Sandia National Laboratories' Programs

1. **Electroactive Ionic Liquids:**
   A New Approach to Flow Batteries

2. **Gallium Nitride Substrates for Power Electronics:**
   Electrochemical Solution Growth

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Sandia National Laboratories

Electroactive Ionic Liquids:

A New Approach To Flow Batteries

Date

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David Ingersoll
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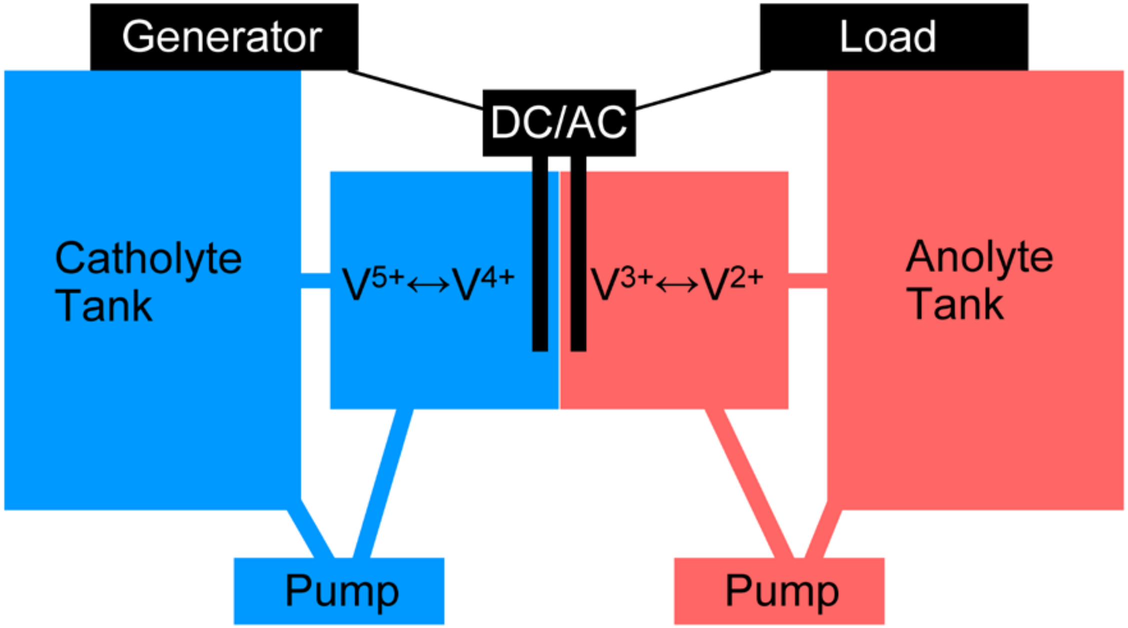
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

Flow Batteries

Vanadium Redox Battery (VRB)

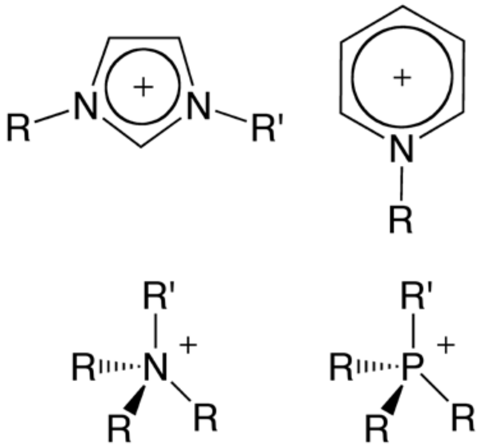


- No cross contamination
- Flexible layout
- High cycle life
- Large, tunable capacity
- Low maintenance

vanadium redox couples are in both cells, separated by a proton exchange membrane

Ionic Liquids

Common Cations



Common Anions

BF_4^- PF_6^- $AlCl_4^-$

Cl^- NO_3^- $CF_3SO_3^-$

ClO_4^- $(CF_3SO_2)_2N^-$

Synthetic "Targets"

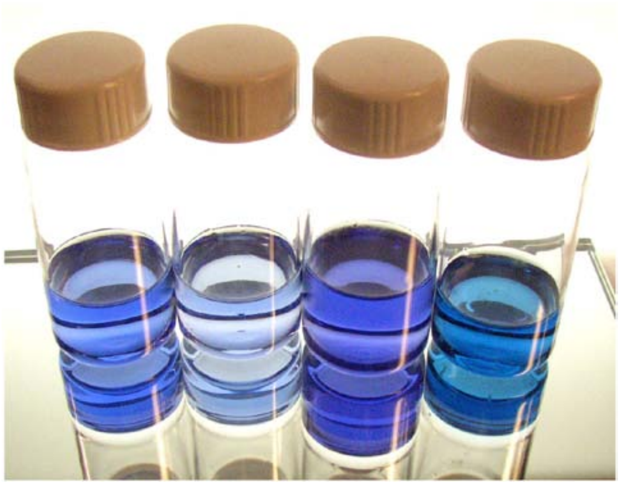
- **Low symmetry**
- **Weak Intermolecular Interactions**
- **Low charge density**

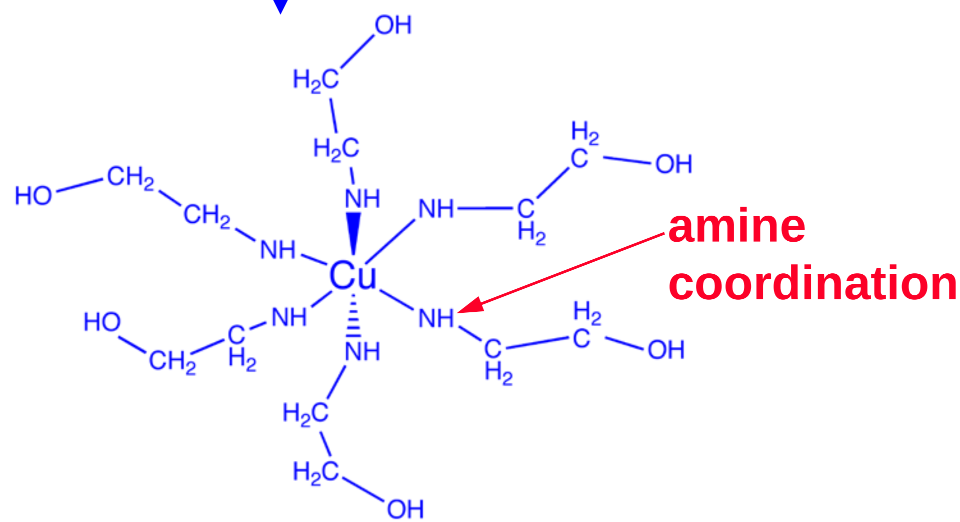
Wasserscheid and Keim *Angew. Chem. Int. Ed.* **2000**, 3772-3789.

Synthesis of Electroactive Ionic Liquids

$(CF_3SO_3)_2Cu$ or $(CH_3(CH_2)_3CH(C_2H_5)CO_2)_2Cu + 6\ NH_2CH_2CH_2OH$

↓ Δ 75 °C, 45 min

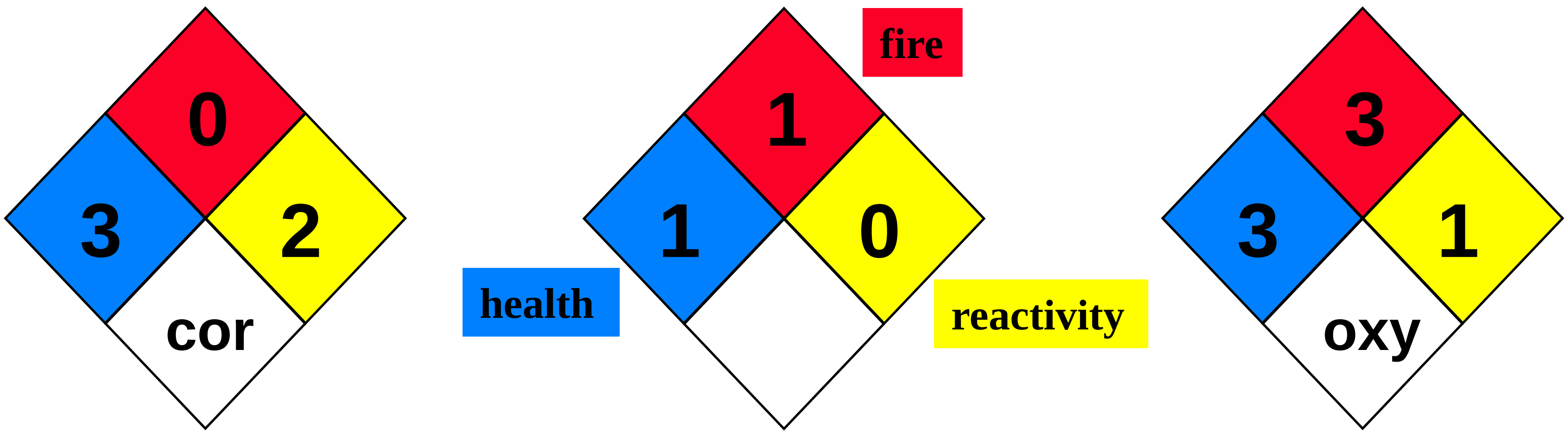




$+ 2\ CF_3SO_3^-$ or $CH_3(CH_2)_3CH(C_2H_5)CO_2^-$

- -scalable
- -versatile
- -low cost
- -two functional groups

Flow Battery Safety



Vanadium Redox Battery

Sandia Ionic Liquid

Zinc Bromine Flow Battery

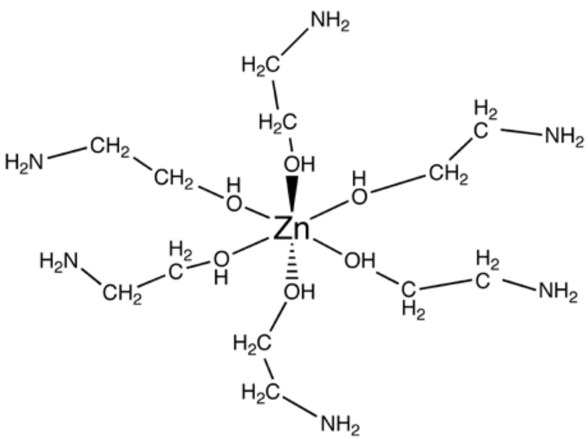
Ionic liquids have no vapor pressure, thus mitigating cell pressurization issues

Data based on individual components

Versatile Synthesis

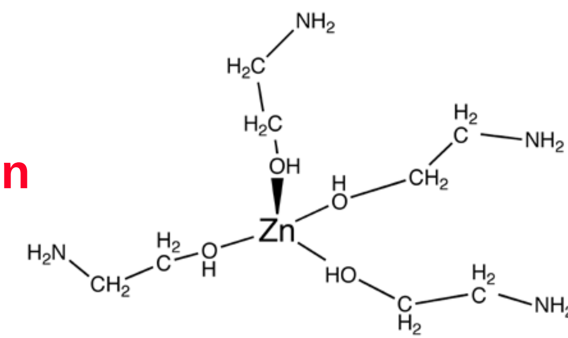
$(CF_3SO_3)_2Zn + 6\ NH_2CH_2CH_2OH$ or $4\ NH_2CH_2CH_2OH$

Δ 75 °C, 30 min



alcohol coordination

Δ 115 °C, 30 min



$+ 2\ CF_3SO_3^-$

The coordination geometry can be varied by changing the reaction stoichiometry.

