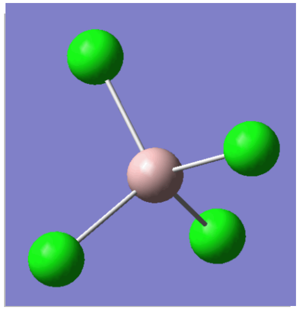
SAND2016-10656PE

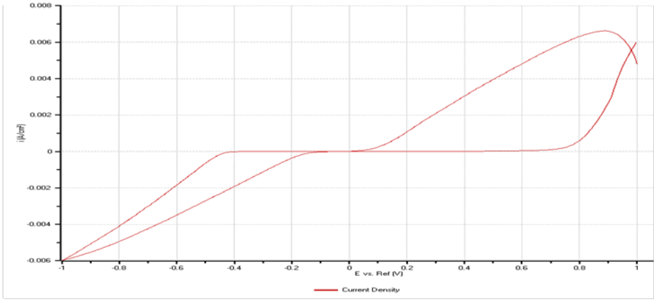
Electrochemical Fabrication of Energetic Thin Films

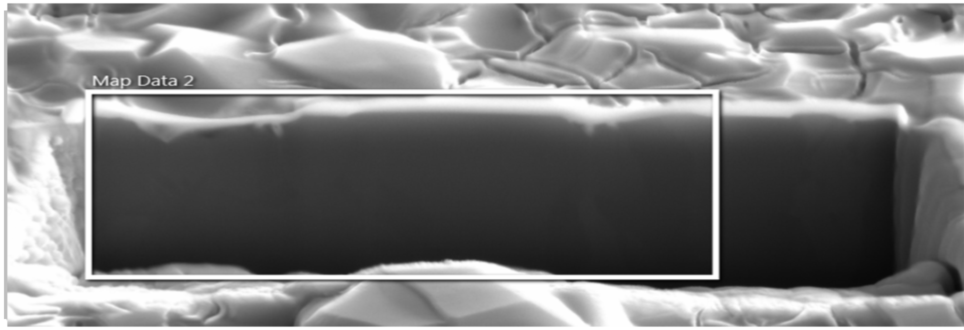
Jonathan J. Coleman

SNL-NM Graduate Intern

Exceptional service in the national interest

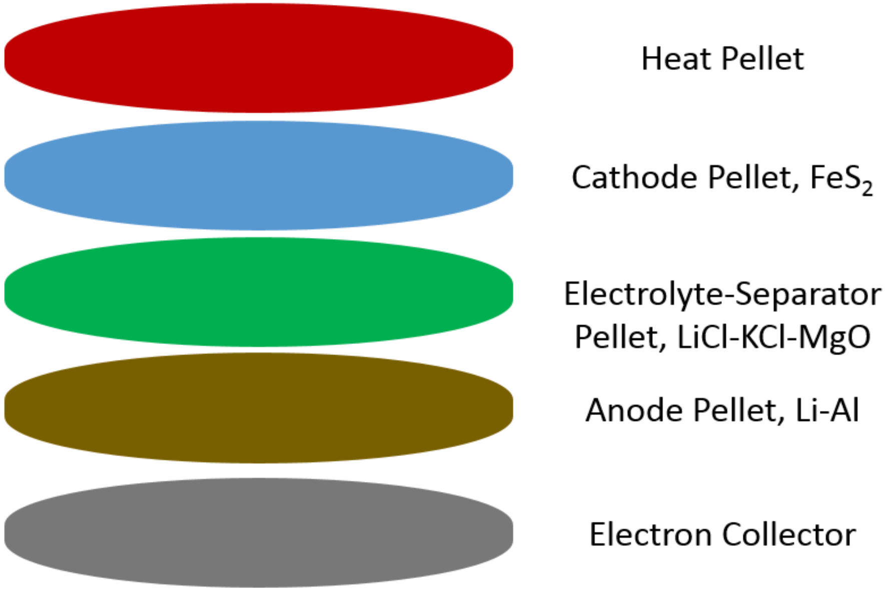






The Problem

- 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



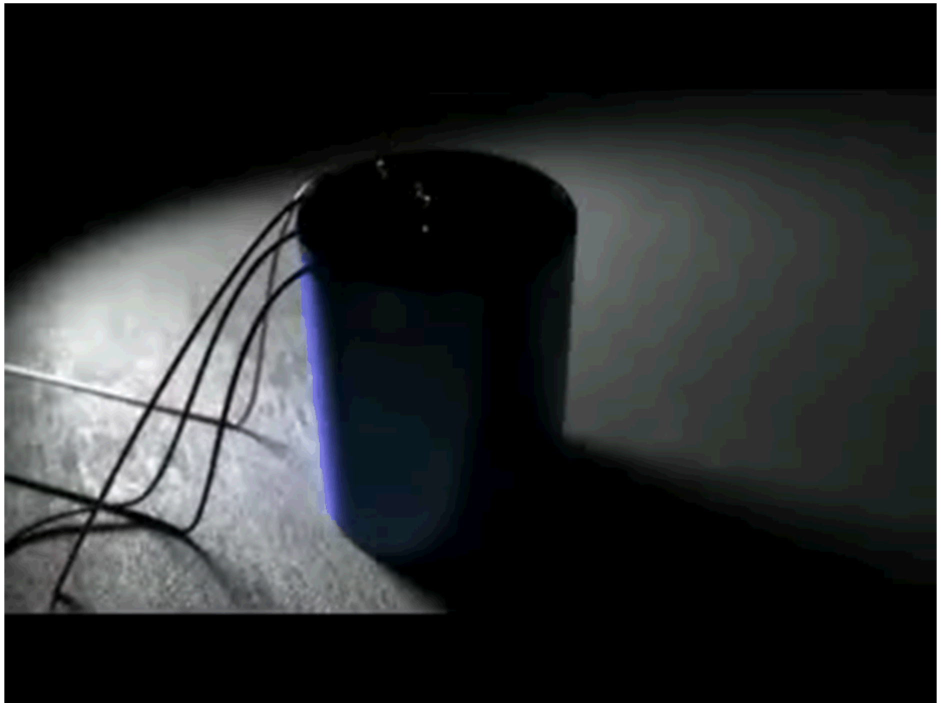
Heat Pellet

Cathode Pellet, FeS_2

Electrolyte-Separator Pellet, LiCl-KCl-MgO

Anode Pellet, Li-Al

Electron Collector



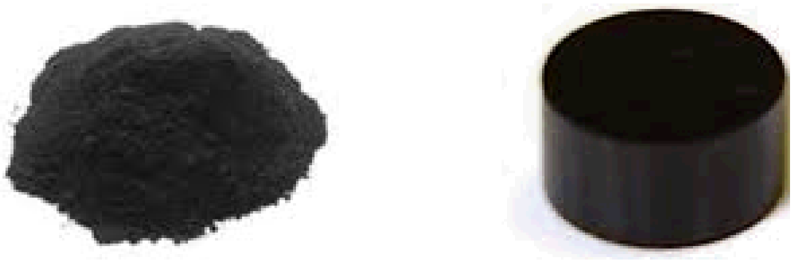
Thermal Battery Function

Outline

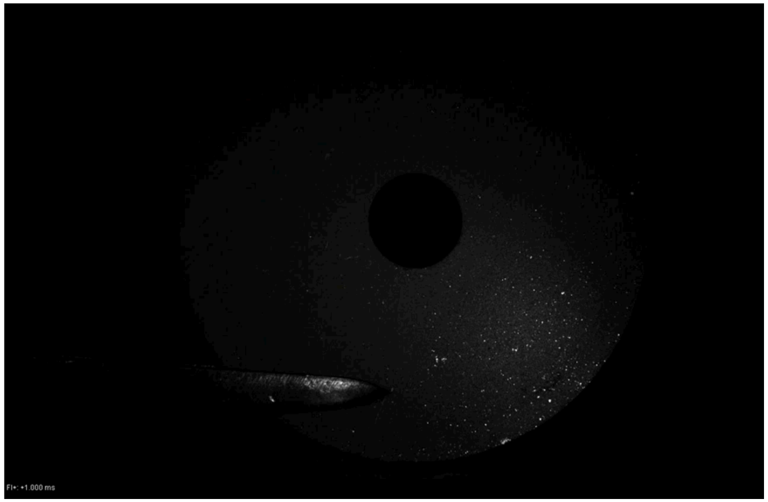
- Current Technology - Packed Powders
- Improved Replacement - Intermetallic Films
- Fabrication of Intermetallic Films
- Electrochemical Codeposition
  - Balance of Forces
  - Importance of Electrodeposition Kinetics and Diffusion Limitations
- Modifying Diffusion with Dilution
- Modifying Kinetics with Temperature
- Codepositions and Particle Incorporation
- Particle Interface Analysis
- Future Work and Conclusions

Current Heat Pellets

- Iron - Potassium Perchlorate powders
- Low packing density (~53%) reduces energy output
- Relatively slow burn rate
- Gas generation



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

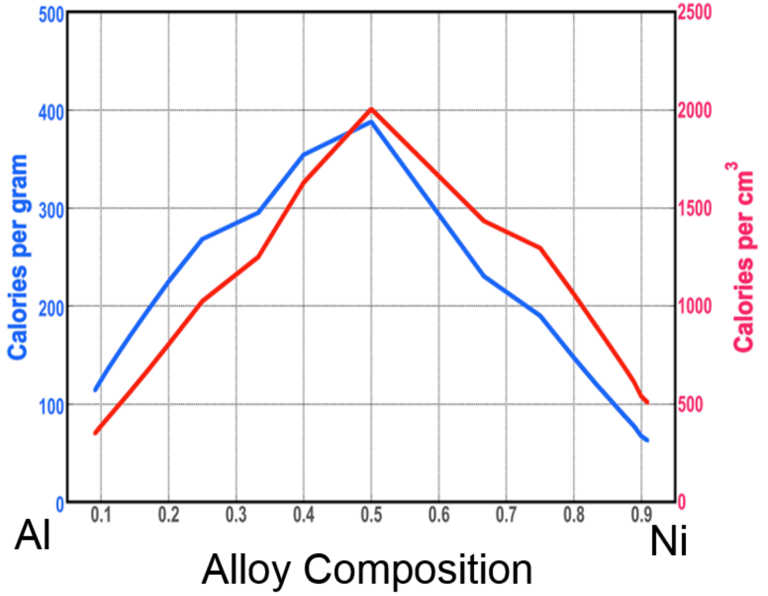


Perchlorate Pellet

Heat Pellet data Adams, Ingersoll

Energetic Heat Sources - Ni/Al

- Fabrication method is important
  - Fast reaction rates
  - No gas generation
  - Max energy at 50% mole fractions
    - 60% Aluminum by volume

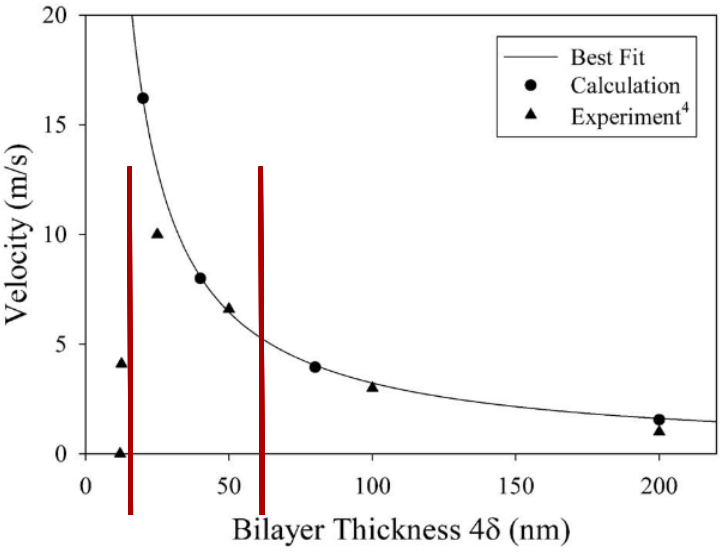


NiAl Pellet

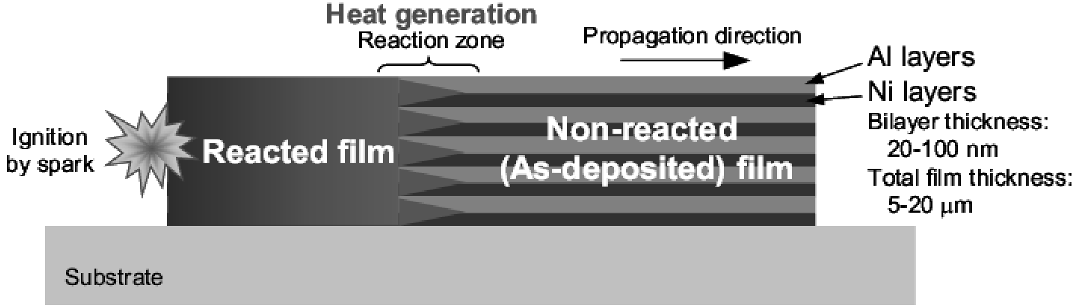
Heat Pellet data Adams, Ingersoll

Ni-Al Intermetallic Fab

- Reaction rate increases with increasing interfacial area
  - Improves propagation reliability and speed
  - Optimum size due to passivation



Metallic Film



Requires high vacuum
Slow fabrication rates
Expensive

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

Energetic Film Requirements

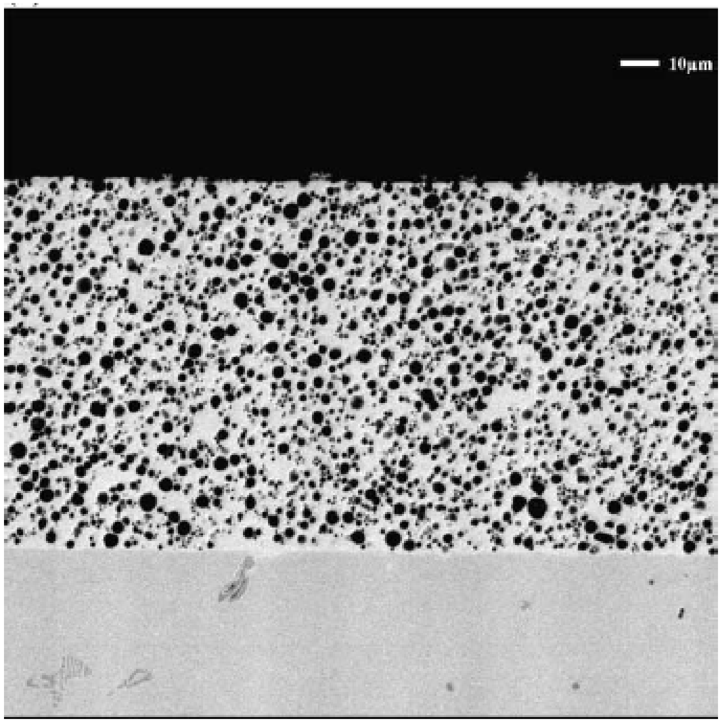
- Nickel and Aluminum
  - Pure, unmixed phases
  - Stoichiometric maximum energy release at 60% Aluminum by Volume, 40% Nickel
- Nanoscale Architecture
  - Required for self propagating reactions and optimal heat release
- Would like to reduce cost
  - Will allow for more widespread application

Electrocodeposition of Al-Ni

- Inherently material efficient
- Does not require vacuum

- Matrix Deposition
  - Want high rate
  - Low Porosity
  - Low temperature/clean interfaces

- Particle incorporation
  - High inclusion (~40%)
  - Well dispersed
  - Nanoscale



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.

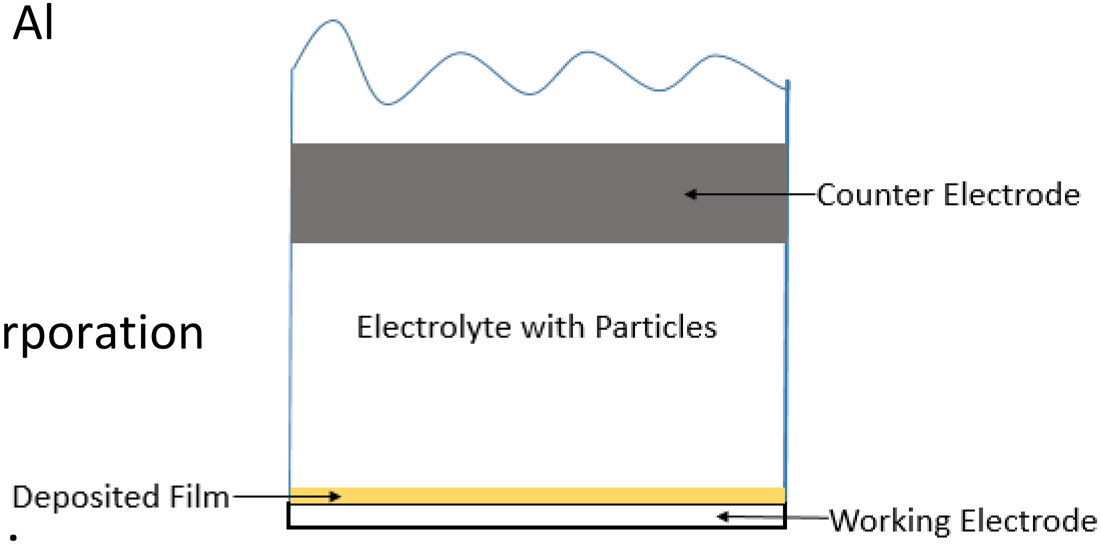
Particle Incorporation Controls

- Particle Characteristics
  - Shape – start with sphere
  - Size - nanoscale
  - Composition – Nickel (Particles are almost always the lower volume phase)

- Particle Quantity and Transport
  - Particle loading in electrolyte
  - Particle convection, flow in reactor

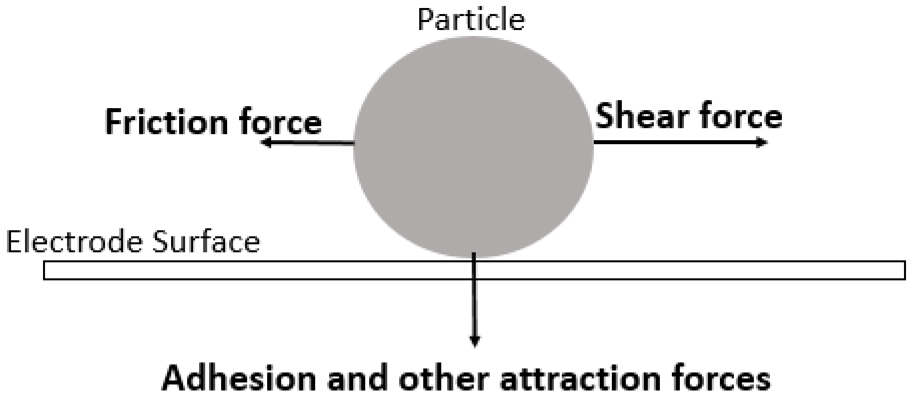
Electrocodeposition Objectives

- Aluminum deposition
  - Necessary to reach high Al volume (60%)
- Nickel incorporation
  - Need High particle in corporation
    - 30%-40%
- Sedimentary Codeposition
  - Use gravity to aid in bringing particles to the surface



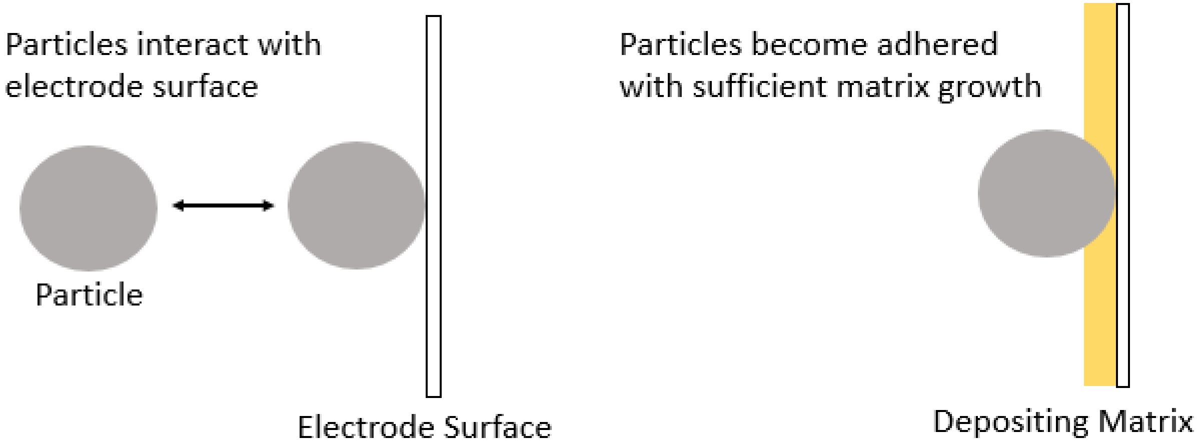
Nanoscale Particles

- Nanoscale shifts influence towards surface forces vs. body forces, reducing particle residence time due to increased shear forces
- Lower solution flow to increases residence time
  - Balance adsorption forces with shear and matrix growth rate



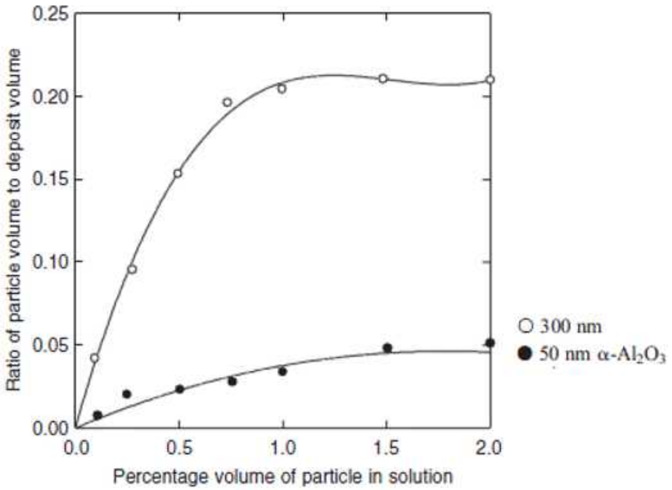
Particle Incorporation Parameters

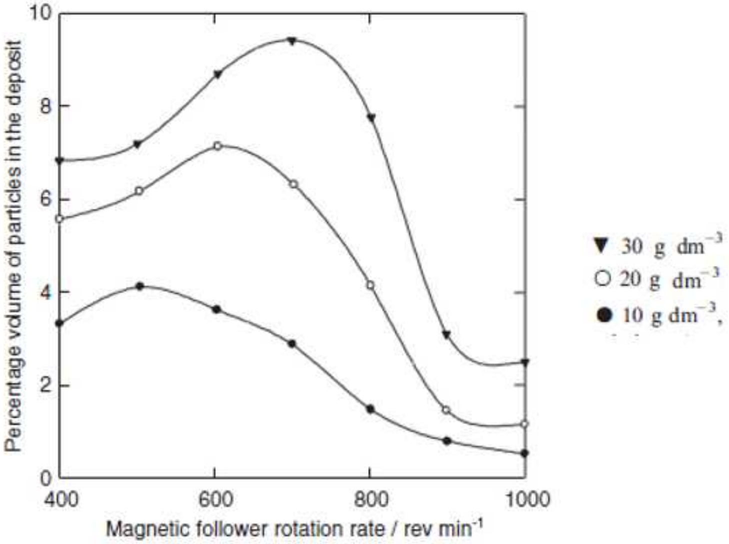
- Particles in equilibrium contact with electrode
  - More particles increase contact probability
- Particles on the electrode become permanently imbedded if the matrix growth is enough
  - Faster deposition rate increases incorporation probability



Controlling Particles

- Competing trends dictate particle arrival and incorporation rates
- Increasing agitation will increase convection toward surfaces but increased shear drives them away without incorporation
    - Decreases residence time





Feng, Q.Y., T.J. Li, and J.Z. Jin, *Research on the mechanism of composite electroplating and its latest progress. Rare Metal Materials and Engineering, 2007.* ***36(3): p. 559-564.***

Particle Incorporation Summarized

- Need to Maximize Incorporation Volume

$$Incorporation\,Volume = \frac{(Particle\ Loading)(Incorporation\ Probability)(Convection)}{(Matrix\ Growth\ rate)}$$

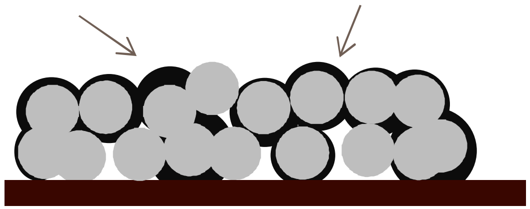
$$Incorporation\ Probability = (Residence\ Time)(Matrix\ Growth\ Rate)$$

$$Residence\ Time = \frac{Adhesion\ forces}{Convection}$$

- Increase particle loading?
- Adhesion forces?

