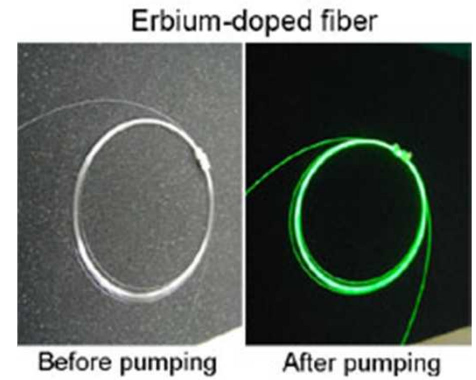
Advanced Materials Laboratory



Recycling Rare Earth Elements Using Ionic Liquids: An Electrochemical Approach

Ryan F. Hess, Timothy J. Boyle, Timothy Lambert, Daniel Kammler, Leo Small, and Jeremiah Sears

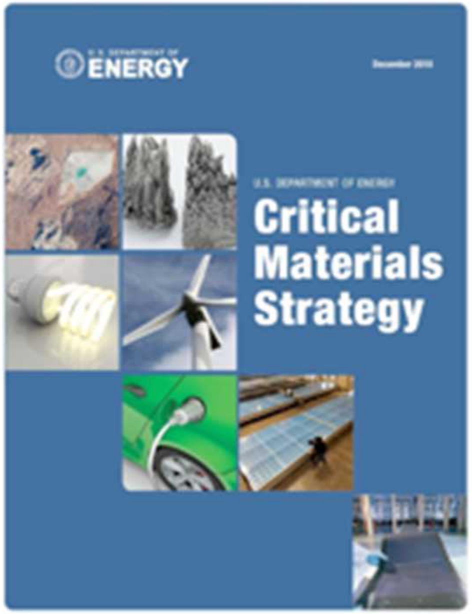
Advanced Materials Laboratory

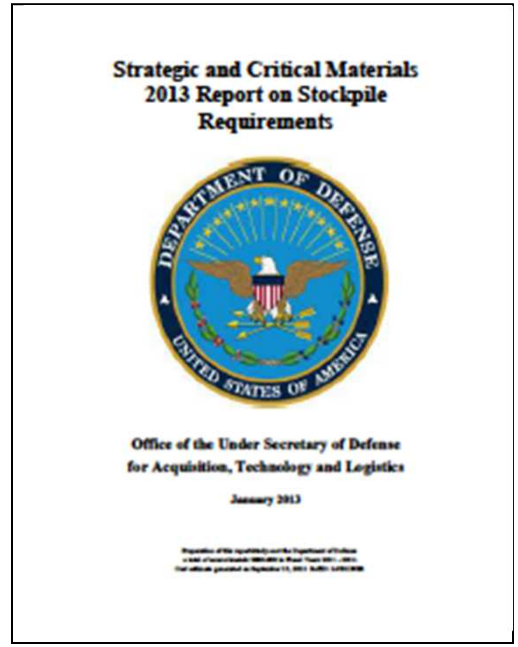
Sandia National Laboratories

This work was supported by the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories and gratefully acknowledge the use of the Bruker X-ray diffractometer purchased via the National Science Foundation CRIF:MU at the University of New Mexico (CHE04-43580). Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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

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

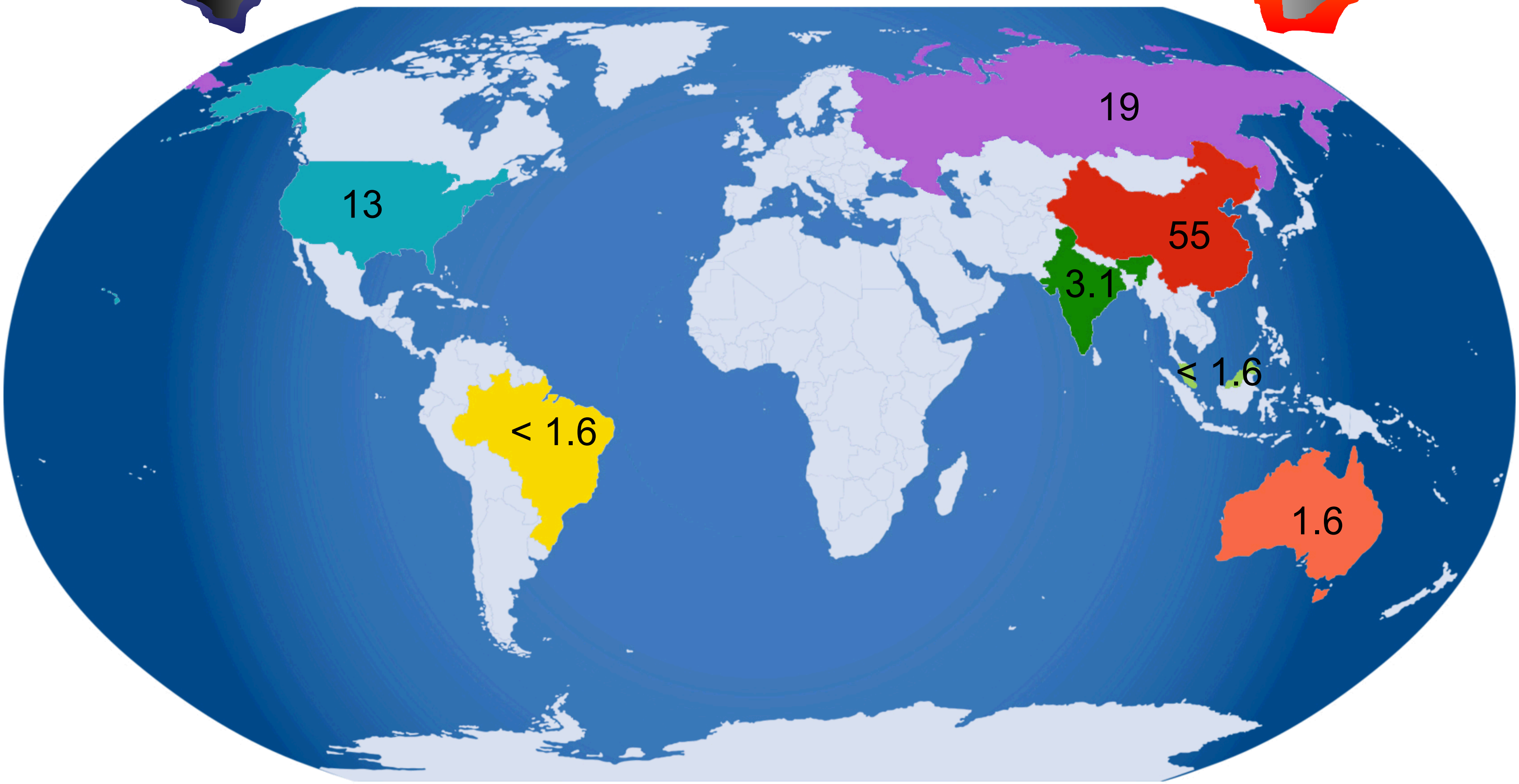




RE elements have found widespread utility:

- *energy technology* • *transportation* • *electronic displays* • *guidance systems*
- *national security* • *lasers* • *radar* • *sonar systems*

Finite Supply



Other: 22 million metric tons in reserve of rare earth elements

Toyota Prius and the lanthanides

Les Terres Rares Uniques, Incontournables, strategiuqes
-J. Lucas *Universite de Rennes*

Sandia National Laboratories

UV Cut Glass
- Ce

Diesel Fuel Additive
- Ce
- La

Glass and Mirrors Polishing Powders
- Ce

Video Display
- Eu
- Y
- Ce

Hybrid NiMH Battery
- La (> 20 lbs)
- Ce

Component Sensor
- Y

Catalytic Converter
- Ce/Zr
- La (> 50 g/Lcat)

25+ Electric Motors Throughout vehicle
- Nd Magnets

High Performance Rubber Tires
- Nd

Headlight Glass
- Nd

Hybrid Electric Motor And Generator
- Nd (> 2 lbs)
- Pr
- Dy
- Tb

"Analysts have called the Prius™ one the most rare-earth–intensive consumer product ever made."

Power Hungry – The myths of 'green' energy and the real fuels of the future
-Robert Bryce (2011) *PublicAffaris*

Also used in vibration units

• **Nd** • **Tb** • **Dy**

Phone polish

• **Ce**

Alloys in speaker and microphone magnets

• **Pr** •**Nd** •**Gd**

Rare Earth Element compounds are used to produce colors in the screen. Some even reduce UV light penetration into the phone

• **Y** •**La** • **Pr** •**Eu** •**Gd** •**Tb** •**Dy**

- IPhone: 8 different rare-earth metals (~74.5 million iPhones sold per quarter)
- Series of phones: 16/17 rare-earth metals used (no promethium)
- Few grams rare-earth per phone

Compound Interest
Smartphone smart chemistry. Brian Rohrig. ACS chem matters.
ACS reactions video
PBS where to find rare earth elements. Ainissa Ramirez
The New York Times

RE-cycle a possible route to reduced dependency

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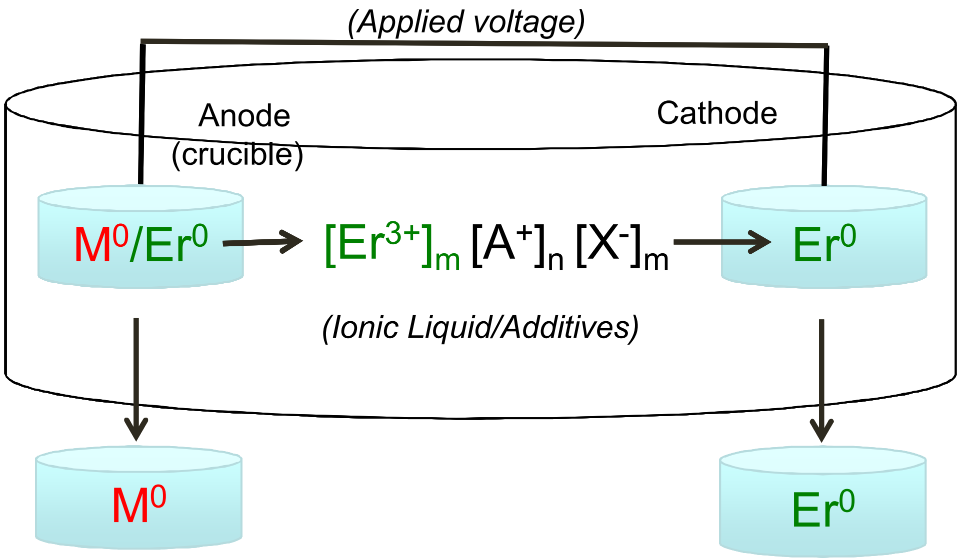
How does one recover elemental Er^0 with high purity?

We are also interested in the chemistry of Sc – often included with the RE's

Standard reduction potentials indicates selective oxidation is thermodynamically possible

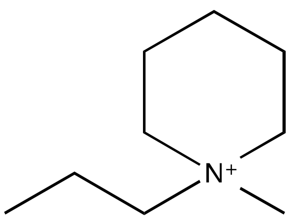
$Er^{3+} + 3e^- = Er^0$ $E^o = -2.32$ V

Precedence for reduction for Rare Earths: La, Sm, Eu, Dy

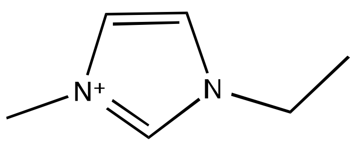


Advantages of Ionic Liquids

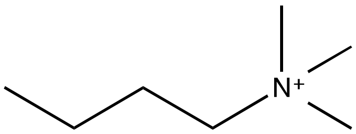
- Low volatility and flammability
- Highly tunable properties
- Wide electrochemical windows
  - Er has a very negative reduction potential! Can't use water.



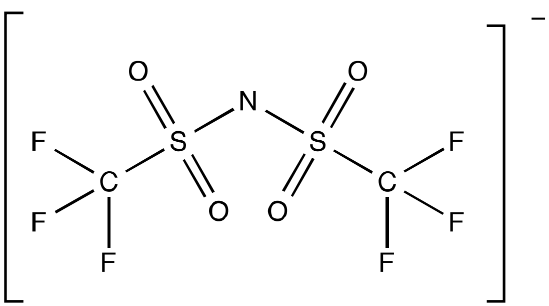
piperidinium



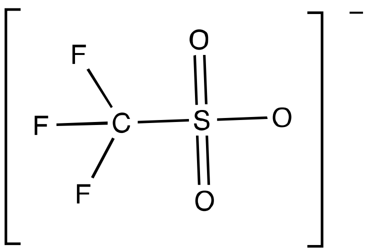
imidazolium



alkylammonium



bis(trifluoromethylsulfonyl)imide
(NTf_2), aka **TFSI**, aka **bistriflimide**



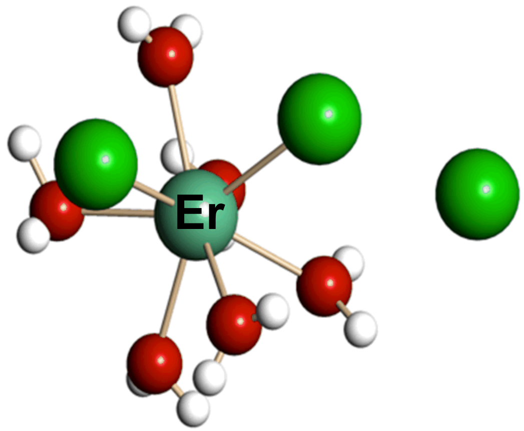
trifluoromethanesulfonate
(OTf), aka **triflate**

Erbium Coordination Chemistry

- For our 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, and bis(trifluoromethylsulfonyl)imide

