

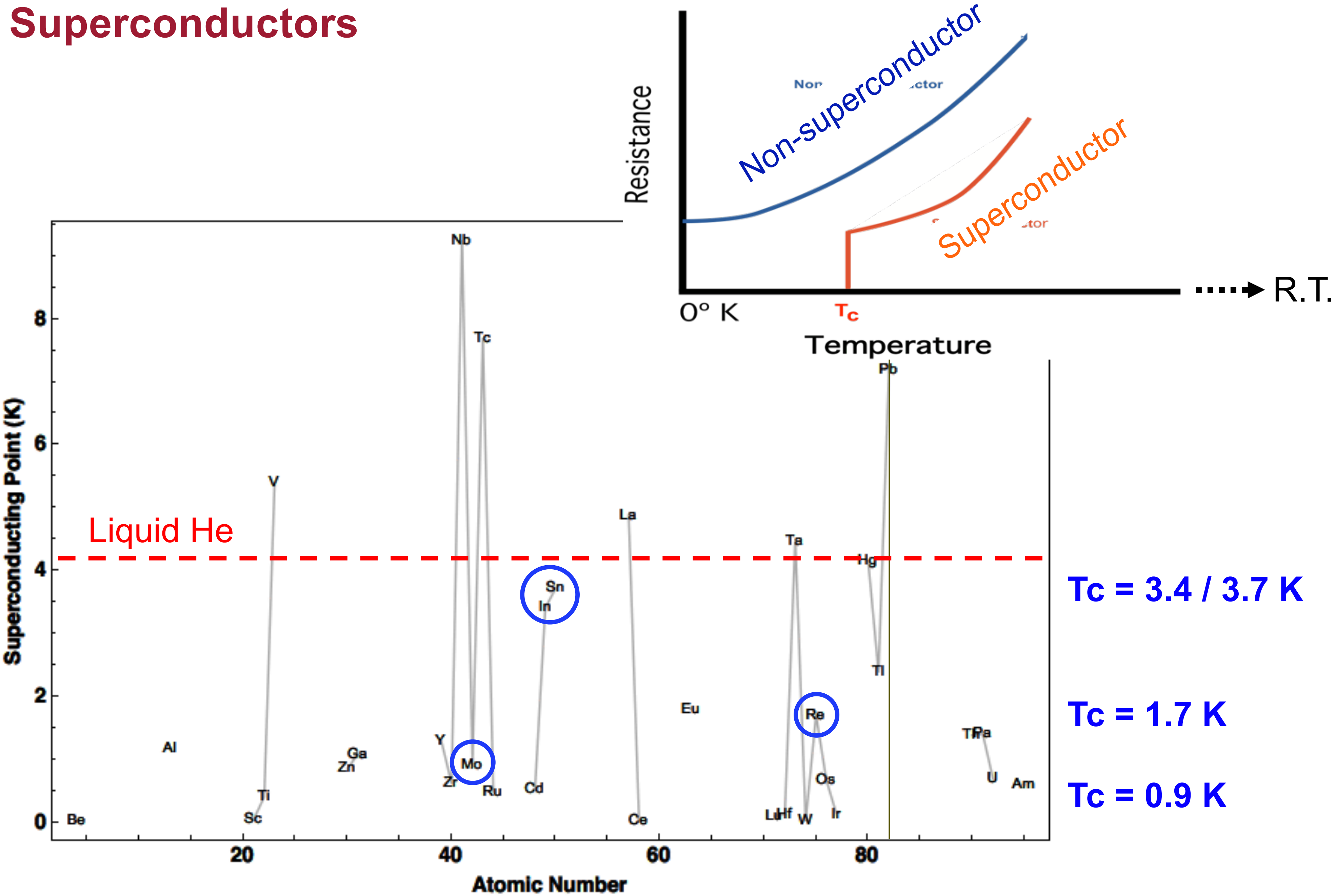




S. W. van Sciver, Helium Cryogenics, 2011.

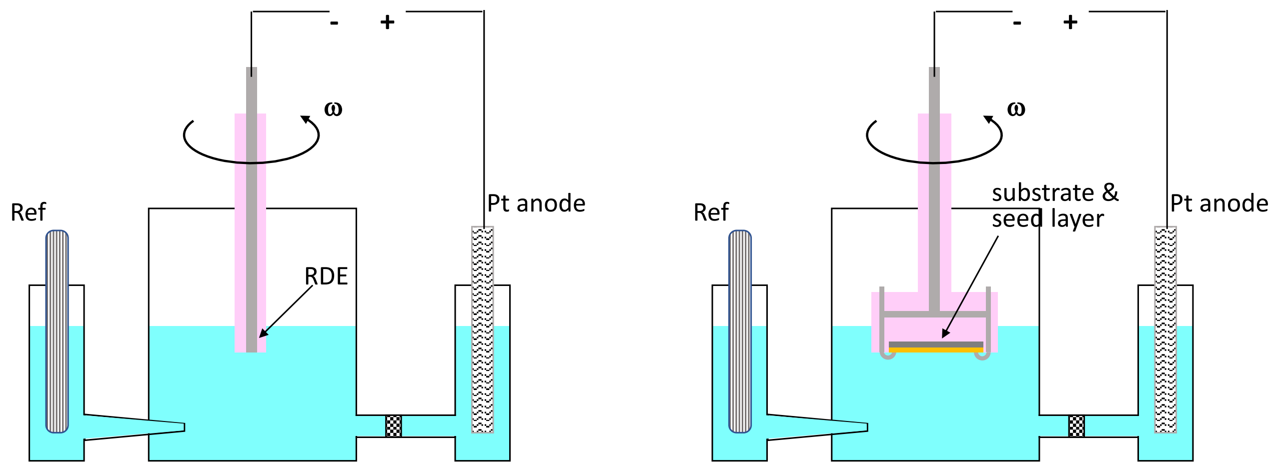
Superconductors with different transition temperatures are needed for applications in different temperature zones.

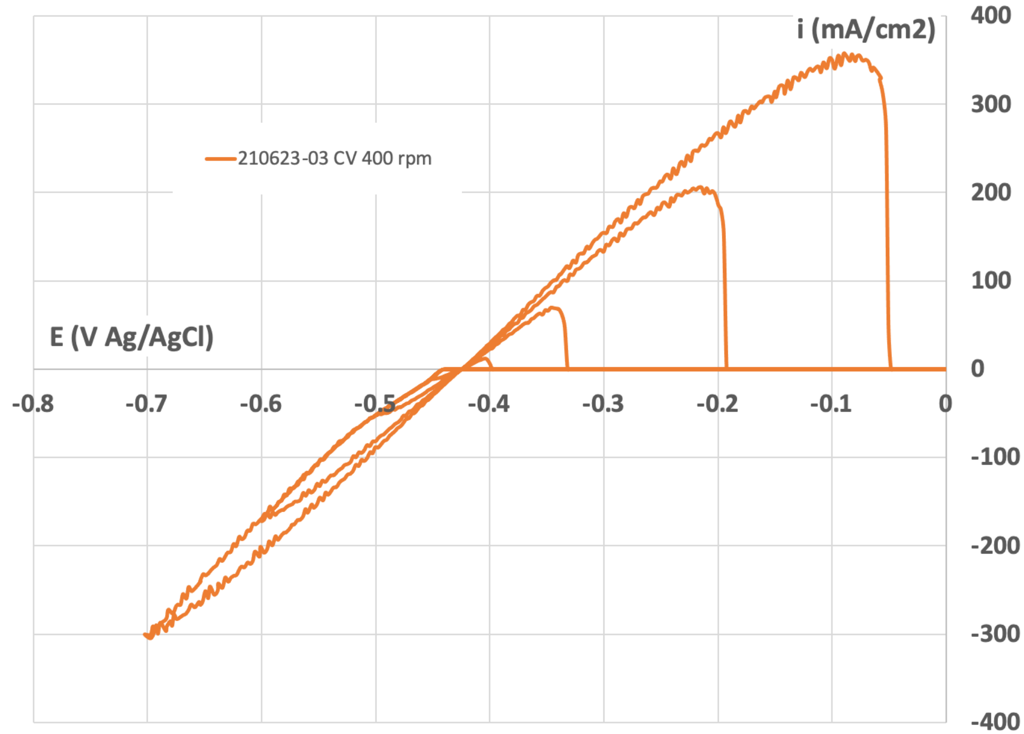
Superconductors



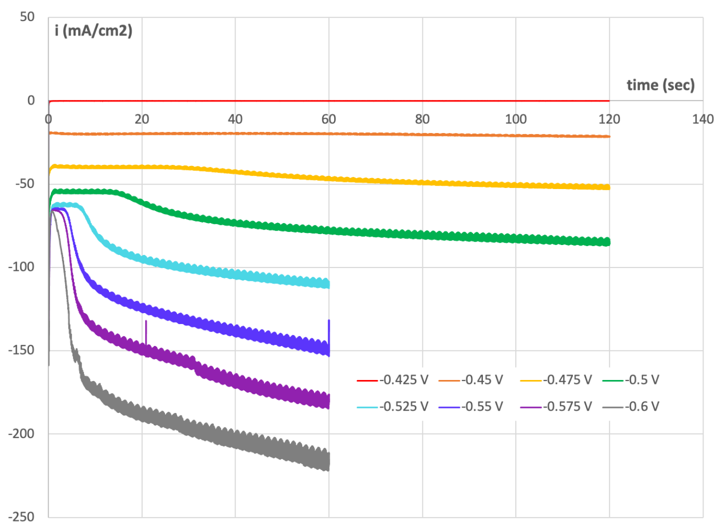
Electrodeposition of Sn

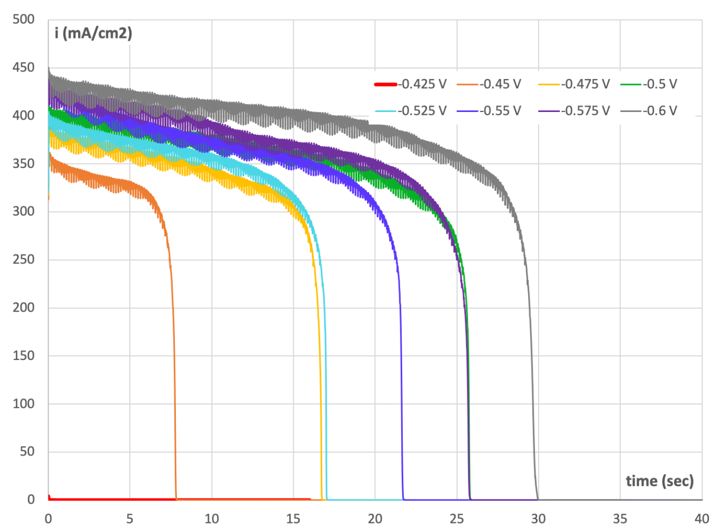
- $SnSO_4$ 0.15 M
- H_2SO_4 1 M
- Organic additives
- Pt RDE
- Sn anode
- Ag/AgCl REF
- Si / SiO_2 / Ti / (100 nm) Au
- Characterization : XRF, SEM, XRD, PPMS

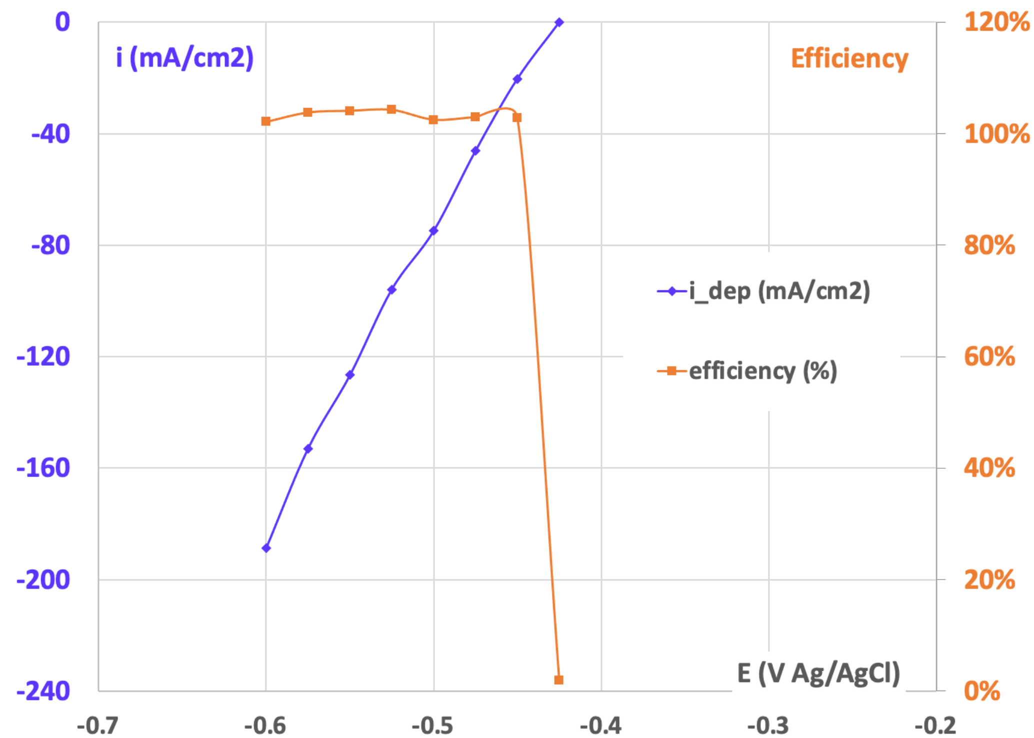




Efficiency of deposition



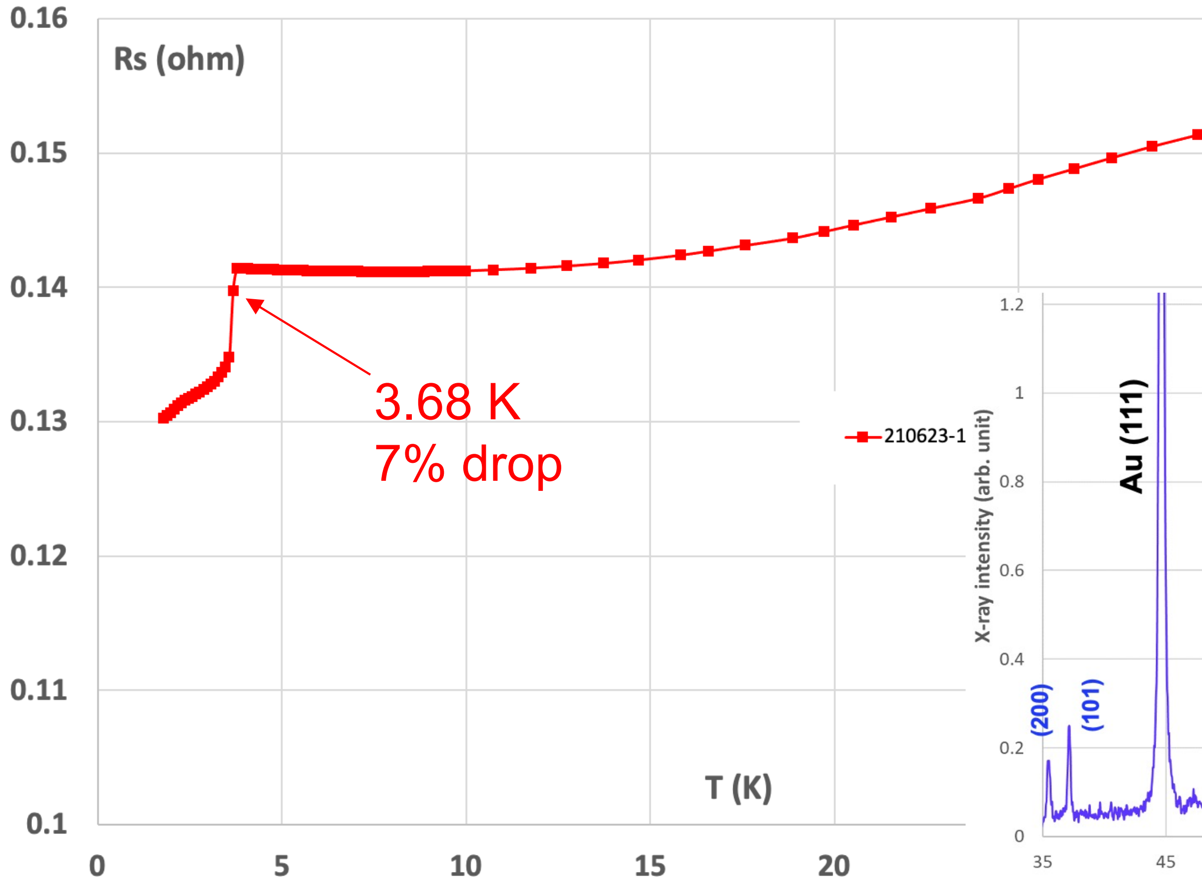


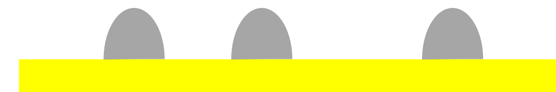


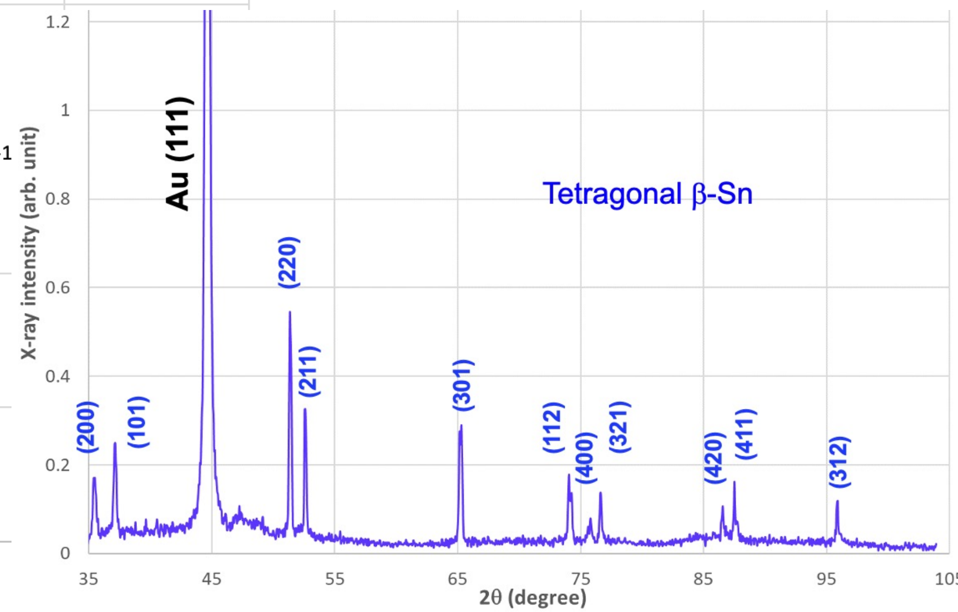
- **Current efficiency of Sn deposition remains at 100% even at high current density up to -200 mA/cm², due to low HER exchange current (on Sn).**
- **Deposition current = deposition rate**

Tc of deposited Sn (on Si/Au pattern)