Conductive Particle Incorporation

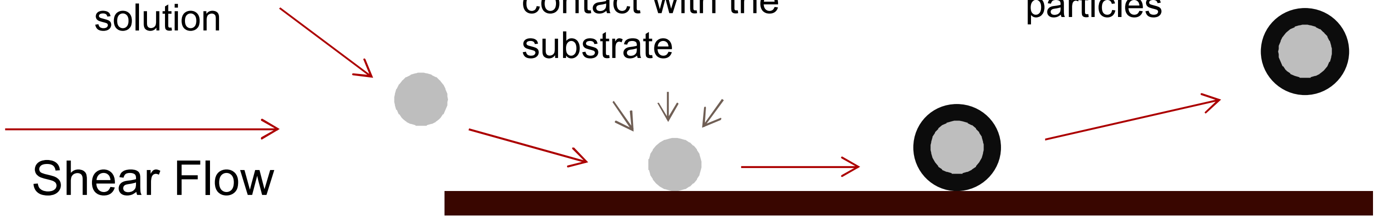
Low Agitation vs. High Loading



Electrical contact with the substrate

Preferential onto the surface of the stack, leading to spongy deposits

High Agitation



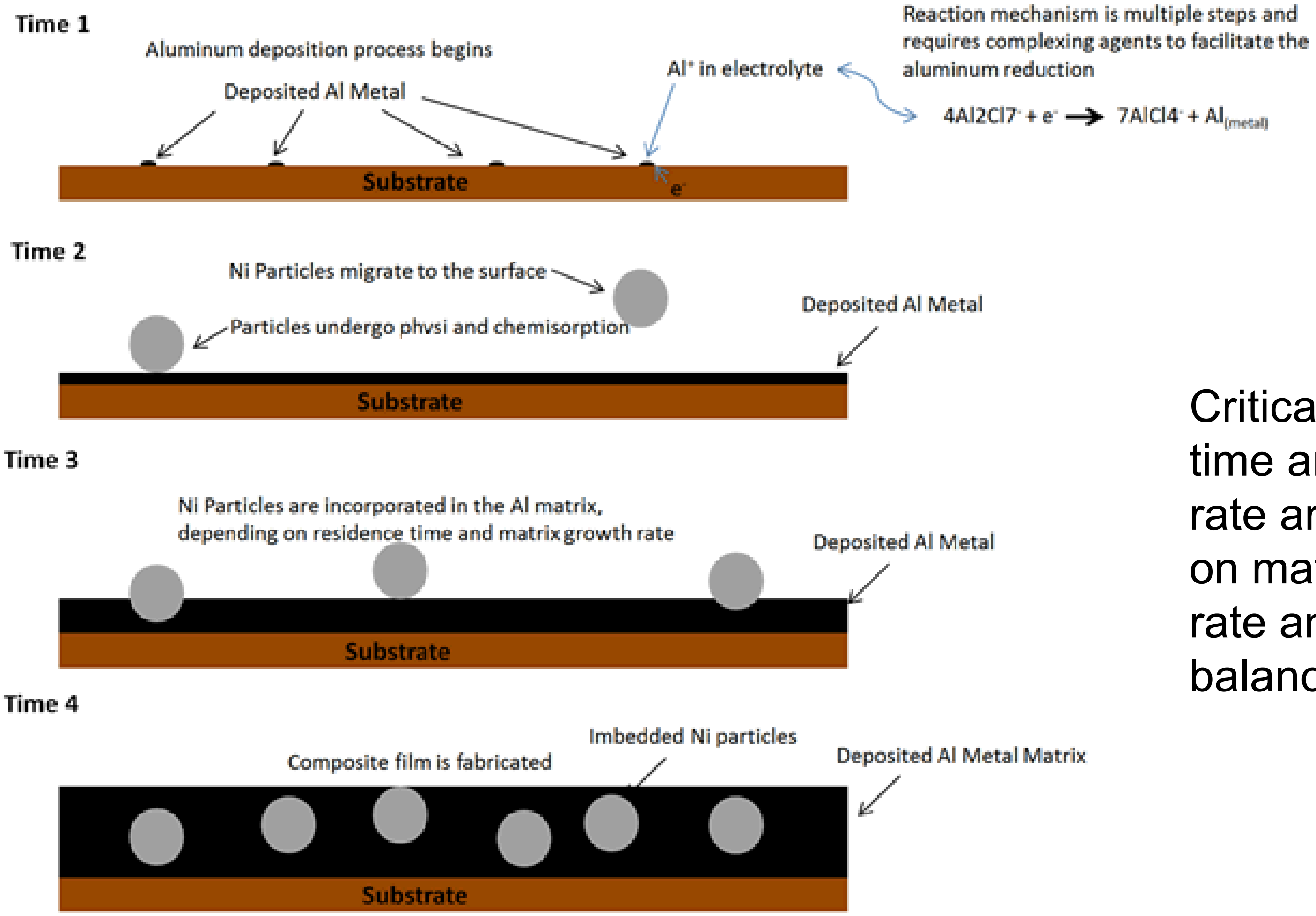
Ni Comes in from solution

Comes into electrical contact with the substrate

Preferential plating onto Ni, and is removed before film can encapsulate the particles

Shear Flow

Particle Incorporation



Reaction mechanism is multiple steps and requires complexing agents to facilitate the aluminum reduction

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

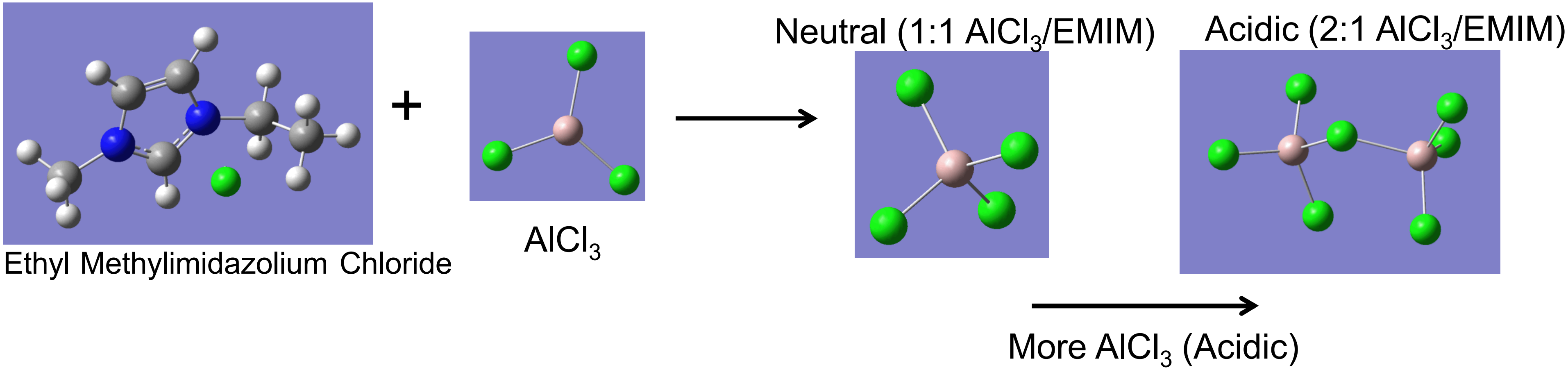
Critical residence time and arrival rate are dependent on matrix growth rate and must be balanced

Conductive Nanoscale Particle Incorporation

- In summation:
  - Interaction with electrode depends on particle loading and arrival rate
  - Low flow increases residence times and improves incorporation
  - Particle loading in electrolyte must be balanced with matrix growth rate
    - Build up of particles on the electrode will result in a porous and spongy deposit
    - Particle that are not incorporated will shift in composition
- Aluminum deposition must be optimized for high rates and low agitation
  - Must detail reduction kinetics and transport properties
  - Flux of reactants to the electrode must exceed the consumption rate

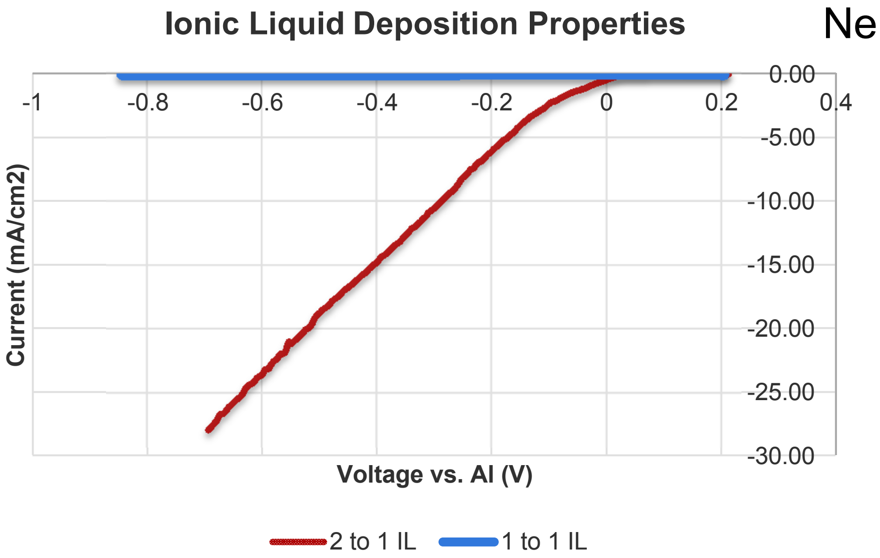
Aluminum Ionic Liquids

- Ionic liquids Uniquely well designed for aluminum deposition we chose dialkyl imidazolium chloroaluminates for their:
  - Large electrochemical window
  - High aluminum concentration
  - High conductivity and deposition rates
  - Moderately low temperature
  - High reliability and low maintenance

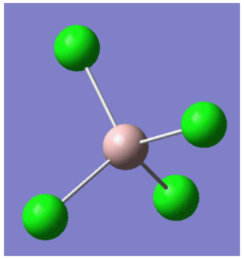


Ionic Liquid Properties

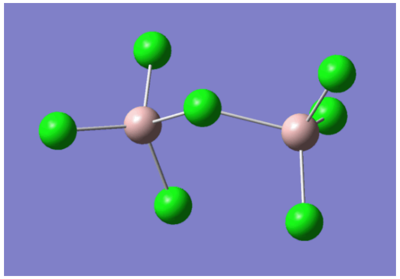
- Really high precursor concentration ($Al_2Cl_7^-$ >3 Molar)
- Low diffusion rates, usually circumvented with agitation
  - We are limited in our mixing (convection) at the electrode due to codeposition
  - Must investigate kinetics and diffusion thoroughly to optimize



Neutral (1:1 $AlCl_3$/EMIM)



Acidic (2:1 $AlCl_3$/EMIM)

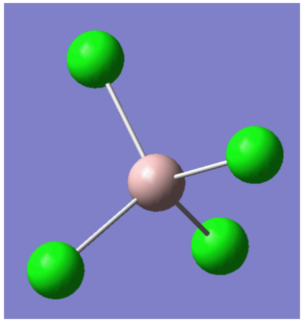


More $AlCl_3$ (Acidic)

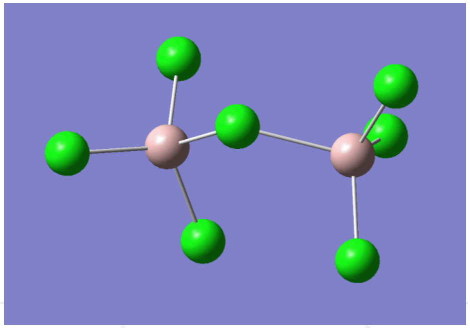
Deposition on RDE 500 RPM, RT, 2 mV/s

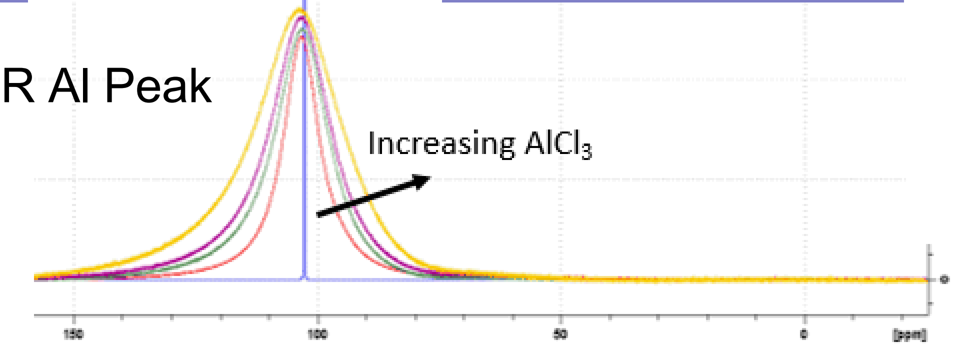
Intermediate Solution Composition

- Al^{27} NMR for Aluminum Speciation
- Aluminum NMR shows response according the aluminum species bonding environment
- Stoichiometric Chloroaluminate speciesAl2Cl7-
  - Single strong peak indicates that all Al precursor is converted to the complexed species

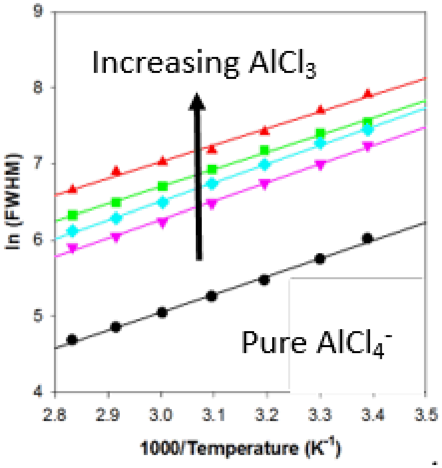


Increasing $AlCl_3$ →



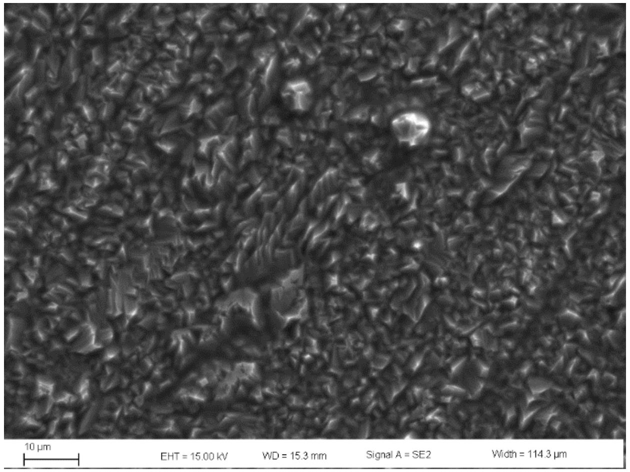


Pure $AlCl_4^-$

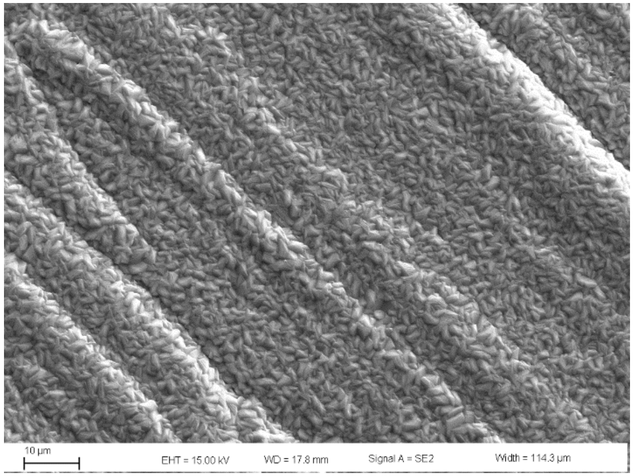


BMImCl:AlCl$_3$ Electrolytes and Dilutions

Neat Ionic Liquid

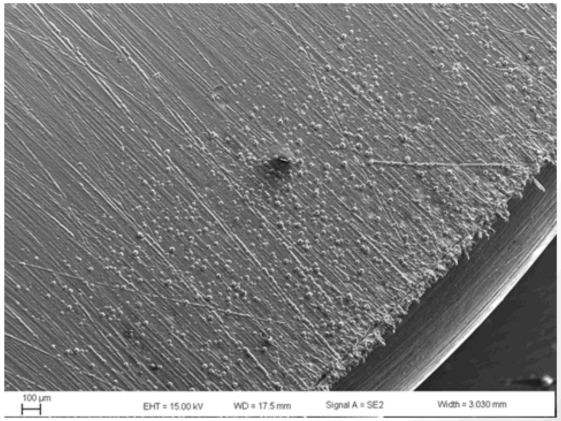


Toluene Diluted Ionic Liquid 1:1

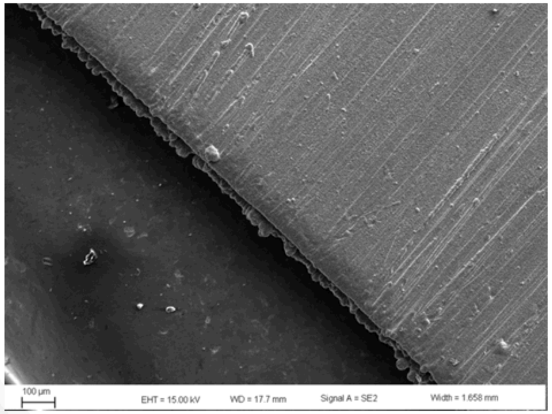


Dilutions and Edge Effects

- Dichlorobenzene decreases edge effects but also reduces rate under the same deposition conditions



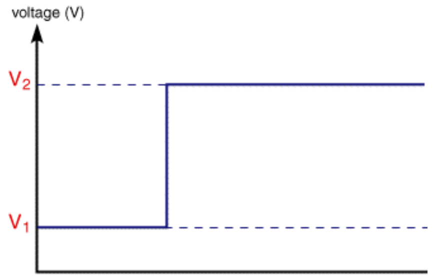
Toluene IL Bath edge effects

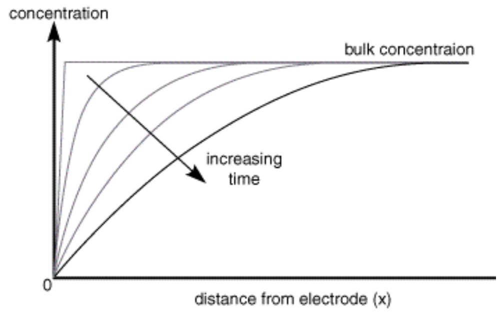


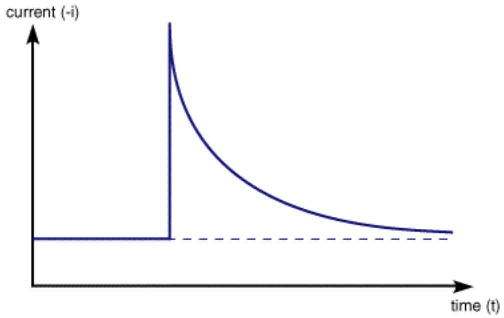
Dichlorobenzene IL Bath edge

$AlCl_3$	BMImCl	Toluene	DCB	mV (-) vs. Al QRE	Appearance	Purity	Cost ($/L)
2	1			600	Acceptable	Acceptable	1468
2	1	1		600	Good	Medium	1120
2	1	3		600	Best	High	768
2	1	6.8		500	Good	Medium	492
2	1	6.8		1000	Poor	Low	492
2	1	6.8		1500	Black powdery	Low	492
2	1		11	600	Best	High	384
2	1		16	600	Not Complete	High	312

Diffusion in IL with Co-solvents

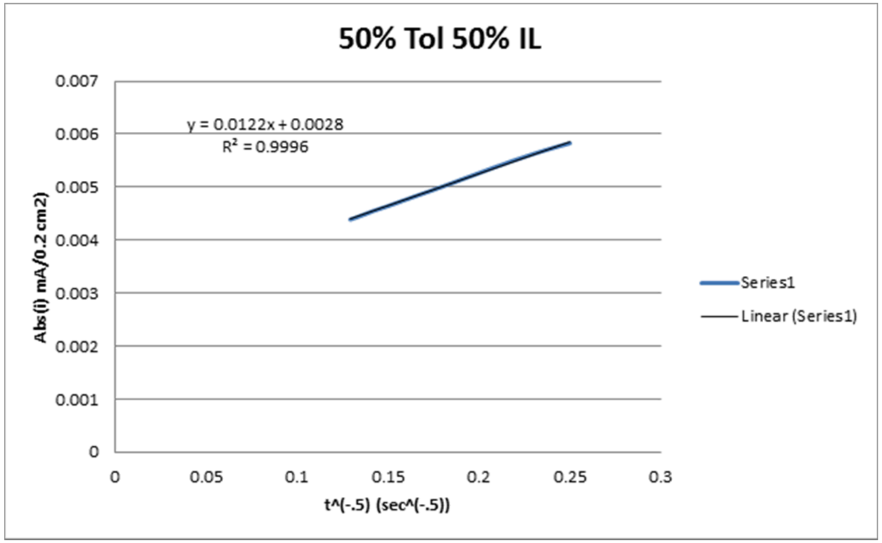






$$i = \frac{nFAc\sqrt{D}}{\sqrt{\pi t}}$$

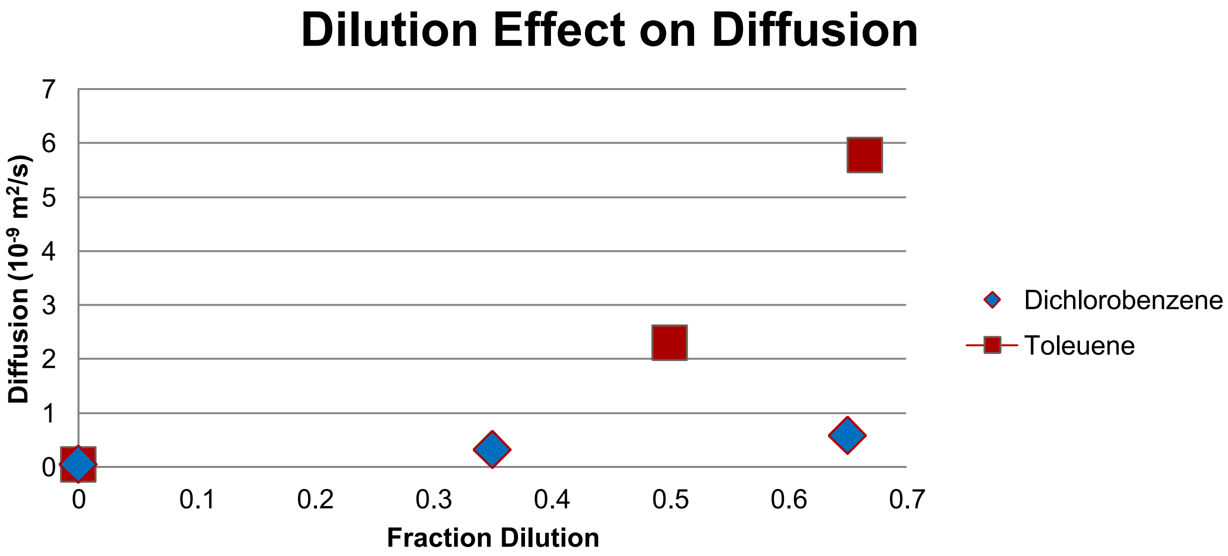
- Diffusion rates shift with dilutions
- Apparent this influences the improved deposition characteristics



http://www.ceb.cam.ac.uk/research/groups/rg-eme/teaching-notes/potential-step-voltammetry

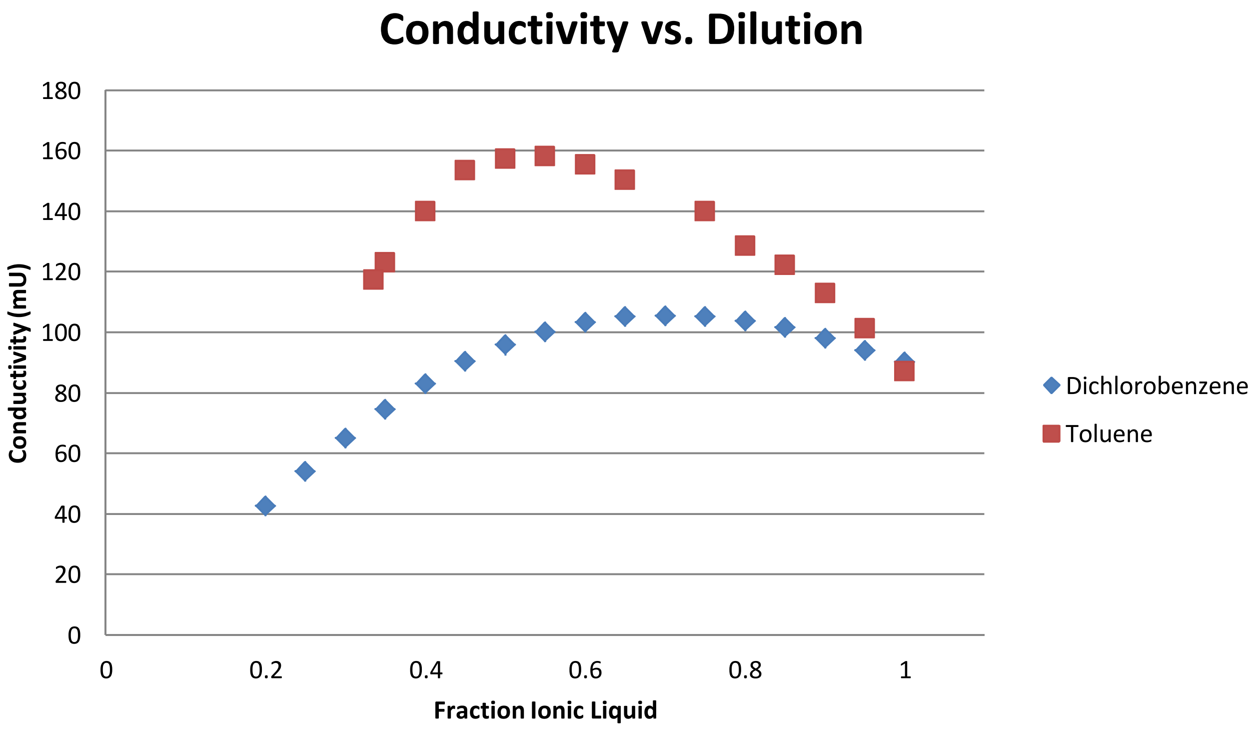
Dilution and Diffusion

- Dilution increases diffusion greatly
  - Lower viscosity in toluene increases diffusion at a higher rate than DCB
- Looking to optimize chemistry without manually testing every make up