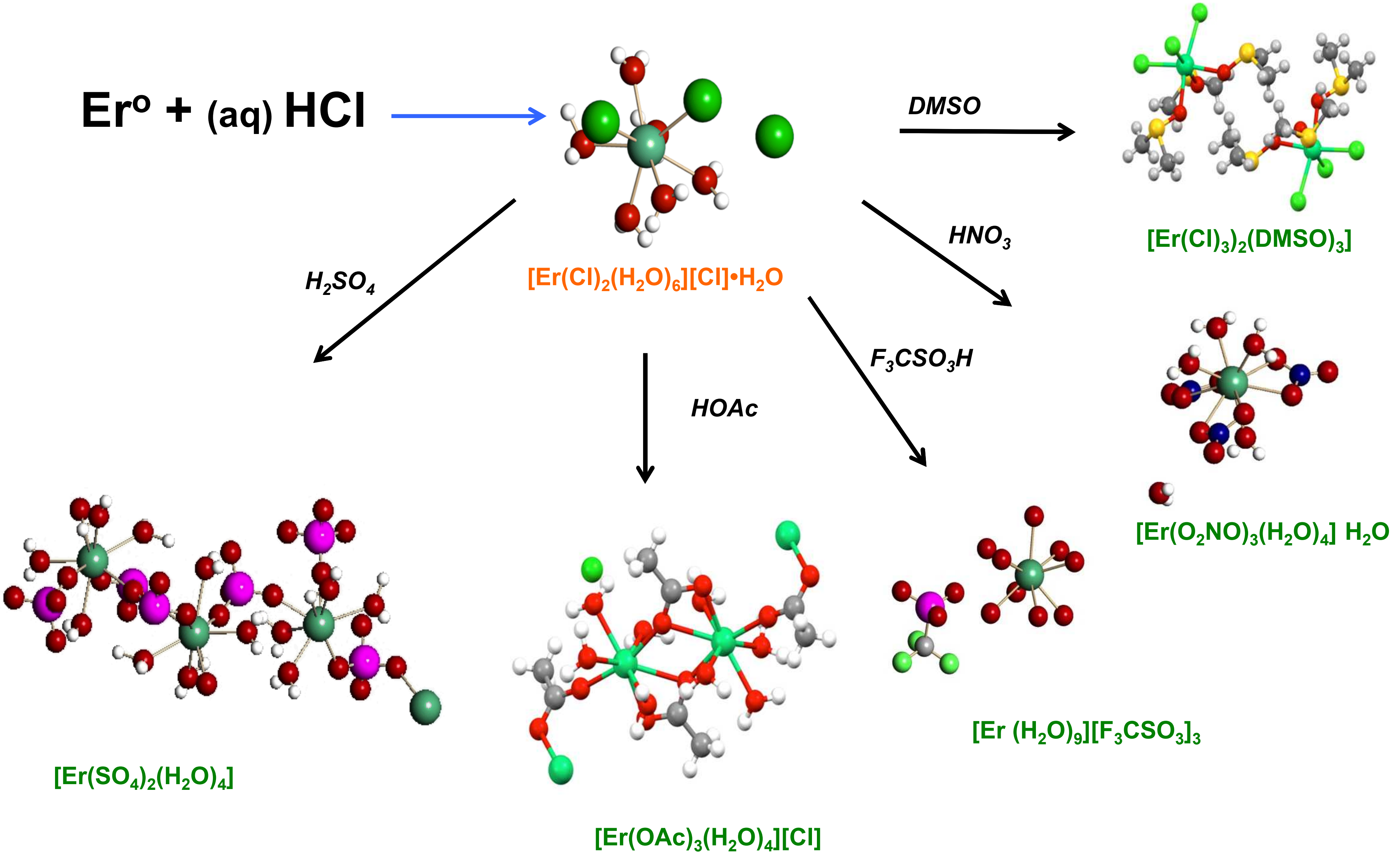
$$Er^0 + HCl(aq) \longrightarrow [Er(Cl)_2(H_2O)_6][Cl] \bullet H_2O$$



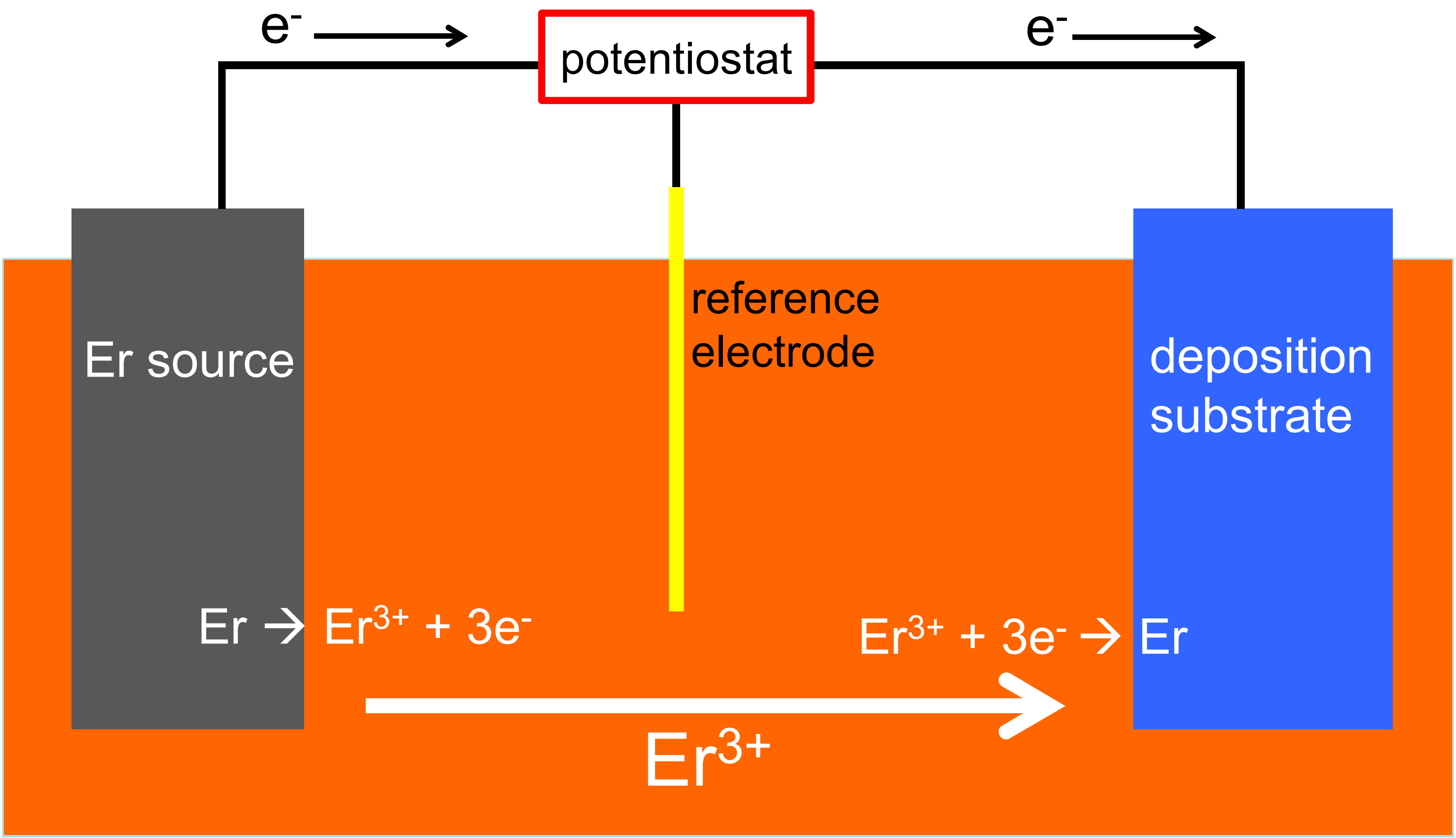
ErO_6Cl_2
Distorted square antiprisms

Initially published by Rogers' group: Rogers R.D., Kurihara L.K. Lanthanide and Actinide Research, 1986, 296-306

Fundamental coordination chemistry of Er being further developed



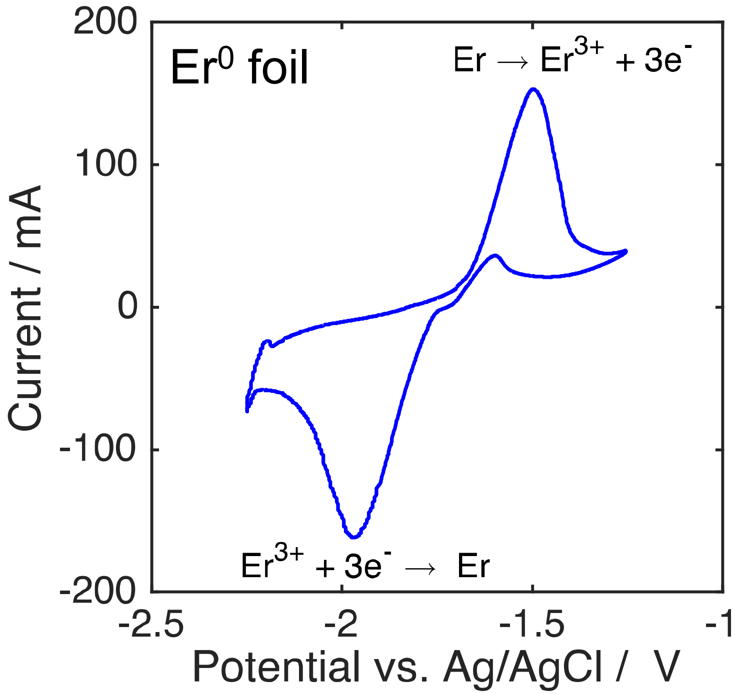
Electrorefining Erbium



Electrochemically move erbium from source to target substrate.

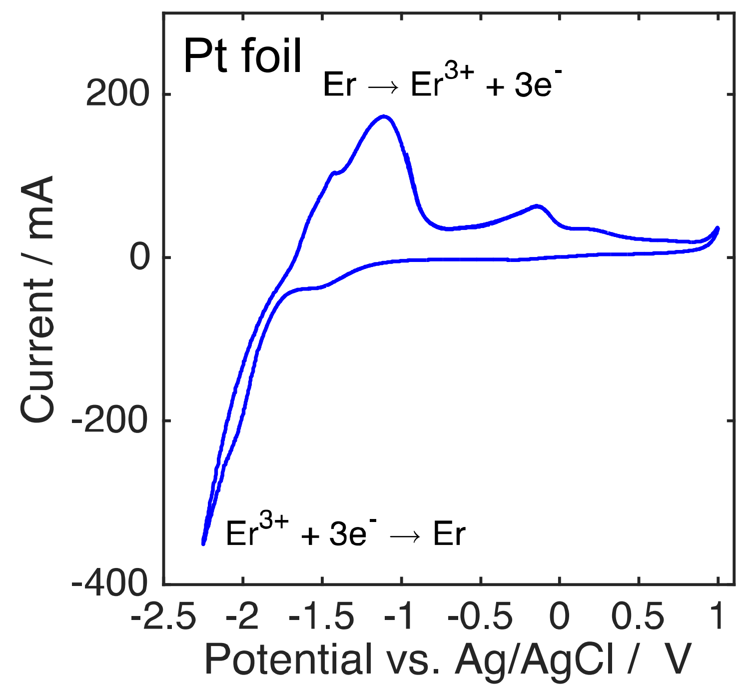
Electrorefining in Molten Salts

Erbium is easily oxidized into solution…



LiCl-KCl-CsCl
2 wt% $ErCl_3$
420 °C
100 mV/s
5th scan
2 cm² electrodes

…and reduced onto platinum.



>90% Coulombic efficiency on 250 mg scale at ***420 °C***

Inert environment with heat-tolerant materials required!

Er^{3+} Electroreduction Experiments

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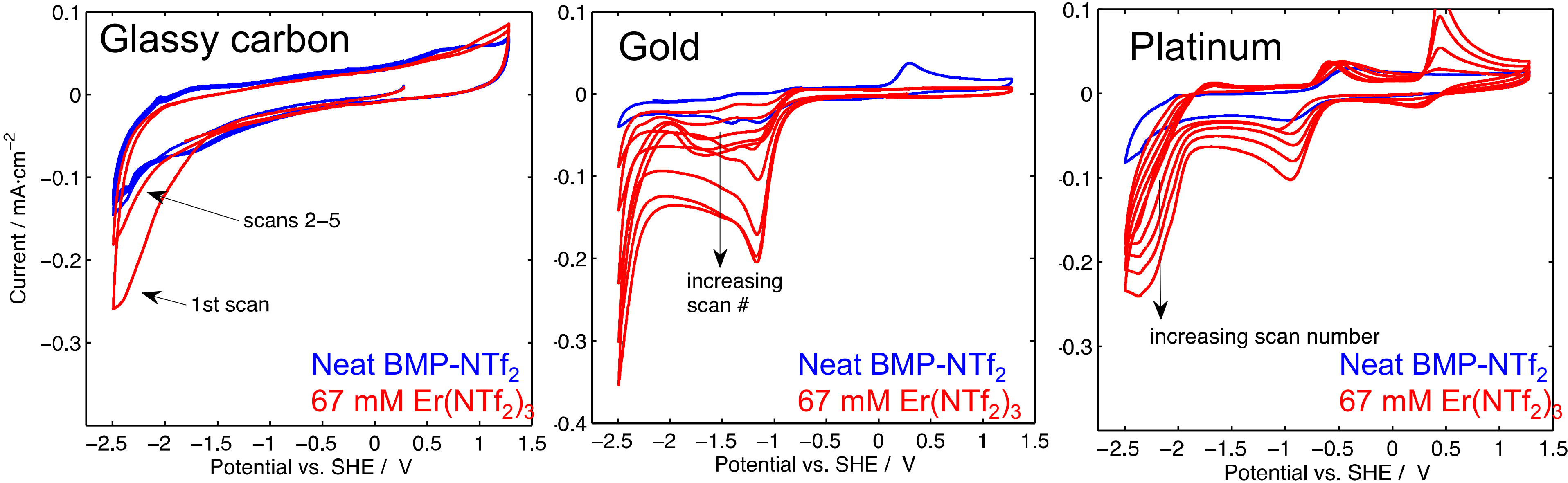
Solvent	Salt	CVs suggest dep?	Deposition Potential	Film contents via EDS
DMF	**100 mM $Er(OTf)_3$**	**Yes**	**-2.0 V vs. Ag/Ag^+**	**Er, O**
butyltrimethylammonium NTf_2	10 mM $Er(OTf)_3$	Yes	-2.5 V vs. Pt wire	Er, C, N, F, O
1-methyl-1-butylpyrrolidinium dicyanamide (tailored IL fromTim Lambert's)	100 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:dicyanamide 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

Effect of Electrode Material



Theoretical $\mathbf{Er^{3+} + 3e^- \rightarrow Er^0}$ is at -2.33 V for 1 M Er^{3+}.