Seven New Electroactive Ionic Liquids

$(CH_3(CH_2)_3CH(C_2H_5)CO_2)_2Cu(NH_2CH_2CH_2OH)_6$	**$Cb_2Cu(EA)_6$**
$(CH_3(CH_2)_3CH(C_2H_5)CO_2)_2Cu(NH(CH_2CH_2OH)_2)_6$	**$Cb_2Cu(dEA)_6$**
$(CH_3(CH_2)_3CH(C_2H_5)CO_2)_2Cu(N(CH_2CH_2OH)_3)_6$	**$Cb_2Cu(tEA)_6$**
$(CF_3SO_3)_2Cu(NH(CH_2CH_2OH)_2)_6$	**$Tf_2Cu(dEA)_6$**
$(CF_3SO_3)_2Zn(NH_2CH_2CH_2OH)_6$	**$Tf_2Zn(EA)_6$**
$(CF_3SO_3)_2Zn(NH_2CH_2CH_2OH)_4$	**$Tf_2Zn(EA)_4$**
$(CF_3SO_3)_3Fe(NH(CH_2CH_2OH)_2)_6$	**$Tf_3Fe(dEA)_6$**

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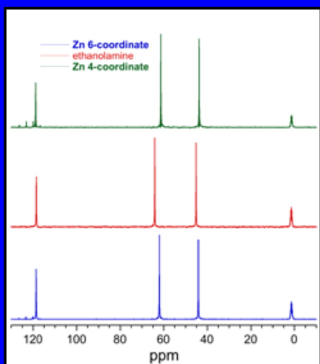
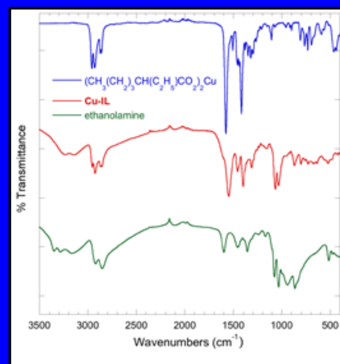
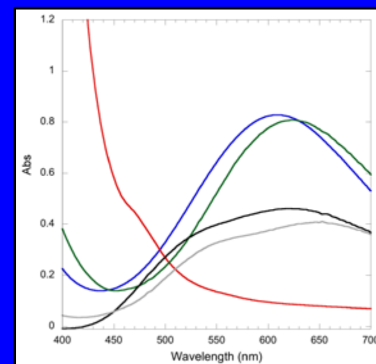
Spectroscopic Studies of Synthesized Ionic Liquids



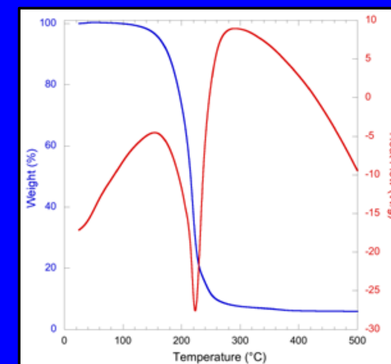
^{13}C NMR Spectroscopy



Infrared Spectroscopy

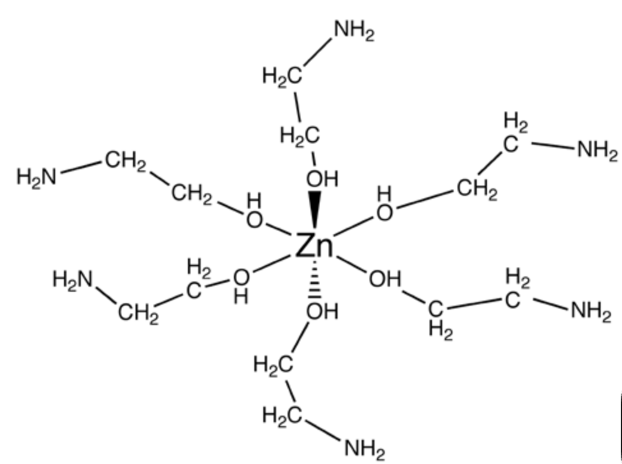


Electronic Absorption



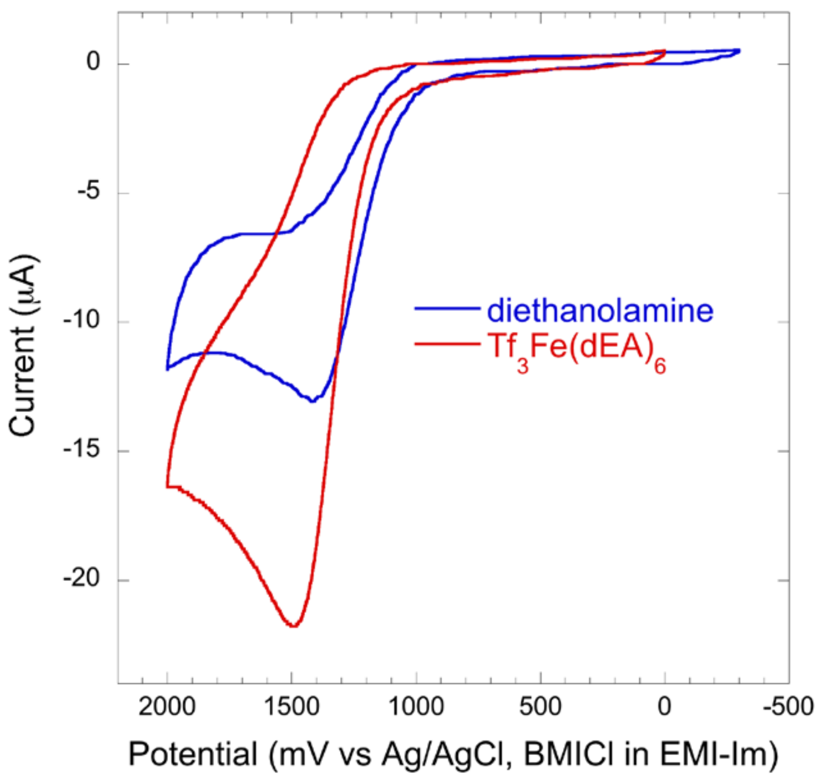
Thermal Stability

- Determine molecular structures
- Relate structure to properties
- Tailor synthesis procedure to obtain molecules with desired properties (e.g., d.p. 150-255C)

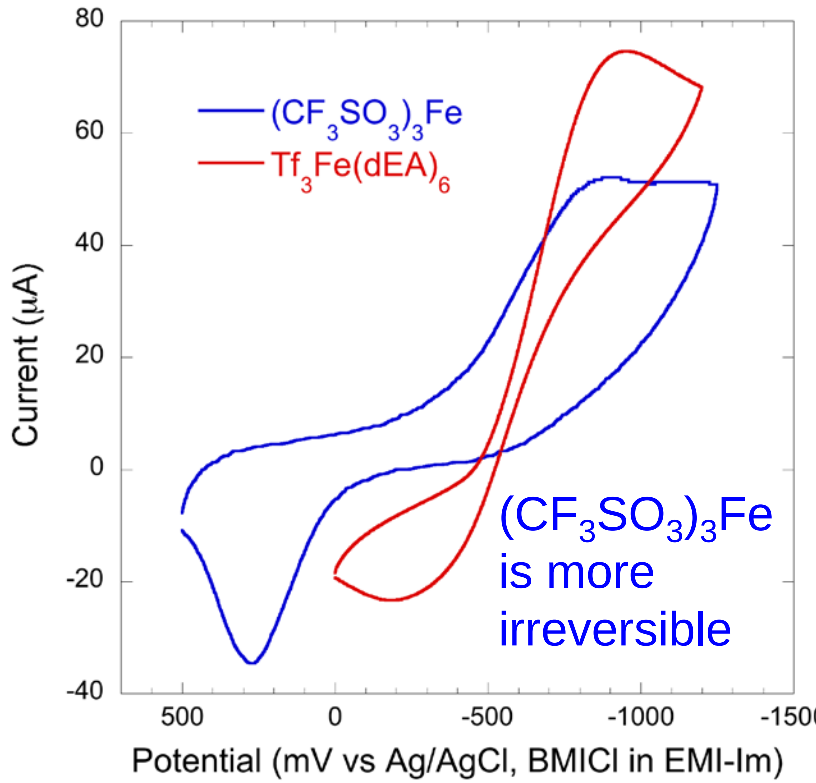


Cyclic Voltammetry

Ligand Oxidation



Metal Redox



Conditions: Pt working electrode, 1 M $TEABF_4$ in CH_3CN

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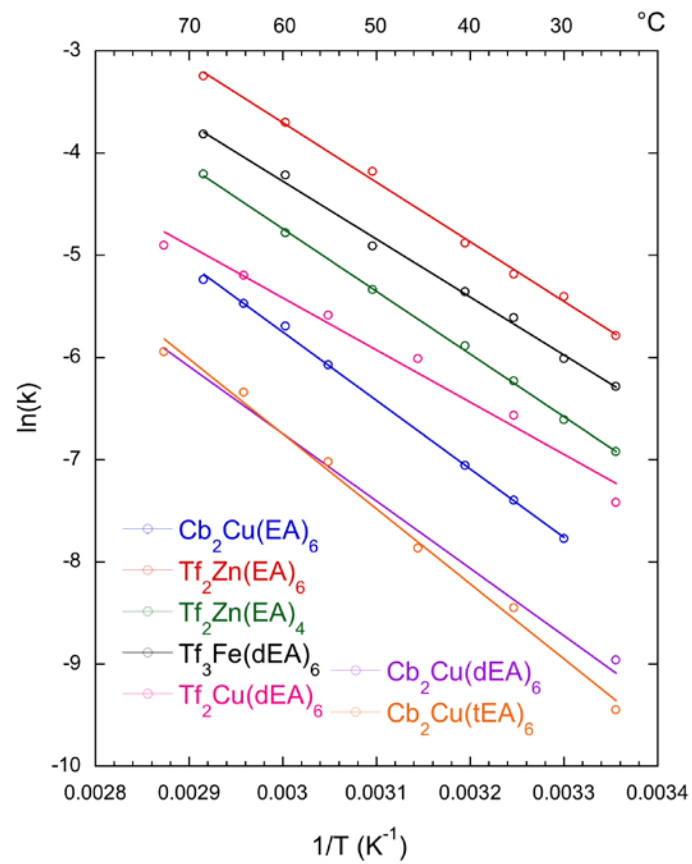
Conductivity Studies

