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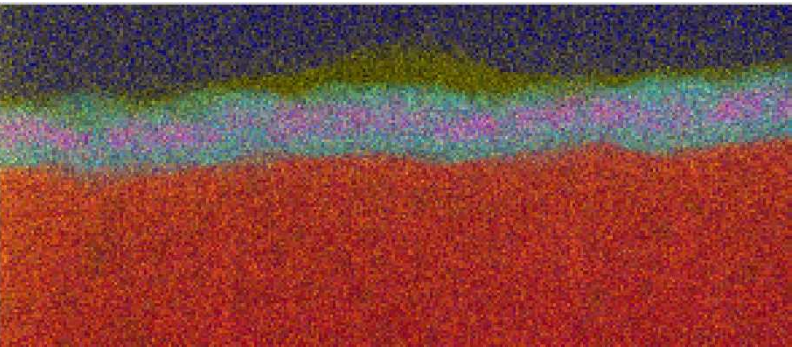

Understanding Inclusion Mechanisms and Effects in Hardened Gold Electrodeposits

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Electroplating Throughout the Ages

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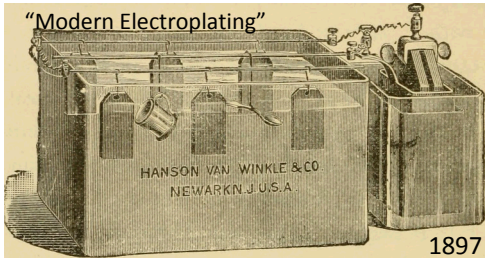
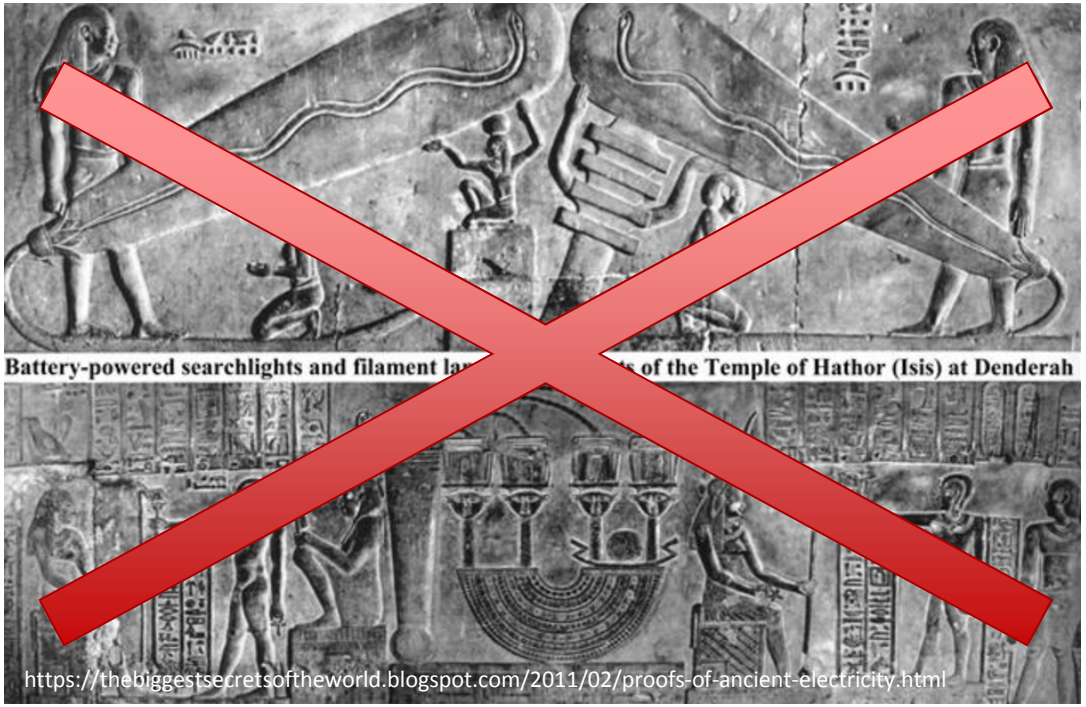
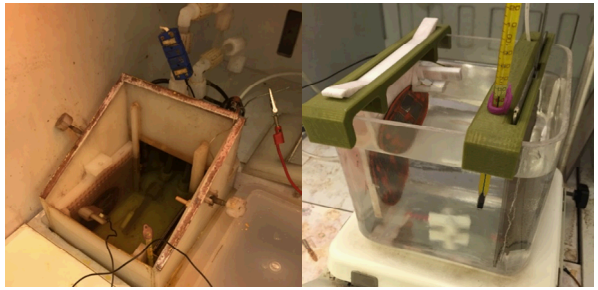






our lab today, and tomorrow!

