Fall 11-9-2015

Reactive Ni-Al nanostructured composites through electrochemical dispersion deposition

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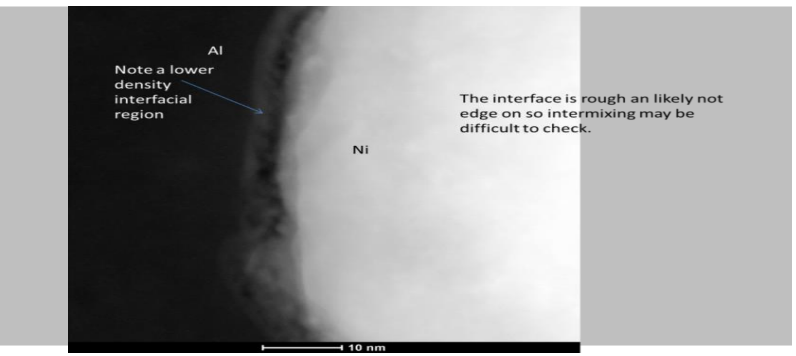
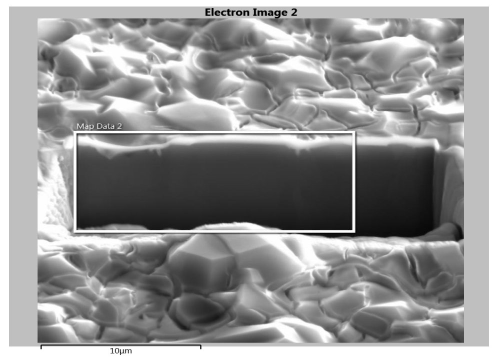
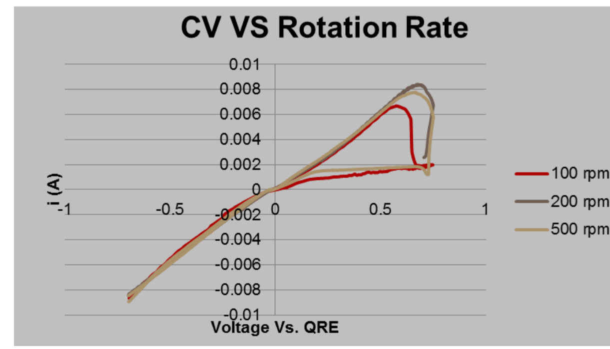
Electrochemical Fabrication of Energetic Thin Films







Christopher Apblett

Composites at Lake Louise 2015

November 8-12, 2015

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

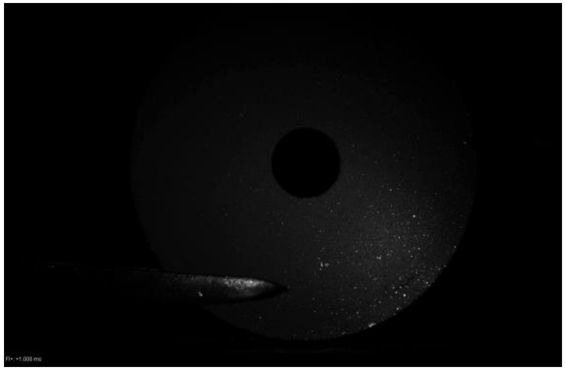
Outline

- Thermal Batteries
- Dispersion plating composite materials
- Electroplating properties
  - Kinetics and diffusion
  - Ionic liquid properties
  - Experimental and characterization
- Adding in the dispersed phase
- Reaction Testing
- Conclusions

Thermal Batteries

- Long shelf life, inert batteries with decades of shelf life
- Can produce very high power densities when activated
- Current thermal batteries have low efficiency, slow burning heat sources
- Faster, more efficient heat sources are commercially available, but are based on time consuming processes and require expensive and risky post processing to shape

Thermal Battery Function

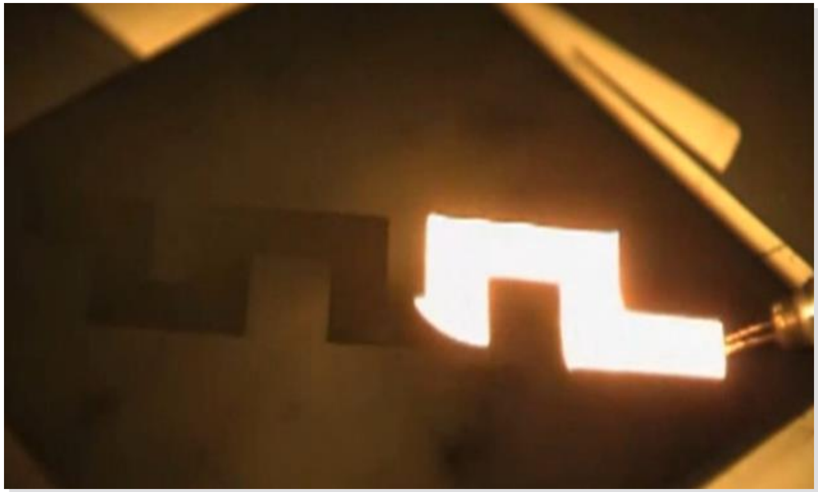


Perchlorate Pellet

Ni-Al pellet

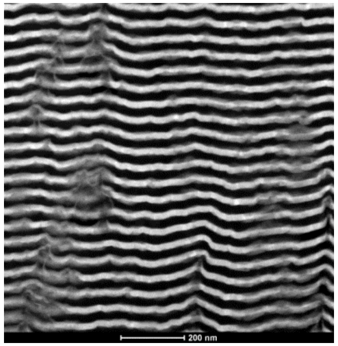
What are Energetic Thin Films?

- Reactive mixture that releases heat upon initiation
  - Ideally gasless
  - High energy local heating
  - Easy initiation
- Requires nanostructure control to promote component mixing and reaction initiation/propagation
  - Solid state diffusion distances must be short for reaction to proceed quickly
  - Requires high surface area between reactants
- Uses
  - Energy sources in thermal batteries
  - Micro brazing/welding



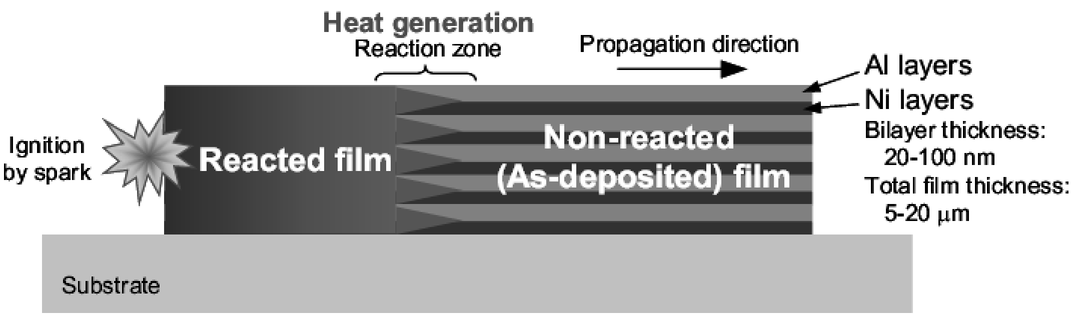
Energetic Films: Fabrication

- Fabrication method is important
  - Requires *high surface area* to improve reaction rates
  - Interfaces must be *atomically defined* as intermixing reduces rates and energy production



