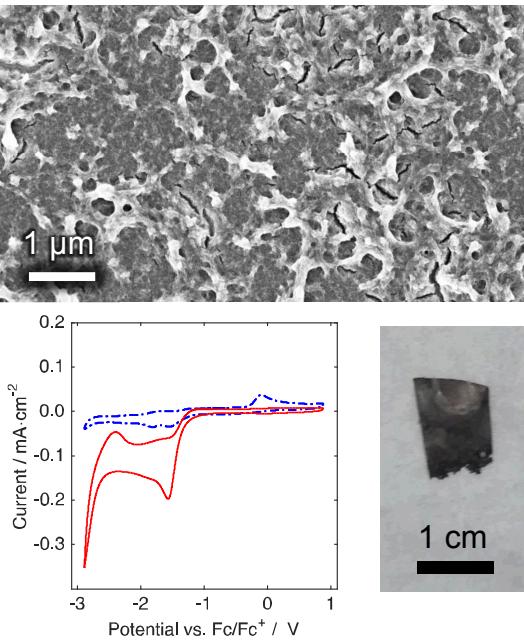


# Electrochemical REcycling of Erbium using Ionic Liquids



Leo J. Small,  
Timothy N. Lambert, Julian A. Vigil,  
Maria Kelly, Timothy J. Boyle,  
Jeremiah Sears, Ryan F. Hess



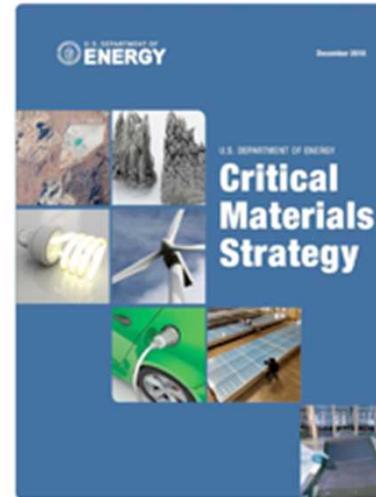
*Exceptional  
service  
in the  
national  
interest*



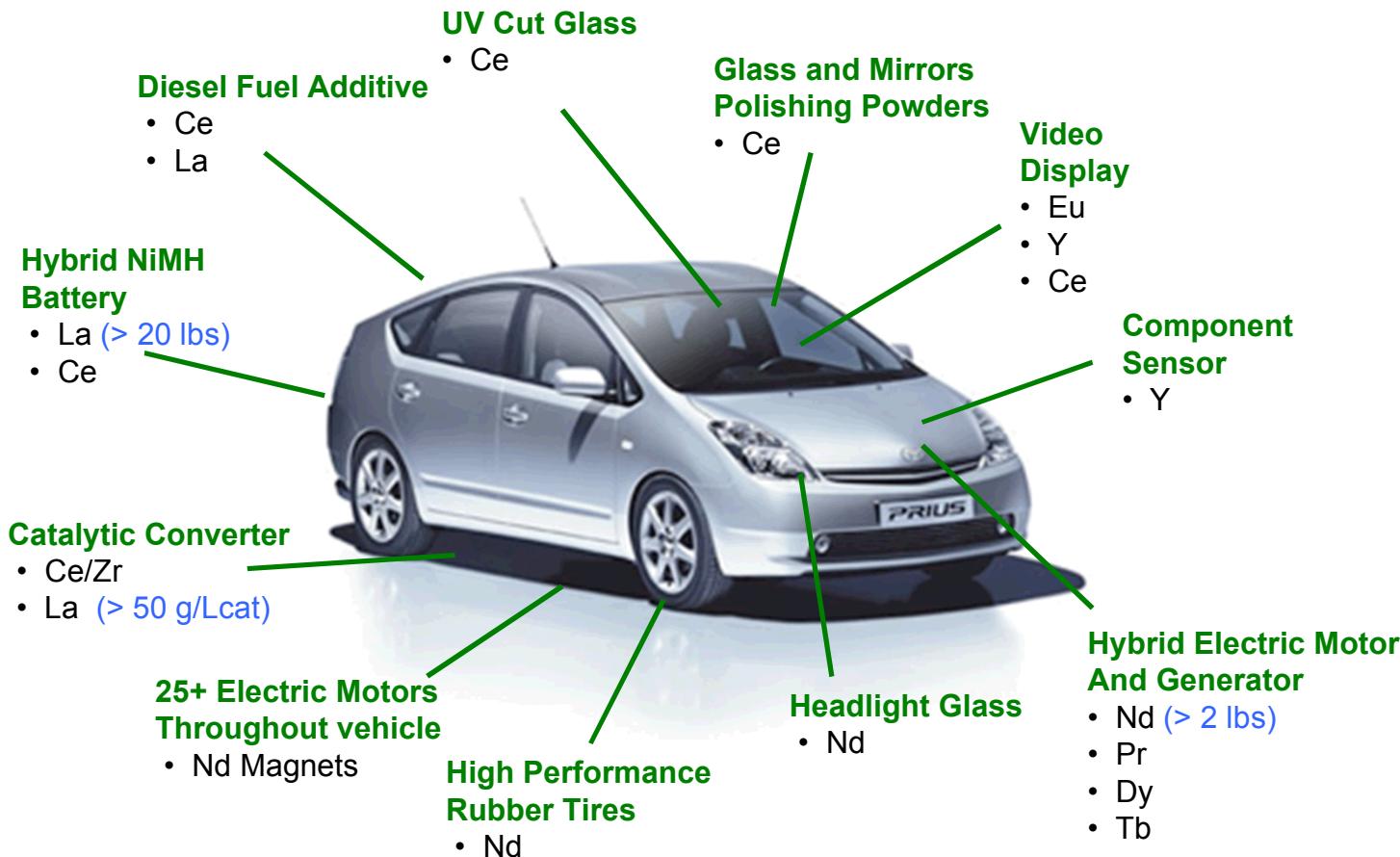
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

