

# Electrochemical REcycling of Erbium using Ionic Liquids

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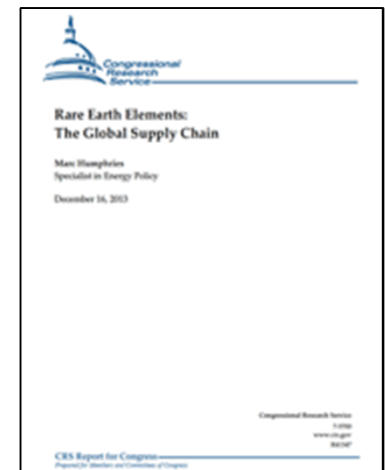
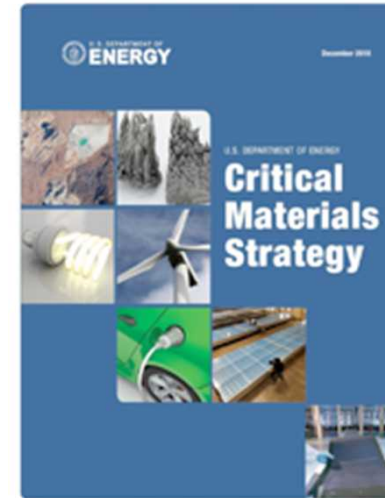
*Exceptional  
service  
in the  
national  
interest*



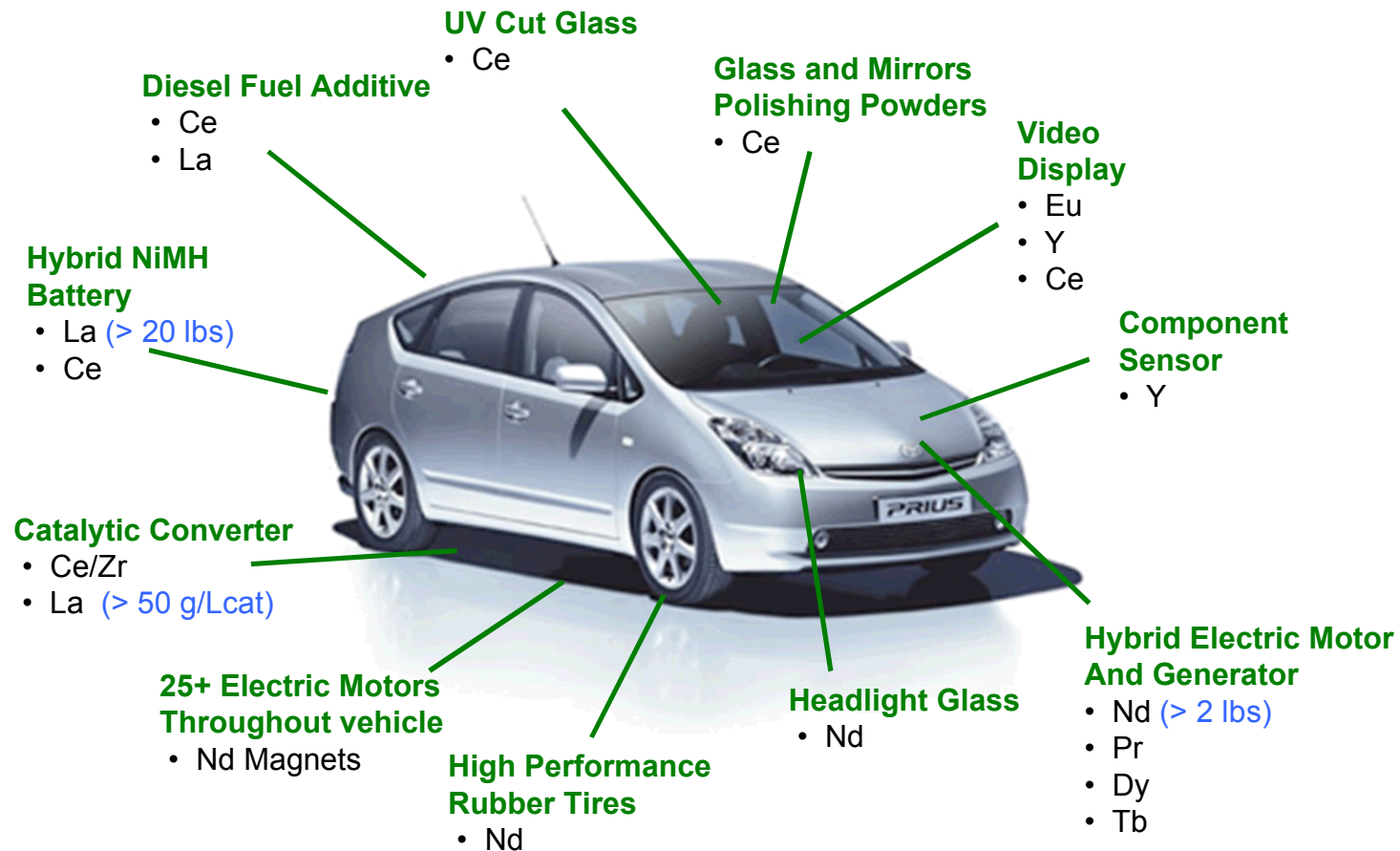
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# Overview

