FARADAY TECHNOLOGY, INC.

2023 Blum Lecture:

Technics in Boundary Layer and Surface Chemistry Control

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Pioneering Electrochemical Technologies
An A3 Global Company

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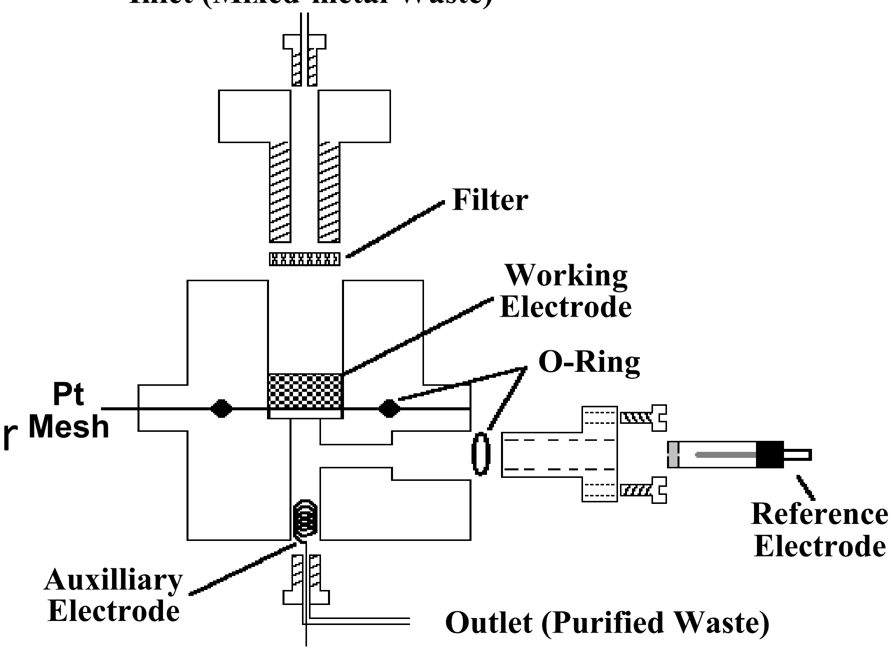
Outline

- First 20 years
  - WVU (Dr. John Zondlo)
  - Notre Dame (Dr. Albert Miller) / NuVant Systems
  - Faraday (EJ Taylor)
- Next 20 years
  - New materials and uses
  - Bring material processing back to the US
  - Training the next generation

WVU
(2001 to 2003)

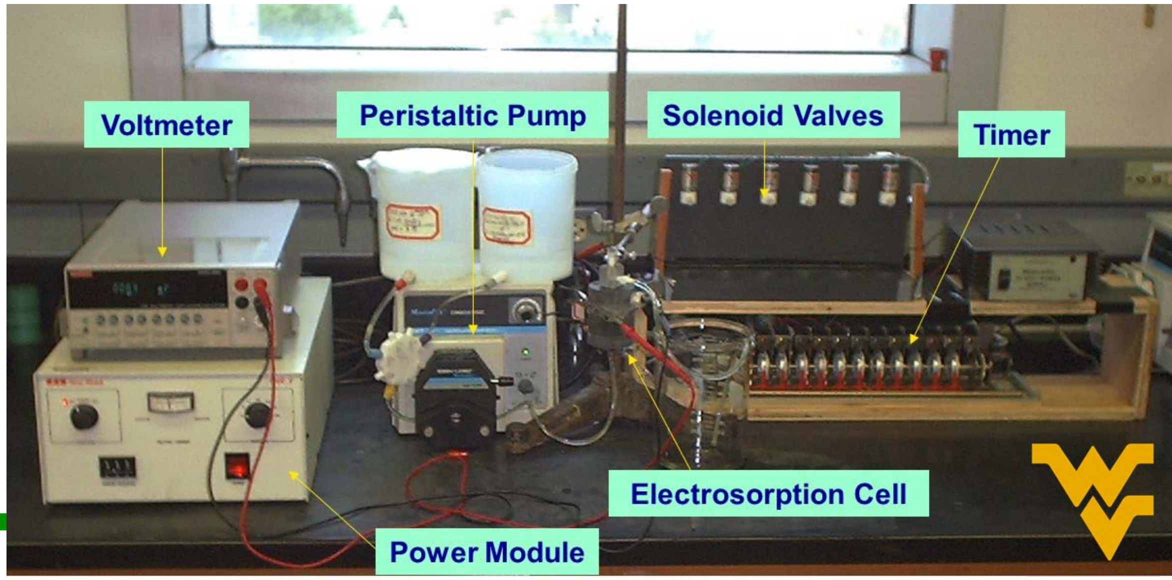
Electrosorption method for uranyl filtration from ground water streams

- First exposure to electrochemistry
  - Critical parameters that would become key for future work
    - Electrochemical induced pH changes near a high surface area electrode surface



Key findings:

- Electrolyte pH and applied voltage critical to absorption capacity
- Density of working electrode affected capacity
- System was inherently reversible by changing polarity.
- System is recoverable



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ND
(2003 – 2007)

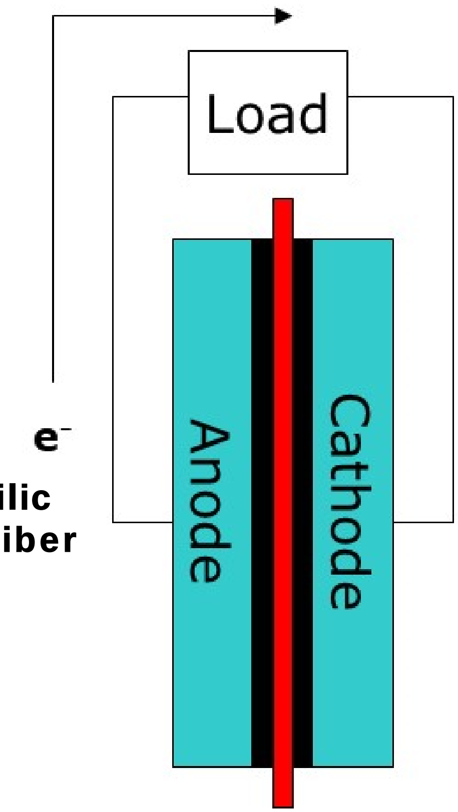
Catalyst and Microporous Layer Design for Low Temperature Polymer Electrolyte Membrane Fuel Cells.

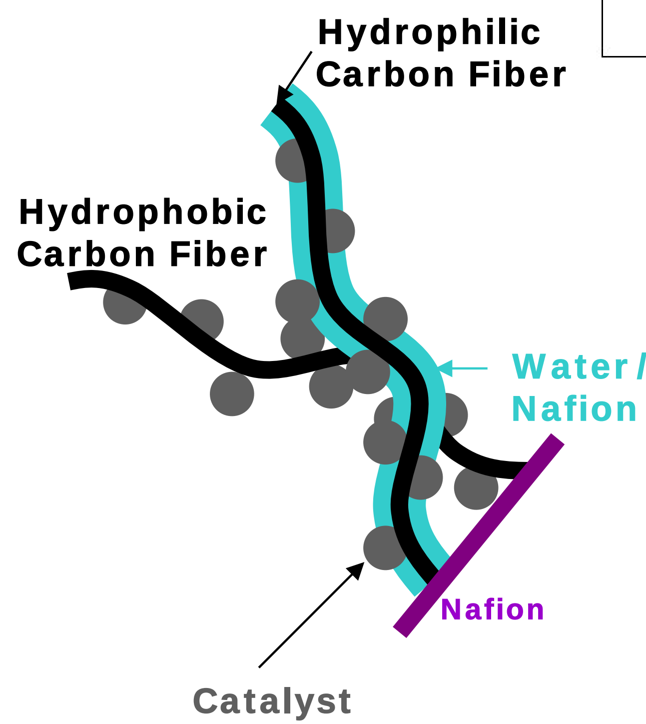
- Pulse electrodeposition of Pt and Pt alloys
- Water management design
- Combinatorial analysis of fuel cell performance
  - Direct methanol (DMFC)

    Anode: $CH_3OH+H_2O \rightarrow 6H^{+}+CO_2+6e^{-}$

    Cathode: $O_2+4H^{+}+4e^{-} \rightarrow 2H_2O$
  - H_2 fueled (PEMFC)

    Anode: $H_2 \rightarrow 2H^{+} + 2e^{-}$





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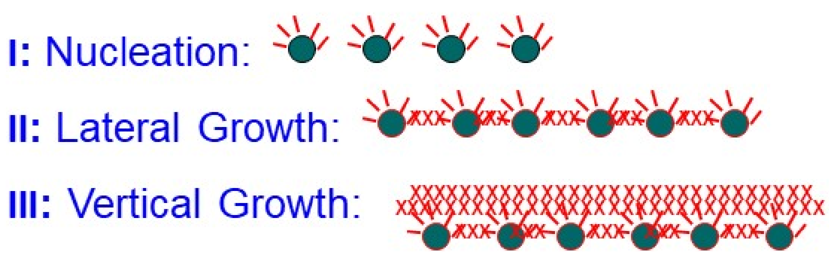
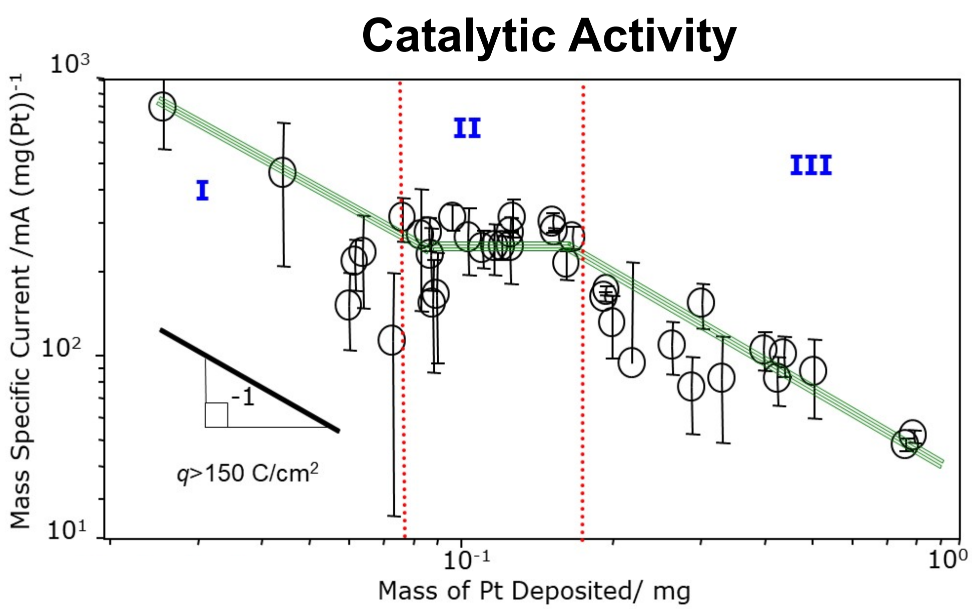
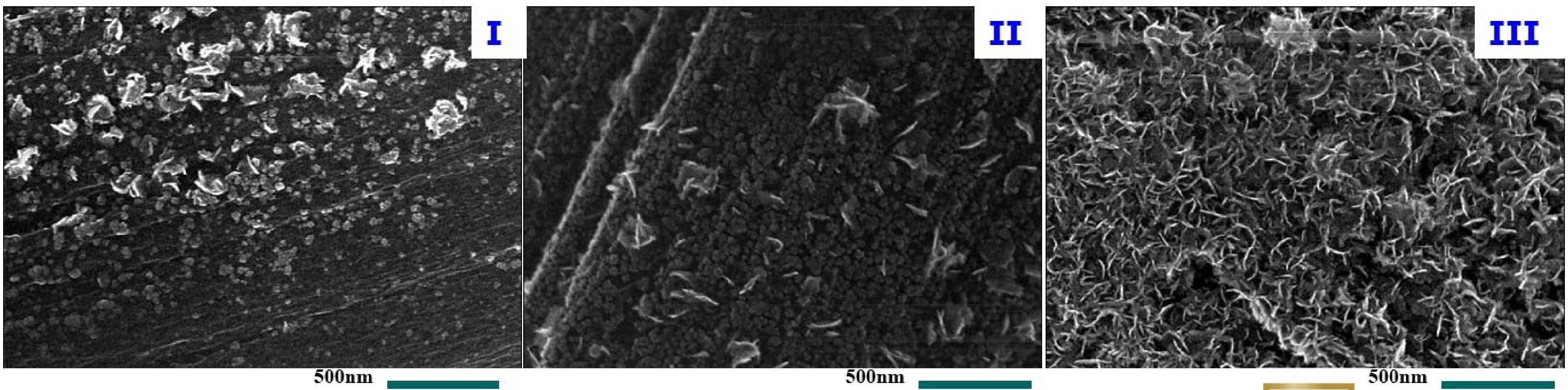
ND (Pulse Deposition)