# Overview

- Motivation
- REcycling scheme
- REcycling in molten salts
- REcycling in ionic liquids
  - Influence of cation
  - Influence of anion
  - Influence of electrode material



# RE Are Ubiquitous in Modern Society

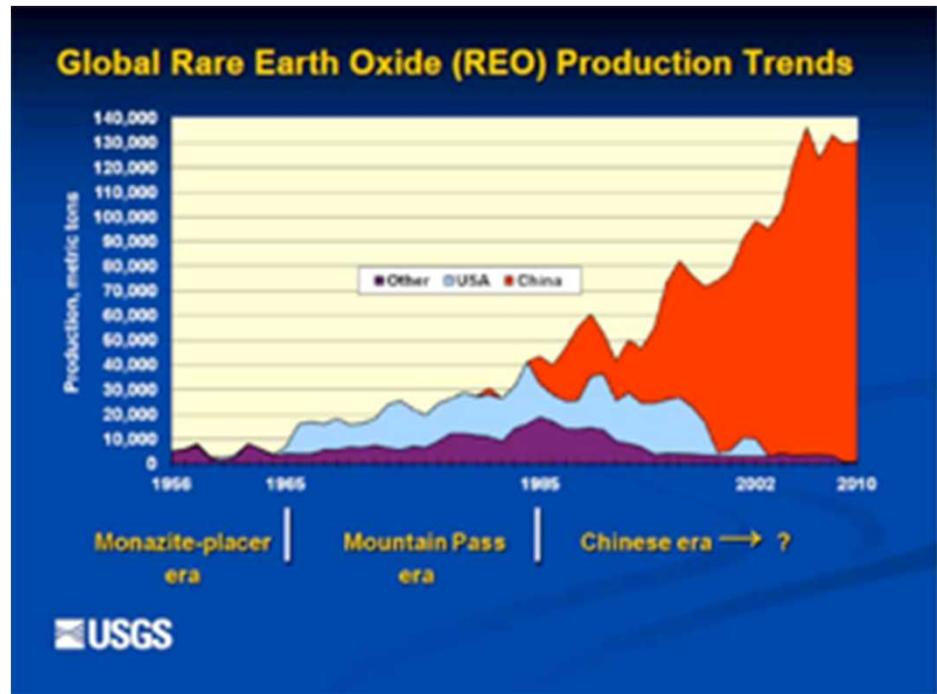


*“Analysts have called the Prius™ one the most rare-earth intensive consumer product ever made.”*

# Over the past few decades China has taken over production of RE materials.

## RE Historically Produced:

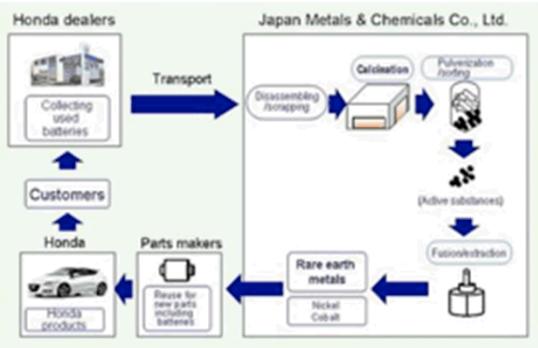
- 1950s: South Africa (monazite)
- 1960-1980: Mountain Pass (CA)
- 2000: Inner Mongolia, China
- 2011: MolyCorp resurrects Mountain Pass (CA)



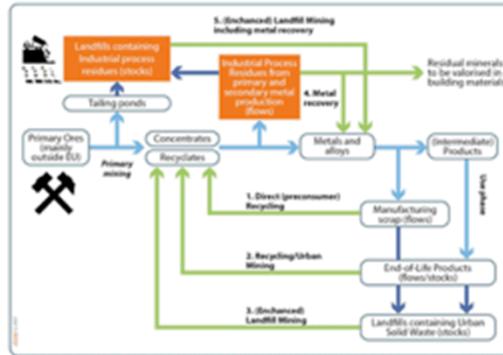
*Molycorp filed for bankruptcy in June 2015.*

*In August 2015, it was reported that the mine was to be shutdown.*

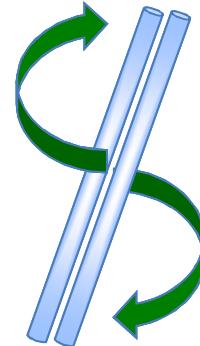
# REcycle: A Route to Reduced Dependency



**Honda** recently announced that key materials for their hybrid automobiles will be recycled.



**Rhodia** (France) has begun to recover Tb and other RE elements from magnets, windmill components, electric vehicles and hard disks.