- 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

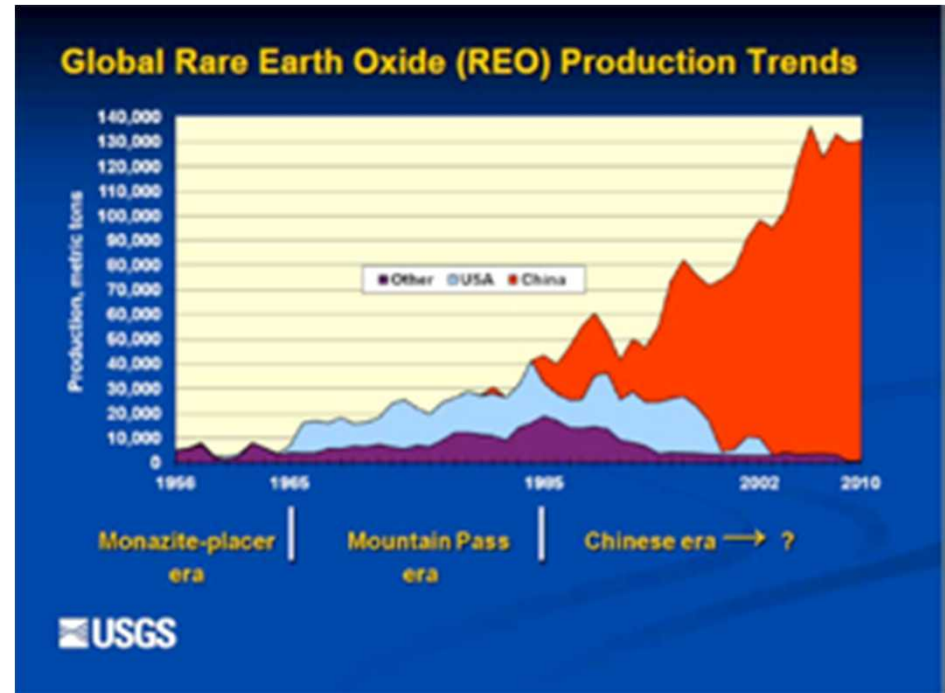


***“Analysts have called the Prius™ one the most rare-earth intensive consumer product ever made.”***

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

RE Historically Produced:

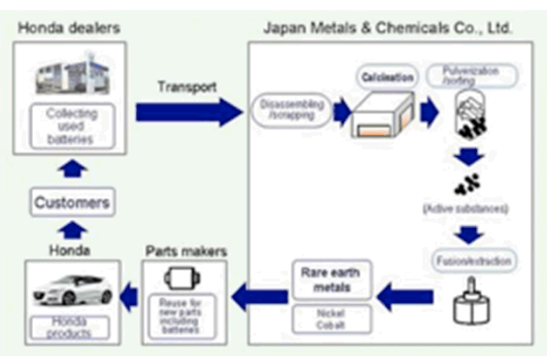
- 1950s: South Africa (monazite)
- 1960-1980: Mountain Pass (CA)
- 2000: Inner Mongolia, China
- 2011: MolyCorp resurrects Mountain Pass (CA)



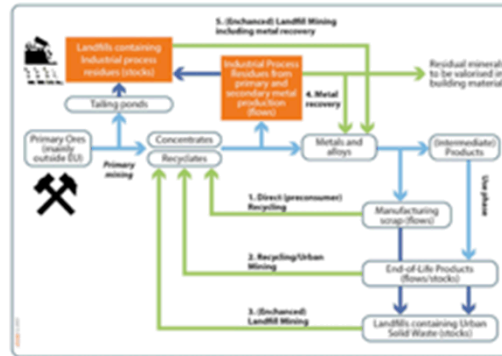
***Molycorp filed for bankruptcy in June 2015.***

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

# REcycle: A Route to Reduced Dependency



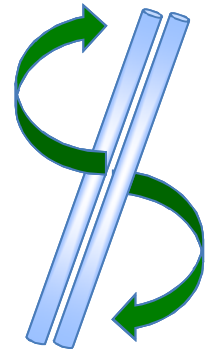
**Honda** recently announced that key materials for their hybrid automobiles will be recycled.