-50 mA/cm2, “1.5” um Sn



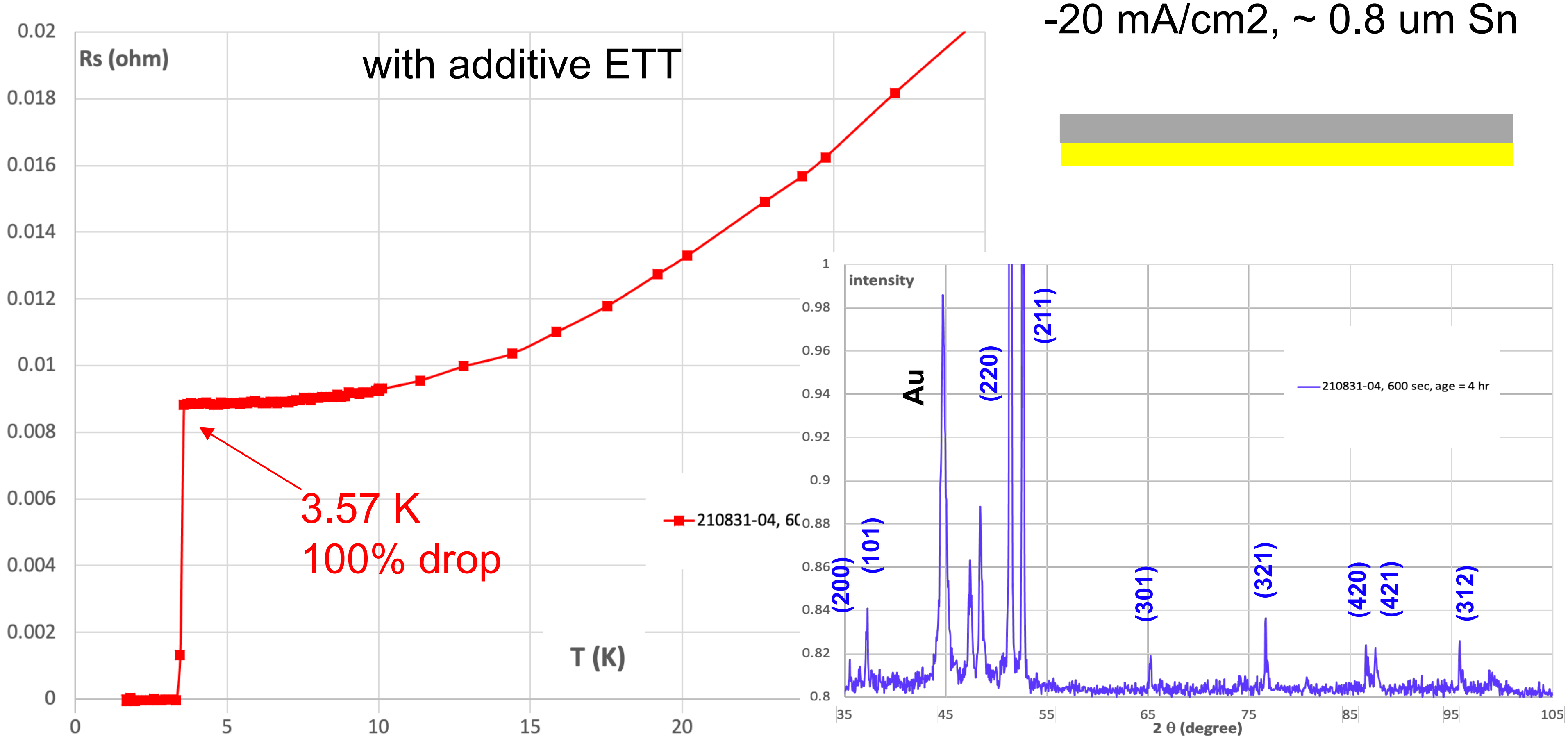




- **Sharp but small (<10%) resistance drop observed at 3.7 K, with a slow transition tail.**
- **The resistance does not drop to 0 – suggesting a non-continuous / non-coalescent Sn film despite of a thickness of 1.5 um.**
- **Tetragonal β-Sn was obtained, with Tc = 3.7 K.**

Tc of deposited Sn with additive ETT (on Si/Au pattern)

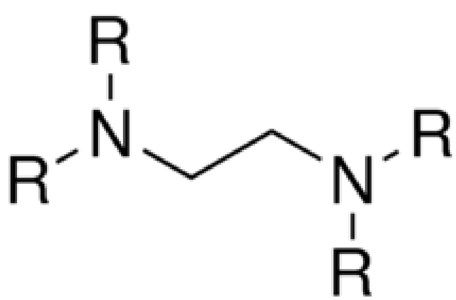
-20 mA/cm2, ~ 0.8 um Sn

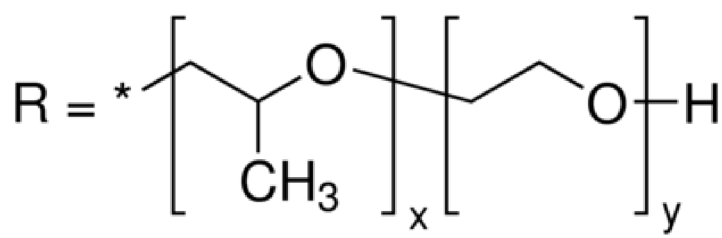


- **Sharp superconducting transition observed at 3.7 K when Sn is deposited with ETT.**
- **A continuous Sn film is deposited with suppressing additives.**

Ethylenediamine tetrakis (propoxylate-block-ethoxylate) tetrol

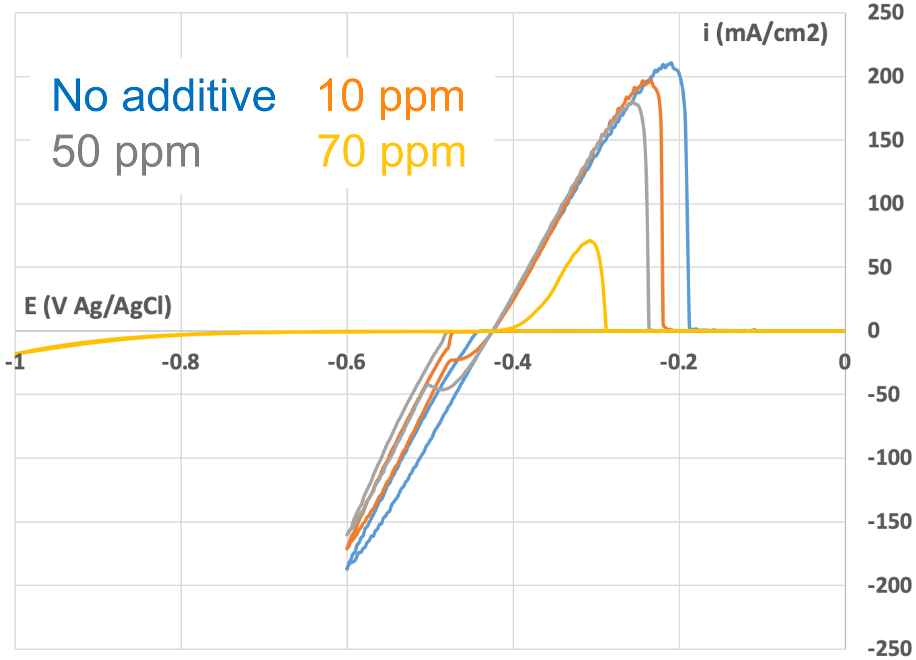
ETT 3600	**ETT 7200**
Average MW = 3,600	Average MW = 7,200
Tetronic 701	Tetronic 90R4
Cloud point 18 C (1wt% aqueous solution)	Cloud point 43 C (1wt% aqueous solution)
More hydrophobic	More hydrophilic

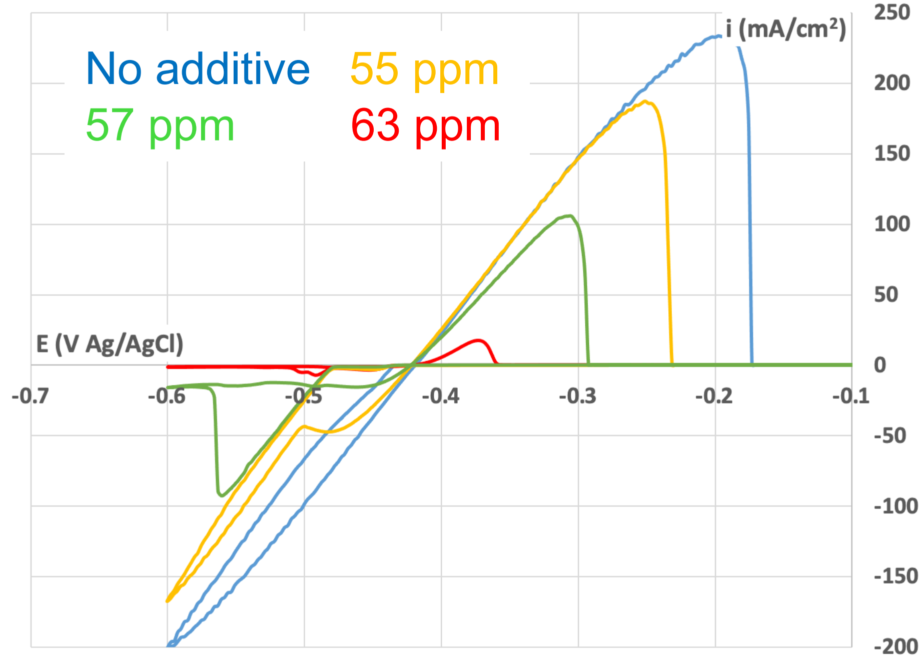




$(PPG)_x$ $(PEG)_y$

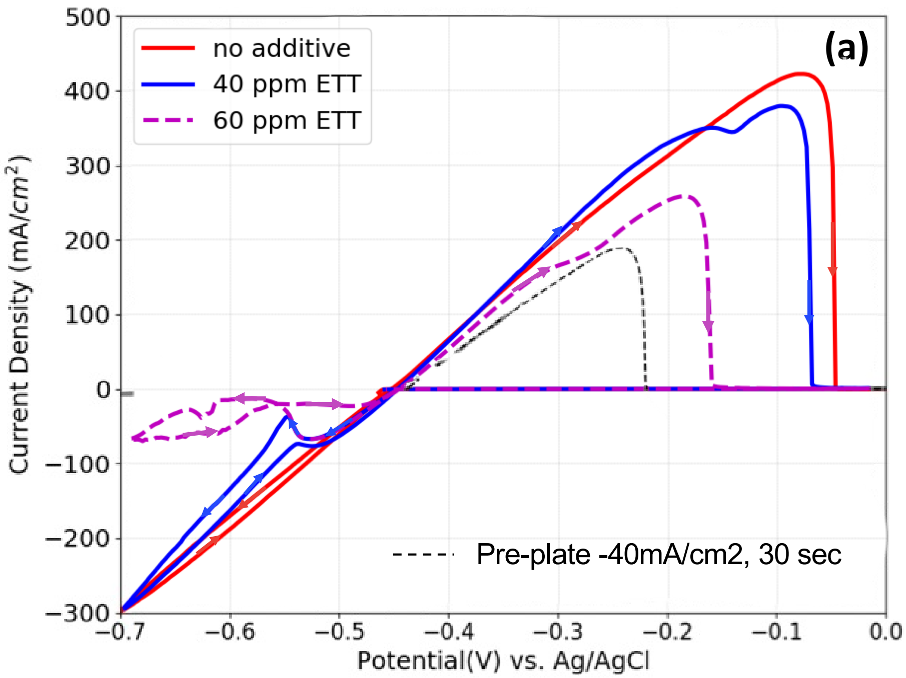
ETT 3600 – concentration effect

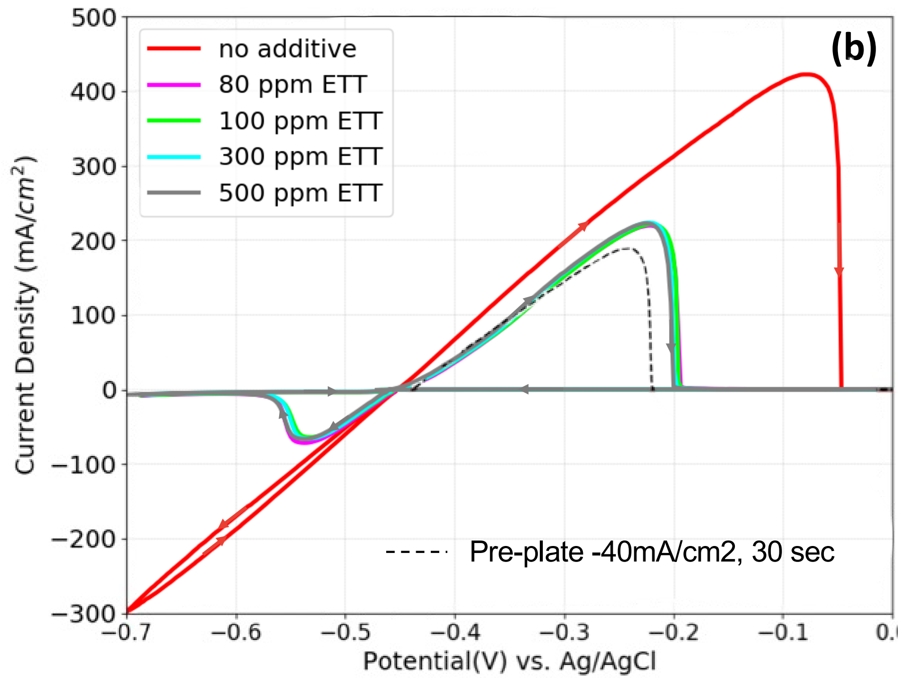




- **ETT 3.6k suppresses Sn deposition, and the suppression saturates at about 60 ppm.**
- **This suppression, when saturated, completely shuts off the Sn deposition.**

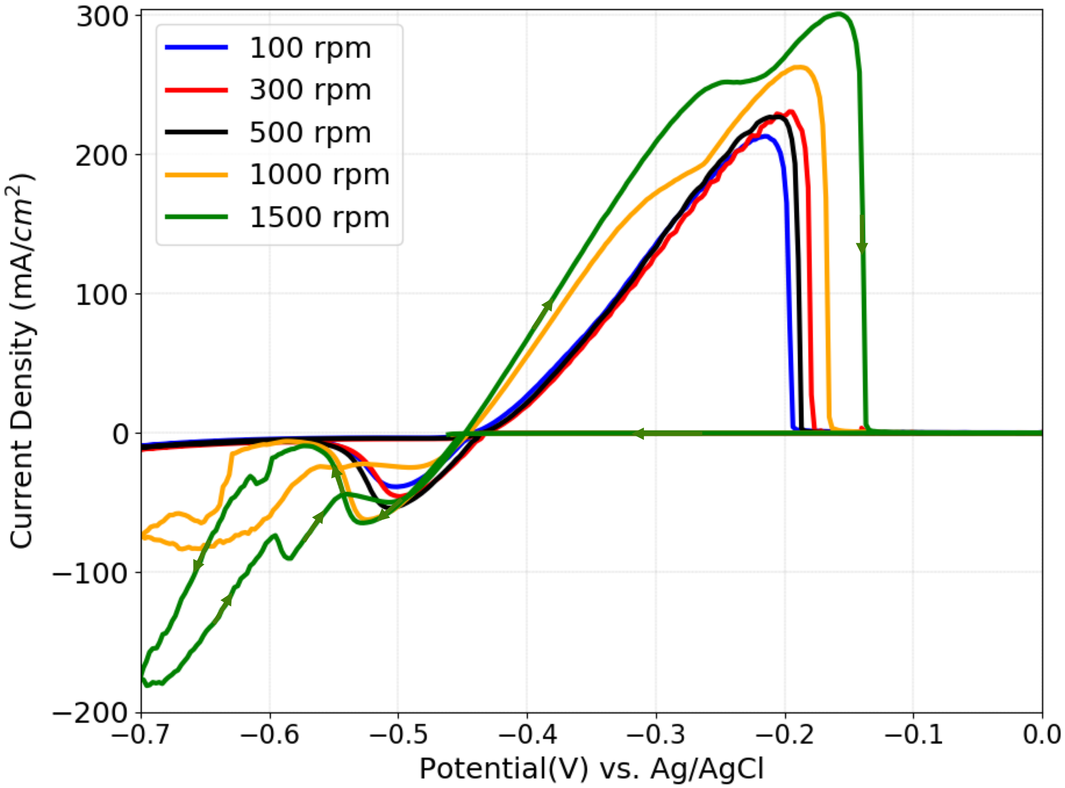
ETT 7200 – concentration effect

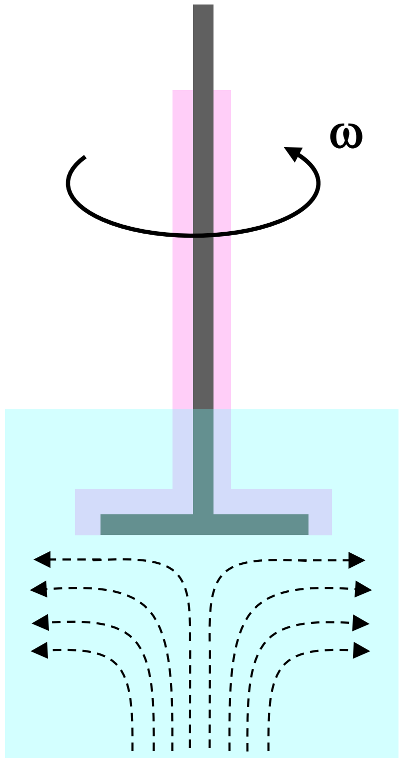




- **ETT 7.2k suppresses Sn deposition, and this suppression saturates at 80 ppm.**
- **Small amount of Sn deposition still occurs with a current peak, even at suppression saturation, suggesting weaker suppression with more hydrophilic additives, despite of higher molecular weight.**

Agitation effect



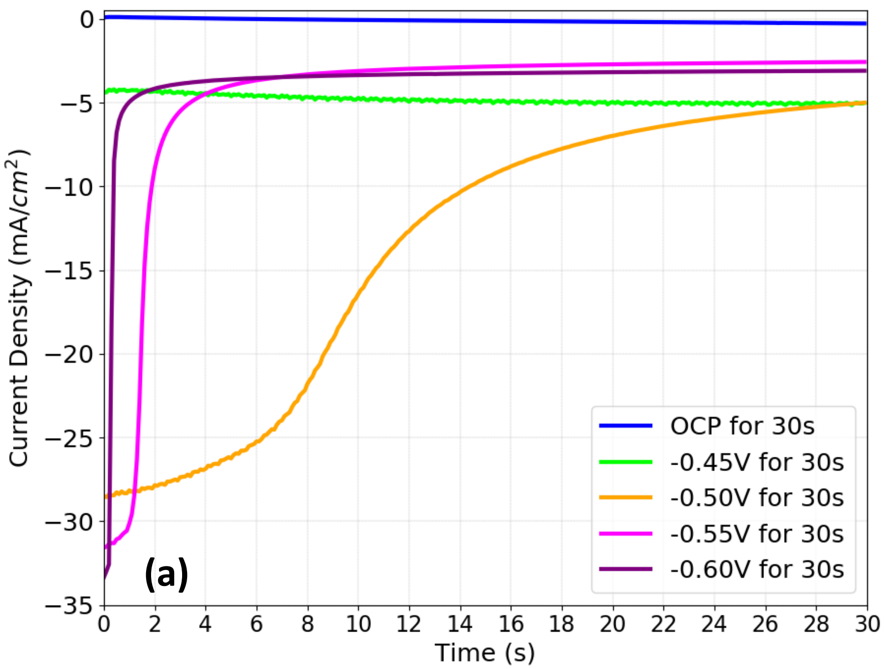


- **Suppression is weakened by stronger agitation.**
- **A weak (physical) adsorption suggested.**
- **Not a diffusion limited process with consumption at surface.**

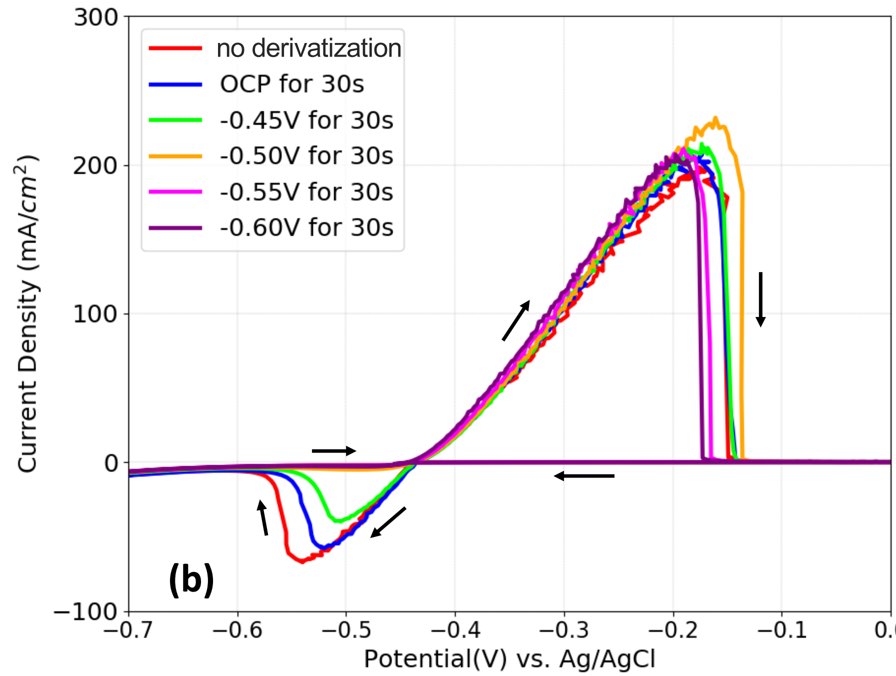
- Y. Hu, et al, *Electrochim. Acta.*, 2022.