Complex	Specific Conductivity ($\mu S\ cm^{-1}$) at 25 °C	Activation Energy ($kcal\ mol^{-1}$)
$Cb_2Cu(tEA)_6$	8.77	13.3
$Cb_2Cu(dEA)_6$	14.3	11.6
$Cb_2Cu(EA)_6$	44.6	12.2
$Tf_2Cu(dEA)_6$	66.7	11.2
$Tf_2Zn(EA)_4$	101	8.9
$Tf_3Fe(dEA)_6$	207	13.1
$Tf_2Zn(EA)_6$	341	14.6

the specific conductivity of common battery electrolytes at 25 °C is ~0.5-1 $S\ cm^{-1}$

E_a of aqueous (and molten) metal salt ~3-5 $kcal\ mol^{-1}$



conductivity is low: suggests significant ion pairing

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Path Forward

Anion Exchange to Increase Conductivity

- ORNL compounds $M(NH_3\text{-}R)_2(CF_3SO_2)_2N$ increased conductivity by three orders of magnitude

Decrease Viscosity to Increase Efficiency

- The increased hydrophobicity of $(CF_3SO_2)_2N$ will decrease the internal resistance to power extraction

Increase Molar Concentration of Metals

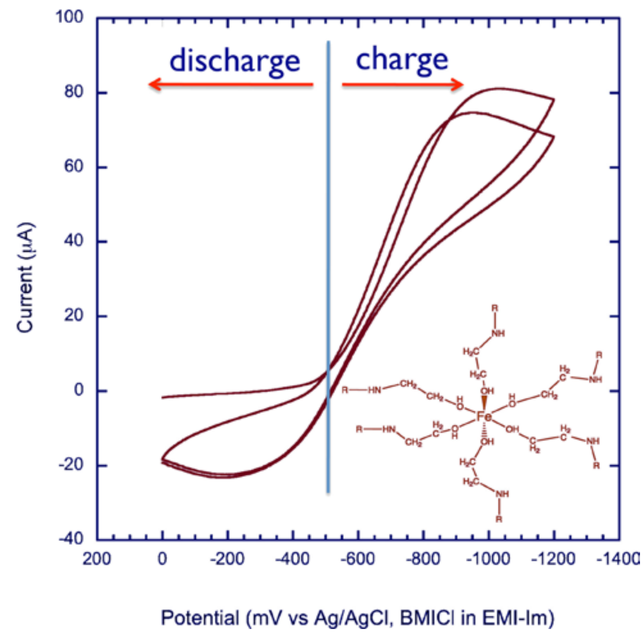
- Increases energy density
- Metal-Ligand exchange, mixed metal systems

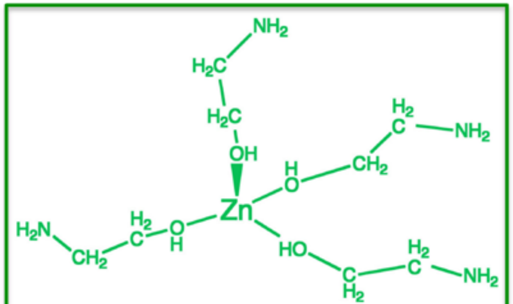
Conclusions and Future Work

•Although we have demonstrated the compounds may serve as a **liquid electrode** they are not yet appropriate as the **electrolyte**

•Future work on the electroactive ionic liquids will focus on both new **ligands** and new **anions** to increase hydrophobicity

•Evaluate the effect of hydrophobicity on the fundamental electrochemical characteristics





Zinc-based ionic liquid
(cation shown)

Electrochemical Solution Growth (ESG) of Gallium Nitride for Power Electronics

Karen Waldrip

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Dave F. Smith

GNOEM Systems, Boulder Creek, CA

Sandia National Laboratories

Combined Figure of Merit

	K (W/cm°C)	E_c (MV/cm)	ε	μ (cm^2/Vs)	v_s	Combined Figure of Merit
Si	1.31	0.3	11.8	1350	1×10^7	1
SiC	4.9	2	10	650	2×10^7	136
GaN	1.3	3.3	9	1200	2.5×10^7	153

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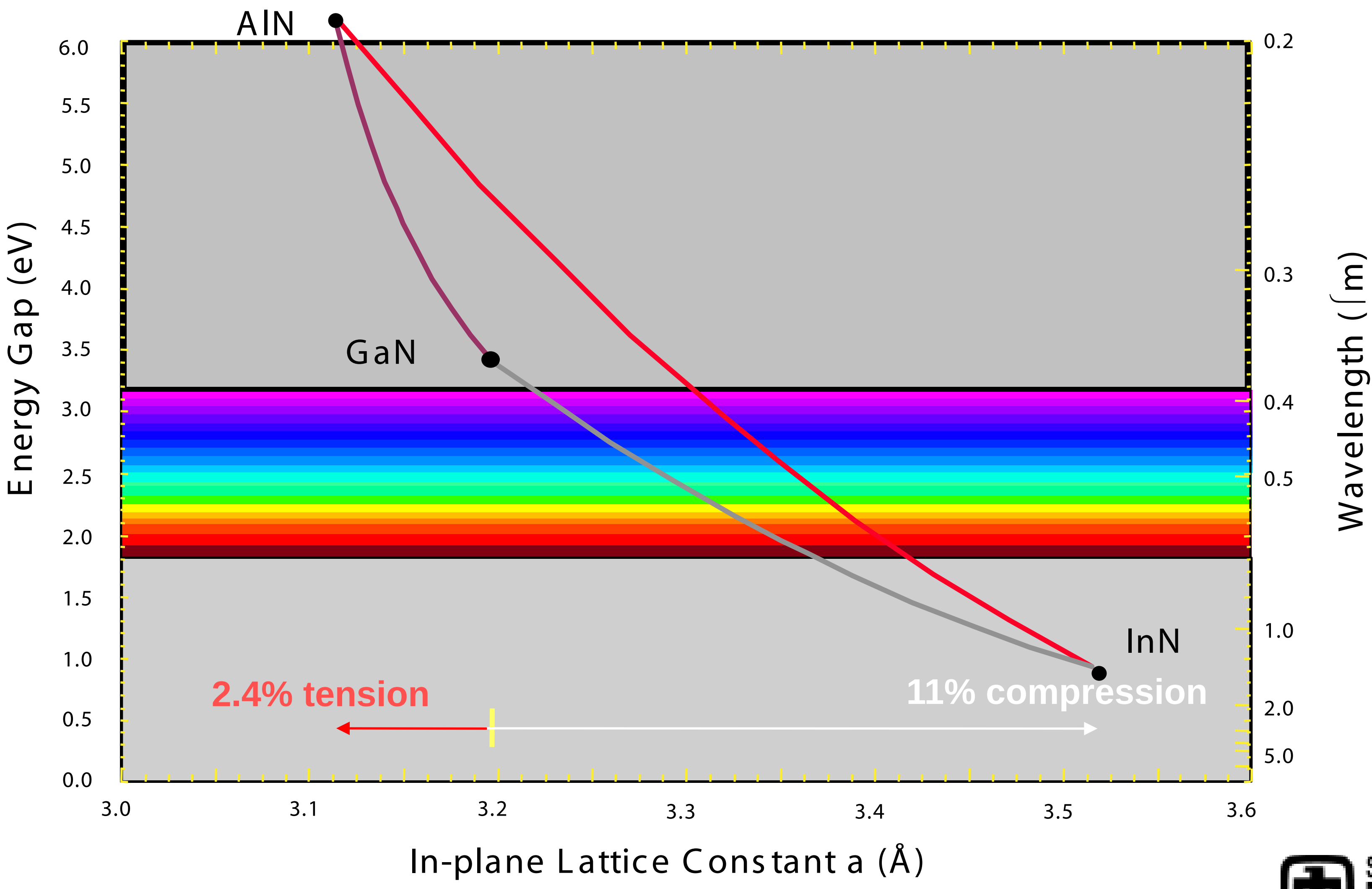
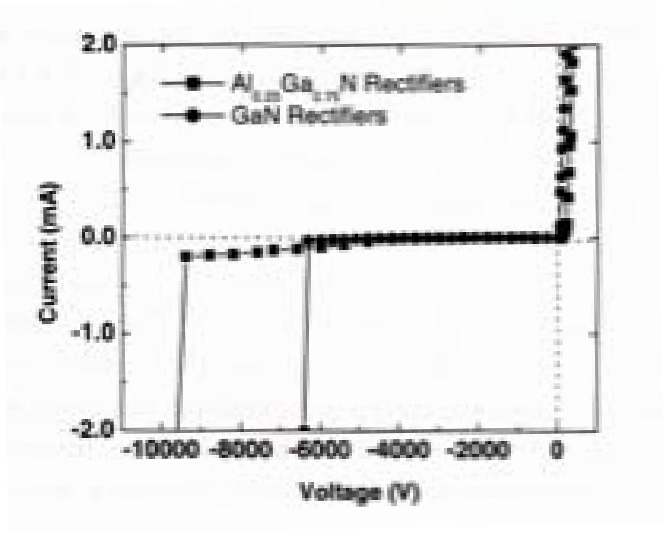
Energy gap - lattice parameter diagram of III-nitrides