**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.



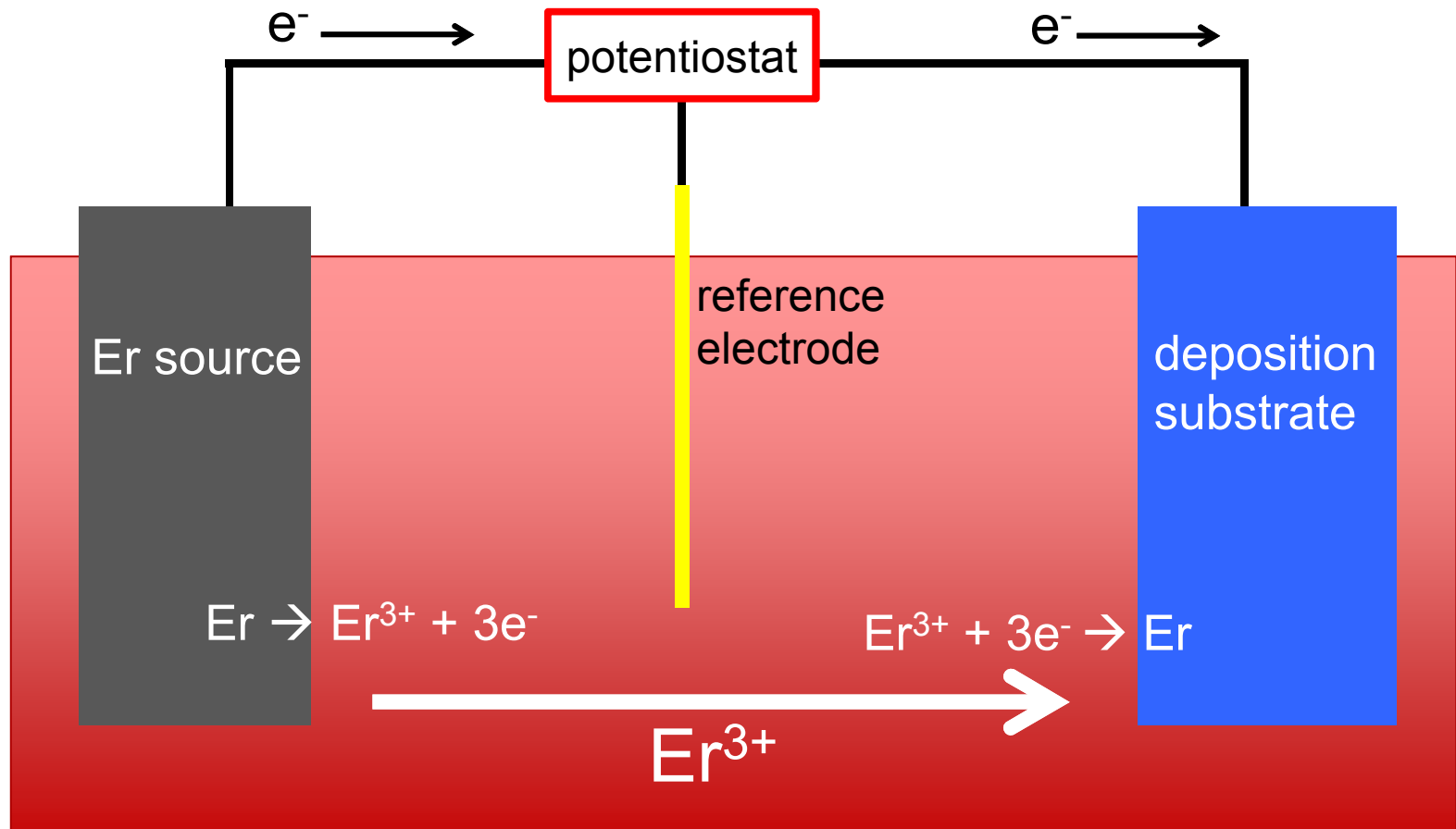
**Sandia** 8700 kg of fluorescent waste, a loss \$900,000 in RE material (per 2 yrs).