**Hitachi**, Ltd. announced plans for recycling RE-magnets from hard disk drive motors, air conditioners, and other compressors.

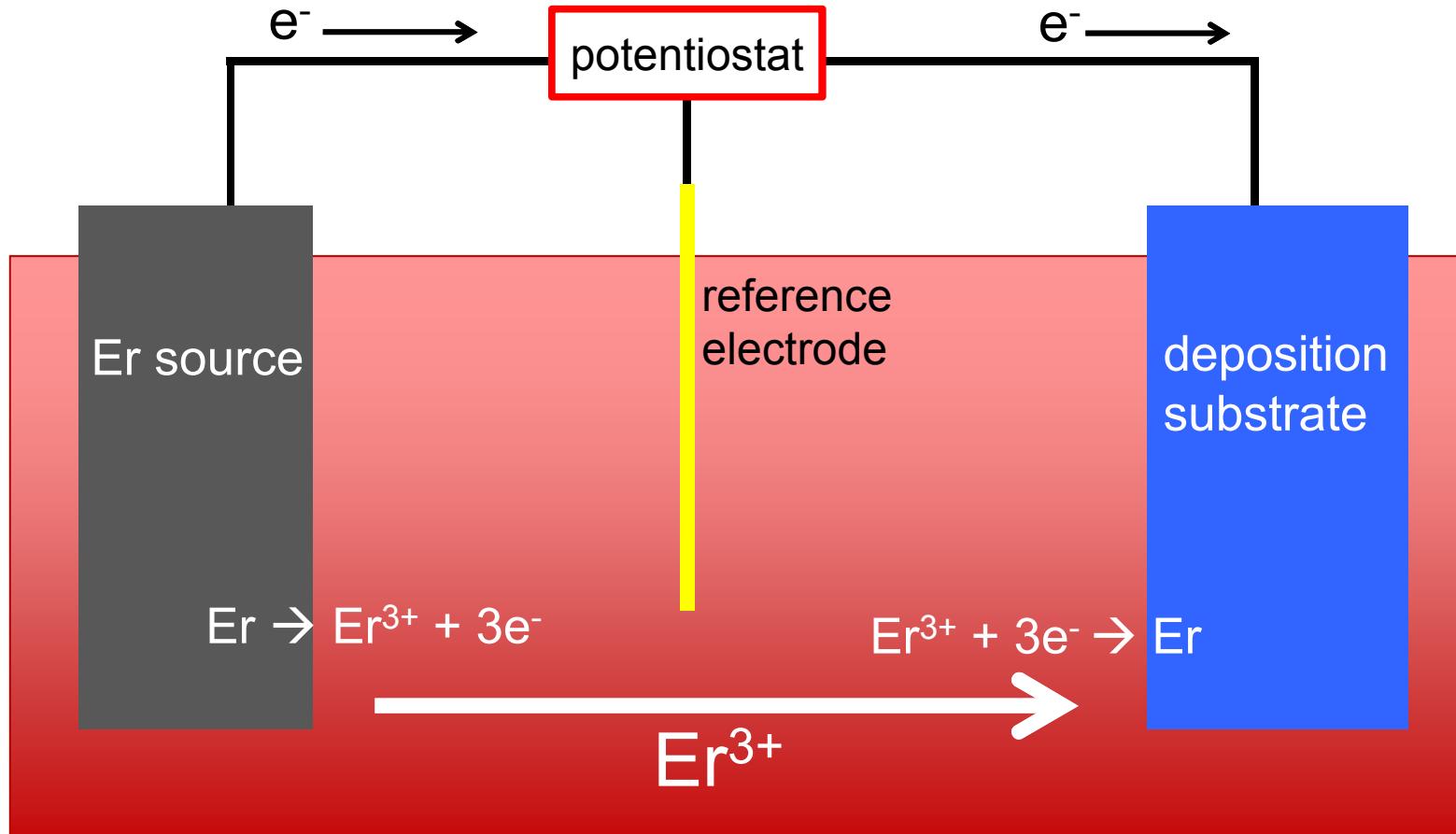
**Sandia** 8700 kg of fluorescent waste, a loss \$900,000 in RE material (per 2 yrs).

## *New extraction methods are necessary to aid in the RE-utilization of other 'waste' RE-materials*

- REEcycle (U. Houston) has a patented method to extract Dy/Nd from magnets.
- Ames Laboratory and Critical Materials Institute has an imidazolium  $\text{BF}_4^-$  ionic liquid to dissolve lanthanide oxides.