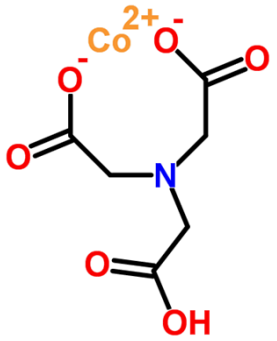
Two centuries in, we've come a long way, but modern plating is recognizable to a 19th century observer

Electroplating Hard Gold

- Gold hardening is mediated by the addition of brighteners which result in smaller gold grains
- Hardened gold is not at equilibrium after plating and so prone to the development of defects, dislocations and grain boundaries forming the starting point of the aging effect
- Some samples may develop discoloration and increase in contact resistance over their lifetimes

- **Objective**: optimize plating process to <u>minimize performance degradation</u>
  - Operating parameters and additives

Potassium dicyanoaurate(I)



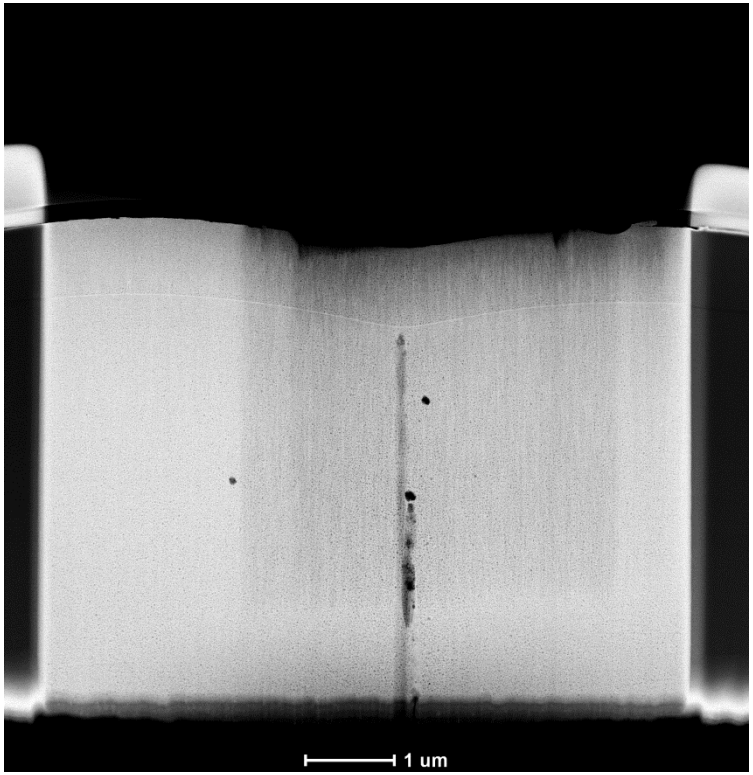
Cobalt(II) nitrilotriacetic acid

Gold discoloration

Kurtz, Olaf, et al. "Thermal Aging of Technical Hard Gold Deposits."

