SAND2014-18357PE

Exceptional service in the national interest

Sandia National Laboratories

Electrochemical Fabrication of Energetic Thin Films

Jonathan Coleman

Sandia National Laboratories, University of New Mexico

Christopher Apblett, Graham Yelton, Robert Knepper

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

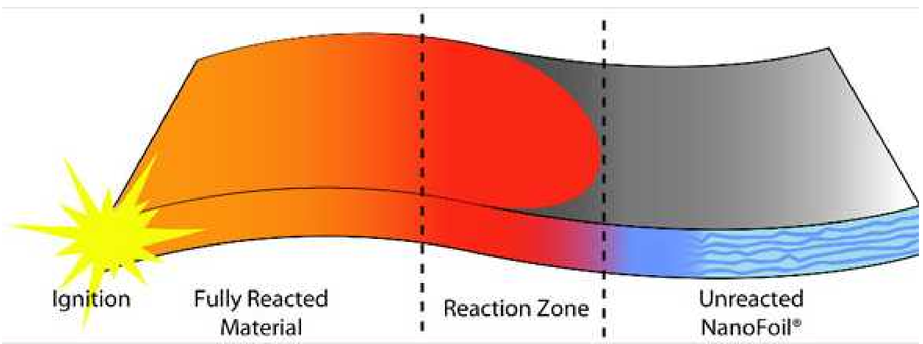
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

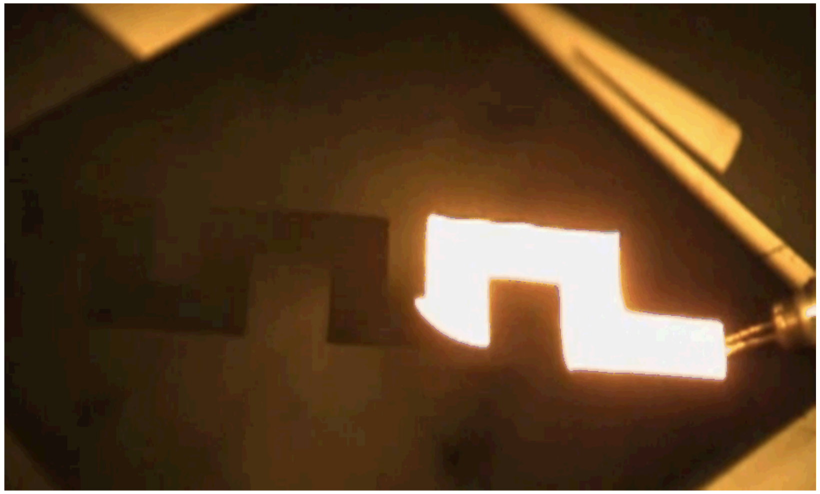
Outline

- Energetic Thin Films
- Reactive Metal Couples
  - Aluminum and Nickel alloying exothermic properties
  - Current fabrication techniques and opportunities
- Aluminum Plating in Ionic Liquids
  - Transport and kinetics investigation
  - Dilution agents and optimization
- Analysis and Results
  - Film codepositions and phase interface
  - Reaction testing
- Conclusions

Energetic Thin Films

- Localized Heat Sources
  - Brazing and welding
  - Electronics assembly
  - Energetics
    - Propellant ignition, munitions and circuit protection applications
    - Heat sources for thermal batteries