Potential to Control the Boundary Layer and Catalyst Structure with Pulse

- Shows a broad range of Pt masses that achieve nearly identical activity for DMFC



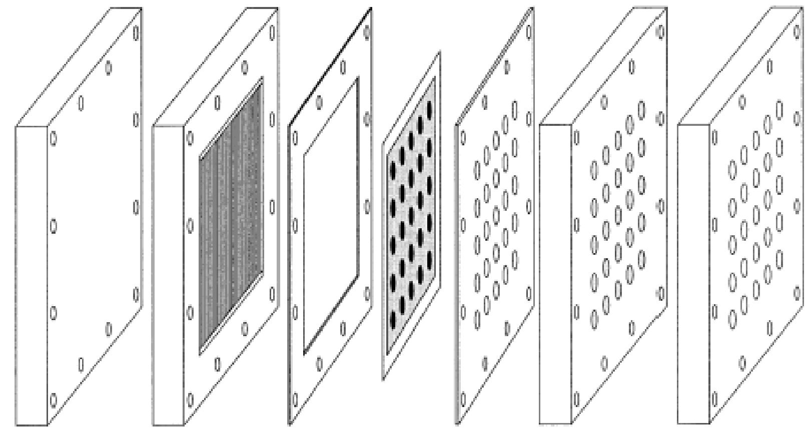


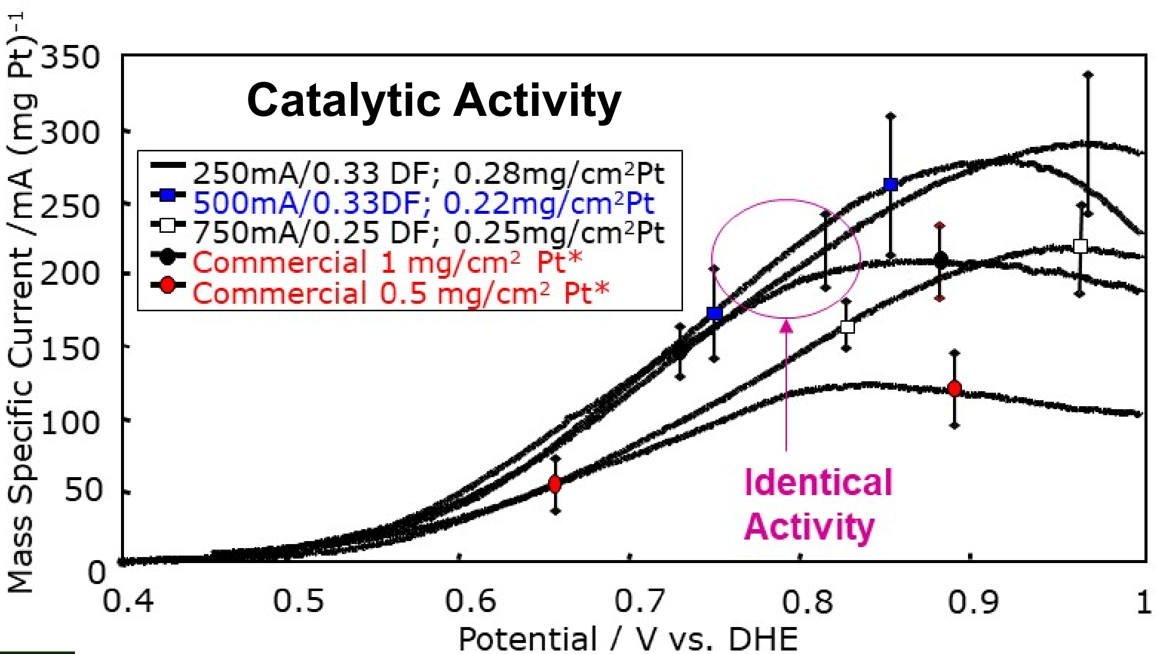


ND/NuVant Systems (2007-2009)

Combinatorial Electrochemical Characterization

- Used NuVant Systems Arraystat
- Showed improved electrocatalyst performance using PP Pt
- Led to my first professional job





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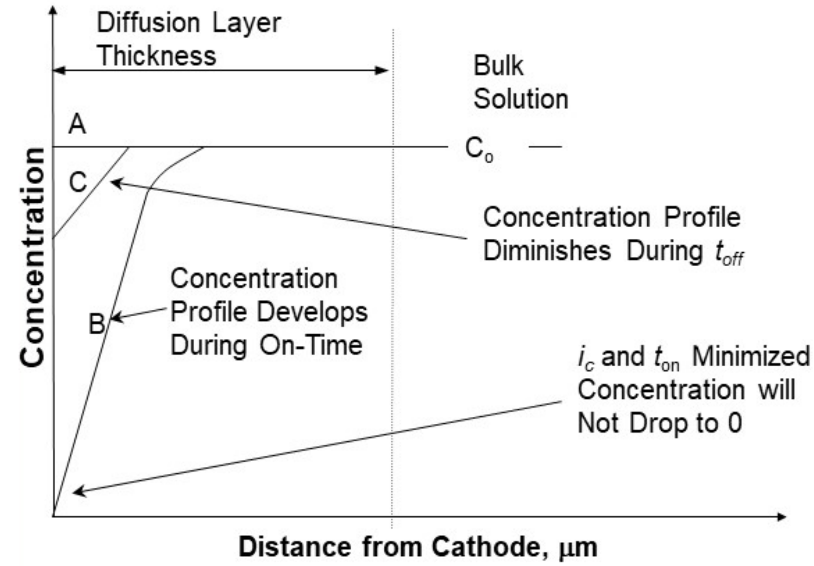
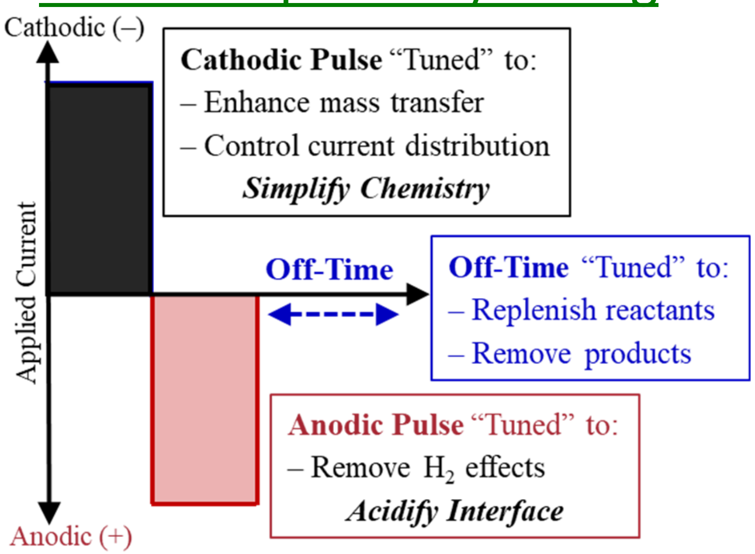
Faraday Technology (2009 to Present)

- Interest in
  - Electrochemistry
  - Electrochemical system design
  - Electronics
  - Boundary layer control
    - Pulse control

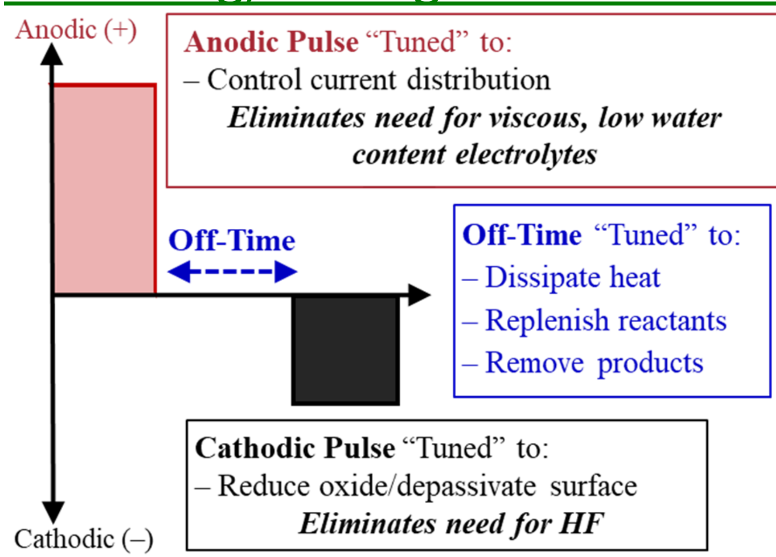


Led me to Faraday

Electrodeposition/Plating



Electrochemical Machining, Polishing, Deburring, Through-Mask Etching



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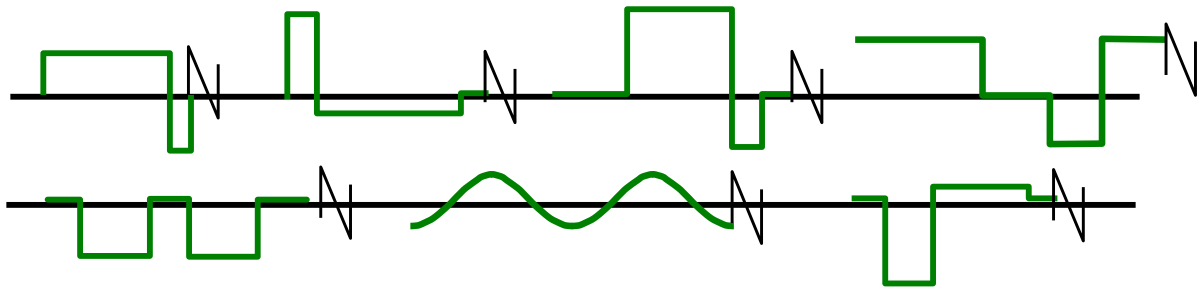
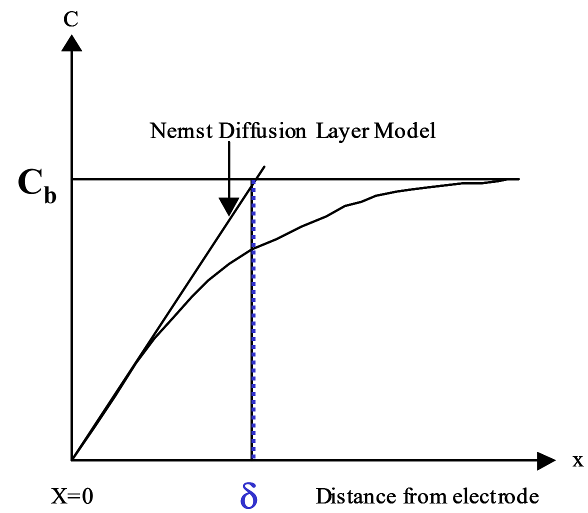