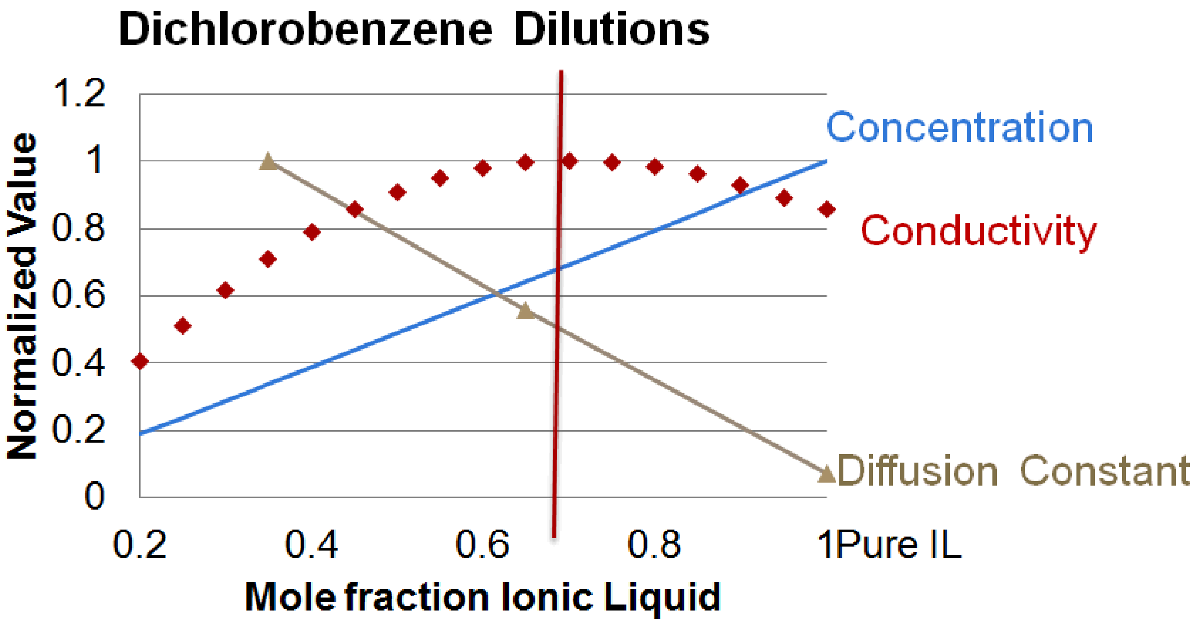
Conductivity Tests

- The lower viscosity in toluene increases the conductivity of the solution more than dichlorobenzene



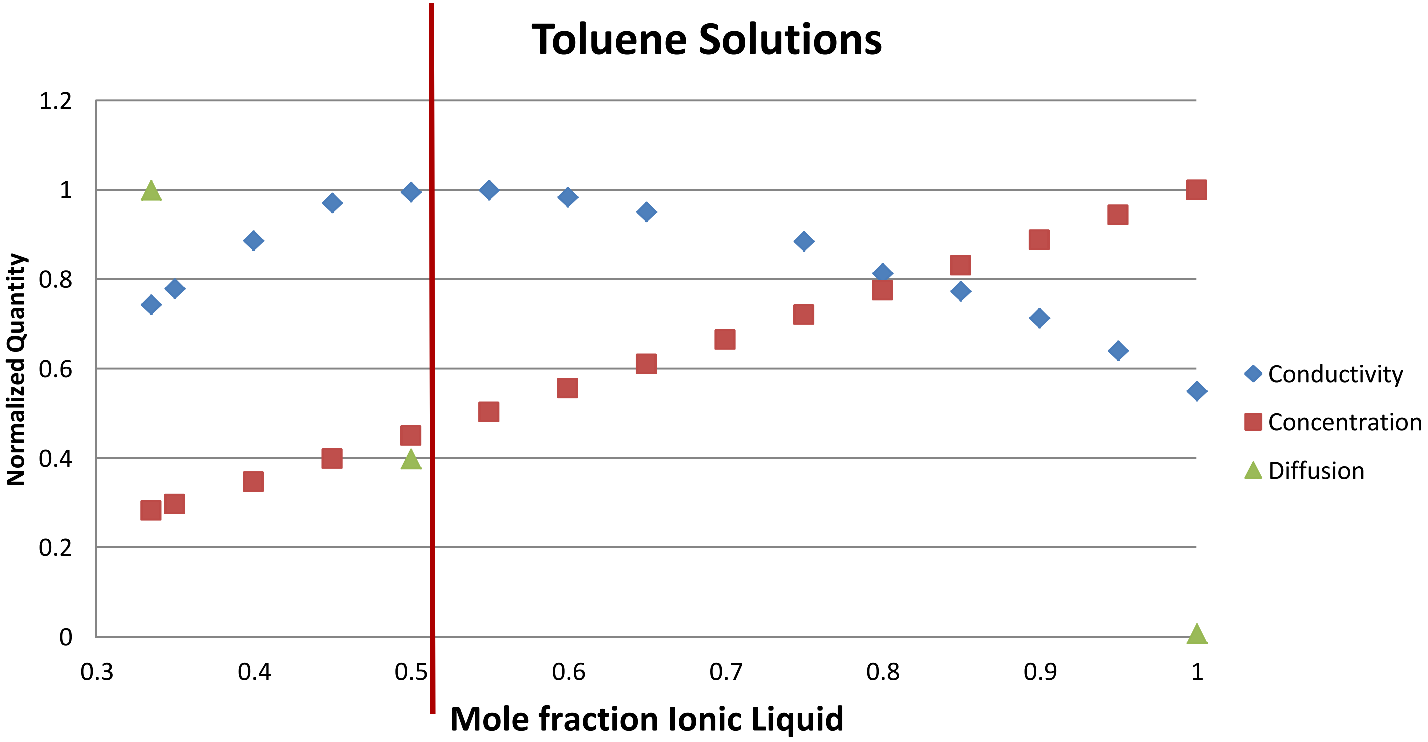
Conductivity - DCB

- Decreasing ionic concentration while increasing mobility leads to a maximum in the conductivity



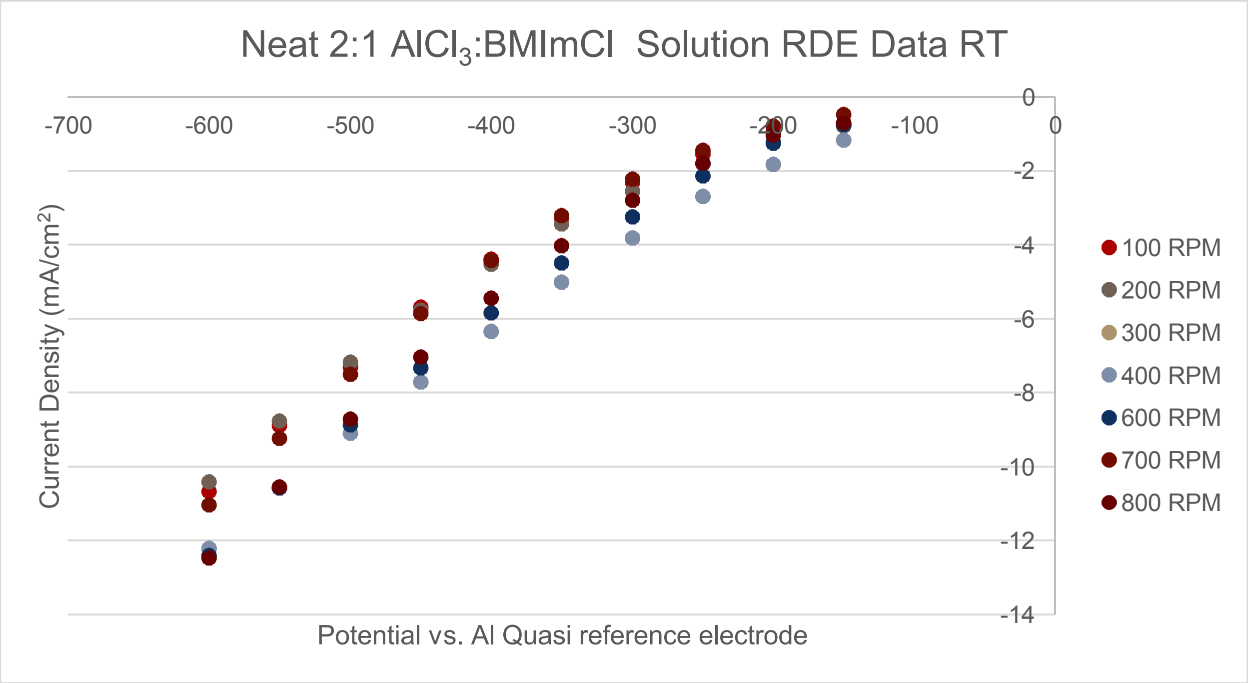
Conductivity - Toluene

- Decreasing ionic concentration while increasing mobility leads to a maximum in the conductivity
  - This maximum correlates to the best observed deposition characteristics (combination max rate and min roughness)



RDE Kinetics Investigation

- Do not reach any diffusion limitations in the window of the electrolyte
- Kinetics are relatively low, no dependence on rotation rate (diffusion)

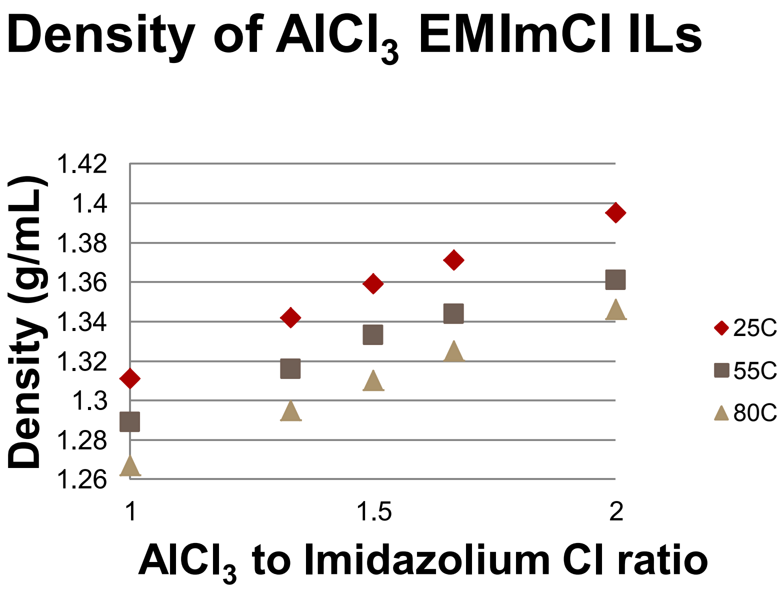


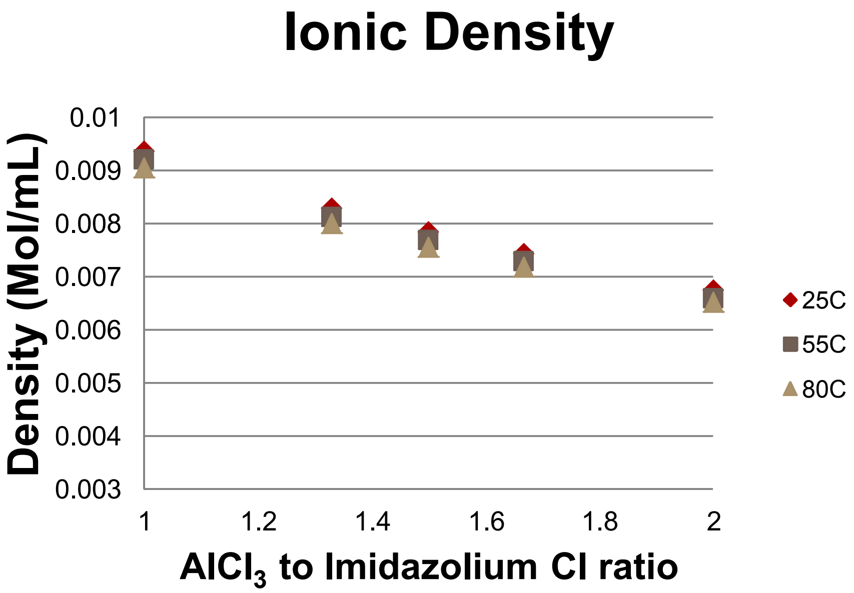
Increasing Kinetics

- EMImCl and $AlCl_3$ without dilutions to simplify analysis
- Modify and map responses
  - Temperature (30, 50 and 80 C)
  - Composition
  - Overpotential (linear voltammetry, 0 - -700 mV vs. Al)
- Requires information on the neat ionic liquid
  - Density/Concentration over temperature and composition range
  - Viscosity

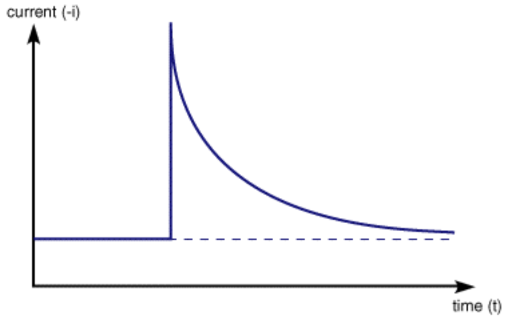
Density and Concentration

- Density increases as you shift from neutral to acidic compositions
    - However, since the anions are more massive in the acidic electrolytes the ionic concentration decreases

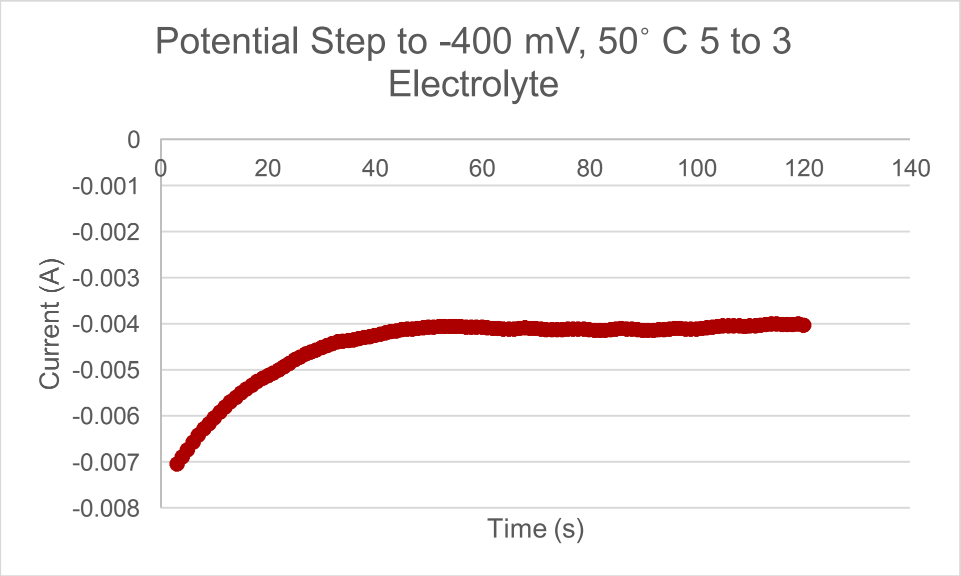

Density of $AlCl_3$ EMImCl ILs

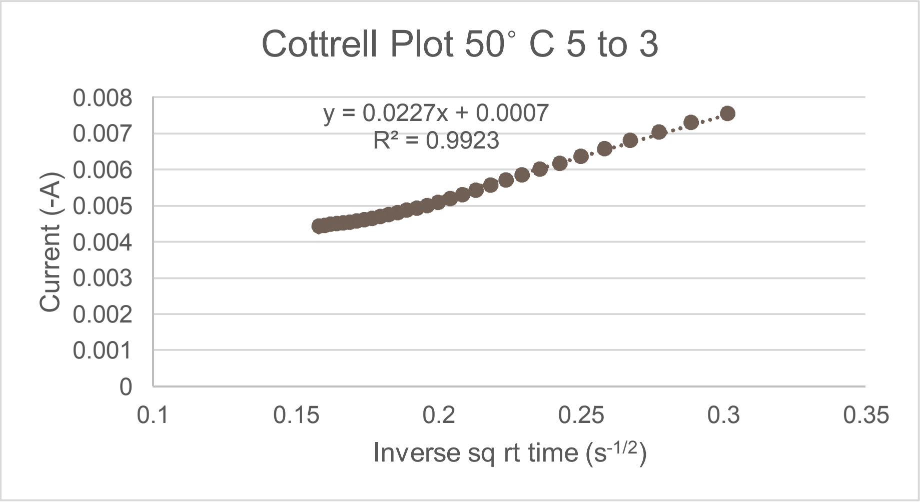

Ionic Density

Diffusion in EMImCl



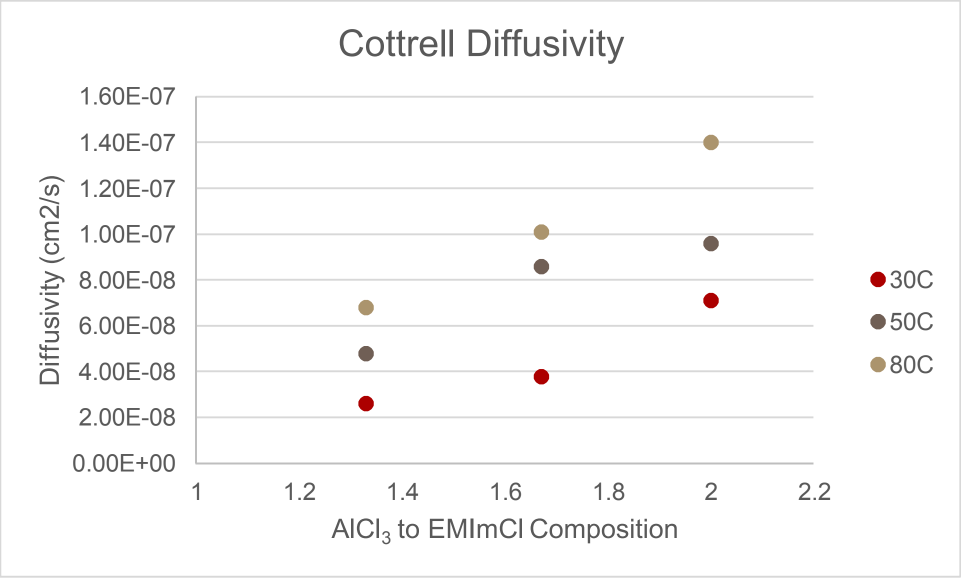
- Solutions were tested for diffusion rates
  - Exhibit Cottrell type response
  - One example is shown below
- Interface response is relatively slow to come to equilibrium
  - Low Diffusion/Polarization rate





Diffusivity in EMImCl

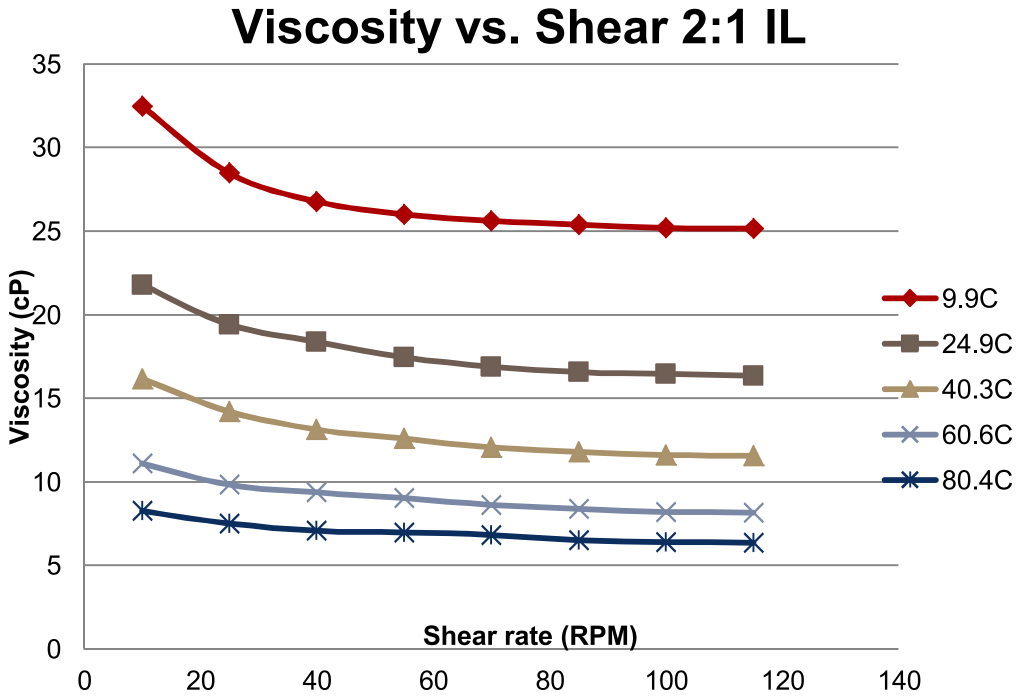
- Diffusion rates increase with temperature and also with increasing $AlCl_3$ content

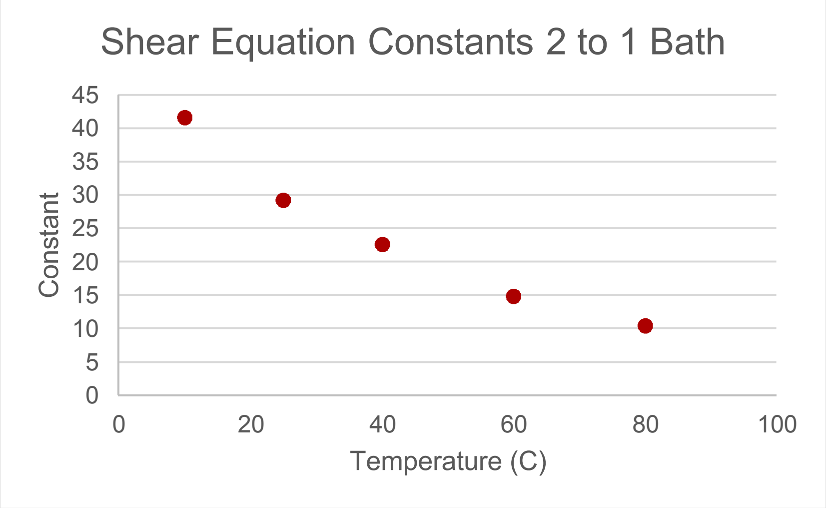


4 to 3 | 5 to 3 | 2 to 1

Bulk Properties - Shear Thinning

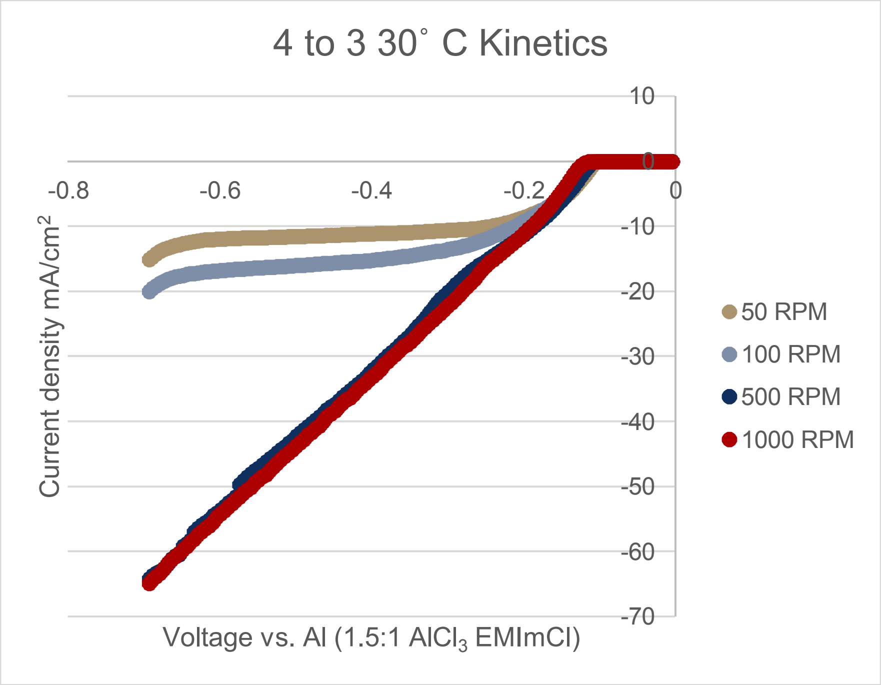
- Short distance structuring shown in non-Newtonian viscosity

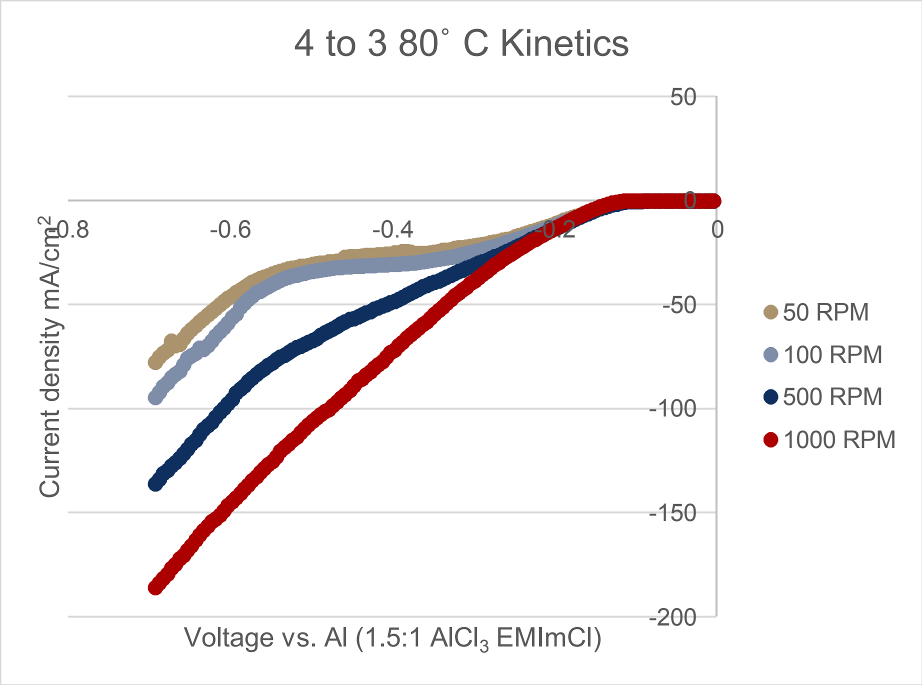




EMImCl:$AlCl_3$ IL RDE, Changing Temp.