Heat Pellets

Metallic Film



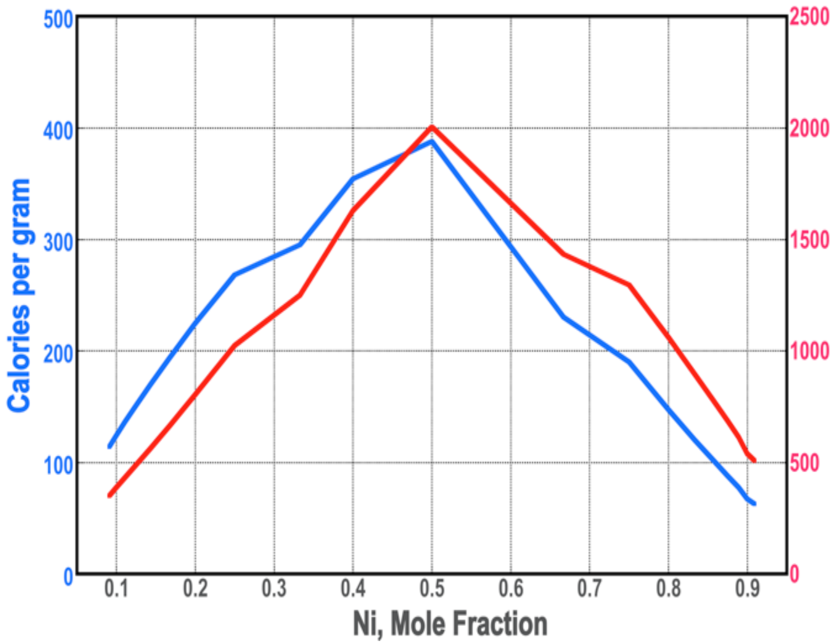
Pressed from powder
Low cost production
Clean interfaces
Difficult to handle (brittle, explosive)
Lower density

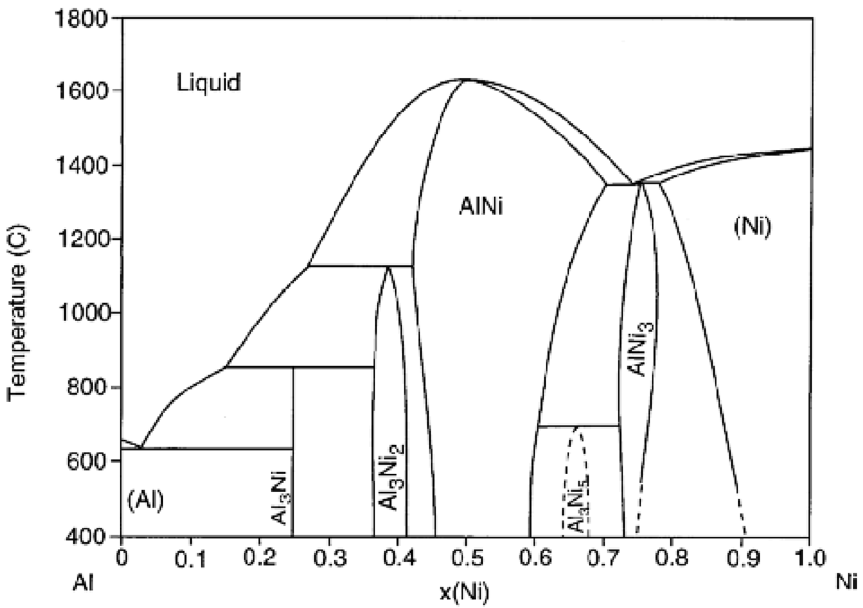
Sputtered
High control over stoichiometry
Clean interfaces
Requires high vacuum
Slow fabrication rates

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

Aluminum Nickel

- Abundant and relatively cheap materials
- Max energy at 50% mole fractions
  - Difference in atomic density translates to 60% Al by volume



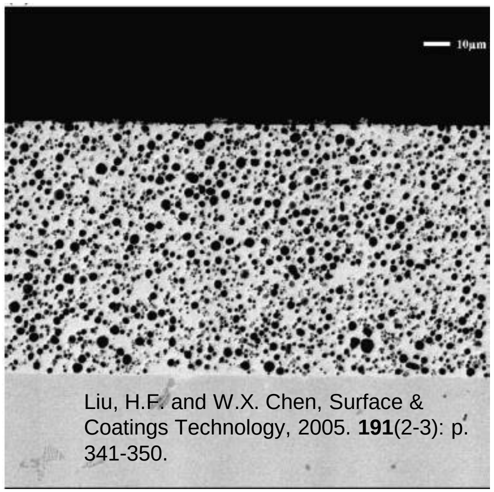


S. Ito, S. Inoue, and T. Namazu "The Size Limit of Al/Ni Multi Layer Rectangular Cuboids for Generating Self-Propogating Exothermic Reaction on a Si Wafer" 2010

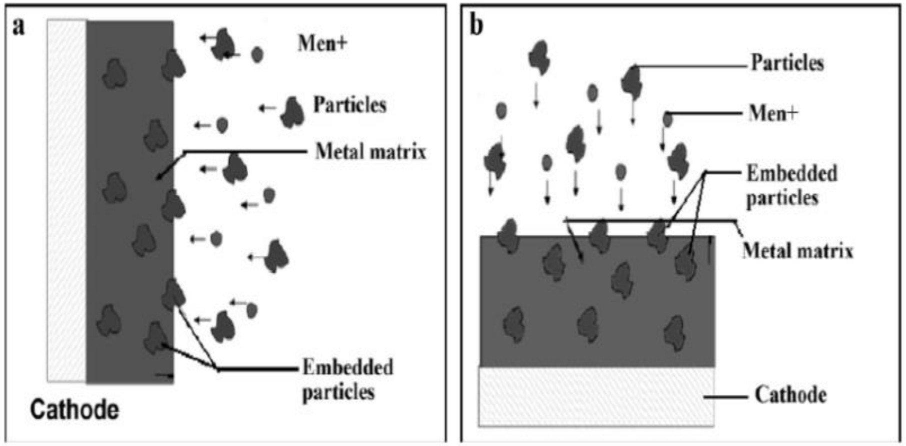
T. Namazu, H. Takemoto, H. Fujita, Y. Nagai, and S. Inoue, "Self-Propagating Explosive Reactions in Nanostructured Al/Ni Multilayer Films as A Localized Heat Process Technique for MEMS", 2006

Dispersion Plating

- Electroplating bath also consists of suspended particles to be incorporated in the deposited film
  - These nanoparticles are high surface area and elementally different than the matrix metal
- Sedimentary codeposition utilizes density difference of the particles to increase incorporation
- Need to understand plating rate and arrival rate of particles to get proper incorporation



