SAND2015-4102C

Exceptional service in the national interest

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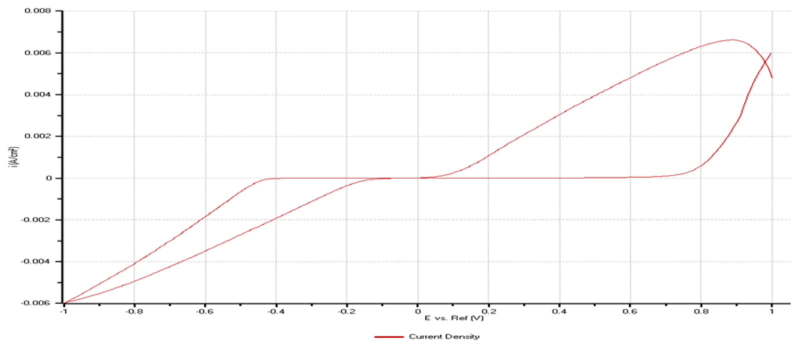
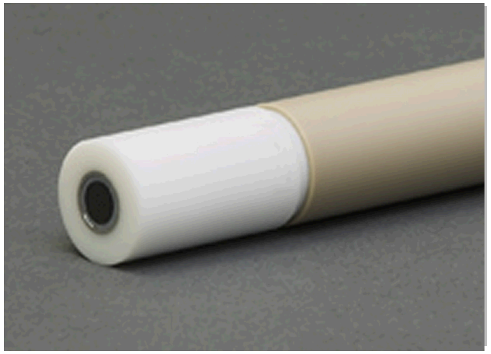
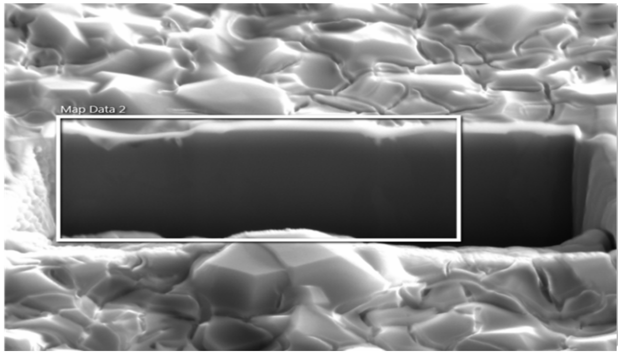
Improving Dispersion Plating of Nickel in Chloroaluminate Ionic Liquids







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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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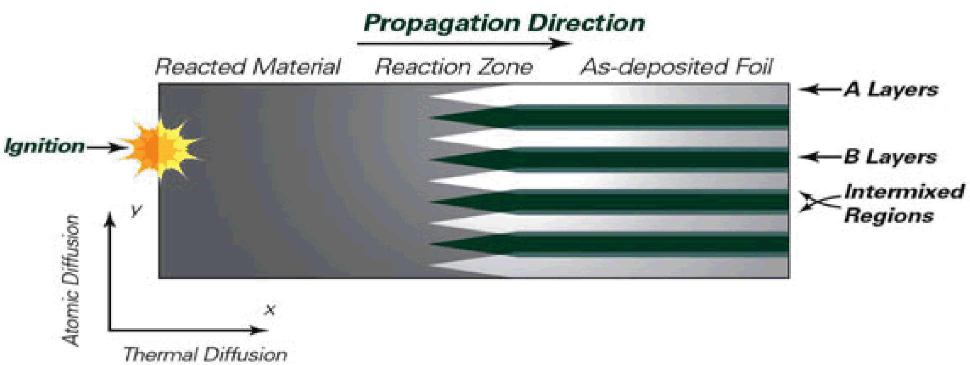
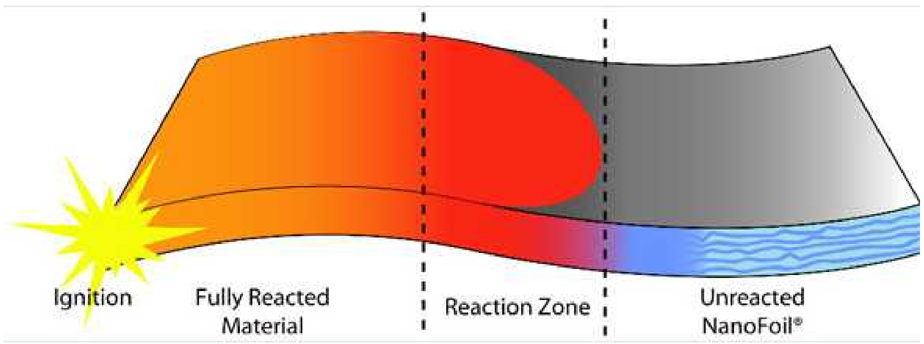
Exothermic Films

- Codeposition of a composite film
  - Allows for composite foil in a single process step
  - Control over nanostructure
  - Relatively low cost and scalable process
  - Potential for electroforming
- Nickel and aluminum exothermic alloying is suitable performance for thermal batteries
- Properties of exothermic films
  - Reaction rate and heat release are controlled by particle size, shape, distribution and total content