# REEcycle

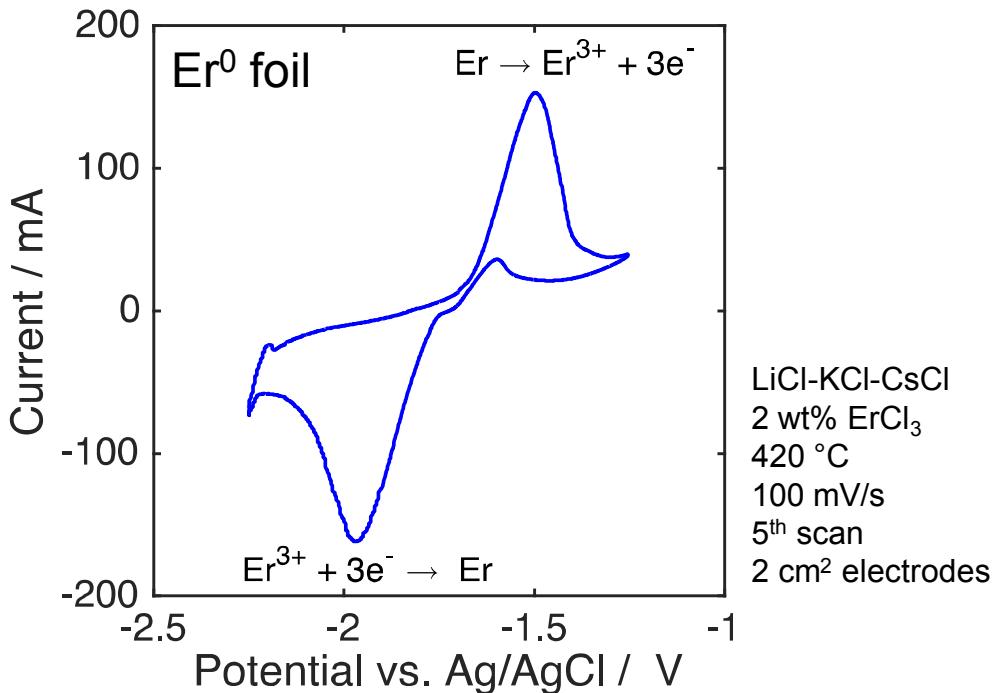
# Electrorefining Erbium



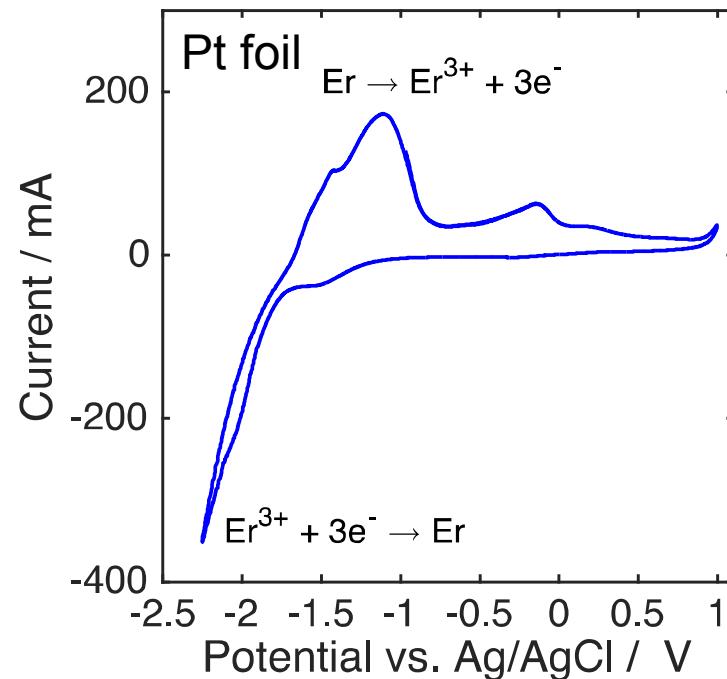
***Electrochemically move erbium from source to target substrate.***

# Electrorefining in Molten Salts

Erbium is easily oxidized into solution...



...and reduced onto platinum.

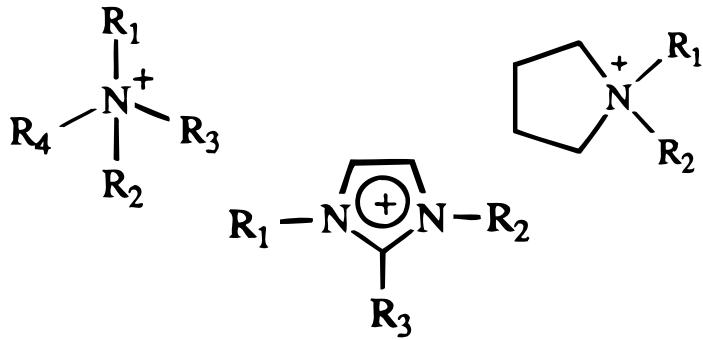


>90% Coulombic efficiency on 250 mg scale at **420 °C**  
***Inert environment with heat-tolerant materials required!***