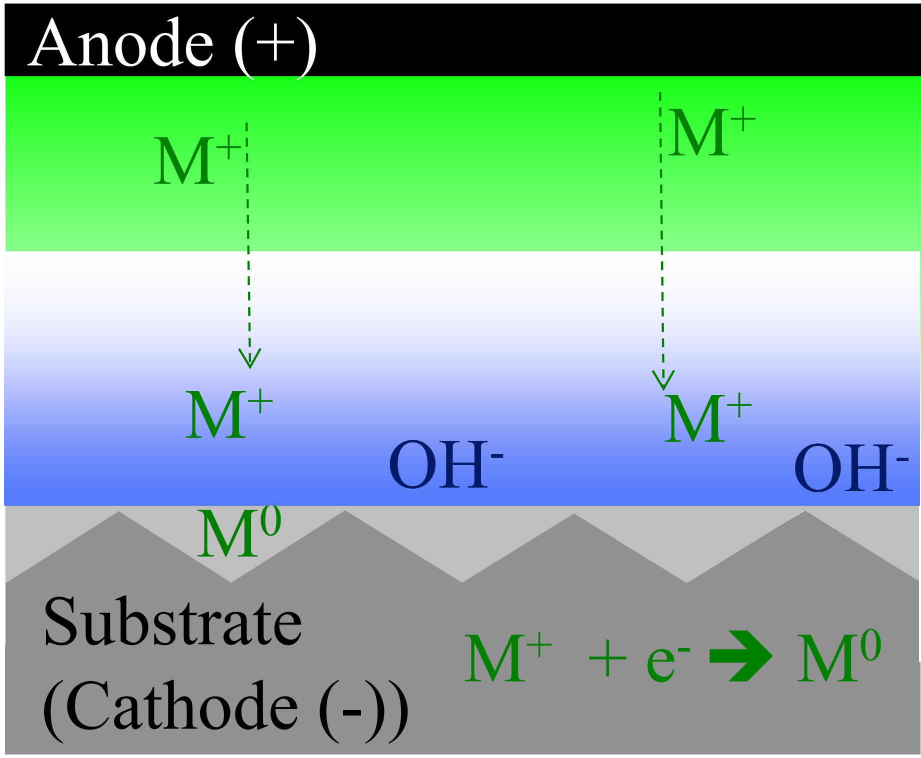
Pulse Deposition

Pulse Electrodeposition

- Generally, multiple reductions occur at the cathode
  - $M^+ + e^- \rightarrow M^0$
  - $H_2O + 2ye^- \rightarrow 2OH^-$
    - (when efficiency <100%)
- Local pH change can lead to side reactions
  - $M^+ + OH^- \rightarrow MOH$

❖Need to consider the pH change in the boundary layer as well as the concentration gradient in the diffusion layer





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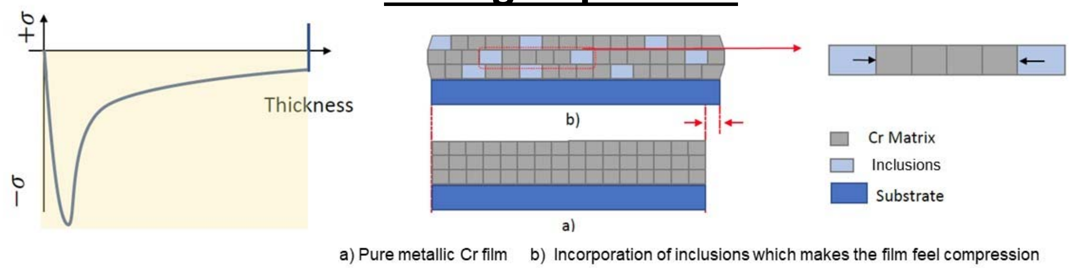
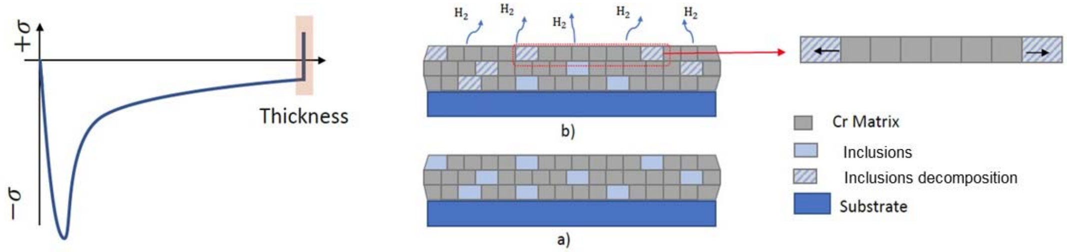
Pulse Electrodeposition with Single Metal

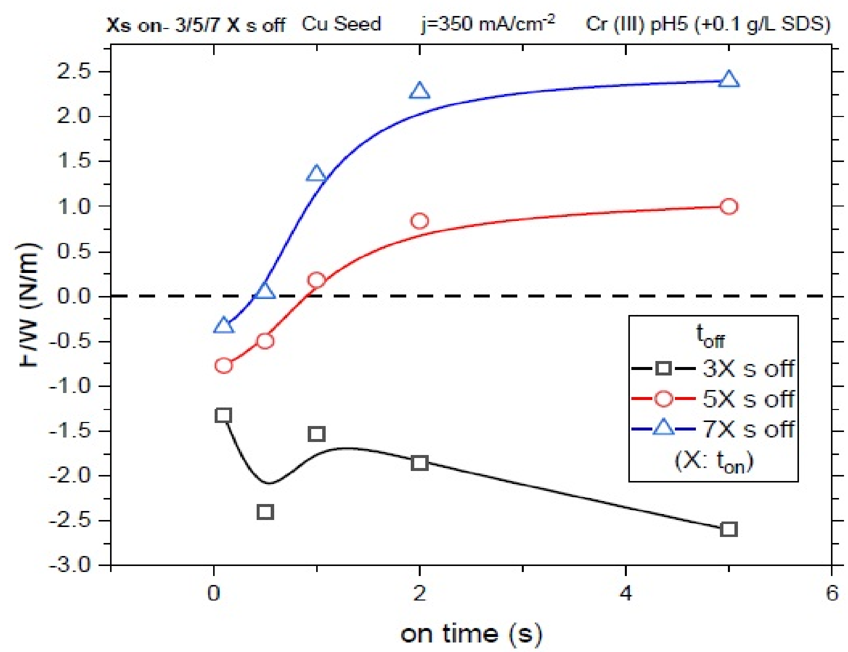
- Cr plating is an excellent example of side reaction affect
  - Efficiency less than 15%
  - Local CrOH formation
  - High current density leads to complexant break down
    - Inclusions of C, O, and presumably H in the deposit

During Deposition

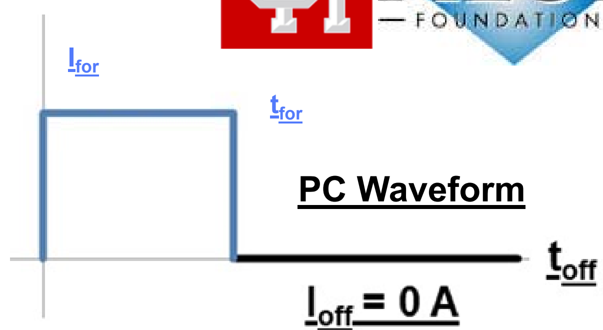


During Relaxation/Off-time





https://www.pfonline.com/articles/nasfaesf-university-funded-research-transitioned-to-industry-practical-performance-improvements-in-functional-reach-compliant-trivalent-chromium-plating



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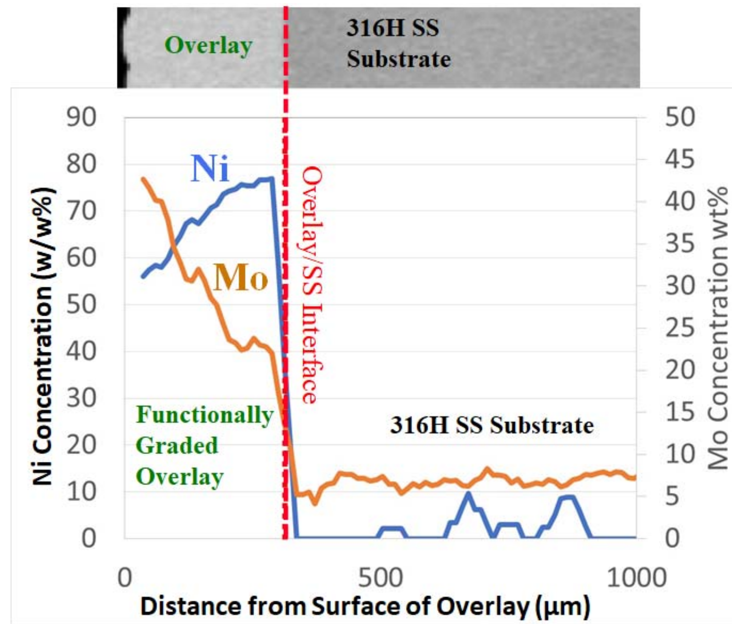
Ahmadi, J. Electrochem Society, 169, 012504 (2022)

Pulse with Alloy Metal Electrodeposition

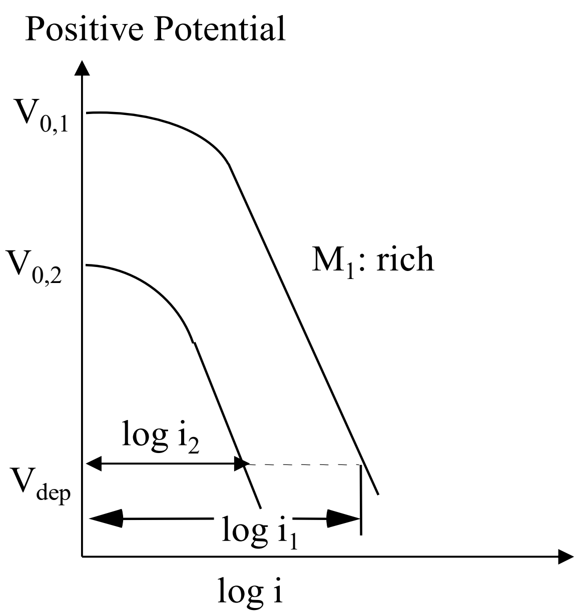
- Functionally graded NiMo coating
  - 0.2 M Ni
  - 0.02 M Mo

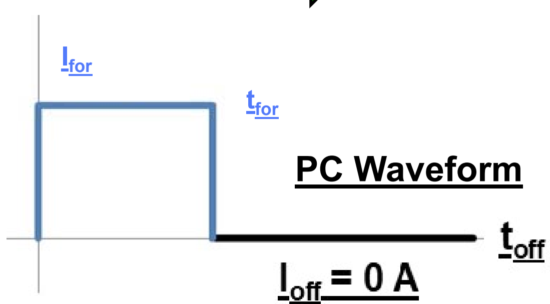
❖ Without electrolyte change large composition variance just with small duty cycle changes.