Electrolyte: 1-butyl-1-methylpyrrolidinium NTf$_2$ – dried >48 h at 100 °C, <0.5 mTorr

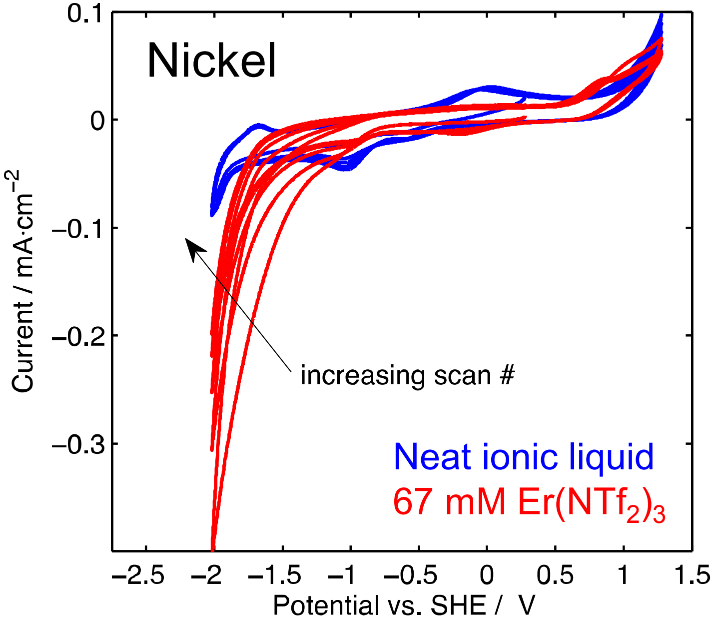
67 mM Er(NTf$_2$)$_3$ from Ryan + Isabella – dried >48 h at 100 °C, <0.5 mTorr

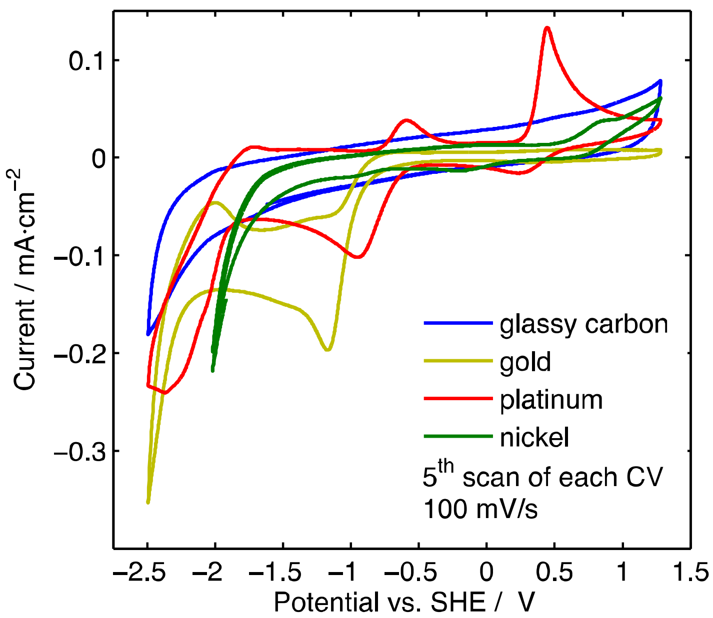
Reference electrode: Ag wire in 10 mM AgNTf$_2$ in electrolyte (no Er). Potentials referenced to ferrocene.

Counter electrode: Pt wire

100 mV/s scan rate

Effect of Electrode Material II





Au, Pt, and Ni show increased reduction currents at potentials < -2 V when $Er(NTf_2)_3$ is in solution, consistent with $Er^{3+} + 3e^- \rightarrow Er^0$.

Electrolyte: 1-butyl-1-methylpyrrolidinium NTf_2 – dried >48 h at 100 °C, <0.5 mTorr

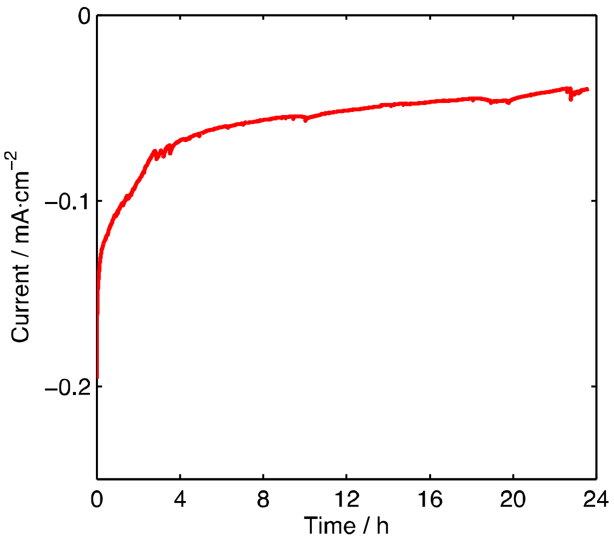
67 mM $Er(NTf_2)_3$ from Ryan + Isabella – dried >48 h at 100 °C, <0.5 mTorr

Reference electrode: Ag wire in 10 mM $AgNTf_2$ in electrolyte (no Er). Potentials referenced to ferrocene.

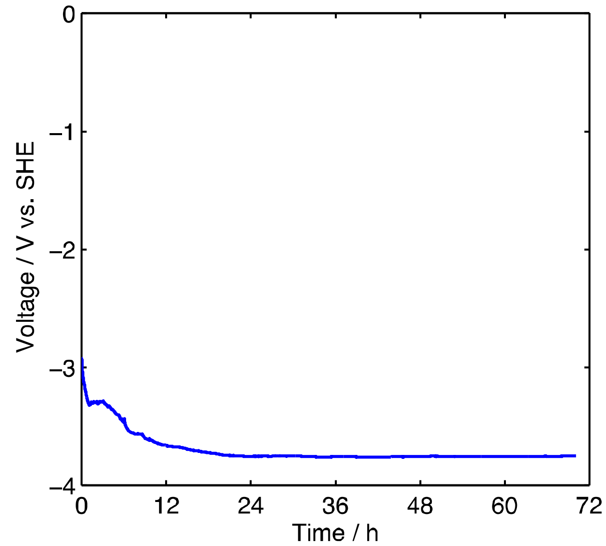
Counter electrode: Pt wire, 100 mV/s scan rate

Bulk Electrolysis onto Platinum

Constant Potential: -2.495 V



Constant Current: -1 mA/cm^2



Electrolyte: 1-butyl-1-methylpyrrolidinium NTf_2
Working electrode: 100 nm Pt on $Ti/SiO_2/Si$ (100)
Reference electrode: 10 mM $AgNTf_2$ in BMP-NTf_2
Counter electrode: Er rod, lightly sanded

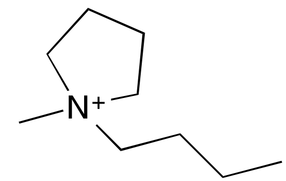
Condition	Mass Change: Pt Film	Mass Change: Er rod	Charge Passed (Coulombs)	% Efficiency
-2.495 V (-50 µA), 24h	0 mg*	0 mg*	-1.5 C	N/A
-1 mA/cm^2 (-3.77 V), 66h	+14 mg	-12 mg	-238 C	9.5%

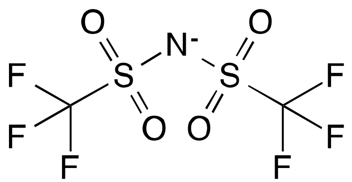
*only 0.4 mg theoretical change.

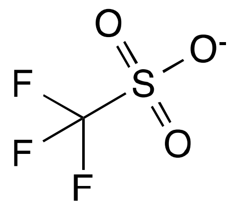
Moved ~13 mg in 66 hours! Need to analyze deposited film.

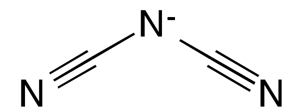
Variation of Ionic Liquid Anion

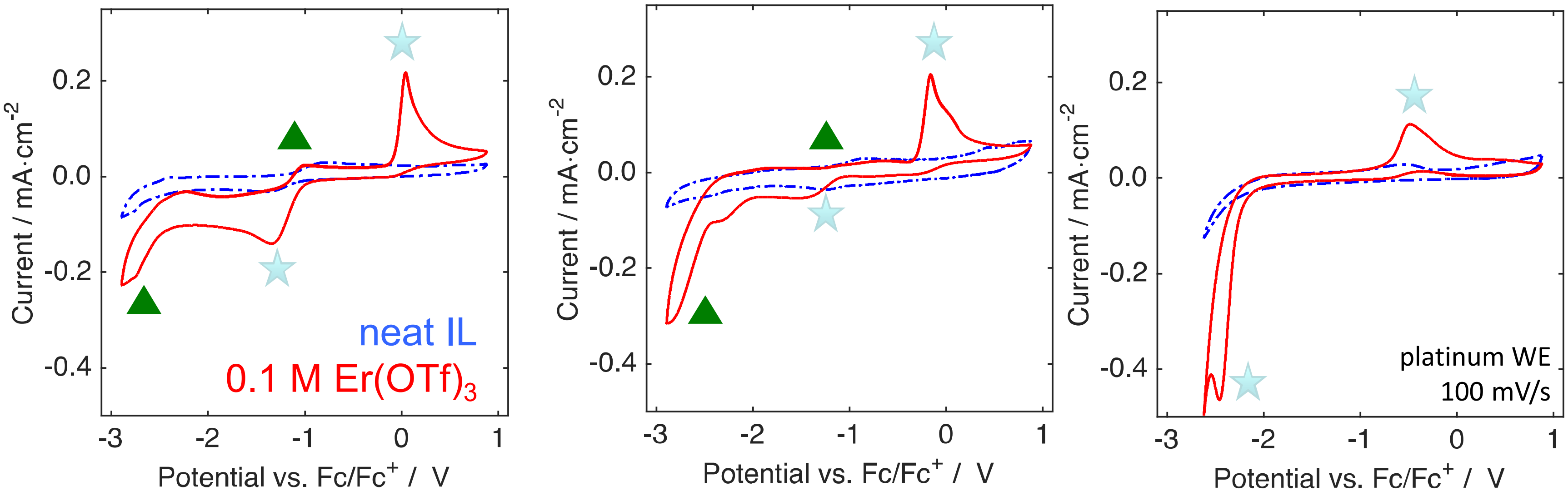
0.1 M $Er(OTf)_3$ in 1-butyl-1-methylpyrrolidinium ionic liquids at a platinum surface







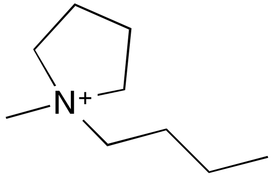


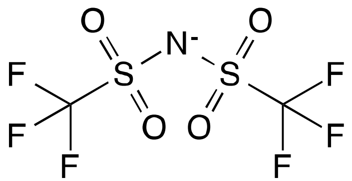


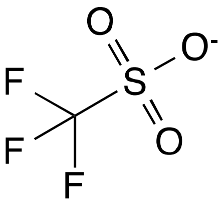
Redox active intermediates formed during Er^{3+} reduction

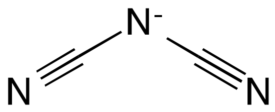
Variation of Ionic Liquid Anion

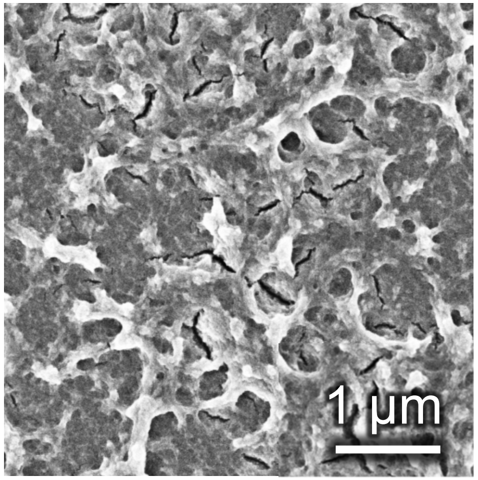
0.1 M $Er(OTf)_3$ in 1-butyl-1-methylpyrrolidinium ionic liquids at a platinum surface

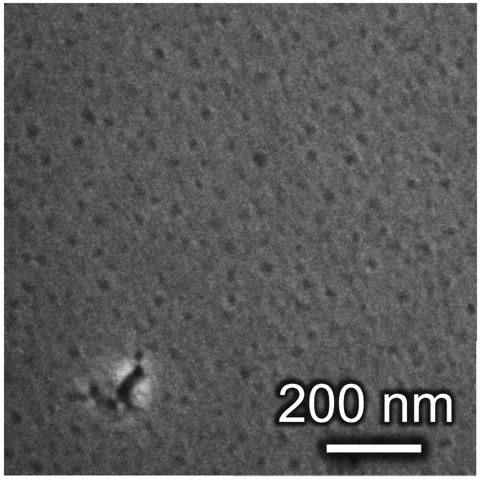


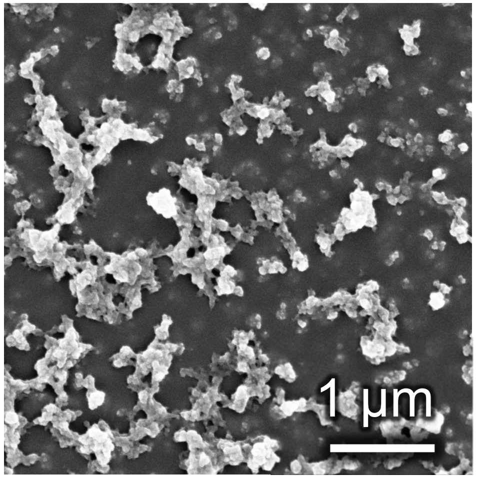












Amorphous, anion-contaminated ErO_x deposited onto Pt.