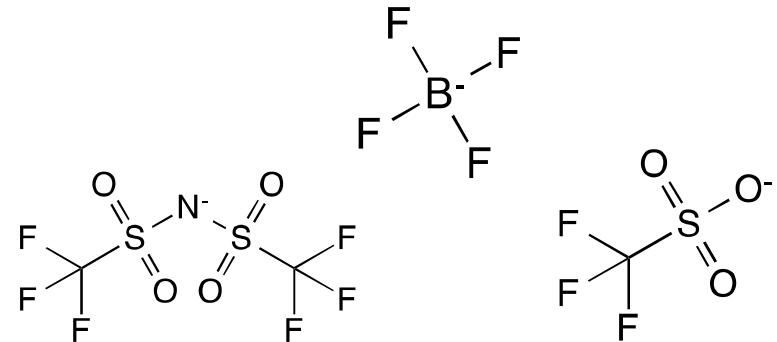
# Ionic Liquids

- Room temperature liquids with negligible vapor pressure
- Bulky non-coordinating ions
- Versatile, highly tunable
- Large (>4 V) electrochemical windows common

Example Cations



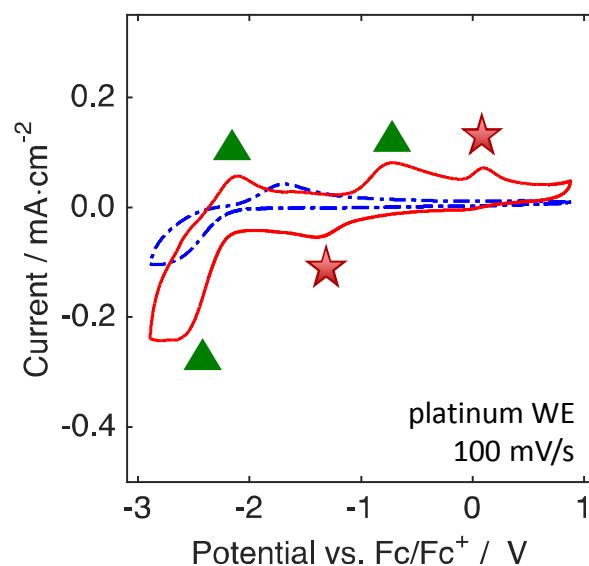
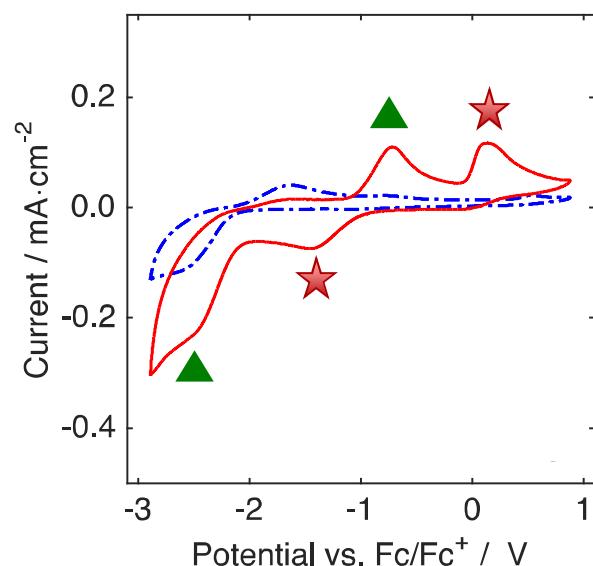
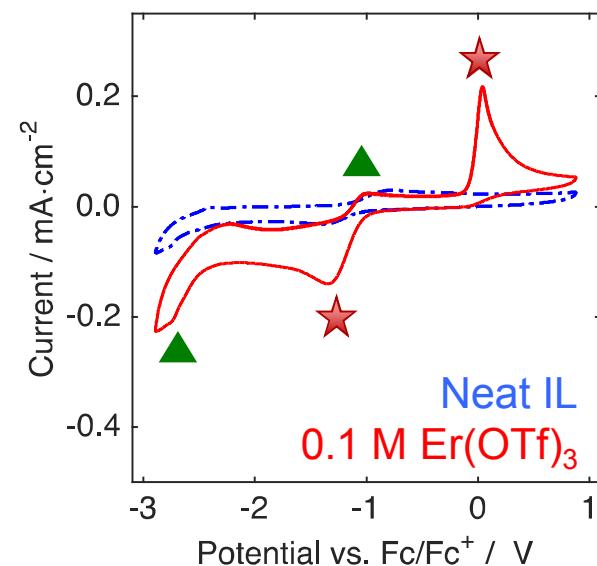
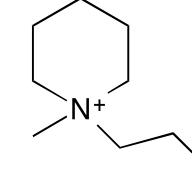
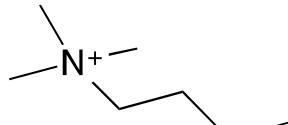
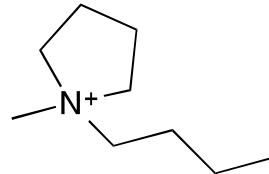
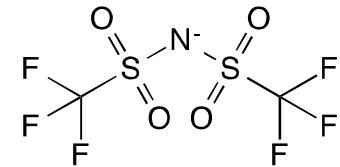
Example Anions



*Ionic Liquids may be tuned to have a wide range  
(electro)chemical properties.*