Heterostructure Rectifiers Offer Improved Breakdown Voltages



- 9.7 kV for $Al_{0.25}Ga_{0.75}N$
- Leakage current due to bulk defects

GaN is Grown Heteroepitaxially on Sapphire (and Silicon Carbide) Substrates

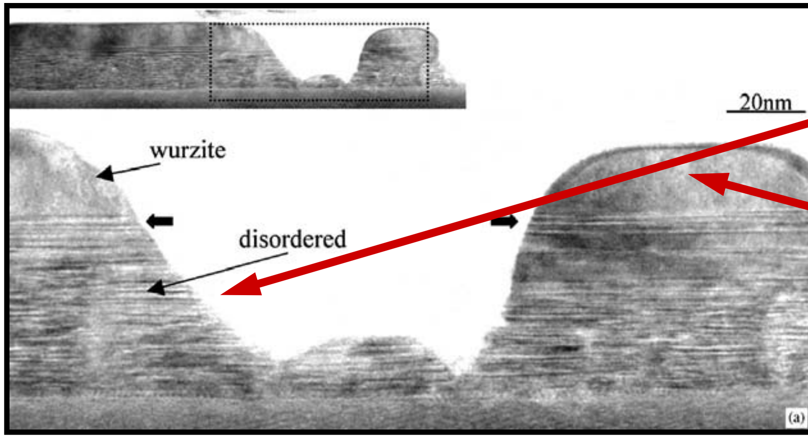
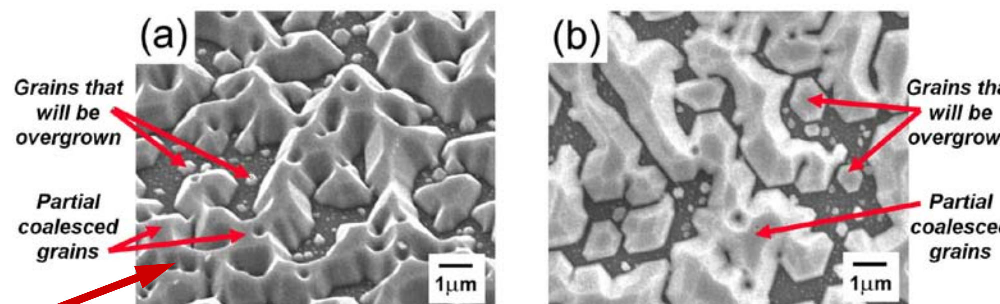


Figure from Lada et al., J. Crystal Growth 258, 89 (2003).

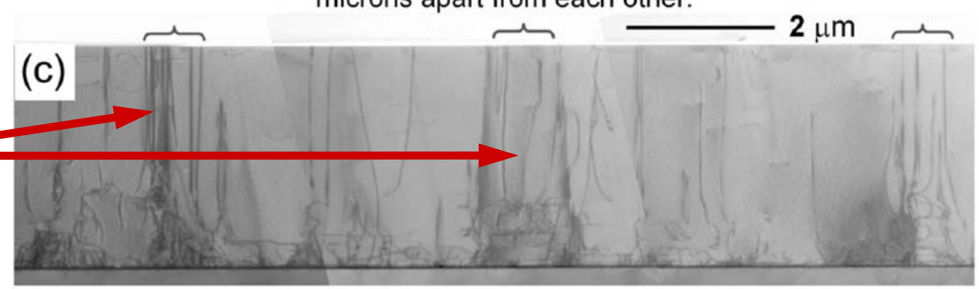
- **As grown GaN nucleation layers contain disordered GaN with many stacking faults.**
- **Once annealed, wurtzite GaN forms on top of disordered GaN NL, forming nano-sized GaN nuclei from which further high temperature GaN growth occurs.**

SEM Images of 3D GaN grain growth



The threading dislocation appear in bunches which are located a few microns apart from each other.

- High temperature growth on the GaN nuclei produces GaN grains.
- Growth conditions can be varied to enhance the <u>pyramidal growth mode</u> or lateral coalescence. Dislocations are bent laterally on pyramidal facets.
- Dislocations are concentrated in bunches located microns apart.



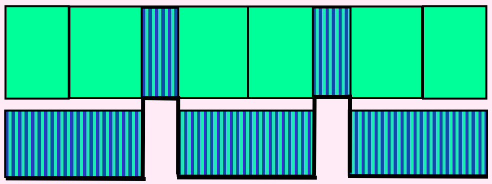
TEM cross section

TEM courtesy of D. M. Follstaedt

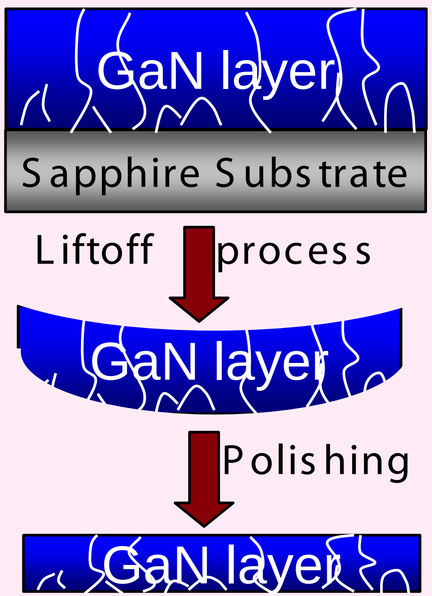
Methods for growing bulk GaN

Dislocation Filtering Techniques

Lateral Overgrowth

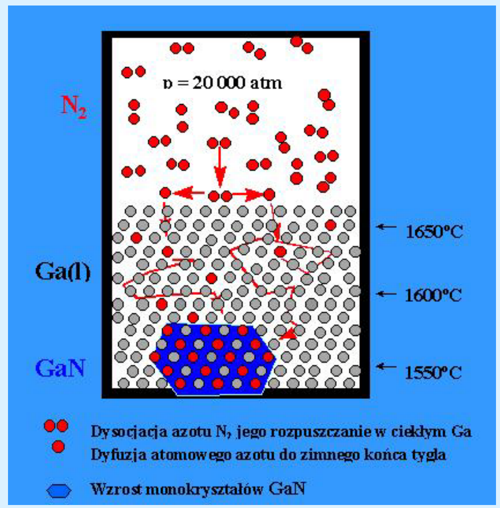


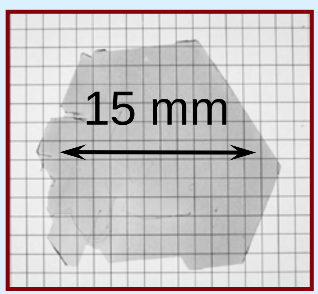
HVPE



"True" Bulk Techniques

High Nitrogen Pressure

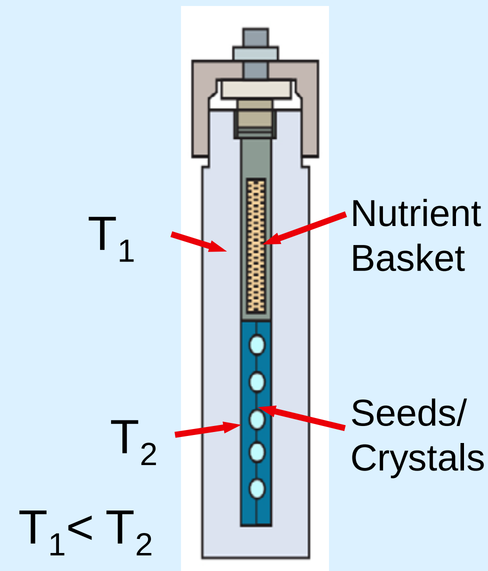




$P = 10^5$ atm
T = 1500C
t = 100 hr
h = 100 μm

Dislocation density = $10^2 cm^{-2}$

Ammonothermal growth



$KNH_2 + GaN + 2NH_3 \rightarrow KGa(NH_2)_4$

$GaN + 2NaNH_2 + 2NH_3 \rightarrow Na_2Ga(NH_2)_5$

4,000 – 5,000 atm
T = 400 – 800°C
G.R. = 50 μm/day
Multiple seeds

Desires/Requirements for a Bulk Growth Technique

- **Good crystalline quality (〉 ≤ $1x10^{5}cm^{-2}$)**
- **High growth rate (~mm/hr): high throughput, high volume production**
- **Low impurity content**
- **Scalable**
- **Controllable**
- **Manufacturable**
- **Reasonably inexpensive**
- **Applicable to InN, GaN, AlN, and III-N alloys**

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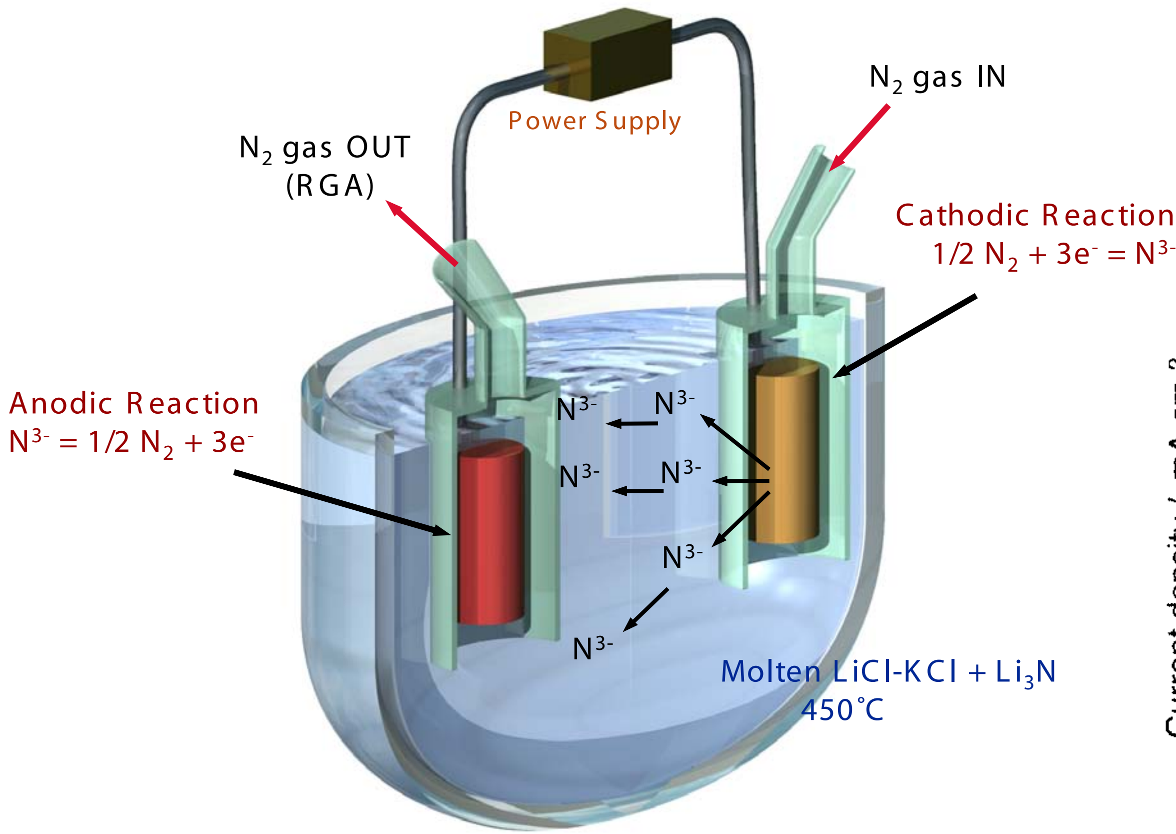
$1/2N_2 + 3e^-$ □ N^{-3}: The **Reactive Intermediate**