EXAFS Studies of RE's in IL's

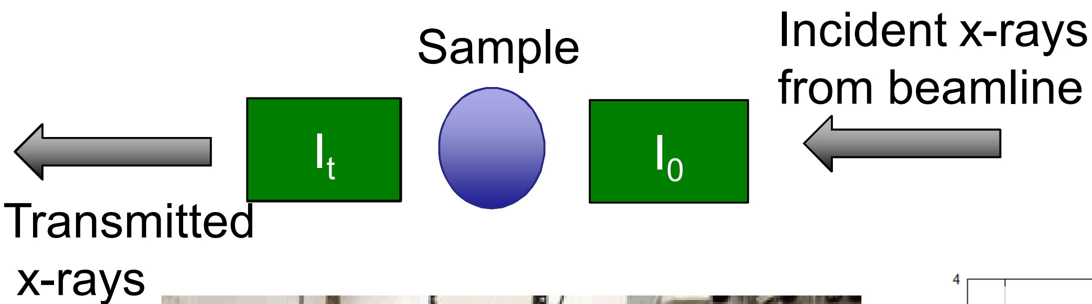
- Er coordination environment in IL's and solvents done at the X23A2 beamline at NSLS-I using the Er L_3 edge (8358 eV)
- Sc coordination environment were conducted at the 20-BM-B beamline at APS using the Sc K edge (4492 eV)
- Data processing and fitting: Artemis and Athena by Bruce Ravel
  - *B. Ravel and M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, Journal of Synchrotron Radiation* ***12****, 537–541 (2005) doi:10.1107/S0909049505012719*

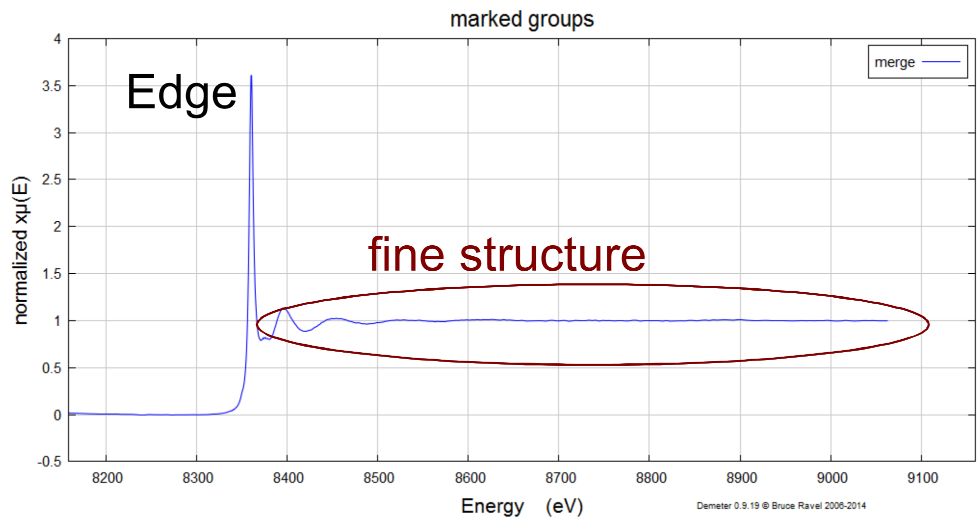
- Solid samples - transmission mode
- Liquid samples - fluorescence mode custom-built cell based on a design Marcos and co-workers

NSLS-I

Marcos, E.S.; et.al.; Rev. Sci. Inst.; 65, (1994), 2153.   image: www.bnl.gov

Quick EXAFS Overview



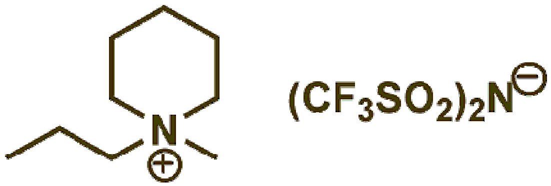


In EXAFS we measure the energy-dependent x-ray absorption spectrum

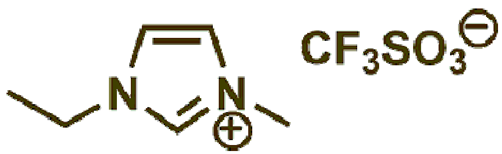
The oscillation that occurs above the absorption edge is the "EXAFS"

EXAFS provides unique information on local coordination environment in liquid samples

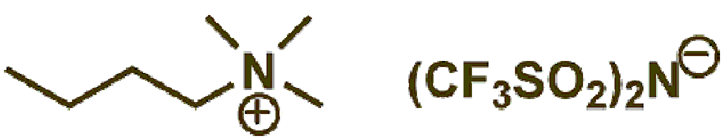
Ionic Liquids used for Er experiments



1-Methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide
"MPP-TFMS"



1-Ethyl-3-methylimidazolium triflate
"EMI-trif"



Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide
"BTMA-TFMS"

Ionic Liquids used for Sc Experiments

1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide "BMP-NTf_2"

1-butyl-1-methylpyrrolidinium Trifluoromethanesulfonate "BMP-OTf"

1-butyl-1-methylpyrrolidinium Dicyanamide "BMP-$N(CN)_2$"

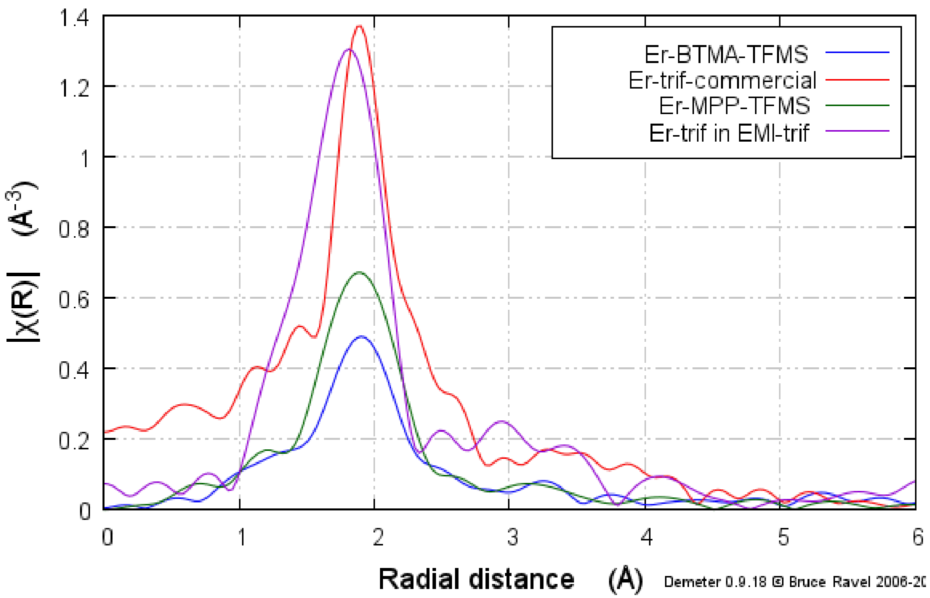
propylmethylpiperidinium bis(trifluoromethylsulfonyl)imide "PMP-NTf_2"

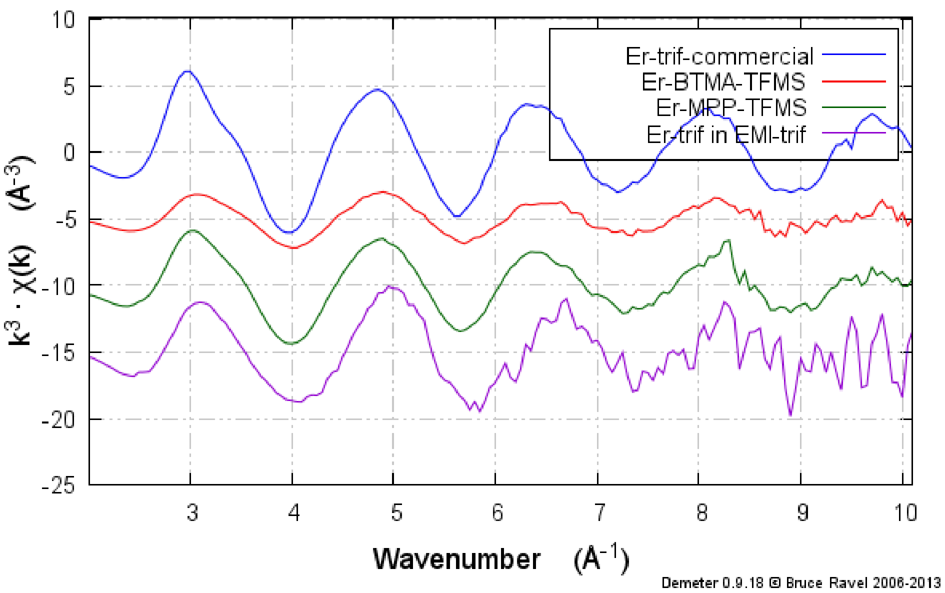
Er Coordination in Ionic Liquids

1.) Do the Er 1st and 2nd coordination shells more closely resemble: direct Er-IL bonding, Er triflate, or Er hydrate?

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

3.) Can we observe Er reduction in real time???

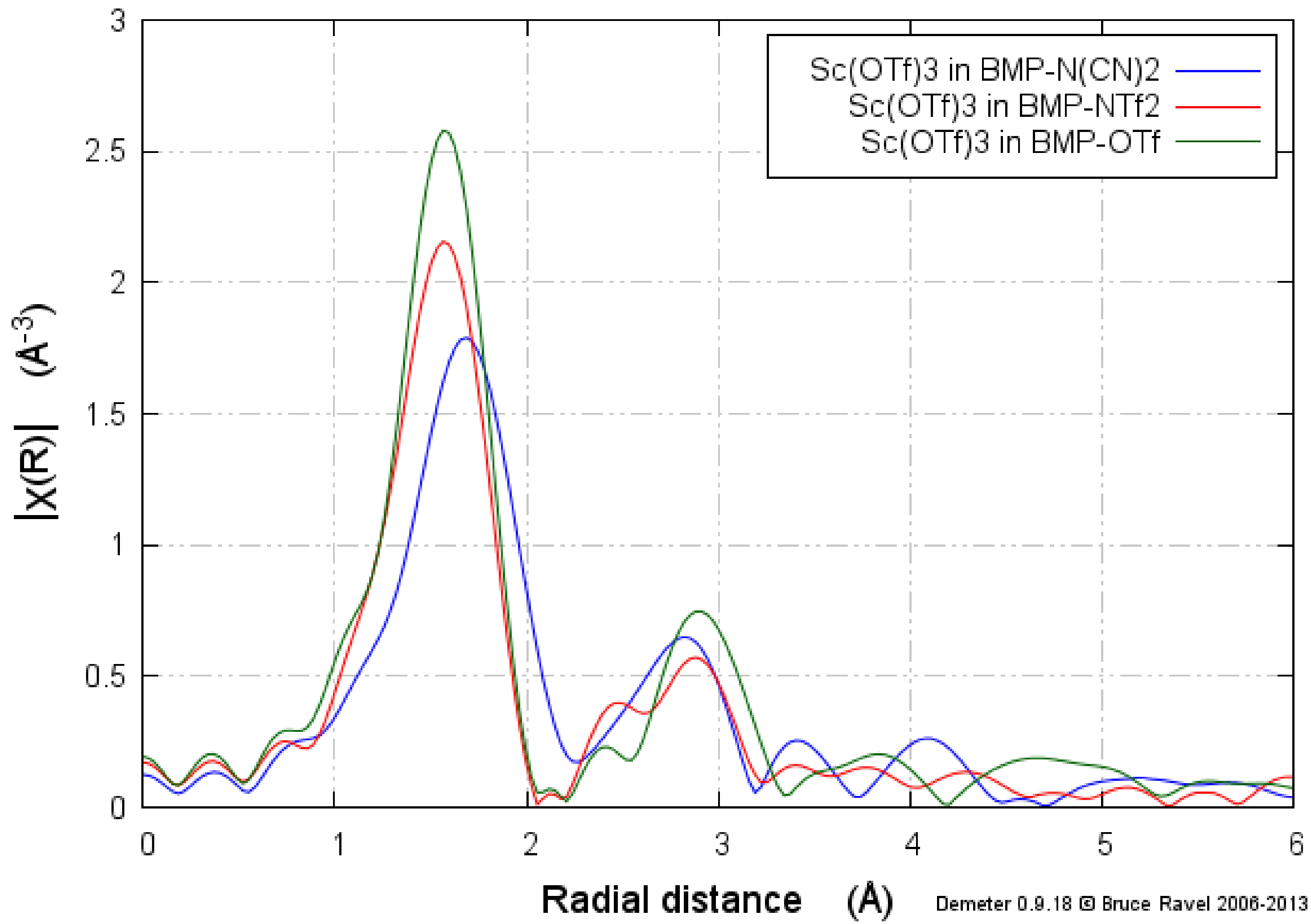




Three IL's tested appear to have same 1st shell and possibly the 2nd
Qualitatively agrees well with work by Persson et.al. in 2008

Persson, I.;et.a.; Chem. Eur. J; **2008**, *14*, 3056-3066.

Sc^{3+} Coordination in Ionic Liquids



Summary

- The reaction of Er^0 with HCl(aq) 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 bistriflimide IL's have wide electrochemical windows and appear to allow for the reduction of Er^{3+} to Er^0 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 likely coordination of the IL with the metal in the 1st or 2nd shell (data analysis is still on-going).