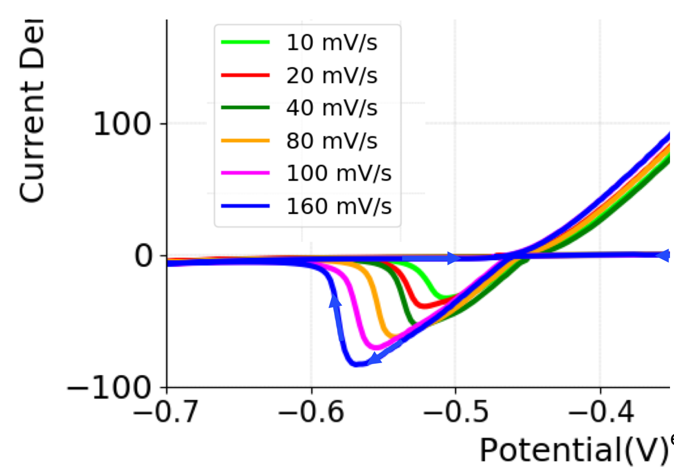
Pre-derivatization study

30 s derivatization at different voltage



CV after derivatization





- **The time-dependent adsorption of ETT is also potential dependent.**
- **The higher current peak at higher scan rate results from both the time effect and potential effect.**

Adsorption rate

- **Langmuir isotherm**

$$\frac{d\theta}{dt} = k_{ad} \cdot (1-\theta) - k_d \cdot \theta$$

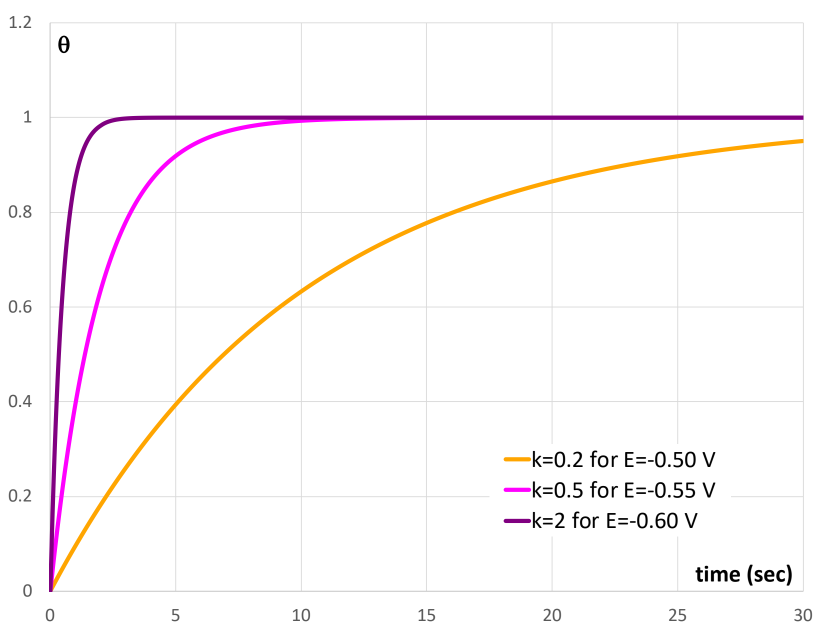
$$\frac{d(1-\theta)}{(1-\theta)} = -k_{ad} \cdot dt$$

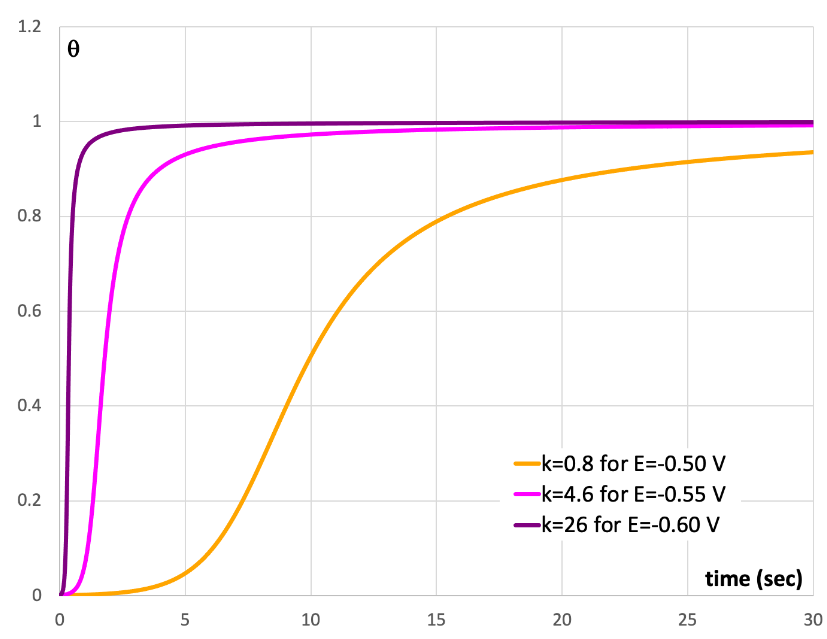
$$\theta = 1 - e^{-k_{ad} \cdot t}$$

- **Coverage dependent**

$$\frac{d\theta}{dt} = k \cdot \theta^m \cdot (1-\theta)^n - desorption$$

- **The S-shape curve suggests dependency on coverage in addition to empty fraction.**



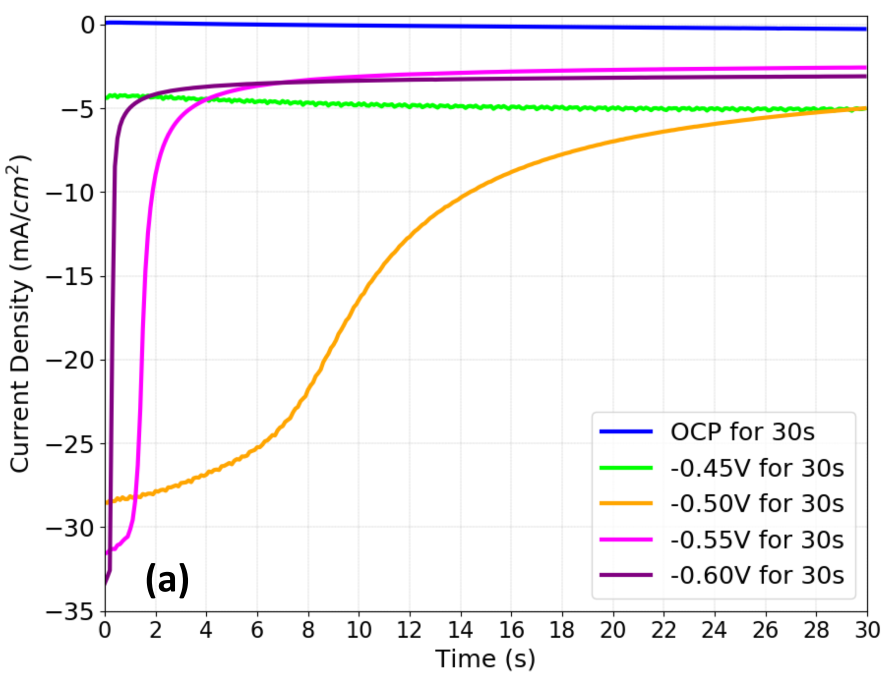


Adsorption rate

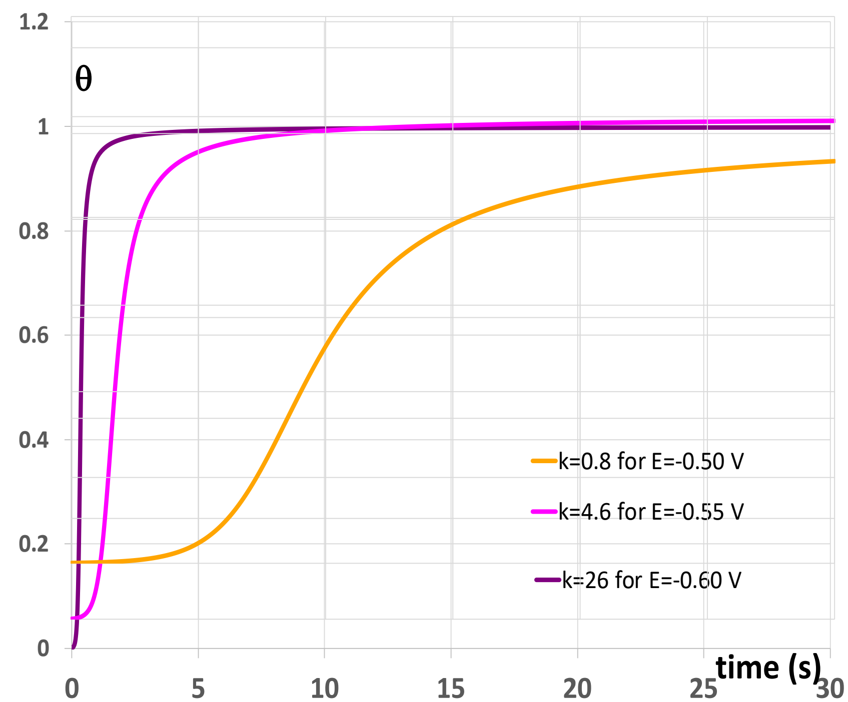
- **Coverage dependent**

$$\frac{d\theta}{dt} = k \cdot \theta^m \cdot (1-\theta)^n - desorption$$

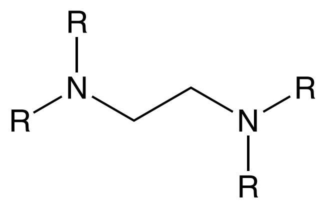
30 s derivatization at different voltage



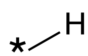
Computed θ with m=1, n=2



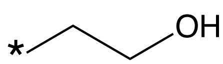
Critical functional groups



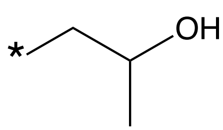
R =



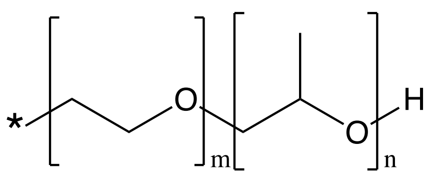
Ethylenediamine



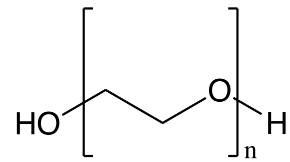
N, N, N', N' - Tetrakis (2-hydroxyethyl) ethylenediamine



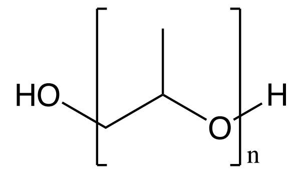
N, N, N', N' - Tetrakis (2-hydroxypropyl) ethylenediamine



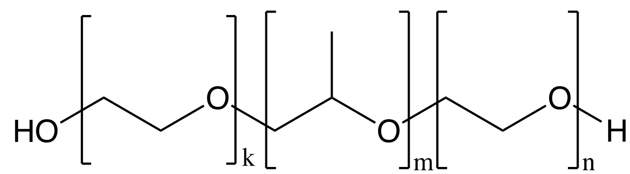
Ethylenediamine tetrakis(ethoxylate-*block*-propoxylate) tetrol (ETT)



Poly(ethylene glycol) (PEG)



Poly(propylene glycol) (PPG)

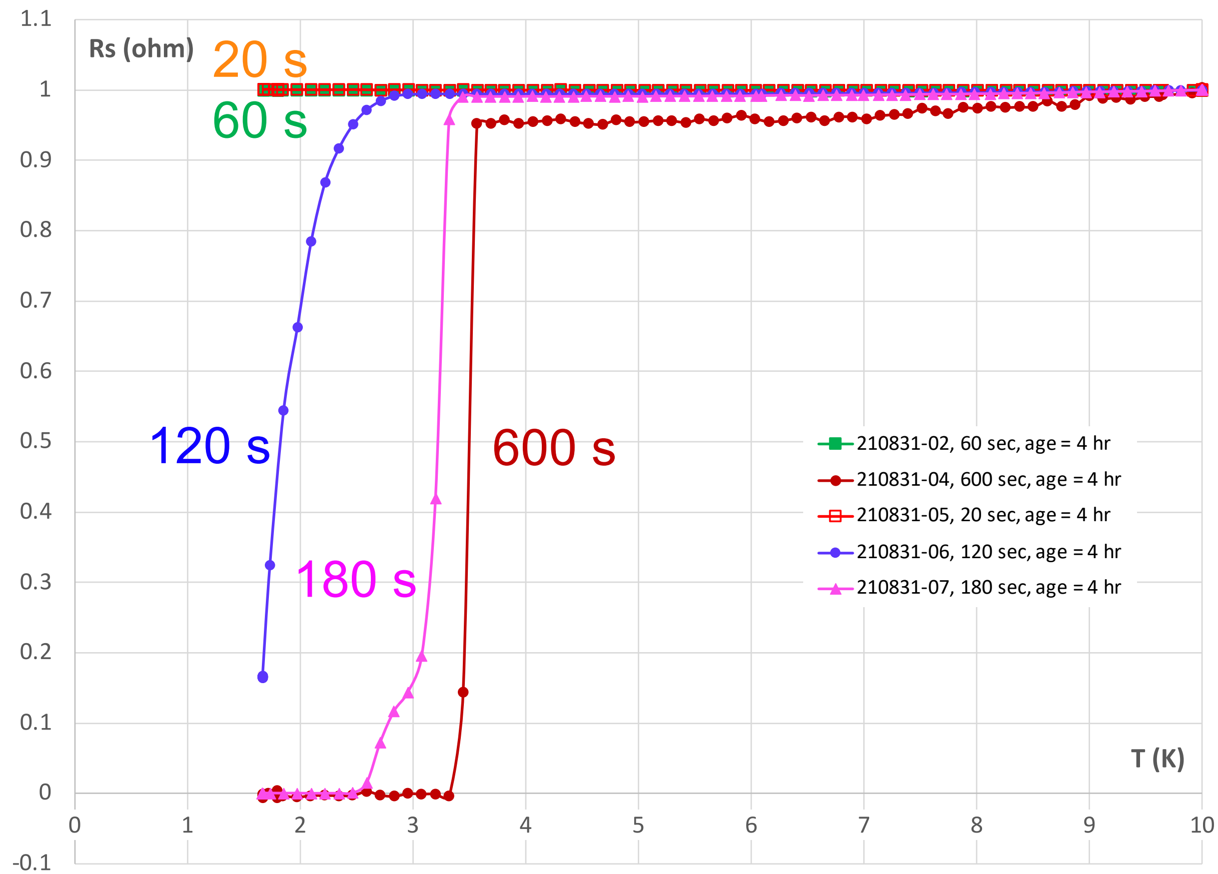


Poly(ethylene glycol) – block – poly(propylene glycol) – block – poly(ethylene glycol) (PEG-PPG-PEG)

- **The polymer branches are the critical groups.**
- **The hydrophobicity and molecular weight strongly impact the suppression effect.**