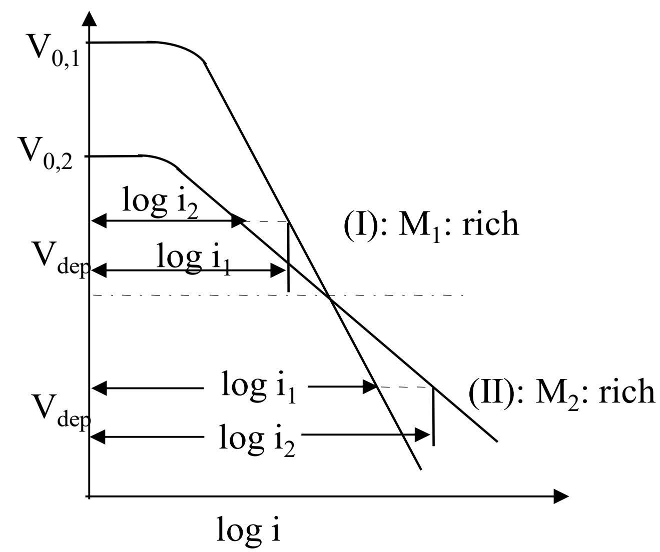
Possibilities With Pulse



Anticipated Deposition w/DC



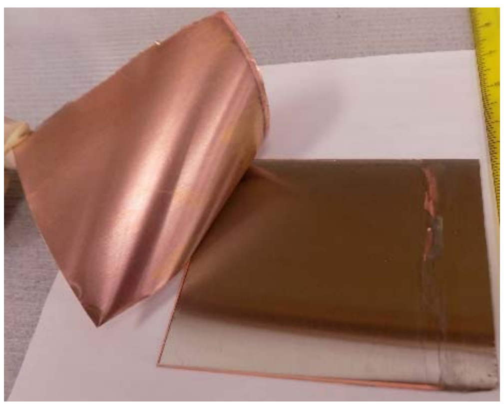




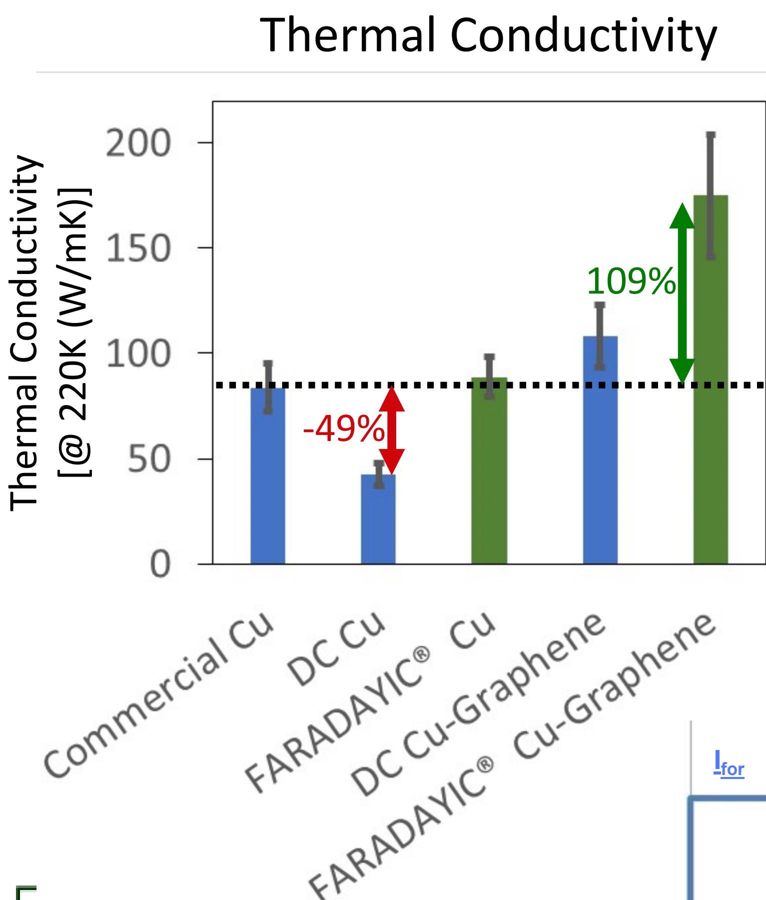
Pulse with Composite Electrodeposition

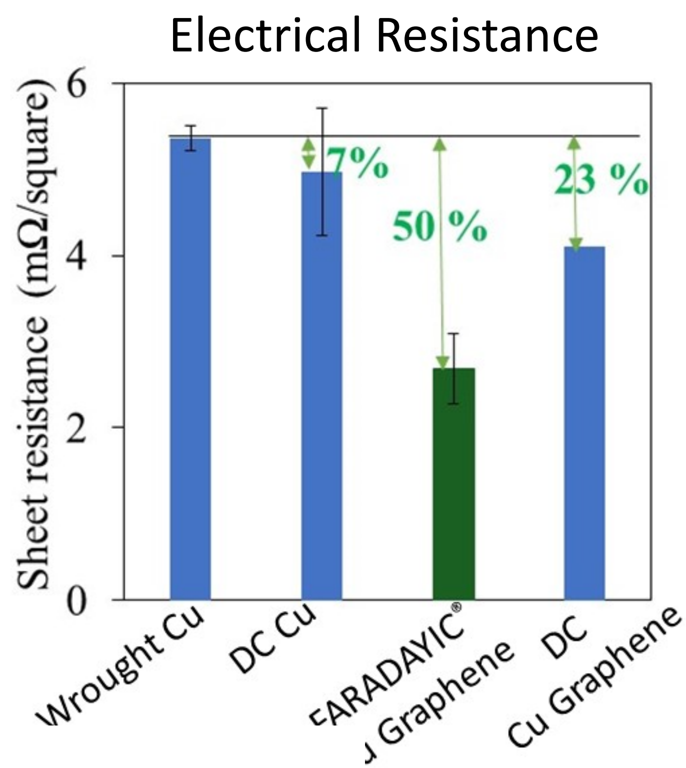
- Graphene inclusion concentration control leads to enhanced electrical/ thermal conductivity

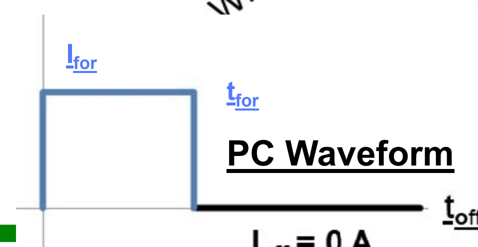
❖ Small on-time and off-time changes lead to large inclusion effect

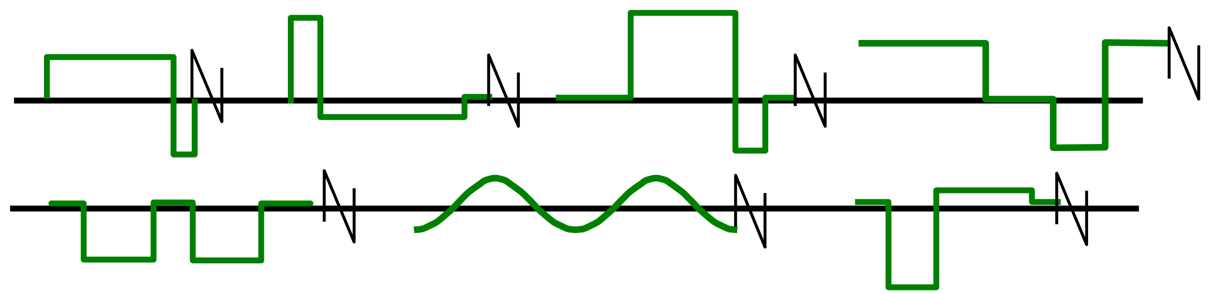


Cu/Graphene Foil





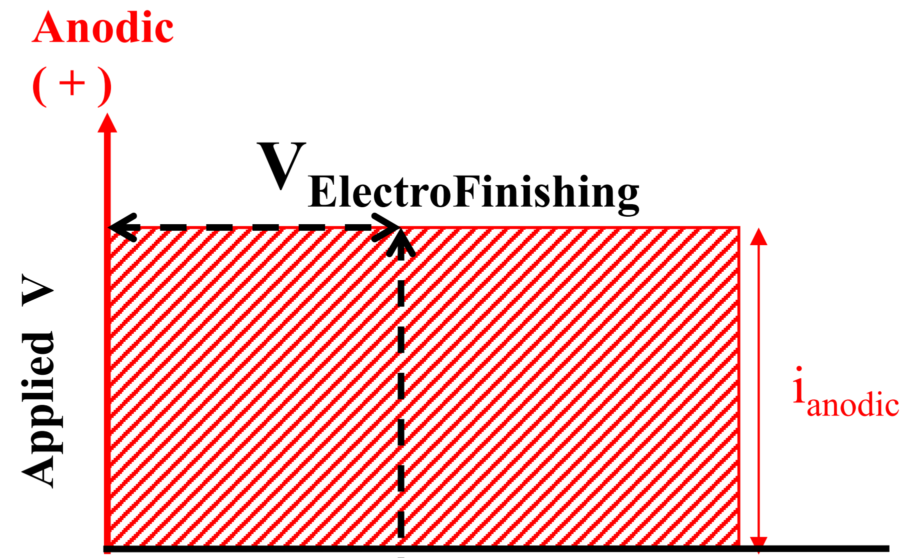


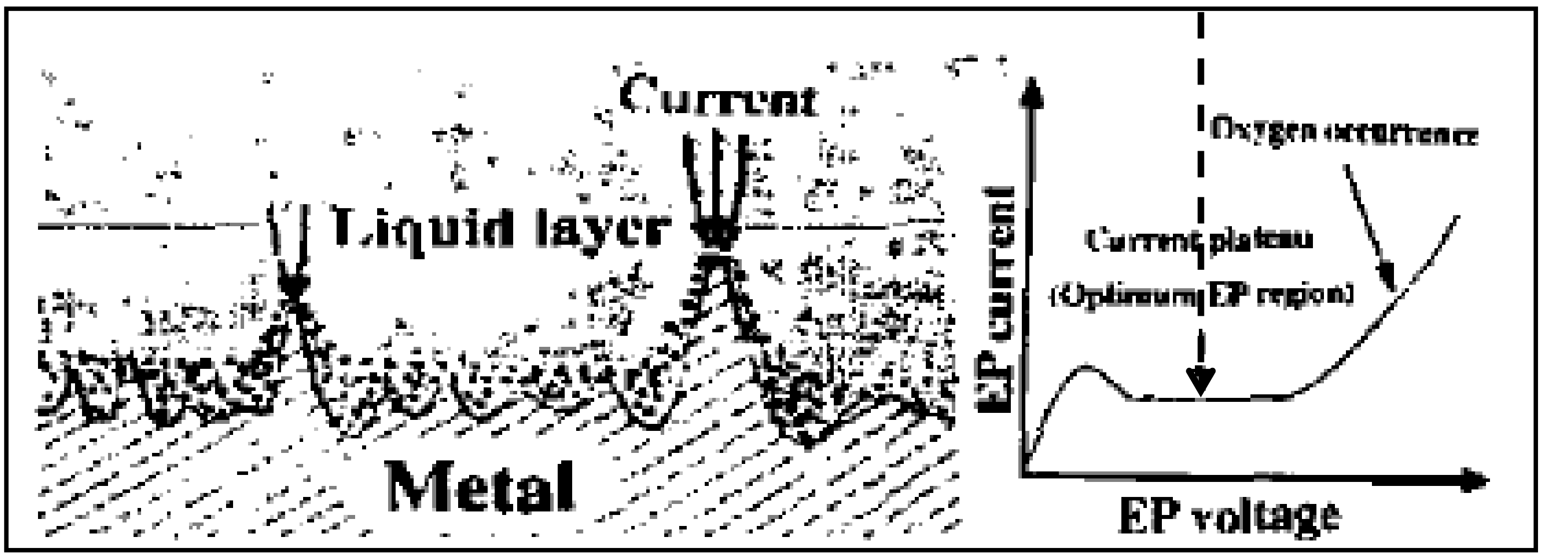


Pulse Surface Finishing

ElectroFinishing – Direct Current (DC)