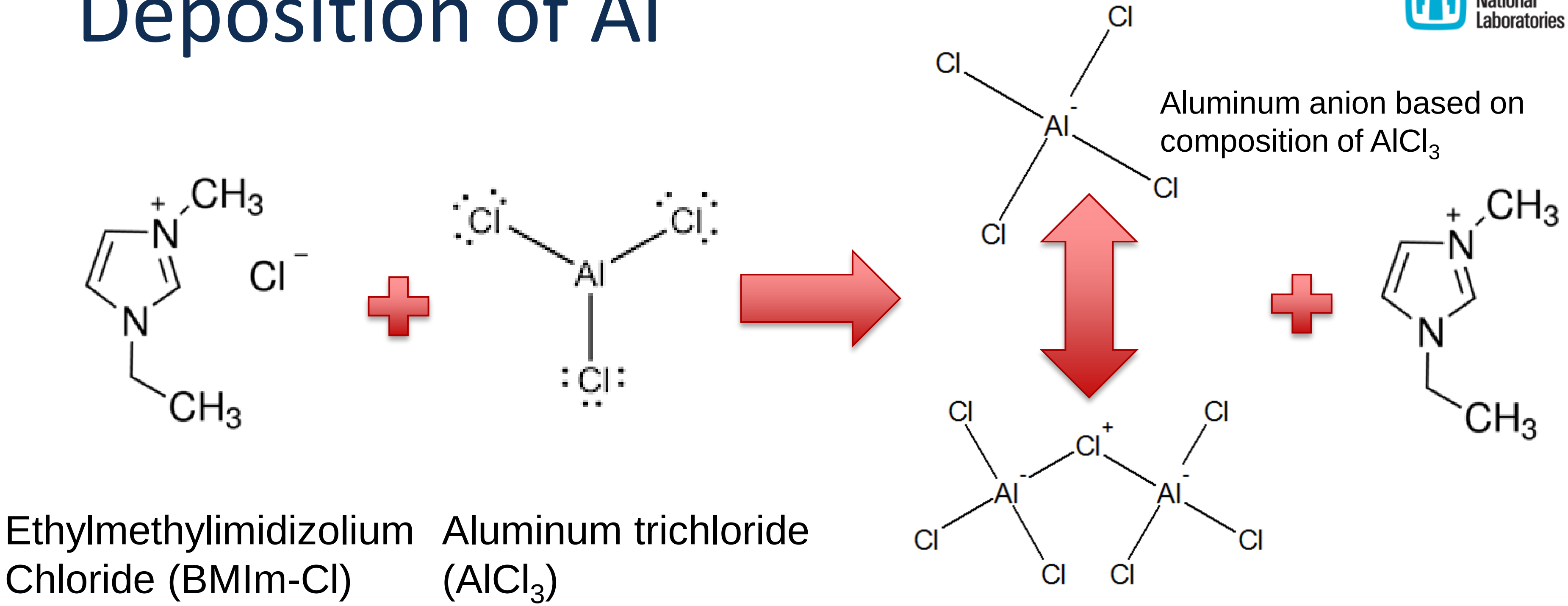
Codeposited film with ~3 um particles

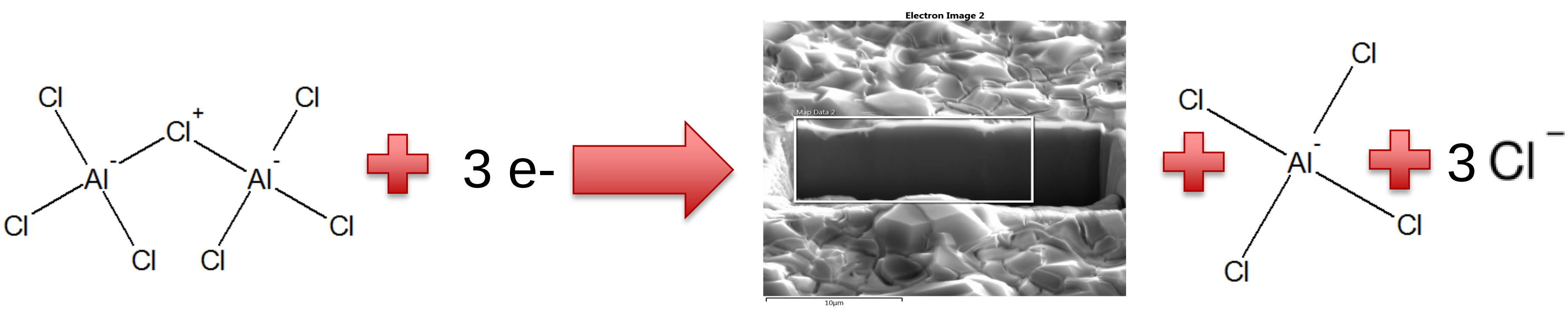


C.T.J. Low, R.G.A. Wills, F.C. Walsh 2005

Conventional and Sedimentary Codeposition

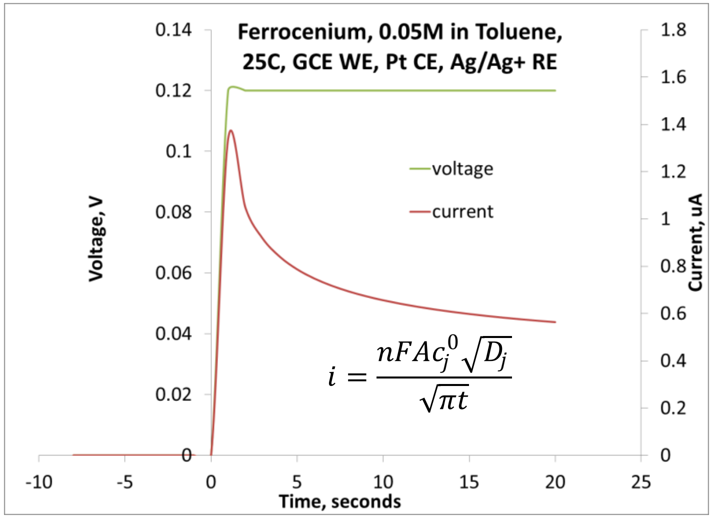
Deposition of Al

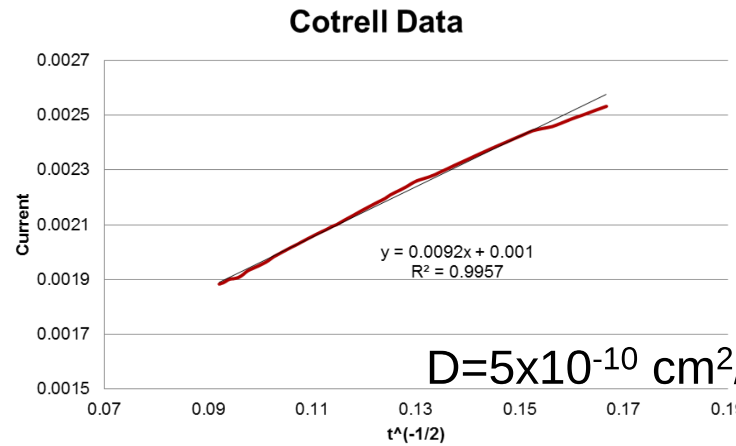




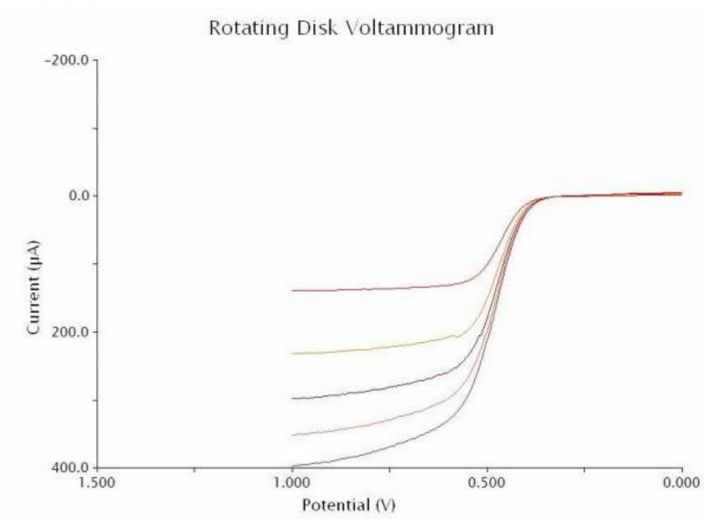
Al deposition

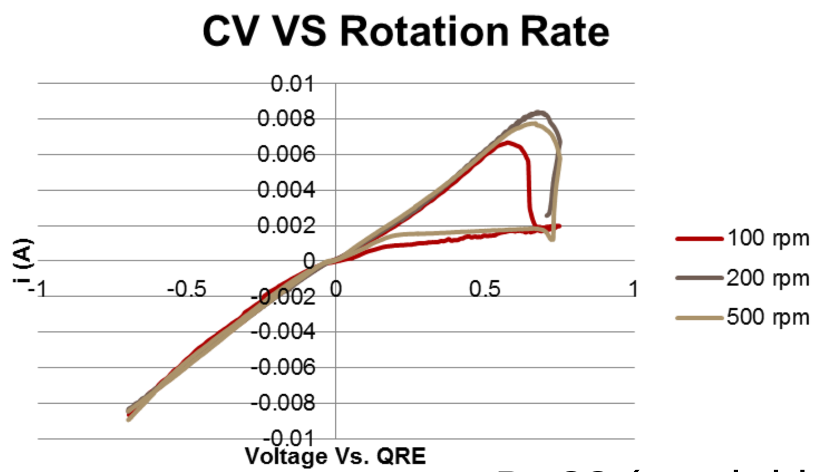
Diffusivity measurements





D=5x10^{-10} cm^2/s

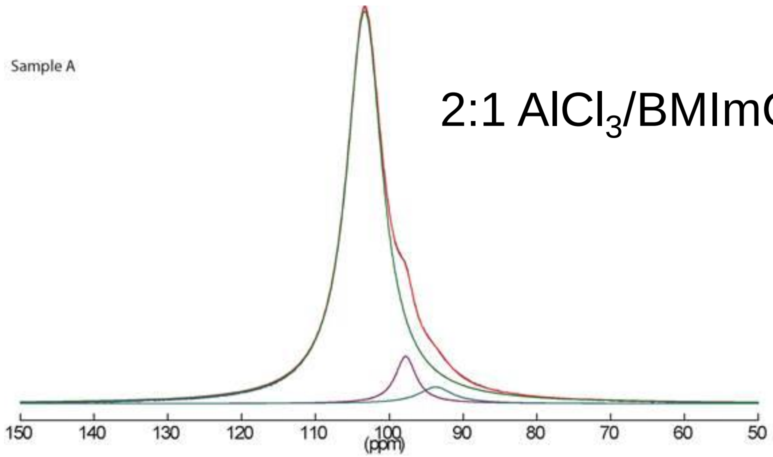




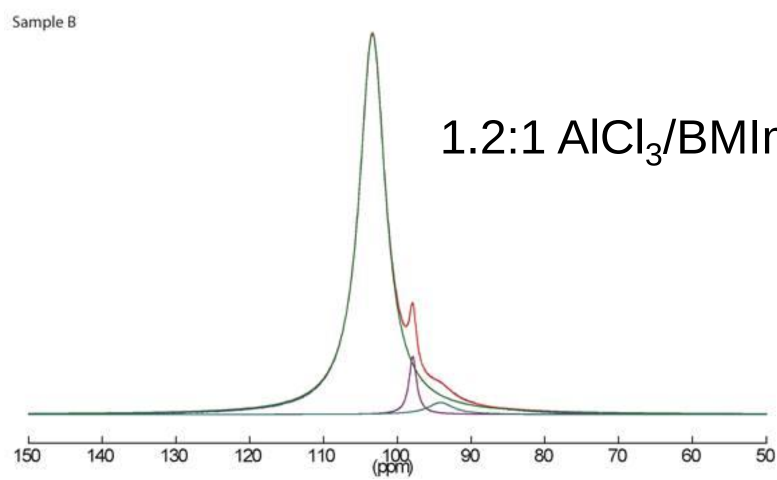
D=?? (much higher)

Different methods produce significantly different results. Why?