## *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**

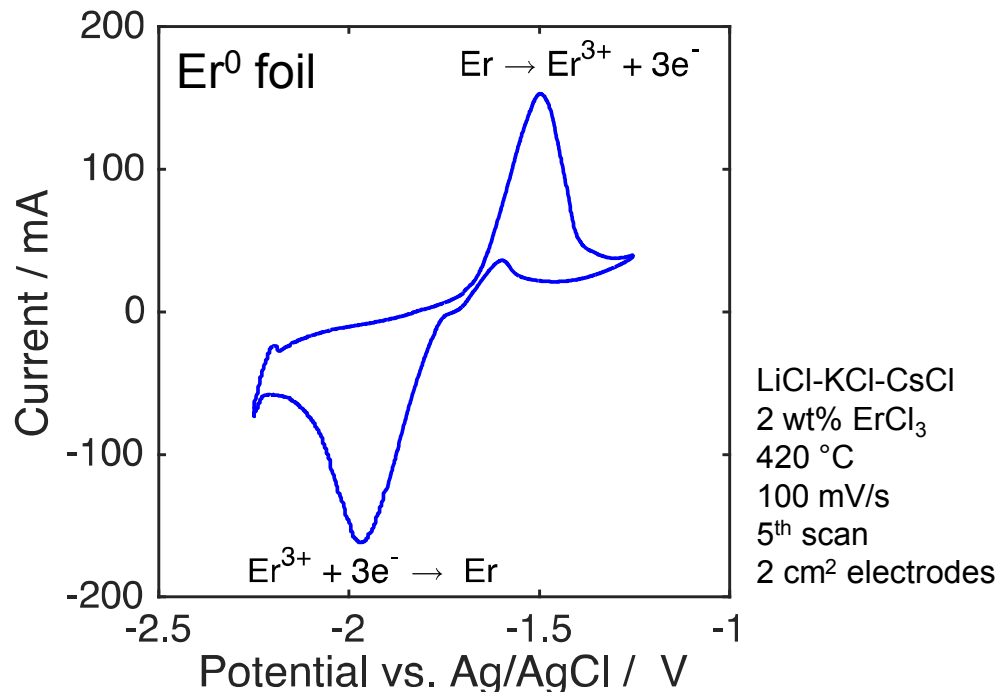
# Electrorefining Erbium



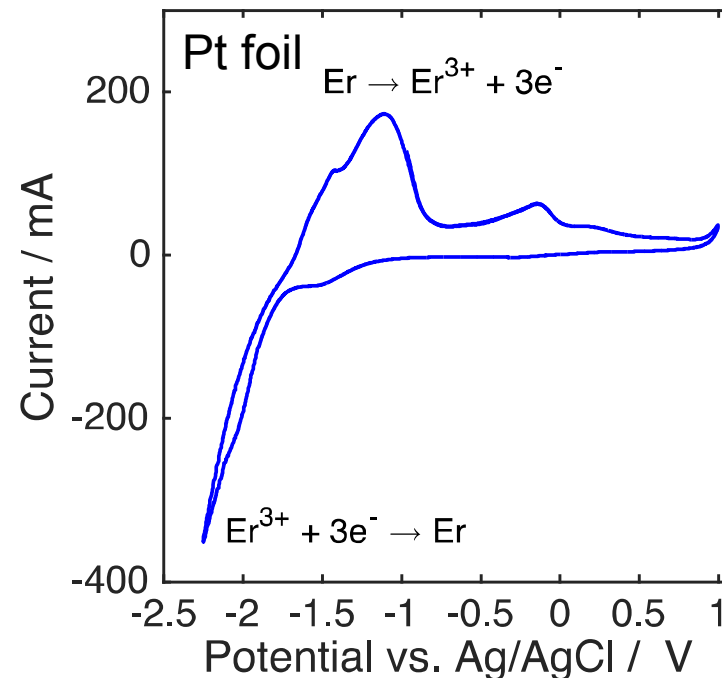
***Electrochemically move erbium from source to target substrate.***

# Electrorefining in Molten Salts

Erbium is easily oxidized into solution...



...and reduced onto platinum.

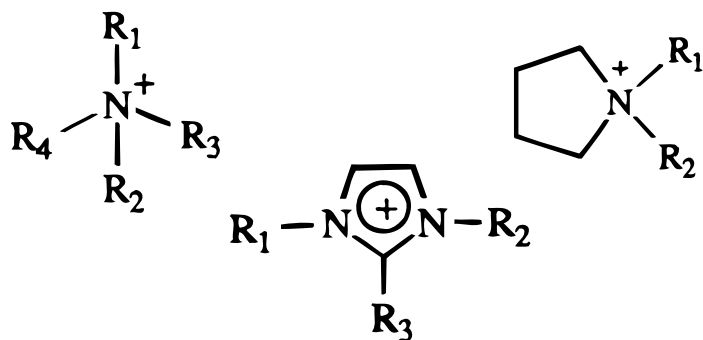


>90% Coulombic efficiency on 250 mg scale at **420 °C**  
***Inert environment with heat-tolerant materials required!***