Film thickness on Superconductivity

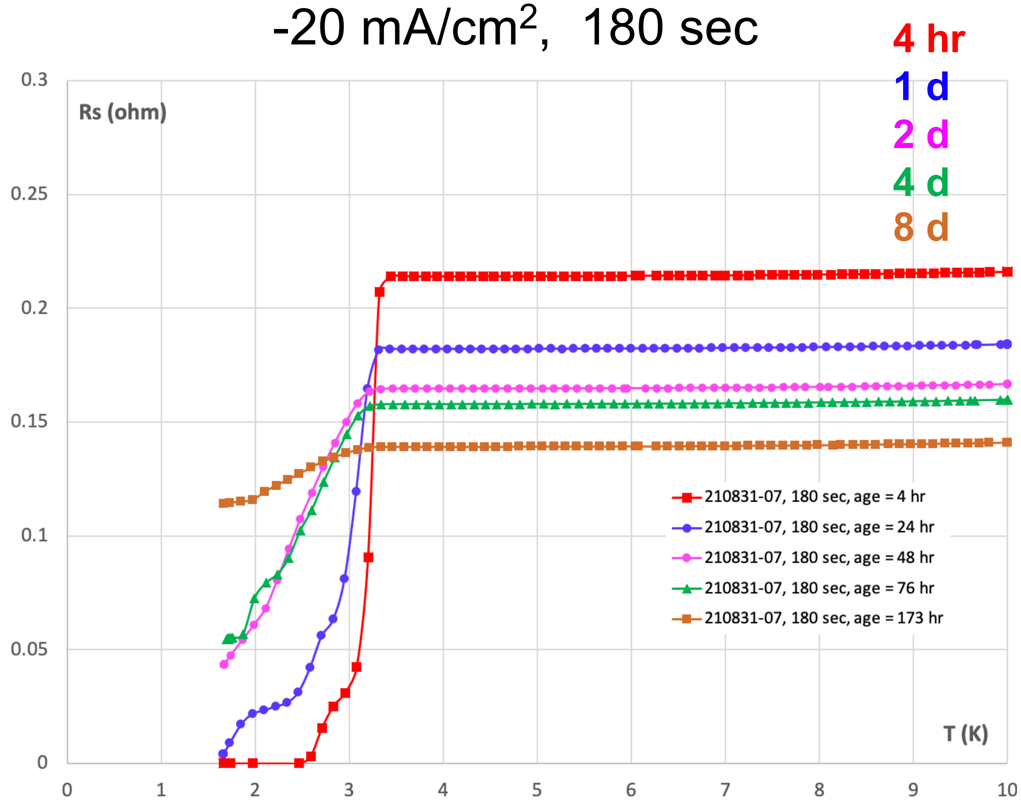
-20 mA/cm^2



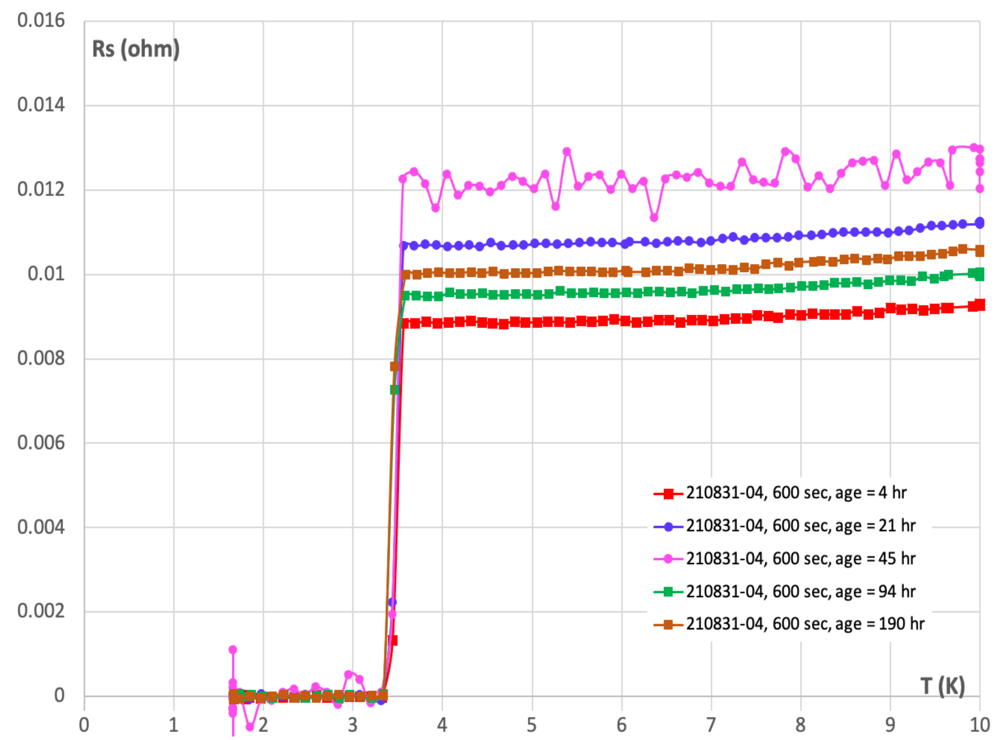
- **The T_c of electrodeposited Sn on Au film decreases as the Sn thickness decreases.**

Film aging on Superconductivity

-20 mA/cm², 180 sec



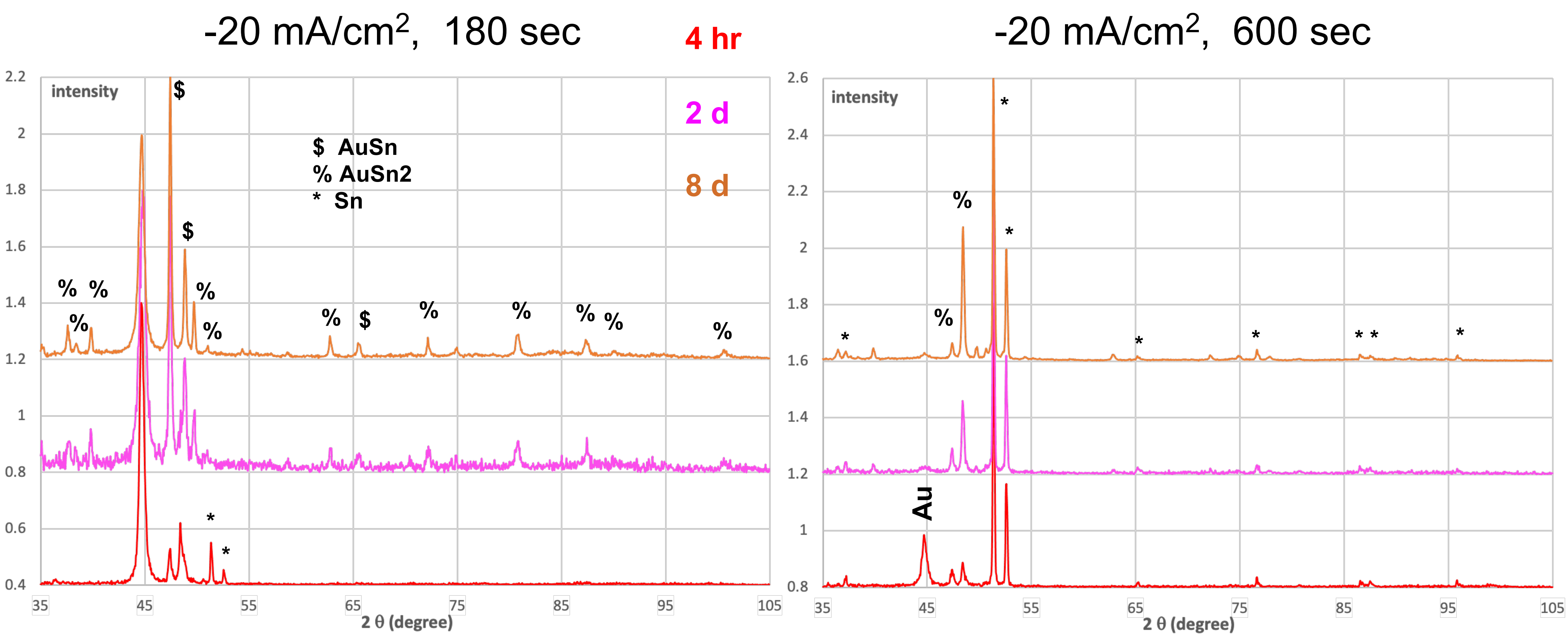
-20 mA/cm², 600 sec



- **The T_c of electrodeposited thin Sn film on Au film decreases as Sn ages.**

- Q. Huang, et al., *in preparation*, 2022.

Sn Film aging on Superconductivity



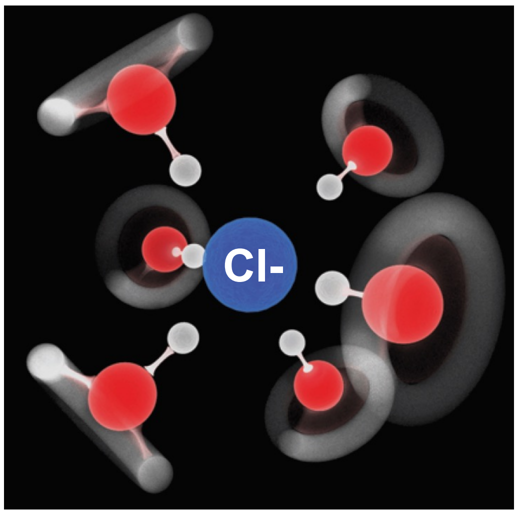
- **No Au peaks observed for 600 sec Sn film after aging – completely consumed.**
- **No tetragonal Sn peak observed for 180 sec Sn film after aging – completely consumed.**
- **Tetragonal Sn still observed for 600 sec Sn after 8-day aging – consistent with the Tc.**

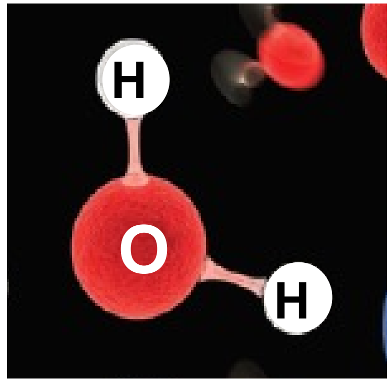
Summary

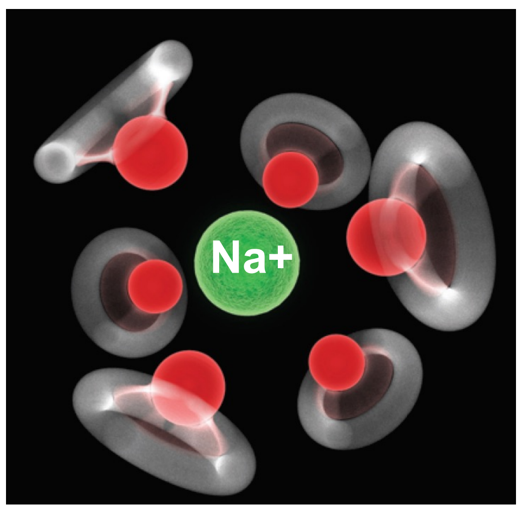
- **Organic additive for Sn electrodeposition to tune the nucleation and growth, as well as the superconducting transition.**
  - Hydrophobicity of additives dominates the adsorption and suppression effect
  - Adsorption dependent on not only the empty fraction but also the covered fraction.
  - Significant interdiffusion between Sn and Au occurs at room temperature, degrading the superconductivity upon aging.

- **Alkaline metal supporting salts and alloying metal cations in Re electrodeposition to tune the hydrogen evolution rate and alloy composition, as well as the superconducting transition.**

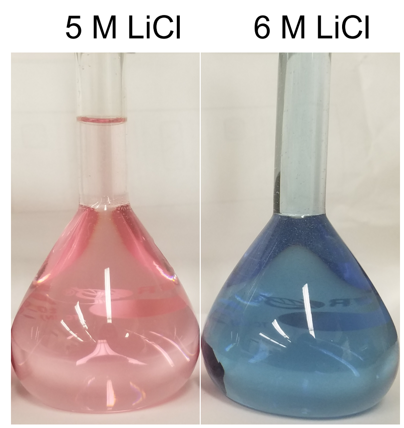
Hydration of Salts

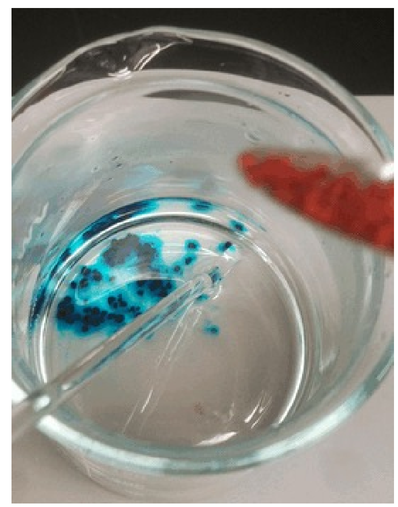




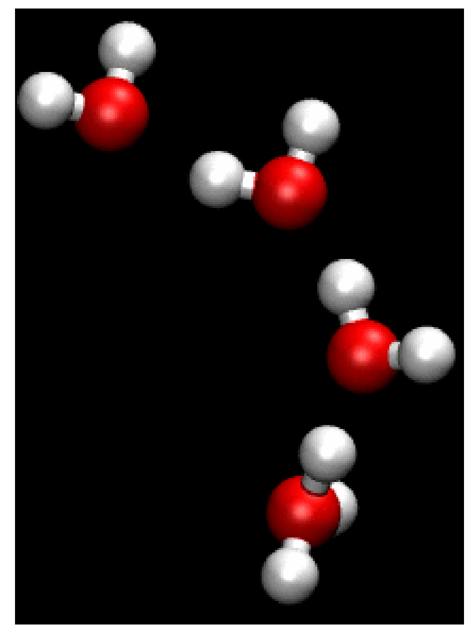


- *Laage et al., J. Phys. Chem. B (2009).*





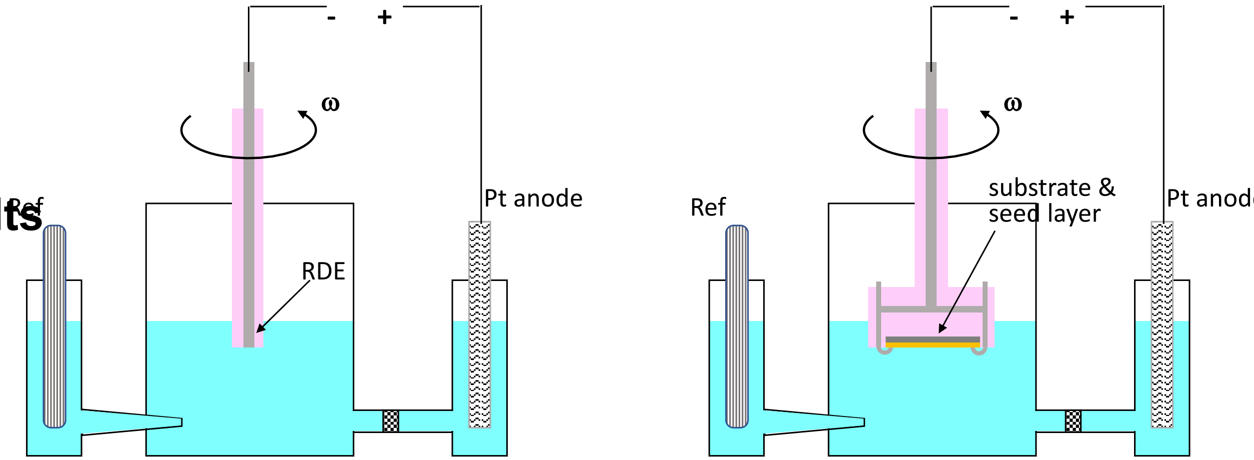
Grotthuss Mechanism
'Proton Jumping'

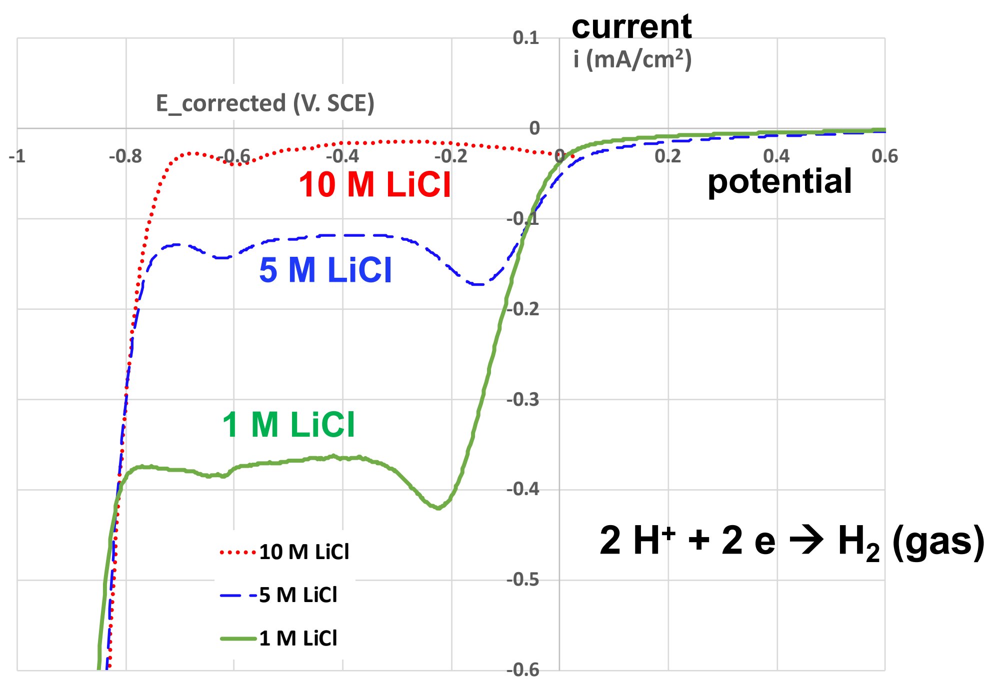


Matt K. Petersen
http://en.wikipedia.org/wiki/Grotthuss_mechanism

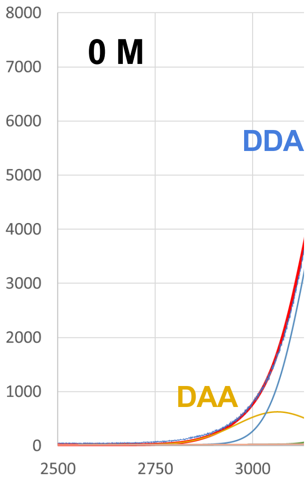
Electrodeposition of Re and alloys

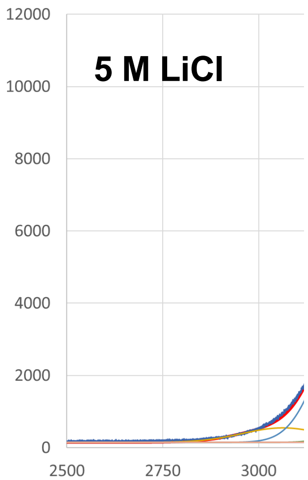
- NH_4ReO_4 0.025 M
- Alloying metal salts
- LiCl or other hydration salts
- Pt RDE
- Pt anode
- Ag/AgCl REF
- Si / SiO_2 / Ti / (100 nm) Au
- Characterization : XRF, SEM, XRD, PPMS, TEM, Raman