Acknowledgements

Sandia National Laboratories

- **Timothy Boyle, Jeremiah Sears, Michael Neville, and Daniel Yonemoto** – erbium precursor chemistry/characterization

- **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) and **Dale Brewe** (APS) – EXAFS data collection

- *Funding: SNL Laboratory Directed Research &Development program*

Extra Slides

Variation of Ionic Liquid Cation

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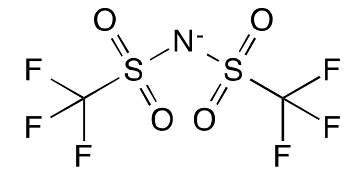
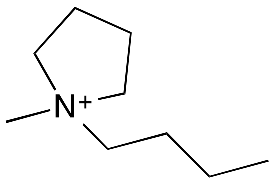
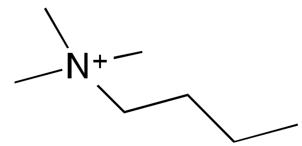
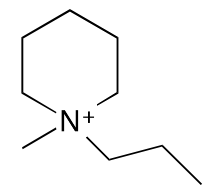
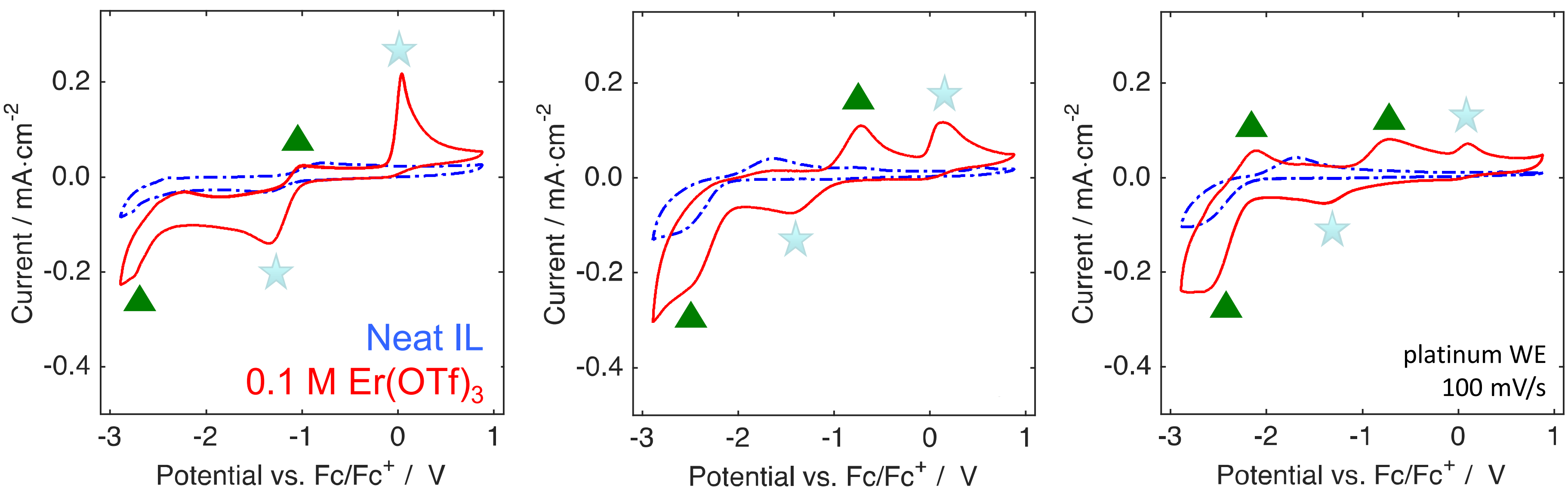
0.1 M $Er(OTf)_3$ in NTf_2 ionic liquids at a platinum surface







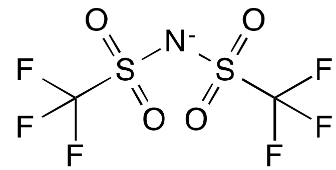


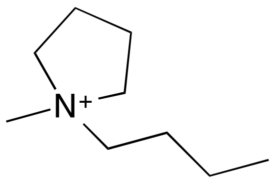


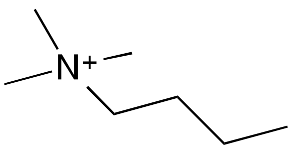
Redox active intermediates formed during Er^{3+} reduction

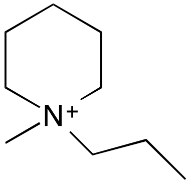
Variation of Ionic Liquid Cation

0.1 M $Er(OTf)_3$ in NTf_2 ionic liquids at a platinum surface

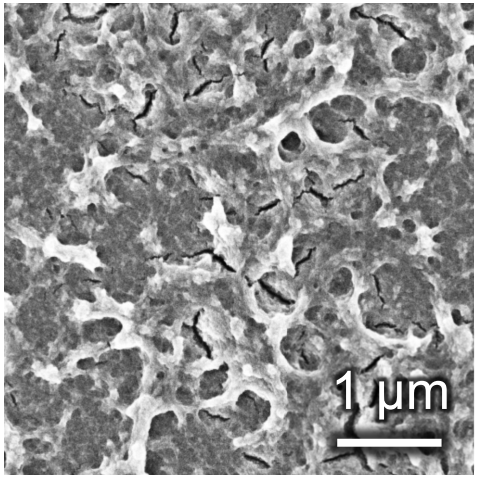


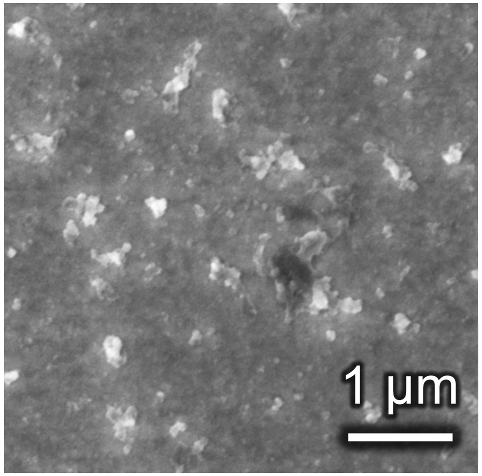


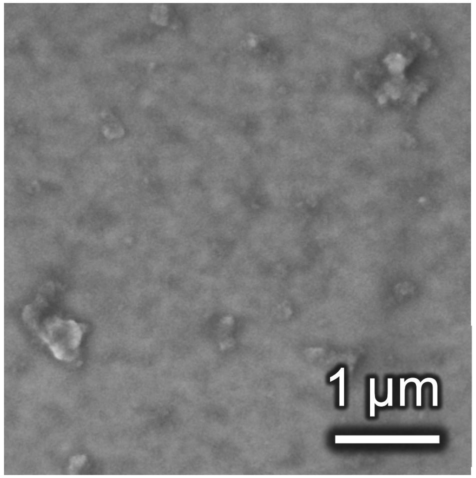




Deposit at -2.9 V for 2 hours







Amorphous, anion-contaminated ErO_x deposited onto Pt.

Er Deposition onto Different Materials

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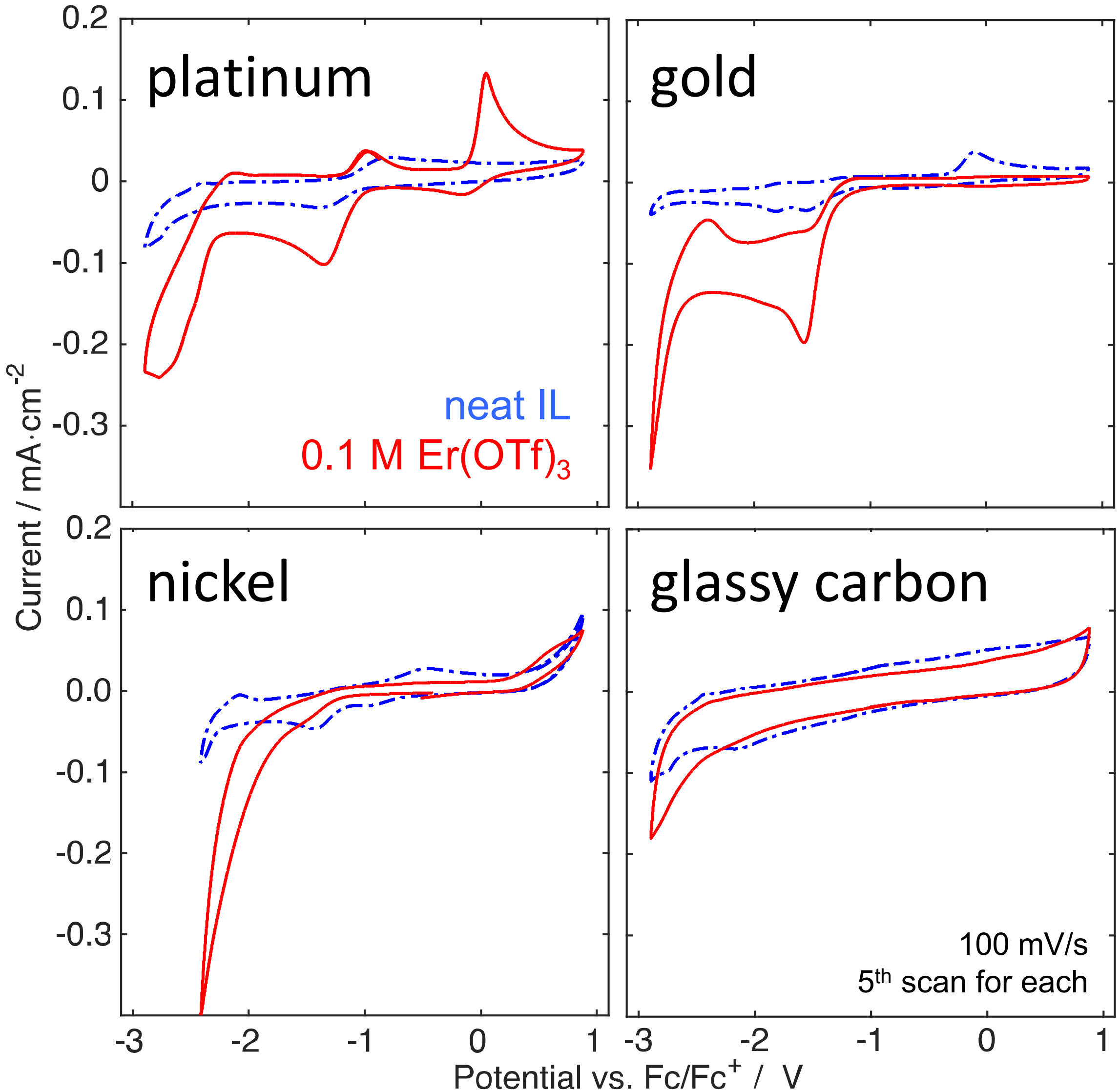
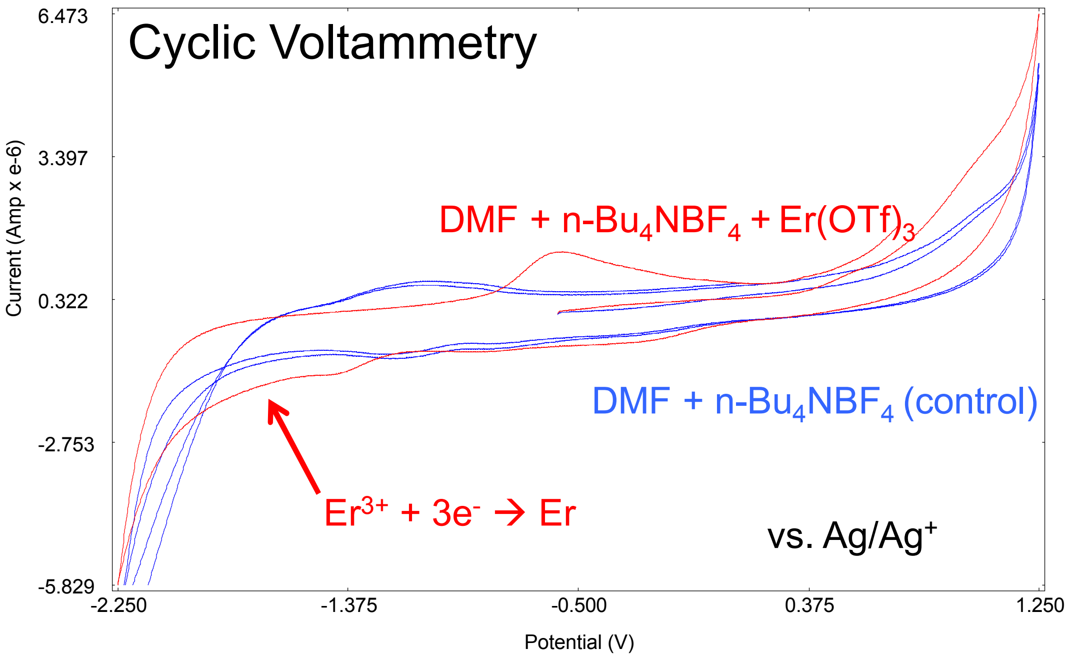
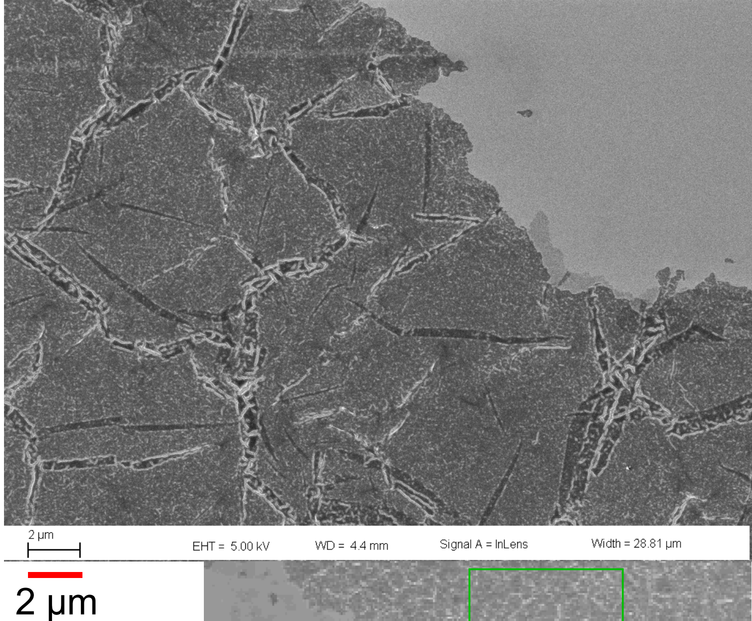


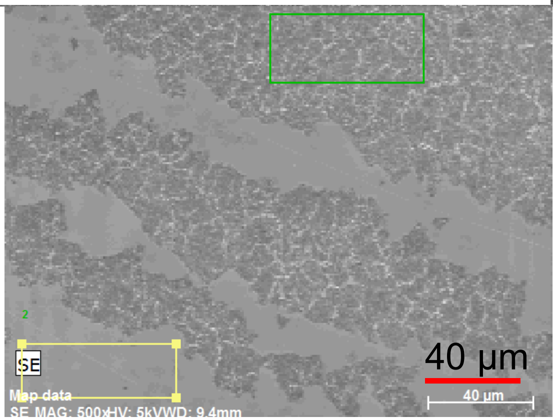
- No deposition on glassy carbon
- Oxidizable species only on platinum
- No intermediate on nickel

