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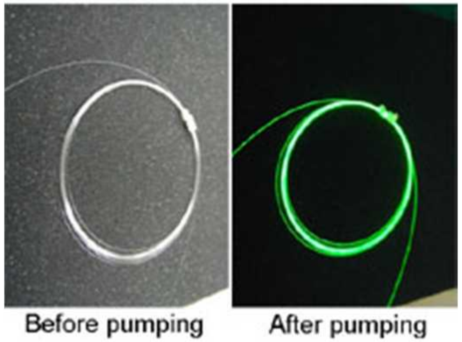
AML

Advanced Materials Laboratory

Erbium-doped fiber



Recycling of the nationally critical element erbium: electrochemical reduction of erbium coordination compounds in ionic liquids

Ryan F. Hess, Timothy J. Boyle, Timothy Lambert, Steven Limmer, Daniel Kammler, Leo Small, Jeremiah Sears, Adam Cook, and Michael Brumbach

Sandia National Laboratories

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Pictures from: en.wikipedia.org/wiki/Erbium and www.ntt.co.jp

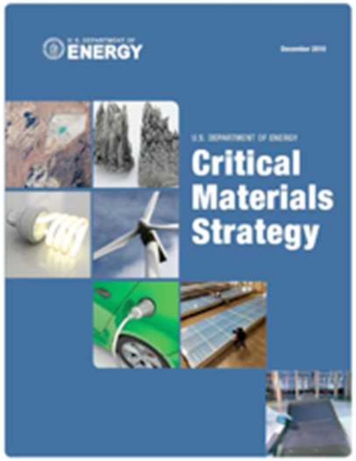
Outline

- The need to recycle lanthanide elements

- Erbium coordination chemistry in ionic liquids
  - Single crystal structures
  - Coordination environment in ionic liquids using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy

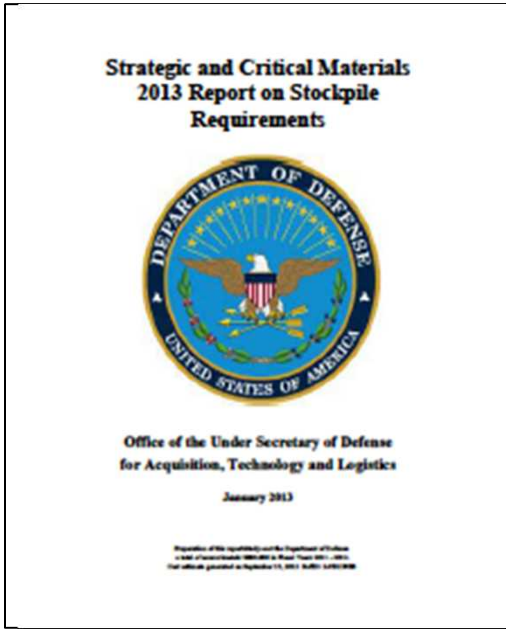
- Erbium electrochemistry in ionic liquids

‘Nationally Critical Materials’ are necessary to maintain the nation’s economy and defense.


ENERGY

Critical Materials Strategy

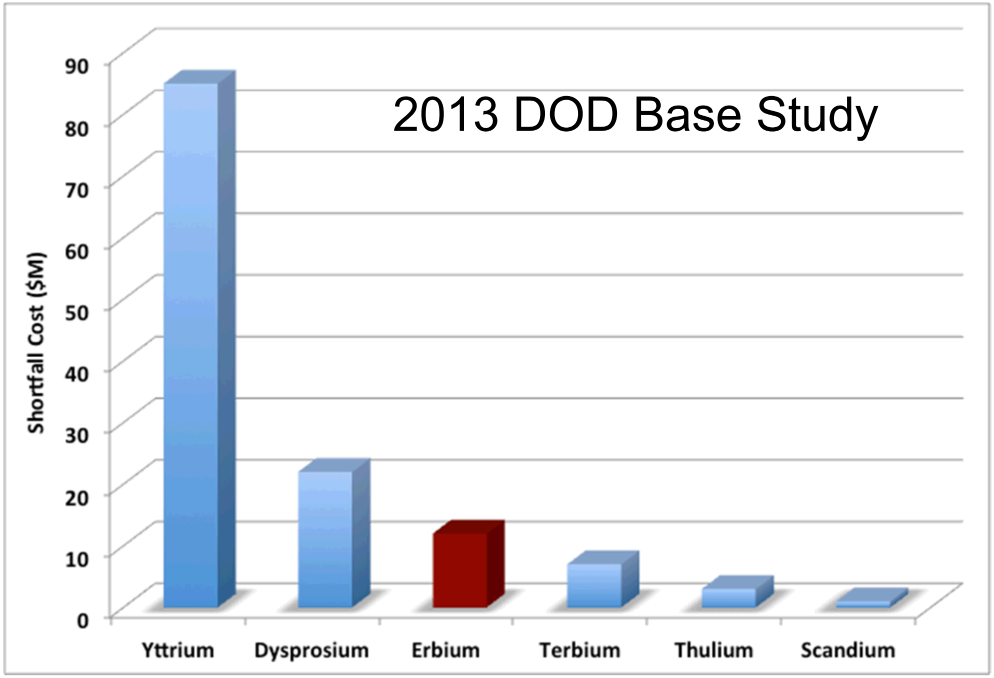
- **no U.S. Government-wide definition exists** - broadly, if a vital sector of the economy requires a mineral in order to function, that mineral would likely be deemed “critical.”
- from a national perspective, a strategic mineral may be defined as one that is important to the Nation’s economy, particularly for defense issues; doesn’t have many replacements; primarily foreign sourced.
- a nation’s ***perception of vulnerability to supply disruptions***, and of a need to safeguard its industries from repercussions of a loss of supplies.


Strategic and Critical Materials
2013 Report on Stockpile
Requirements

Office of the Under Secretary of Defense
for Acquisition, Technology and Logistics

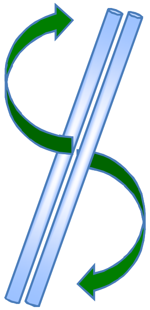
January 2013

This is an expensive problem!!


2013 DOD Base Study

RE-cycle a possible route to reduced dependency

New extraction methods are necessary to aid in the RE-utilization of other 'waste' RE-materials (i.e., fluorescent bulbs and magnets).