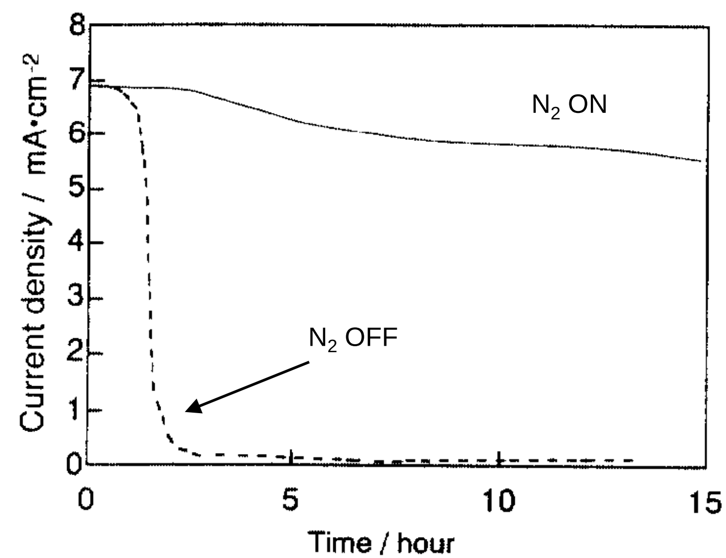
- T. Goto and Y. Ito, "Electrochemical reduction of nitrogen in a molten chloride salt" Electrochimica Acta, Vol. 43, Nos 21-22, pp 3379-3384 (1998).

Found that nitrogen was continuously and nearly quantitatively reduced to nitride ions

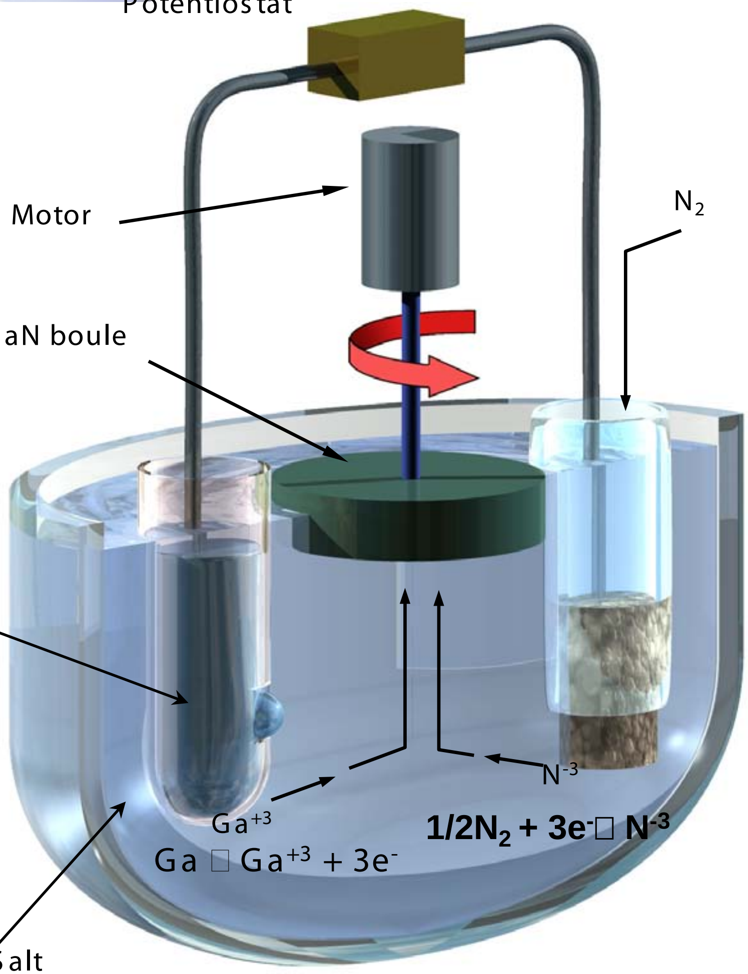


Report of nitride concentration in LiCl in literature: 12 mole %

Advantages of using N_2 gas:
- Clean
- Inexpensive
- Control over precursor conc.
- Continuous, controlled supply



New Bulk Growth Technique: Electrochemical Solution Growth (ESG)



Note that this is not electrodeposition!
- Avoids requirement for conductive materials
- Avoids purity, crystalline quality issues

Uses rotation of seed/boule to deliver ionic precursors (changes growth physics!)

Highlights of Advantages:

- Highest quality crystals produced by solution growth (disl. densities ~10^2 cm^{-2})
- Manufacturable process because electrochemistry controls concentrations
- Fully Scalable because seed/boule rotation produces uniform lateral Temp/Concentration and T, C gradients
- Inexpensive because relatively high concentrations enable mm/hr growth rates

Path Forward:
Demonstrate seeded growth (*in situ* seed prep)
Tune growth parameters to produce high quality boules
Transfer process to commercial 6” reactor (available for use)

U.S. Patent issued October 14, 2008

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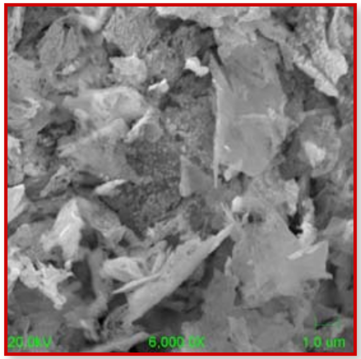
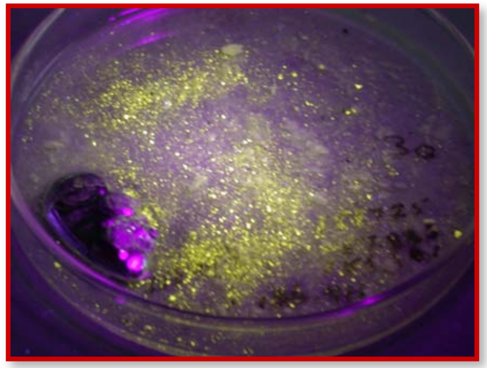
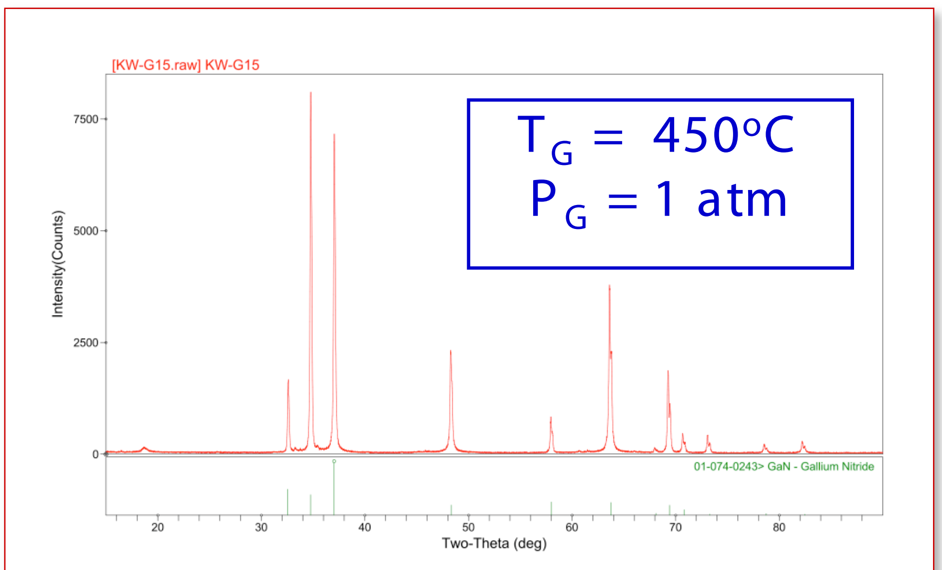
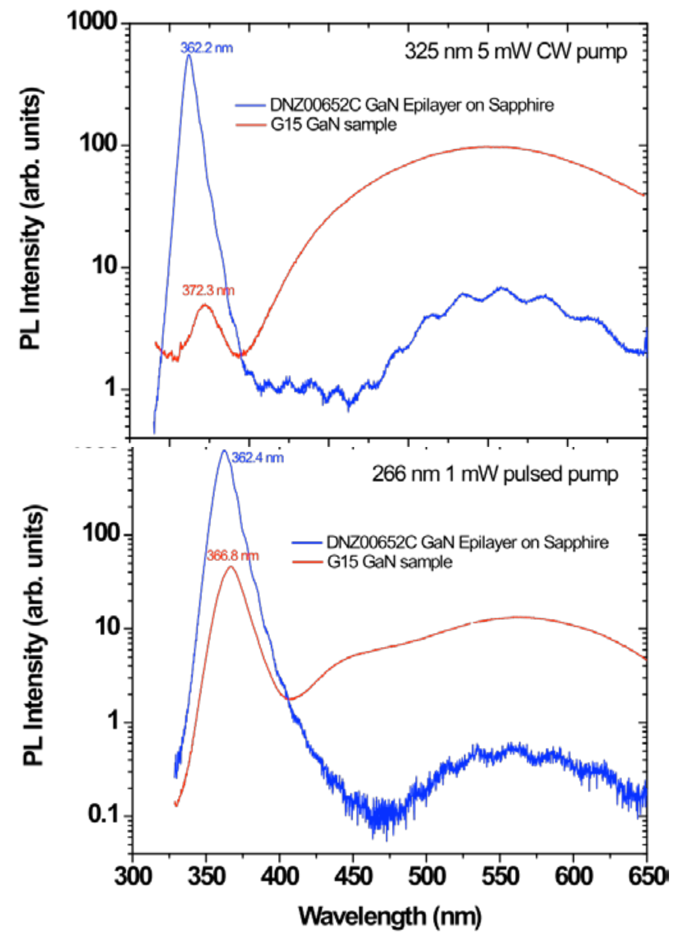
GaN ESG Produces Photoluminescent GaN Crystallites