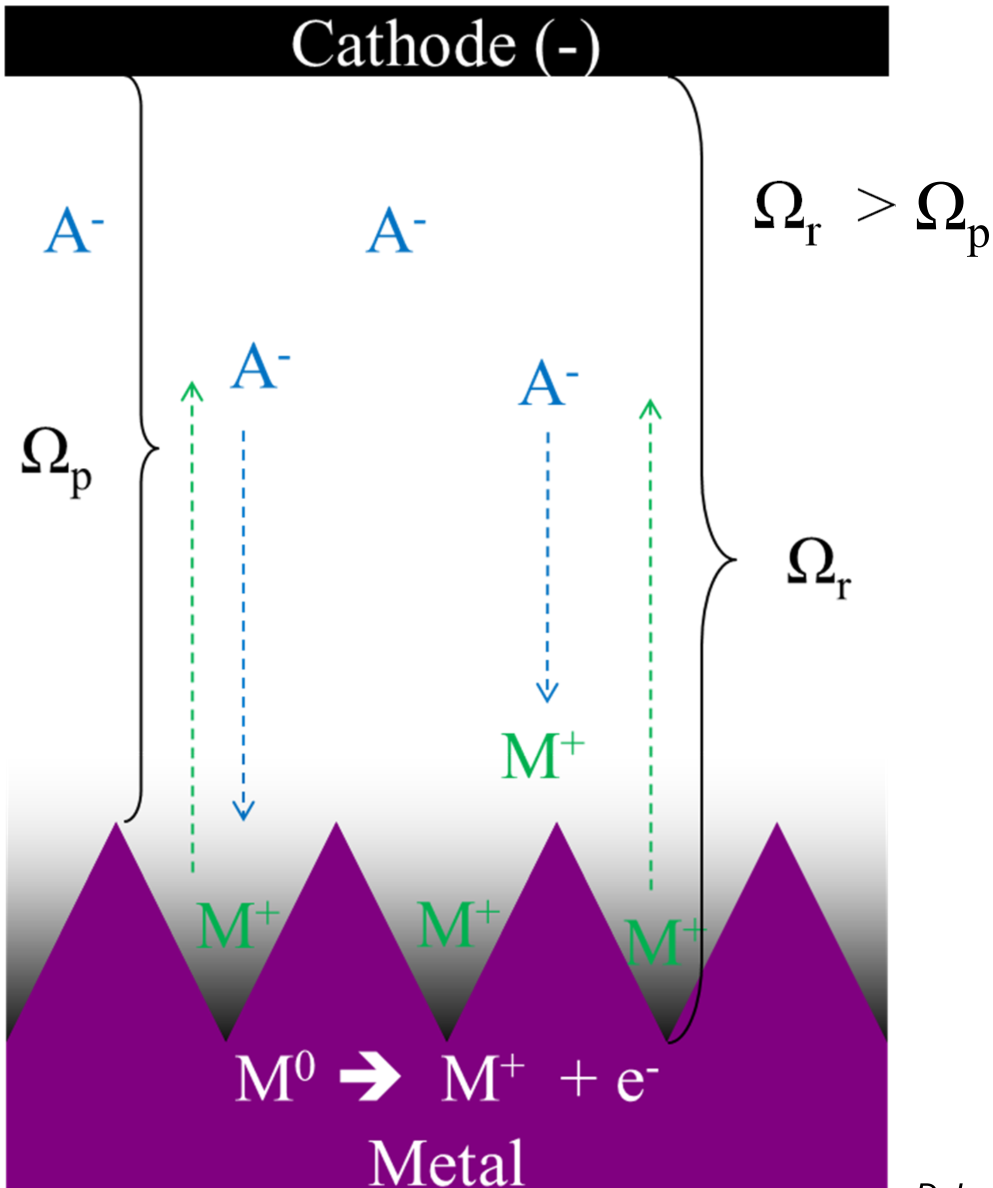
- Rectification:
  - DC - Constant voltage
  - Viscous salt film per Jacquet
  - Passive (oxide) film formation
- Electrolyte:
  - Concentrated/viscous acid
  - Chilled to increase viscosity
  - HF add to remove oxide





† *P.A. Jacquet, Trans. Electrochem. Soc.,* ***69*** *629 (1936).*

Conventional (DC) Surface Finishing



DC Finishing Challenges:

1st Challenge: Current distribution, i.e. focusing current preferentially on peaks or asperities

- ➢ Large Features > ~1 μm Macro-smoothing or leveling
- ➔ Chilled Resistive electrolytes
- ➢ Small Features < ~1 μm Micro-smoothing or brightening
- ➔ Chilled Viscous electrolytes

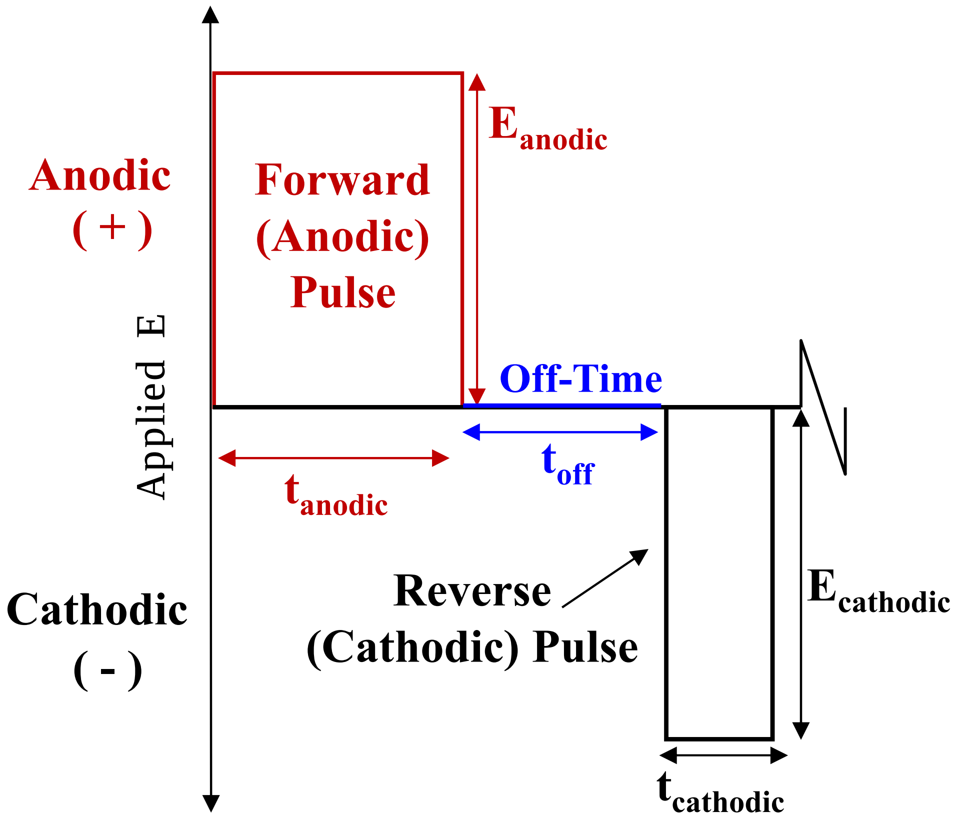
2nd Challenge: Polishing materials which form a passive (protective) or strongly passive layer

$$xM + yH_2O \rightarrow M_xO_y + 2yH^+ + 2ye^-$$

- ➢ Requires either water free or oxide preventing electrolyte (HF)

D. Landolt, Electrochimica Acta 32(1) 1-11 (1987).

Pulse/Pulse Reverse (P/PR) ElectroFinishing



Anodic Pulse – focus the current distribution to smooth surface

➔ Eliminates need for viscous electrolyte

Cathodic Pulse – depassivates surface/ removal of surface oxide

➔ Eliminate need for HF and/or low water content electrolytes

Off-time – no applied voltage

➔ Dissipates heat – simplifies cell design

➔ Replenishment of reacting species

➔ Remove reaction products

1. E.J. Taylor, M. Inman, *The Electrochemical Society Interface* 23(3), 57, Fall 2014
2. M. Inman, E.J. Taylor, T. Hall, *J. Electrochem Soc* 160(9), E94-E98, 2013
3. E.J. Taylor, M. Inman, T. Hall, B. Kagajwala, *ECS Trans* 45(8), 13-20, 2013

P/PR ElectroFinishing shifts the paradigm ➔ enabling use of aqueous, non-viscous electrolytes free of F^- /HF acid

P/PR ElectroFinishing Demonstrations

- Titanium Alloys
  - Nitinol (Ni:Ti 50:50)
  - Ti-15Mo
  - Ti-6Al-7Nb
  - **Ti-6Al-4V**
  - CP Ti (Grade 2/4)
- Mo
  - Pure Molybdenum
  - Spherical Mo-Hf
  - 52.5Mo-47.5Re
- Co-Cr
- **Nb**
- SAE 4159 Steel
- **Ta**
- Ta 10W
- **Cu**
- Stainless Steels
  - **316L**
  - 301/304
  - 430
  - C450
- Ni Alloys
  - **718 Inconel**
  - **625 Inconel**
  - Hastelloy
  - Haynes 230
- Aluminum Alloys
  - 6061
  - 7075

For P/PR (Generally);