Currently, only 1% of the RE-containing consumables are recycled.

- Honda (Japan) recently announced that key materials for their hybrid automobiles (which include RE oxides) will be recycled.
- Rhodia (France) has begun to reactivate its production plant to recover Tb and other RE elements from magnets, windmill components, electric vehicles and hard disks.
- REEcycle (U. Houston) has a patented method to extract Dy/Nd from neo-magnets.
- Ames Laboratory and Critical Materials Institute has an imidazole borate ionic liquid to dissolve lanthanide oxides.

Primary Question: How does one recover elemental Er^0 with high purity?

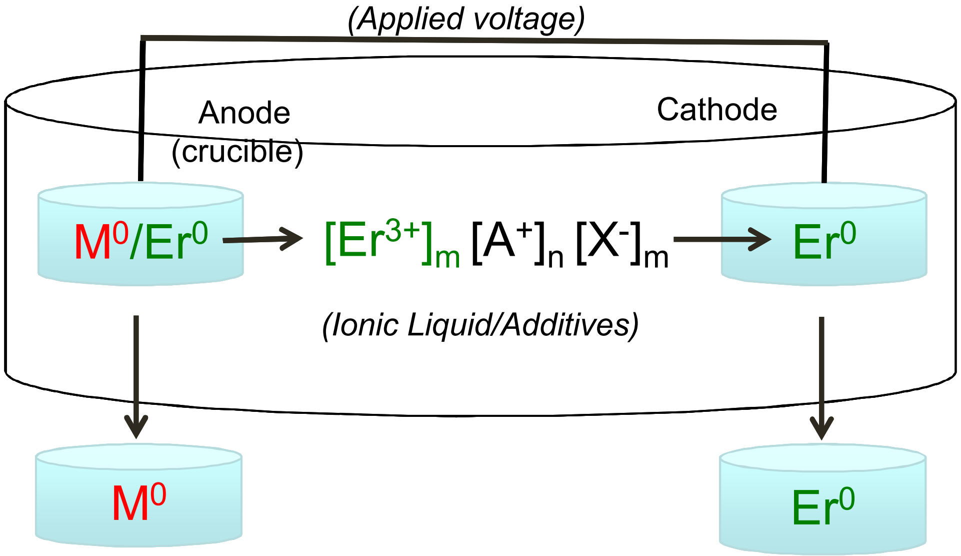
Standard reduction potentials indicates selective oxidation is thermodynamically possible

$Er^{3+} + 3e^- = Er^0$ $E^o = -2.32$ V

Ionic Liquids$[A^+][X^-]$:

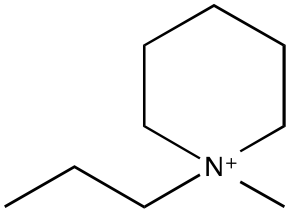
- electro-chemical window > 4-5 V
- negligible vapor pressure
- low viscosity
- no H_2 generation
- IP opportunities

- Precedence for reduction for Rare Earths

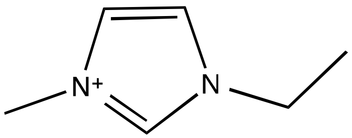


Advantages of Ionic Liquids

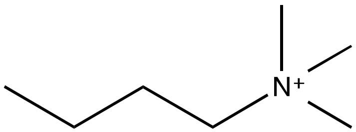
- Low volatility and flammability
- Highly tunable properties
- Wide electrochemical windows
  - Er has a very negative reduction potential! Can’t use water.



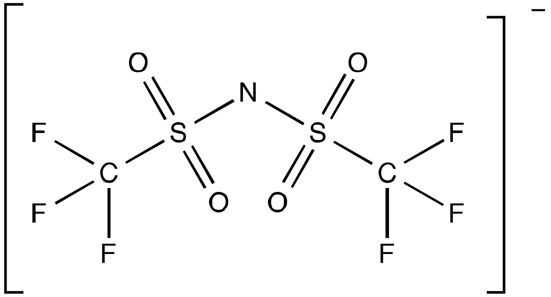
piperidinium



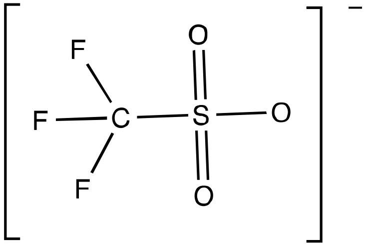
imidazolium



alkylammonium



bis(trifluoromethylsulfonyl)imide
(NTf_2)



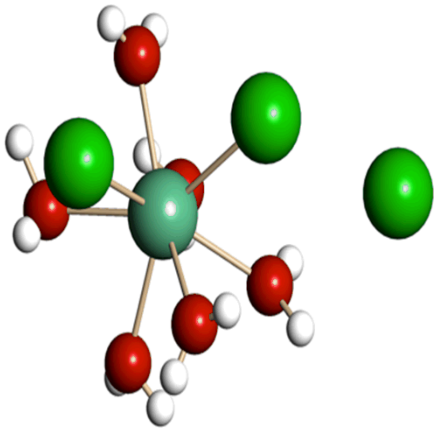
trifluoromethanesulfonate
(OTf)

Erbium Coordination Chemistry

- For our early studies we have focused on using impure Er metal as our starting material

- We have explored a range of options for dissolving Er metal including: 3M HCl, triflic acid, bis(trifluoromethylsulfonyl)imide, and hydrogen peroxide