Mary Crawford, SNL

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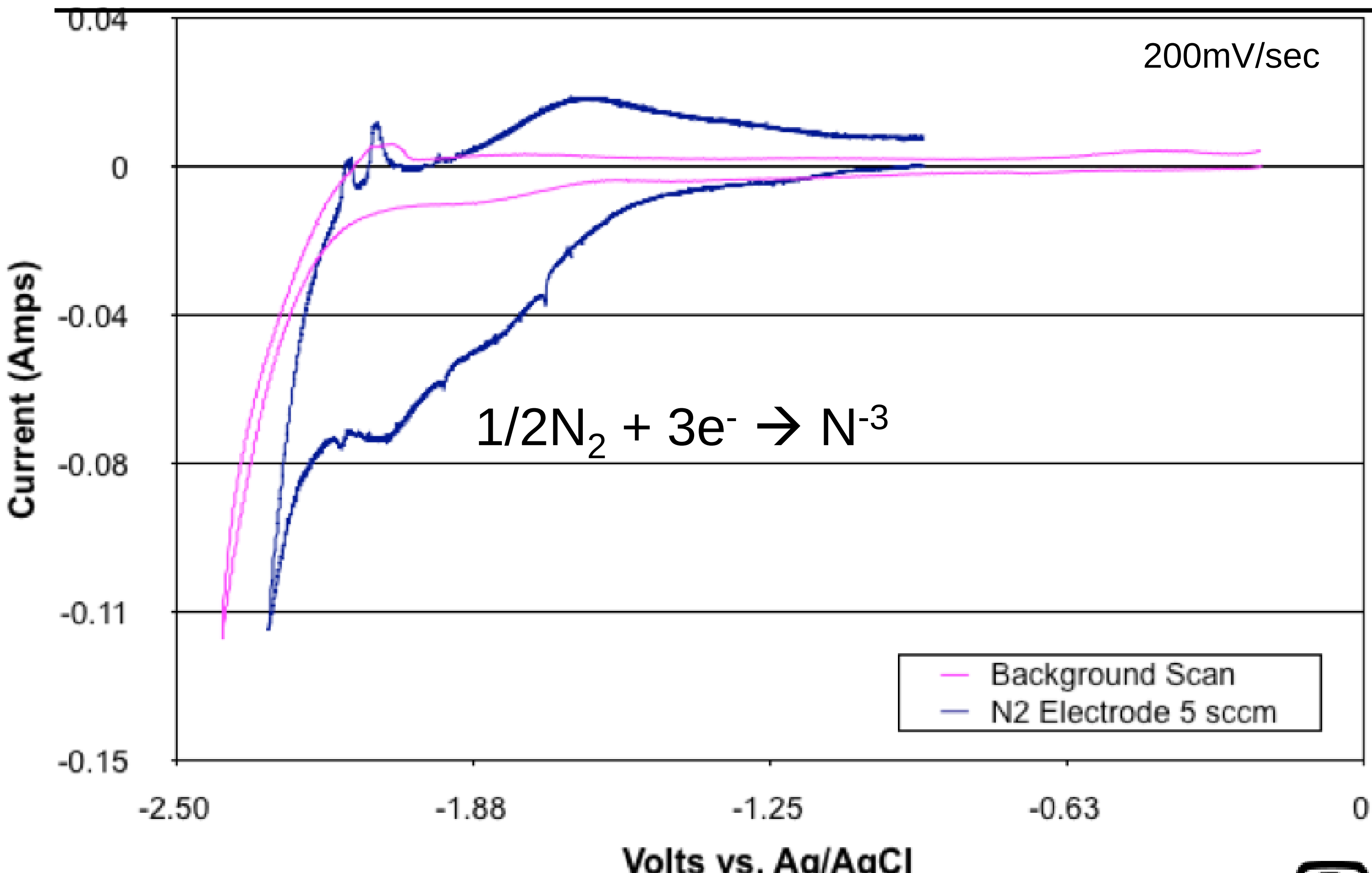
GNOEM Systems, Inc. Boulder Creek, CA

Example of Nitrogen Gas Reduction Cyclic Voltammograms



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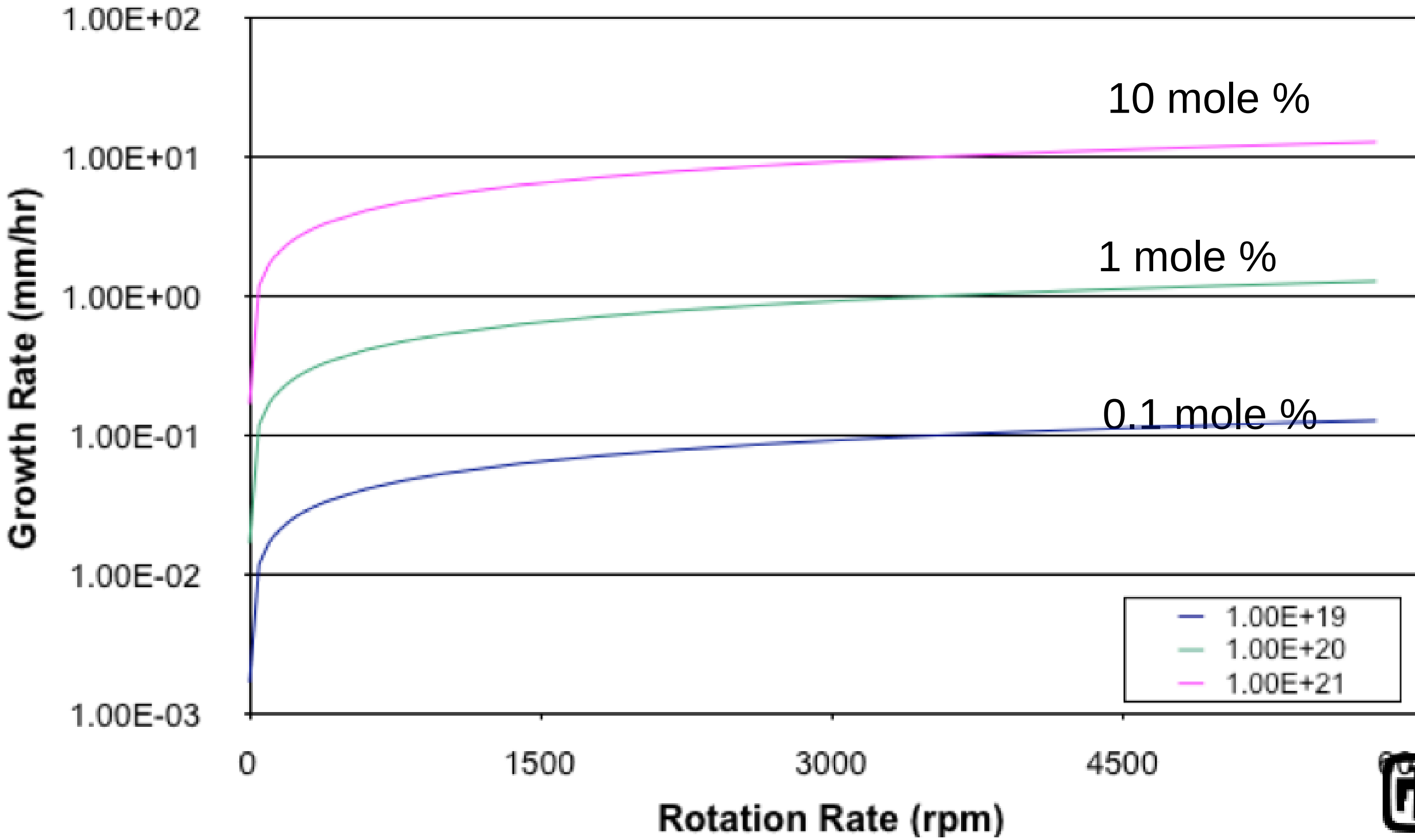
Industrial Partner (GNOEM) Hardware Development

Growth Rate vs. Rotation Speed and Concentration

$$GR\ (mm/hr) = \frac{a^2\ c\ (3)^{1/2} * 0.62 D_o^{2/3}]^{1/2} v^{-1/6} C_o^*}{4} \times \frac{10mm * 3600s}{cm * hr}$$



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Summary: Path For Development

✓ • Demonstrate that chemistry is viable
  – Kinetics and thermodynamics are favorable in this setup

✓ • Check for dissolution and precipitation approach

✓ • Develop N_2 electrochemical reduction methods

✓ • Develop initial fluid dynamics schemes

⇨ • Deposit GaN on a seed crystal

• Improve crystal quality

• Optimize growth rate

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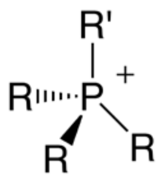
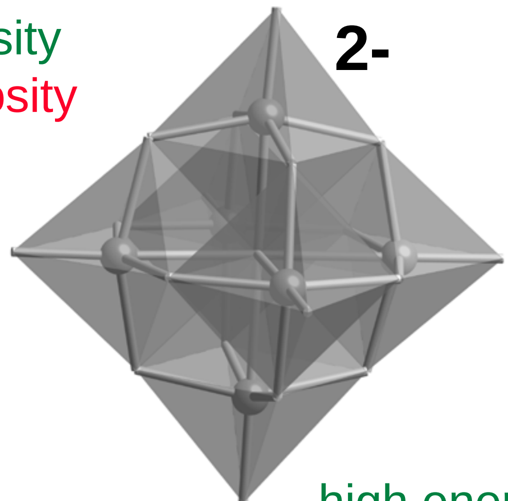
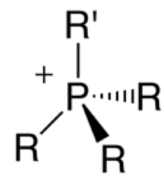
Electroactive Ionic Liquids

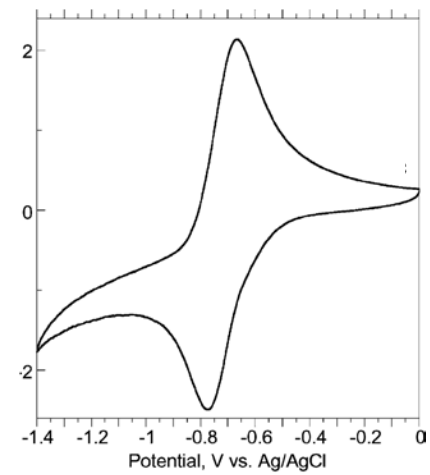
high energy density
detrimental viscosity

ANL Work









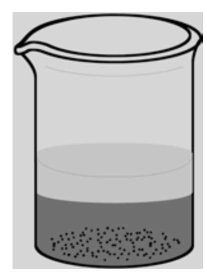
high energy density
low yield
expensive synthesis

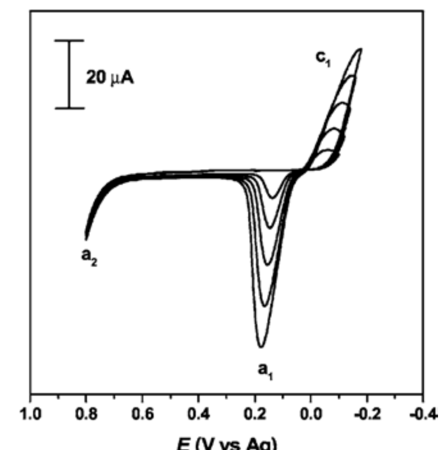
ORNL Work

$AgNO_3$ + 2 H_2N-R

↓ H_2O

$Ag(H_2N\text{-}R)_2NO_3$ —$(CF_3SO_2)_2NLi$→





P. G. Rickert et al. *Dalton Trans.* **2007**, 529-531.
J.-F. Huang et al. *J. Electrochem. Soc.* **2006**, *153*, J9-J13.