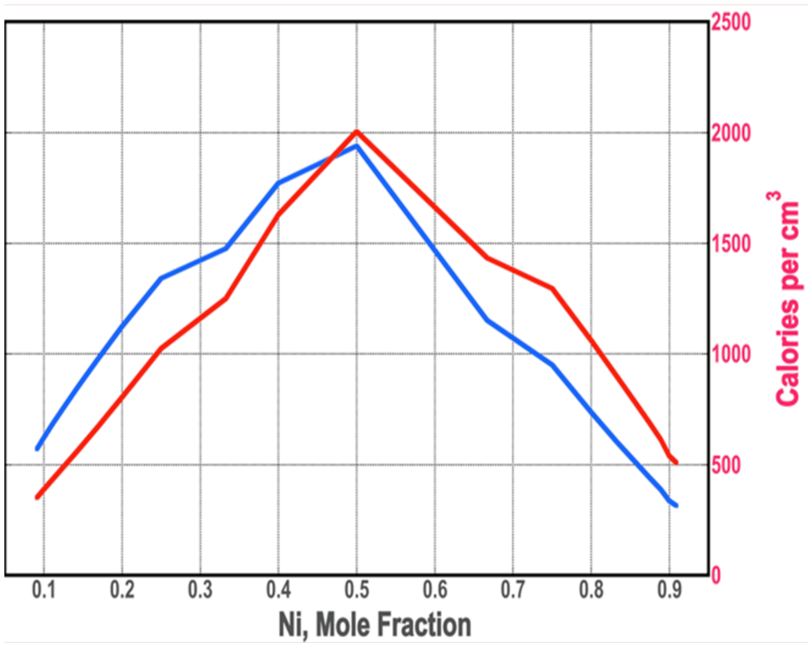




http://www.indium.com/nanofoil/

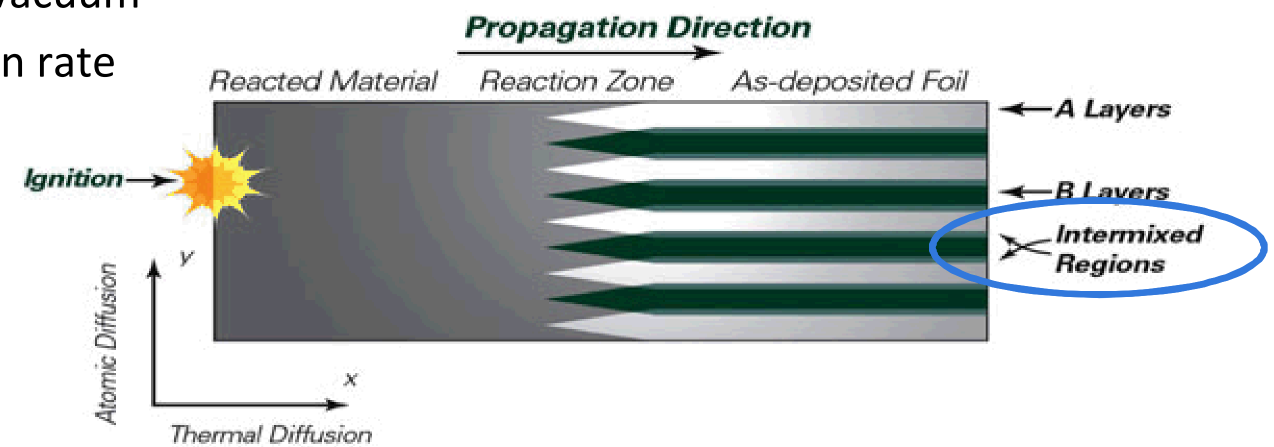
Reactive Metal Couples (Ni-Al)

- Reaction rate increases with increasing interfacial area
  - Improves propagation reliability and speed
  - Higher rates generate higher maximum temperatures
  - Metals can diffuse between the interface, decreasing energy of reaction
- Abundant and relatively cheap materials
  - High energy output
  - Inherently conductive
- Max energy at 50% mole fractions
  - 60% Aluminum by volume



Current Fabrication Method

- Physical Vapor Deposition
  - Alternating Nickel and Aluminum multilayer process
    - Reliable layer thickness and composition
    - High quality and sharp interfaces
  - Drawbacks
    - Requires high vacuum
    - Slow fabrication rate

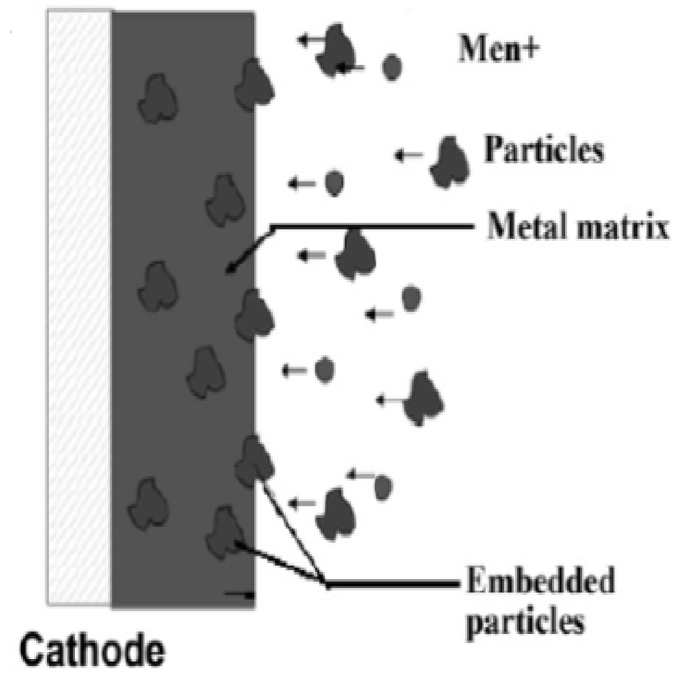


S. Ito, S. Inoue, and T. Namazu "The Size Limit of Al/Ni Multi Layer Rectangular Cuboids for Generating Self-Propogating Exothermic Reaction on a Si Wafer" 2010

T. Namazu, H. Takemoto, H. Fujita, Y. Nagai, and S. Inoue, "Self-Propagating Explosive Reactions in Nanostructured Al/Ni Multilayer Films as A Localized Heat Process Technique for MEMS", 2006