$$Er^0 + HCl(aq) \rightarrow [Er(Cl)_2(H_2O)_6][Cl]\bullet H_2O$$



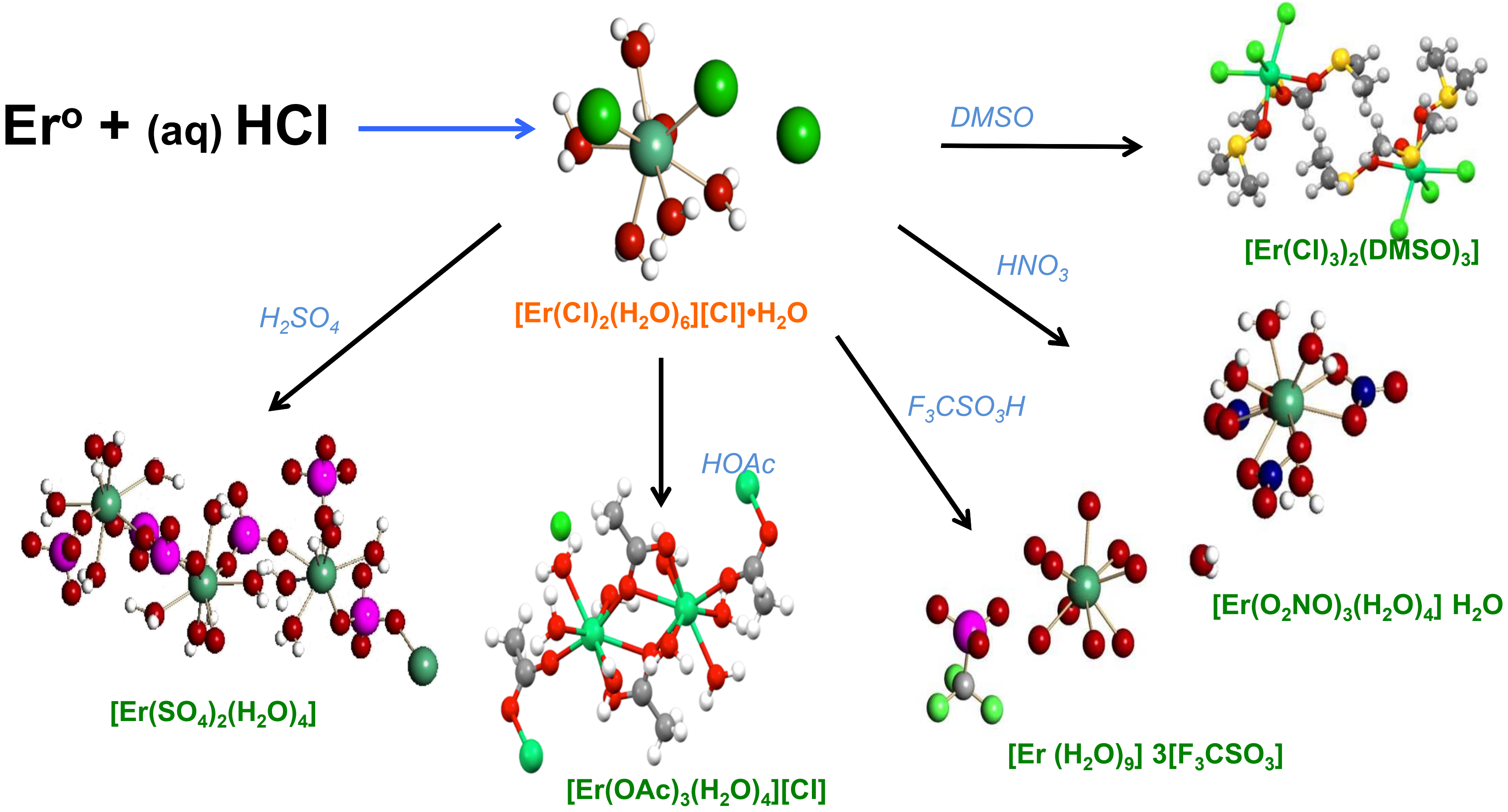
Solubility Issues in IL’s of Interest

- The Er chloride hydrate formed on reaction with HCl isn’t very soluble in the triflate and sulfonylimide IL’s

- Xxxx has shown that lanthanide sulfonylimides can be formed on reaction of the metal with an aqueous bis(trifluoromethylsulfonyl)imide solution

- We also found that Er metal rapidly dissolves in triflic acid in the presence of a small amount of water

- To address the soluble issue in a less expensive fashion we synthesized a number of erbium coordination compounds in the hopes of finding one with a high solubility in IL’s and will allow for easy electrochemical reduction



Er^o + (aq) HCl

$[Er(Cl)_2(H_2O)_6][Cl]•H_2O$

DMSO

$[Er(Cl)_3)_2(DMSO)_3]$

HNO_3

$[Er(O_2NO)_3(H_2O)_4]\ H_2O$

F_3CSO_3H

$[Er\ (H_2O)_9]\ 3[F_3CSO_3]$

HOAc

$[Er(OAc)_3(H_2O)_4][Cl]$

H_2SO_4

$[Er(SO_4)_2(H_2O)_4]$

EXAFS Studies of Erbium in IL’s

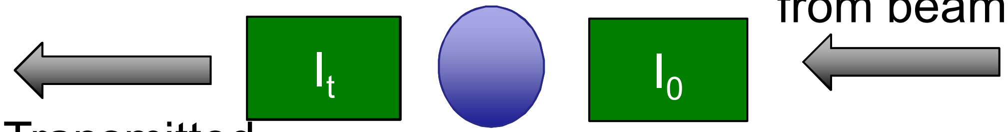
- Extended X-ray Absorption Fine Structure (EXAFS) provides valuable information regarding the local coordination environment of specific elements of interest

- We studied the Er coordination environment in IL’s and solvents of interest at the X23A2 beamline at Brookhaven National Lab’s National Synchrotron Light Source (NSLS-I) using the Er L_3 edge

- Solid samples were collected in transmission mode while liquid samples were collected in fluorescence mode using a custom-built cell based on a design by XXXX

- Attempts were made to collect in-situ electrochemical reduction data during the EXAFS and XANES experiments