Nanostructured Thin Films

- Want high energy but no gas generation (using Ni-Al intermetallic)
- Inherently conductive
- Reaction depends on solid state diffusion
  - Can be controlled with nanostructuring and increasing reaction area
    - Improves propagation reliability and speed
    - Higher rates generate higher maximum temperatures
- Achieve this with sputtering
  - Cost prohibitive
    - Material inefficient and can't be made in complex shapes
    - Slow fabrication process that requires high vacuum



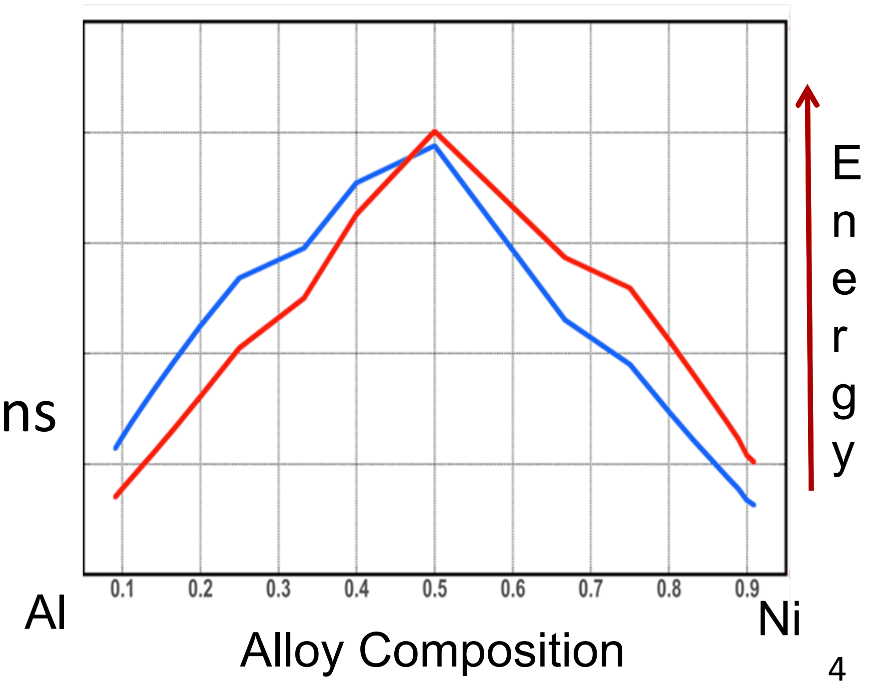


S. Ito, S. Inoue, and T. Namazu "The Size Limit of Al/Ni Multi Layer Rectangular Cuboids for Generating Self-Propogating Exothermic Reaction on a Si Wafer" 2010

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

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

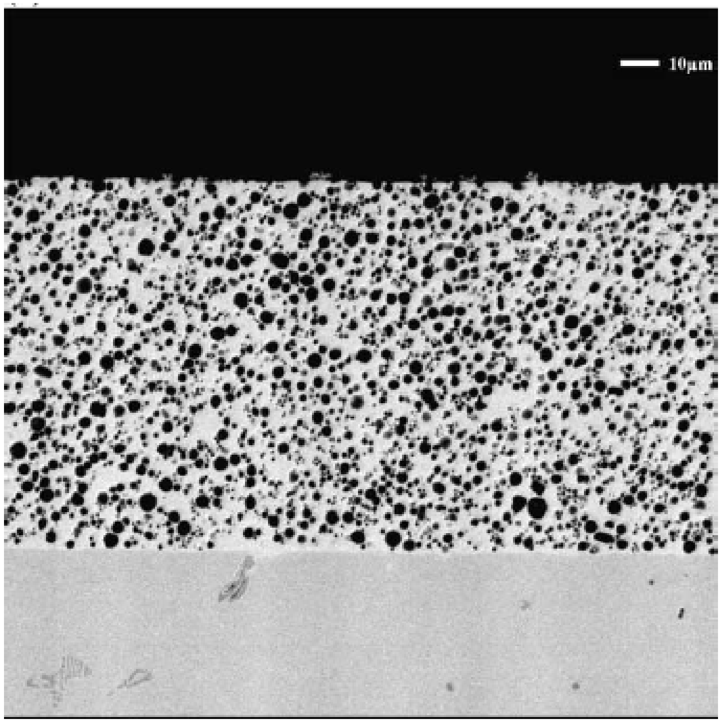


Objectives

- Aluminum deposition
  - Want high deposition rate
  - Smooth and compact deposition
  - High purity and efficiency
- Nickel incorporation
  - Control over inclusion size
  - Well dispersed
  - Low Ni-Al interfacial alloying

$$x_v = \frac{Kc_v}{1+Kc_v}\frac{zF\cdot\rho_M\cdot v_0}{M\cdot i}\left(\frac{i}{i_0}\right)^{\beta}$$

$$V = \frac{2\Delta\rho g a^2}{9\eta}$$



Composite Film Example:
~30% 3 μm particle incorporation

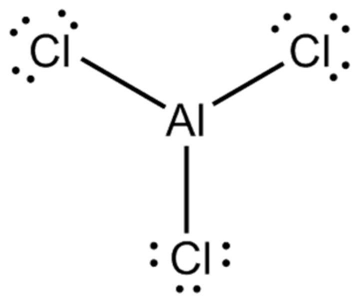
Liu, H.F. and W.X. Chen, *Electrodeposited Ni-Al composite coatings with high Al content by sediment co-deposition.* Surface & Coatings Technology, 2005. **191**(2-3): p. 341-350.