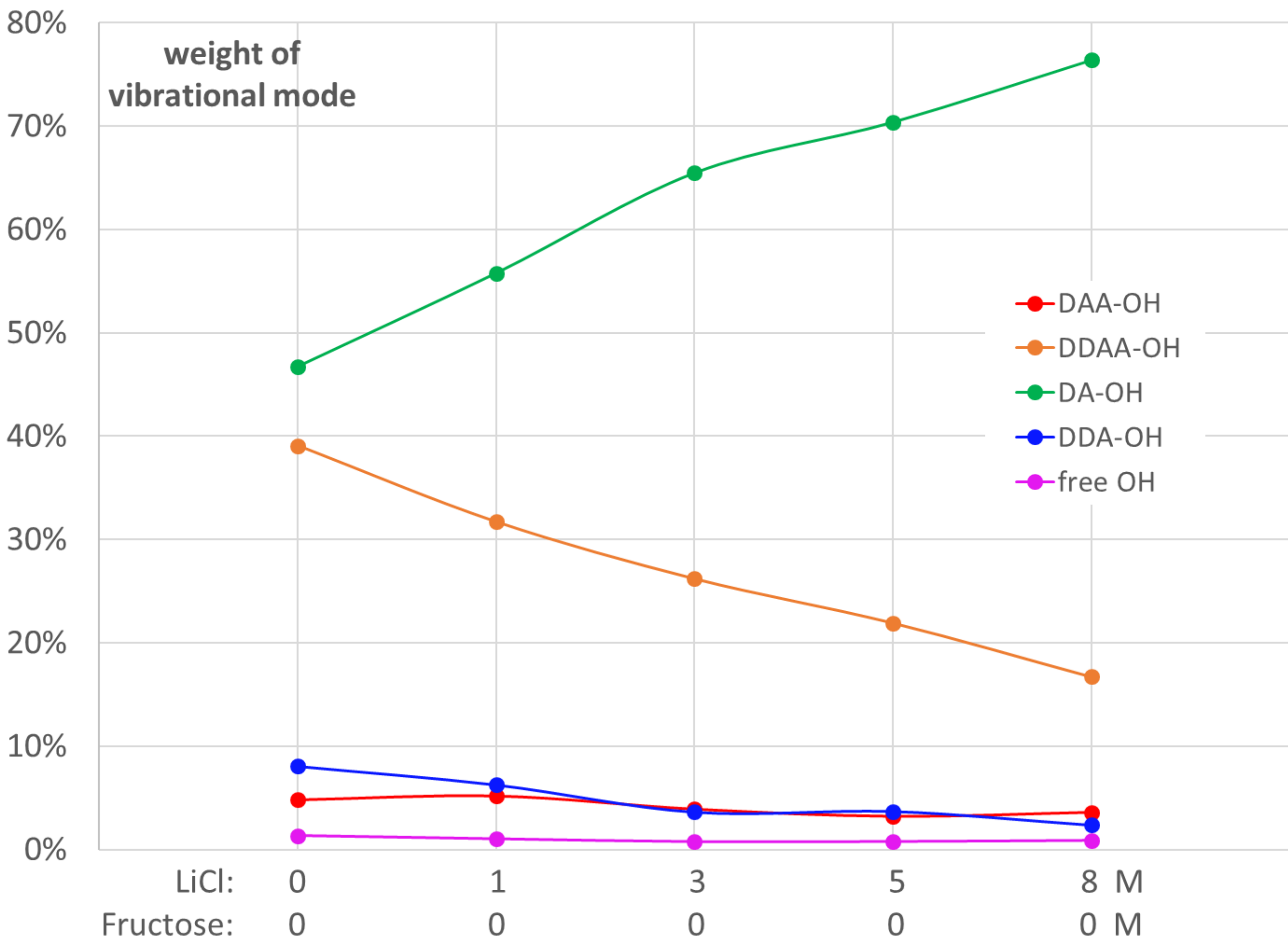


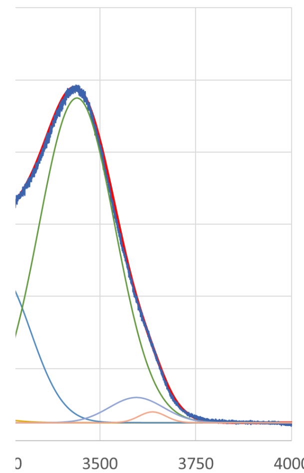


Hydration of LiCl

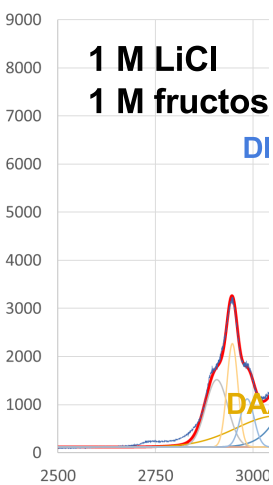


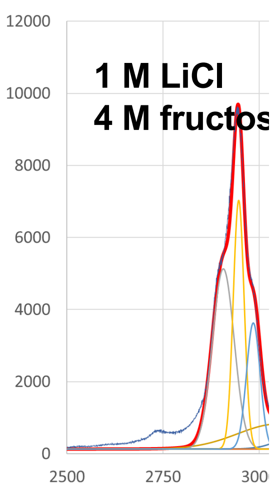


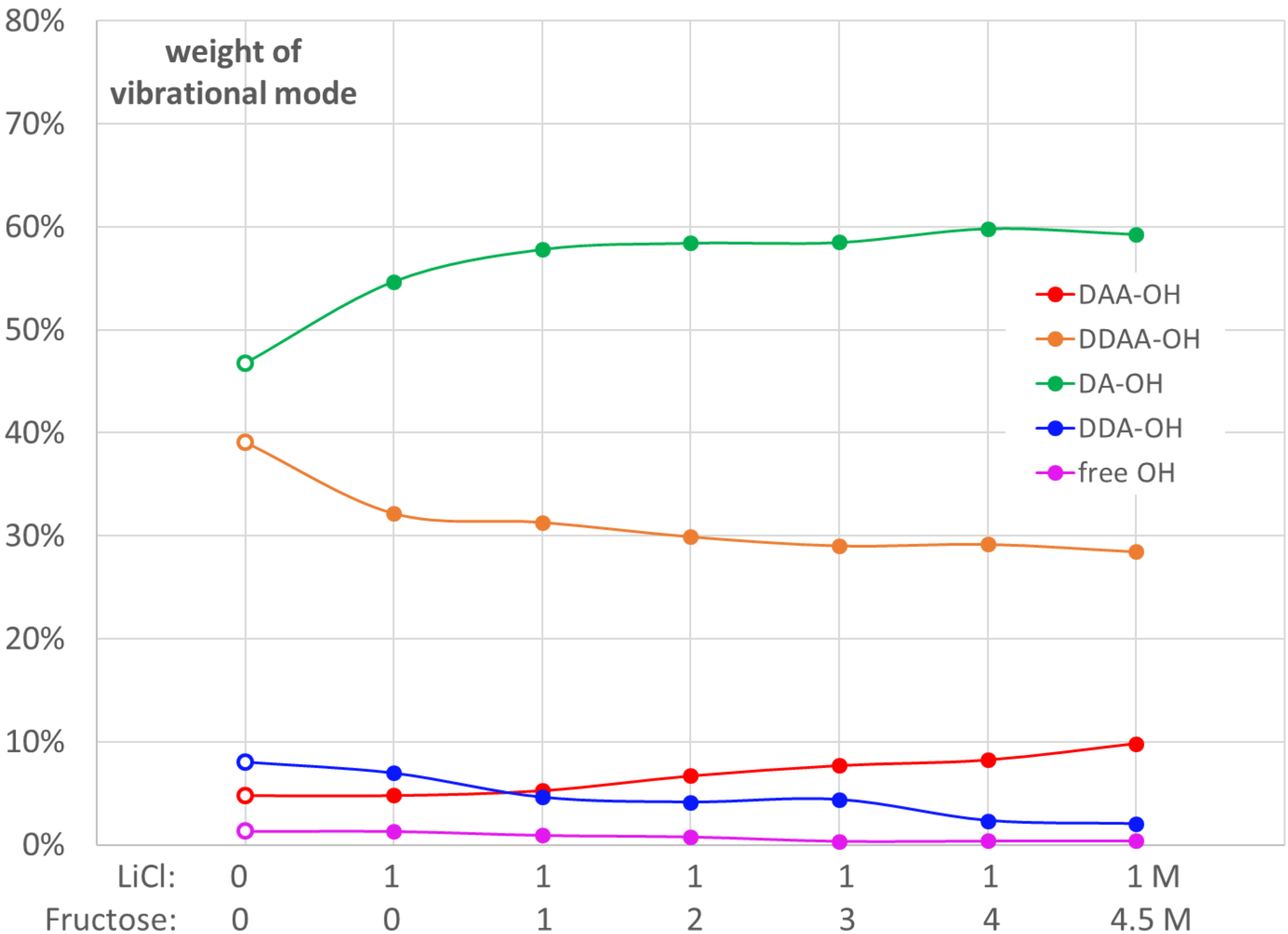


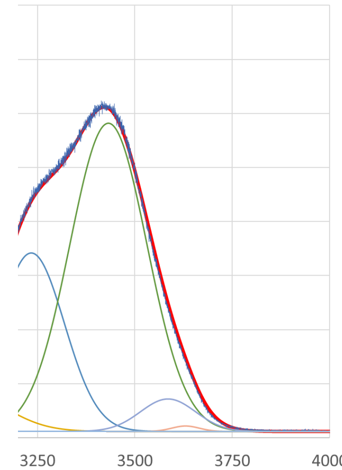


Hydration of organic solute









- **Hydration of fructose (hydroxyl group) increases the viscosity, but not to disrupt the H-bond network as strongly as alkaline metal cations.**

- Q. Huang, *J. Electrochem. Soc.*, 2022.

Hydration of different alkaline metal cations

Diffusion of H^+ and acidity of solution

LiCl (M)	ν (cm^2/sec)	D_H (cm^2/sec)	γ_H
1	0.01128	6.30E-5	1.412
3	0.01422	3.70E-5	1.457
5	0.01853	1.31E-5	1.981
8	0.03030	5.08E-6	2.254

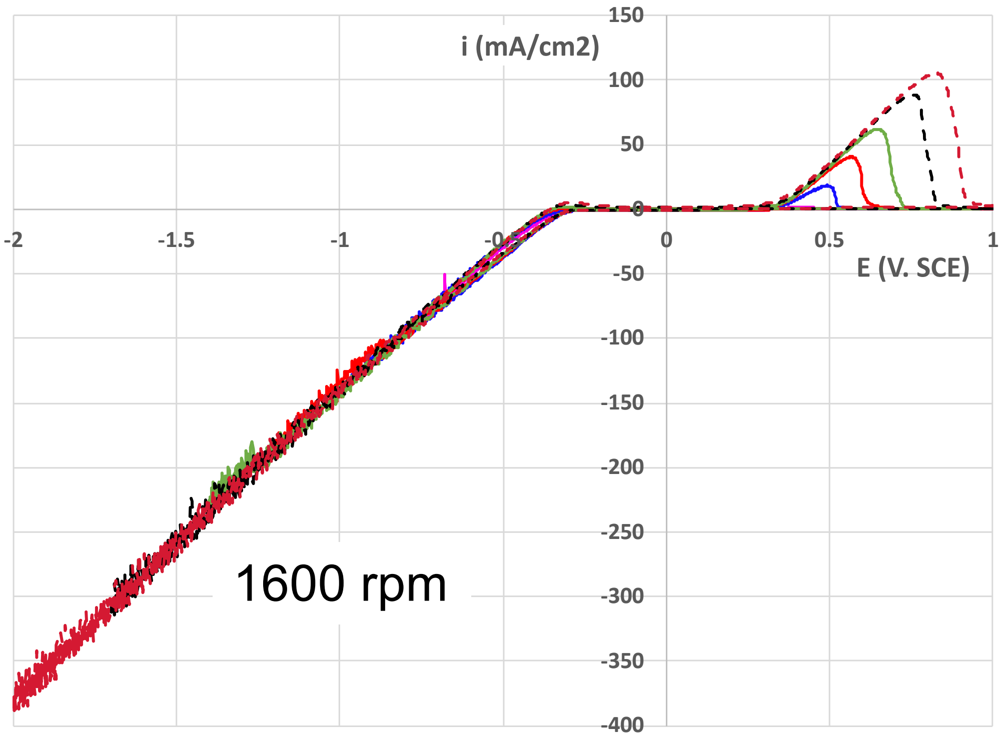
Salt	D_H (cm^2/sec)	γ_H
3 M LiCl	3.70E-5	1.457
3 M NaCl	4.43E-5	1.485
3 M KCl	6.42E-5	1.303
5 M LiCl	1.31E-5	1.981
5 M NaCl	3.31E-5	1.325

- **H-bond network disruption : Li^+ > Na^+ > K^+.**

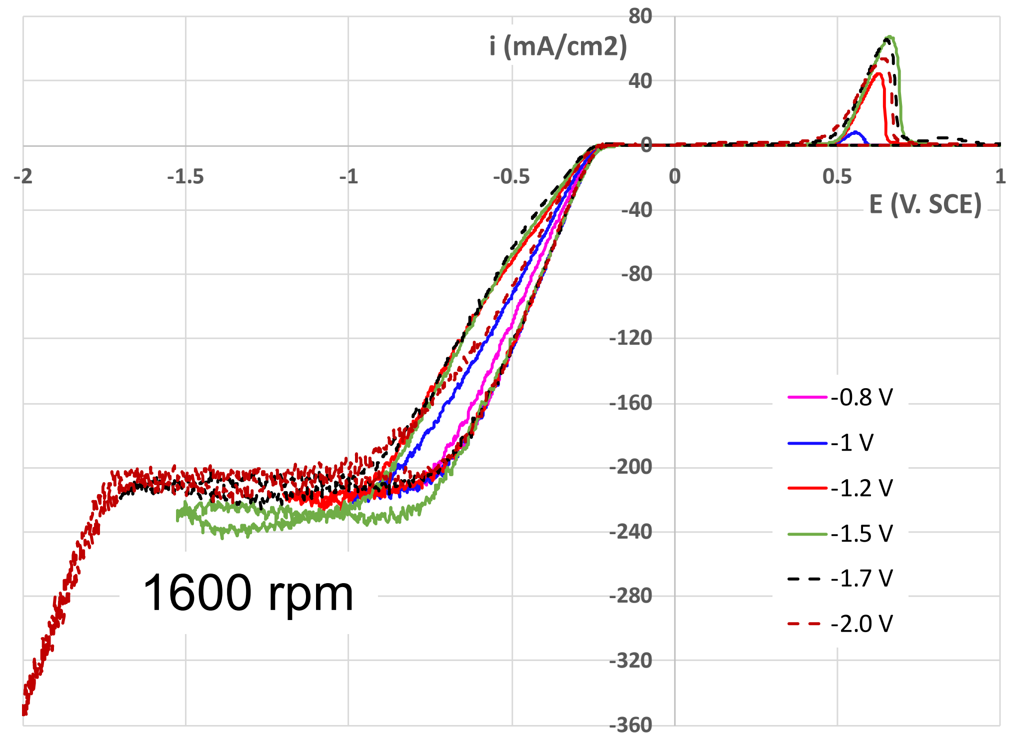
- S. De, *Electrochim. Acta.*, 2020.

Water-in-Salt for Re deposition

0.025 M NH_4ReO_4, 0.1 M H_2SO_4



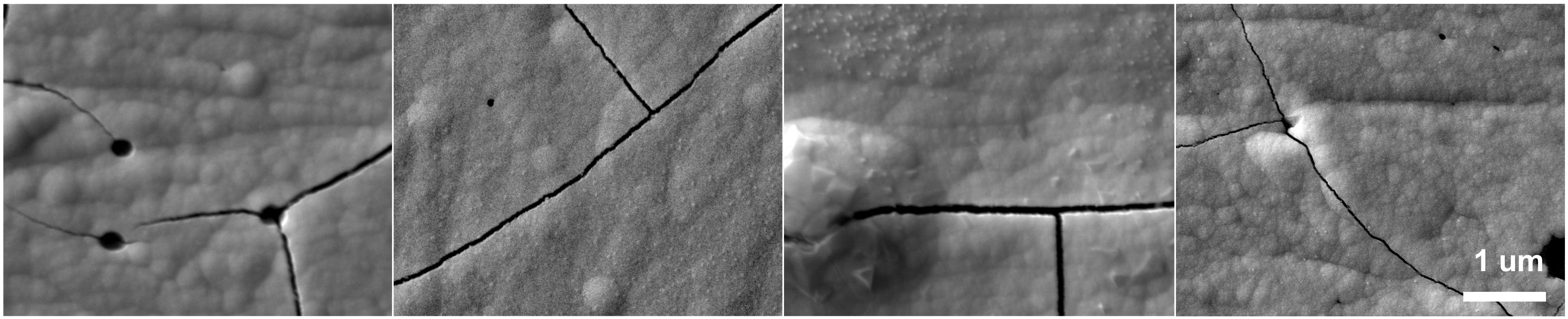
0.025 M NH_4ReO_4, 0.1 M H_2SO_4 , <u>5 M LiCl</u>



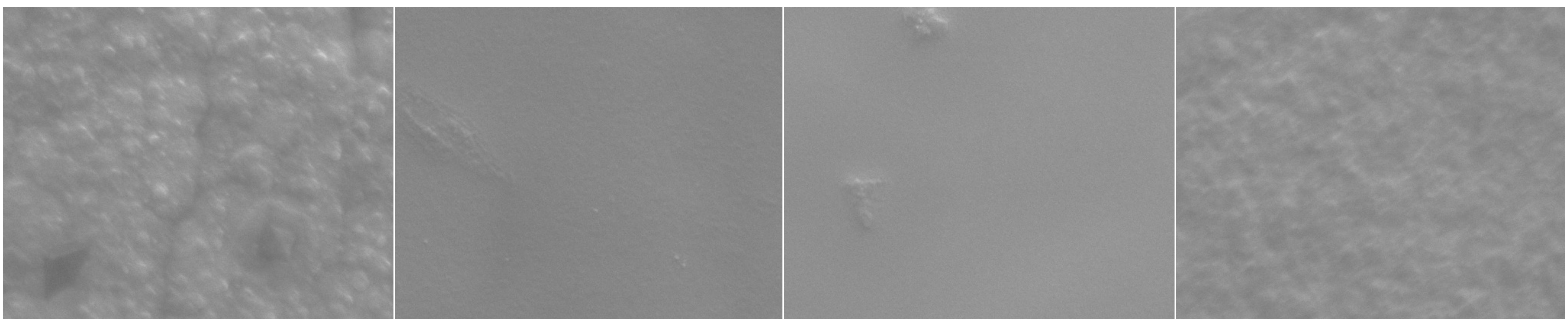
- Q. Huang, T. Lyons, *Electrochem. Comm.*, 2018.