Quick EXAFS Overview



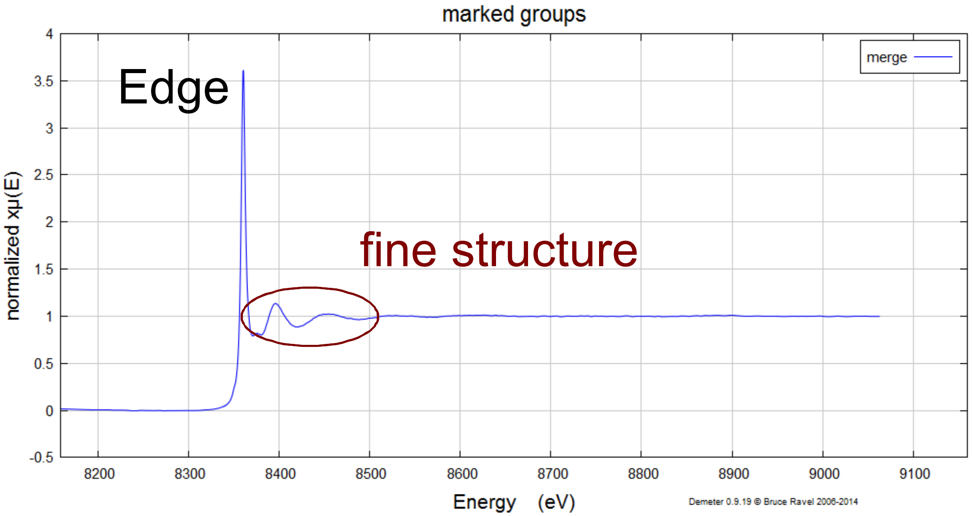
Sample

Incident x-rays from beamline

I_t

I_0

Transmitted x-rays

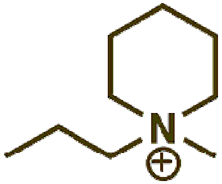


In EXAFS we measure the energy-dependent x-ray absorption spectrum

The oscillation that occurs above the absorption edge is the “EXAFS”

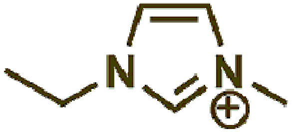
EXAFS provides unique information on local coordination structures in liquid samples

Ionic Liquids used for Er experiments



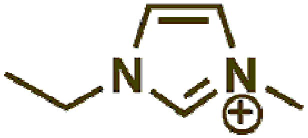
$(CF_3SO_2)_2N^{\ominus}$

1-Methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide



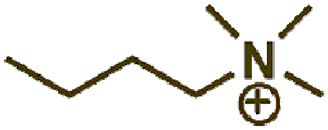
$CF_3SO_3^{\ominus}$

1-Ethyl-3-methylimidazolium triflate



$(CF_3SO_2)_2N^{\ominus}$

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide



$(CF_3SO_2)_2N^{\ominus}$

Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide

$(CF_3SO_2)_2N^{\ominus}$

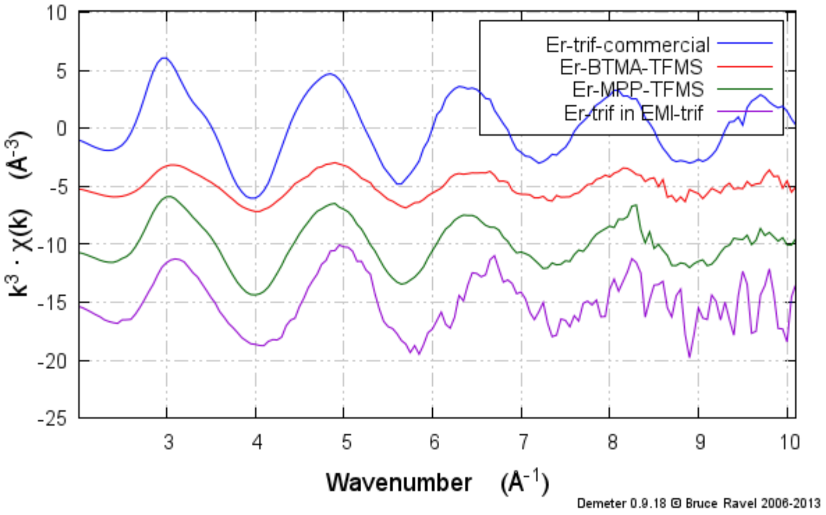
1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide

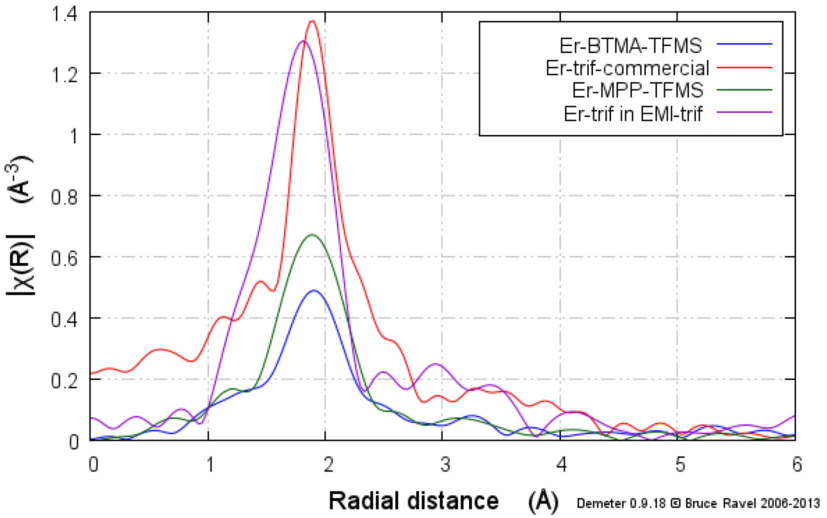
Er Coordination in IL's

In IL's of interest do the Er 1st and 2nd coordination shells more closely resemble: direct Er-IL bonding, Er triflate, or Er hydrate?

Does the Er environment change with different IL's or solvents?

Can we observe Er reduction in real time???