Dispersion Plating

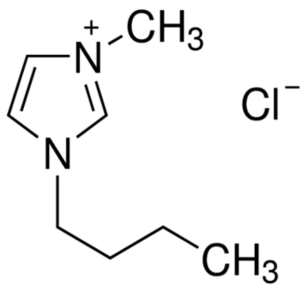
- Electroplating bath also consists of suspended particles that are incorporated in the film
  - Nanoparticles are high surface area and phase separated from the matrix metal
- Particle incorporation is lower volume than deposited matrix
  - ***Since 60% of the volume will be Aluminum, the matrix must be Aluminum***



"Electrodeposition of composite coatings containing nanoparticles in a metal deposit" C.T.J. Low, R.G.A. Wills, F.C. Walsh 2005
"Synthesis, characterization and comparison of sediment electro-codeposited nickel–micro and nano SiC composites" P. Narasimmana, Malathy Pushpavanama, V.M. Periasamyb

Aluminum Deposition

- Ionic liquids based on chloroaluminate anions deposit aluminum readily with limited hazards
  - Low vapor pressure and non flammable
  - Very high aluminum concentration
- Low diffusion rates
  - Large bulky ions
  - High ionic interactions



Butyl methylimidazolium Cl (BMIC)

- ***Butyl methylimidazolium is stable at overpotentials required to deposit aluminum***
  - ***Diffusion is very low which leads to dendritic deposits***
  - Implement dilution agents to improve transport properties

Co-Solvent Additions

Sandia National Laboratories

- Diffusion and conductivity are increased by adding co-solvents
  - Aromatics are inert in the ionic liquid
  - Impart new properties into the electrolyte
  - Decreases viscosity and improves mobility
  - Decreases ionic concentration

	O-Dichlorobenzene	Toluene
Viscosity	1.32	0.56
Polarity (dipole moment)	2.3	0.36
Vapor pressure (mmHg)	1.3	22

Need to optimize overall electrolyte properties

↓ Viscosity ↑ Diffusion Rate

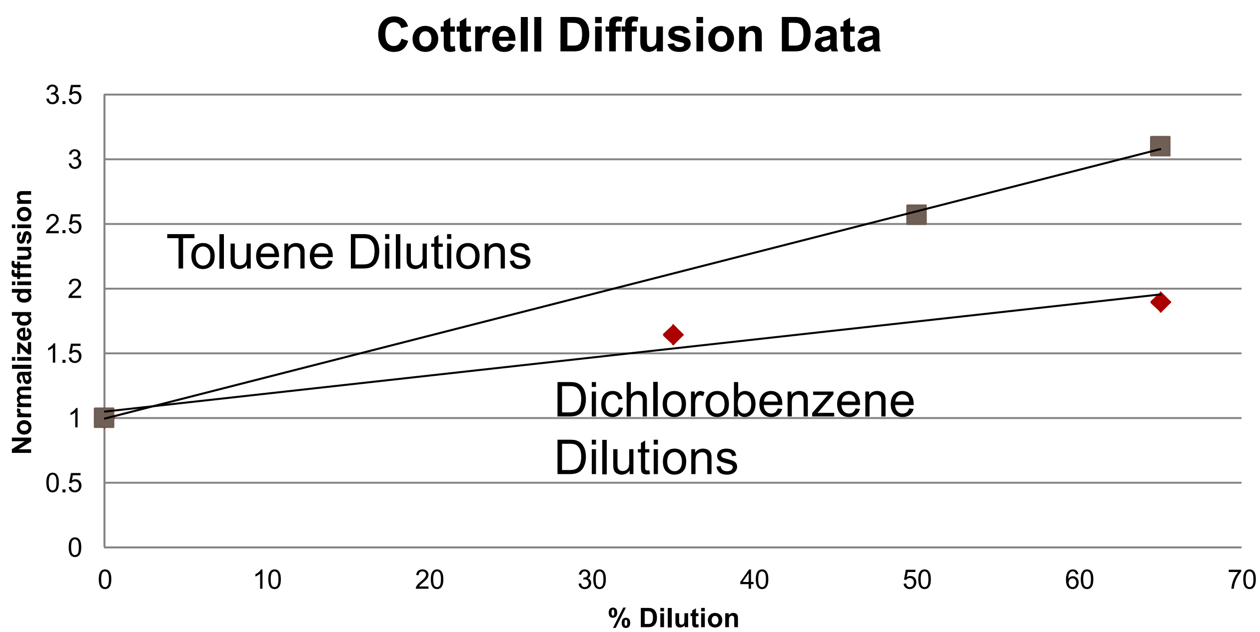
↓ Polarity ↑ Miscibility

↓ Vapor Pressure ↑ Ease of Use

Chronoamperommetry for Diffusion Parameters

- Co-solvents increase conductivity by modifying diffusion
  - Need to look into diffusion parameters specifically to investigate rate limitations
- Correlation to the theoretical model indicates diffusion limited regime
- Dilution ***greatly*** affects diffusion