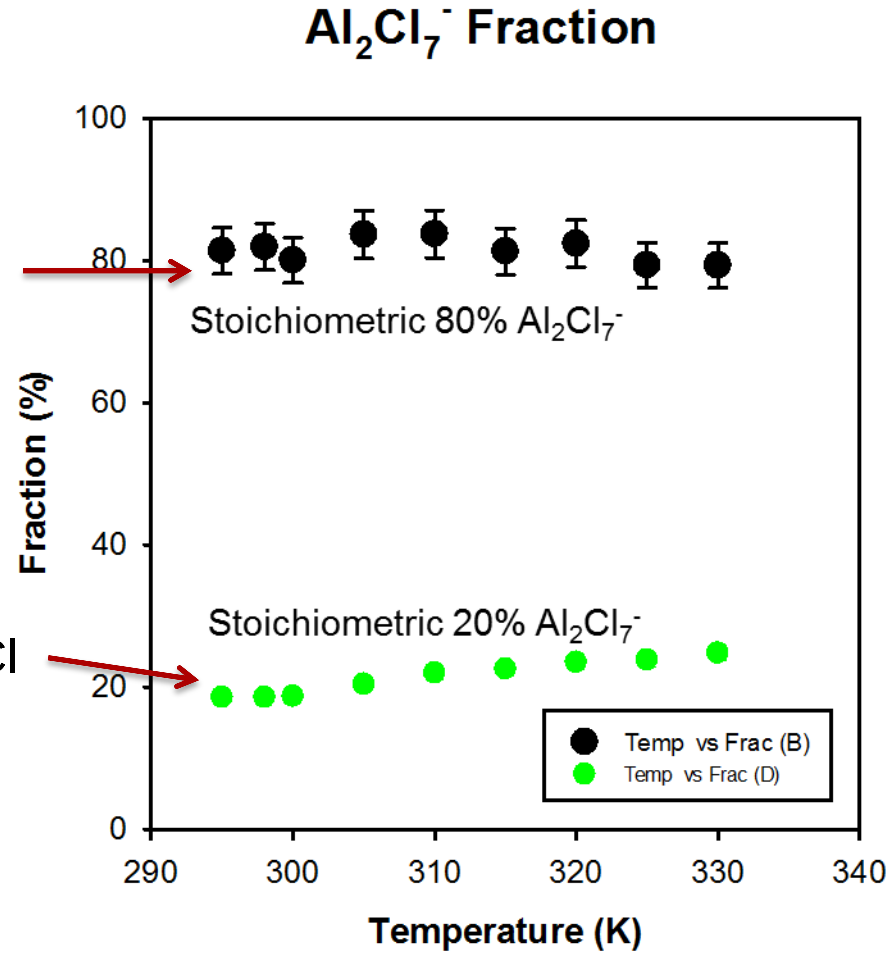
NMR for Concentrations



2:1 $AlCl_3$/BMImCl

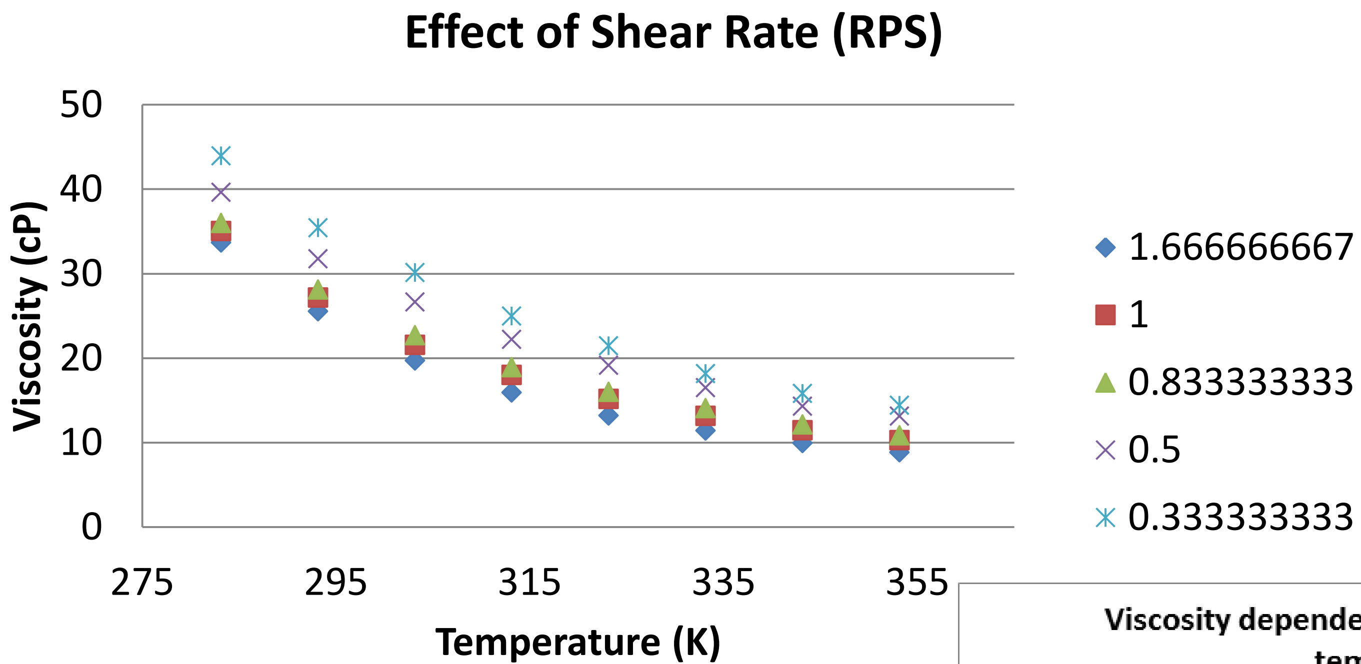


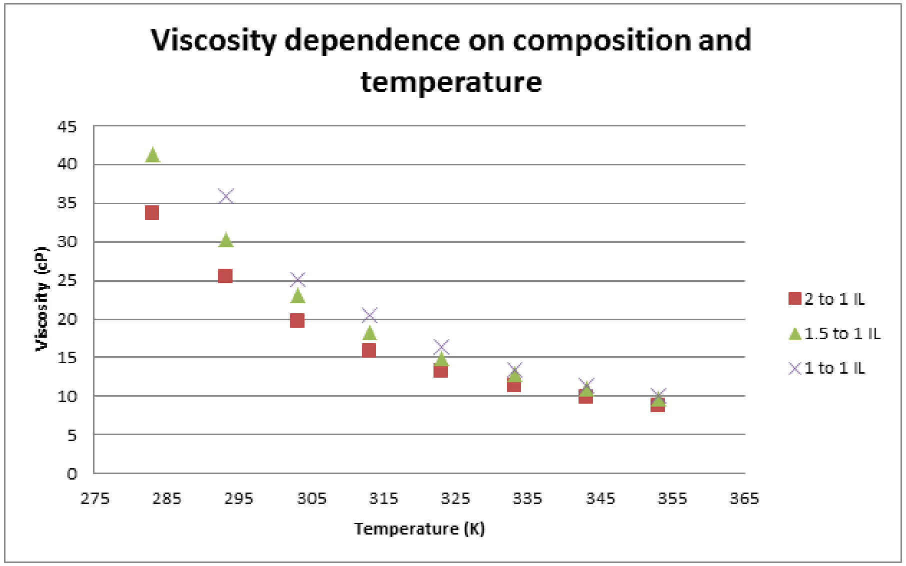
1.2:1 $AlCl_3$/BMImCl



Compositions in the salt of active species are correct

Viscosity is affected by conditions

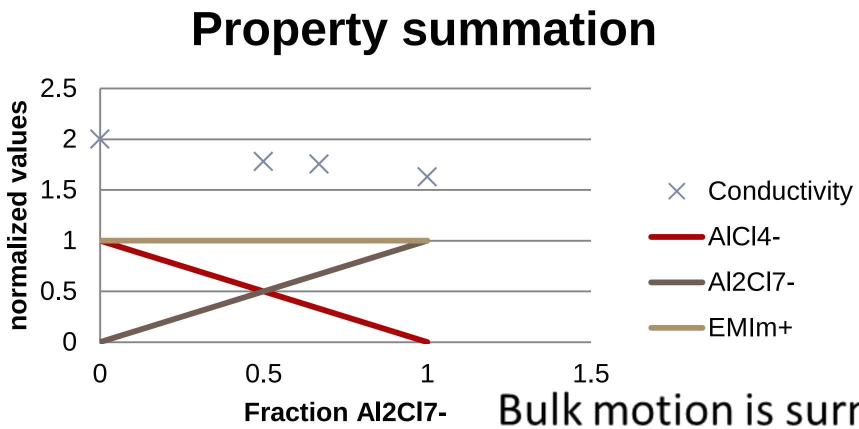




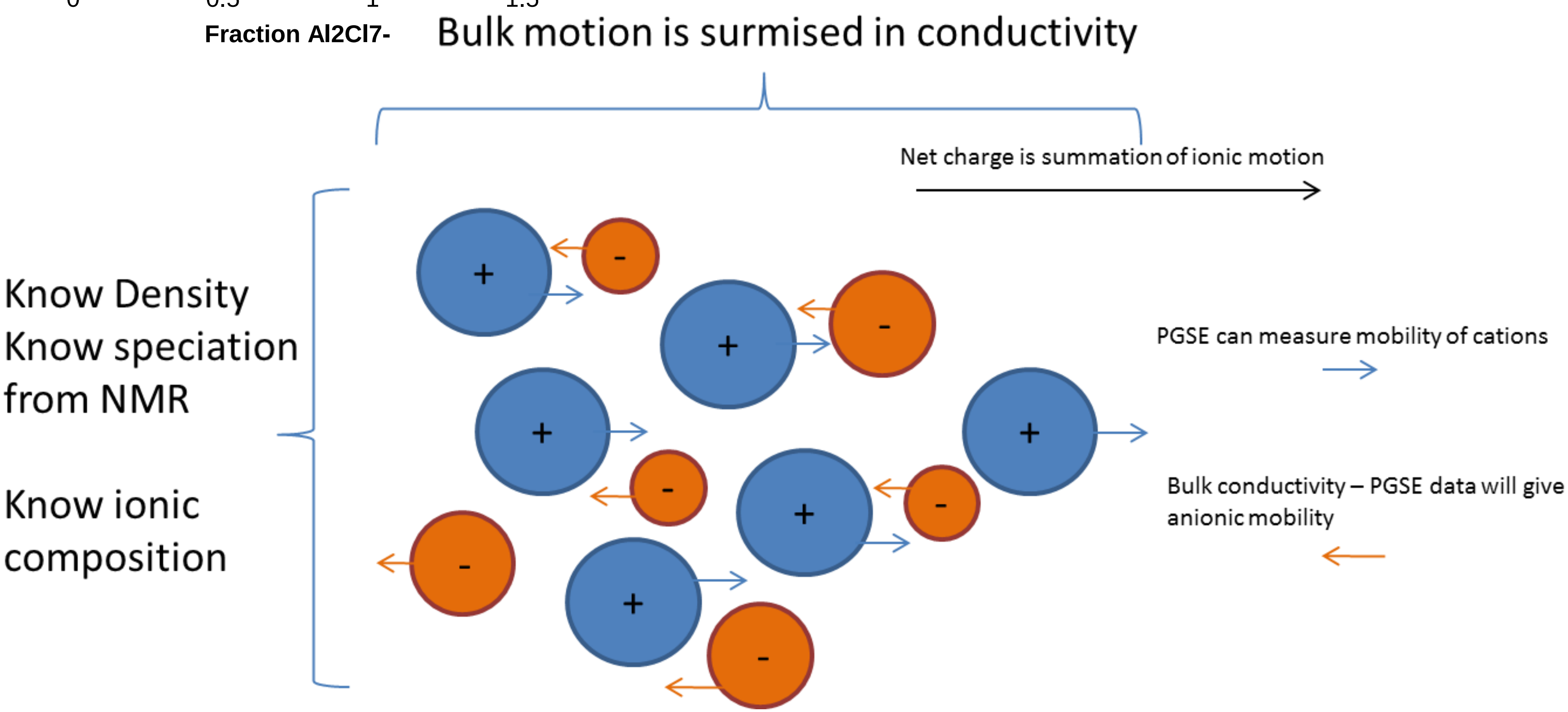
Since plating rate is proportional to viscosity, the plating rate is changing with all of these conditions as well