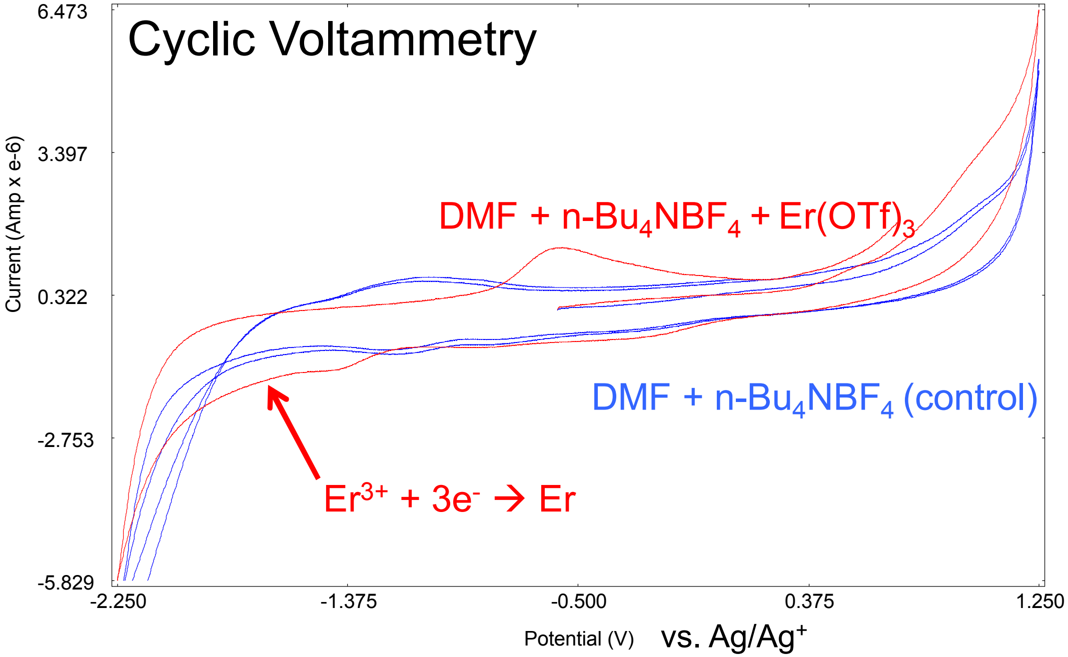
For three IL's tested it appears that they all have at least the same 1st shell and possibly the 2nd – very similar to Er(trif)$_3$

Er^{3+} Electroreduction Experiments

Solvent	Salt	CVs suggest dep?	Deposition Potential	Film contents via EDS
DMF	10 mM $ErCl_3$	Yes	N/A	N/A
DMF	100 mM $Er(OTf)_3$	Yes	-2.0 V vs. Ag/Ag^+	Er, O
butyltrimethylammonium NTf_2	10 mM $Er(OTf)_3$	Yes	-2.5 V vs. Pt wire	Er, C, N, F, O
1-methyl-1-butylpyrrolidinium dicyanamide (Tim Lambert's IL)	100 mM $Er(OTf)_3$	Yes	-2.5 V vs. Pt wire	Er, Ag, C, N, O gel-like film in areas Ag(111) in XRD
1-methyl-1-propylpiperidinium NTf_2	10 mM $Er(OTf)_3$	Yes	-2.5 V vs. Pt wire	Er, C, N, O, S, F
1:1 DMF:Tim Lambert's IL	100 mM $Er(OTf)_3$	Yes	-2.5 V vs. Ag/Ag^+	Er + some C,N (no F)
[1-ethyl-3-methylimidazolium $Cl]_3Er(OTf)_3$	(25 mol% $Er(OTf)_3$)	Yes	-2.5 V vs. Pt wire	No deposition. Lots of bubbles during dep (Cl_2?)
[1-butyl-3-methylimidazolium $Cl]_3Er(OTf)_3$	(25 mol% $Er(OTf)_3$)	Yes	-2.5 V vs. Pt wire	No deposition. Lots of bubbles during dep (Cl_2?)
[1-butyl-3-methylimidazolium $Br]_3Er(OTf)_3$	(25 mol% $Er(OTf)_3$)	Yes	-3.0 V vs. Pt wire	No deposition.

- All ILs and Er salts dried at 75 °C, <0.5 mTorr for 72 hrs
- Anhydrous DMF kept with 3Å sieves.
- Deposit onto 100 nm Pt/40 nm Ti/SiO_2/Si (100).
- Hold for 2 hours at deposition potential.