# Variation of Ionic Liquid Cation

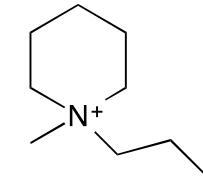
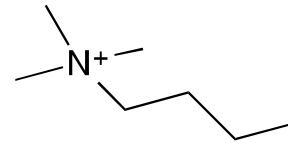
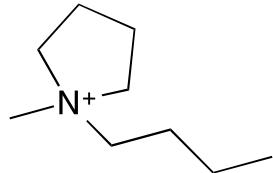
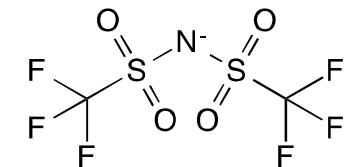
0.1 M  $\text{Er}(\text{OTf})_3$  in  $\text{NTf}_2$  ionic liquids at a platinum surface



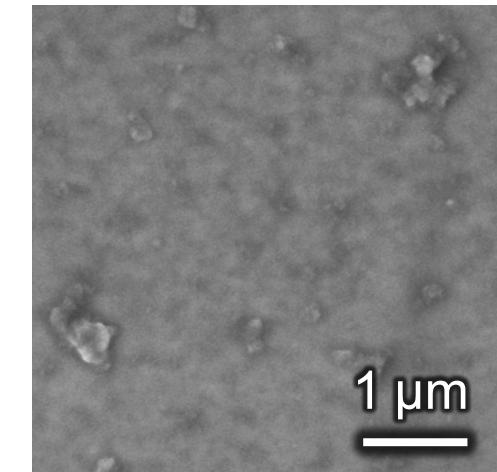
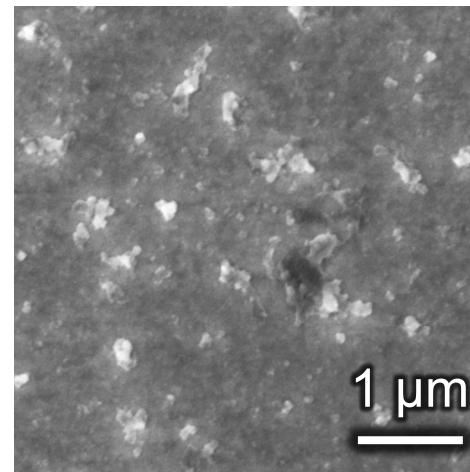
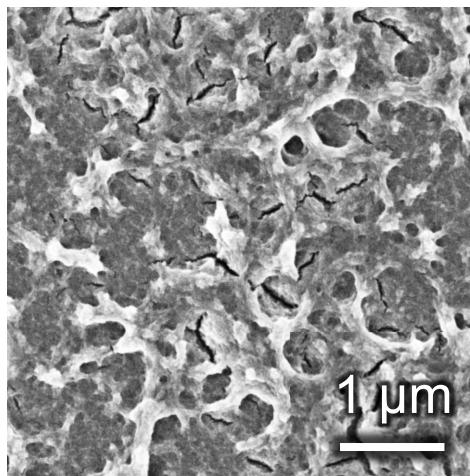
***Redox active intermediates formed during  $\text{Er}^{3+}$  reduction***