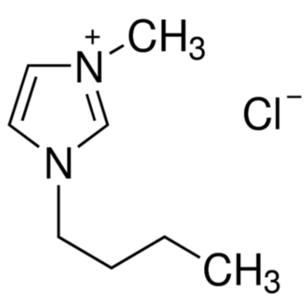
Methods

- Investigate particle properties in the electrolyte
  - Agglomeration, surface modifications, migration from settling, diffusion or other means, and effect of different particle geometries
- Important parameters
  - Electrolyte viscosity
  - Particle shape and size
  - Particle-particle interaction
  - Particle-electrolyte interactions

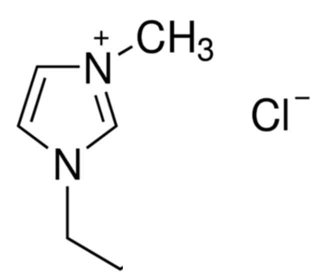
Deposition of Aluminum Matrix

- Ionic liquids
  - Chloroaluminate anions deposit aluminum readily
    - High efficiency
    - High purity
  - Low vapor pressure and non flammable
  - Low diffusion rates
    - Large bulky ions
    - High ionic interactions
- *Particle interactions are not well researched*





Butyl methylimidazolium Cl (BMIC)



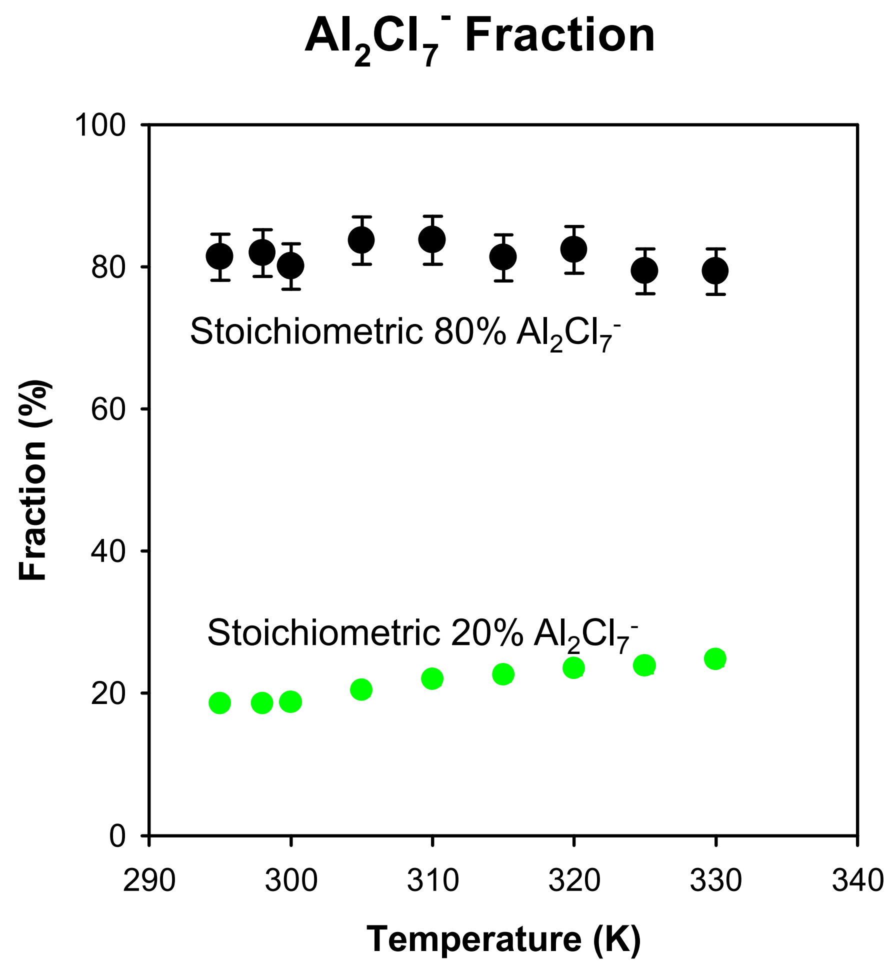
Ethyl methylimidazolium Cl (EMIC)