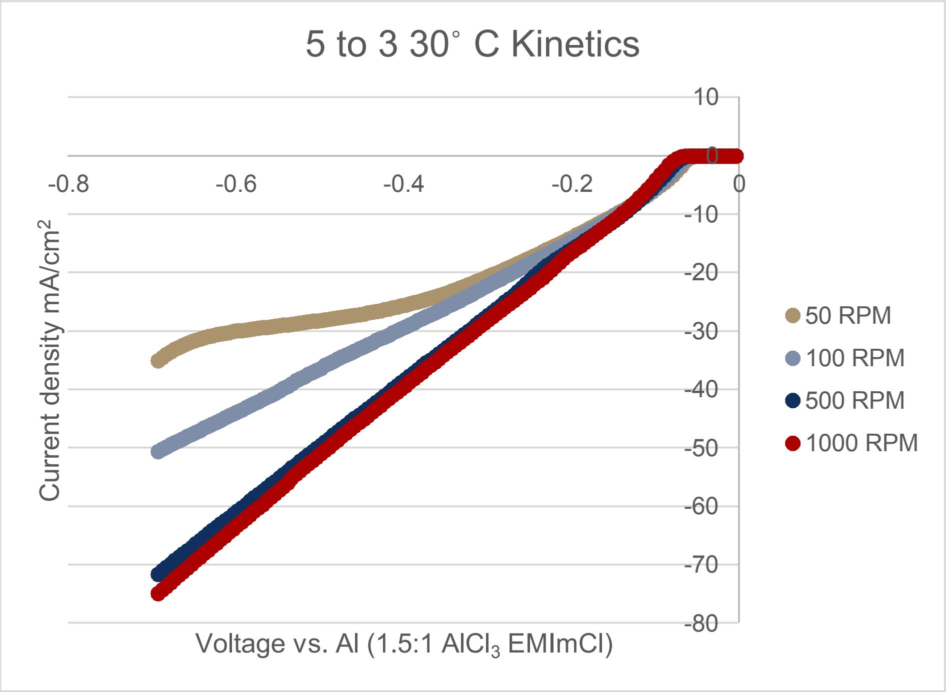
- 4 to 3 electrolyte shows diffusion limitation in low rotation rates
- Kinetically limited at high rates and low temperatures
- Increasing temperature increases kinetics more than diffusion
  - Low temperature kinetically limited condition is now diffusion limited

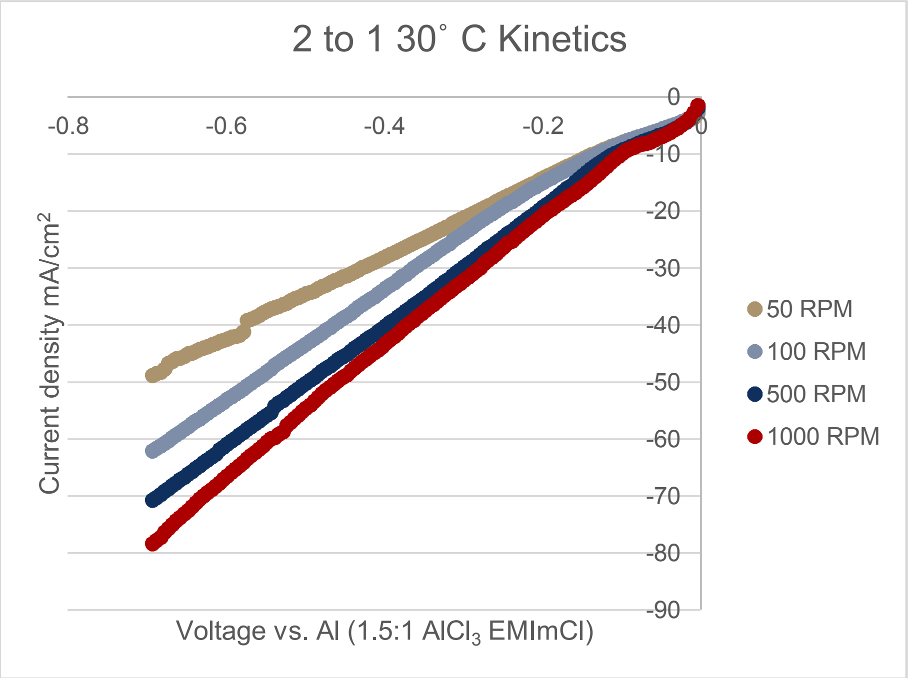




Modifying composition

- Increasing precursor concentration decreases diffusion limitations and shifts toward all mixed or pure kinetically limited





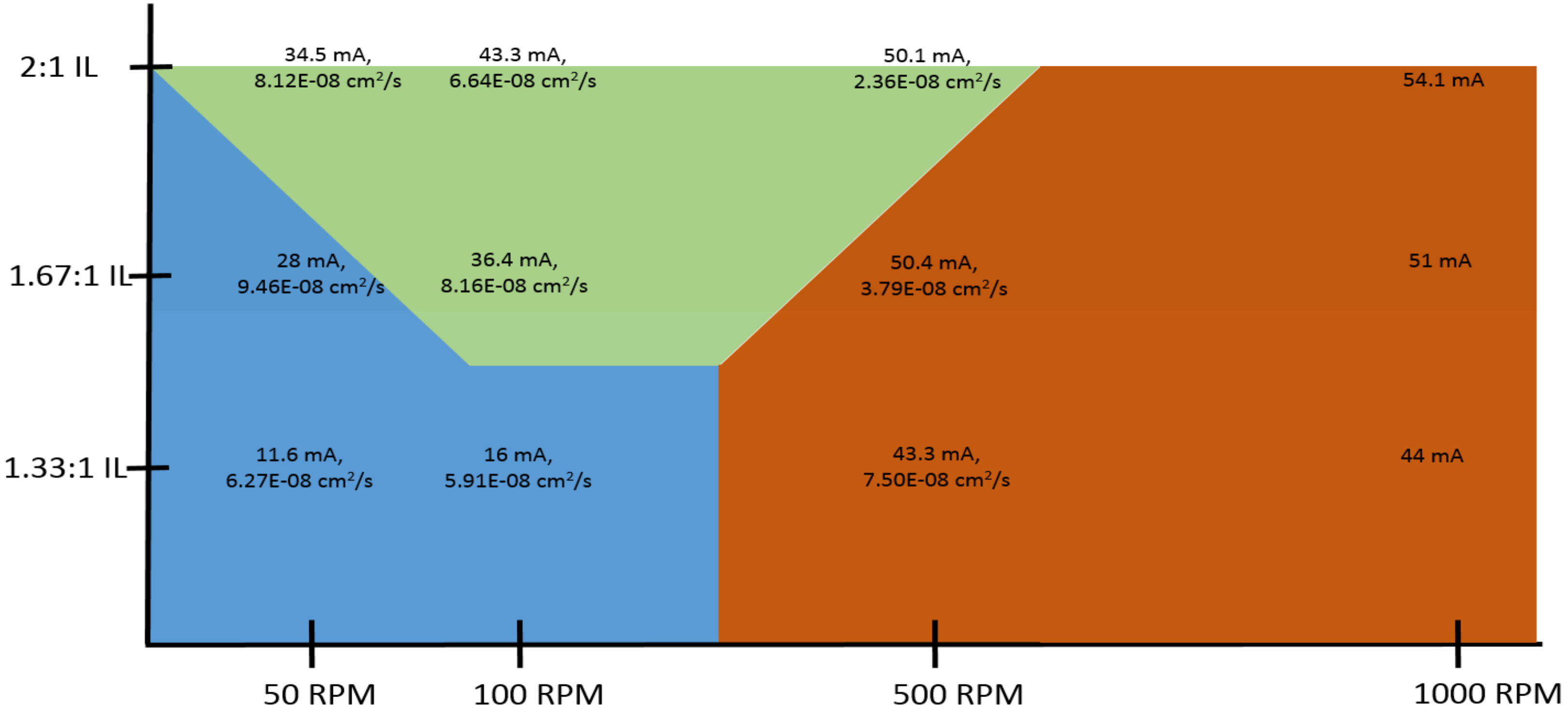
Linear Scan Profile – 30˚ C

Diffusion Limited – Blue

Mixed – Green

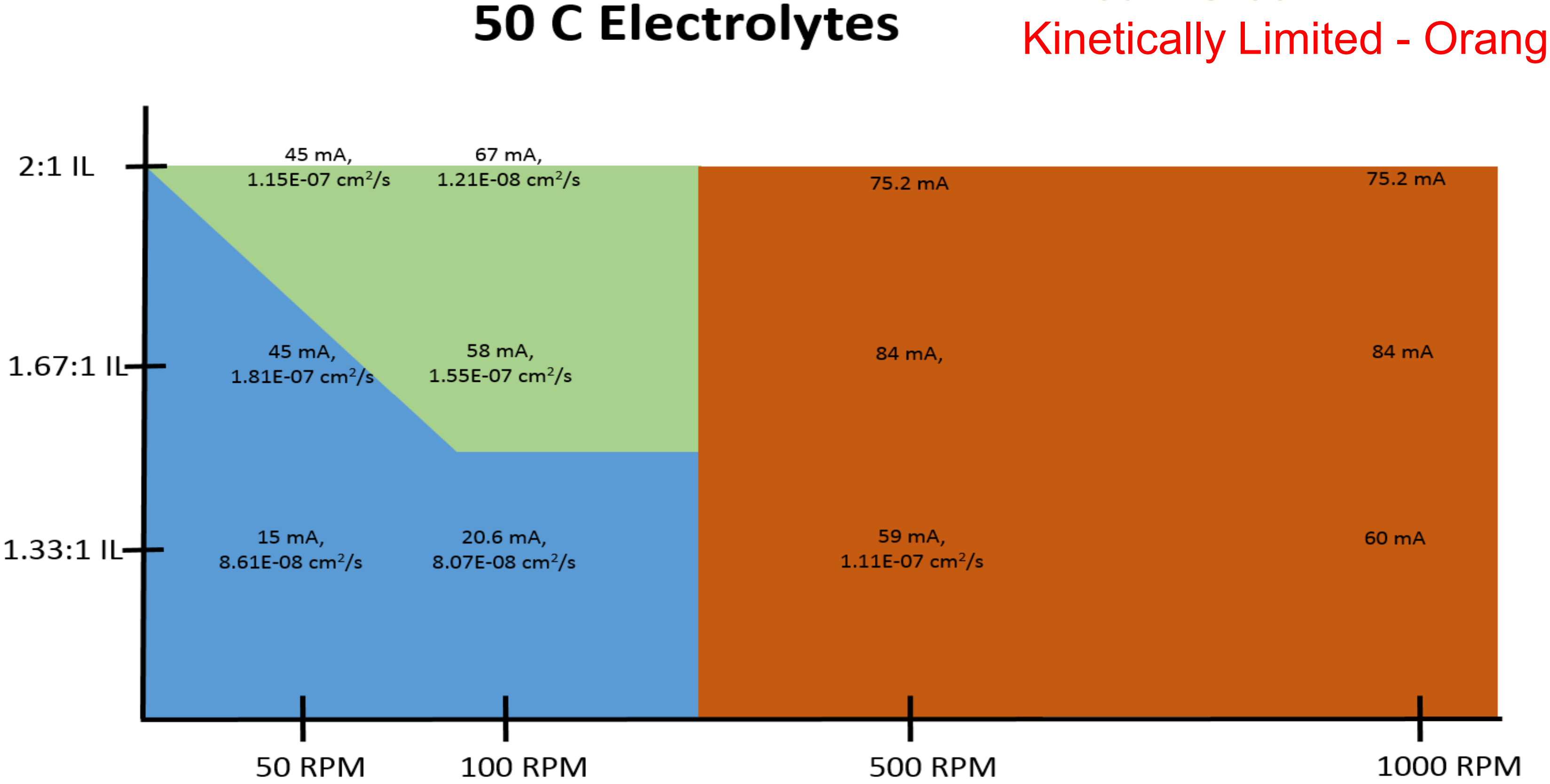
Kinetically Limited - Orange

30 C Electrolytes



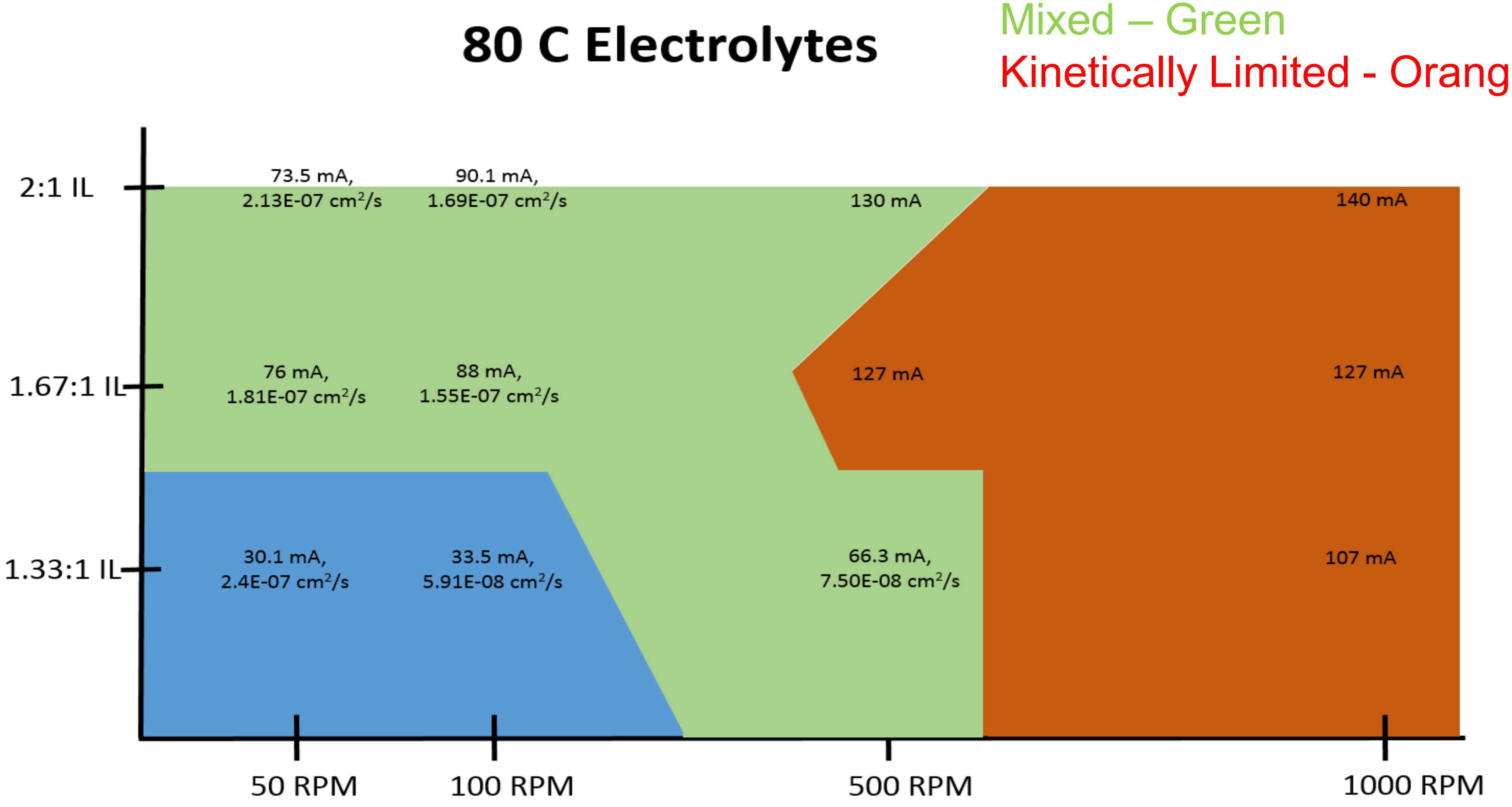
Linear Scan Profile – 50˚ C

Diffusion Limited – Blue
Mixed – Green
Kinetically Limited - Orange



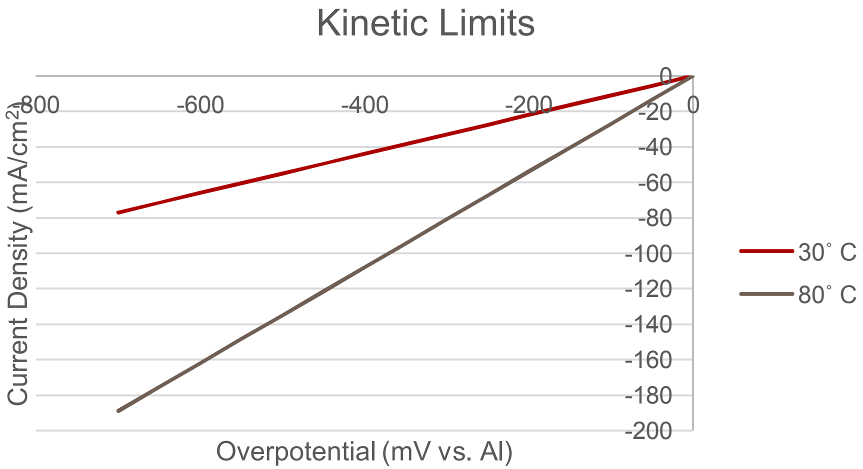
Linear Scan Profile – 80˚ C

Diffusion Limited – Blue
Mixed – Green
Kinetically Limited - Orange



Composition and Temp Control

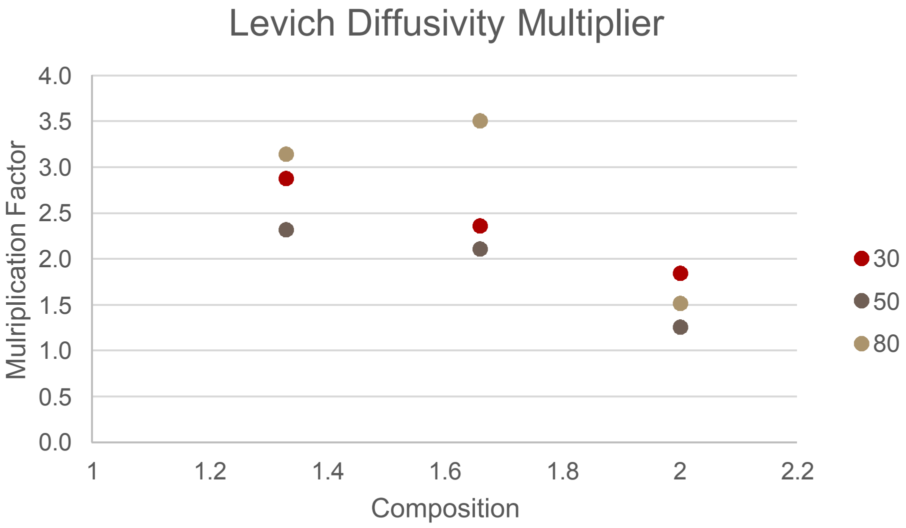
- Diffusion limitations seen at low rotation and low concentration
- Kinetics are the same in all baths
- Kinetics increase with temperature



- Kinetics increase faster than diffusion (with temperature)
- Kinetics rates are higher than should be allowed by diffusion rates determined by Cottrell

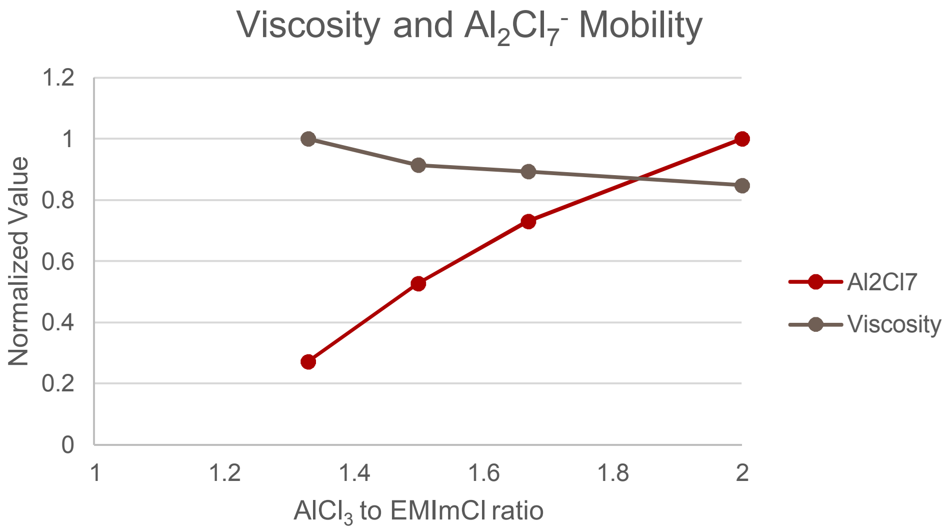
Cottrell Diffusion vs. Levich

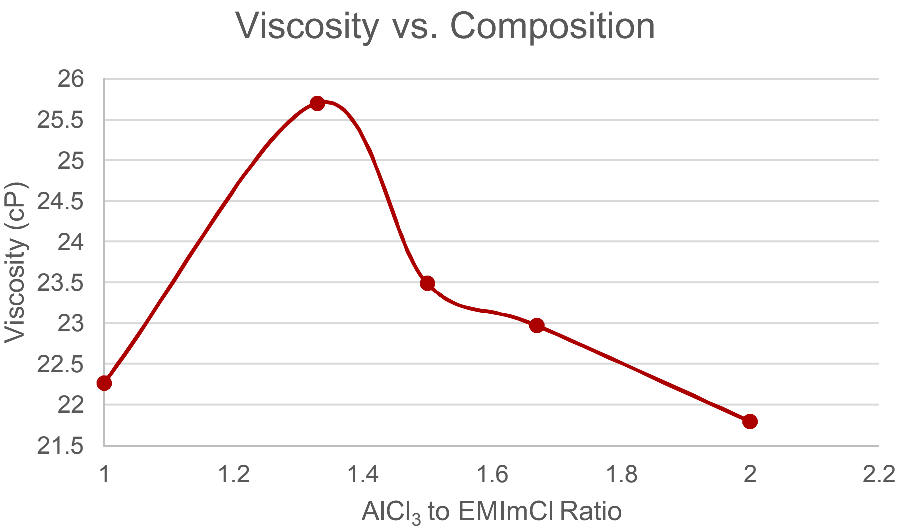
- Levich is multiple times higher than Cottrell, it shouldn't be possible to reach even the kinetically limited rates
- Going from static to dynamic regimes increases the diffusion rates