Need to control this to get the right stoichiometry of dispersion plating

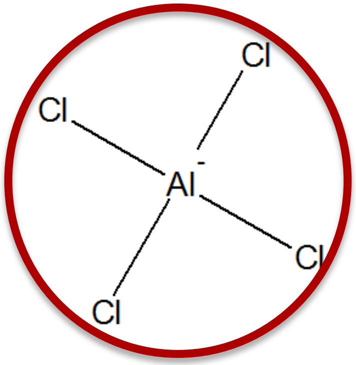
Conductivity of ILs, Quiescent

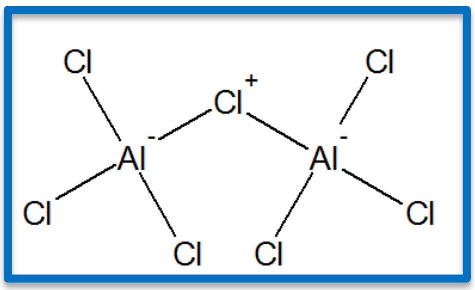


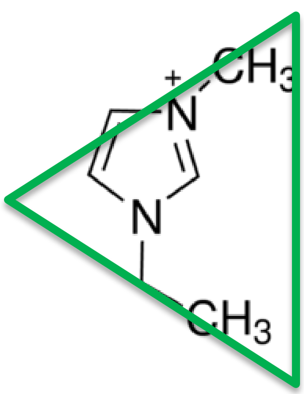
Understanding how conductivity is affected by composition and temperature allows prediction of total ionic species mobility (in static situations)