Investigation - Speciation

- Aluminum deposition only occurs from specific reduction complexes

$$4Al_2Cl_7^- + e^- \longrightarrow 7AlCl_4^- + Al_{(metal)}$$

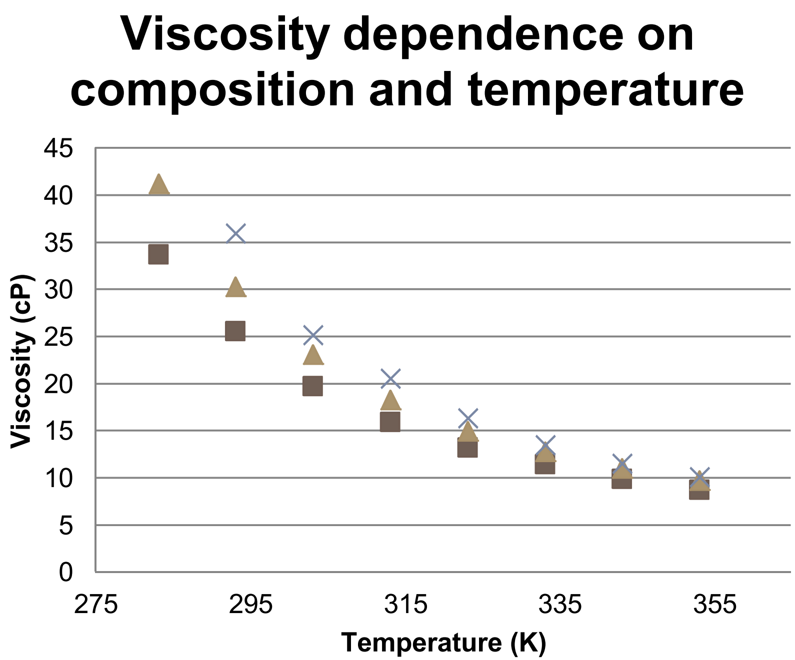
  - Optimizing these complexes is crucial
    - Concentration
    - Viscosity
    - Particle interaction