Viscosity and Mobility

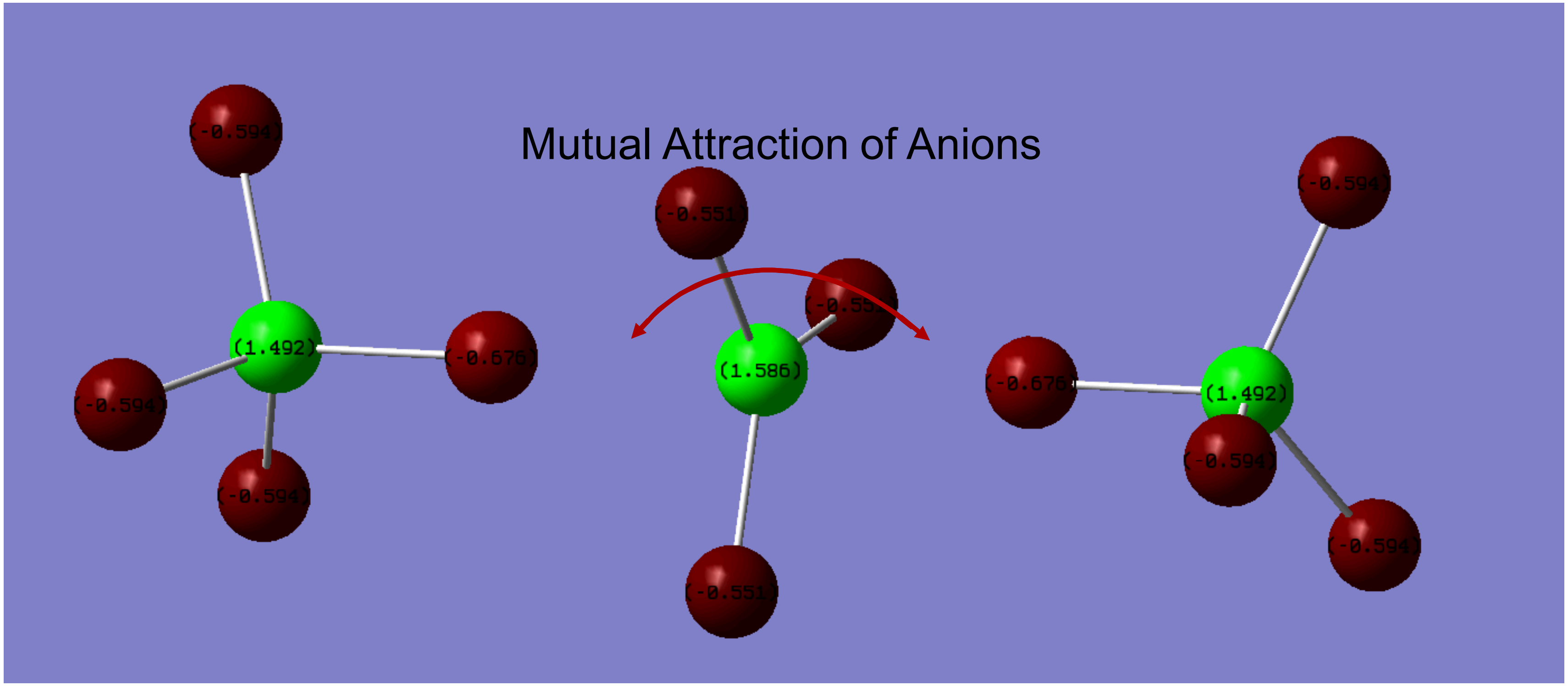
- Viscosity decreases with increasing composition
- $Al_2Cl_7^-$ mobility increases with composition
- What is the correlation between mobility and viscosity
  - Only occurs with presence of mixed anionic species





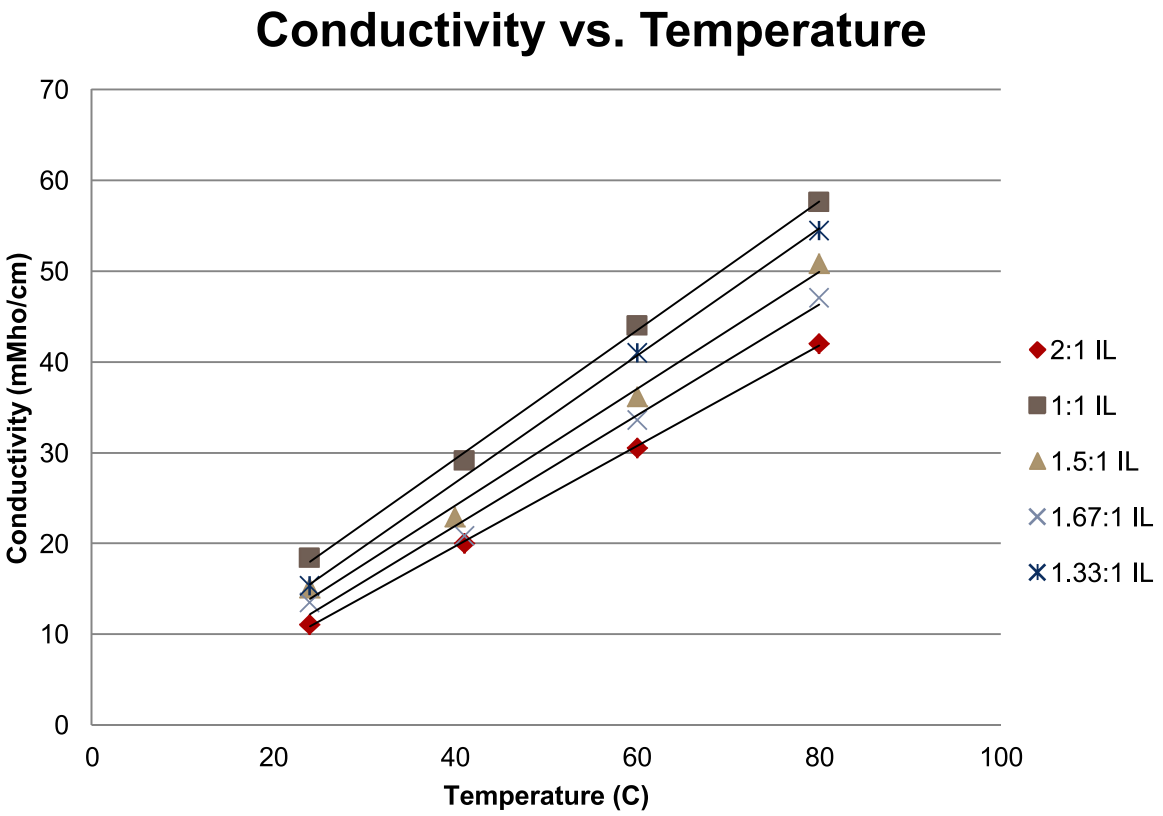
Anionic Attraction?

- Anionic attraction through fluctuance could be the predominant contributor to the low anionic mobility
  - Leads to long range association, increased in static conditions
  - Calculate $AlCl_4^-$ mobility, it should be suppressed as well



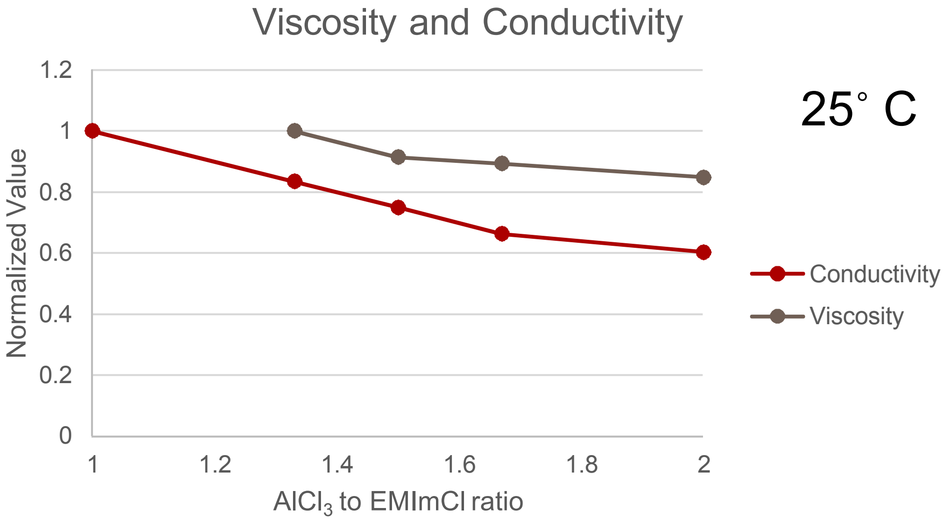
Conductivity

- Can’t calculate $AlCl_4^-$ mobility directly
  - As neat ionic liquids there should be correlations between ionic conductivity, viscosity and ionic mobilities



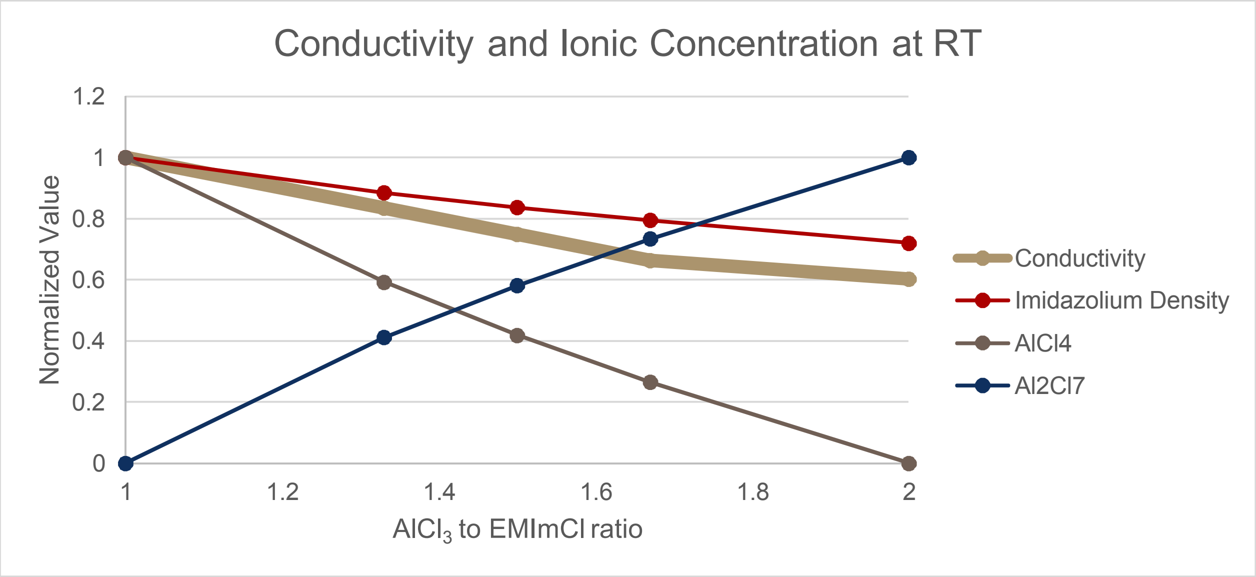
Conductivity and Viscosity

- Conductivity and viscosity should be inversely proportional
- No corresponding trend between conductivity and viscosity based on composition changes



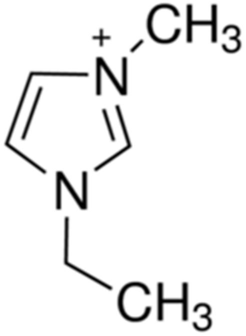
Conductivity and Ionic Density

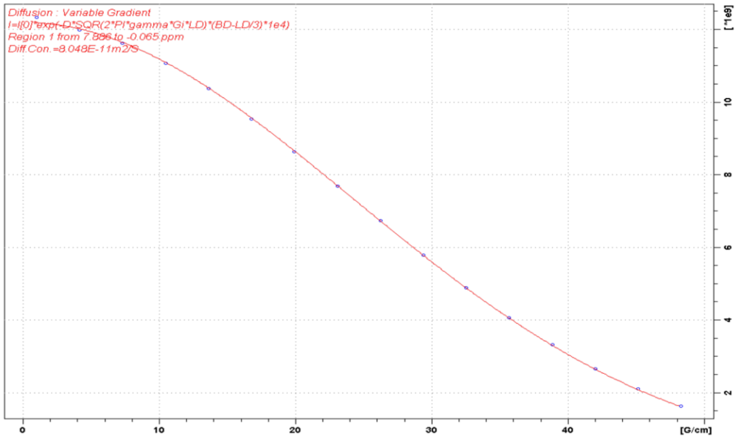
- Conductivity decreases approximately linearly with composition shifts
  - Trends with **imidazolium** density strongly, with influence from increasing anionic size



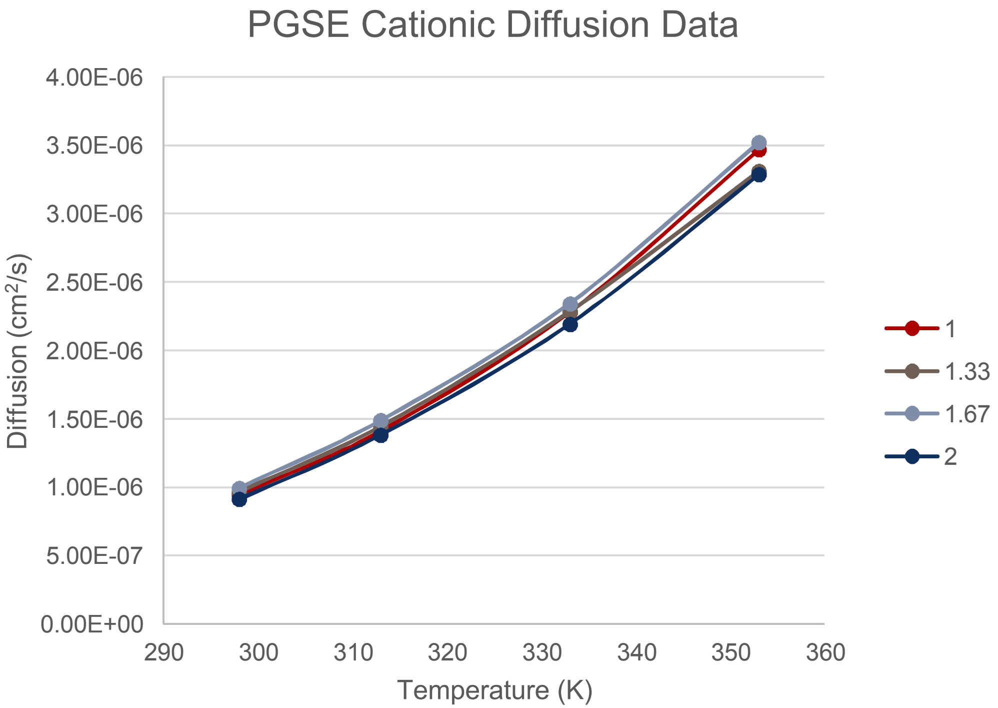
NMR PGSE – Imidazolium Mobility

- Proton pulse field gradient spin echo nuclear magnetic resonance (PGSE NMR) spectroscopy for Imidazolium mobility
  - ~10^{-6} cm^2/s at RT, invariable with composition





```
Diffusion : Variable Gradient
I=I[0]*exp(-D*SQR(2*PI*gamma*Gi*LD)*(BD-LD/3)*1e4)
Region 1 from 7.886 to -0.065 ppm
Diff.Con.=8.048E-11m2/S
```

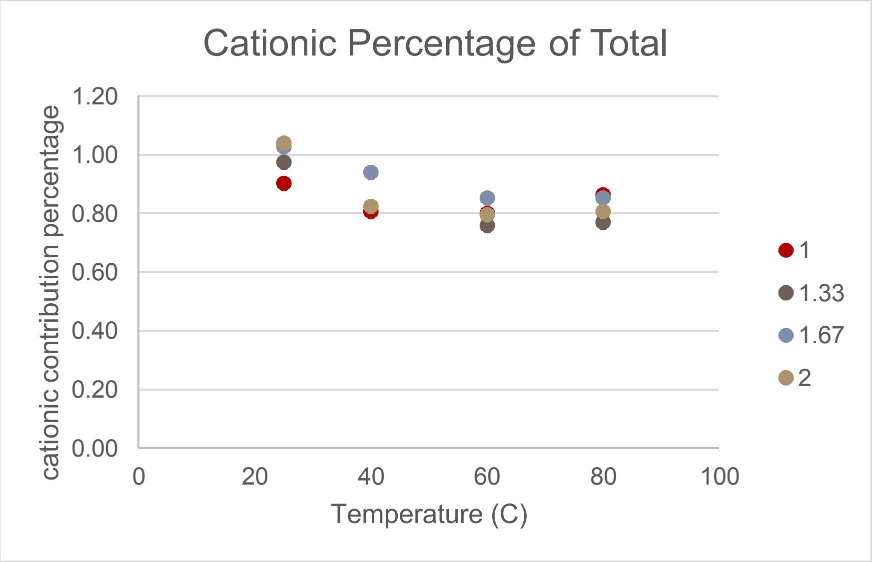


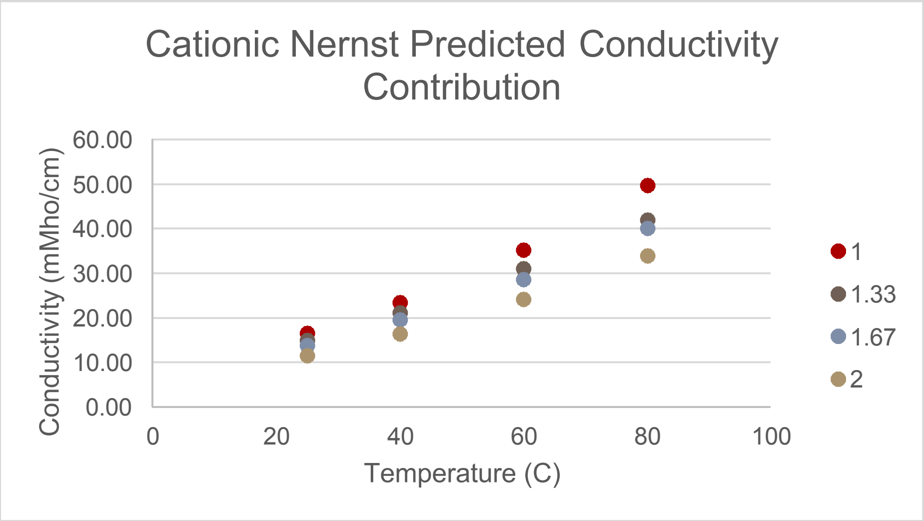
Contribution to Mobility

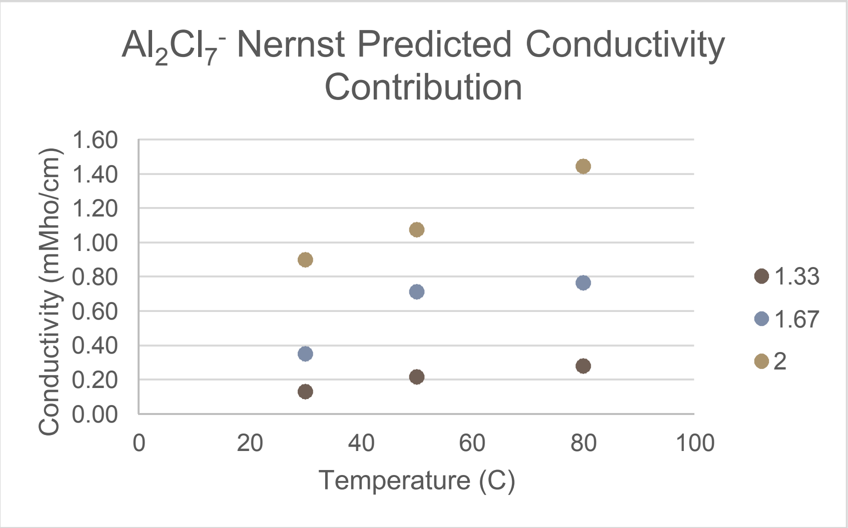
- Cations can account for almost all of the conductivity under all conditions

$$\Lambda_{\mathrm{NMR}} = N_A e^2 (D_{\mathrm{cation}} + D_{\mathrm{anion}})/kT = F^2 (D_{\mathrm{cation}} + D_{\mathrm{anion}})/RT$$

Nernst Einstein equation

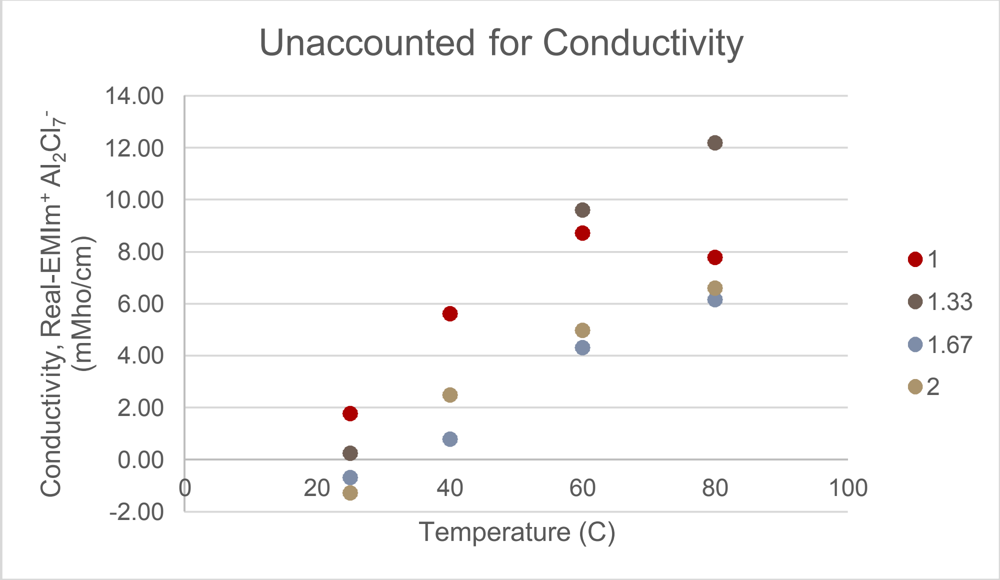

Cationic Percentage of Total

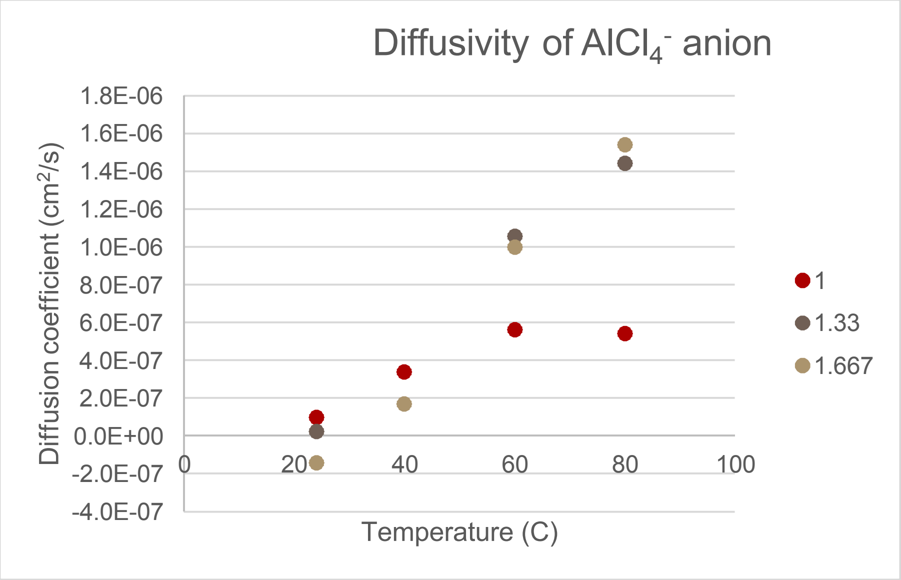

Cationic Nernst Predicted Conductivity Contribution


$Al_2Cl_7^-$ Nernst Predicted Conductivity Contribution

Conductivity and Mobility

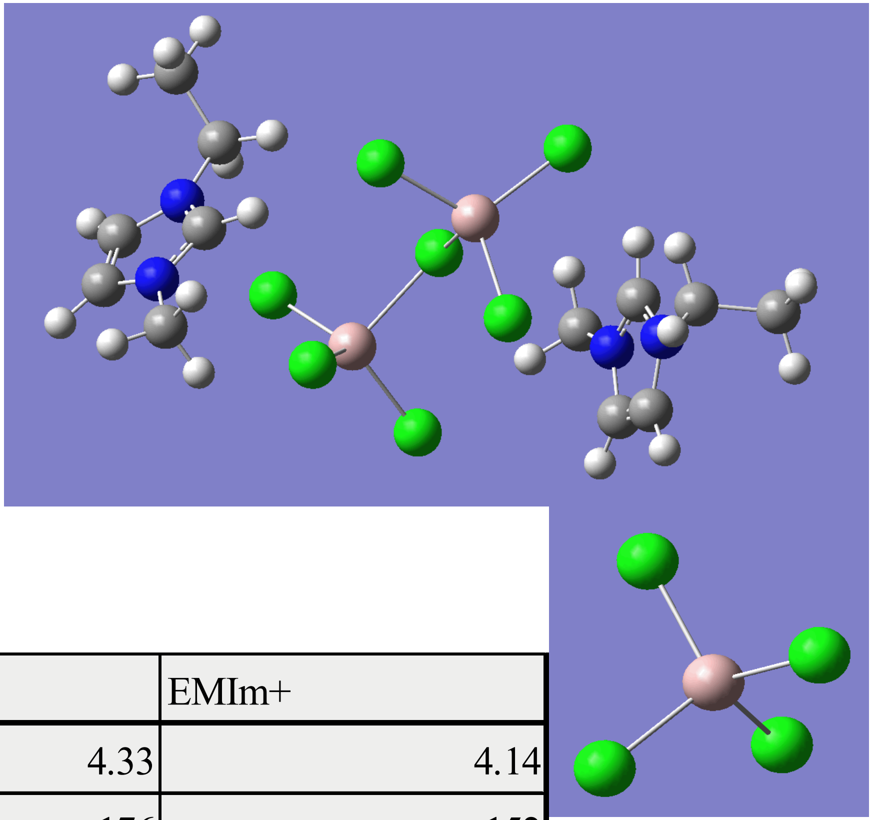
- Imidazolium is 12-40 times more mobile than the Al_2Cl_7 complex
  - Al_2Cl_7 is minimally contributing to conductivity
  - Factoring the remaining ions, $AlCl_4$ is a contributor to conductivity with mobility close to but lower than the $EMIm^+$ cation