$V_{Anodic} / V_{Cathodic}$ → **Material specific**

$t_{anodic} / t_{cathodic} / t_{off}$ → **Part/Cell geometry specific**

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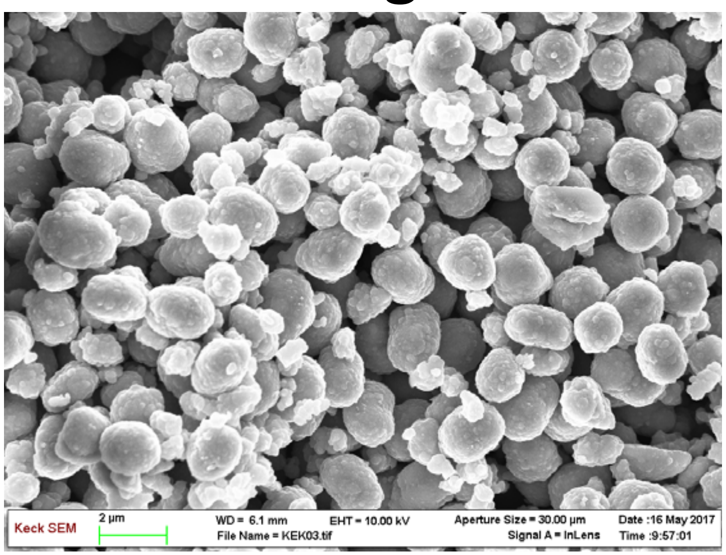
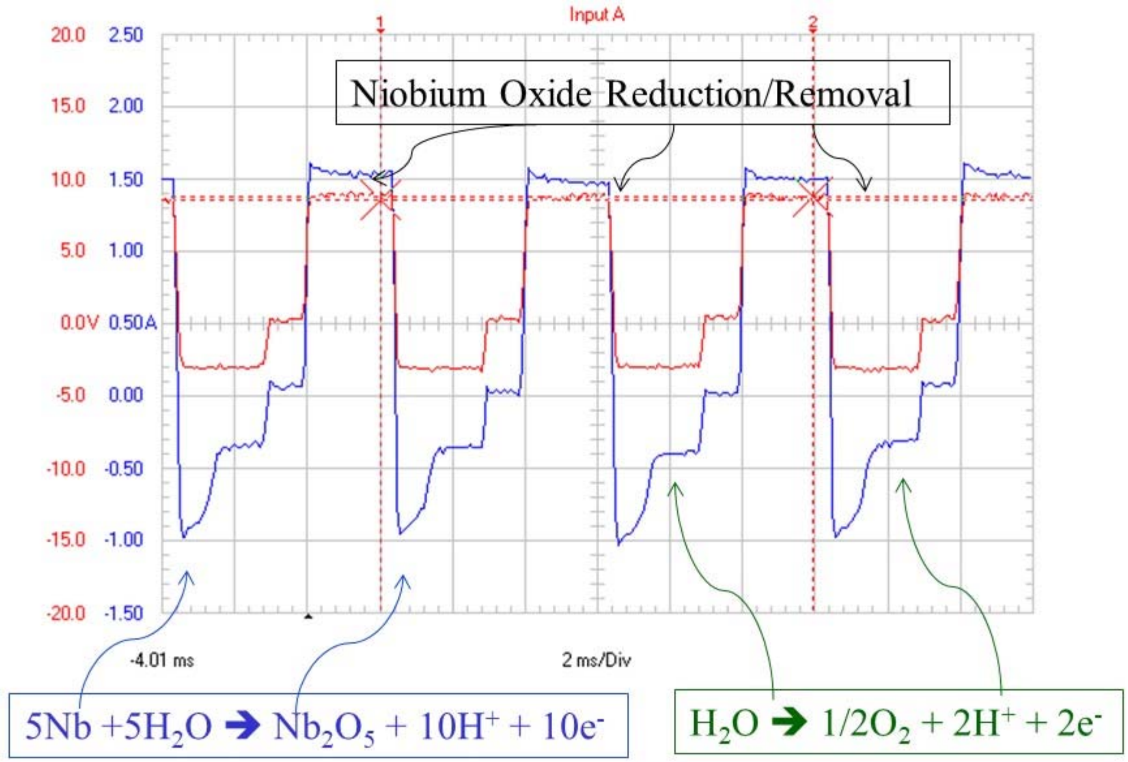
Electropolish Passive Materials with Pulse

- Highly passive materials form strong oxides
  - Commonly electropolished in 9:1 H_2SO_4: HF
- Control of surface oxidation enable water-based EP
  - $NaNO_3$ and water
  - 5 w/w% H_2SO_4 and water
- Cathodic etching???

Resulting Nb Powder



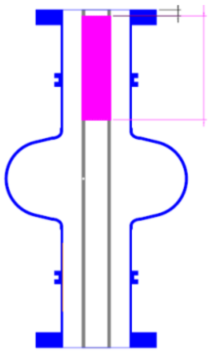


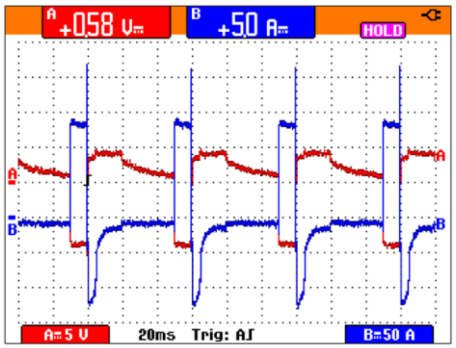
Electropolish Passive Materials with Pulse