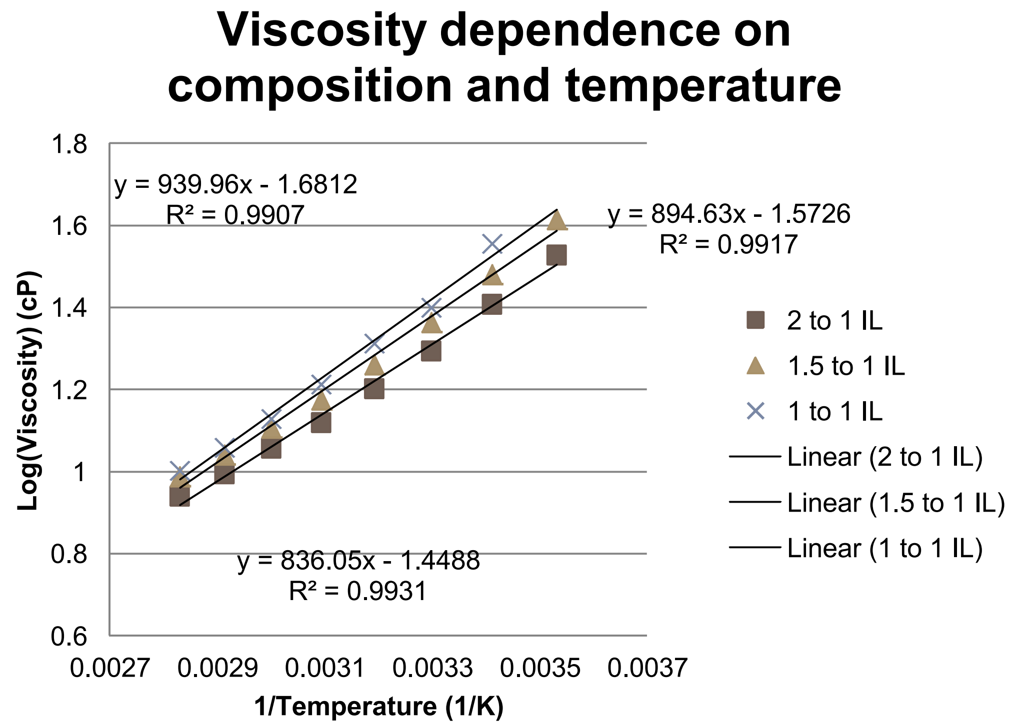


NMR data on speciation at variable temperatures

Viscosity Arrhenius behavior

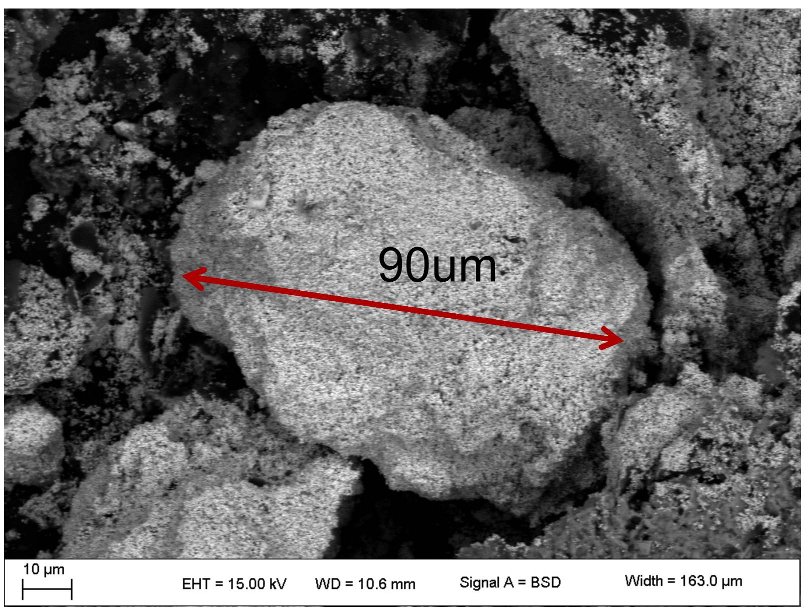
$$Viscosity = \mu_0 * e^{\frac{E}{RT}}$$

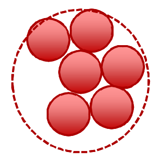




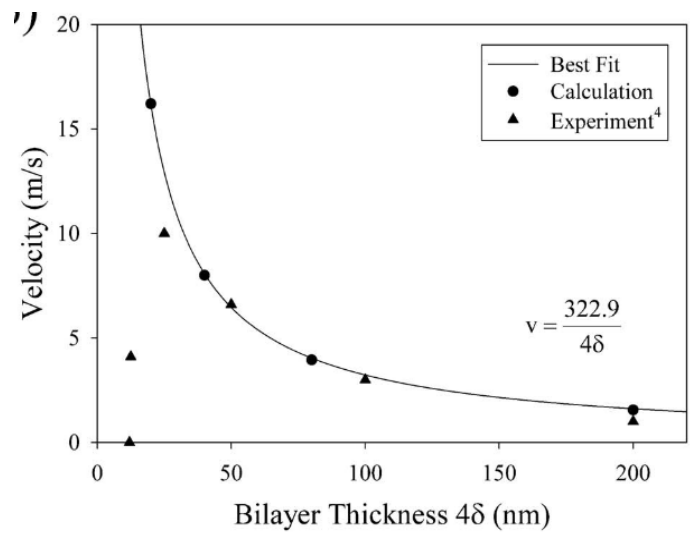
Particle Size Effects

- Smaller particles increase reaction rate
- Need to keep agglomeration to a minimum with agitation and electrolyte properties/surface functionalization
  - Preventing agglomeration in the electrolyte will minimize agglomerations in the deposited film