Re morphology

-100 mA/cm2, 600 sec | -150 mA/cm2, 600 sec | -200 mA/cm2, 300 sec | -250 mA/cm2, 200 sec

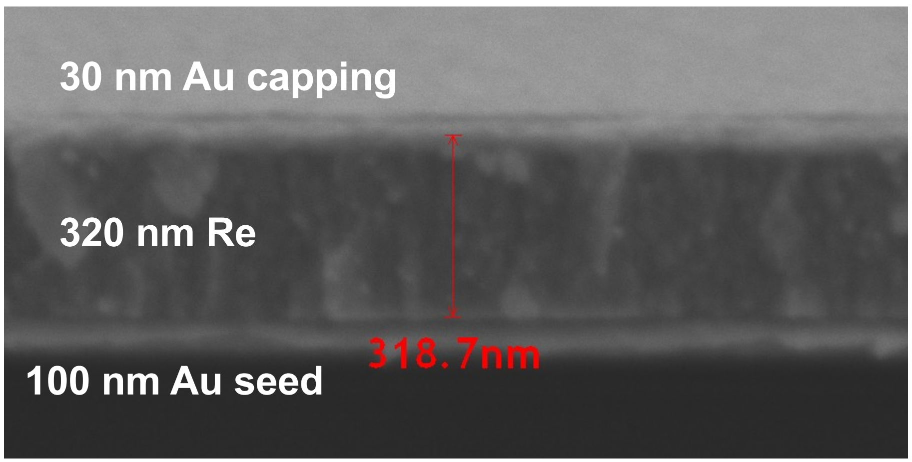


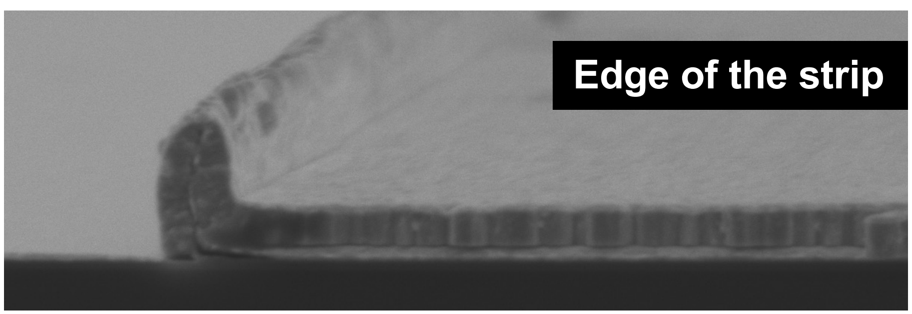
-0.9 V, 900 sec | -1 V, 900 sec | -1.1 V, 600 sec | -1.2 V, 600 sec

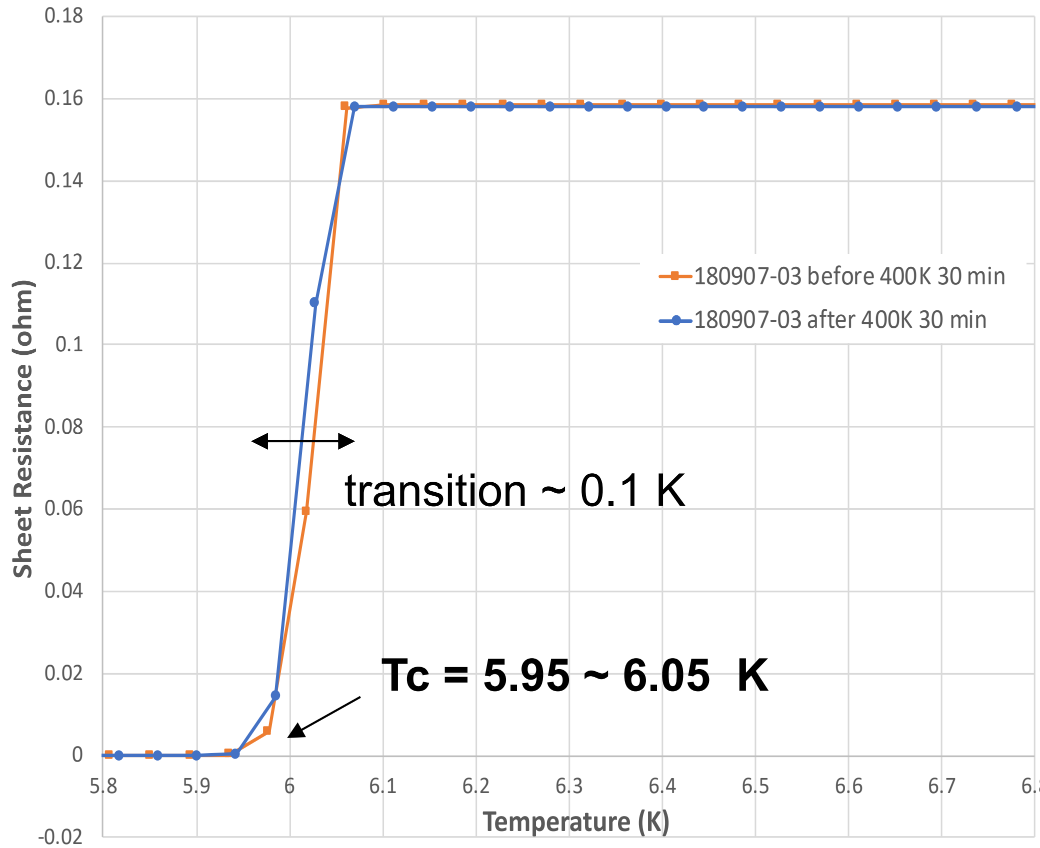


- Q. Huang, Y. Hu, *J. Electrochem. Soc.*, 2018.

XSEM & Superconductivity







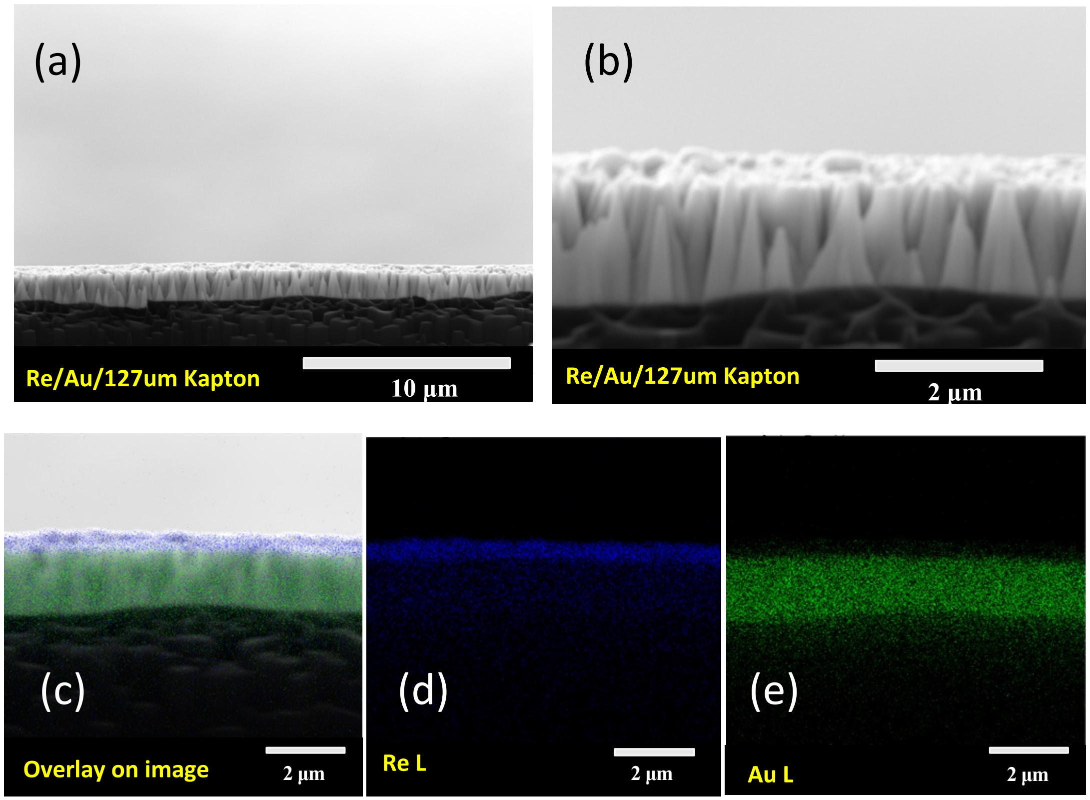
- Q. Huang, Y. Hu, *J. Electrochem. Soc.*, 2018.

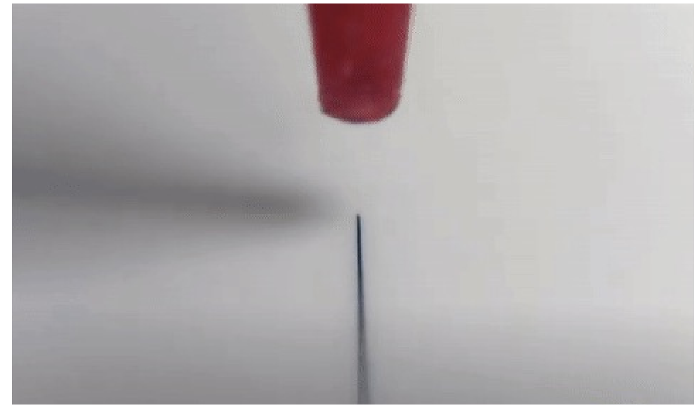
- **Enhanced Tc of 6 K was obtained for as deposited amorphous Re film, as compared with 1.7 K for bulk crystalline Re.**

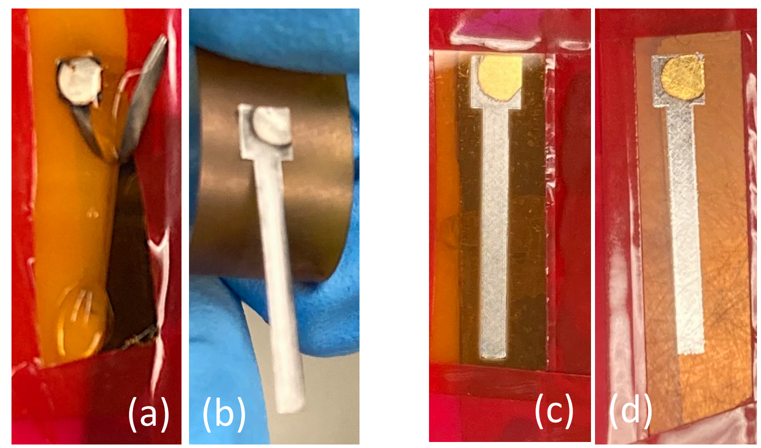
Electrodeposition of Re for flexible connector

Late E-2504 - Digital Presentation, by L. Tsui

- **Aerosol Jet Printing of metal seed followed by Re electrodeposition**





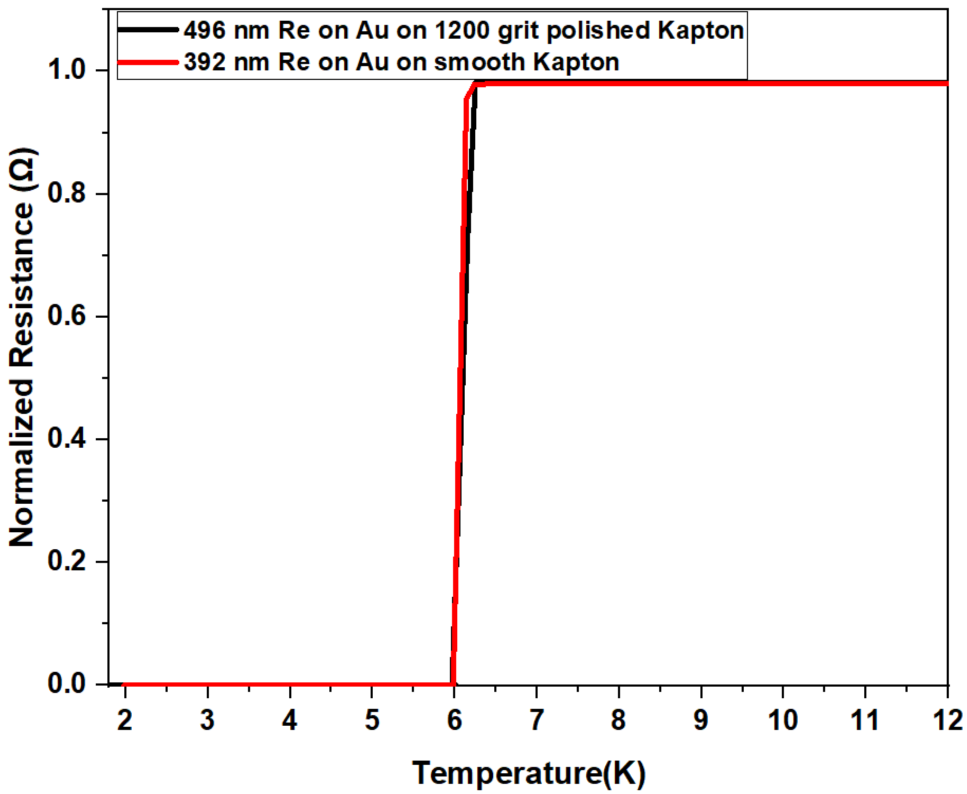


- **Columnar grains observed for AJP Au, clear interface between Kapton / Au / Re.**
- **Adhesion strongly depends on the AJP metal, poor adhesion for Ag.**

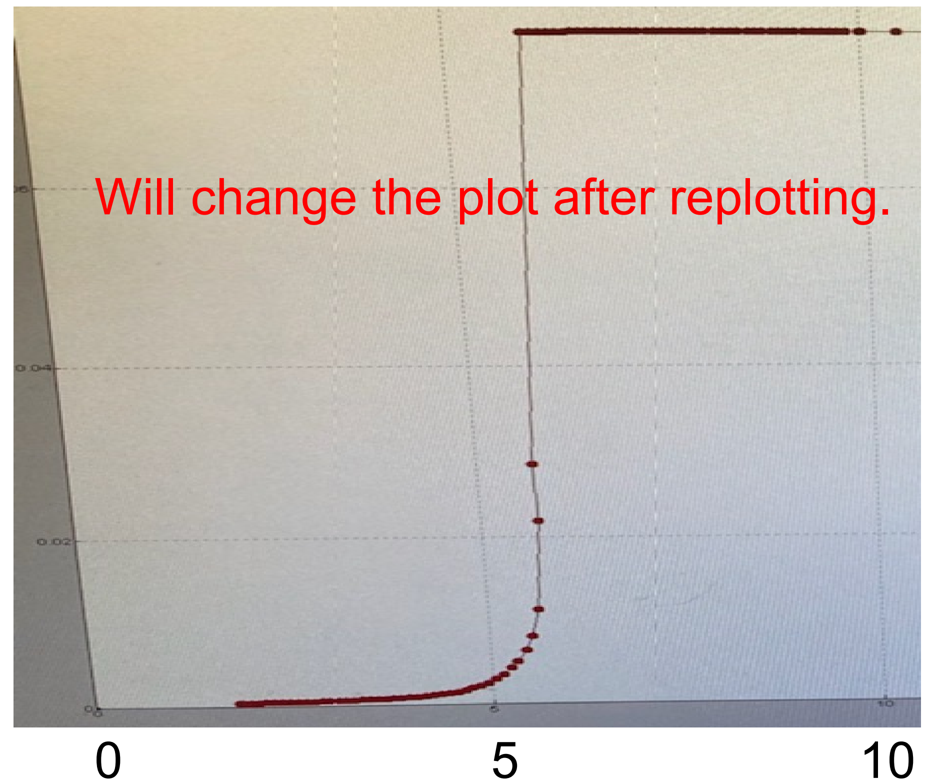
Electrodeposition of Re for flexible connector

Late E-2504 - Digital Presentation, by L. Tsui

Typical as deposited Re film



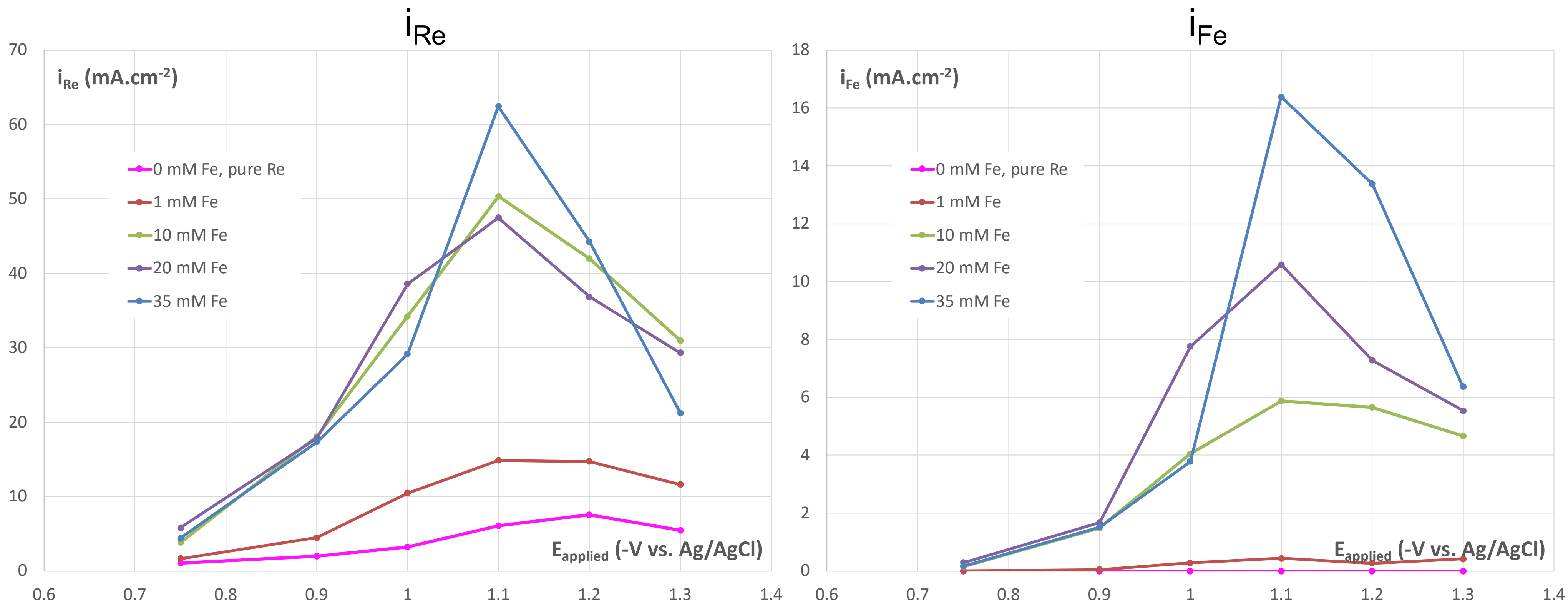
After flexure of 200 cycles



- **Improved Tc of 6 K (as compared with 1.7 K for crystalline Re) is demonstrated on AJP Au on Kapton, consistent with results on silicon coupons.**
- **Flexure for 200 cycles did not significantly alter the Tc, small tail observed is believed to relate to corrosion of Re.**

- K. Ahammed, et al, *in preparation*, 2022.

Effect of Fe & Co on Re deposition

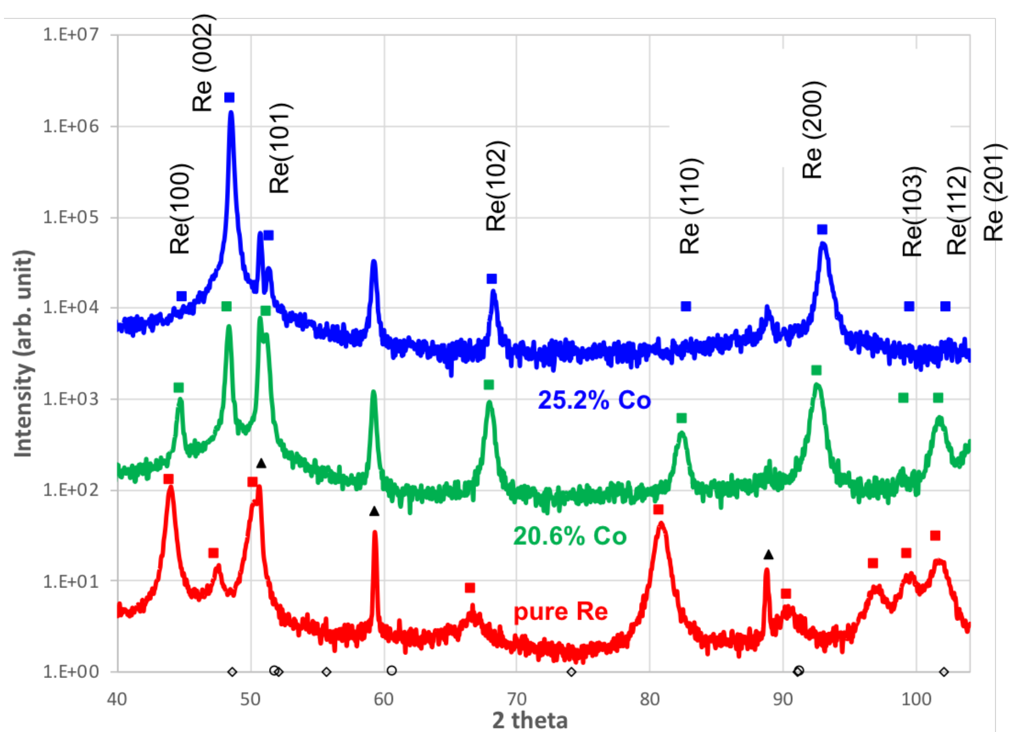


- **The presence of Fe^{2+} promotes the Re deposition rate, up to 10 times faster.**
- **Presence of Co^{2+} also promotes Re deposition, but the effect is less pronounced.**

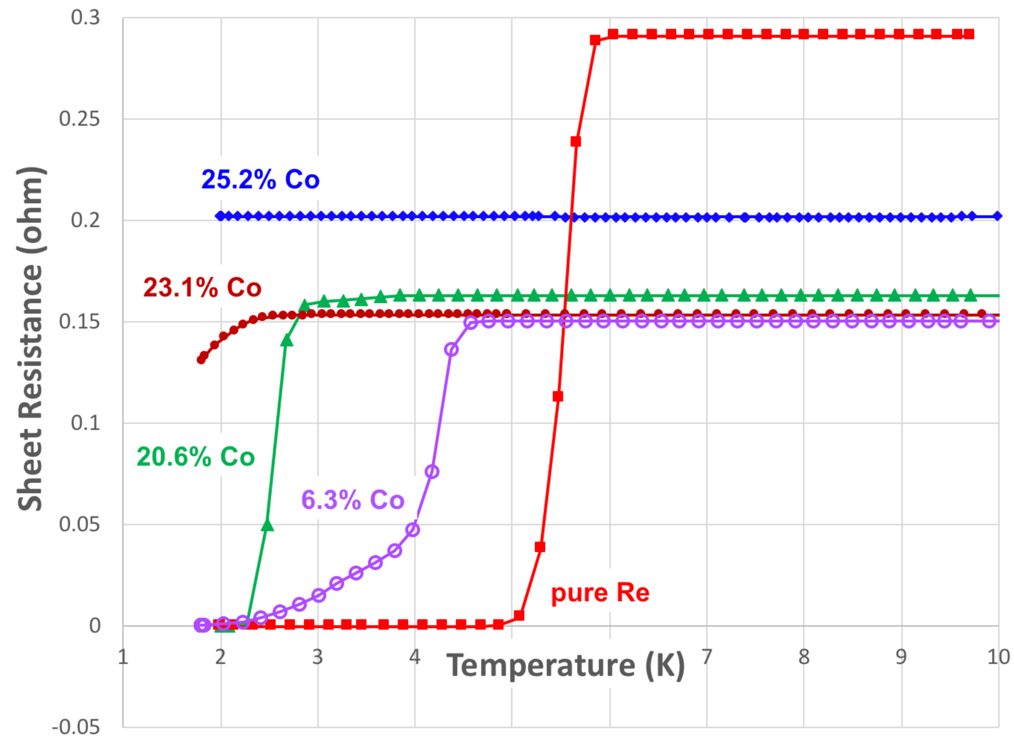
- B. Malekpouri, Q. Huang, *J. Alloy Comp.*, 2022.