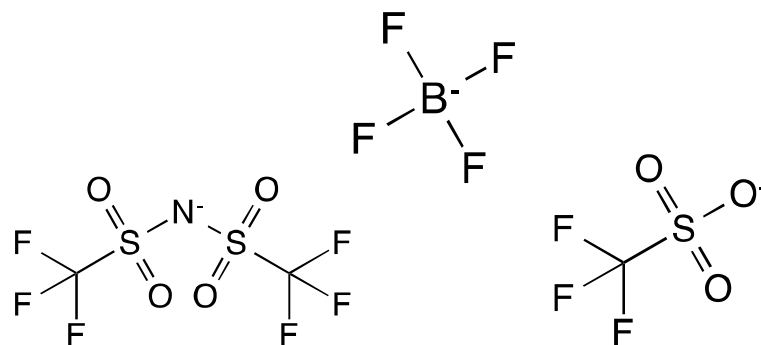
# Ionic Liquids

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

## Example Cations



## Example Anions

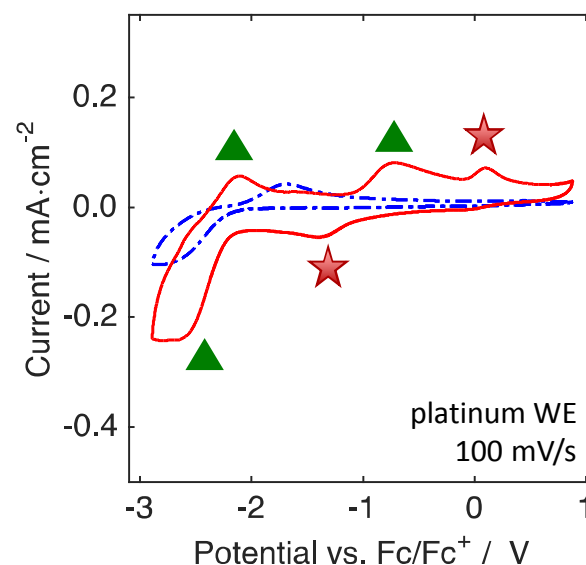
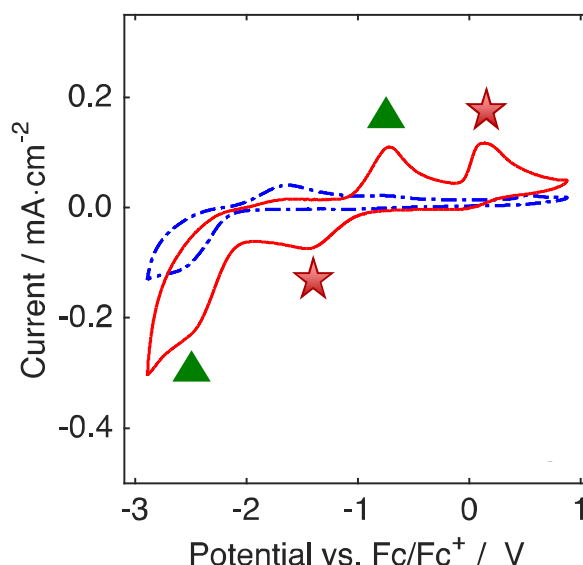
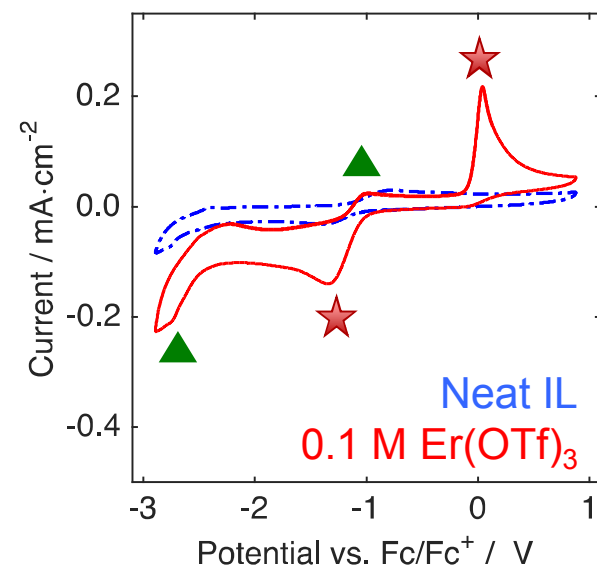
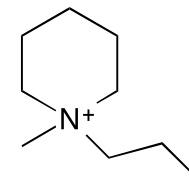
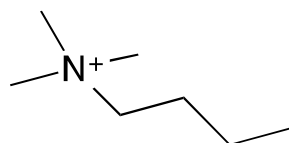
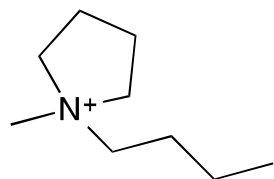
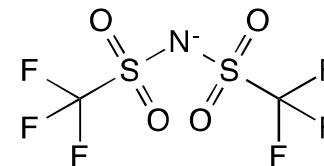