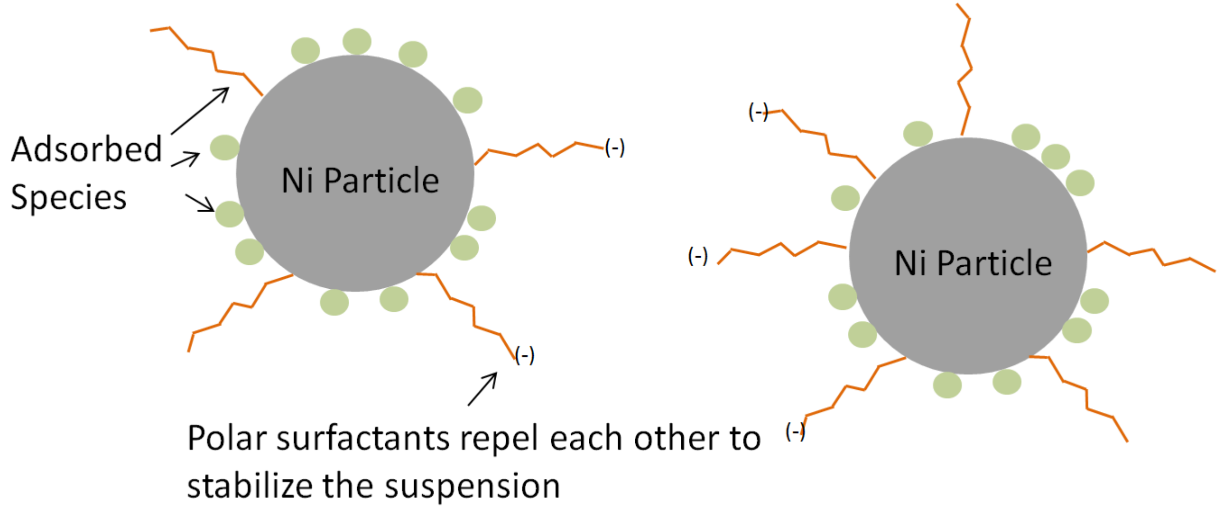


Agglomerations of small particles can mimic large particles



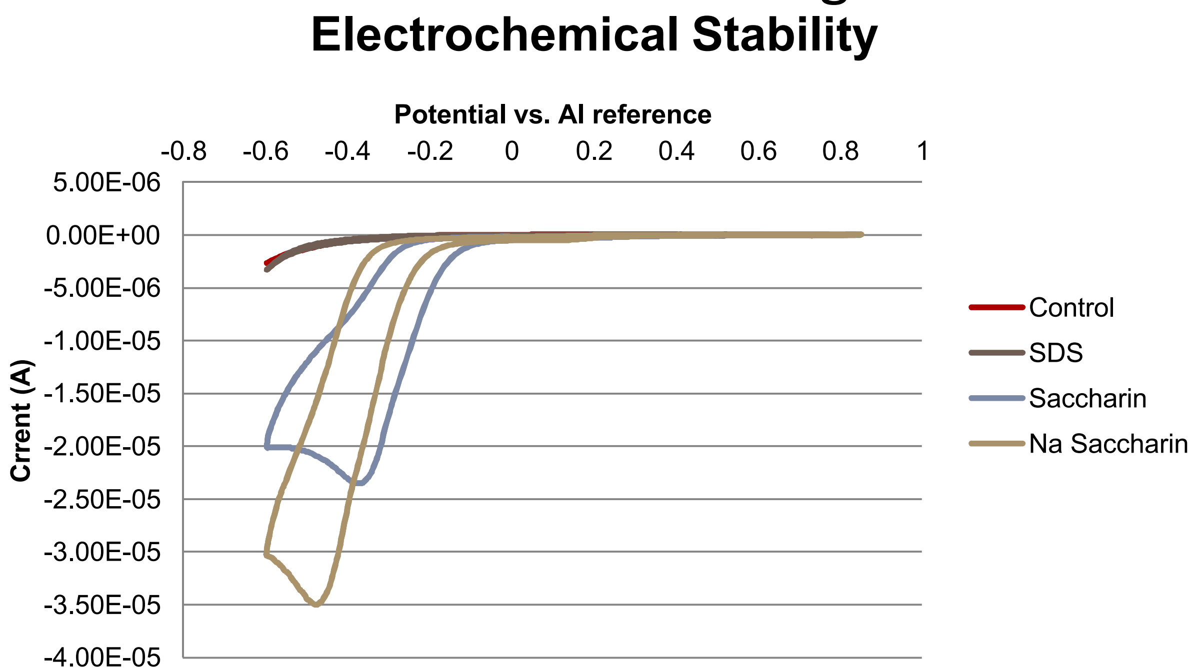
Particle Properties and Modifications

- Particle size, shape and composition
  - Flakes or spheres
  - 10 nm to microns (PVD comparison indicates that ~20 nm particles will be optimal)
  - Ni, NiO, Cu and other options will change the burn properties
- Surface functionalization
  - Surfactants or oxides
  - Modify electrolyte composition



Electrochemical Stability of Surfactants

- Saccharins reduce in the range of Aluminum deposition and are not compatible
- Sodium dodecyl sulfate (SDS) and Centronium Bromide (CTAB) are compatible
- Particle interaction needs to be investigated



Zeta Results (Needs more analysis)

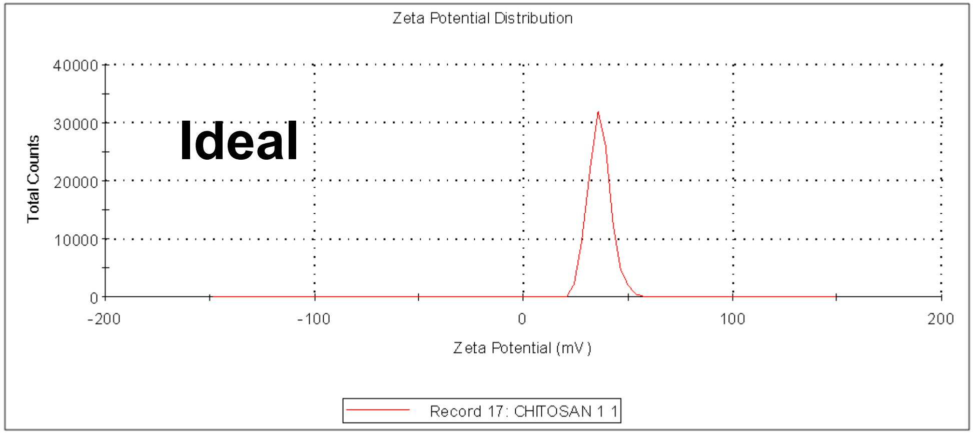
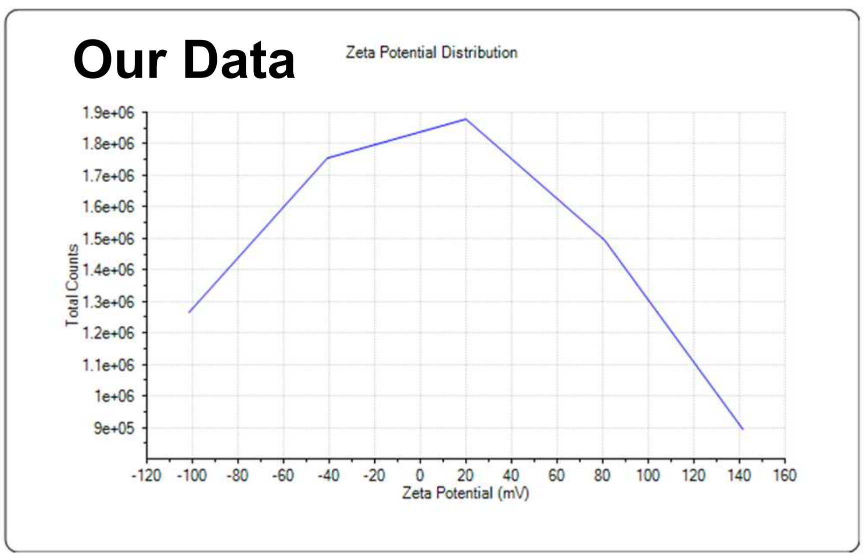