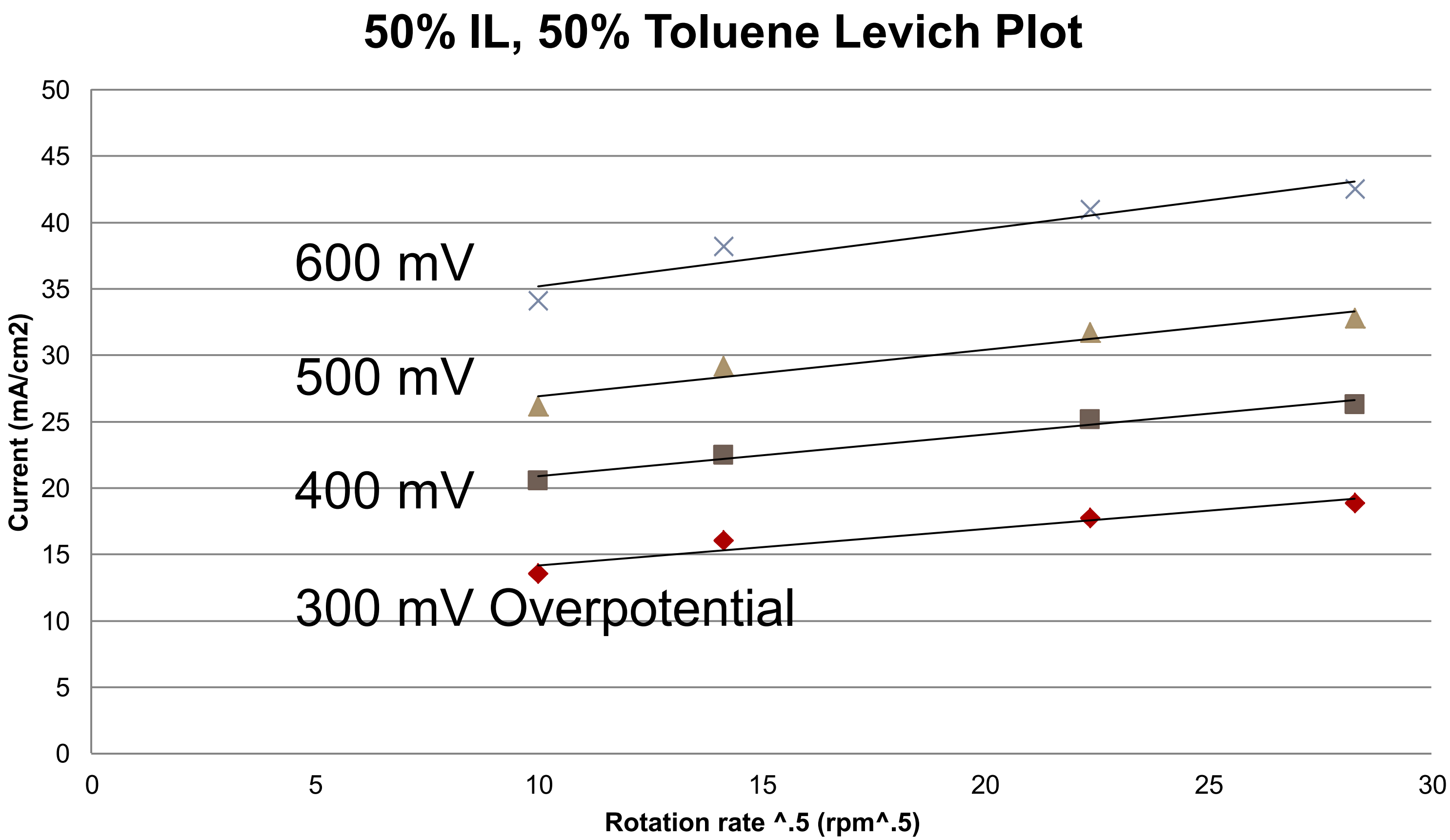
$$i = \frac{nFAc_j^0\sqrt{D_j}}{\sqrt{\pi t}}$$