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Magnetic Susceptibility Studies

Compound	Calculated χ	Measured χ (±0.05)
$Cb_2Cu(EA)_6$	1.73 BM	1.50 BM
$Cb_2Cu(dEA)_6$	1.73 BM	1.69 BM
$Cb_2Cu(tEA)_6$	1.73 BM	1.72 BM
$Tf_2Cu(dEA)_6$	1.73 BM	1.60 BM
$Tf_2Zn(EA)_6$	0	0
$Tf_2Zn(EA)_4$	0	0
$Tf_3Fe(dEA)_6$	5.90 BM	5.87 BM

diamagnetic

-smaller ligands and anions promote
antiferromagnetic coupling

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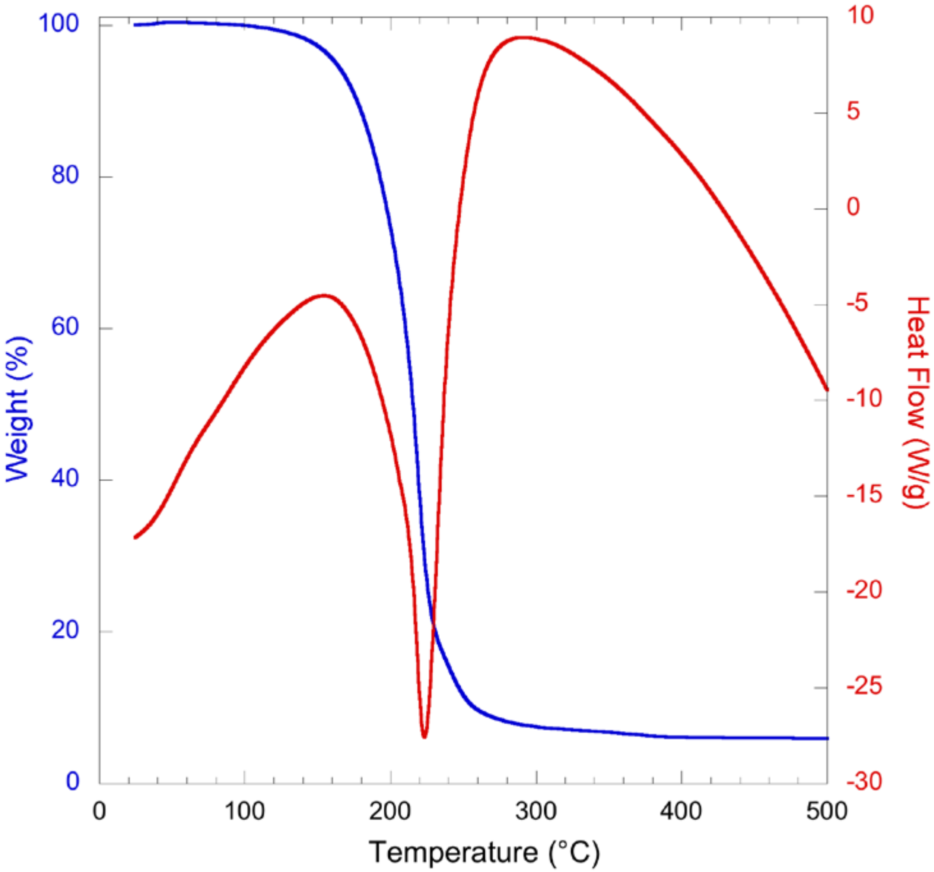
Thermal Stability Studies

tunable based on metal, ligand, and anion

$Tf_2Cu(dEA)_6$



Complex	Disassociation Temperature
$Tf_2Zn(EA)_4$	150 °C
$Tf_2Zn(EA)_6$	150 °C
$Cb_2Cu(EA)_6$	185 °C
$Tf_2Cu(dEA)_6$	210 °C
$Cb_2Cu(dEA)_6$	225 °C
$Cb_2Cu(tEA)_6$	250 °C
$Tf_3Fe(dEA)_6$	255 °C

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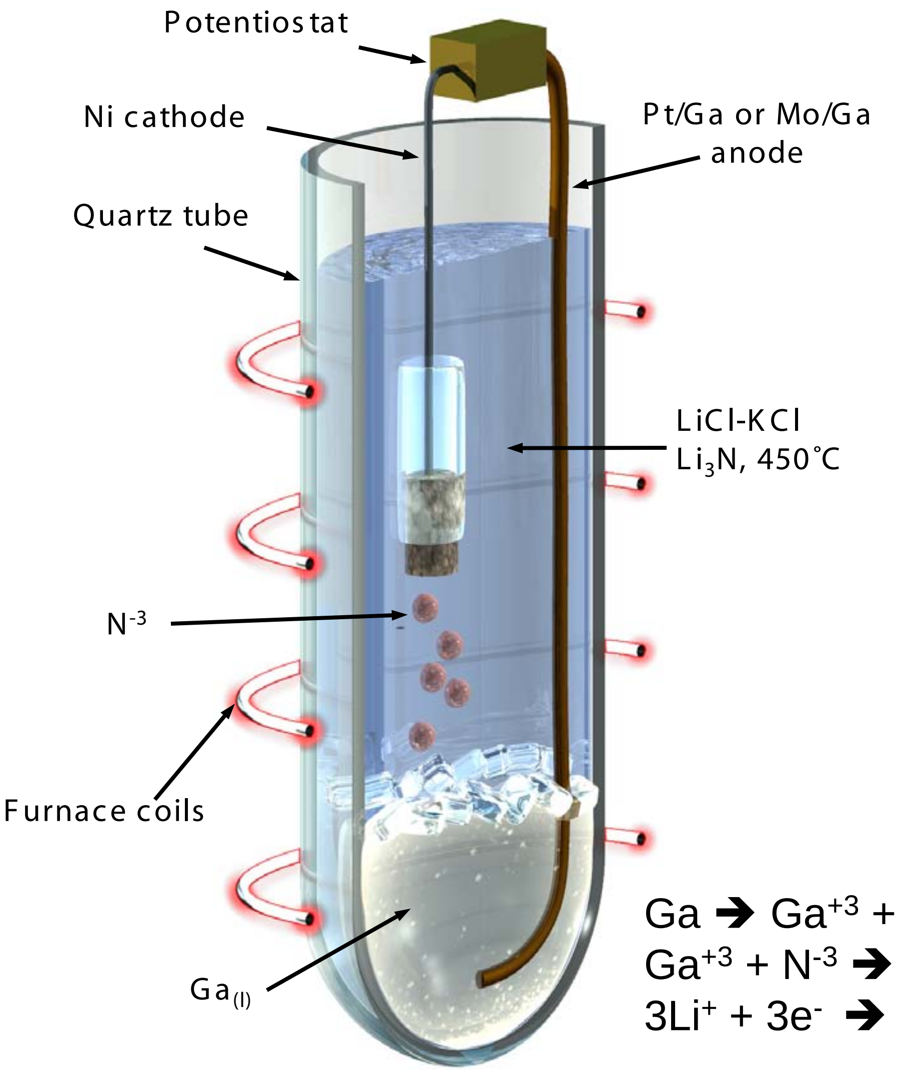
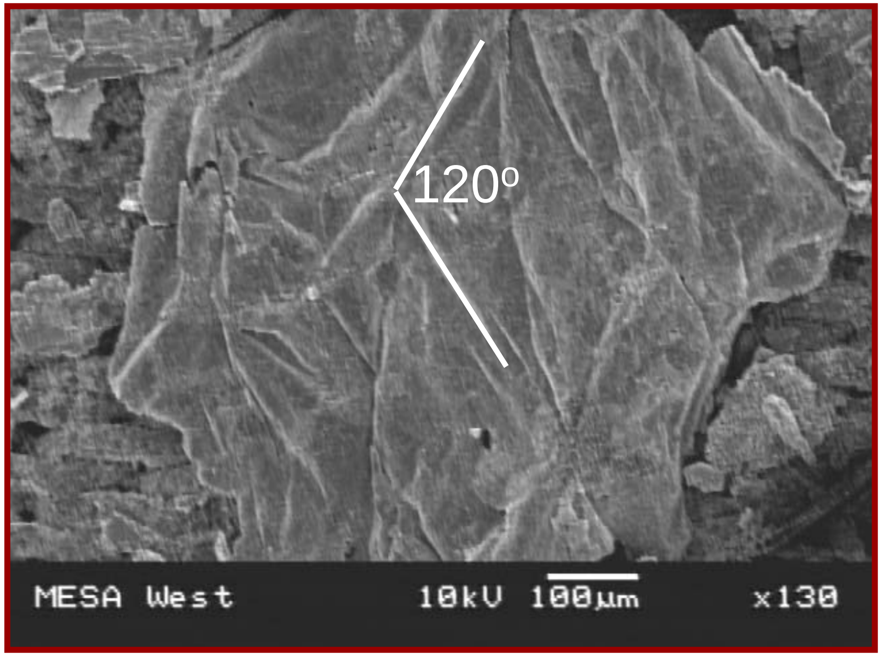
Initial Experimental Setup: Unseeded Growth of GaN in a Test Tube

$$\frac{Li_3N \text{ or } (Li_3N + N_2) + Ga,\ 450^\circ C,\ \text{current}}{\text{sweep, 2 hours}}$$





Produced numerous wurtzite GaN crystals;
This crystal was ~1.25mm long x 0.8mm wide