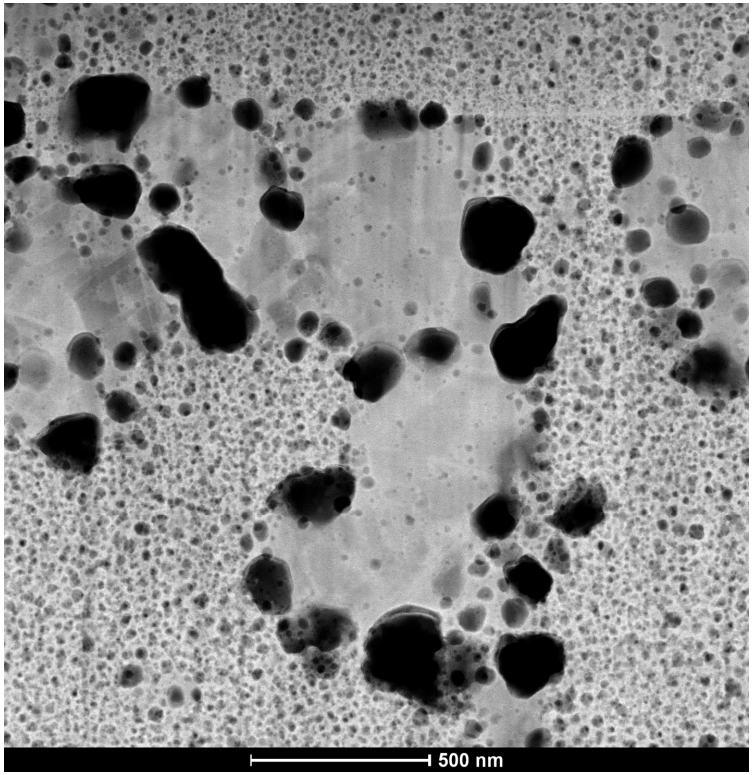
Cross-sections - Voids

Good



Smaller, more uniform pores, with a small number of larger pores likely from plating