Transition to complex cavity polishing

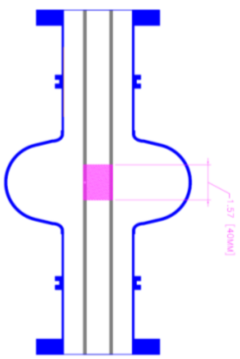
- Pink is open cathode area

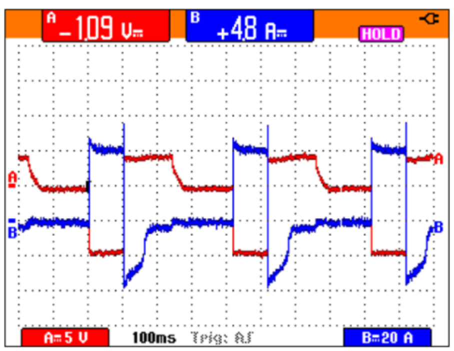
Trial 12



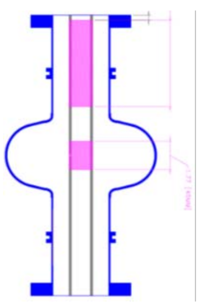


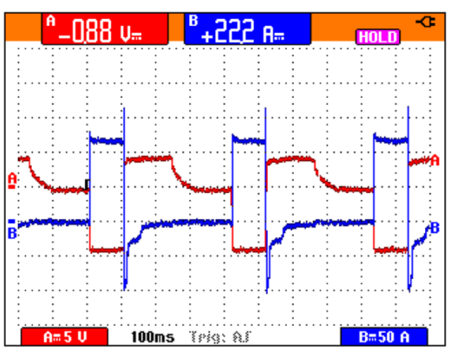
Trial 13



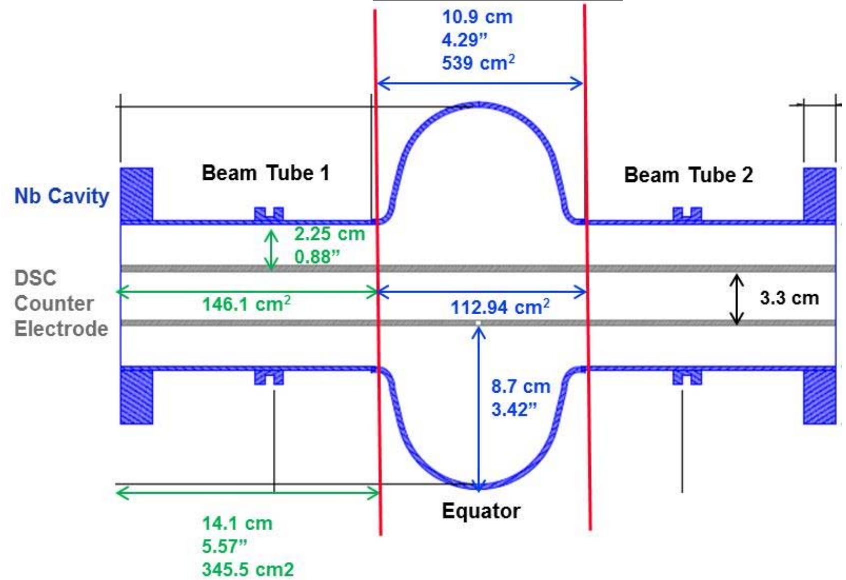


Trial 14



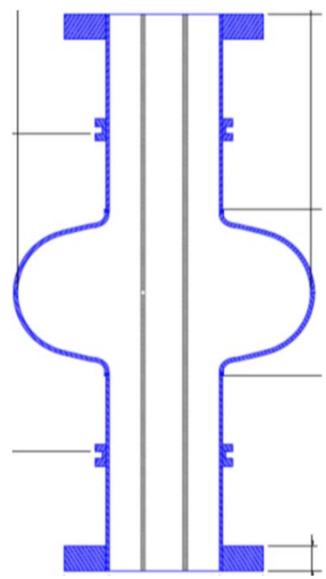


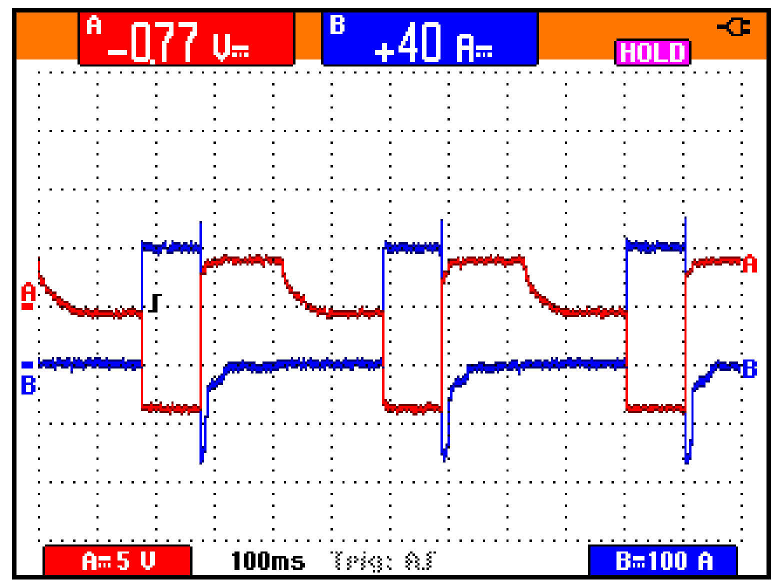
Cavity Shape



Unmasked Cavity

Trial 17





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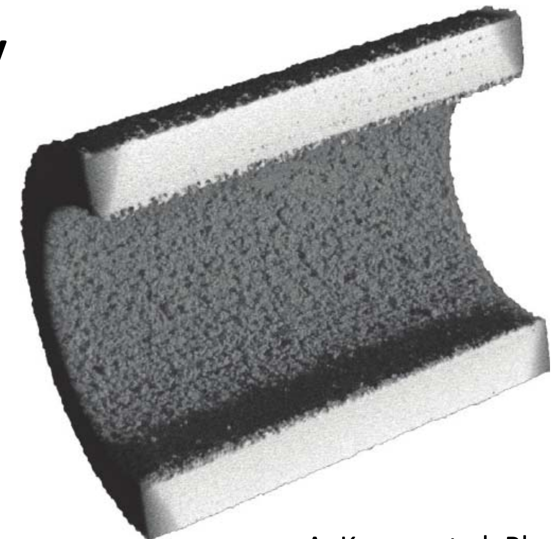
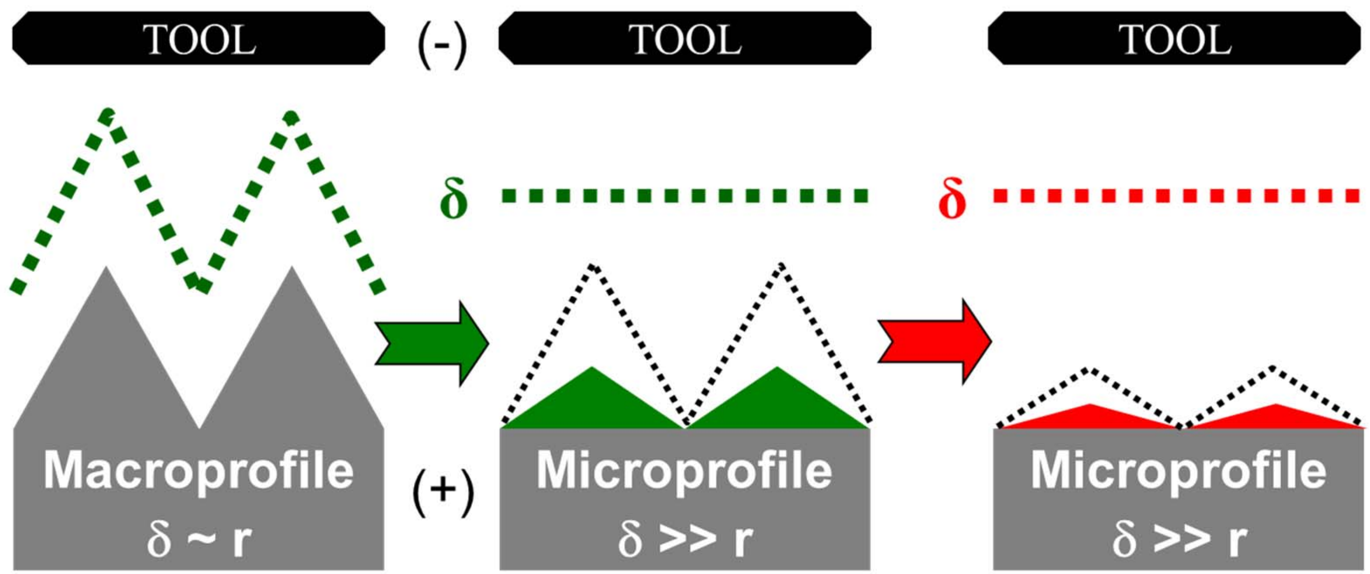
Finishing Complex Materials with Pulse

- Additively manufactured parts have a many levels roughness
  - As you finish the surface:
    - Surface area and profile height changes
    - Required boundary layer changes



A. Karme et al, Physics Procedia, 78, 347-356 (2015)

❖ Design polishing conditions to accommodate changing surface



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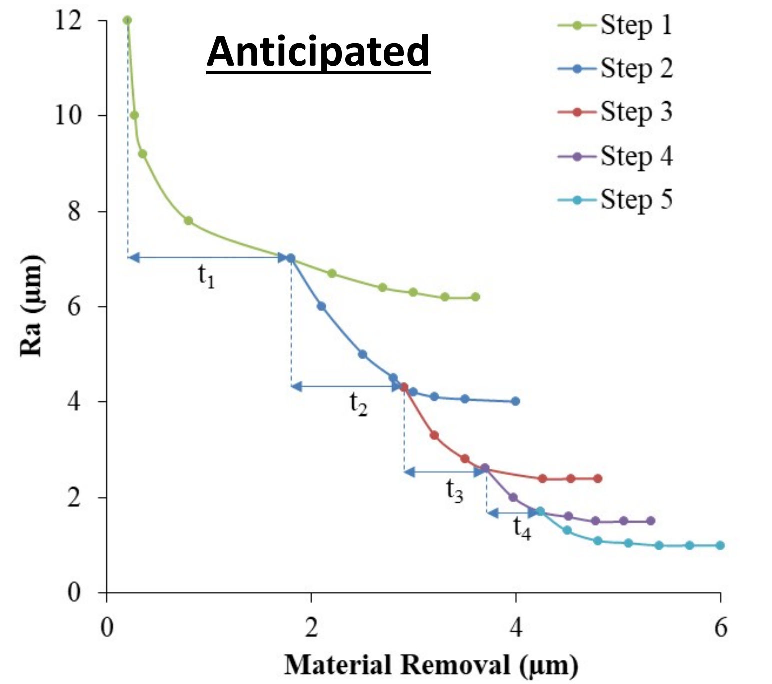
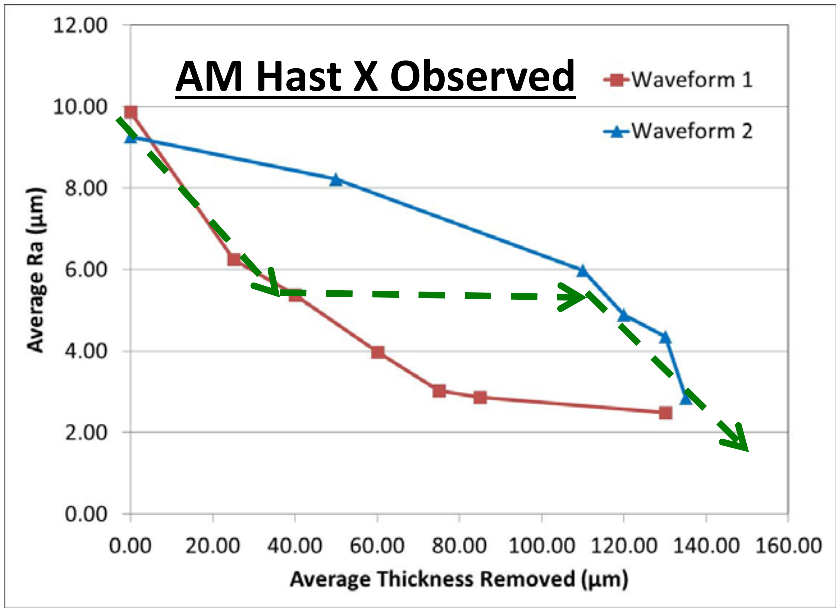
Finishing Complex Materials with Pulse

- **CHALLENGE:** Improve Ra < 2 µm while minimizing material removal
  - ***Waveform 1:***
    - Initial rapid ΔRa/Δmaterial removed until ~6 µm Ra reached
    - Decrease in ΔRa/Δmaterial removed after ~6 µm Ra reached
  - ***Waveform 2:***
    - Initially slow ΔRa/Δmaterial removed until ~6 µm Ra reached
    - Increase in ΔRa/Δmaterial removed after Ra < 6 µm
- **SOLUTION:** Initiate process with Waveform 1(4 min) until Ra ~6 µm then switch to Waveform 2(1 min) until next critical Ra ~1.8 with 80 µm removed.





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US Patent 11,118,283

Electropolishing Precipitating Alloys

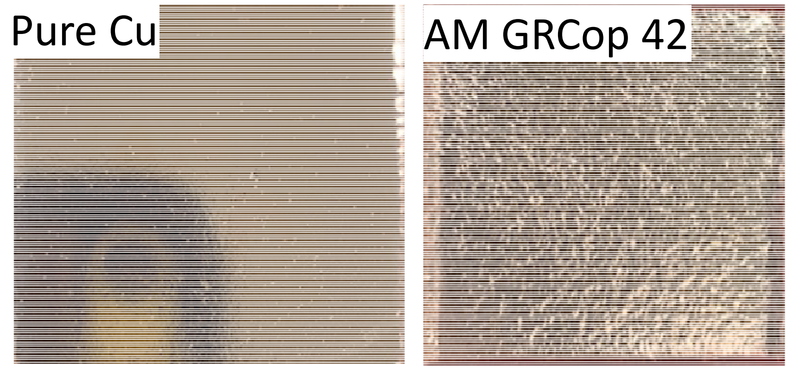
- GRCop 42
  - 0.06% Al; 3% Nb; 0.04% Si; 3.4% Cr; 0.03% Fe

❖ Complex alloys require special consideration

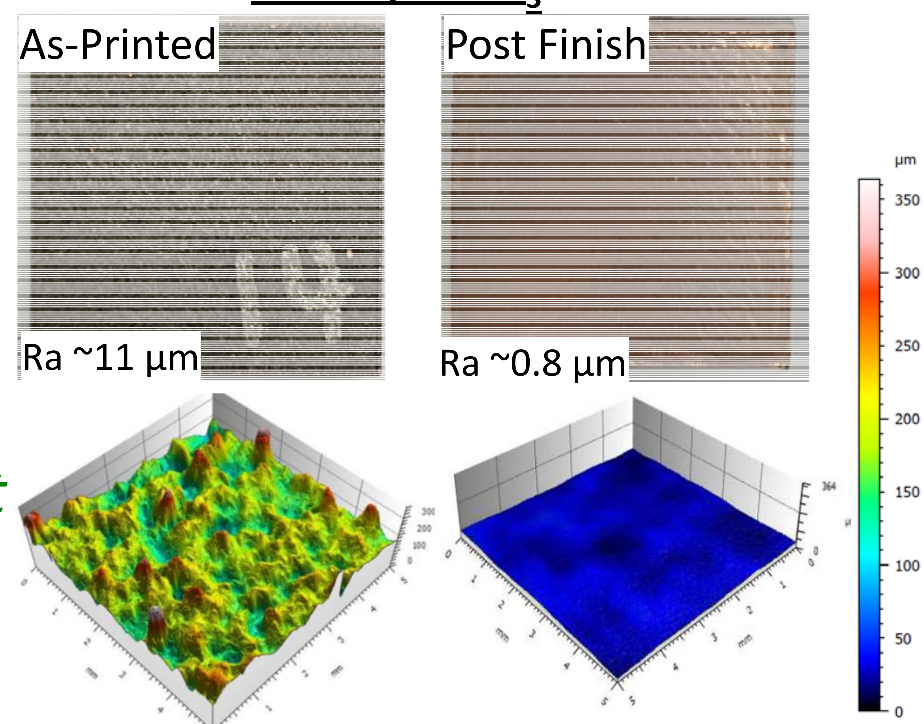
- ➢ Nb/Al are passivating but low concentration
  - ❖ Must <u>exceed</u> *breakdown voltage* or provide *cathode breakdown*
- ➢ Cr and Fe are known to ppt at surface
  - ❖ Must <u>consider</u> *flow and off-time* to control the movement of the ppt.

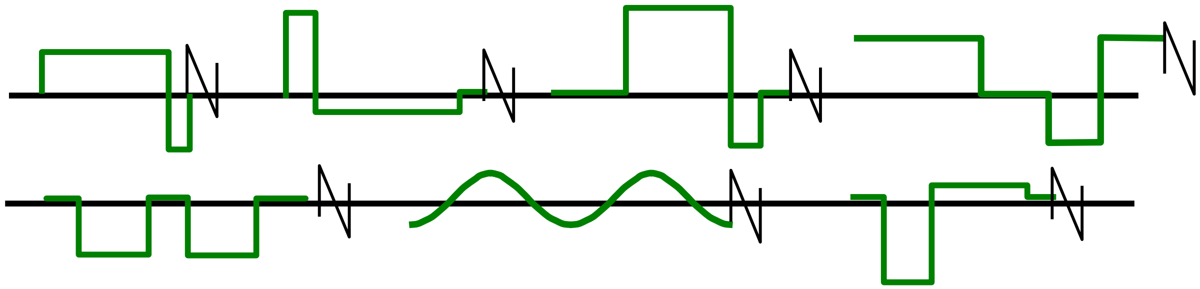
Changes in roughness leads to changes in ppt thickness and mobility

<u>Electropolishing in SO_4/PO_4</u>



<u>AM GRCop 42 Electropolishing in $NaCl/NaNO_3$</u>





What is next?