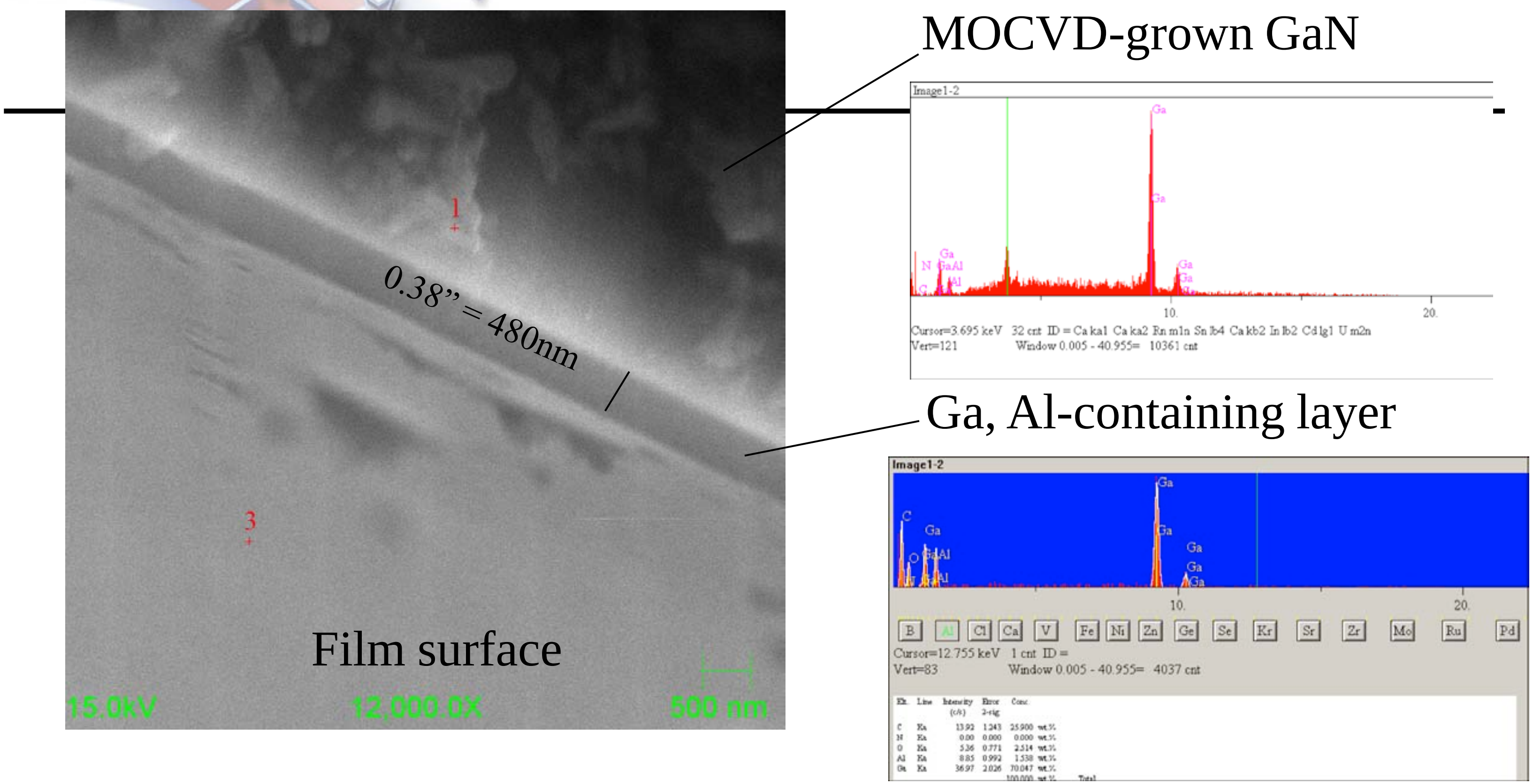
$Ga \rightarrow Ga^{+3} + 3e^-$

$Ga^{+3} + N^{-3} \rightarrow GaN$

$3Li^+ + 3e^- \rightarrow 3\ Li$

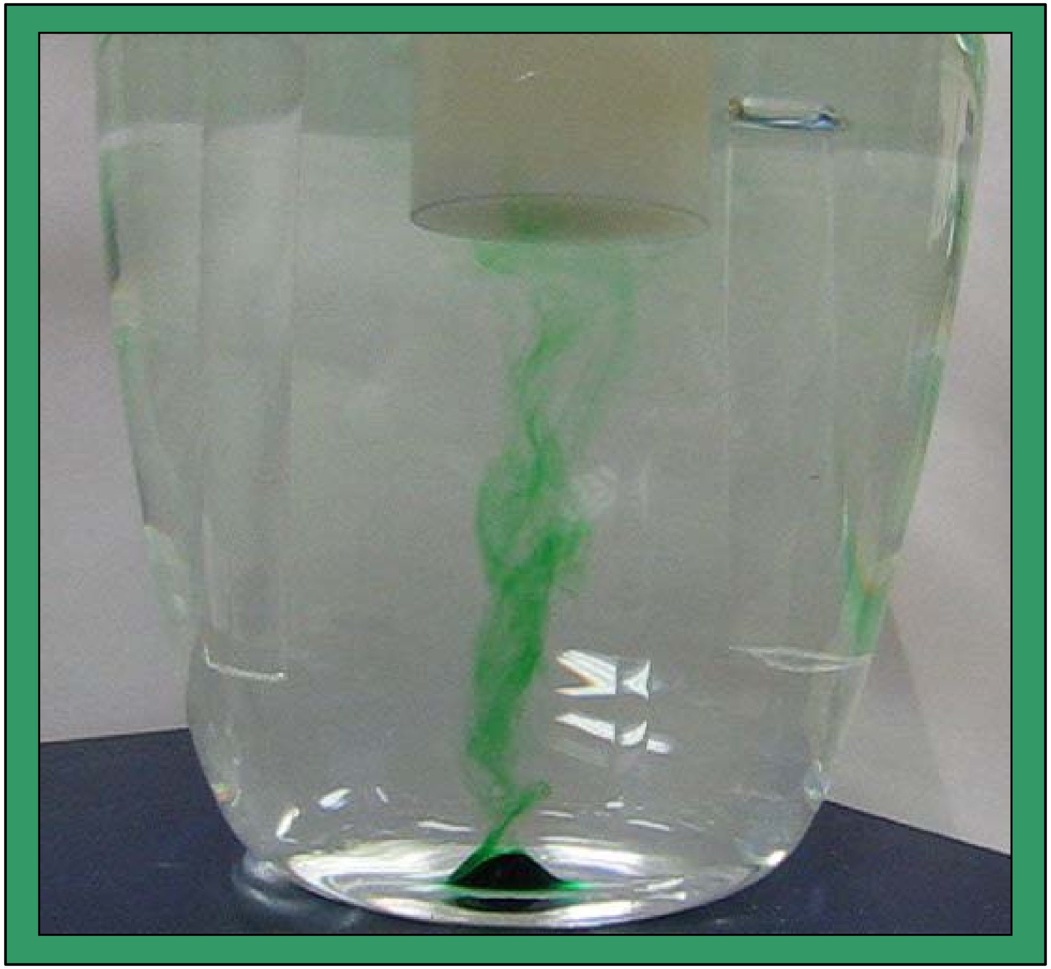
Sandia National Laboratories

SEM of RD-ESG Growth Run #1



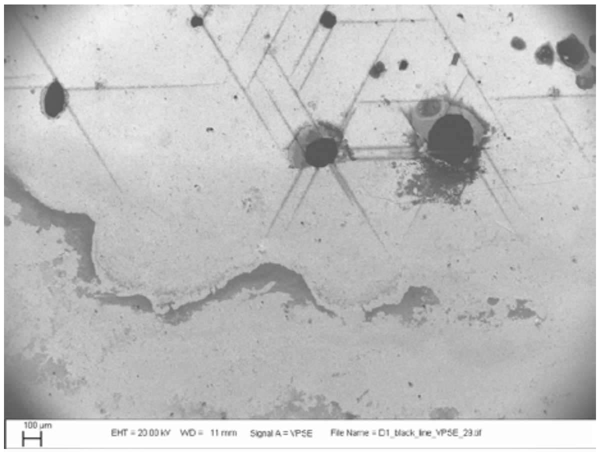
- SIMS revealed the layer to be a graphitic carbon layer, with Ga, N, and GaN clusters
  - GaN content was about 10%
  - Profile was consistent with an increasing concentration
- Problem with salt purity from supplier
  - Working it out with supplier
  - Developing in-house purification technique for reagent grade salt

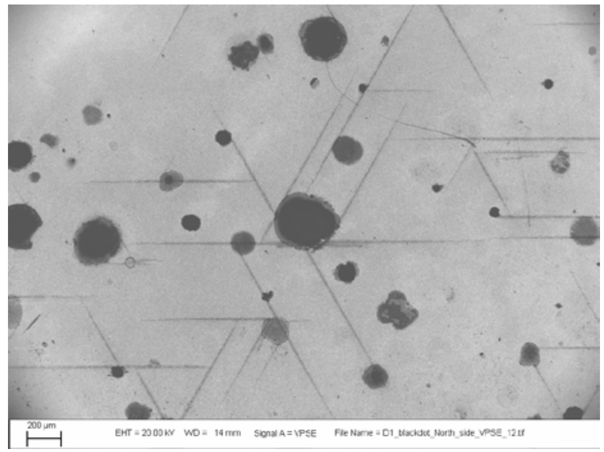
Room Temperature Convection Experiments

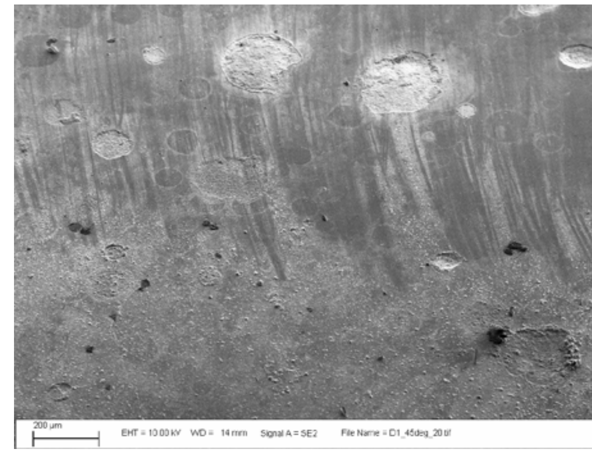


Under laminar flow conditions, the spinning seed will draw nutrient-containing fluid to the surface– if the electrodes are properly shaped and located.

First GNOEM RD-ESG Experiment







- **Hardware failure– susceptor sheared, not sure when**
- **Black line on sample surface delineated a higher, specular region and lower, roughened area**
- **Defect selective etching observed (several microns/hr)**
- **Highly encouraging for crystal quality**
  - **Must identify the conditions under which this takes place**
- **Polished cross sections of control and experiment sample consistently measure about 1⌠m thicker for experiment**