Gaussian - DFT

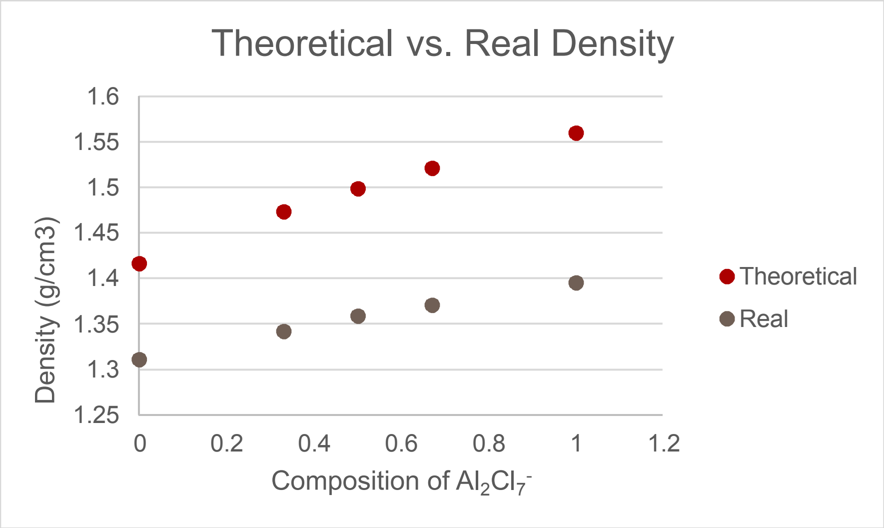
- Comparing ionic sizes gives insight to why diffusion rates are so varied

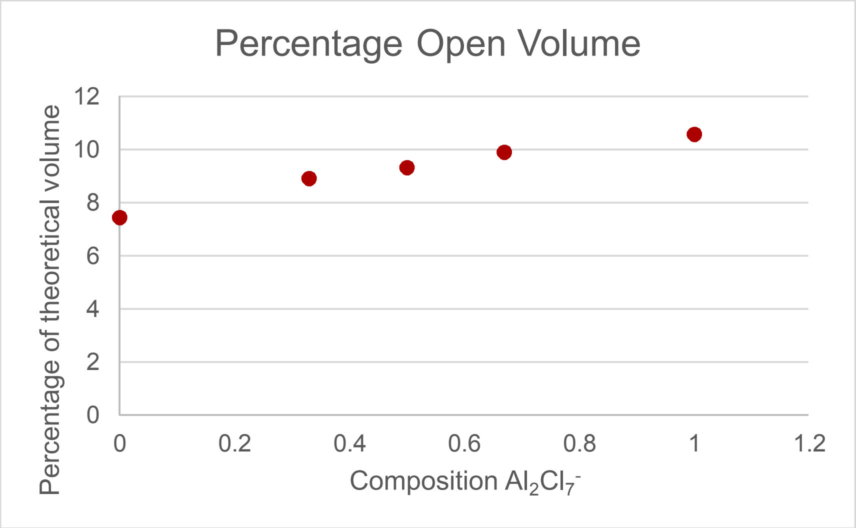


	$Al_2Cl_7^-$	$AlCl_4^-$	EMIm+
Stokes radius (Angs)	5.004	4.33	4.14
Volume (Angs^3)	288	176	152
Normalized values	$Al_2Cl_7^-$	$AlCl_4^-$	$EMIm^+$
Radius	1.00	0.85	0.81
Volume	1	0.61	0.53

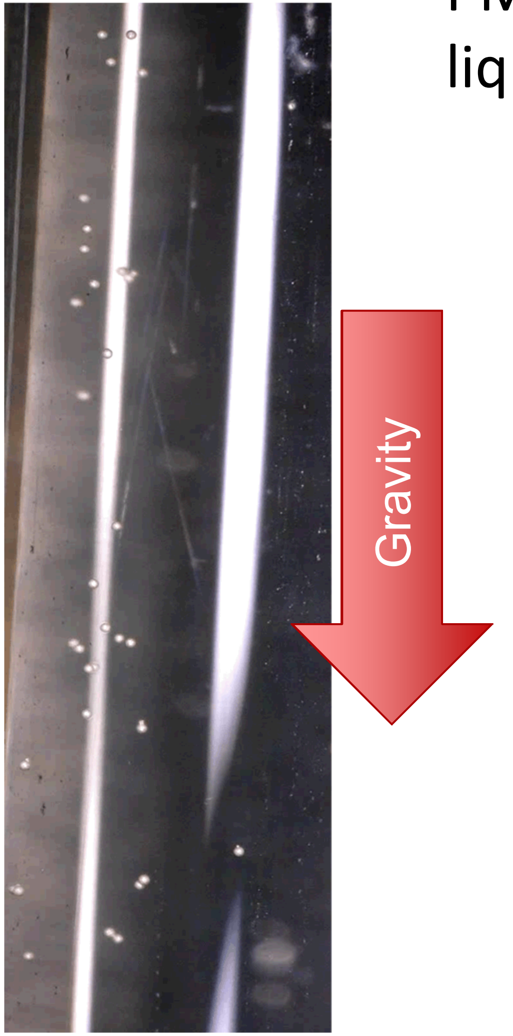
Hole Transport – Diffusion vs. Composition

- Matches $Al_2Cl_7^-$ trend
  - Initial open volume and hole sizes may be large enough to accommodate smaller ions
- Peak in viscosity is determined by competing:
  - Increase in anionic size, increase viscosity
  - Increasing open volume, increase $Al_2Cl_7^-$ mobility, decrease viscosity





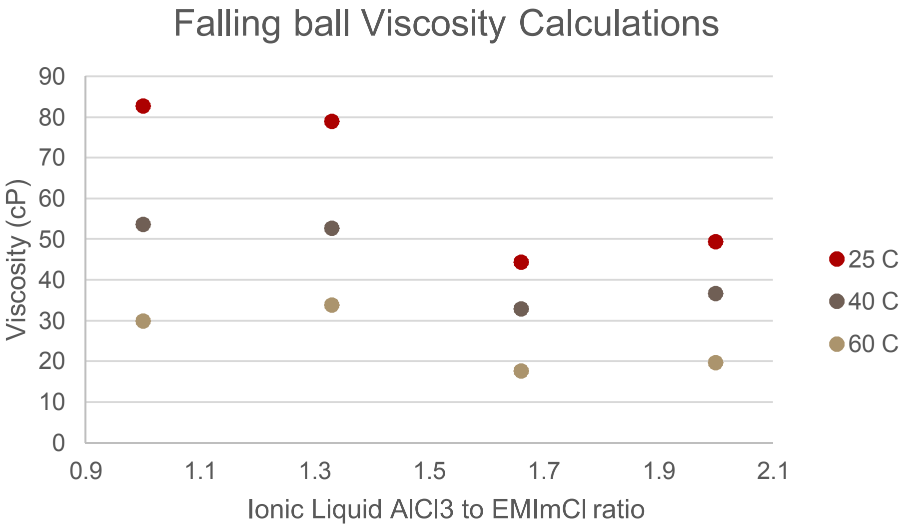
Falling sphere Experiments - Diffusion vs. Shear



PMMA spheres with similar density to the ionic liquid settle at very slow velocities

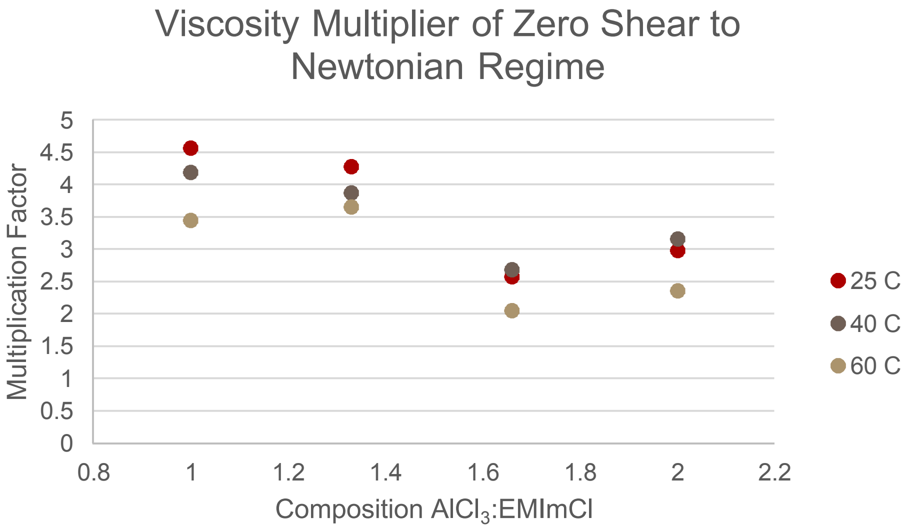
$$\mu = \frac{2}{9}\frac{g R^2}{V_T}(\rho_s - \rho_l)$$

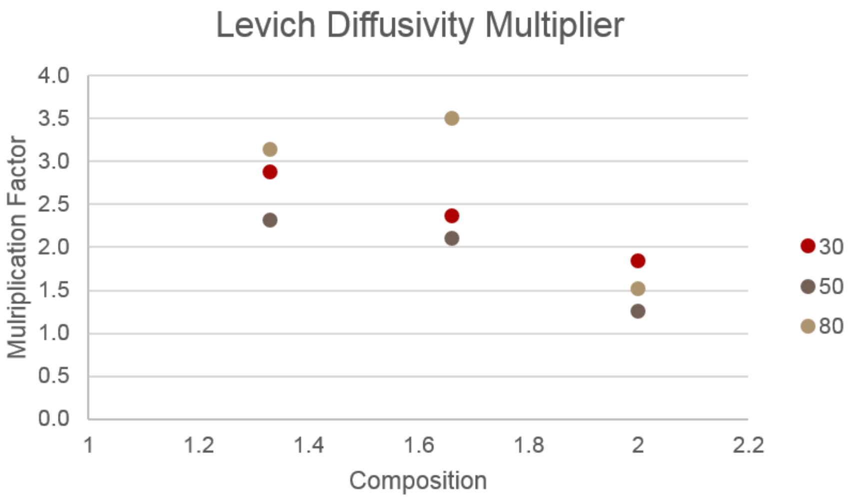
Creeping flow $10^{-6}<Re<10^{-4}$
~ Zero Shear



Zero Shear Viscosity

- Same order of magnitude decrease in viscosity going from static to shear regime as increase in $Al_2Cl_7^-$ diffusion going from static to dynamic conditions
- Likely due to break up of electrostatic interactions


Viscosity Multiplier of Zero Shear to Newtonian Regime

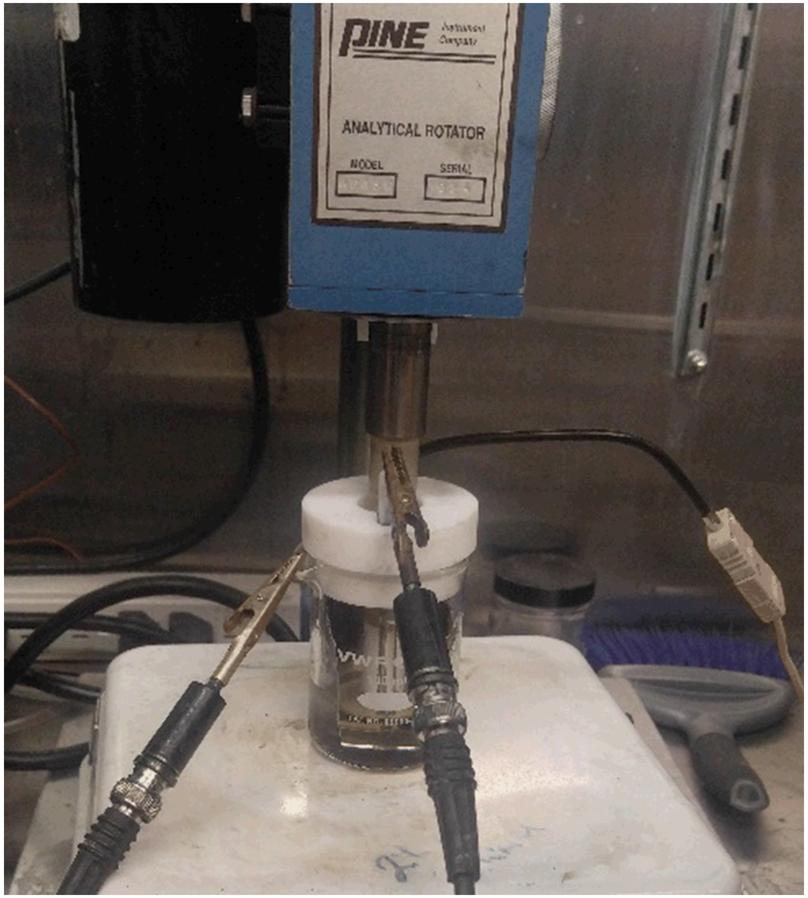

Levich Diffusivity Multiplier

Matrix Growth - Summation

- The $Al_2Cl_7^-$ ion is responsible for aluminum deposition and diffusion rates are inversely correlated to viscosity
  - Both change with composition, temperature and shear
    - Convection is very influential
  - Diffusion can be modified by adding dilutions
    - Optimal conditions at the maximum of conductivity, optimization of concentration and mobility
- Conductivity (in neat ILs) is determined primarily by the smaller, more mobile ionic species, the cation and the $AlCl_4^-$
- Kinetics can be modified with temperature
  - Kinetics increase faster than diffusion rates with temperature
- All properties are mapped, can now incorporate particles

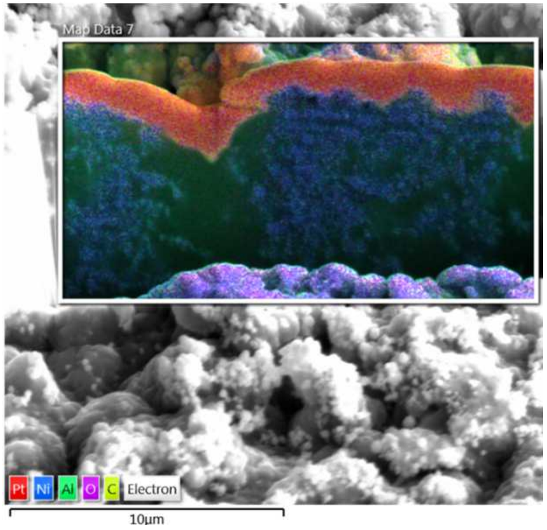
Codeposition on Rotating Disc

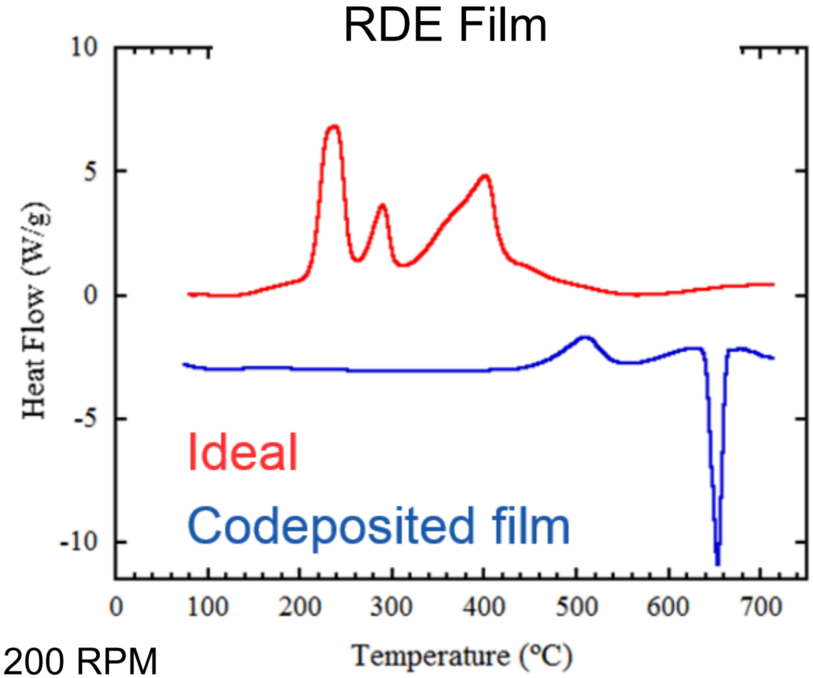
- Control flow with RDE
- Start with room temperature
- Diluted electrolyte system



Calorific Data

- Low nickel leads to low energy output
  - Increased content between runs
- Larger particle sizes (agglomeration) leave unreacted components
  - Cloud resolution of peaks vs. time (broadened and shifted to higher temperatures)

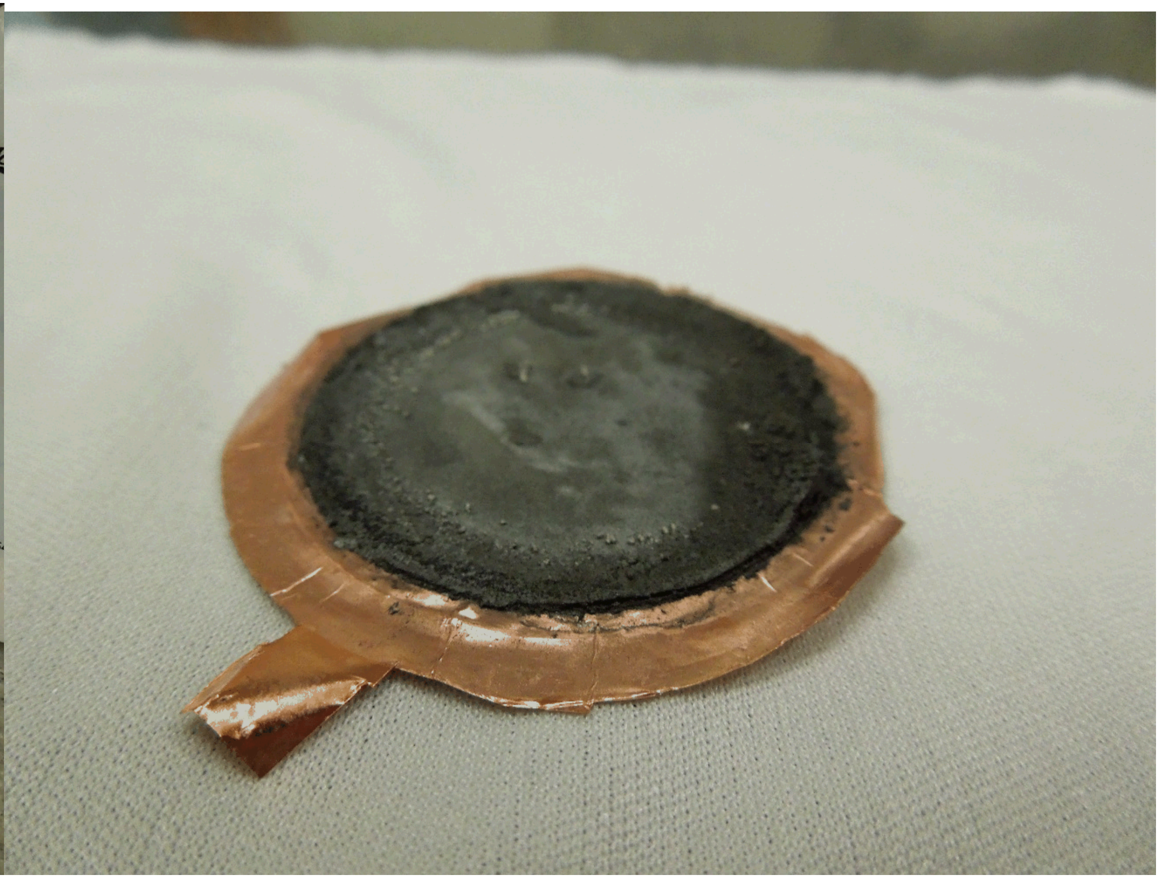




Room temperature, -400 mV vs. Al, 5 hours, 50g/L Ni, 200 RPM

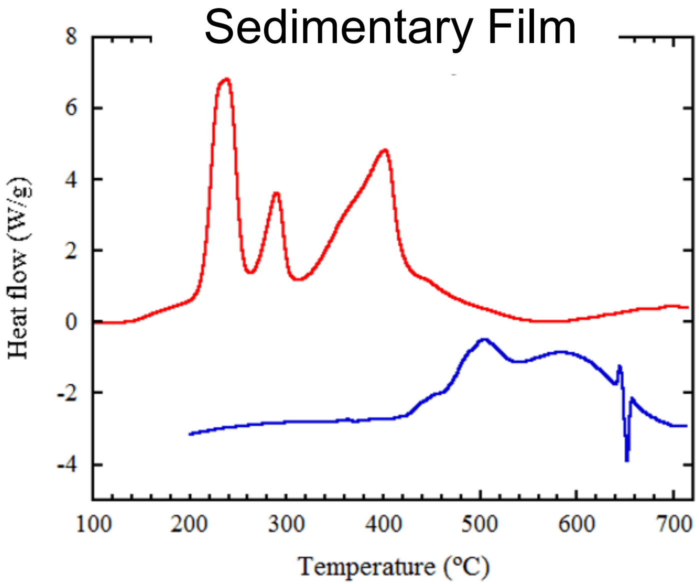
Sedimentary Deposition

- Improves particle incorporation but poor morphology



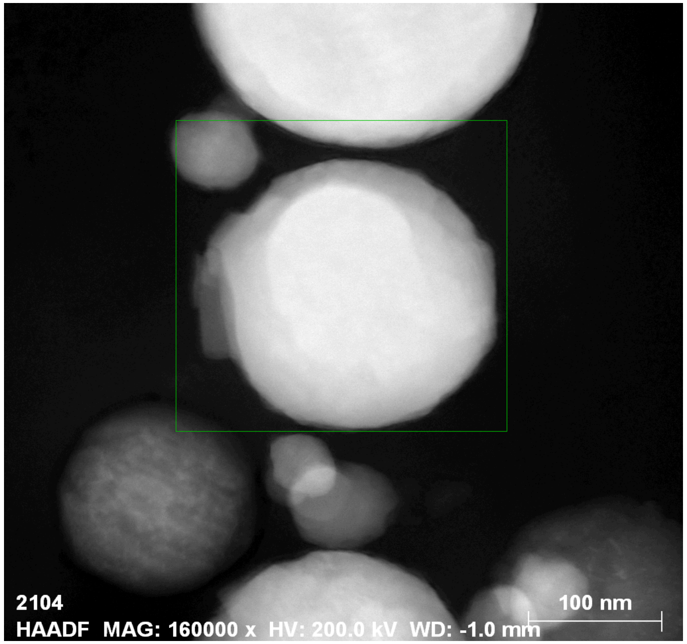
Sedimentary Deposition

- Sedimentary deposition increases energetic output
- Still shifted to higher temperature initiation
- Broad smeared peaks likely due to particle size being too large
  - Due to agglomeration

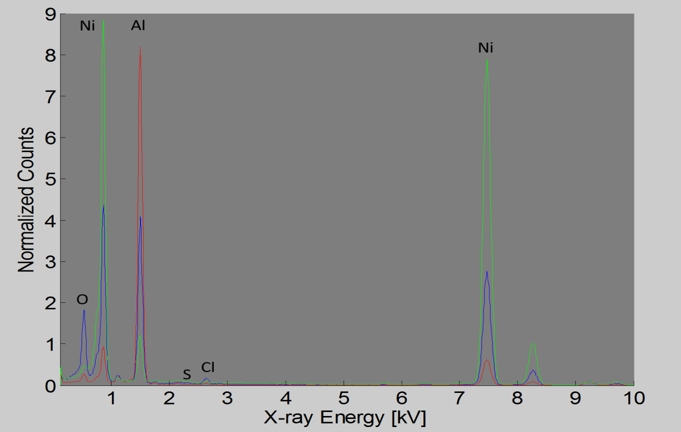


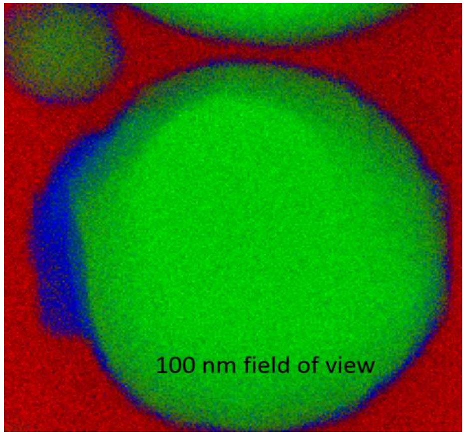
EDS on Particle/Matric Interface

- Shows Oxygen contamination on Nickel particles, indication to why initiation shifts are toward higher temperatures



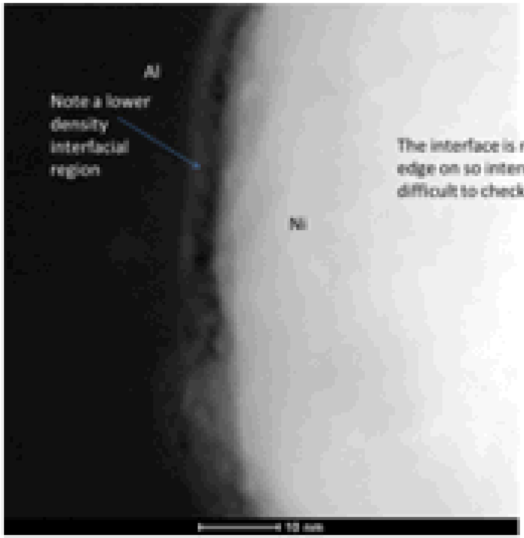
Red = Al
Green = Ni
Blue = Ni, Al, O, Cl, S