Effect of Co alloying

vacuum 200 C 30 min



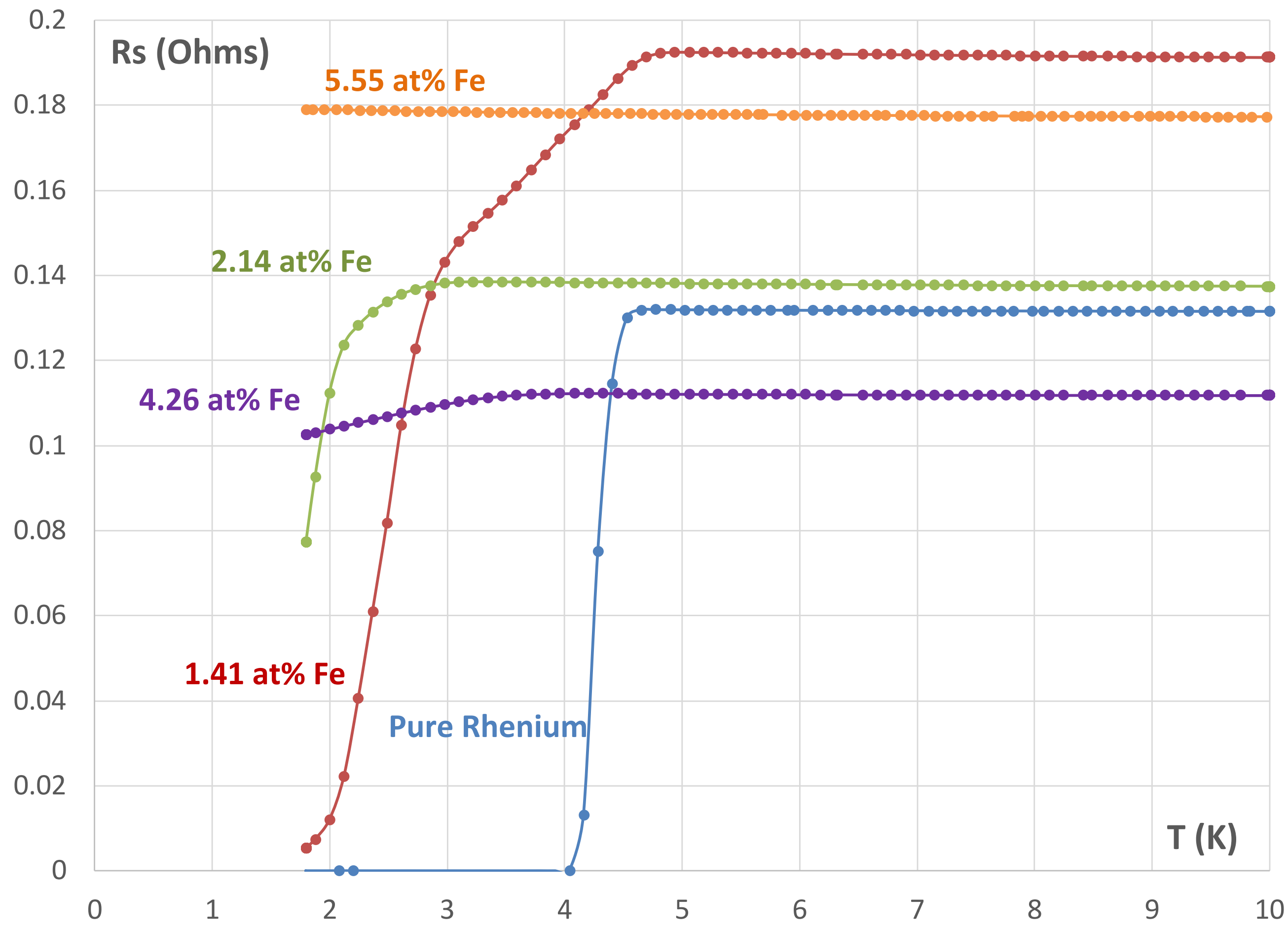
T_c before annealing



- S. De, et al., *J. Electroanal. Chem.*, 2020.

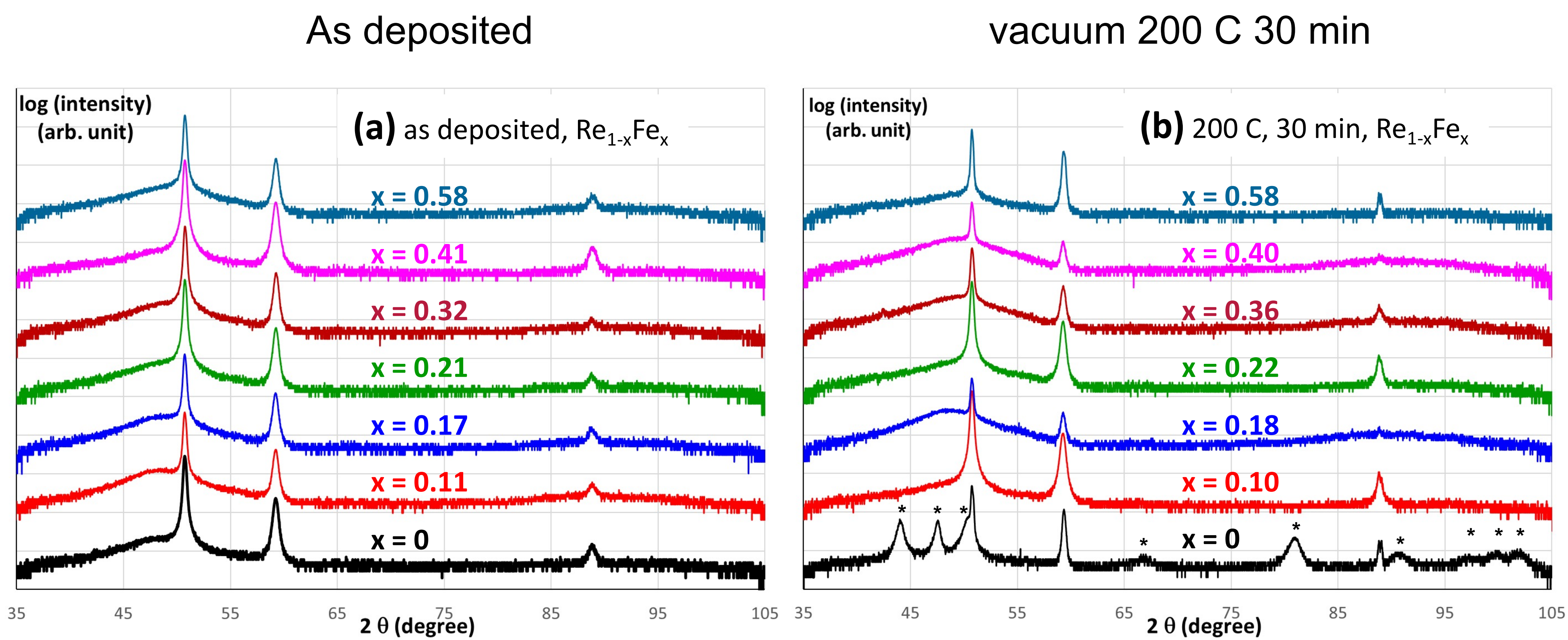
- **Tc gradually decreases upon alloying of Co into Re.**
- **As deposited ReCo alloys are amorphous, films re-crystallizes upon 200 C anneal.**
- **HCP single phase solid solution can be obtained for ReCo after annealing.**

Effect of Fe on Tc



- **Alloying with Fe also decreases the Tc of Re, and the effect of much stronger than Co.**

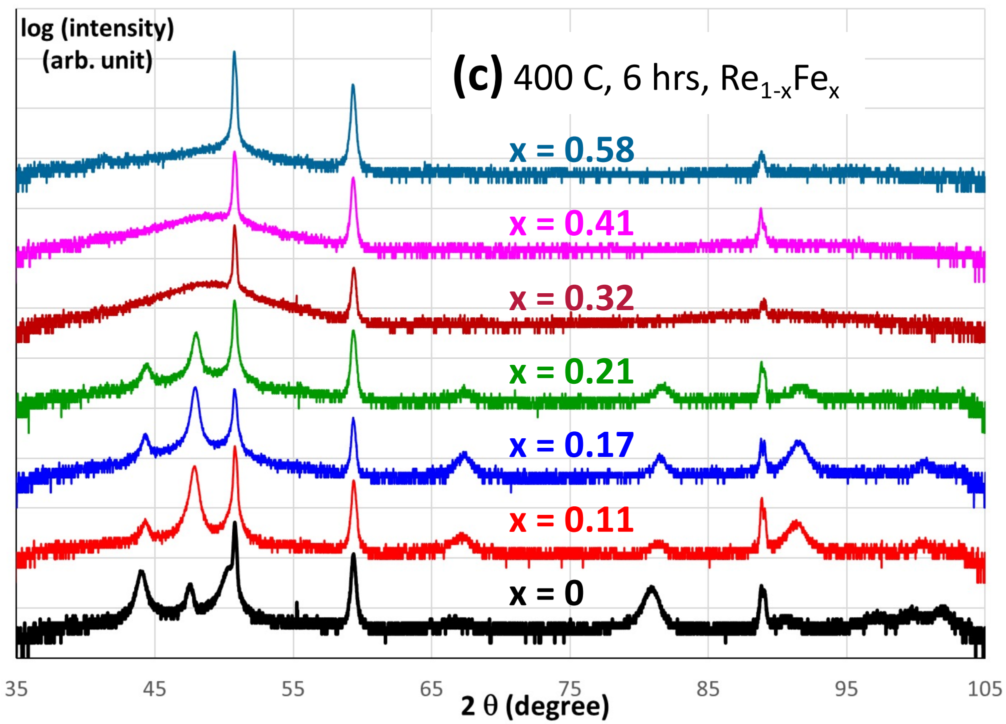
Effect of Fe on Re recrystallization



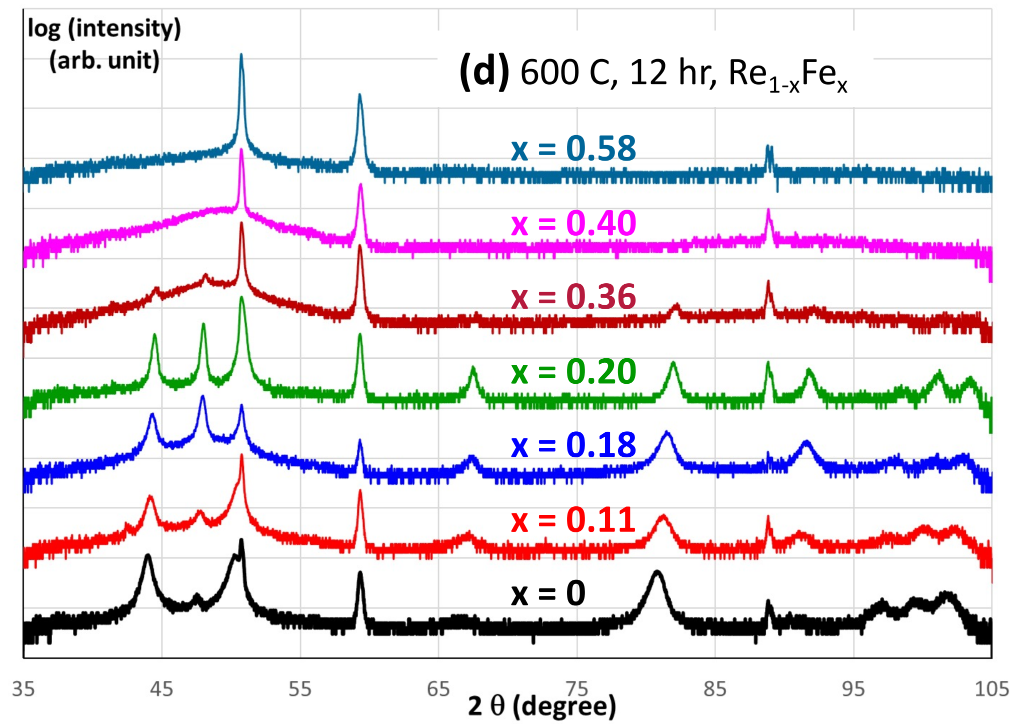
- **As deposited ReCo alloys are amorphous, 10% Fe prevents the film from re-crystallization at 200 C.**

Effect of Fe on Re recrystallization

vacuum 400 C 30 min



vacuum 600 C 30 min

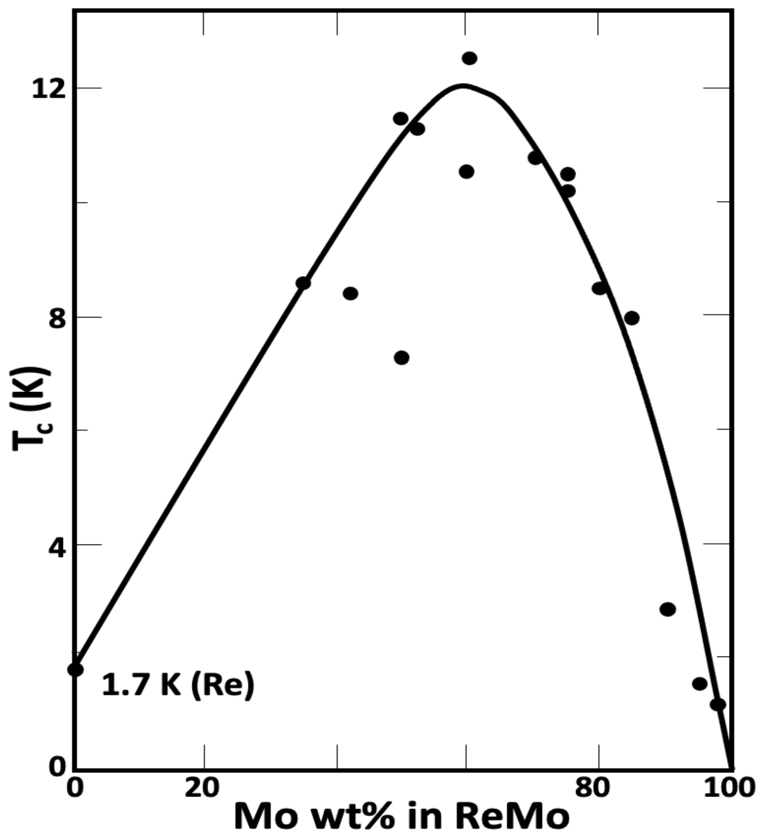


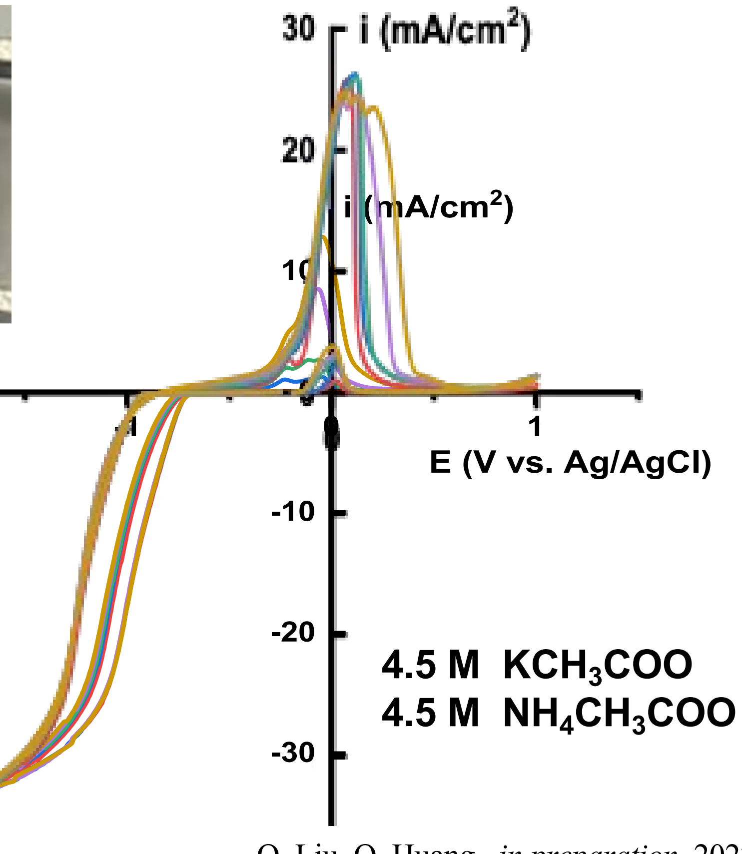
- B. Malekpouri, Q. Huang, *J. Alloy Comp.*, 2022.

- **Higher temperature annealing enables the recrystallization of films with higher Fe%.**
- **600 C annealing is not able to crystallize films with 40+ % Fe.**

Electrodeposition of Mo from Aqueous solution

Late E-2536 – Poster, by Q. Liu





- Q. Liu, Q. Huang, *in preparation*, 2022.