Rotating Disk Electrode

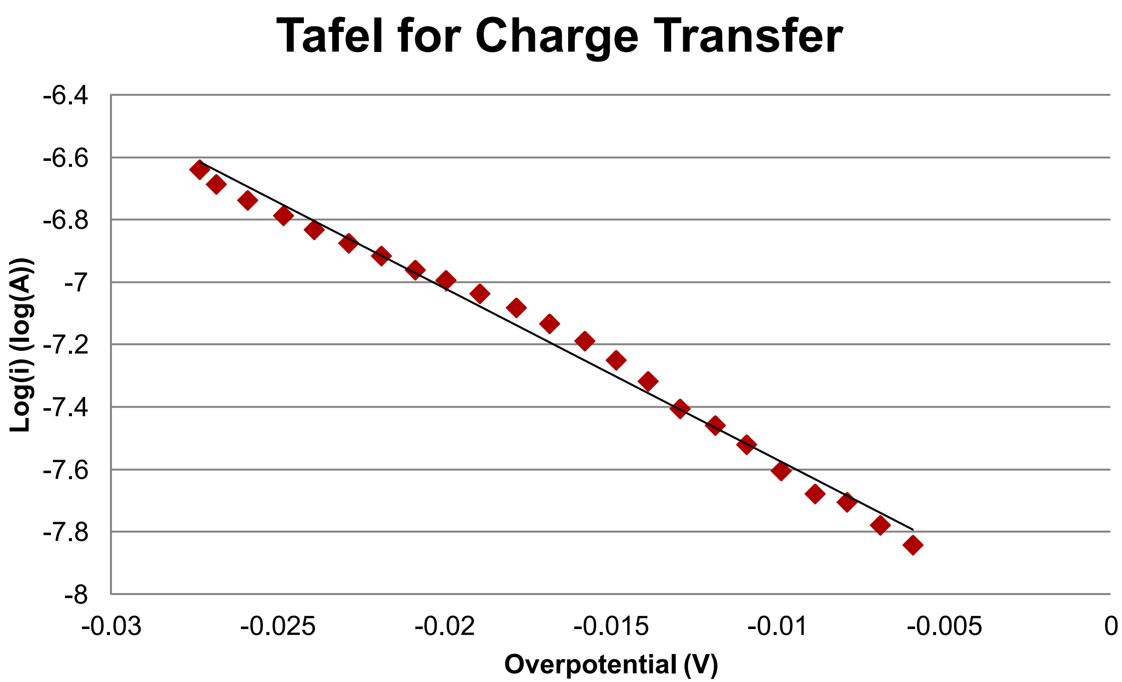
- Rotation rate changes diffusion distance
- Non-zero intercept indicates kinetic limitations

$$I_L = (0.620)nFAD^{\frac{2}{3}}w^{\frac{1}{2}}v^{\frac{-1}{6}}C$$



Charge Transfer Limitations

- Tafel investigates charge transfer rate by extrapolating overpotential vs. Log(current) plot to zero overpotential
- The exchange current density is on the order of $5x10^{-9}$ A/cm^2
  - Charge transfer is indeed slow (Technically Irreversible)



Results

- Kinetic limiting current densities are similar in toluene and dichlorobenzene
  - 3-8% higher in Toluene, assume negligible
- Levich diffusion rates are higher than Cottrell derived
  - Reddy reported 2 x 10 $^{-11}$ m^2/s in similar IL at 90° C
- Neat IL does not correlate well with RDE models
- Exchange current density: $5x10^{-9}$ A/cm^2

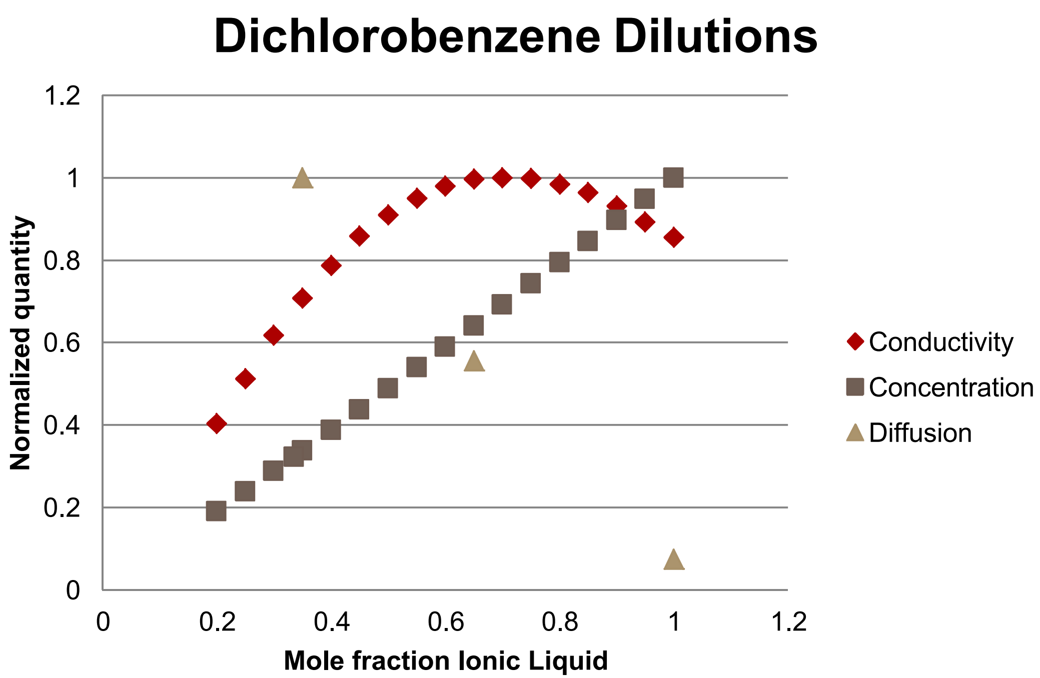
	Cottrell	Levich	
pure	4.28E-11	3.98E-10	m^2/s
35% DCB	3.21E-10	1.49E-09	m^2/s
65% DCB	5.78E-10		m^2/s
50% tol	2.3E-09	4.42E-09	m^2/s
66% Tol	5.78E-09	4.52E-09	m^2/s