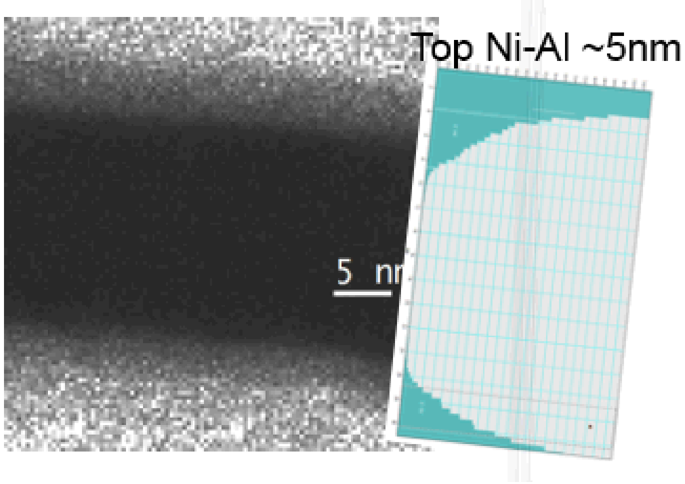
Deposited Films Alloy Interface

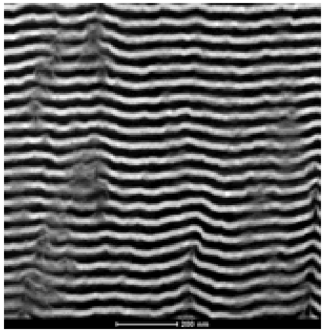
- Small alloying interface seen in both PVD and electrodeposited films



Note a lower density interfacial region

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

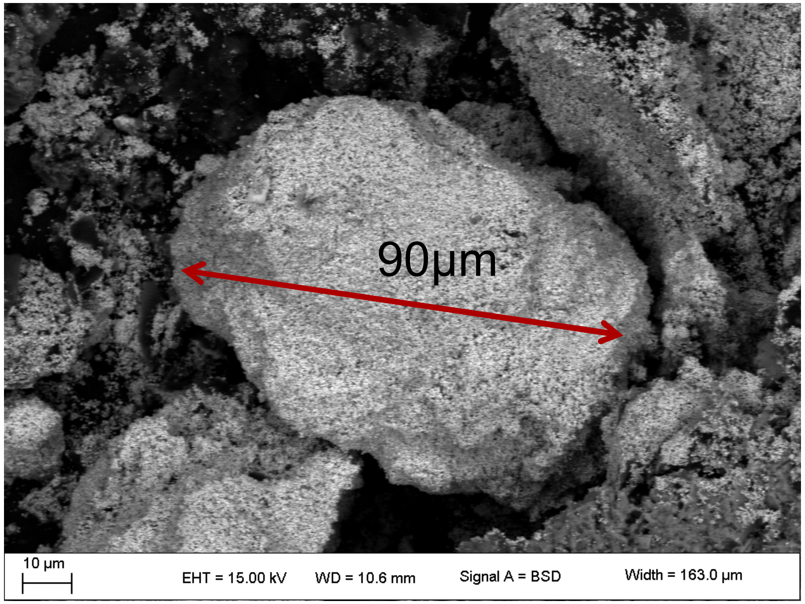


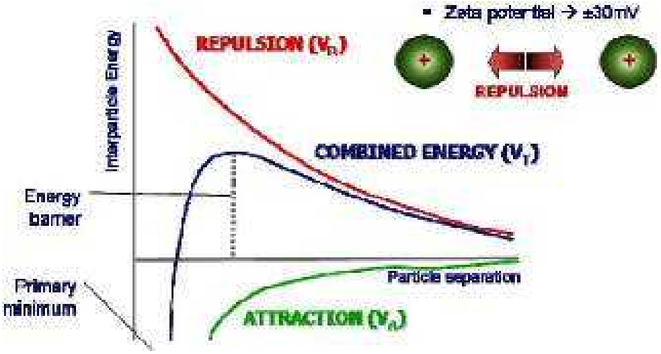


Indium Corp Foil

Challenges in Sedimentary Dep

- Particle flocculation
  - Assume dispersion in electrolyte will lead to dispersion in film
- Test surfactants to reduce agglomerations
  - Not effective
- Use physical agitation to break up agglomerations





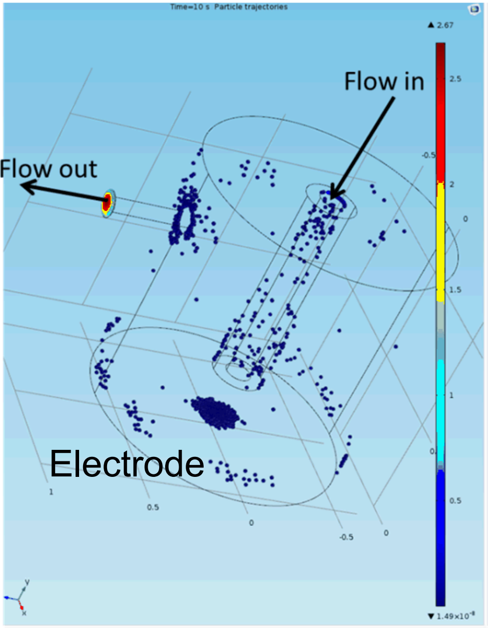
Colloid stability based on zeta potential[55]

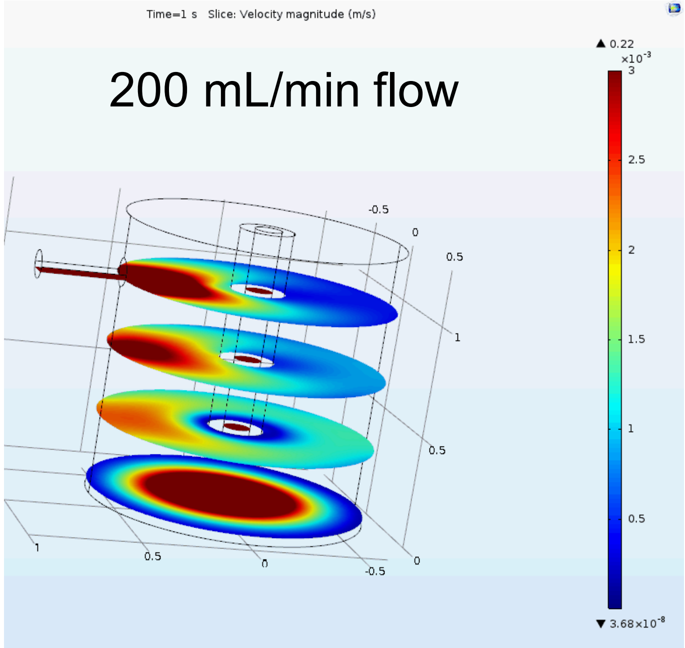
Reactor Design

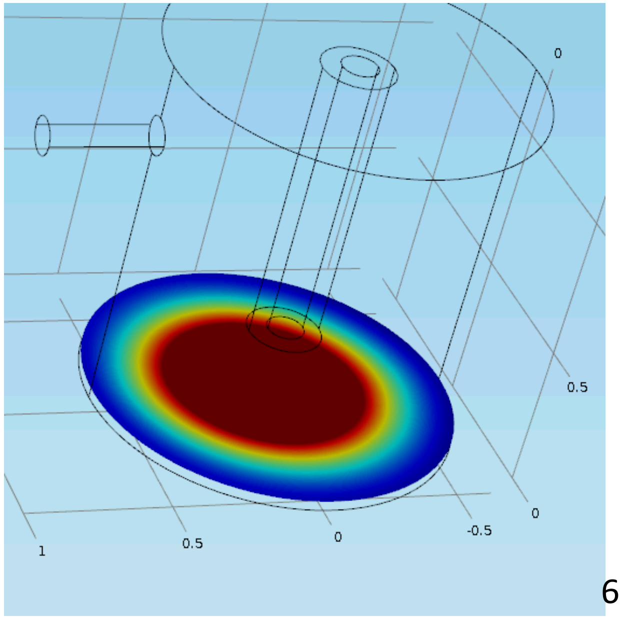
- Agitation in separate reservoir to keep particles dispersed
- Controlled flow over electrode to manipulate electrodeposition and particle motion

Optimizing Particle Motion

- Shift to modelling to test the many conditions
  - Particle tracing shows where nickel encounters the electrode
    - Can adjust particle loading and flow profile to optimize incorporation
- As expected, high shear results in higher percentage of particles at the electrode, but increased shear
  - No interaction at <10 mL/min, mixed from 10 to 100 mL/min, Shear forces is too high at >100 mL/min
- Balance arrival with Matrix growth







Conclusions

- Looked into viscosity correlations to conductivity and ionic mobility
  - Precursor mobility determines electrodeposition quality, and is related to viscosity
  - Viscosity is influenced by structuring, shear, temperature and composition
  - Mapped mobility of precursor under all viable composition (including dilutions), shear and temperature conditions
    - Clarified why viscosity and mobility change with composition and shear
  - Mapped kinetic limits over the operating temperature range
- Incorporated nickel particles in aluminum films and tested energetic output
  - Films are influenced by agglomeration and low particle loading
  - Investigated particle and matrix interface, some alloying and oxidation seen
- To achieve higher particle loading
  - Use COMSOL modelling and Investigate adsorbtion characteristics
  - Incorporate more forces to bring and keep particles on the electrode

Thank you

SNL NM

Chris Apblett, David Wheeler,

Alex Tappan, Robert Knepper,

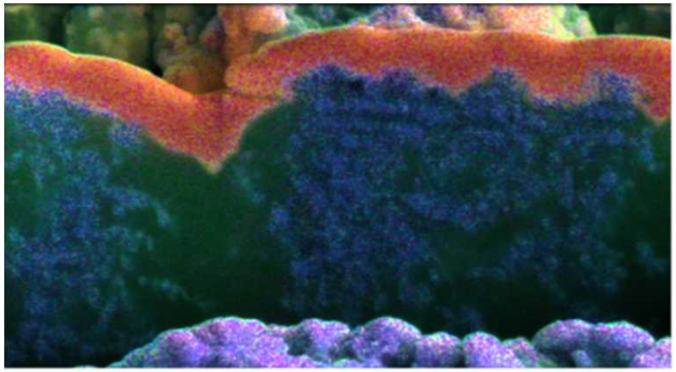
Todd Alam

Brian Perdue, Chelsea Ehlert, Hannah Height,

Josey McBrayer, Jaclyn Coyle

UNM

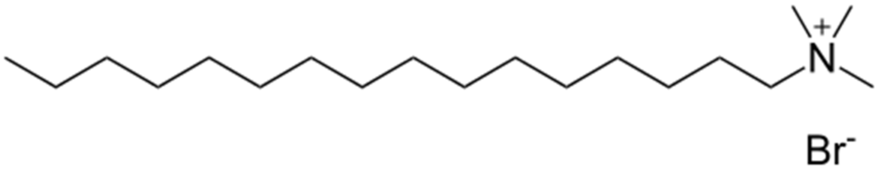
Plamen Atannasov, DimiterPetsev



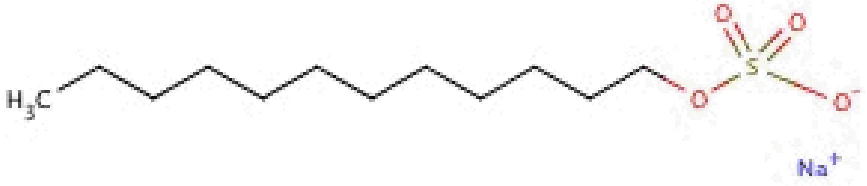
Surfactants and Compatibility

- Sodium dodecyl sulfate, Centronium bromide and Saccharin have high solubility (>2 wt%)
  - Sodium saccharin salt dissociates more slowly but is soluble
- Tartaric acid Diammonium salt has lower solubility (<2 wt%)
- Ethylene diamine tetra acetic acid (EDTA) shows no solubility

CTAB

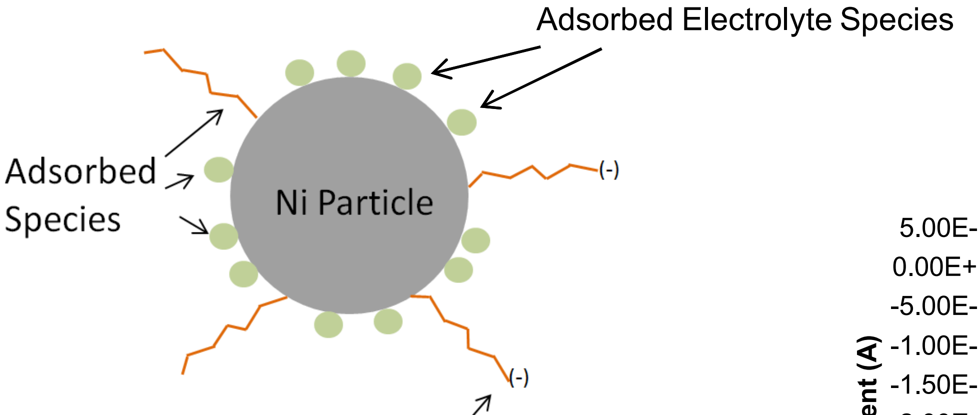


SDS

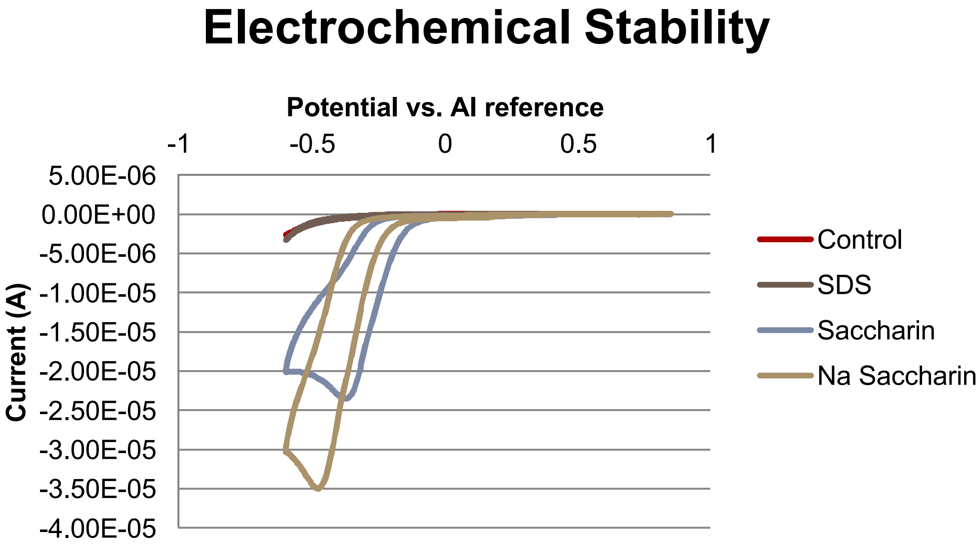


Particle Properties and Modifications

- Particle size, shape and composition
  - 10 nm – microns, Flakes or spheres, Ni, NiO, Cu etc.
- Surface functionalization (control zeta potential)
  - Modify electrolyte composition, surfactants or oxides



Polar surfactants repel each other to stabilize the suspension



Zeta Potential Results (Needs more analysis)

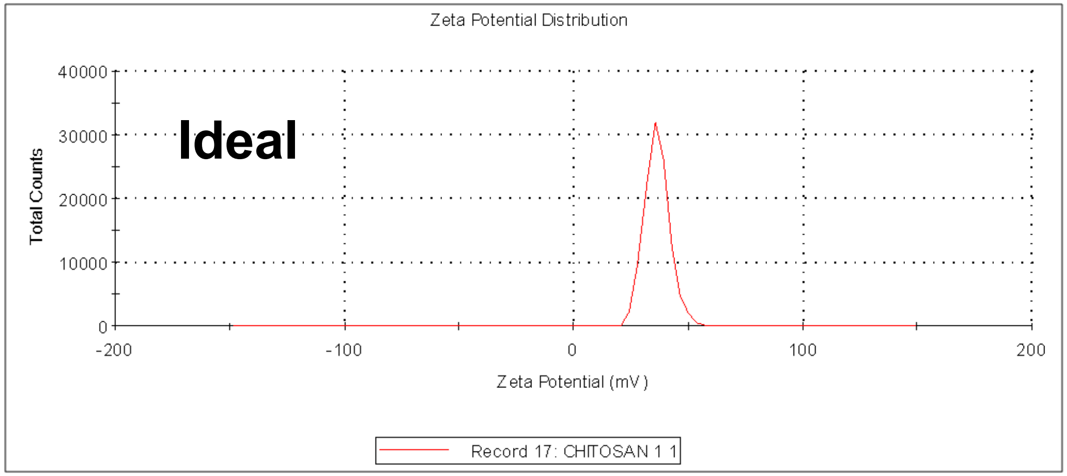
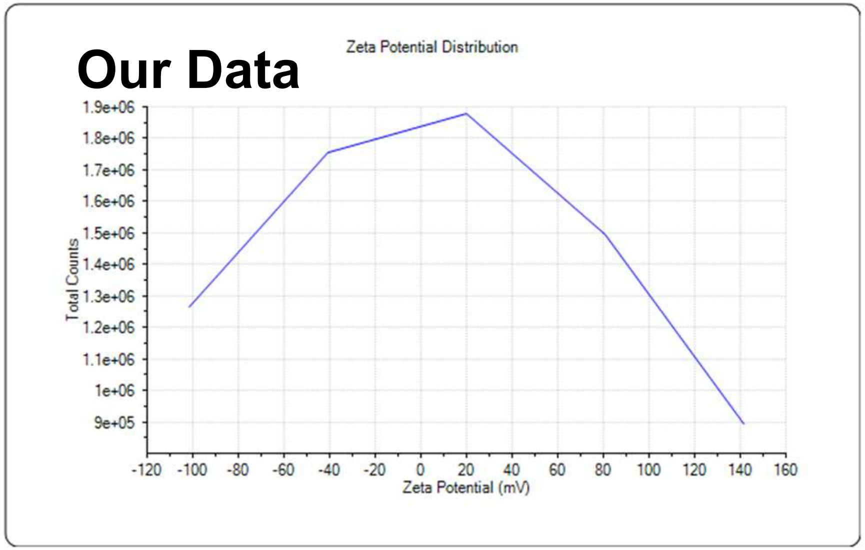
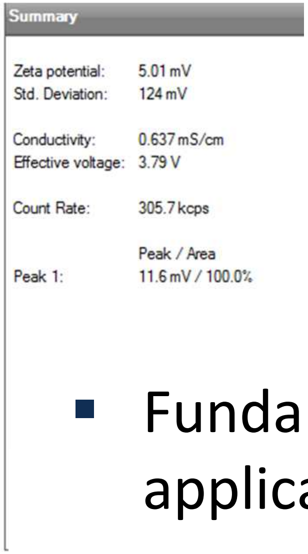


Figure 2: Zeta potential analysis of chitosan nanoparticles, showing mean zeta potential of 40mV as determined by Malvern zeta analyzer

- Non-conducting particles
- Well understood double layer in aqueous
  - Fixed charge on surface
- Notice resolved at 30,000 counts





Summary

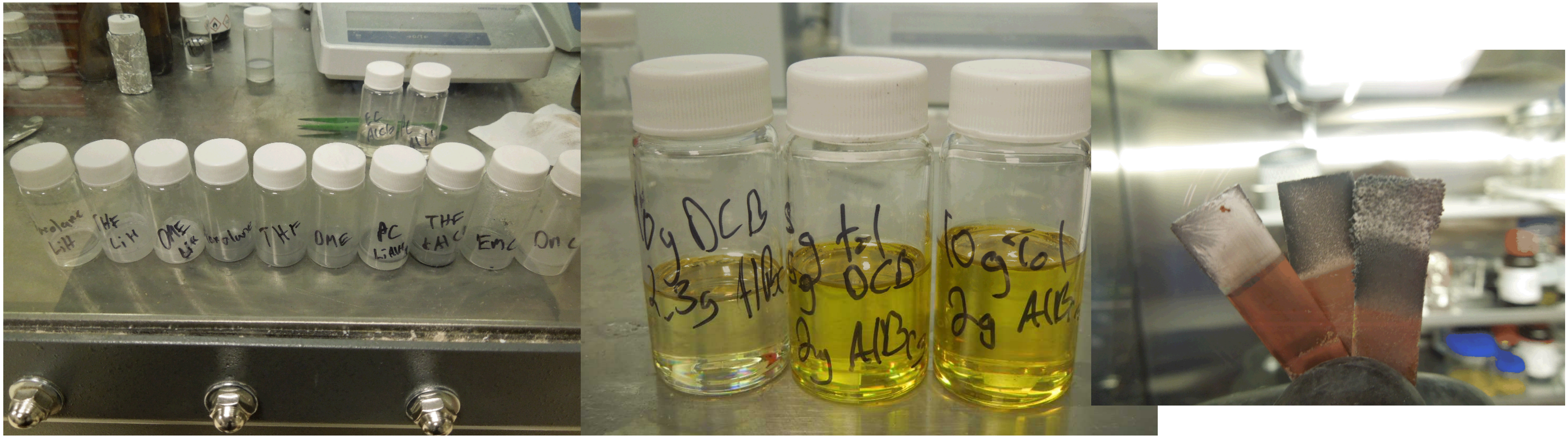
Zeta potential:	5.01 mV
Std. Deviation:	124 mV
Conductivity:	0.637 mS/cm
Effective voltage:	3.79 V
Count Rate:	305.7 kcps
	Peak / Area
Peak 1:	11.6 mV / 100.0%

- Metal (conducting) particles
- Magnetic particles
- Lacking understanding of IL media
- ~2 million counts and no resolution

- Fundamental research leading to application

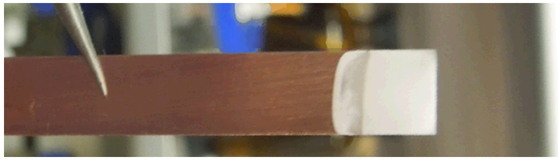
Kumar V, Dandapat S, Kumar A, Kumar N (2014). Preparation and characterization of chitosan nanoparticles “alternatively, carrying potential” for cellular and humoral immune responses. Adv. Anim. Vet. Sci. 2 (7): 414 –417.

Aluminum Deposition



Aprotic and aromatic depositions

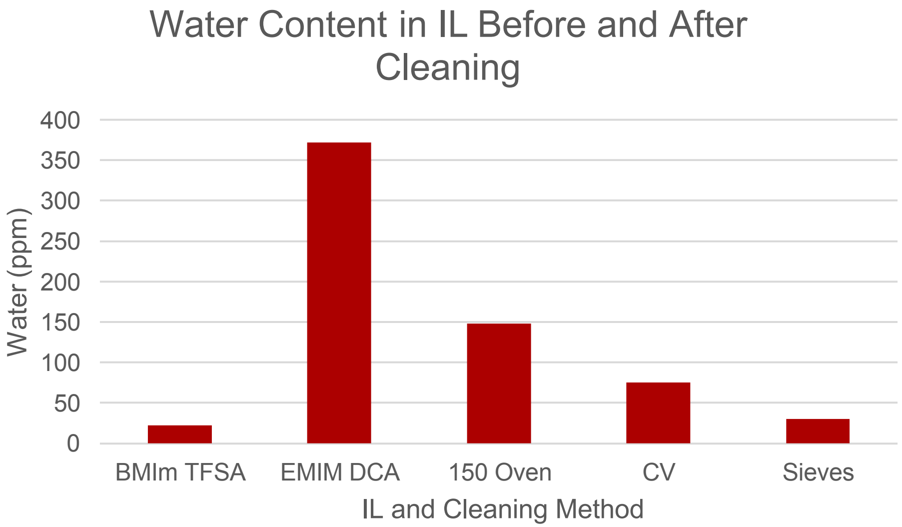
Ionic Liquid and aromatic Dilution -600 mV vs. Al QRE DC



Ionic Liquid and aromatic Dilution -850 mV vs. Al QRE Pulse deposition

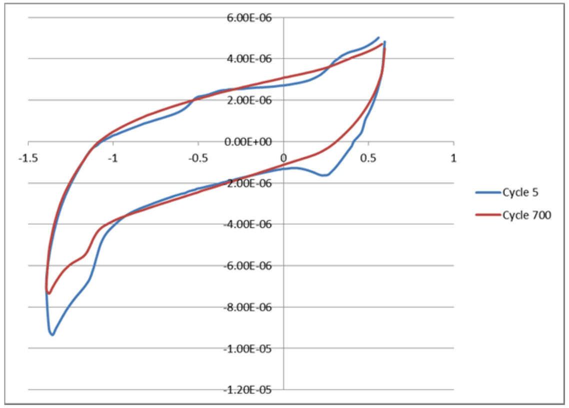
Chemical Cleaning

- Impurities and water contamination are prevalent unless mitigated
  - Multiple cleaning methods

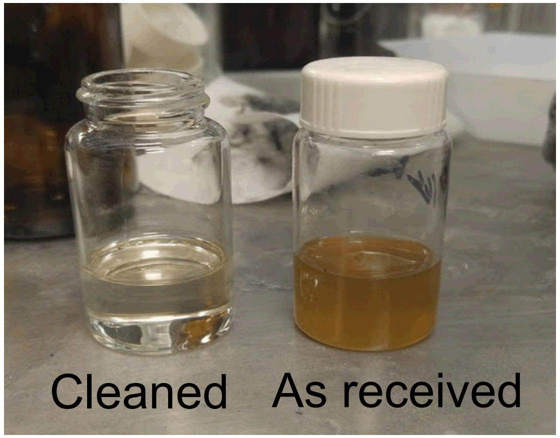


Precursor sublimation (Chemical)

Cyclic Voltammetry (electrochemical)