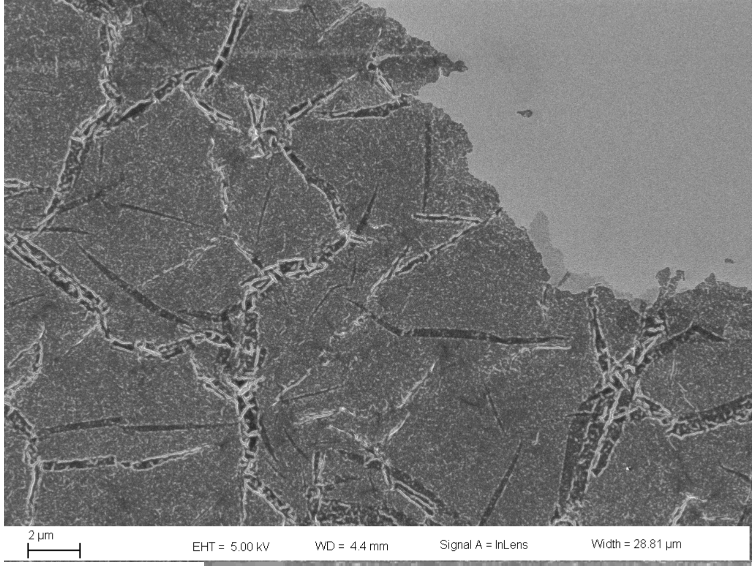
Er(OTf)$_3$ Reduction in DMF

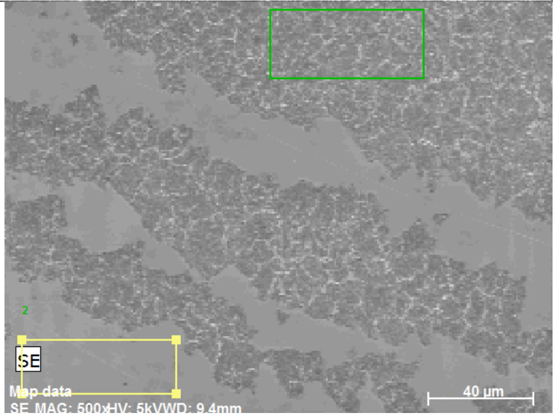

Cyclic Voltammetry

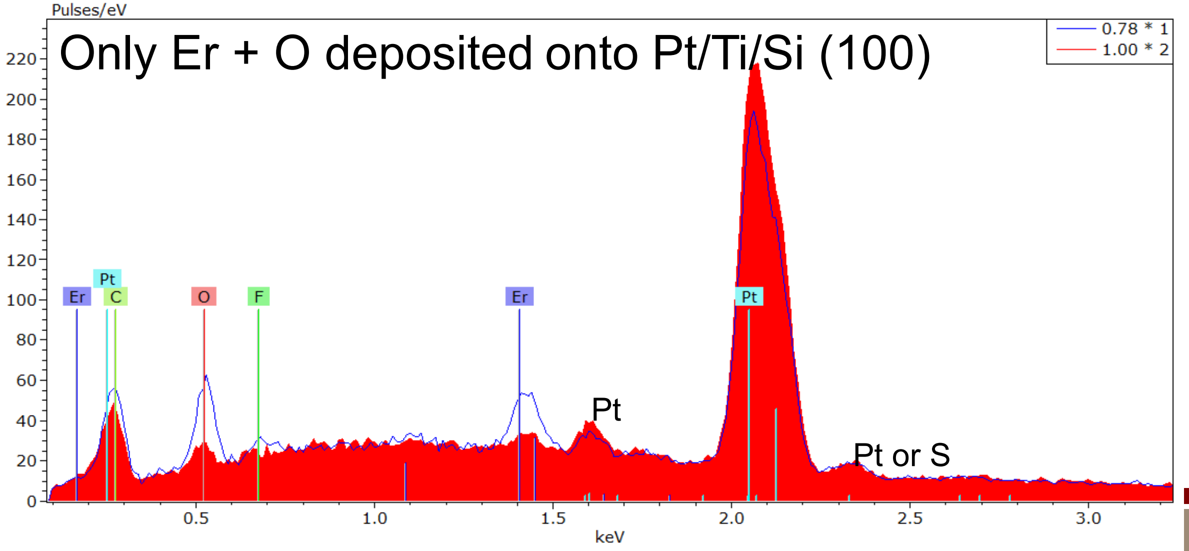
DMF + n-Bu$_4$NBF$_4$ + Er(OTf)$_3$

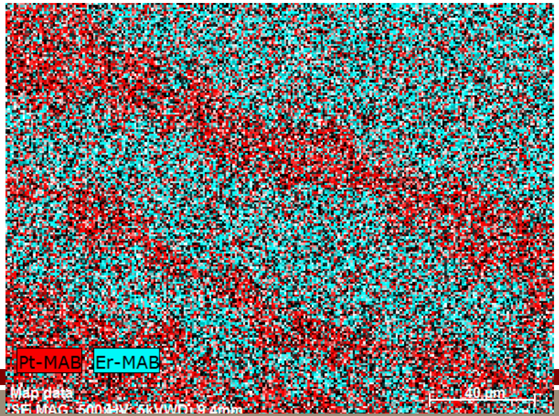
DMF + n-Bu$_4$NBF$_4$ (control)

Er^{3+} + 3e$^-$ → Er





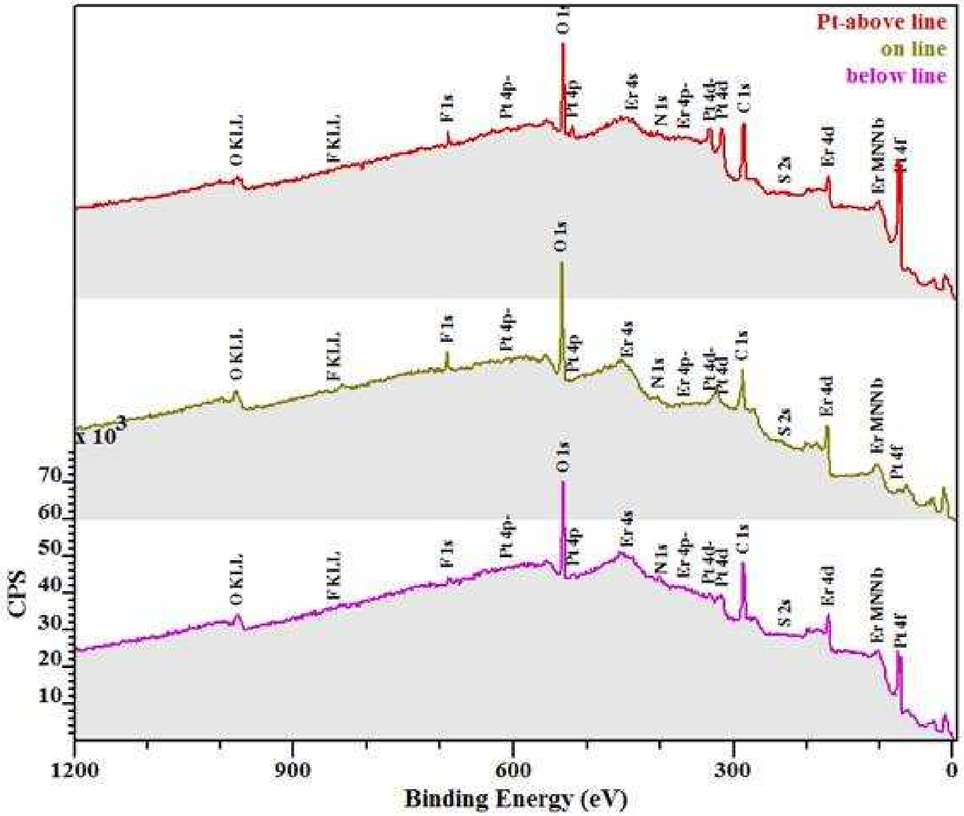

Only Er + O deposited onto Pt/Ti/Si (100)



Characterization of film from $Er(OTf)_3$ reduction in DMF X-ray Photoelectron Spectroscopy