	Kinetic Current Limit (mA/cm^2)		
mV vs. QRE	35% DCB	50% Tol	tol/dcb
300	19.8	21.4	1.08
400	27.3	28.8	1.06
500	34.9	35.7	1.03
600	42.8	46.0	1.07

“Mechanistic study of Al electrodeposition from EMIC–AlCl3 and BMIC–AlCl3 electrolytes at low temperature” Pradhana, D; Reddy, R. G. 2014

Conductivity Trend

- Conductivity, diffusion rates and active species concentration vs. dilution

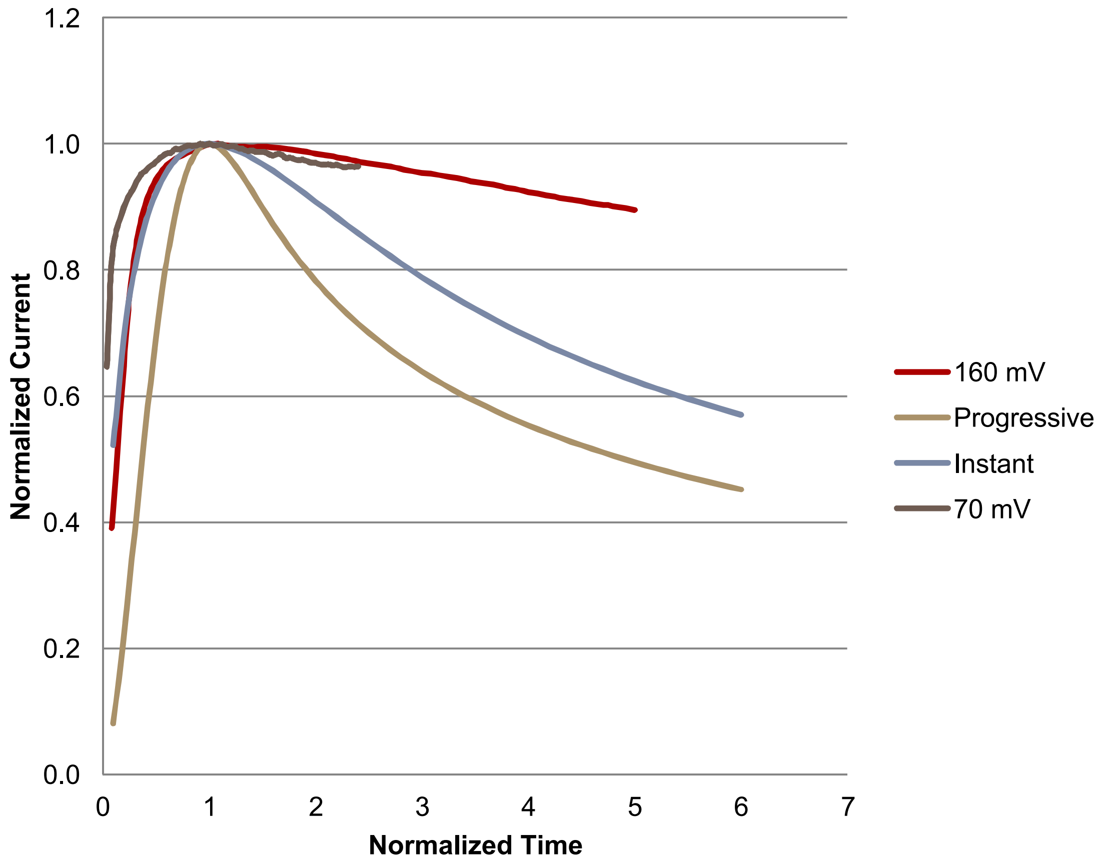


Pure Co-Solvent   Composition   Pure IL

- Combination of Kinetic and diffusion limitations
- Co-solvents greatly improve diffusion and deposition rates
- Will be able to control deposits with dilution and equipment parameters