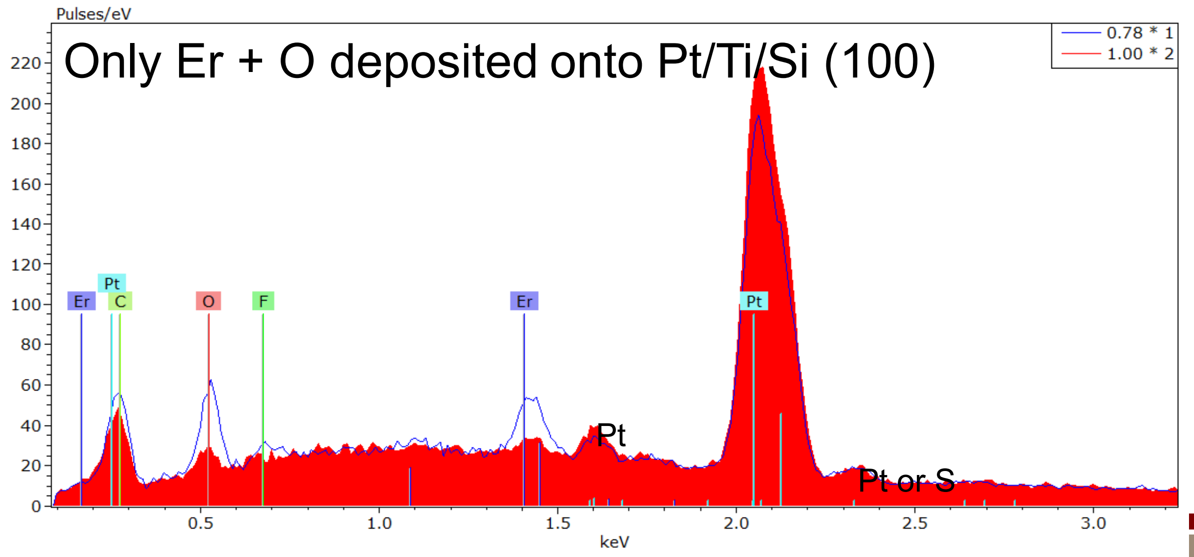
Electrode material greatly influences deposition electrochemistry.

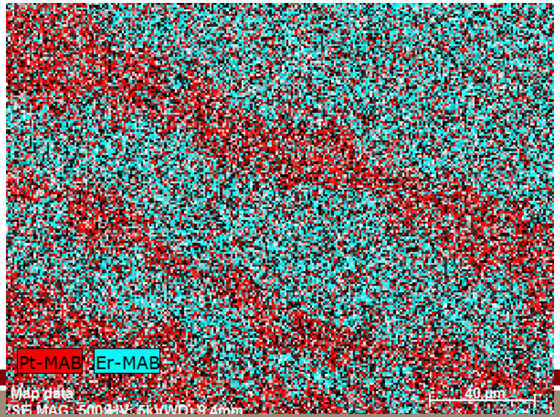
$Er(OTf)_3$ Reduction in DMF









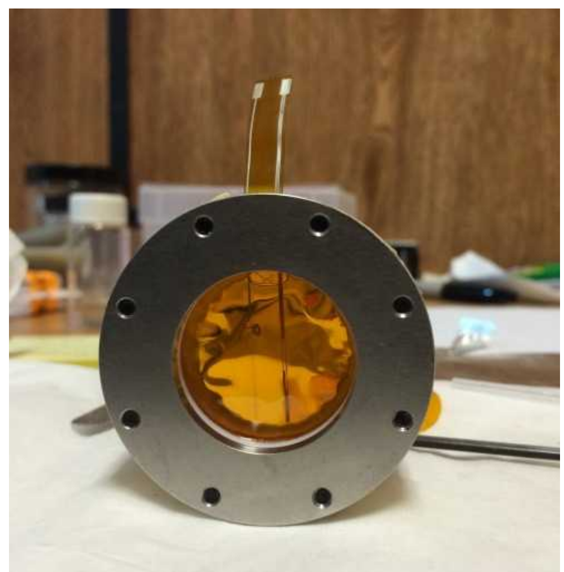


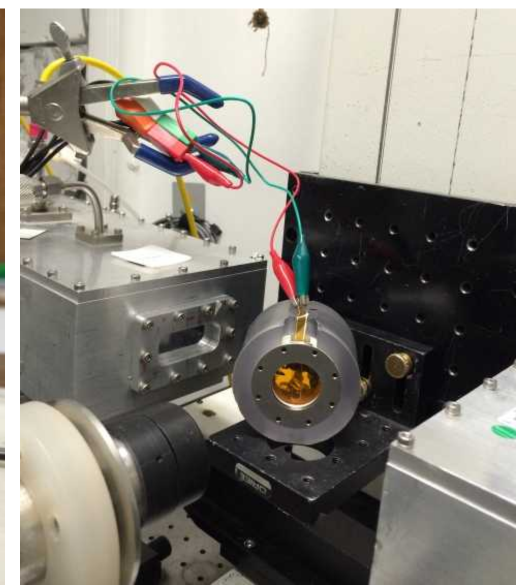
Attempt at In-situ XAS E-chem

- 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}

- One of the more promising CV's we recorded at the beamline was not in IL but in **acetonitrile using TBA/TFSI** as a supporting electrolyte

- Held constant potential at -2.6 V for two hours while collecting XANES spectra

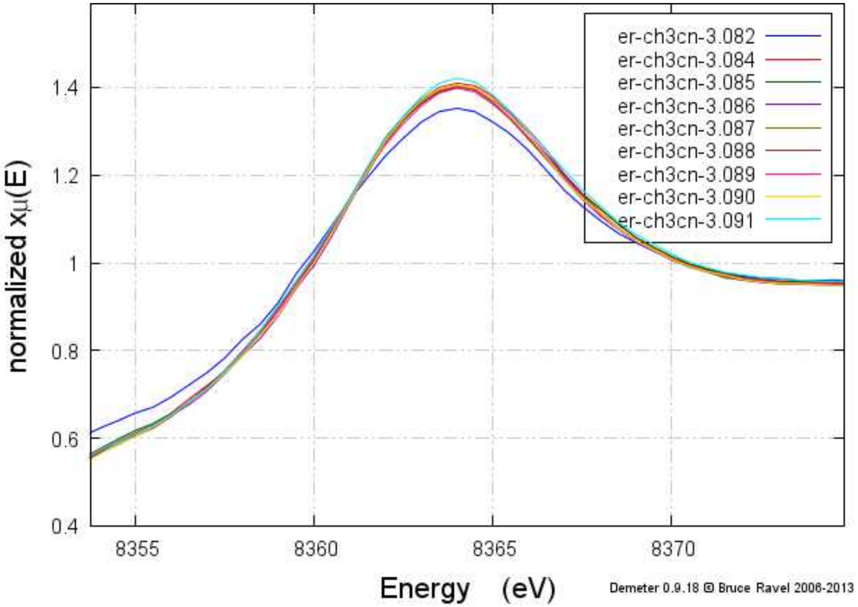




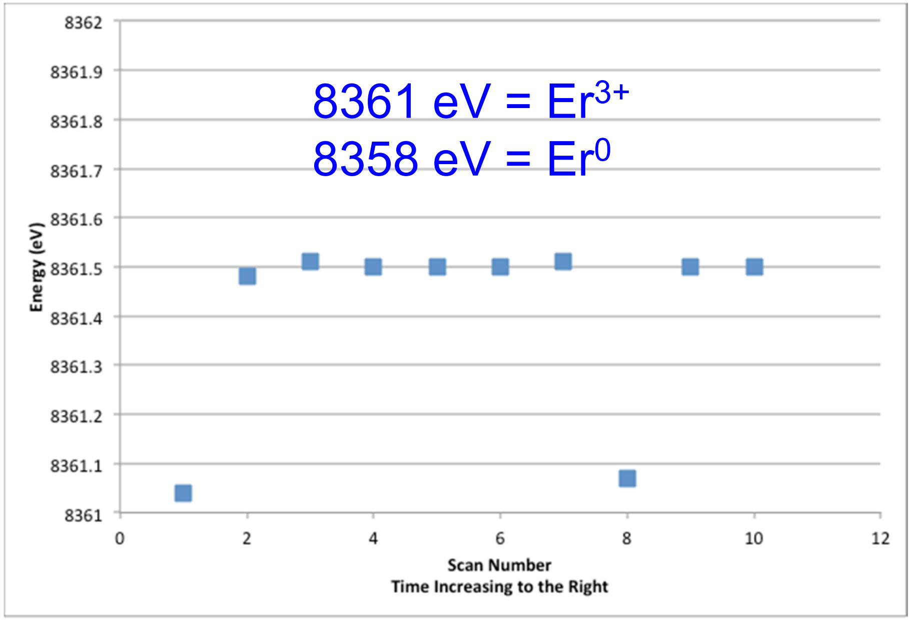
In-situ XAS and Chronoamperommetry

Er(OTf)$_3$ in CH_3CN with TBA/TFSI as a supporting electrolyte

Close-up of the
Er L_3 absorption edge



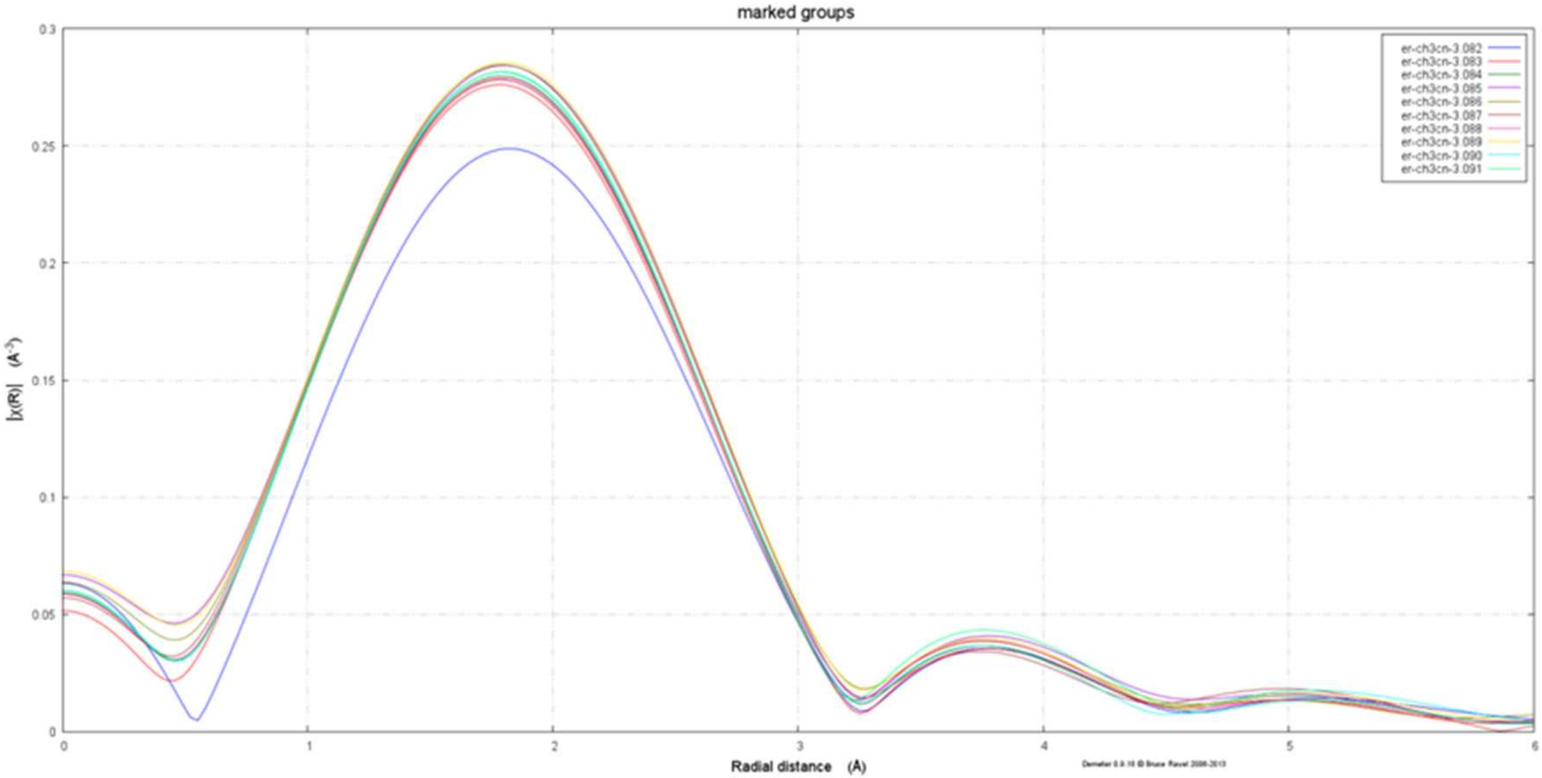
Data from the peak of
the 1st derivative of the energy spectrum



One would expect to see the position of the edge shift to lower energy as the amount of Er^{3+} decreased and Er^0 increased – not observed here

In-situ XAS and Chronoamperommetry

$Er(OTf)_3$ in CH_3CN with TBA/TFSI as a supporting electrolyte



pseudo-radial distribution plot

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

Summary

- The reaction of Er^0 with HCl(aq) 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 bistriflimide IL's have wide electrochemical windows and appear to allow for the reduction of Er^{3+} to Er^0 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 likely 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/characterization