- **Metallic Mo obtained from super high concentrate acetate solutions**
- **K+ is necessary for Mo deposition, and the Mo deposition rate increases with K+ concentration**
- **Substrate makes big difference – also suggesting HER inhibits Mo deposition.**

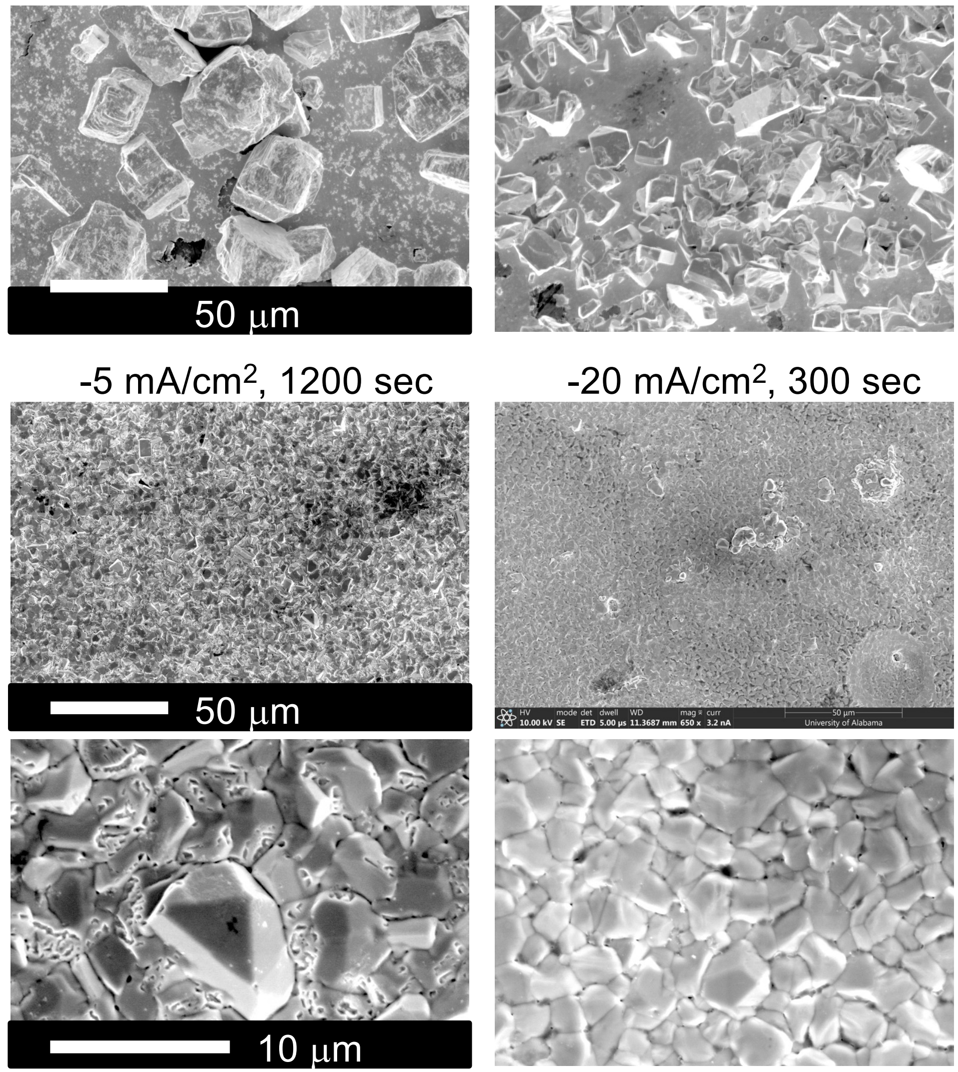
Summary

- **Organic additive for Sn electrodeposition to tune the nucleation and growth, as well as the superconducting transition.**
  - Hydrophobicity of additives dominates the adsorption and suppression effect
  - Adsorption dependent on not only the empty fraction but also the covered fraction.
  - Significant interdiffusion between Sn and Au occurs at room temperature, degrading the superconductivity upon aging.
- **Alkaline metal supporting salts and alloying metal cations in Re electrodeposition to tune the hydrogen evolution rate and alloy composition, as well as the superconducting transition.**
  - Deposition of superconducting Re demonstrated on flexible substrates
  - Iron group metals failed to improve Tc, but to degrade the Tc
  - Mo deposition was demonstrated from Water-in-Salt, with strong substrate effects.

-5 mA/cm², 1200 sec | -20 mA/cm², 300 sec

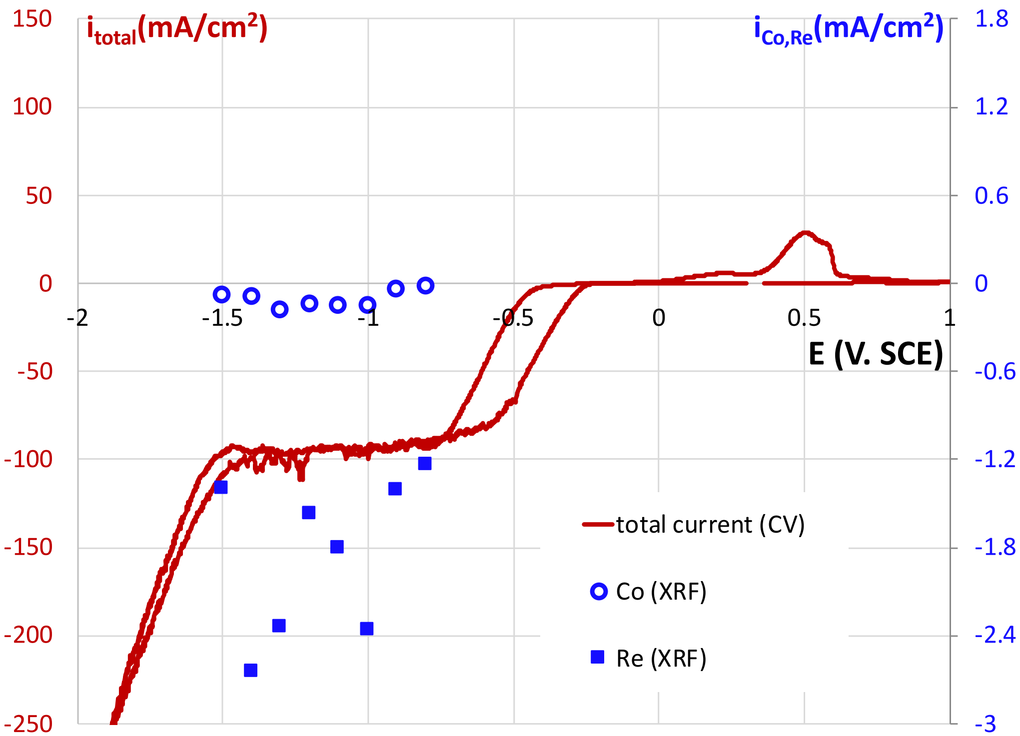
No ETT

500 ppm ETT

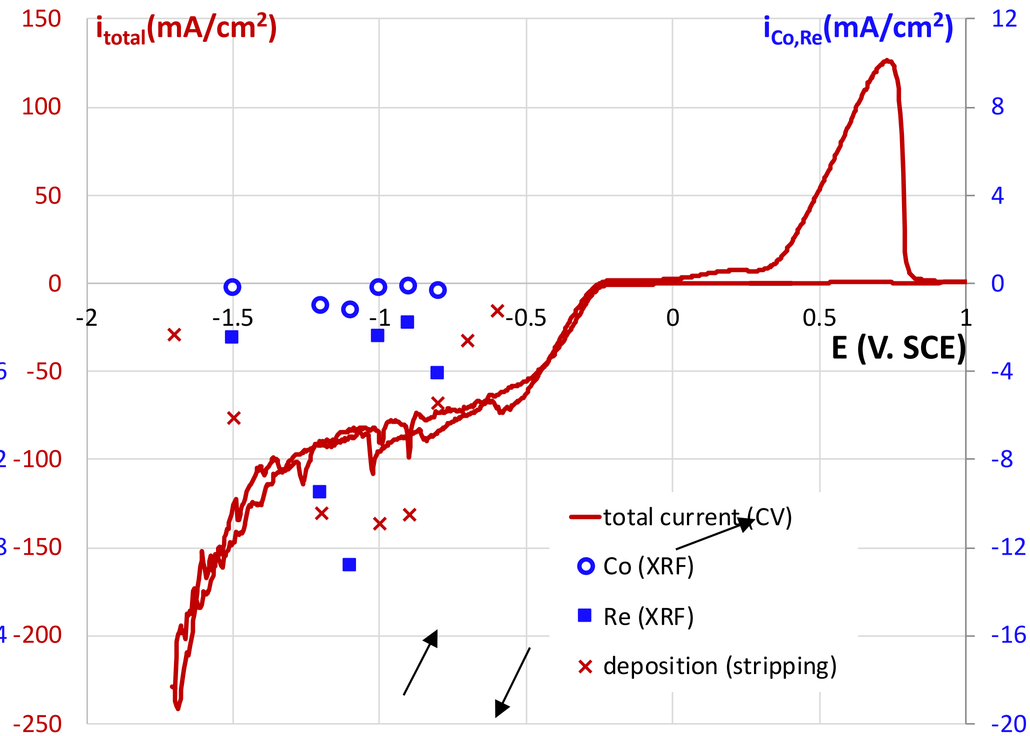


Back up – Co on Re

Re 0.025 M
Co 0.001 M

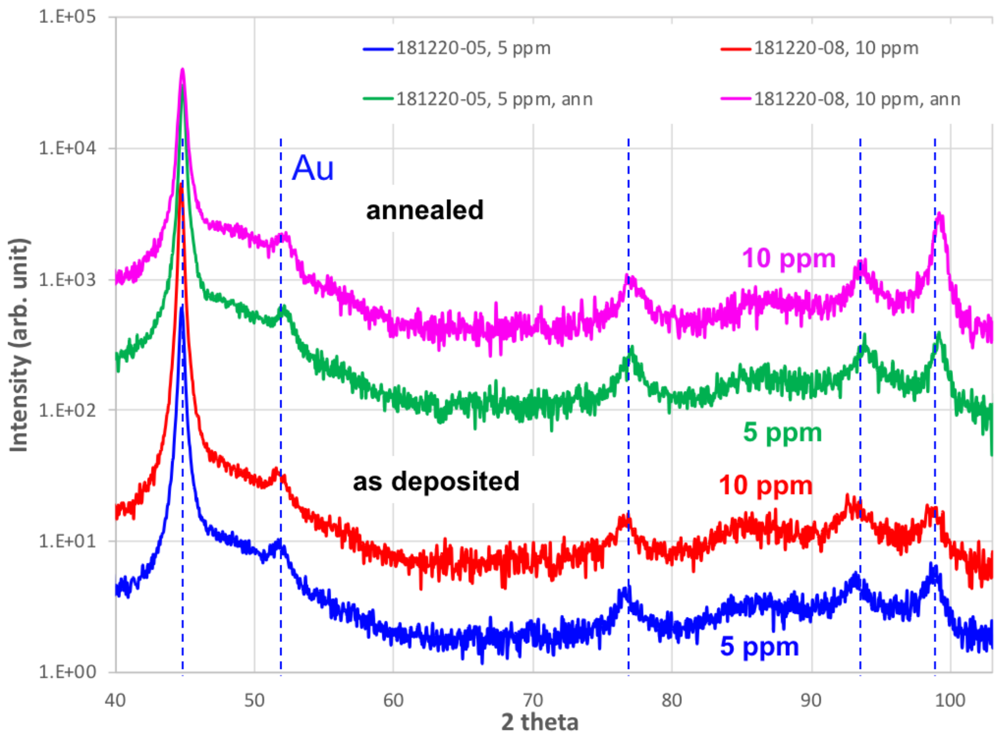


Re 0.025 M
Co 0.01 M

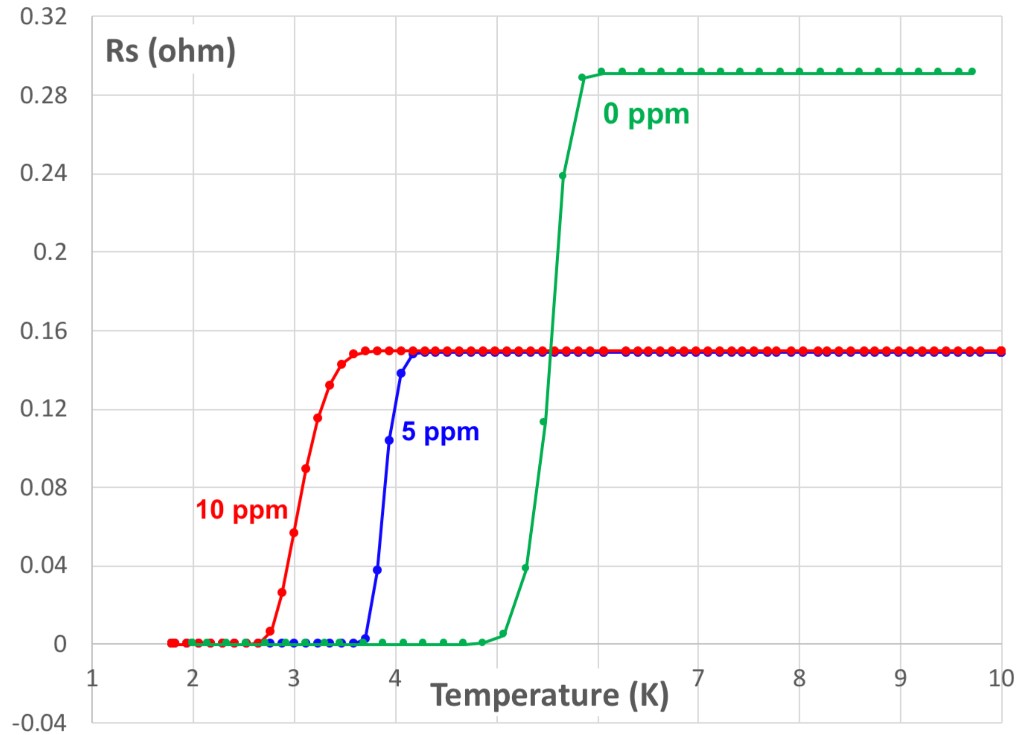


S doping (thiourea)

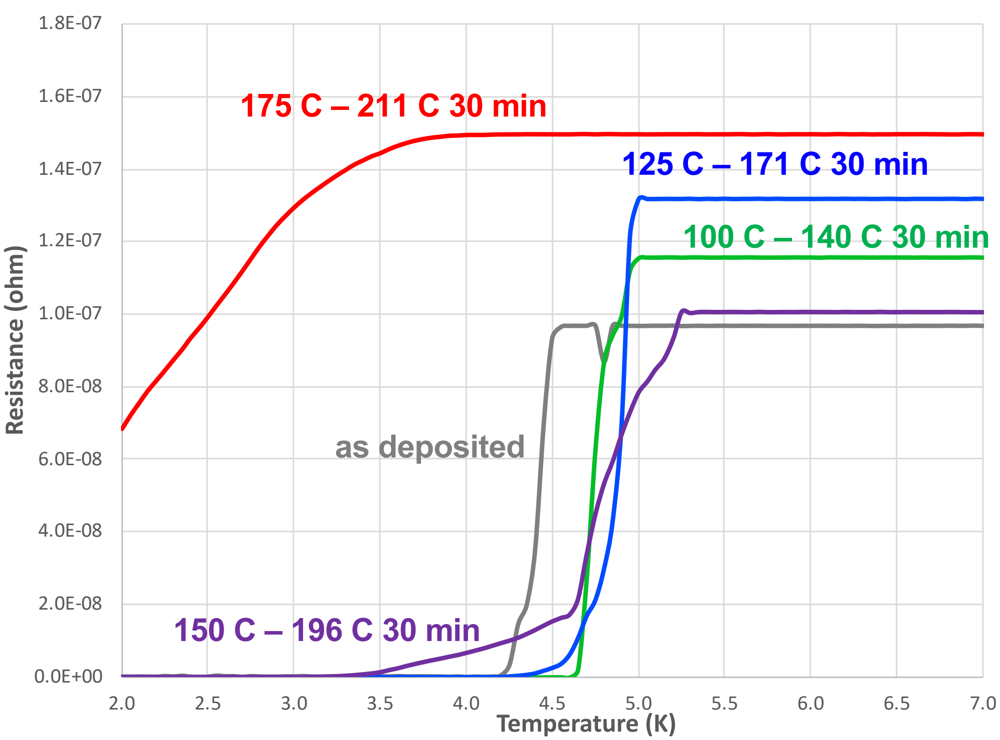
vacuum 200 C 30 min

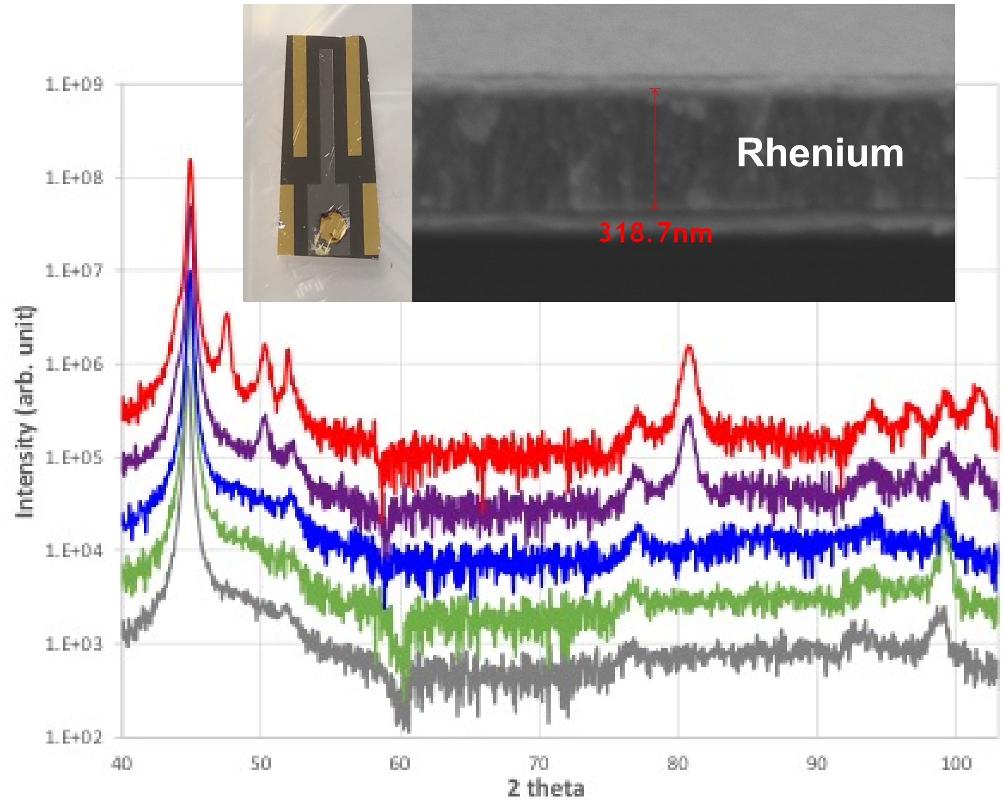


T_c before annealing



Back up – crystallization of Re





- Sides & Huang, *J. Appl. Phys., 2020*.

- **Recrystallization of as-deposited amorphous Rhenium film results in degradation of superconductivity.**
- **Critical temperature above He boiling point (4.2 K) is desired for connector application.**