***Ionic Liquids may be tuned to have a wide range  
(electro)chemical properties.***



# Variation of Ionic Liquid Cation

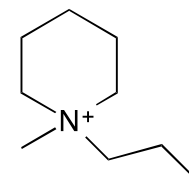
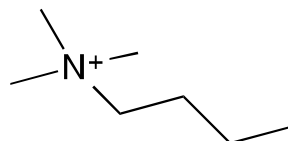
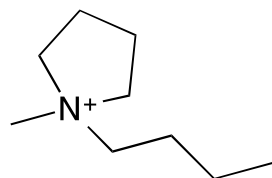
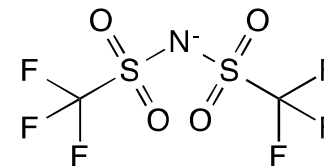
0.1 M  $\text{Er}(\text{OTf})_3$  in  $\text{NTf}_2$  ionic liquids at a platinum surface



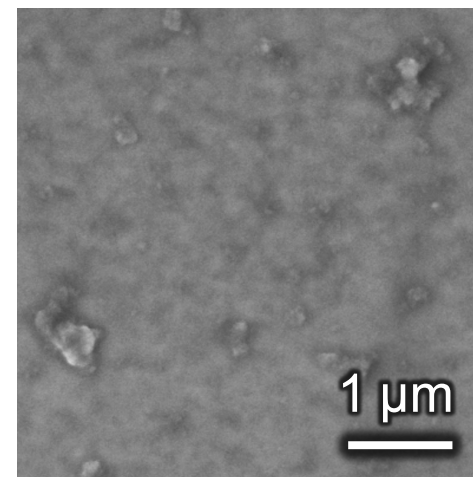
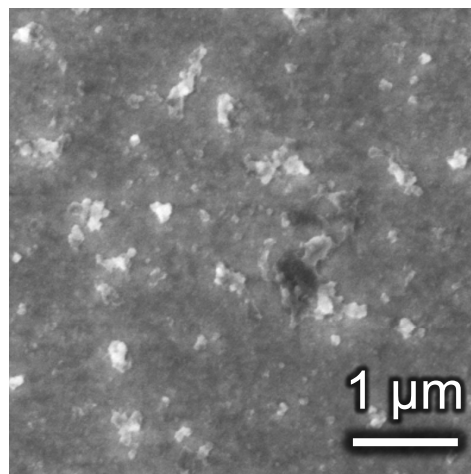
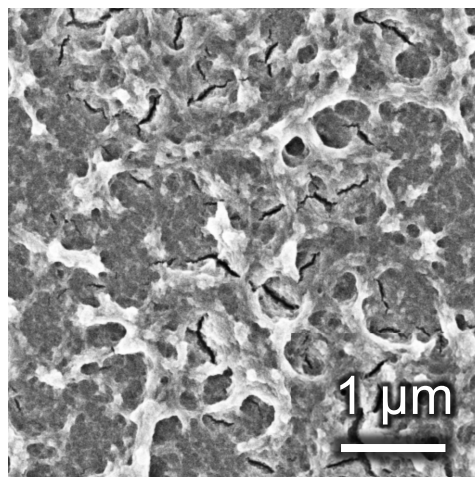
***Redox active intermediates formed during  $\text{Er}^{3+}$  reduction***