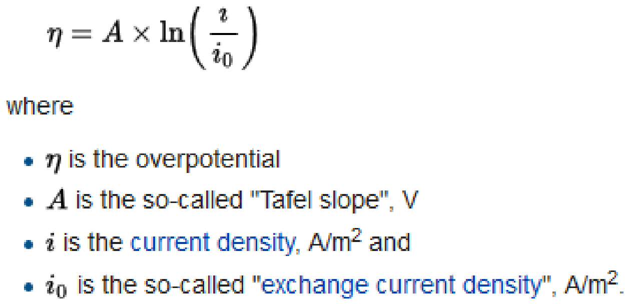


Results



Kinetic Limitations

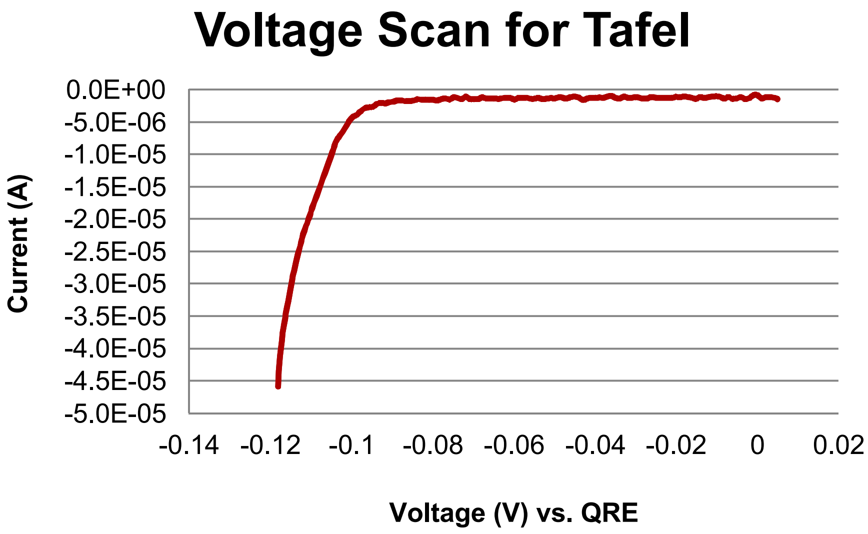
- Room Temp. 2 mV/s 2:1 $AlCl_3$:BMImCl
- 9 x 10^-8 is very low

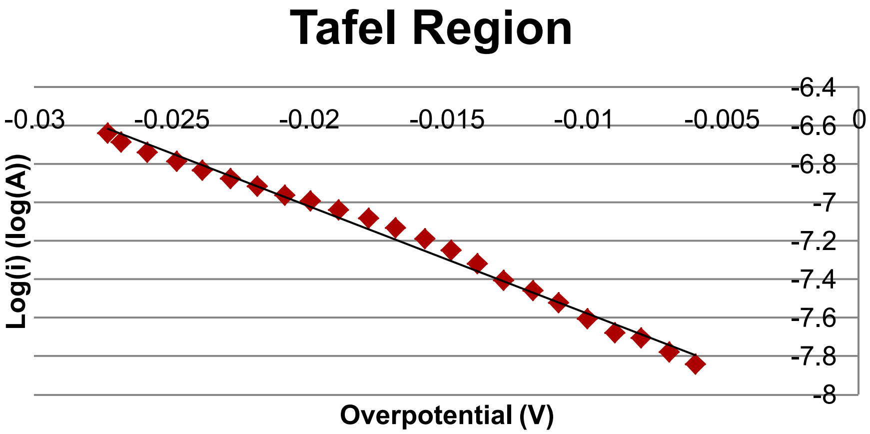


$$\eta = A \times \ln\left(\frac{i}{i_0}\right)$$

where

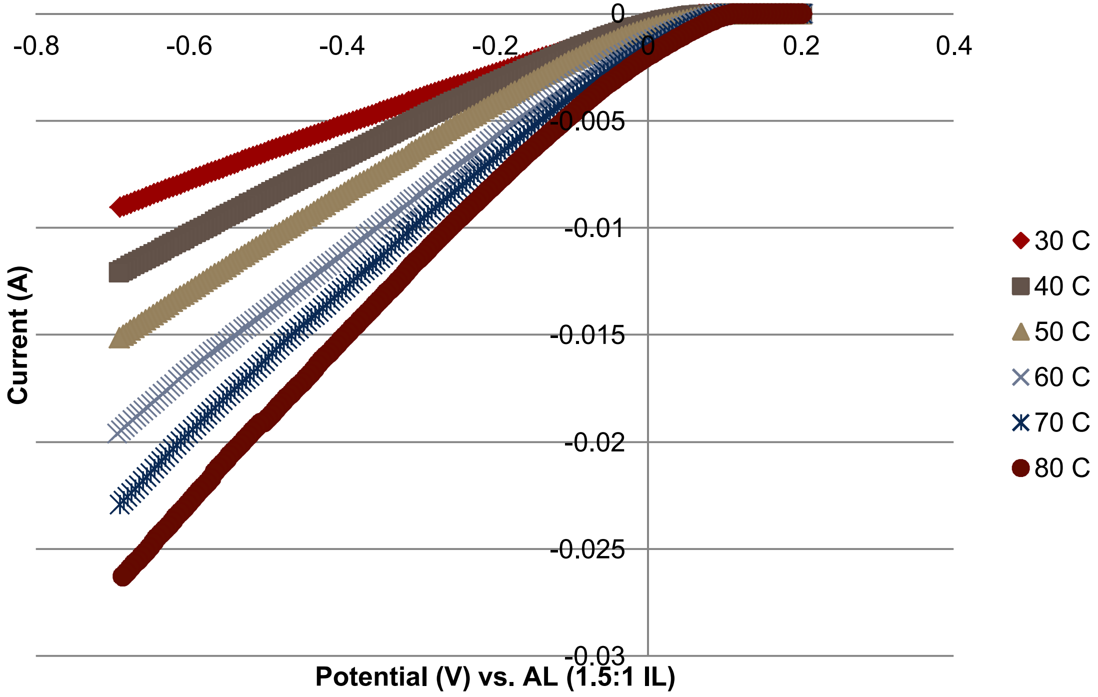
- η is the overpotential
- A is the so-called "Tafel slope", V
- i is the current density, A/m^2 and
- i_0 is the so-called "exchange current density", A/m^2.



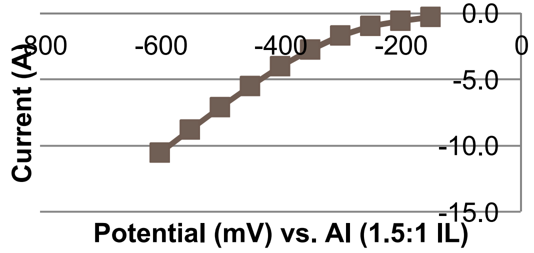


Reaction Kinetics

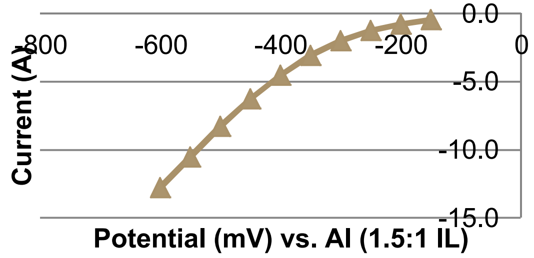
- Heavily dependent on temperature and potential
- Agitation quickly shifts deposition regimes from diffusion to kinetic and mixed limitations



2:1 $AlCl_3$ to EMImCl 500 RPM 2 mV/s

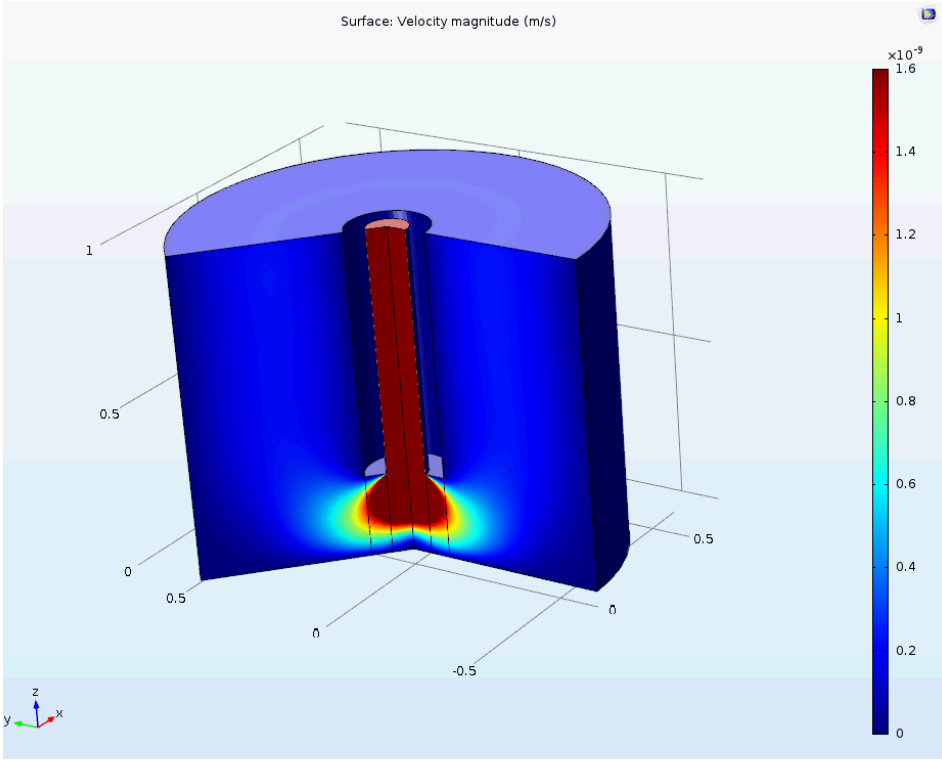


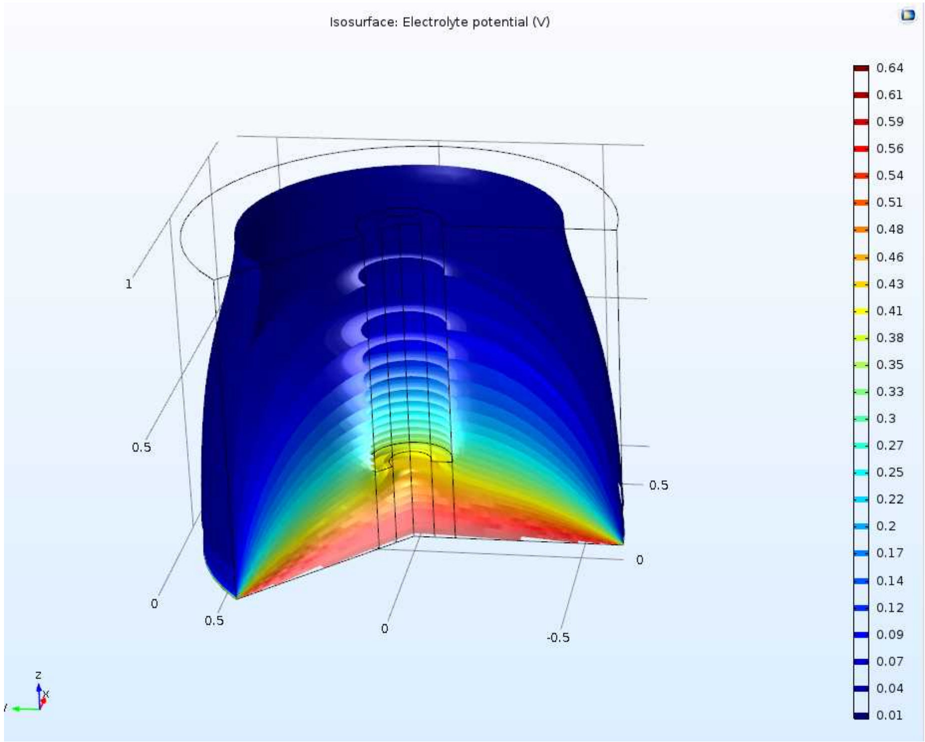
800 RPM 40C 2 mV/s



1400 RPM 40C 2 mV/s

Comsol Electrochemistry





Electrostatic Ionic Attraction

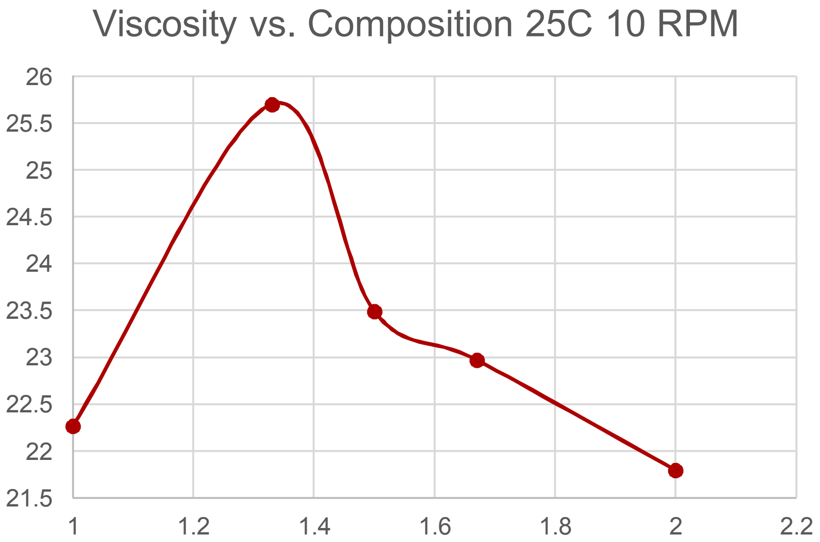
- Use energy of interaction from rheology and theoretical ionic separation distance from DFT modelling
  - Limited accuracy due to charge dispersion and ionic structure
    - More than just attraction force, also requires opening to move into
  - Increase accuracy with statistical mechanics, parameterize ions with DFT, input into LAMMPS but outside scope

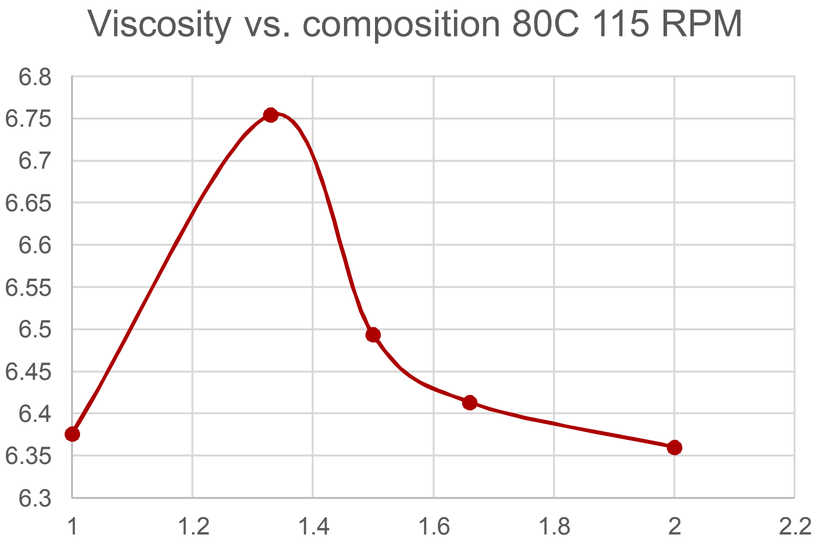
Plans

- Finish last data set
- Analysis
- Writing
- Lots of codep
- Modelling comsol

Structuring varies?

- See anomalies in viscosity dependent on composition
  - Consistent trend over temperature and shear range
- Well known that structuring factor in ionic liquids is a dominant contributor to it’s properties

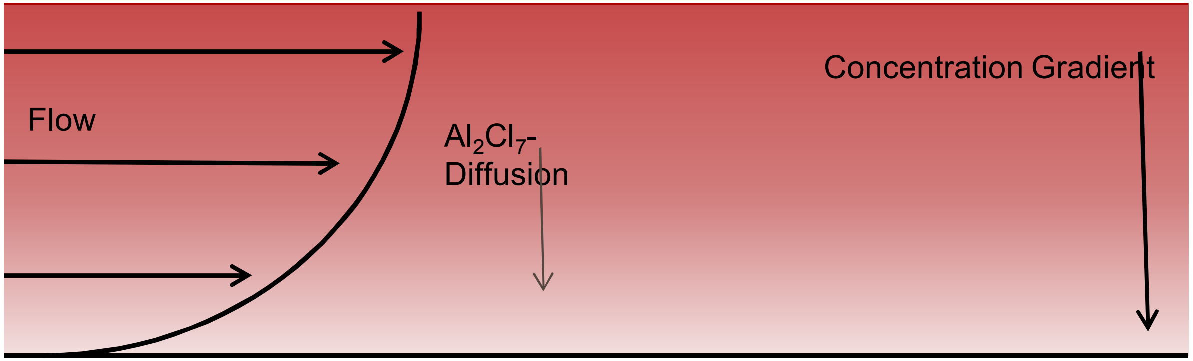

Viscosity vs. Composition 25C 10 RPM


Viscosity vs. composition 80C 115 RPM

Double layer evaluation

- Composition and viscosity changes with z
- Diffusion changes with both
- Diffusion changes with z
  - More complex than simple Cottrell model, sub D with D(z)
  - Shear thinning, may increase mobility

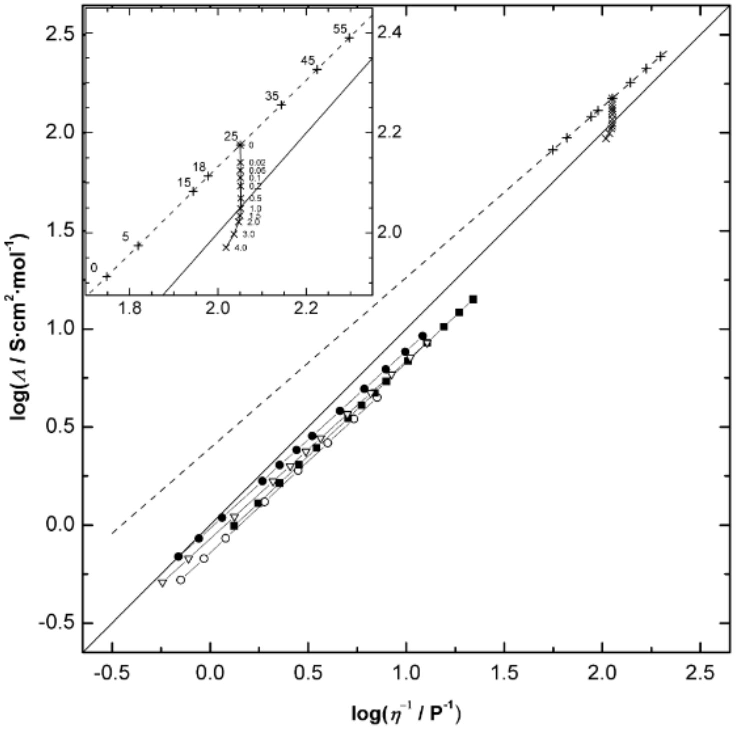
Al_2Cl_7- Rich Bulk (higher diffusion, *maybe)



$AlCl_4$- Rich at surface (slower diffusion, maybe*)

Al_2Cl_7- → $AlCl_4$- Reaction at electrode
surface

Micro and Macro Properties



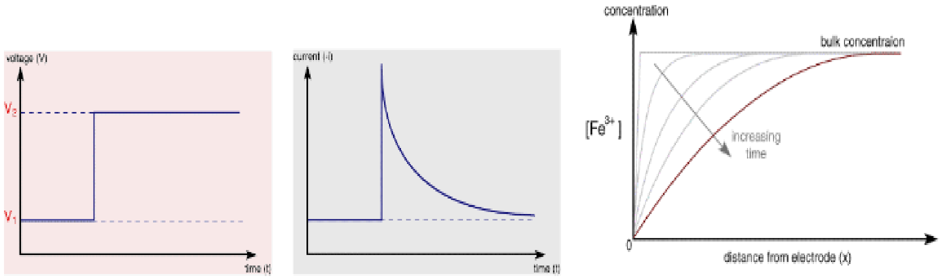
- In molten salts and ionic liquids all species are ionic
  - Conductivity is the relative motion of charges, all species are charged
- Viscosity is dictated by the ability of solution components to move
- Viscosity and conductivity are expected to be correlated in this system

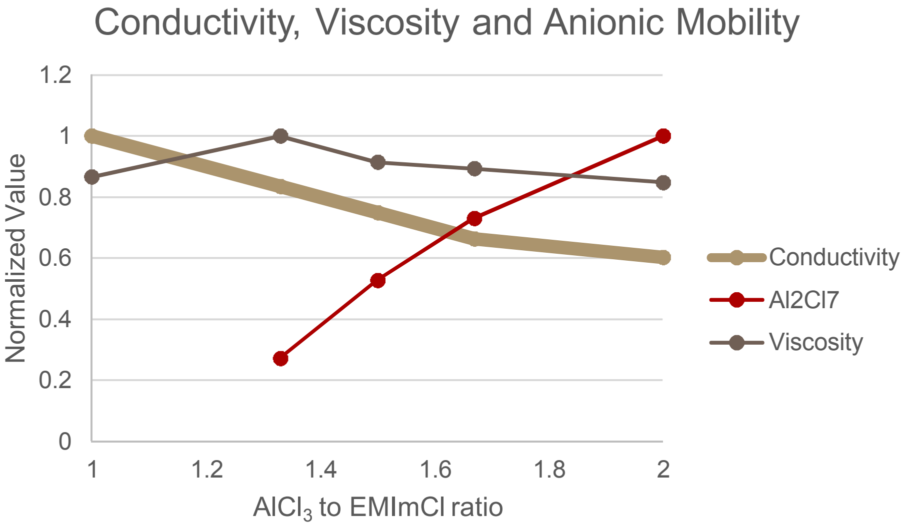
Electrochemical Aspects of Ionic Liquids, Ohno 2005

Conductivity from Mobility

- Cottrell for $Al_2Cl_7^-$
  - $2 - 9 * 10^{-8}$ cm^2/s

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

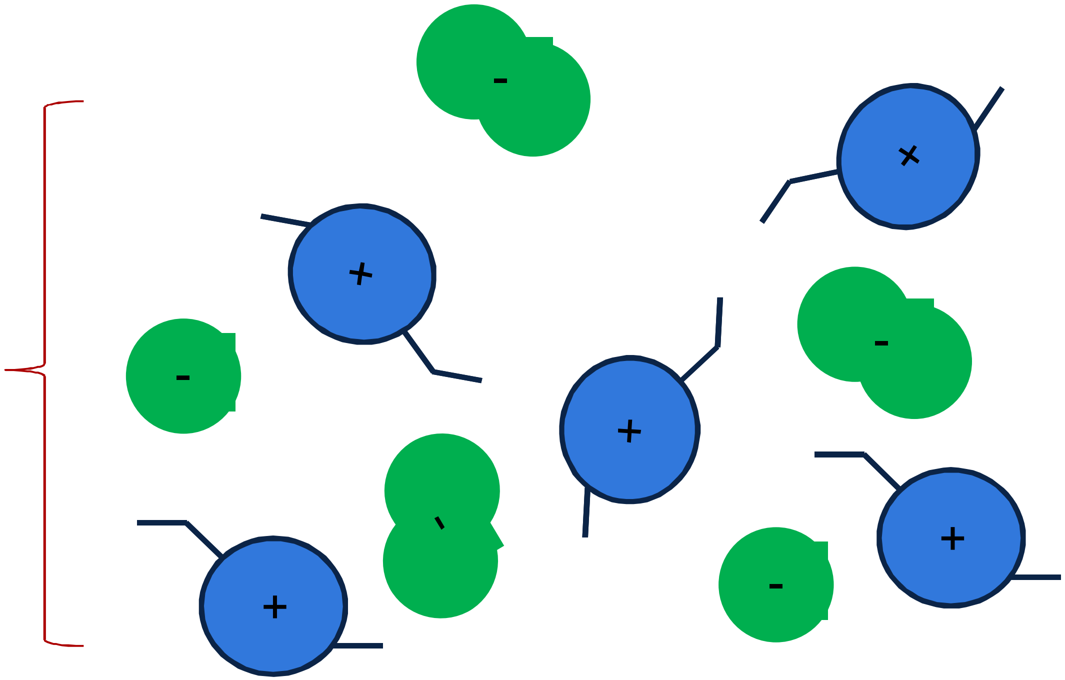




- Remember imidazolium mobility (from PGSE NMR) ~10^{-6} cm^2/s
  - Order of magnitude higher

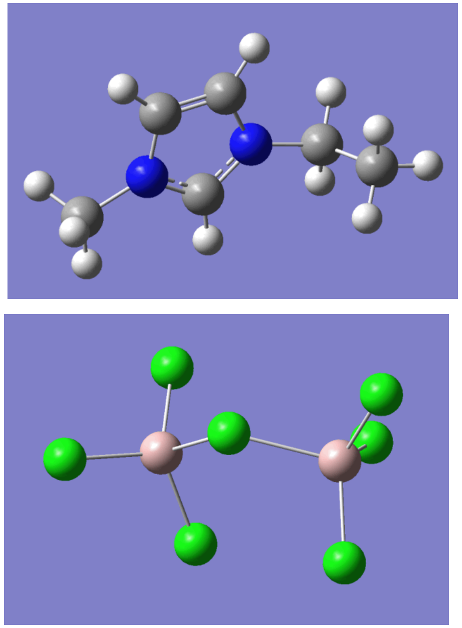
Ionic liquids

- Ionic liquids are liquid state solutions that are entirely composed of ions
- Electrostatic and dipole interactions heavily influence the attractive forces, and packing asymmetry force a liquid state



Strong interactions between ions

Structuring and packing is very influential



Nucleation Testing

- Matches literature even at very low overpotentials
- Always instant nucleation modes