- **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

Precedence for Ln Reduction in IL's

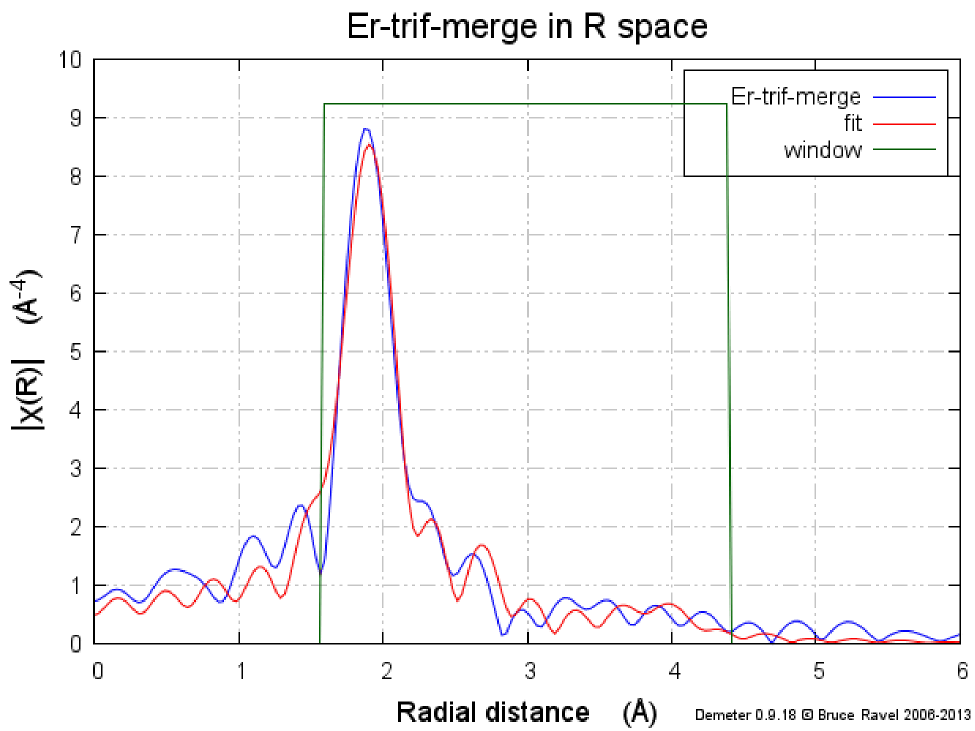
- 2005: May and co-workers from the University of Manchester and Ural State Technical University were able to reduce La, Sm, and Eu triflate hydrates in trimethyl-n-butylammonium NTf_2 on a Pt electrode at ambient temperature[1]

- 2008: Legeai and co-workers from the Universite Paul Verlaine Metz were able to reduce $La(NO_3)_3$ in 1-octyl-1-methylpyrrolidinium NTf2 on a Pt electrode at 25 to 85 ° C [2]

- 2009: Nagarajan and co-workers from Indira Gandhi Centre for Atomic Research were able to reduce $Eu(NTf_2)_3$ in N-butyl-N-methylpyrrolidinium NTf_2 on a glass carbon and stainless steel electrodes at 100 ° C [3]

1. Bhatt, A.I.; May, I.; et.al.; *Inorg. Chem.*; 44; (2005); 4934-4940
2. Legeai, S.; et.al.; *Electrochem. Comm.*; 10; (2008); 1661-1664
3. Rao, Ch.J.; Nagarajan, K.; et.al.; *Electrochim. Acta*; 54; (2009); 4718-4725

Commercial Er(OTf)$_3$ EXAFS



R-factor = 0.016

name	N	S02	sigma^2	e0	delr	Reff	R
O1.1	6.000	0.974	0.00336	7.274	-0.02217	2.34670	2.32453
O2.1	3.000	0.974	0.00336	7.274	-0.01467	2.48850	2.47383
O4.1	12.000	0.974	0.02070	7.274	-0.03413	4.55100	4.51687
O1.1	6.000	0.974	0.00336	7.274	-0.02217	2.34670	2.32453
O2.1	3.000	0.974	0.00336	7.274	-0.01466	2.48850	2.47384
O4.1	12.000	0.974	0.02070	7.274	-0.03413	4.55100	4.51687

$Lu(OH_2)_9(CF_3SO_3)_3$ by Harrowfield et. al.

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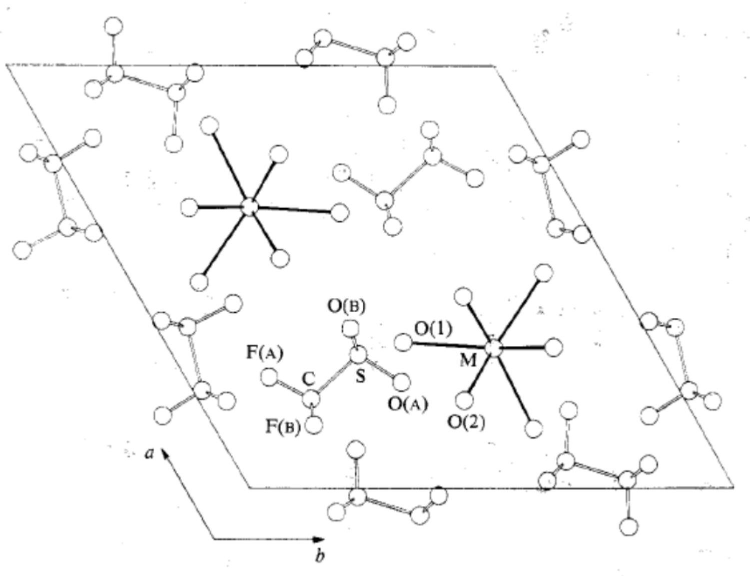
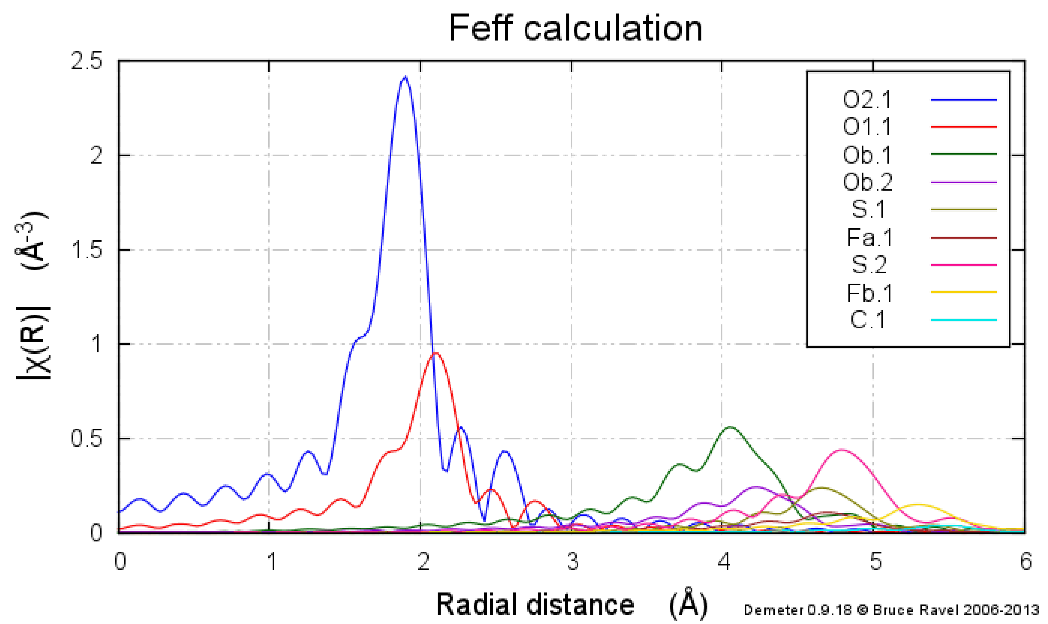


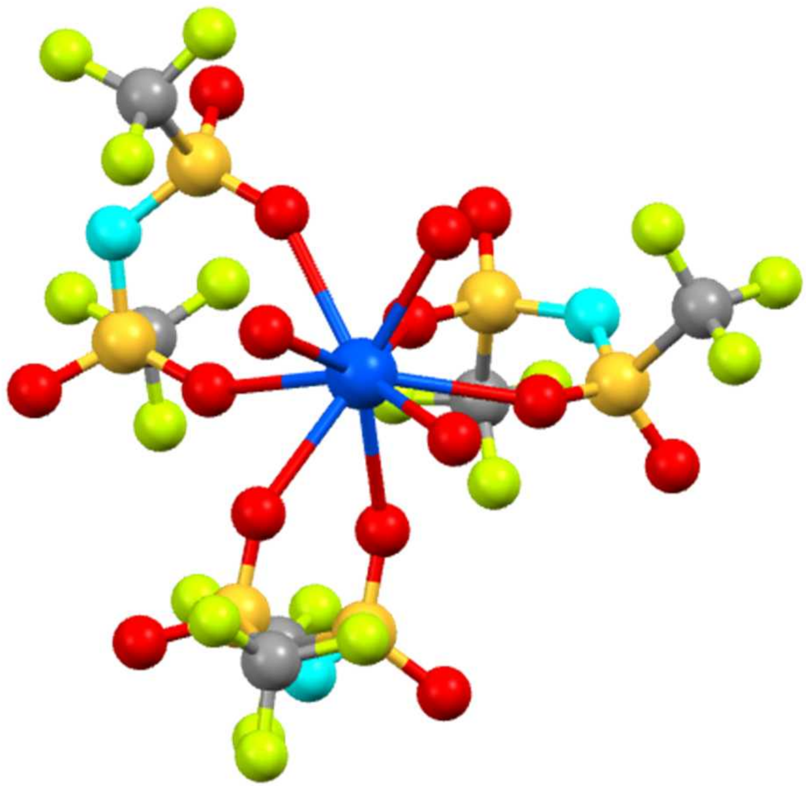
Fig. 1. Unit cell contents projected down c.



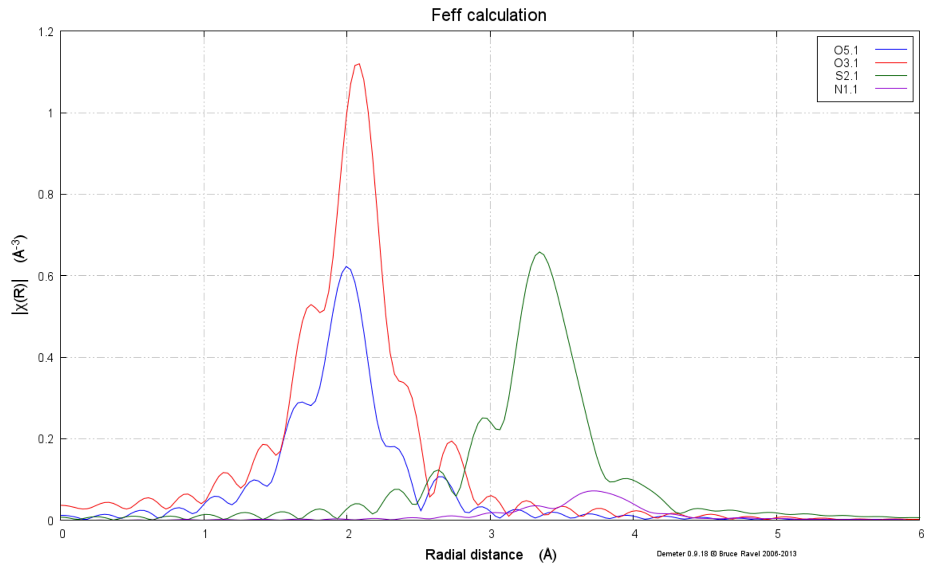
Harrowfield et.al. Aust. J. Chem, 1983, 36, 483-92

Our FEFF6 calculation

Bhatt and May's La Bistrfilimide



Their crystal structure



Our FEFF6 calculation

LaO_9 with 3 bidentate NTf2 ligands and 3 H_2O

La bistriflimide from Ian May icsd 048199, Bhatt, A.I.; May, Iain; et.al. Inorg Chem, 44, 2005, 4934-4940

$Er(OTf)_3$ in EMI-trif EXAFS Analysis

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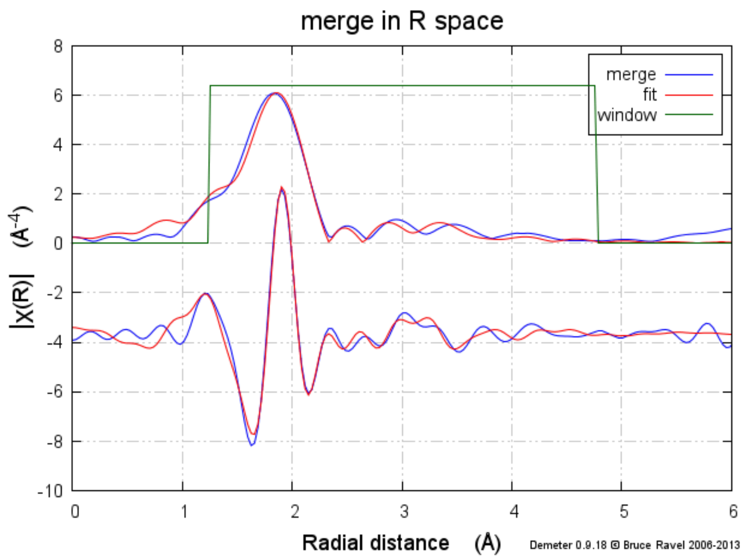
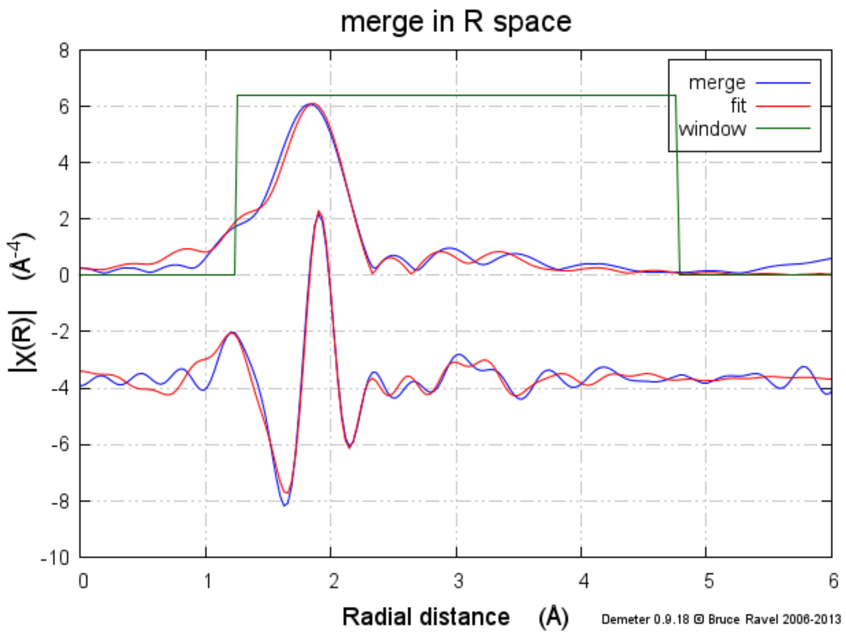


name	N	S02	sigma^2	e0	delr	Reff	R
O1.1	9.000	2.729	0.02638	-5.149	-0.07337	2.34670	2.27333
O4.1	12.000	2.729	0.03179	-5.149	-0.10601	4.55100	4.44499
H1B.1	24.000	2.729	0.01642	-5.149	-0.15165	2.85010	2.69845
O1.1 H1B.1	24.000	2.729	-0.00367	-5.149	-0.63255	2.98500	2.35245
O1.1	9.000	2.729	0.02638	-5.149	-0.07337	2.34670	2.27333
O4.1	12.000	2.729	0.03179	-5.149	-0.10601	4.55100	4.44499
H1B.1	24.000	2.729	0.01642	-5.149	-0.15165	2.85010	2.69845
O1.1 H1B.1	24.000	2.729	-0.00367	-5.149	-0.63255	2.98500	2.35245