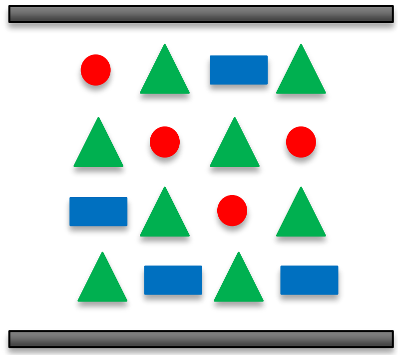


Structuring of Ionic Liquids

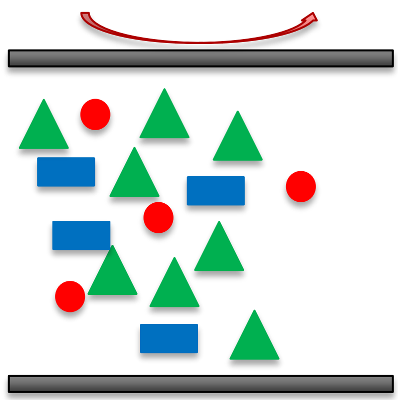








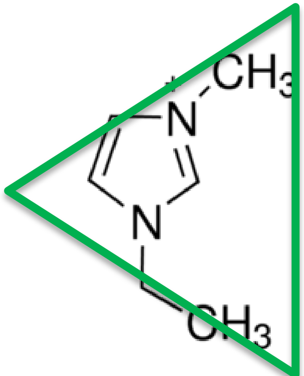
Quiescent Solution
Higher viscosity
Lower Plating rates
Lower Apparent diffusivity



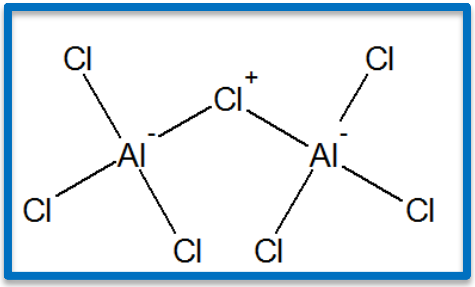
Mixed Solution
Lower viscosity (Thixotropic)
Higher Apparent Diffusivity
Faster plating rates

Ionic motion is directly correlated to viscosity, and therefore plating rate

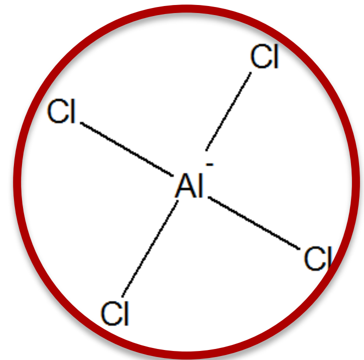
Diffusions under Different Shears



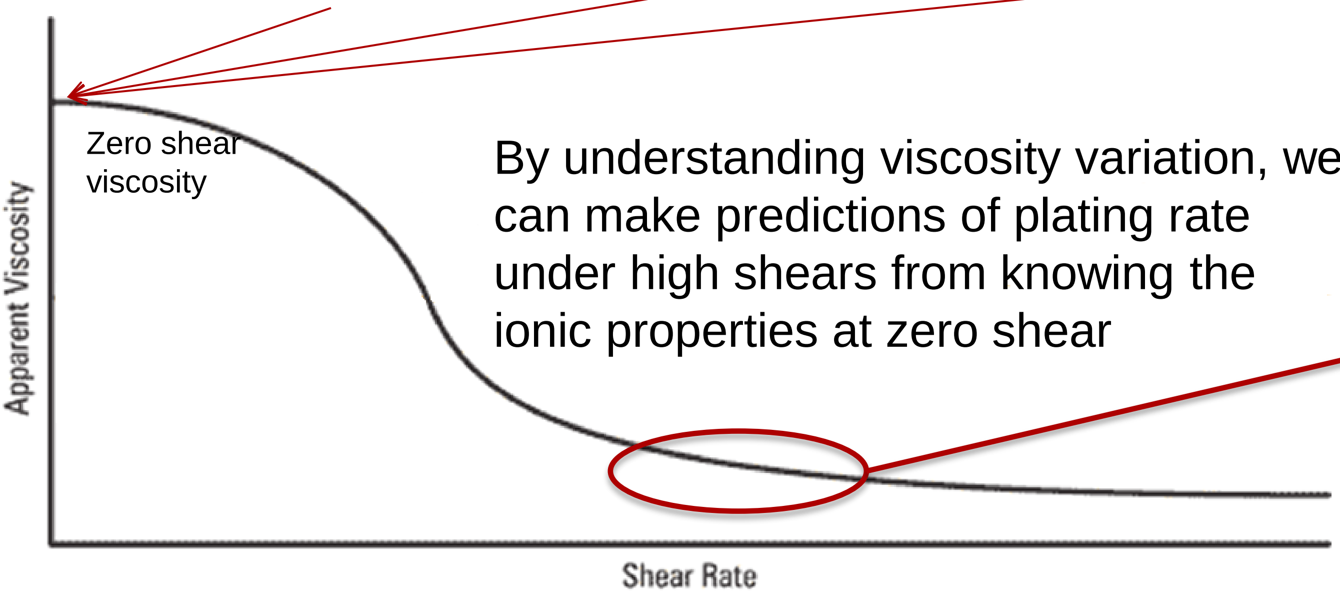
PGSE
NMR



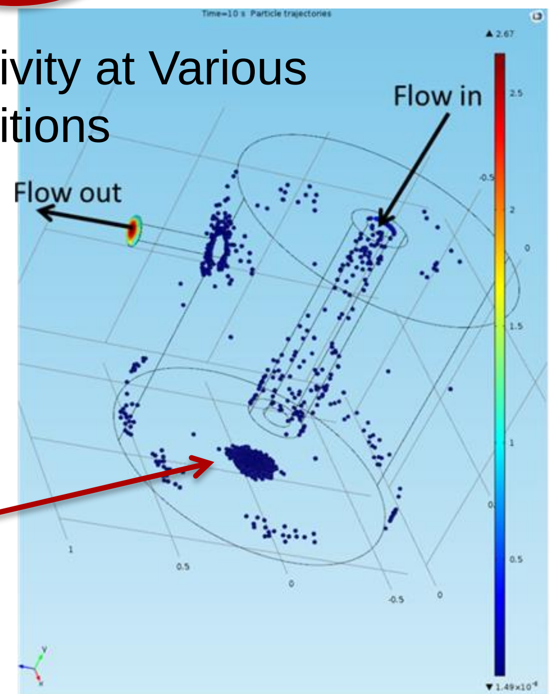
Cottrell,
Plating Rates



Conductivity at Various
Compositions

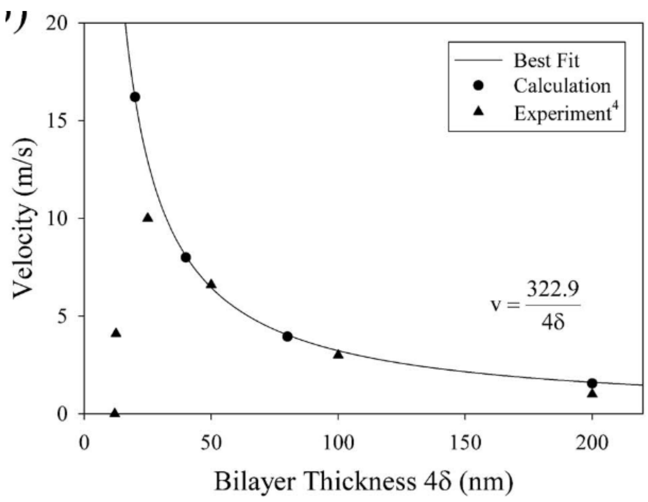


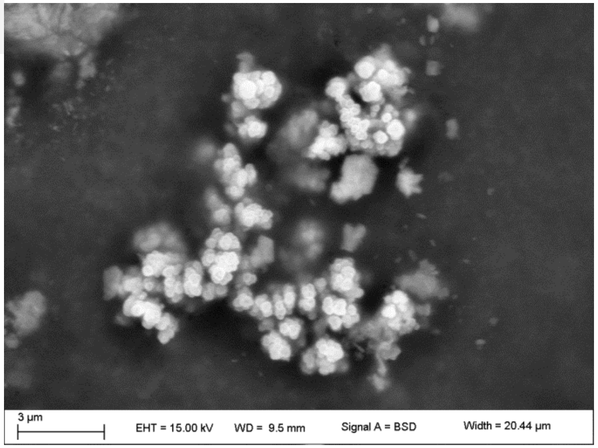
By understanding viscosity variation, we can make predictions of plating rate under high shears from knowing the ionic properties at zero shear