Figure 2: Zeta potential analysis of chitosan nanoparticles, showing mean zeta potential of 40mV as determined by Malvern zeta analyzer

Notice resolved at 30,000 counts

- Well understood in aqueous
- Non-conducting particles
- fixed charge on surface



Summary

Zeta potential: 5.01 mV
Std. Deviation: 124 mV

Conductivity: 0.637 mS/cm
Effective voltage: 3.79 V

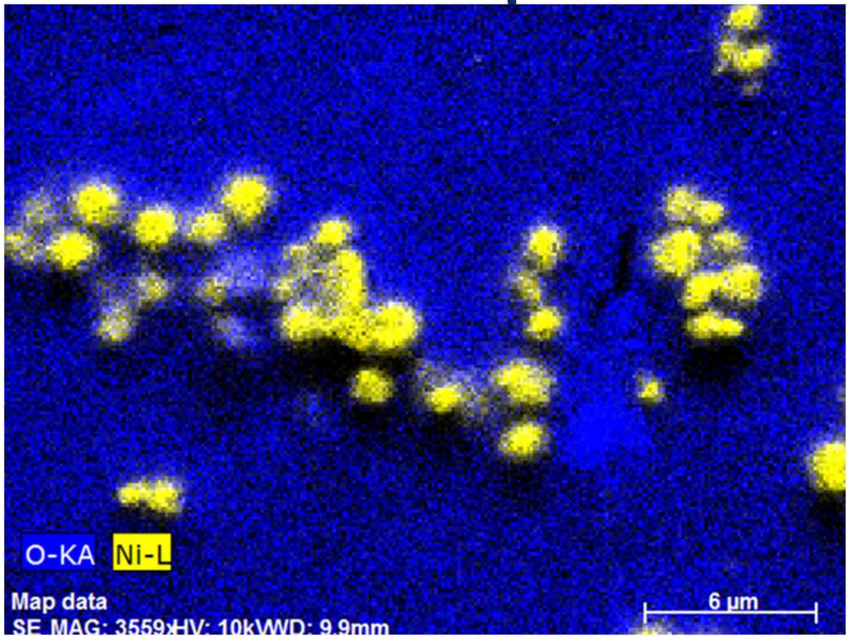
Count Rate: 305.7 kcps

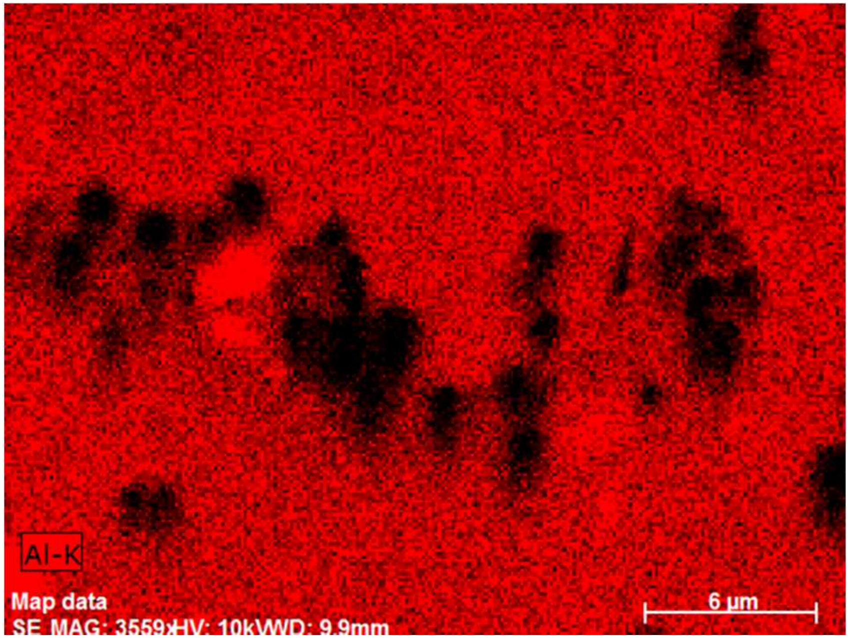
Peak 1: Peak / Area 11.6 mV / 100.0%

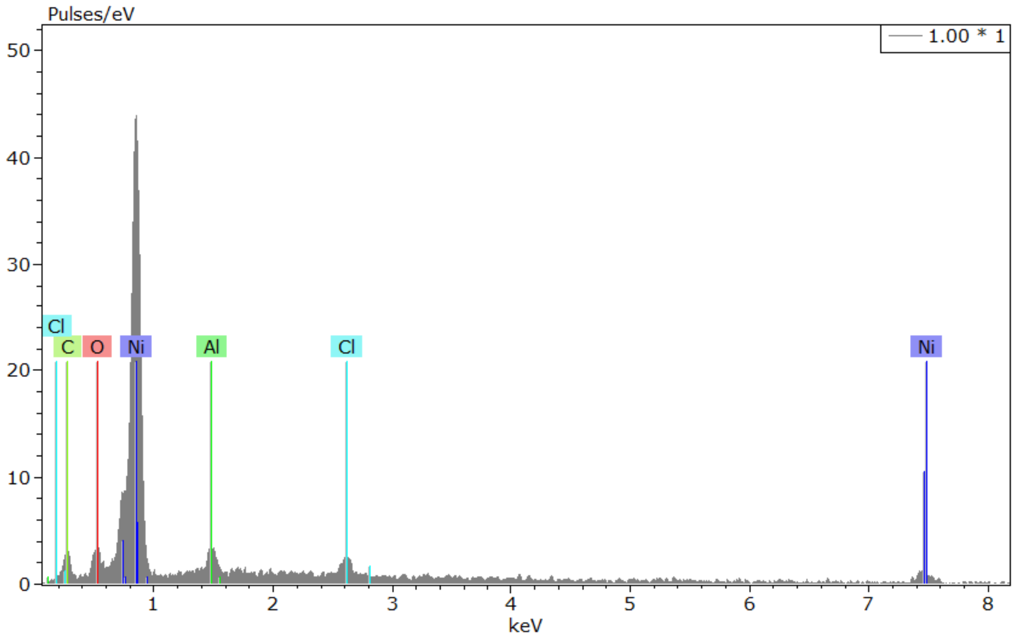
Ni metal (conducting) particles
Magnetic particles
Lacking understanding of IL media
2 million counts and no resolution

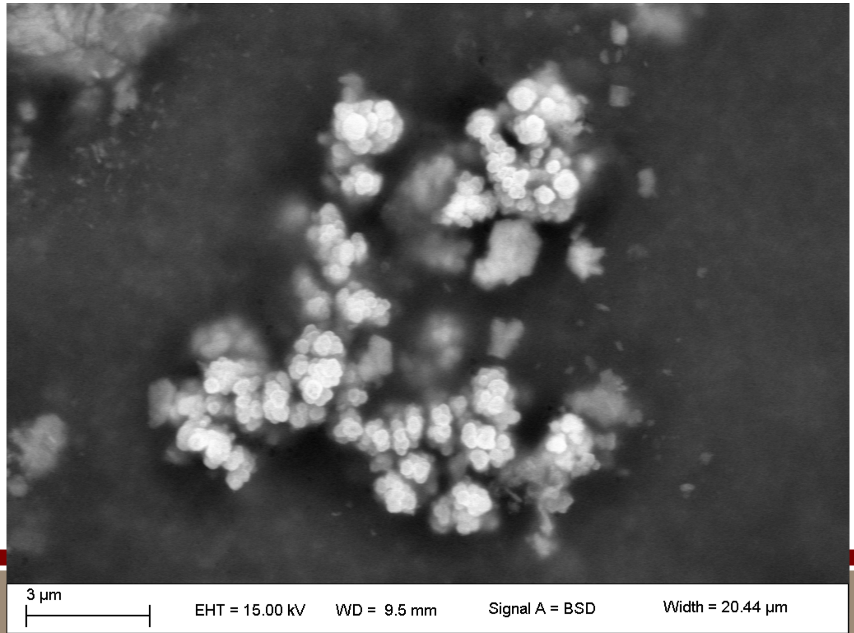
Kumar V, Dandapat S, Kumar A, Kumar N (2014). Preparation and characterization of chitosan nanoparticles "alternatively, carrying potential" for cellular and humoral immune responses. Adv. Anim. Vet. Sci. 2 (7): 414 –417.

NiO Example Data









Conclusions

- Viscosity
  - Temperature and composition
- Speciation effects
  - Particle interaction
  - Deposition precursor
- Surfactants in electrolyte
  - Needs investigation
    - Particles are not acquiring specific zeta potentials
  - NiO is not compatible with AlCl precursors
- Tailoring agitation is crucial
  - Physical properties of ILs need to be well documented and deposition vessel well designed

Acknowledgements

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