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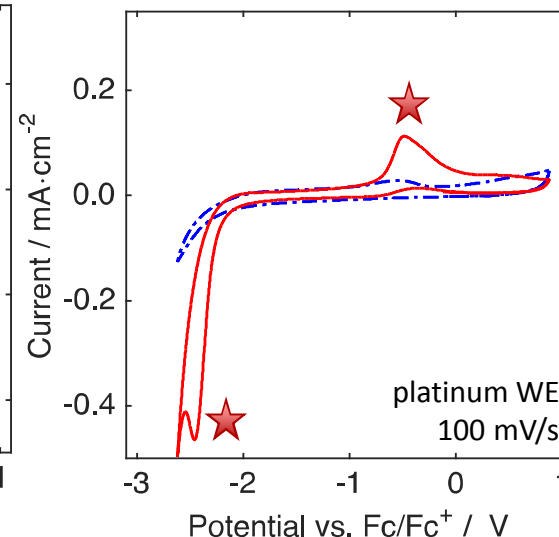
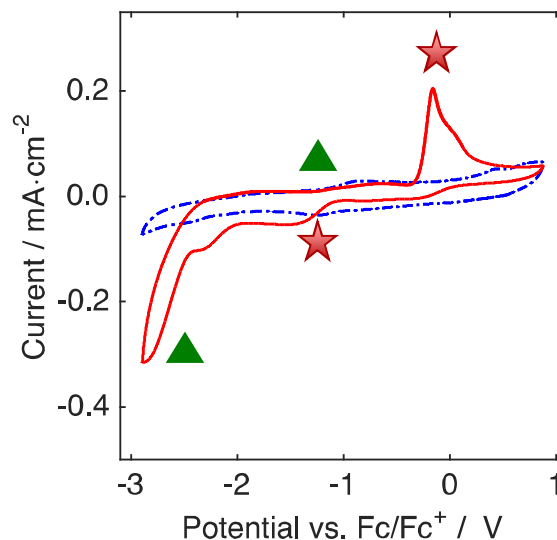
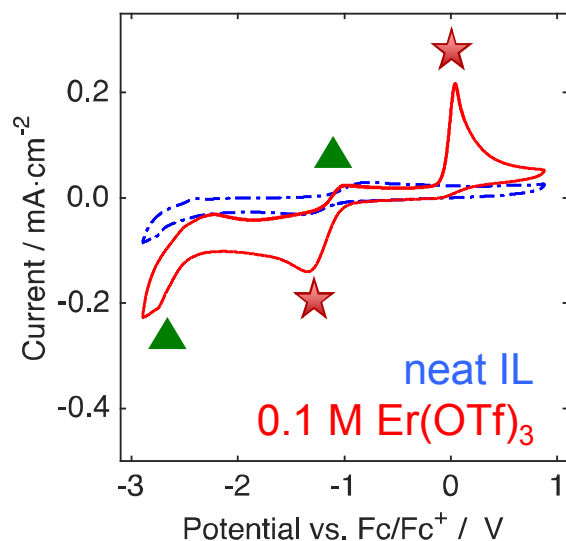
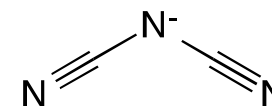
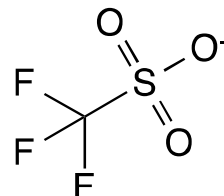
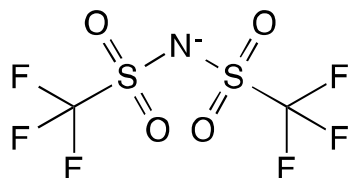
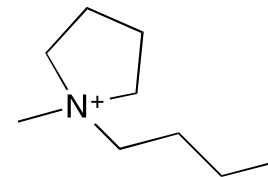
Deposit at -2.9 V for 2 hours



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

# Variation of Ionic Liquid Anion

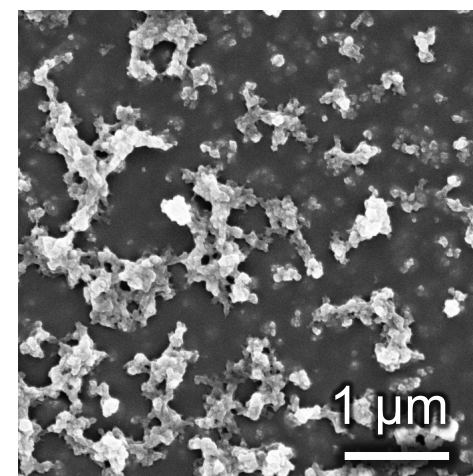
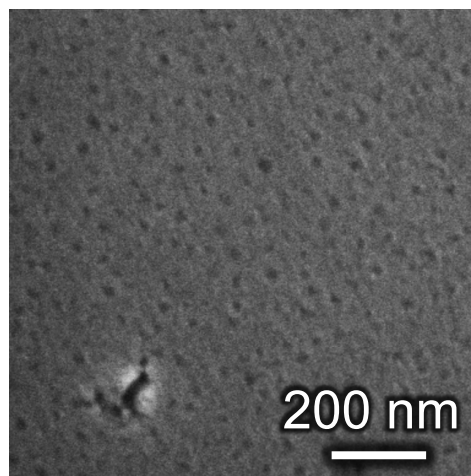
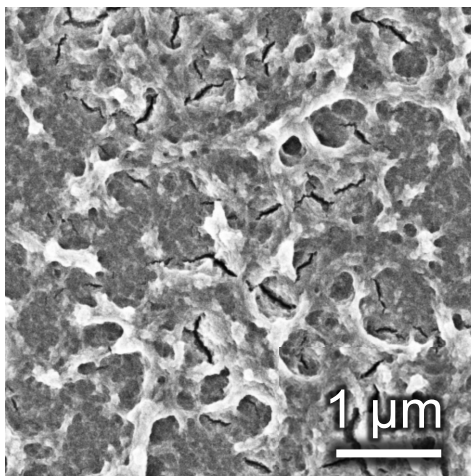
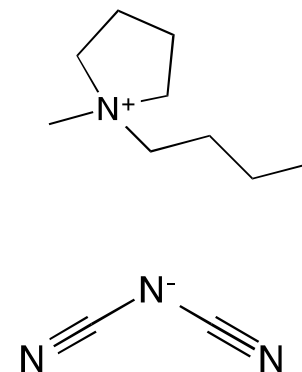
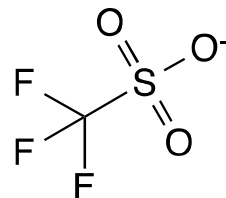
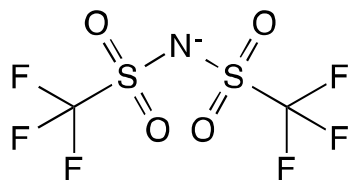
0.1 M  $\text{Er}(\text{OTf})_3$  in 1-butyl-1-methylpyrrolidinium ionic liquids at a platinum surface