Adding the Dispersed Phase

- Poor dispersion will imitate larger particle sizes
  - Increased volume of inclusion phase
  - Likely lead to voids/porosity during deposition
  - Diffusion during burn testing will require longer



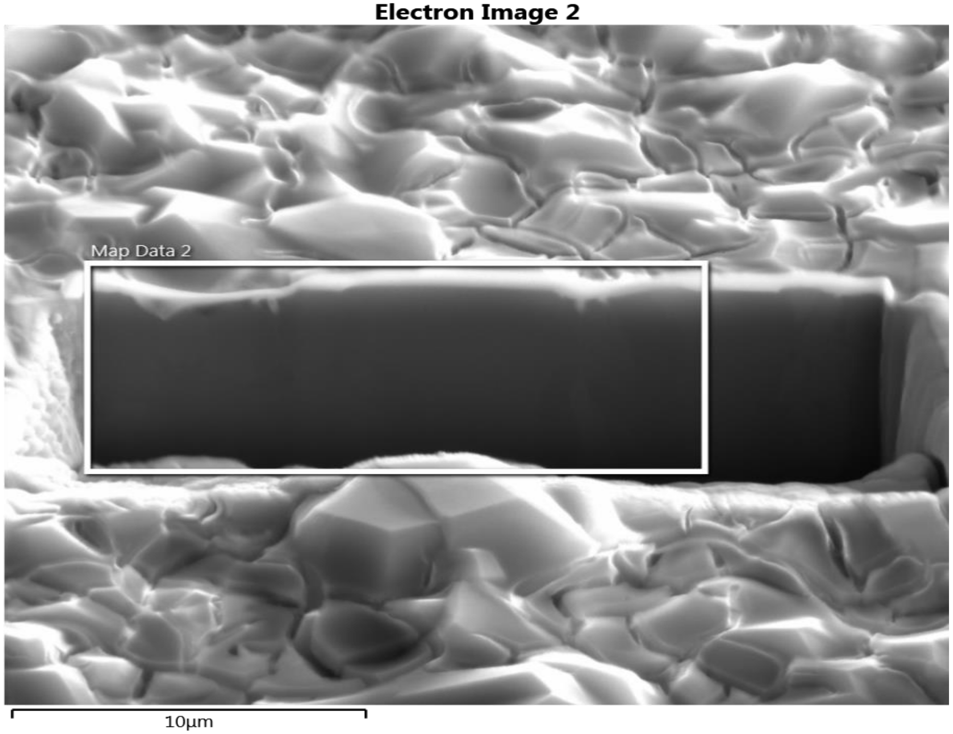


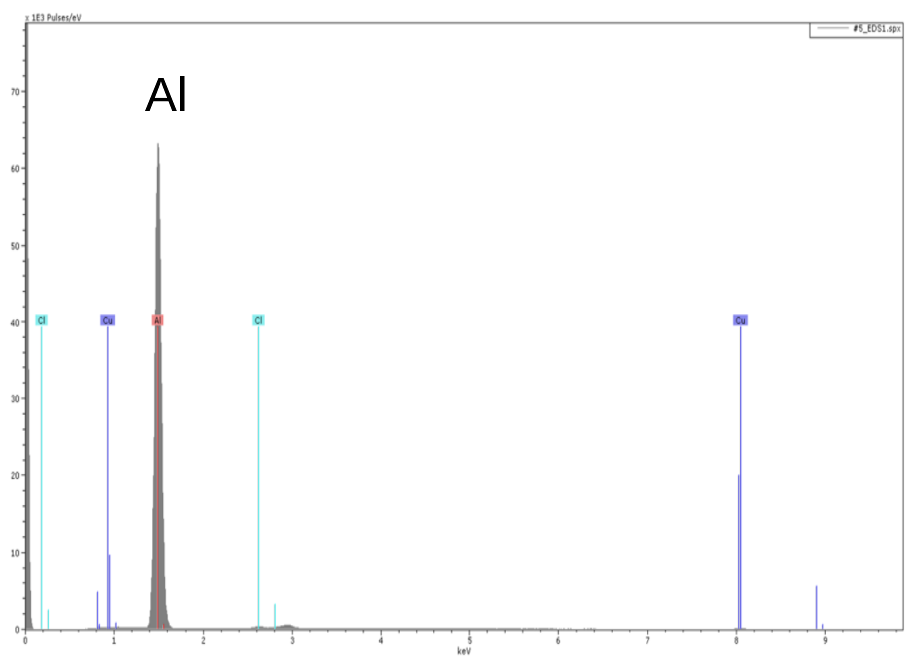
Need to keep agglomeration to a minimum with agitation and electrolyte properties/surface functionalization

Aluminum Film Analysis

- Need XRD on different deposition potentials determined by chronoamperommettry to identify crystal structure and develop pulse plating regime

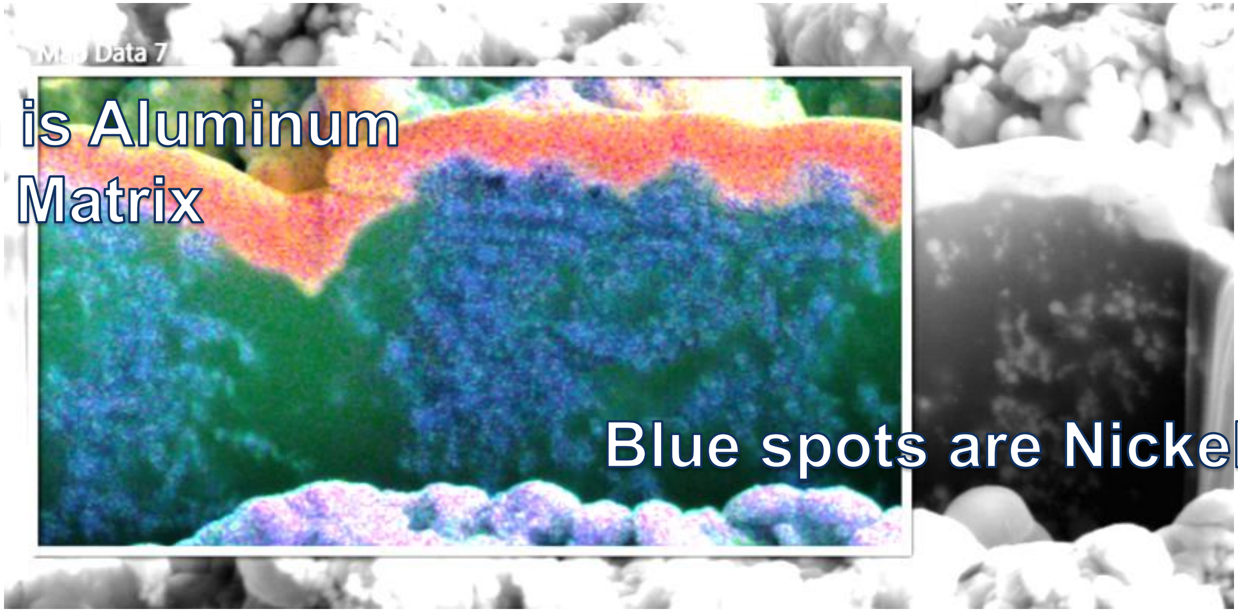
Electron Image 2





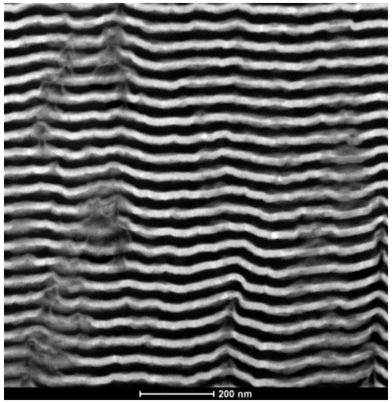
Post deposition Analysis

- Codeposited film properties
  - SEM/TEM for morphology and interface investigation
  - Burn properties
    - Energetic output (Differential Scanning Calorimetry (DSC))
    - Propagation rates (high speed camera)