35% Dichlorobenzene Dilution

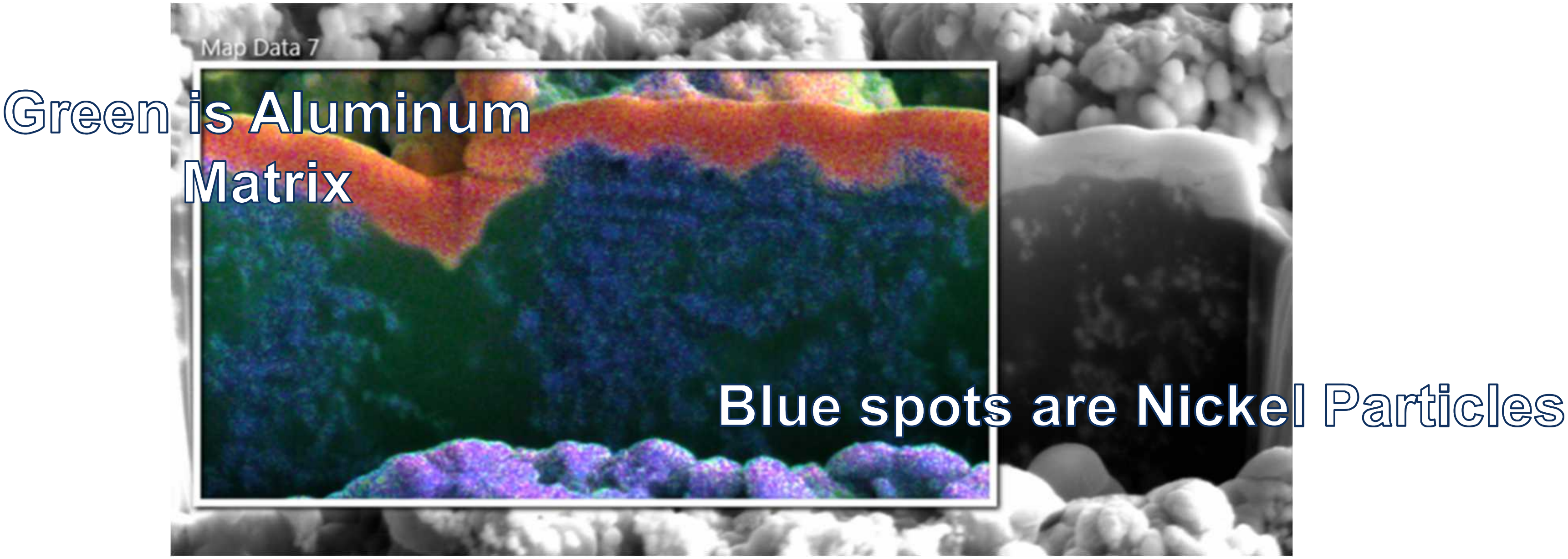
- Instantaneous nucleation even at very low overpotentials
  - Compares to literature (instantaneous profile at -600 mV)



“Mechanistic study of Al electrodeposition from EMIC–AlCl3 and BMIC–AlCl3 electrolytes at low temperature” Pradhana, D; Reddy, R. G. 2014

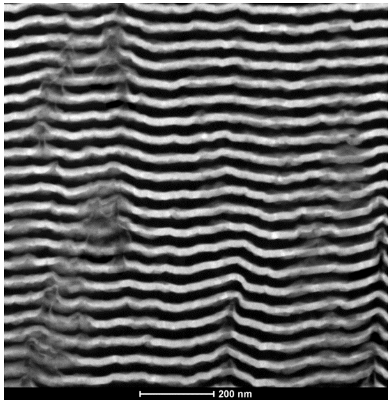
Codeposition Results

- Initial codeposition did achieve nickel particle incorporation
  - Moderate agitation
  - Inverted cathode face (electrode facing down)
  - Ni Concentration is low and non-uniform