Bad

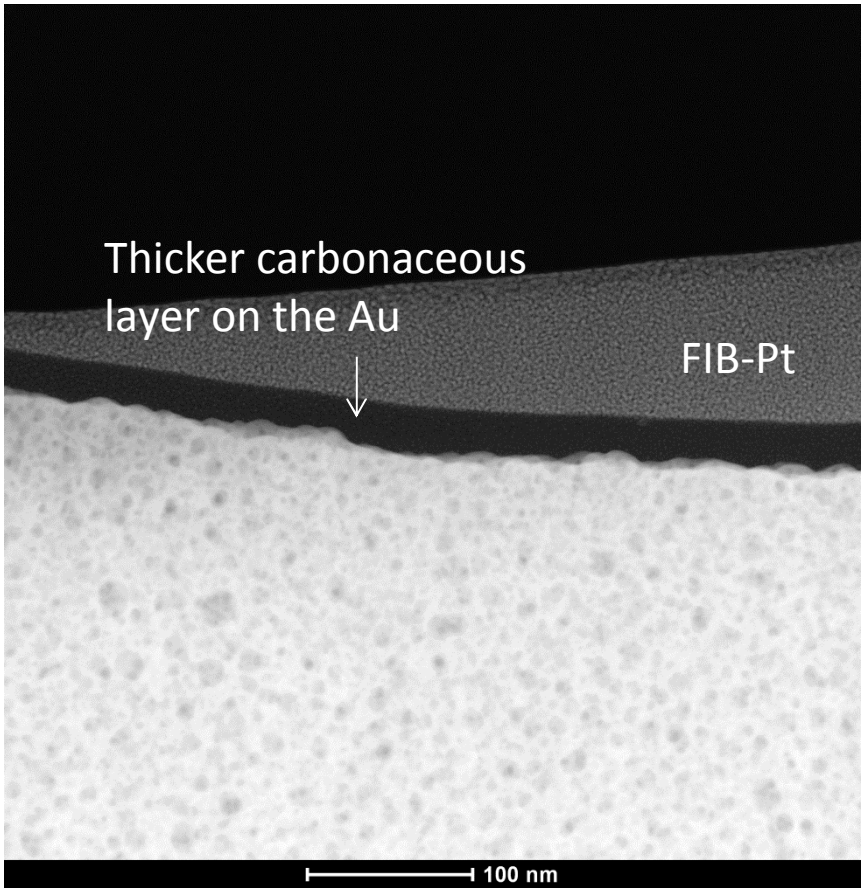


Coarsened pores with likely exaggerated grain growth

SEM images courtesy Paul G. Kotula, SNL

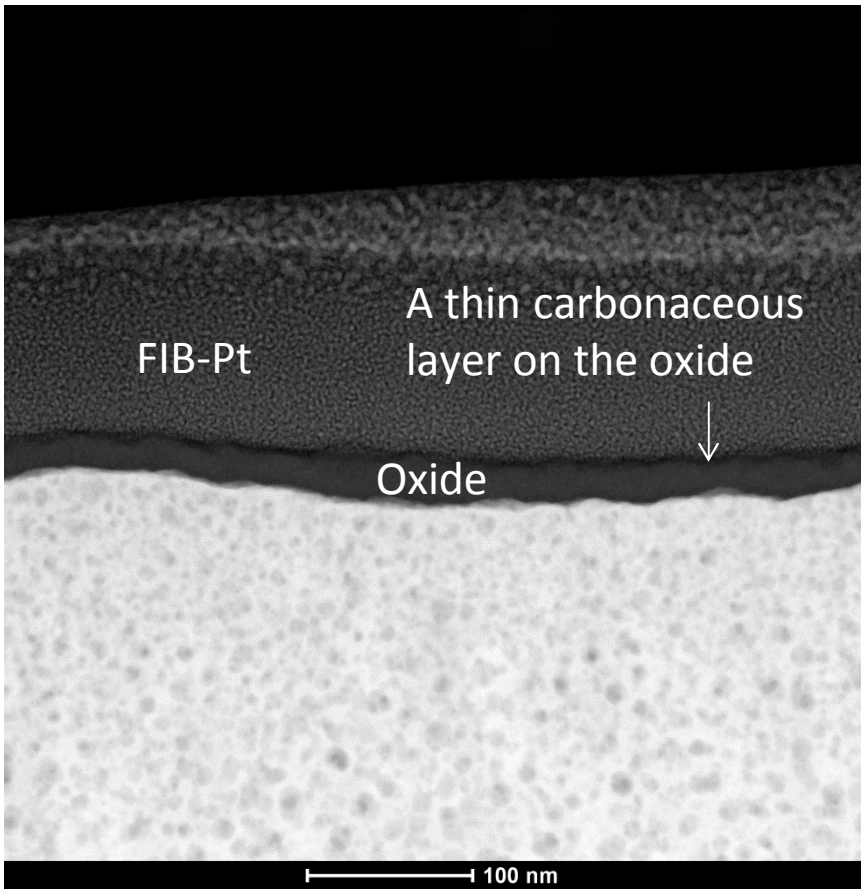
Cross-sections - Films

Good



Carbonaceous surface layer on the good sample consists of C-O-Si with **no** evidence of Co-Fe-O

Bad



30 nm surface layer is Co-Fe-O which is somewhat inhomogeneous but shows evidence of some crystallinity consistent with a spinel structure

Cross-sections - Composition

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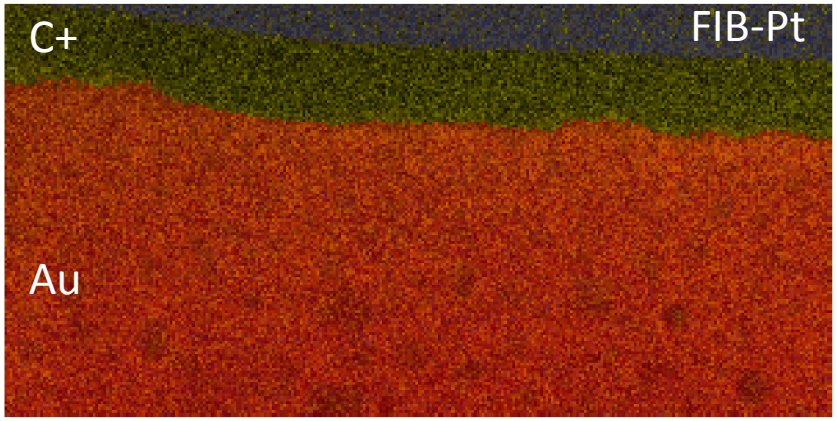
Good



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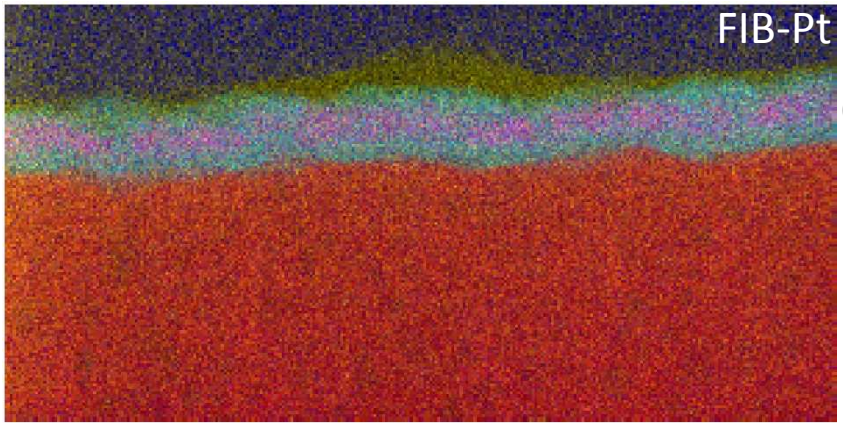