$Er(OTf)_3$ in EMI-trif EXAFS Analysis



name	N	S02	sigma^2	e0	delr	Reff	R
O1.1	9.000	2.729	0.02638	-5.149	-0.07337	2.34670	2.27333
O1.1 H1B.1	24.000	2.729	-0.00367	-5.149	-0.63255	2.98500	2.35245
H1B.1	24.000	2.729	0.01642	-5.149	-0.15165	2.85010	2.69845
O4.1	12.000	2.729	0.03179	-5.149	-0.10601	4.55100	4.44499

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

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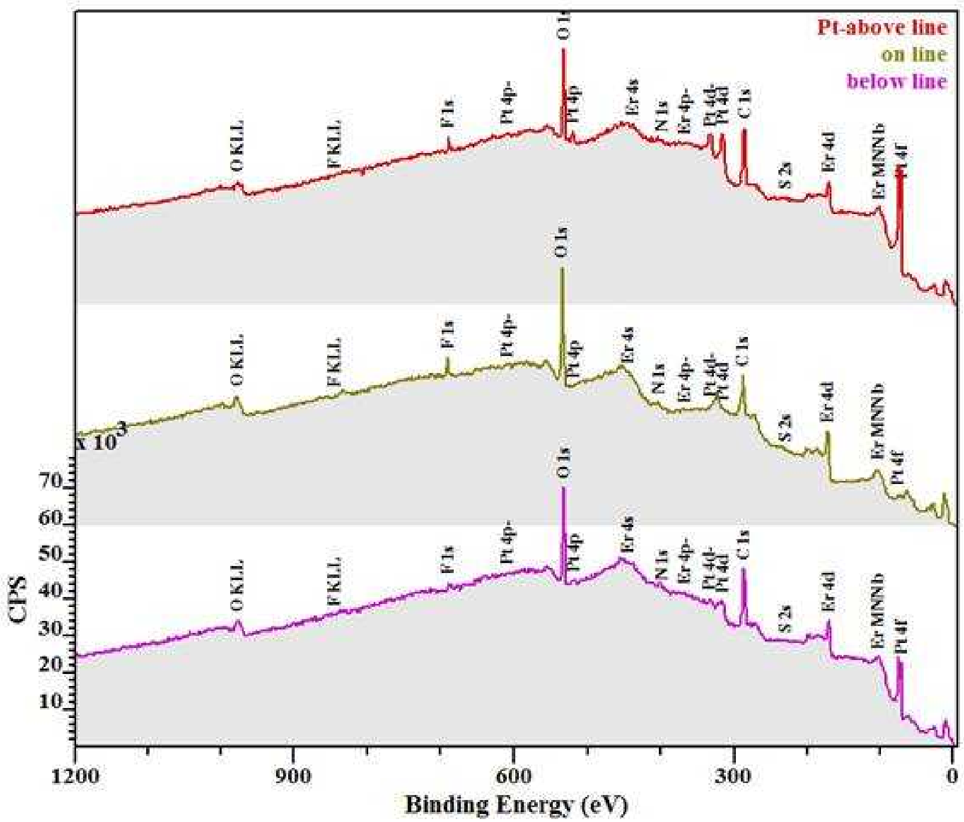
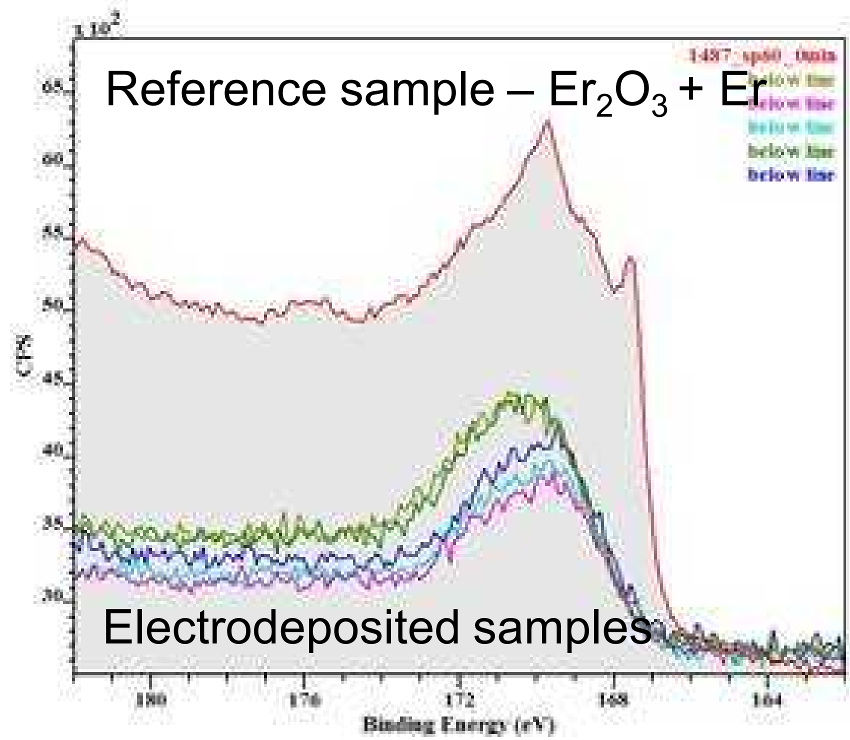
Only Er, O, C, Pt present

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



Survey spectra – above, on, below "water" line

All erbium is oxidized (by air?).



Erbium 4d

Er^{3+} Electrochemistry

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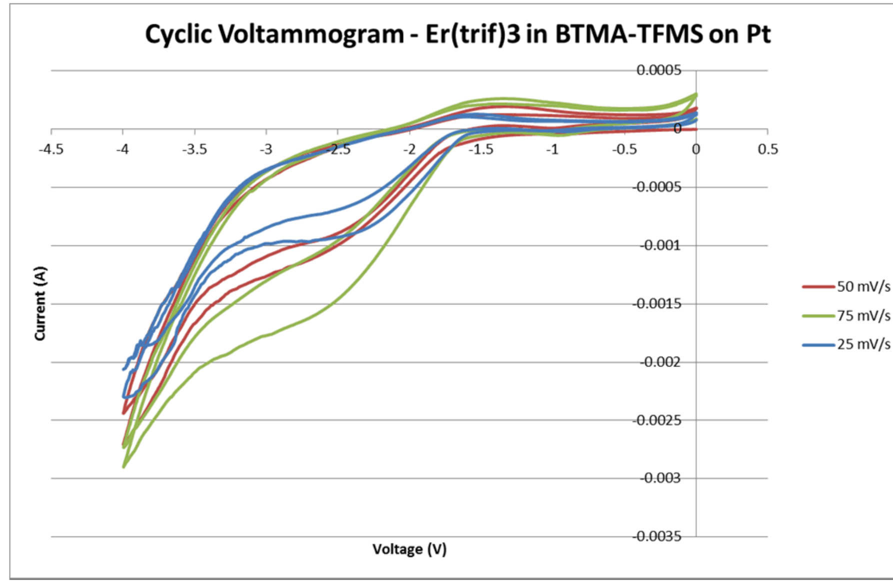
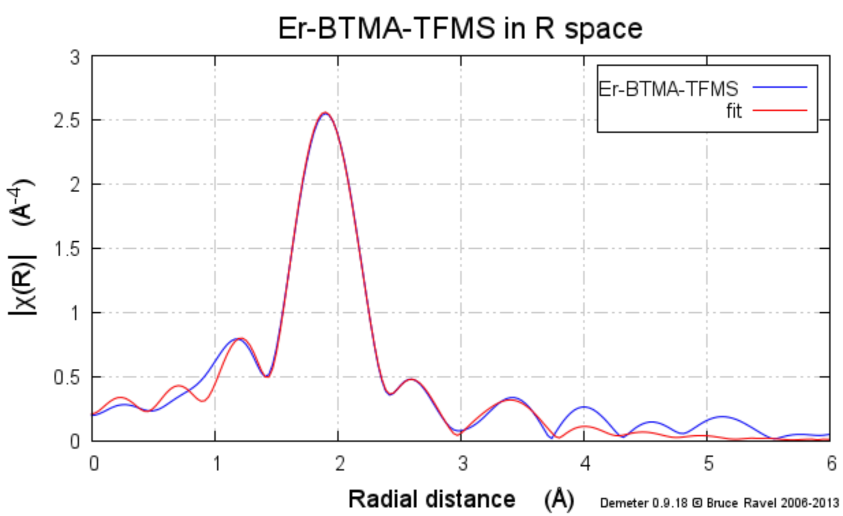
- Studied electrochemistry of Er triflate in BTMA-TFMS ionic liquid – looking for Er reduction and effect of scan rate
  - Also did some experiments looking at C and Au working electrodes

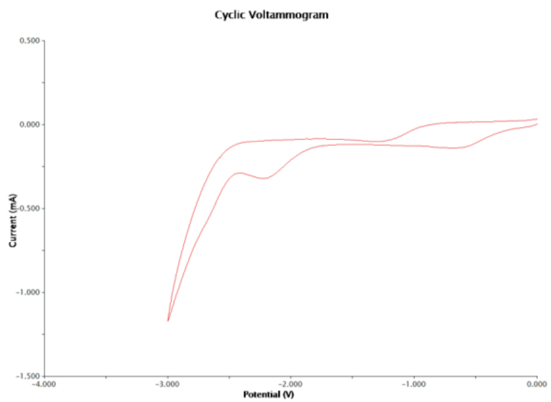


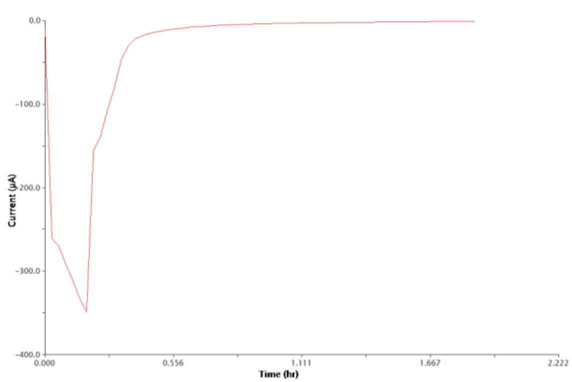


name	N	S02	sigma^2	e0	delr	Reff	R
O4.1	4.000	0.609	-0.00024	-3.278	-0.07454	2.32310	2.24856
O6.1	2.000	0.609	0.00566	-3.278	-0.37693	2.43560	2.05867
O1.1	2.000	0.609	-0.00307	-3.278	-0.06295	2.46550	2.40255
Er3.1	2.000	0.609	0.01414	-3.278	0.09988	3.47110	3.57098
N1.1	1.000	0.609	0.01051	-3.278	0.07628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

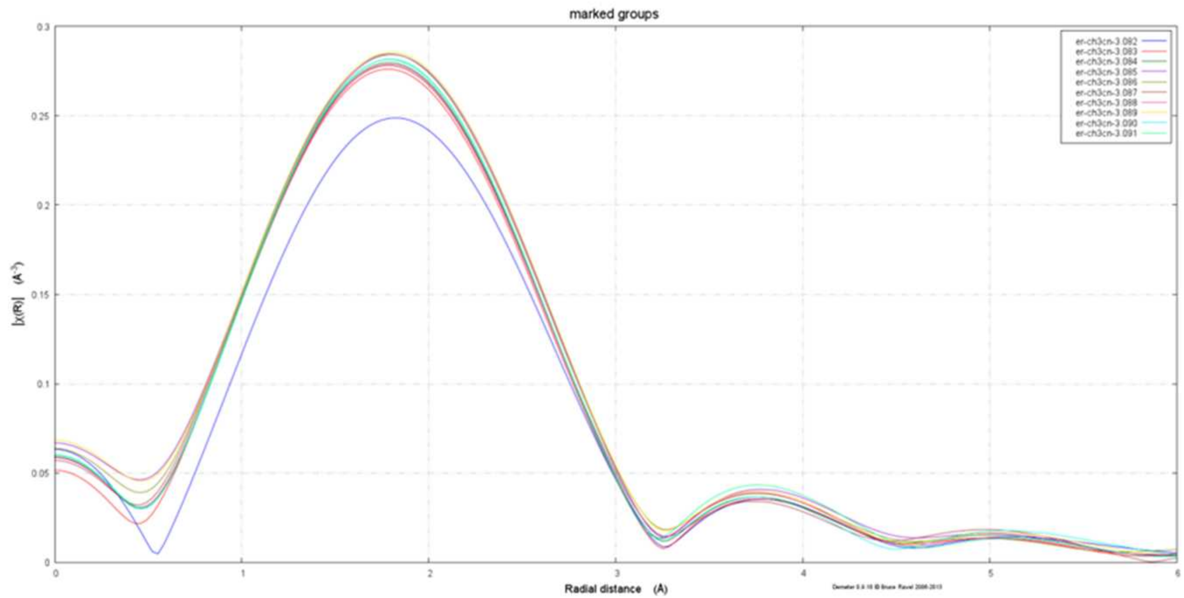
In-situ XANES and Chronoamperommetry

- 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