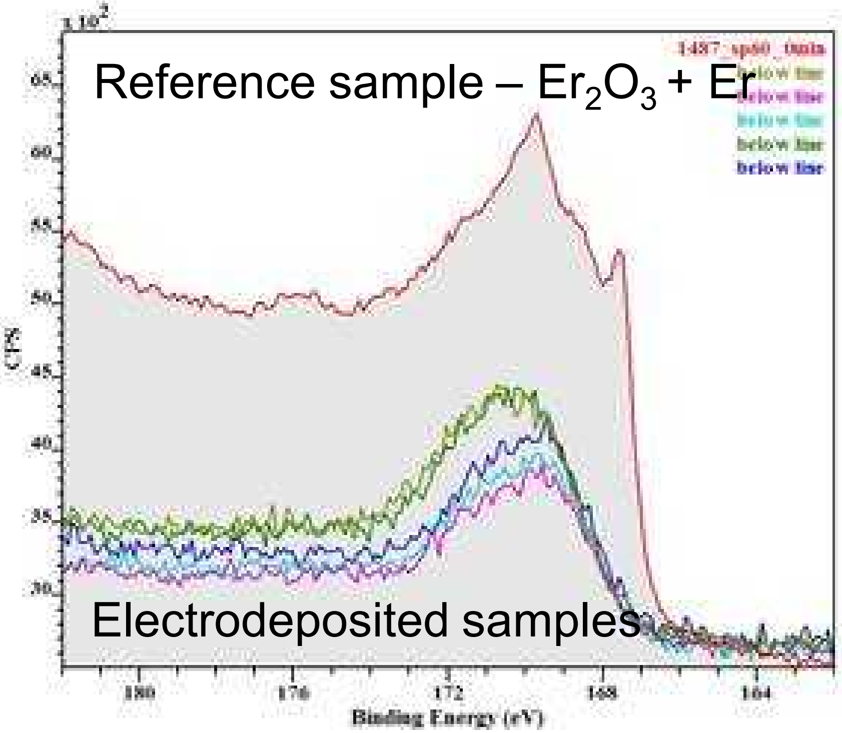
Only Er, O, C, Pt present

No S, N, minimal F → no triflate left in electrodeposited area



Survey spectra – above, on, below “water” line

All erbium is oxidized (by air?).



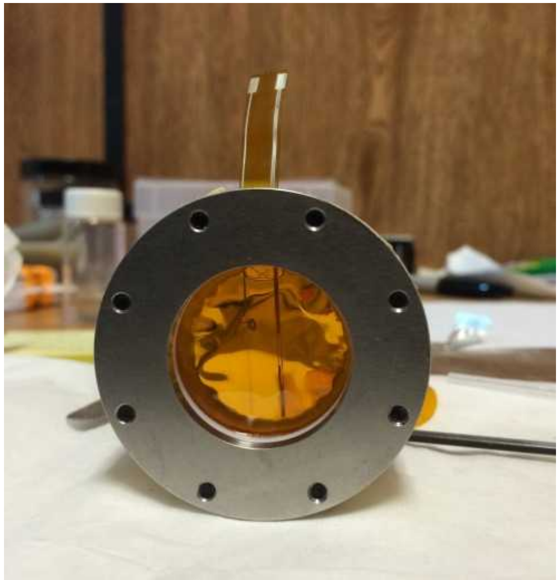
Reference sample – Er_2O_3 + Er

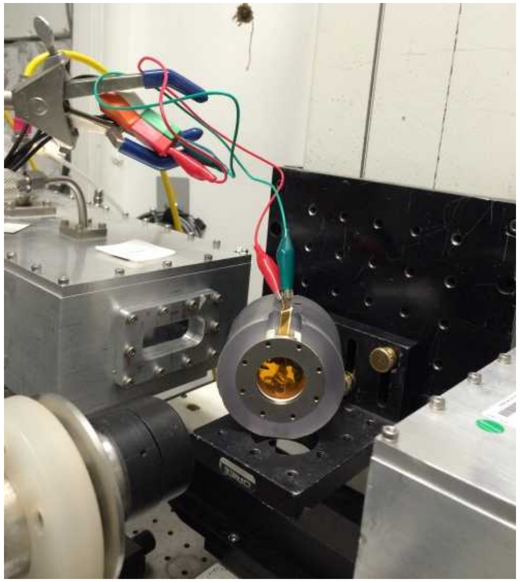
Electrodeposited samples

Erbium 4d

Attempt at In-situ EXAFS E-chem

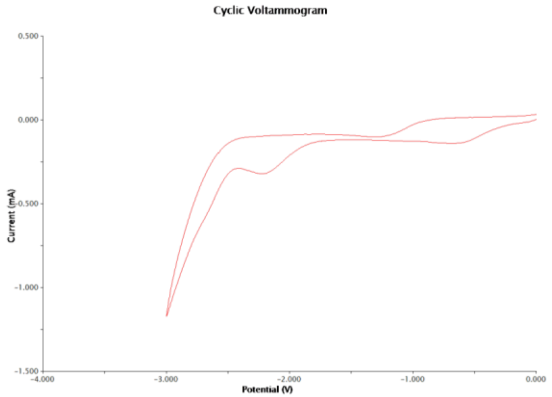
- We carried out a series of cyclic voltammetry and chronoamperometry experiments in search of a system that will allow for the clean reduction of Er^{3+} to Er^0