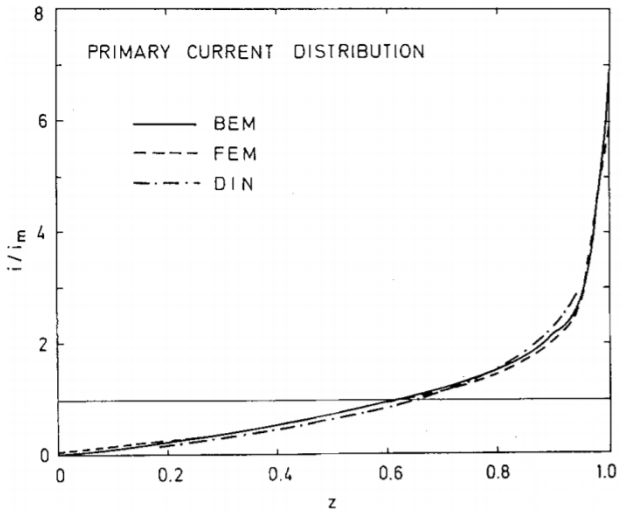
300 nm by 150 nm field of view

Red: Au
Blue: FIB-Pt
Cyan: Fe-O
Magenta: Co-O
Yellow: C-O-Si (low K, Cl)

Co and Fe are inhomogeneous in the surface layer, with Co:Fe about 1:2 consistent with $CoFe_2O_4$

What is happening?

Hull Cell and Test Pattern



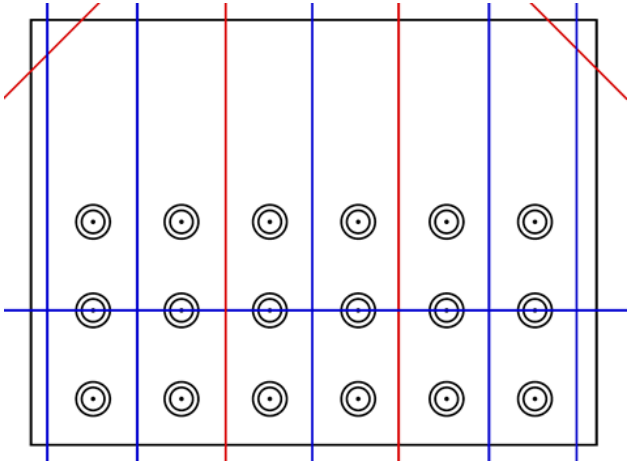
J. Electrochem. Soc. **1987** v.134, i.12, ppp.**3015-3021**

- Current density is:

  $i(x)/i_{AVE} = 2.33 \log(1/(1-x)) - 0.08$

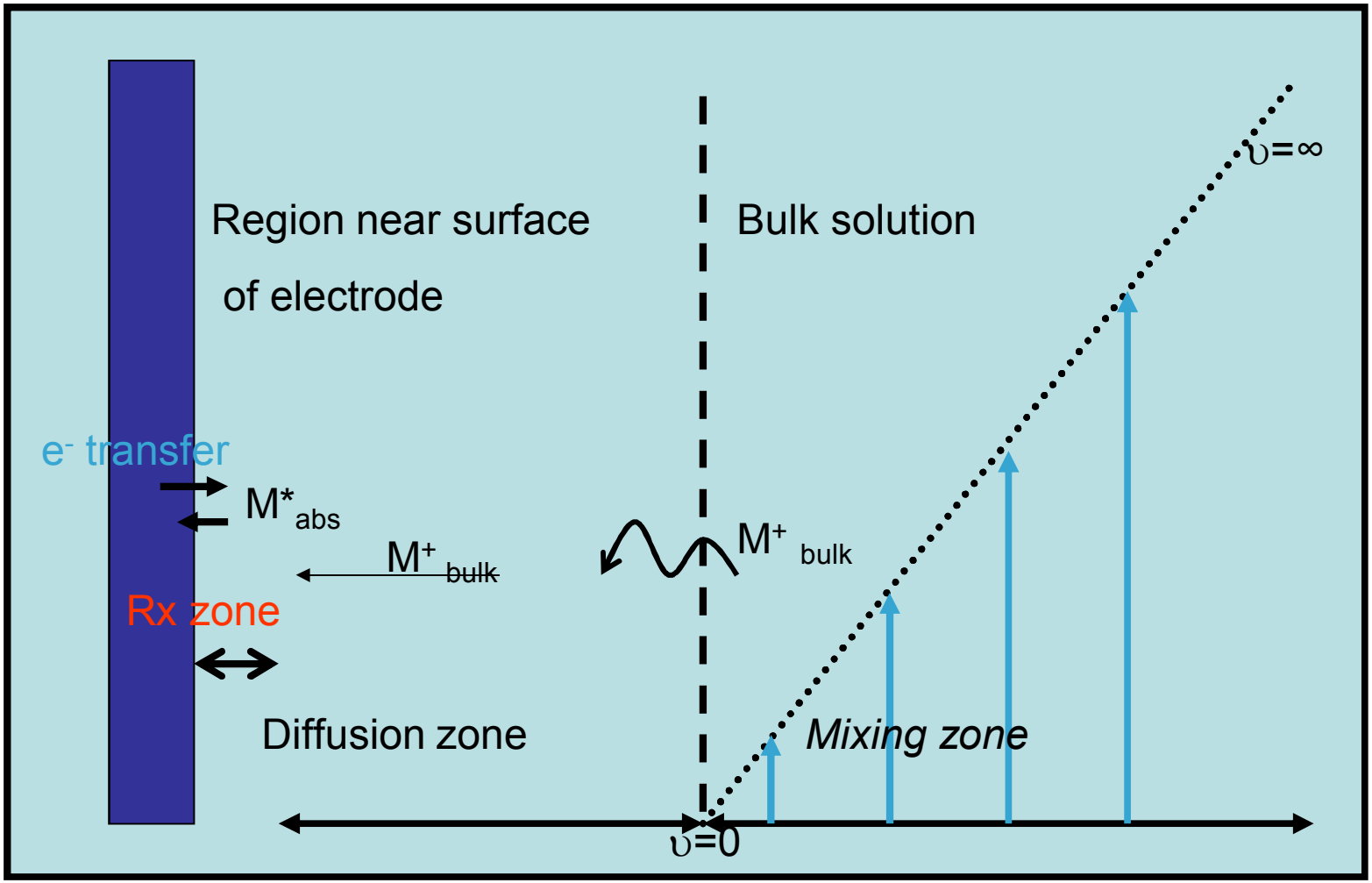
  for $0.186 < x < 0.941$ (DIN 50950)
- Over 2 decades between high (left) and low (right) current density sides
- Allows for concurrent testing of wide range of j
- Rows experience varying agitation and aeration

Sample Preparation



- Nickel-alloy substrate
- Photolithographically defined 3x6 pattern
- 5 minute HCL activation
- 1-3 minute Ni strike
- Immediately proceed to gold bath
- Samples sectioned, polished for analysis
- One side kept, other can be annealed

Ions in the Interphase



Testing Parameters

Cobalt Concentration		x1		x3		x5	
Current (mA)		12	120	12	120	12	120
pH	Strike Duration (min)						
~4.2	3	✓	✓	✓	✓	✓	✓
	1	✓	✓	✓	✓	✓	✓
~3.5	3	✓	✓	✓	✓	✓	✓
	1	✓	✓	✓	✓	✓	✓

- Current density at the test patter spans three orders of magnitude (with some overlap)
- Three cobalt concentrations above commercial bath
- Suggested pH and “extreme” lower pH
- Thinner Ni strike to probe substrate diffusion
- No agitation to induce starve solution near substrate

The goal is to probe regimes of additive drag under mass transport limitation conditions