# Variation of Ionic Liquid Cation

0.1 M  $\text{Er}(\text{OTf})_3$  in  $\text{NTf}_2$  ionic liquids at a platinum surface



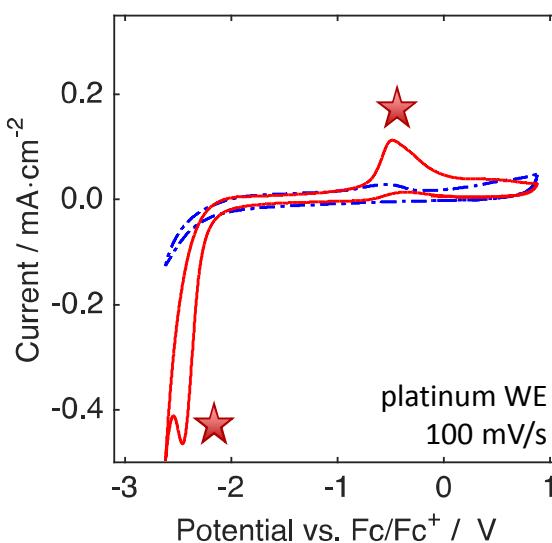
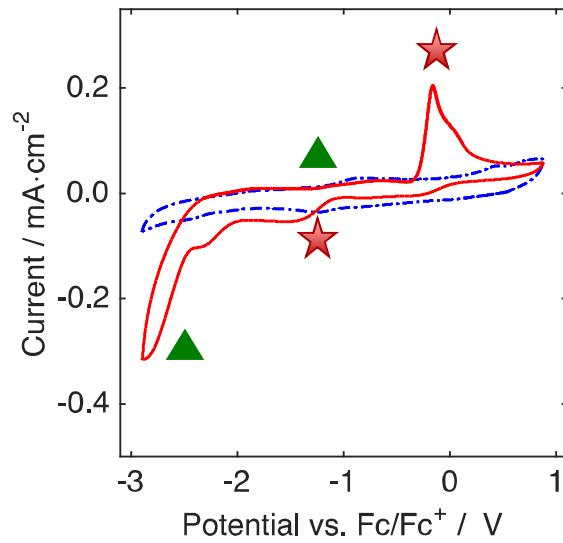
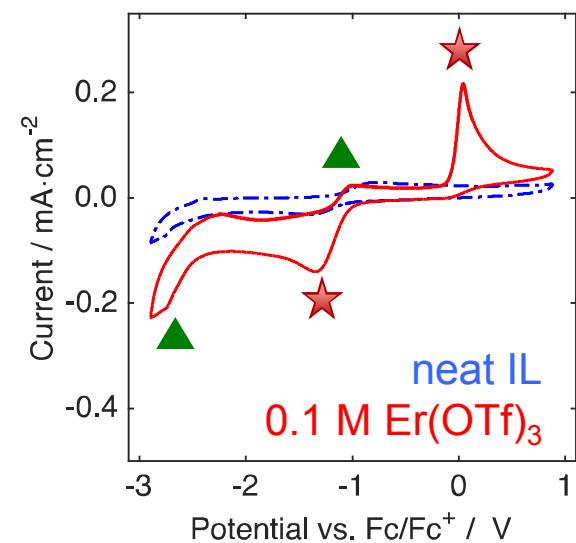
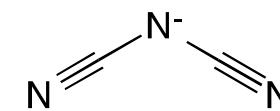
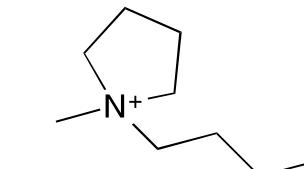
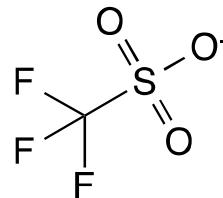
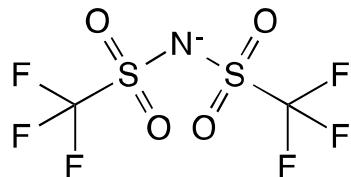
Deposit at -2.9 V for 2 hours



*Amorphous, anion-contaminated  $\text{ErO}_x$  deposited onto Pt.*

# Variation of Ionic Liquid Anion

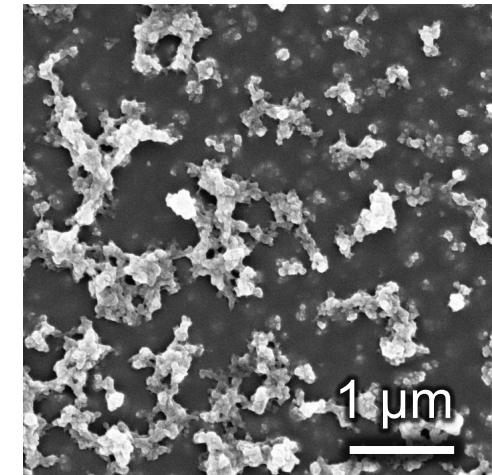
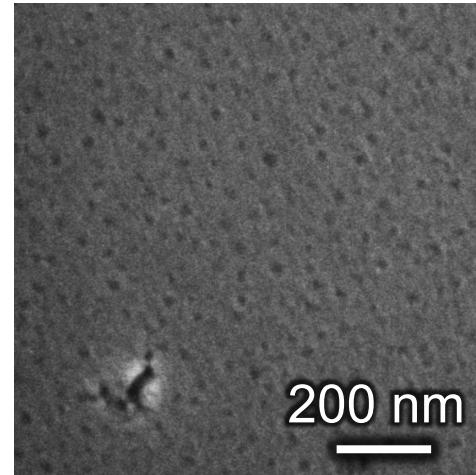
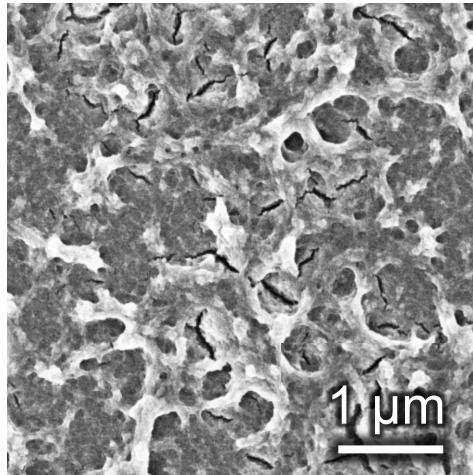
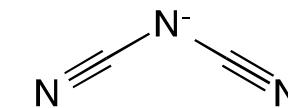
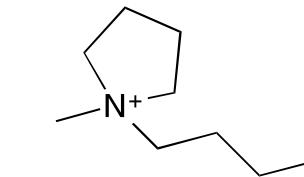
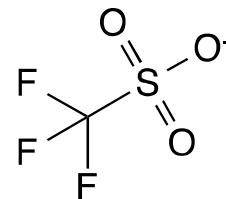
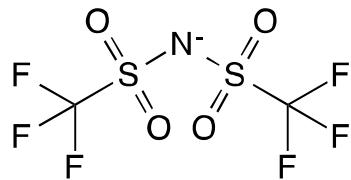
0.1 M  $\text{Er}(\text{OTf})_3$  in 1-butyl-1-methylpyrrolidinium ionic liquids at a platinum surface