Electrodeposition

- Identify new alloys and materials
- Enable new performance properties
  - Electrical Resistance
  - Fatigue Resilience
  - Hardness
  - Corrosion Resistance
  - Embrittlement mitigating
  - Wear Resistance
  - Thermal Resistance
  - Thermal Expansion Match
  - Environmental Stewardship

Single metals that can be electrodeposited

Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	o
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 SC	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

Alloy metals that can be electrodeposited

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Se	Zr	Mo	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	W	Re	Ir	Pt	Au
Au																									
Pt																									X
Ir																								X	
Re																								X	
W																						X			X
Sb																					X				X
Sn																				X	X			X	X
In																			X	X					X
Cd																		X	X	X	X			X	X
Ag																	X	X	X	X	X	X	X	X	X
Pd																X			X					X	X
Rh															X	X					X		X	X	X
Ru														X	X			X						X	
Mo																X			X		X				X
Zr																	X								
Se																X	X			X					X
Zn										X	X	X				X	X	X	X	X	X			X	X
Cu									X	X		X			X	X	X	X	X	X	X	X		X	X
Ni								X	X	X		X	X	X	X	X	X	X	X	X	X	X		X	X
Co							X	X	X			X	X	X	X	X	X		X		X	X		X	X
Fe						X	X	X	X			X			X	X	X		X		X	X		X	X
Mn					X	X	X	X	X	X		X							X		X				X
Cr				X	X	X	X			X		X				X			X	X	X	X			
V			X	X	X	X			X																
Ti			X		X	X	X		X								X								

Eliaz, N., et al., *Modern Aspects of Electrochemistry* **42** Springer, NY, (2008), p 191, Ch. 4

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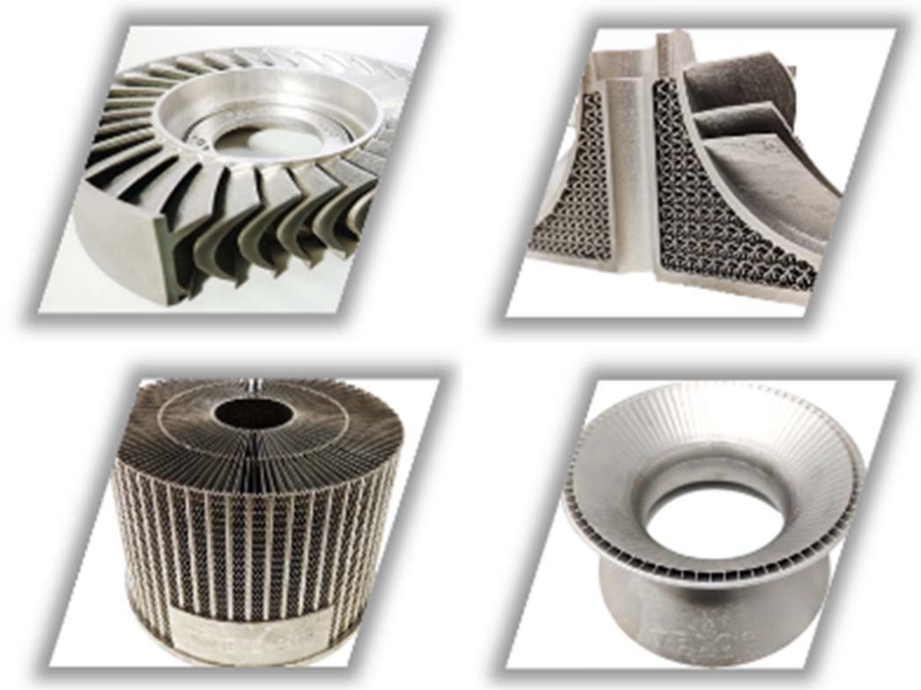
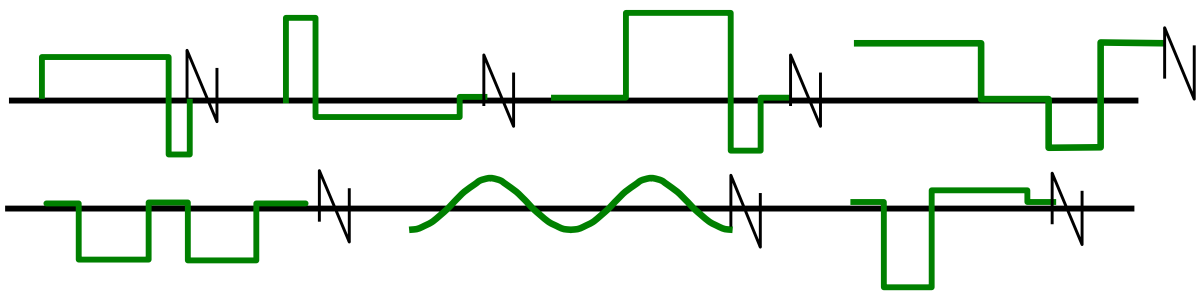
Surface Finishing

- Enable operations with new AM based material systems
- Align existing manufacturing processes with new complex parts and structures
- Develop new software to predict operations and tool designs



FARADAY TECHNOLOGY, INC.



Where is NASF and AESF?

Research Approach

- European View:
  - Government funded interest led to:
    - German and France have master level programs to train and develop new techniques in electrochemical engineering (plating and finishing)

TECHNISCHE UNIVERSITÄT ILMENAU

UBFC UNIVERSITÉ BOURGOGNE FRANCHE-COMTÉ

- US View:
  - Broad range of electrochemical professors across the US
    - Very little funding to drive students to advance technologies in traditional electrofinishing

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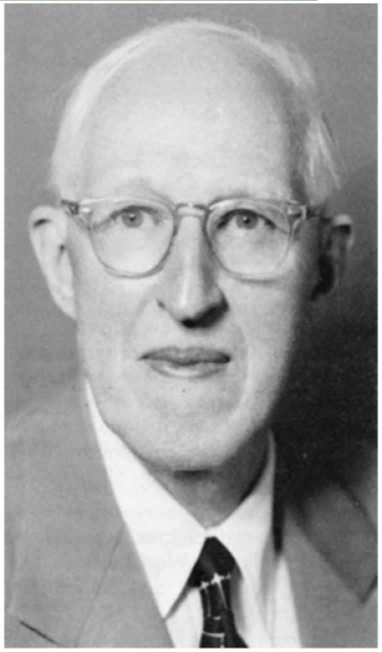
AESF

- Dr. William Blum's first lecture (1959):

  Education and the Electroplating Industry

- Key findings:

The society needs to educate apprentices, platers, works chemists/engineers, research chemists/engineers, plant executives, designers and the purchasing public



- AESF offers an extensive educational course load
  - These opportunities serve traditional plating industries
- AESF offers 4 University grant scholarships
  - These opportunities foster focused future research on advance technology needs for the community
- NASF leads the public education through lobbying activities

FARADAY TECHNOLOGY, INC.

AESF/NASF Role in Surface Finishing Ecosystem

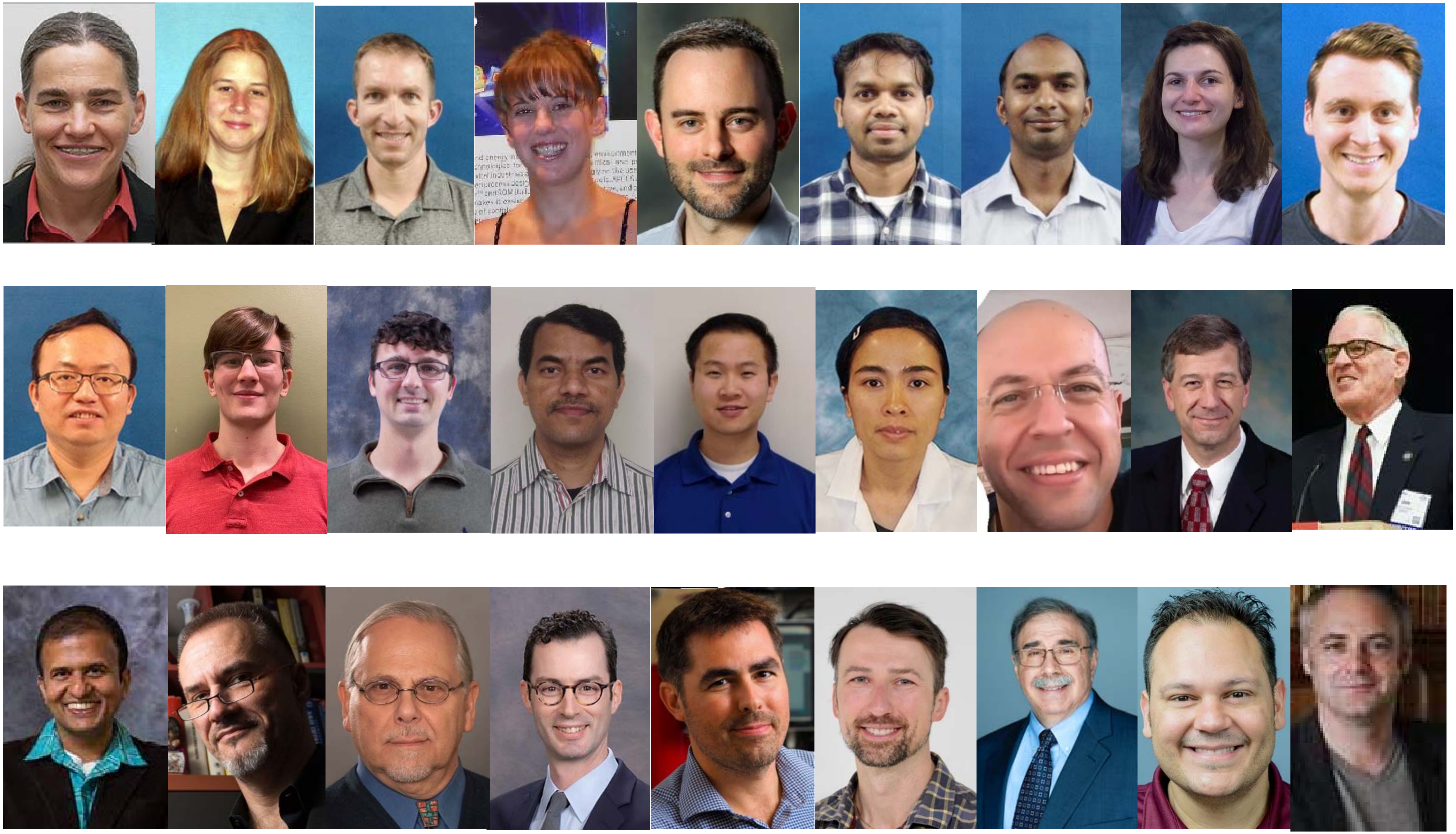
- An international organization
  - Encompassing BOTH US & European & Asian "research view"
- Unique membership
  - Symbiotic nature of industry and academia
- Develops educational content
  - Coursework and training for certification of today's workforce
- Student scholarships & internships
  - Real world experience AND introduction to industry opportunities
- Research grants
  - Foundation for tomorrow's innovative products/services
  - Introduction of student researchers to industry opportunities
  - Travel to SURFIN conferences

Next Steps

- Reach out and identify professors progressing our mission
- Learn more about opportunities in NASF/AESF
- Look to enable new opportunities to
  - Foster future mentors
  - Receive hands on experiences
  - Drive government funding

In order to create one must first question that which exists!!!

Mentors, Colleagues, Collaborators, and Friends



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