Standard Conditions

- 3 min Ni strike
- Au plating
  - 12 mA
  - x1 Co
  - 4.2 pH

This current density was insufficient to cause as-plated discoloration

Higher Current Density

- 3 min Ni strike
- Au plating
  - 120 mA
  - x1 Co
  - 4.2 pH

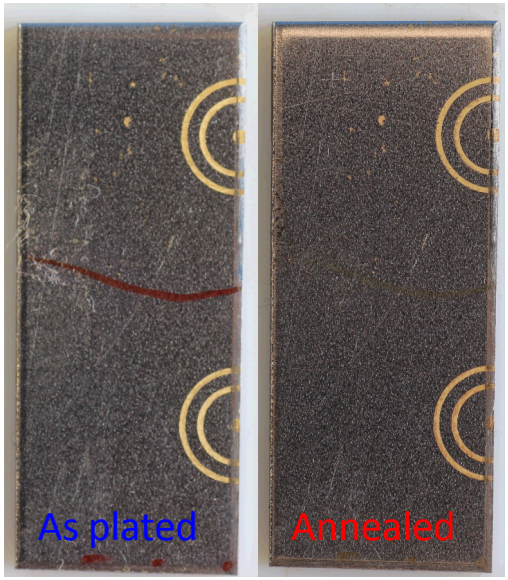
Dendritic gold at higher current density area; also effect of bubbling

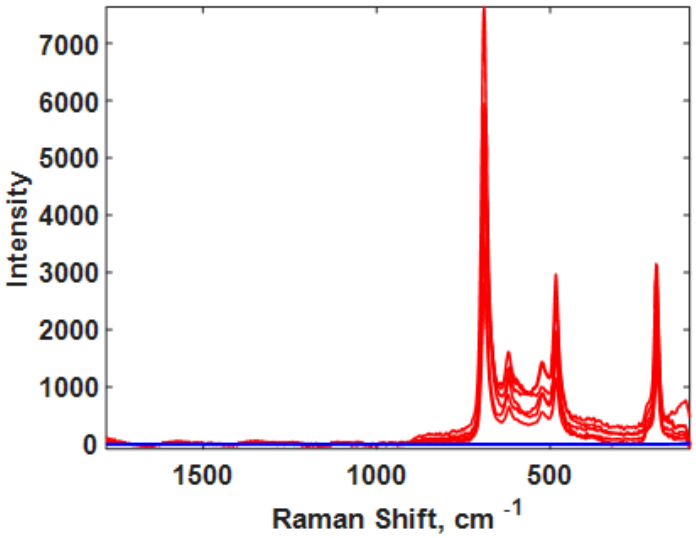
Higher Current and Cobalt Density

- 3 min Ni strike
- Au plating
  - 120 mA
  - x3 Co
  - 4.2 pH

Additional cobalt extends region of “bright” gold

Effect of Annealing





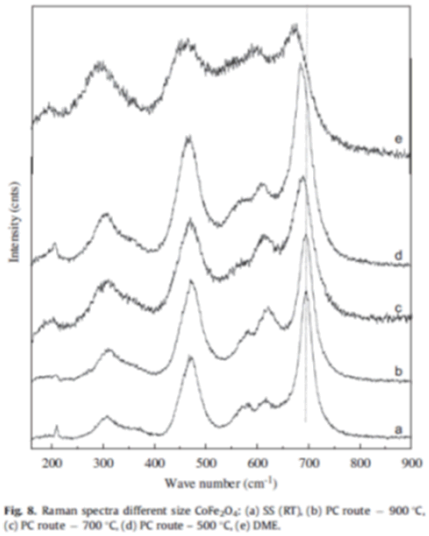


Fig. 8. Raman spectra different size $CoFe_2O_4$: (a) SS (RT), (b) PC route – 900 °C, (c) PC route – 700 °C, (d) PC route – 500 °C, (e) DME.

Plate develops inverse spinel signature consistent with $CoFe_2O_4$

RAMAN spectra courtesy Kathleen M. Alam, SNL

P. Chandramohan et al., J. Solid State Chem., V.184, I.1, 2011, pp.89-96

Conclusions

- Factors contributing to discoloration and rapid aging
  - Higher current density
    - Higher rate of incorporation
    - Voids through gas evolution
  - Poor agitation (mass transport limitation)

- Still under consideration
  - Effect of nickel layer thickness
  - Optimal cobalt content

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Thanks to Lyle Menk, Kathy Alam, Paul Kotula, and Cliff Loucks

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