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

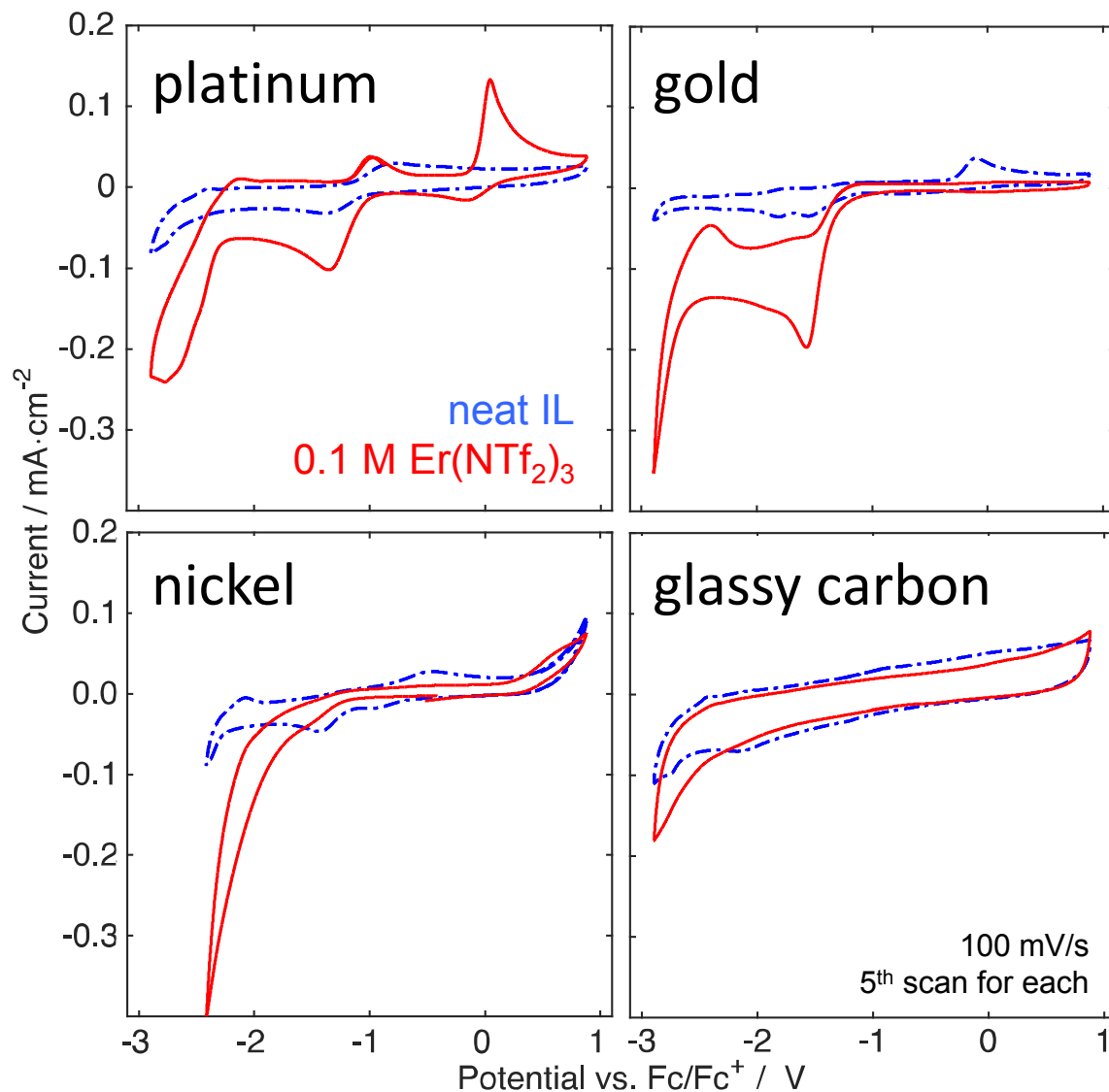
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***Amorphous, anion-contaminated  $\text{ErO}_x$  deposited onto Pt.***

# Er Deposition onto Different Materials



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

# 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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