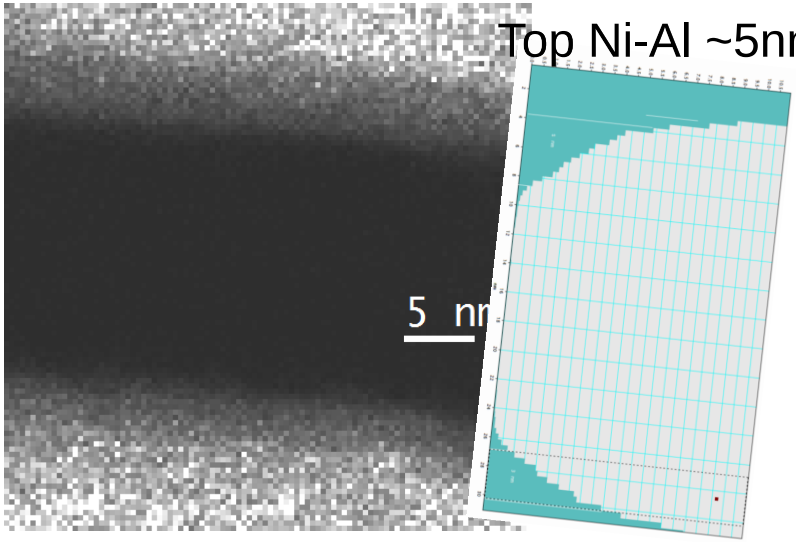
SEM/EDS map of codeposited film

Comparison of PVD vs. Dispersion Plating

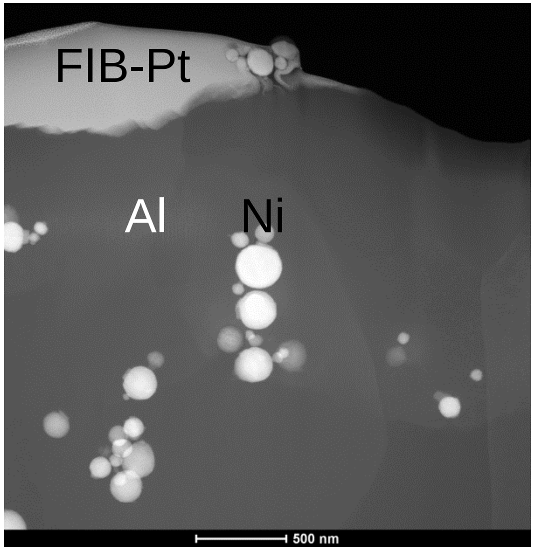


Indium Corp Foil

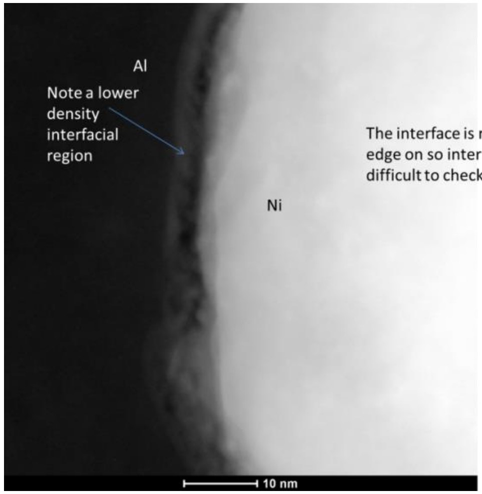
Top Ni-Al ~5nm



Bottom Ni-Al ~3nm



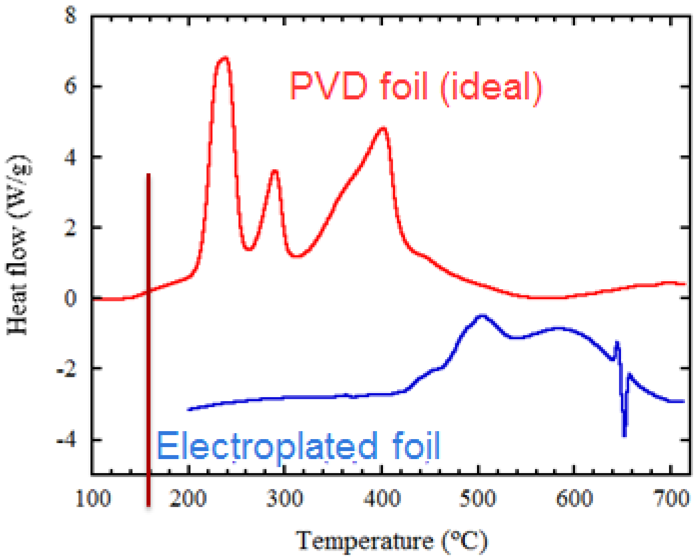
EP Foil (50um thick, plated in 5 hours)

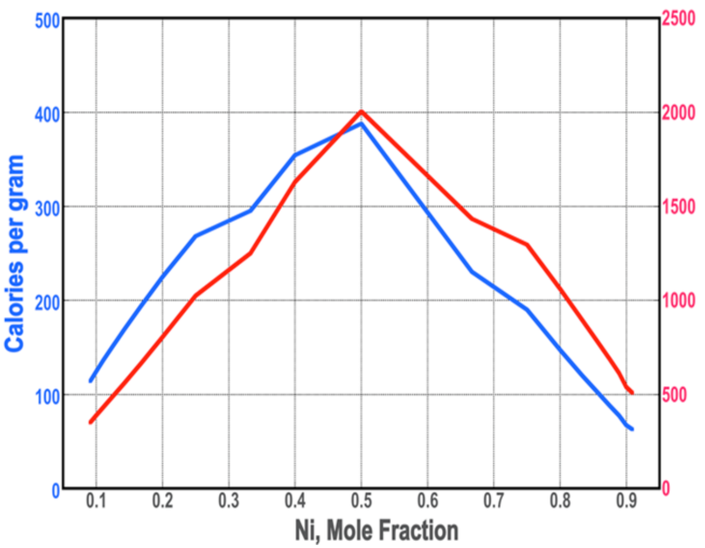


The interface is rough an likely not edge on so intermixing may be difficult to check.

Reaction Testing

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





Initiation of mixing~140C

Conclusions

- Formation of dispersed phase composite of reactive precursors can lead to an energetic film
  - But, for right now, energy levels are lower than sputtered materials
- Ionic liquids are proving to have very complex mechanical behavior
  - Rheology and diffusion that is related to composition complicates matters
  - Fully charged solution complicates analysis
  - "Everything is interrelated"
- Getting full, dispersed incorporation is the key to realizing the full potential

Acknowledgements

- Jonathan Coleman, SNL/UNM
- Plamen Atanassov, University of New Mexico
- Todd Alam, NMR
- Ed Matteo, Zeta Potential Measurements
- Paul Kotula, TEM
- Robert Knepper, Calorimetry
- Laboratory Directed Research and Development Office