***Redox active intermediates formed during  $\text{Er}^{3+}$  reduction***

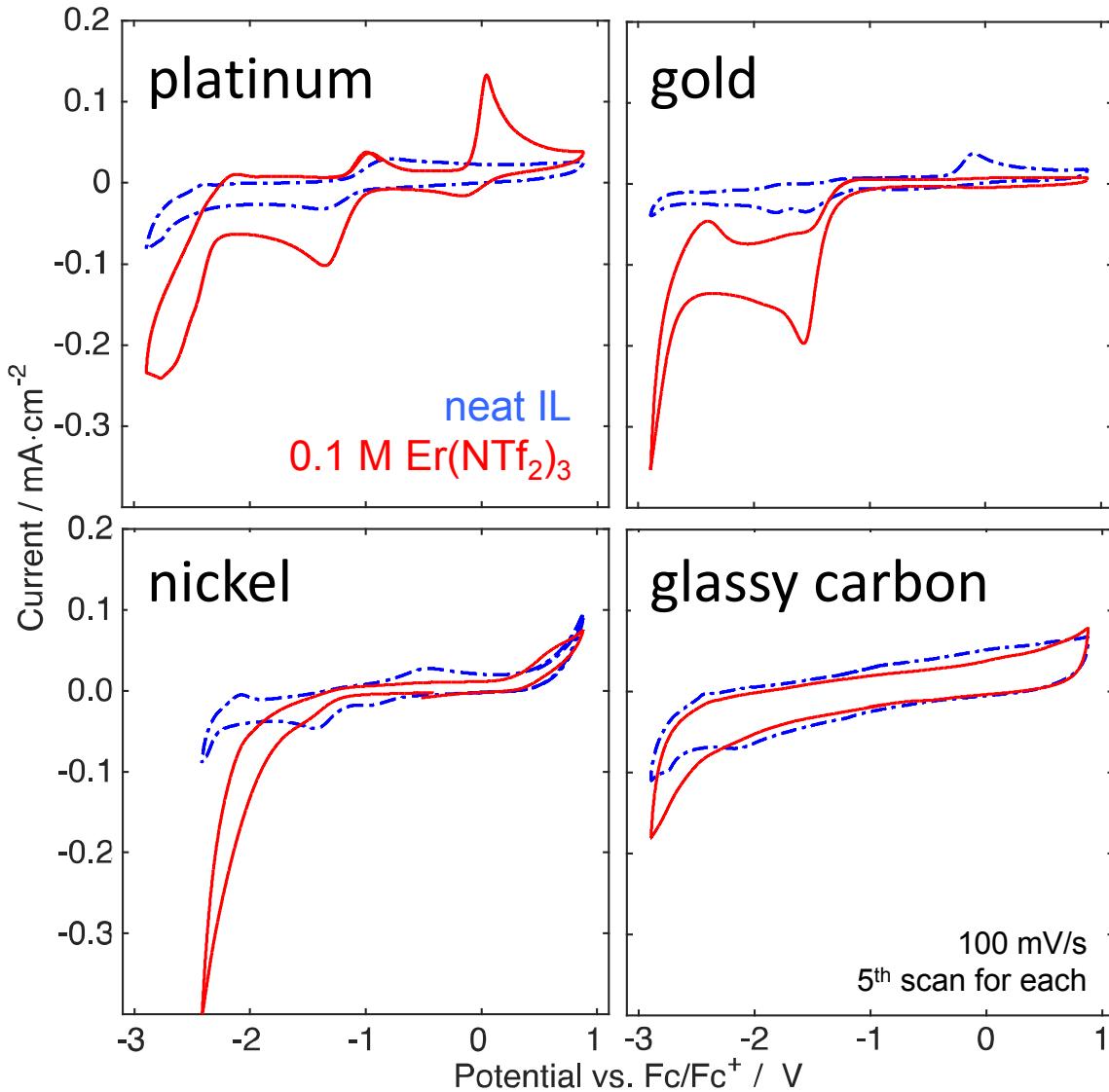
# Variation of Ionic Liquid Anion

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



*Amorphous, anion-contaminated  $\text{ErO}_x$  deposited onto Pt.*

# Er Deposition onto Different Materials



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

*Electrode material greatly influences deposition electrochemistry.*

# Summary

- REcycling of “nationally critical” erbium needed to provide alternative to foreign sources.
- Molten salts offer facile erbium redox, but severely limit processing flexibility.
- Ionic liquids offer a versatile medium for electroreduction.
- Investigation of processing space to improve  $\text{Er}^{3+}$  solubility, ionic liquid stability, deposition rate, and  $\text{Er}^0$  film purity.

# Acknowledgments

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- Dr. Timothy N. Lambert, Julian A. Vigil, Maria Kelly, Dr. Timothy J. Boyle, Jeremiah Sears, Dr. Ryan F. Hess
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