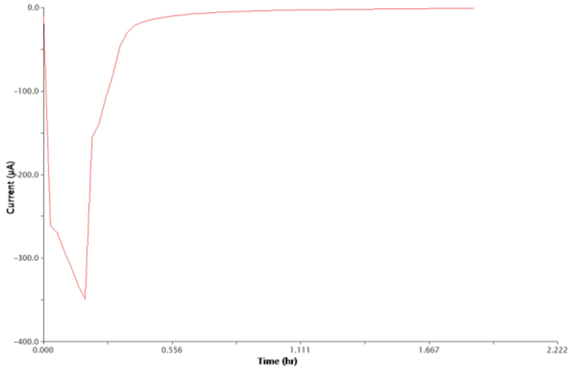




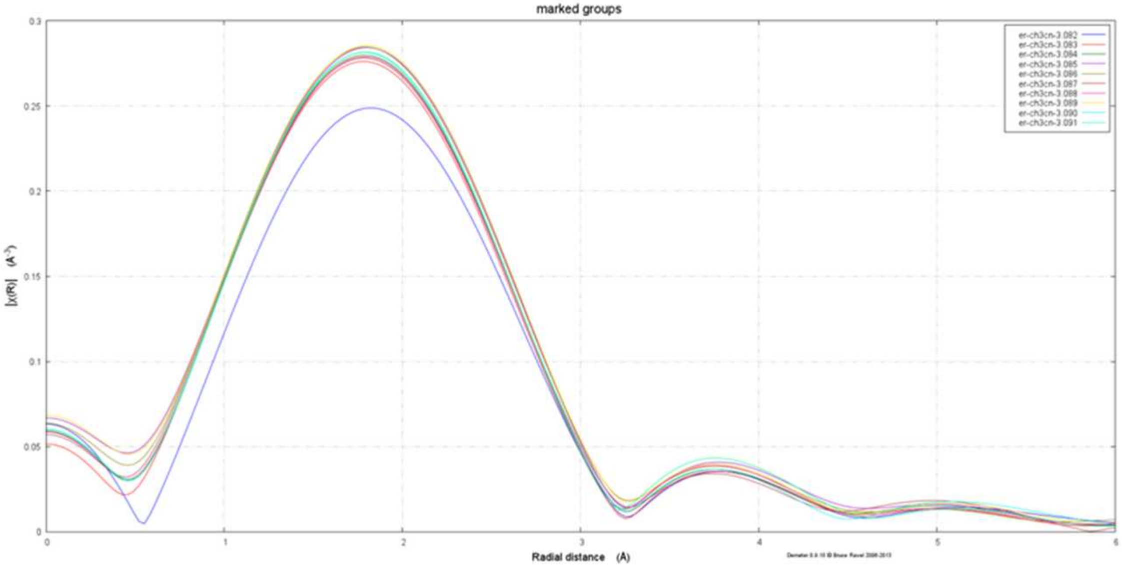
In-situ XANES and Chronoamperommetry

- In-situ experiment using acetonitrile solvent with TBA/TFMS as supporting electrolyte
- Consists of Kapton windows with silver working and counter electrodes printed on them using SNL direct write technology





Chronoampergram



XANES pseudo-radial distribution plot

Held fixed potential of -2.6V for approximately 2 hours while collecting X-ray absorption data

Unfortunately we did not see a detectable change in Er structure over time nor a change in oxidation state

Summary

- The reaction of Er0 with HCl generates a chloride-hydrate complex which can be used as a spring board for the synthesis of a range Er coordination compounds with varying degrees of solubility in IL’s

- The family of triflate and sulfonylimide IL’s have wide electrochemical windows and appear to allow for the reduction of Er3+ to Er0 though the deposited Er material to date is poorly formed though the cleanest film so was deposited in DMF not an IL

- EXAFS experiments conducted at NSLS-I in three different IL’s using Er(OTf)3 as the starting material do not show any coordination of the IL with the metal in the 1st or 2nd shell (data analysis is still on-going)

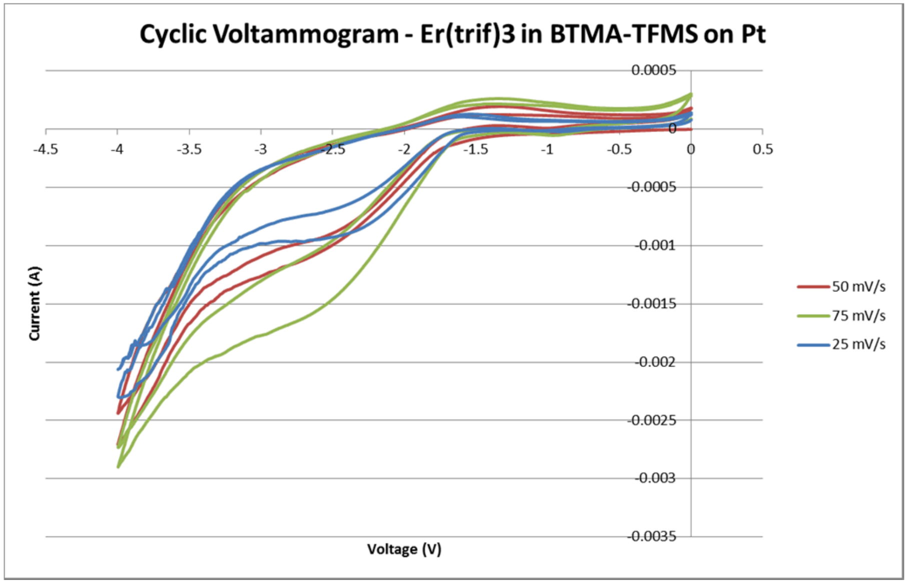
Acknowledgements

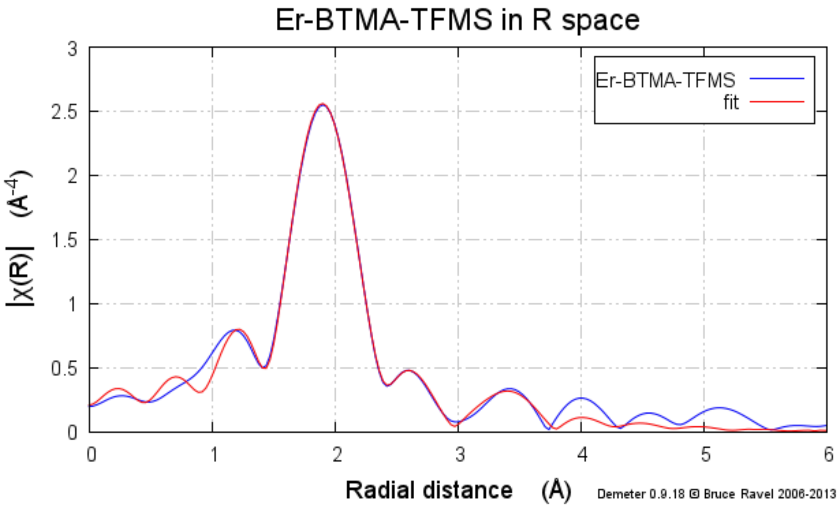
- Timothy Boyle, Jeremiah Sears, Michael Neville, and Daniel Yonemoto – erbium precursor chemistry
- Timothy Lambert – ionic liquid and extractant synthesis
- Steven Limmer and Leo Small - electrochemistry
- Michael Brumbach and Adam Cook – EXAFS data collection and in-situ electrochemistry cell design
- Joseph Woicik (NIST) – EXAFS data collection
- Funding: SNL Laboratory Directed Research &Development program

Extra

Er^{3+} Electrochemistry

- Studied electrochemistry of Er triflate in BTMA-TFMS ionic liquid – looking for Er reduction and effect of scan rate
  - Also did some experiments looking at C and Au working electrodes





```
name      N      S02    sigma^2    e0      delr       Reff       R
=====================================================================
O4.1     4.000  0.609  -0.00024  -3.278 -0.07454  2.32310  2.24856
O6.1     2.000  0.609   0.00566  -3.278 -0.37693  2.43560  2.05867
O1.1     2.000  0.609  -0.00307  -3.278 -0.06295  2.46550  2.40255
Er3.1    2.000  0.609   0.01414  -3.278  0.09988  3.47110  3.57098
N1.1     1.000  0.609   0.01051  -3.278  0.07628  2.93750  3.01378
```