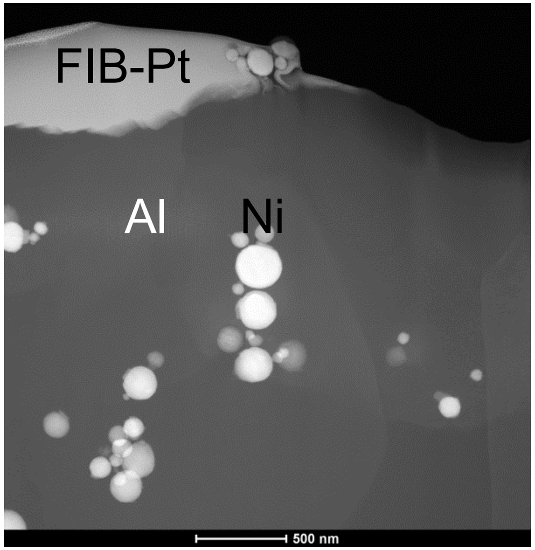


SEM/EDS map of codeposited film

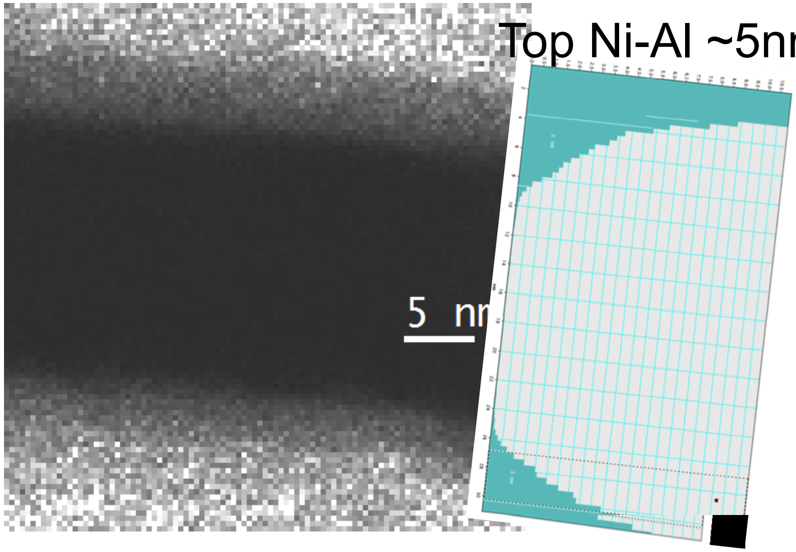
Comparison of PVD vs. Dispersion Plating



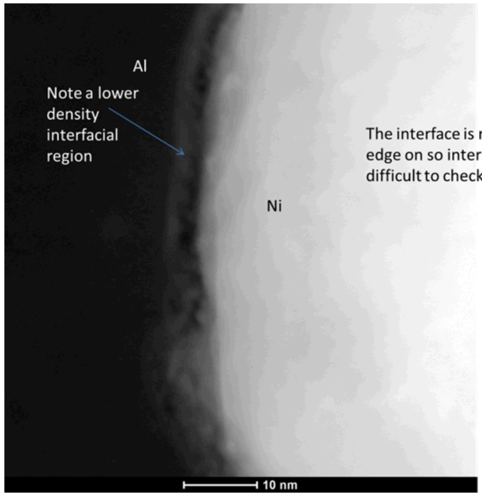
Indium Corp Foil



Top Ni-Al ~5nm



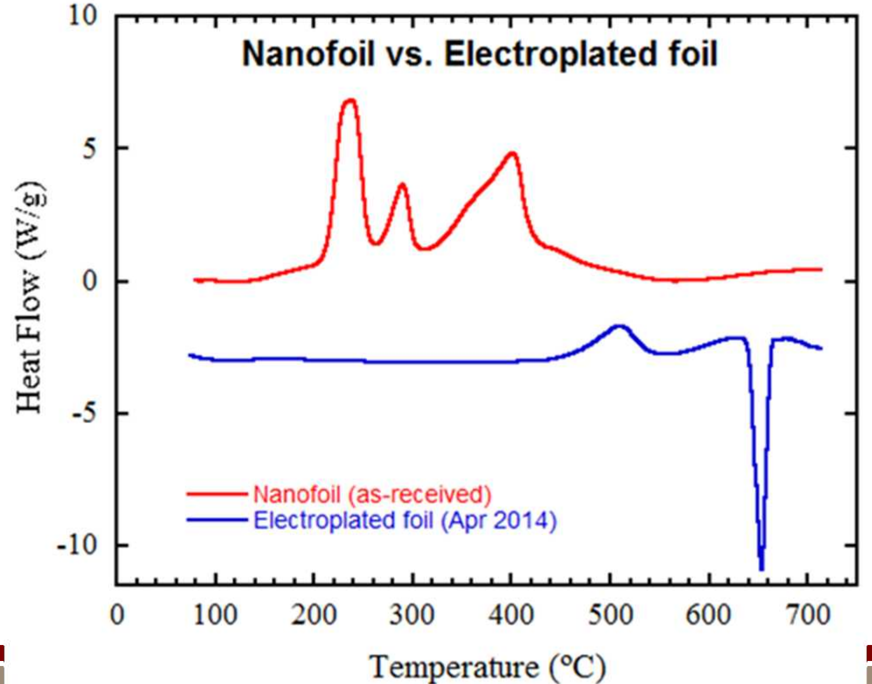
EP Foil (50um thick, plated in 5 hours)



Bottom Ni-Al ~3nm

Reaction Testing

- Very low heat output
- Interface between Al and Ni are similar to PVD sample
- Analysis post burn indicates very low nickel content in the tested samples
  - Focus has been on aluminum deposition, is now shifting to particle incorporation



Conclusions

- Diluted ILs are a reliable electrolyte
  - Diffusion, concentration and kinetic properties are investigated here
  - Optimal conditions are in line with the maximum conductivity compositions
    - 65% Ionic liquid with Dichlorobenzene
    - 50% Ionic liquid with Toluene
  - Dichlorobenzene solutions are easier to use while toluene solutions are less expensive and lower viscosity
- Nickel incorporation is low
  - Energy release was low due to poor stoichiometry
  - Need to modify deposition parameters to incorporate more nickel

Acknowledgements

Sandia National Laboratories:

William Averill

Alexander Tappan

University of New Mexico:

Plamen Atanassov

Funding: Sandia National Laboratories LDRD Program