RIL-343

Efficient Rare Earth Separation Technology

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Motivation

- Rare earth metals are valued for their unique magnetic, optical and catalyst properties. These materials are used in many high tech and clean energy applications including wind turbines, electric vehicles, photovoltaic thin films and fluorescent lighting.

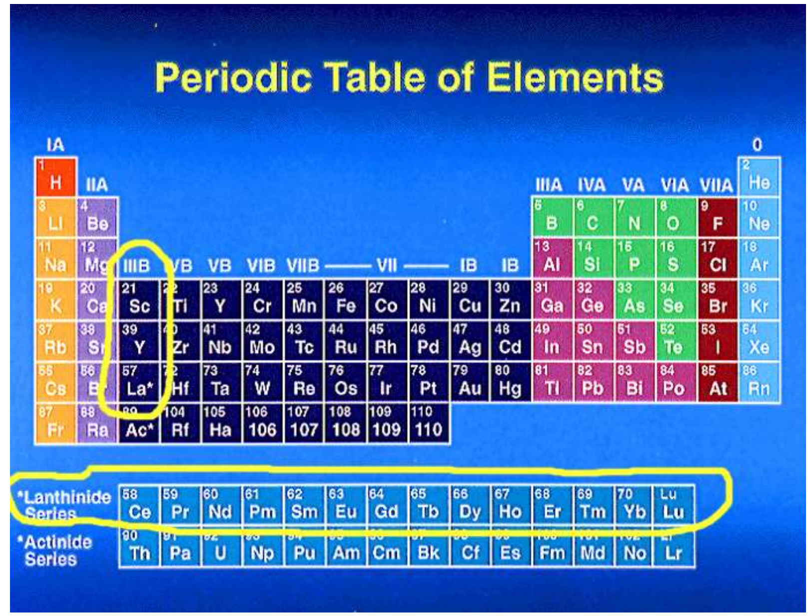
- Mineral and clay deposits in China and the United States represent the largest percentage of the world's rare earth economic resources.

- Currently, China produces 95-97% of the world supply of rare earth metals and oxides.

- Establishing a US rare earth mining and processing industry is of national interest to avoid a disruption in the supply of these strategic materials.

Rare Earth Elements

- What are they?
  - **lanthanide series**: cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum, lutetium, neodymium, praseodymium, samarium, terbium, thulium, holmium, ytterbium
  - **plus scandium and yttrium**



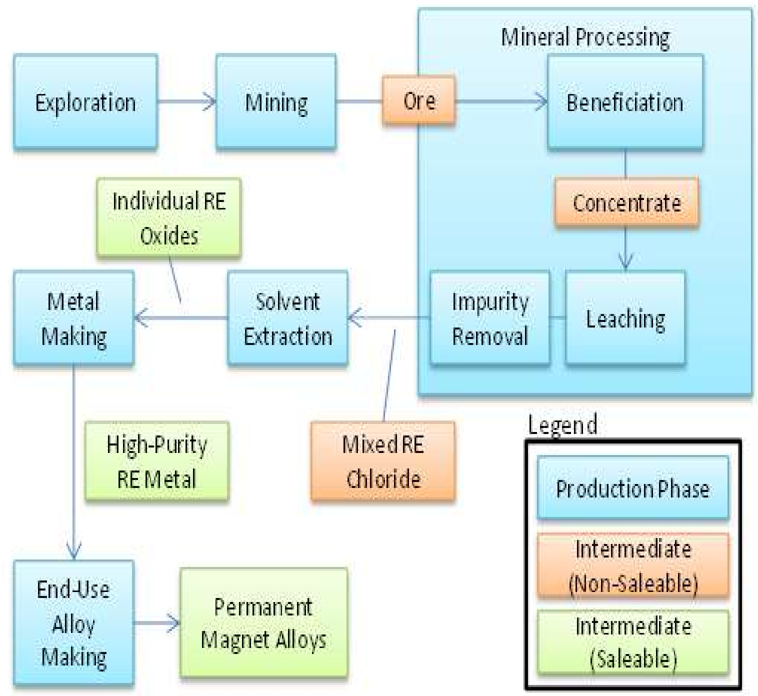
- Further classification
  - Light REE (LREE): atomic numbers 57-62 (La-Sm)
  - Heavy REE (HREE): atomic numbers 63-71 (Eu-Lu)

Rare Earth Processing: *Mine-to-Magnets*

- Processing the ore consists of beneficiation, leaching, and then separation to result in separated rare earth metals/oxides

- **Separating the rare earths is challenging**

- Currently, refineries exploit the slight differences in solubility in multi-stage solvent extraction technology to separate and purify the rare earths
  - ***Ytterbium requires 1000 stages*** for complete separation.



Reactive's Approach

- Improve the production of rare earth metals by essentially **combining the extraction and separation processes**.
  - Want to selectively electrodeposit individual light rare earth (lanthanide) metals from a mixture containing their respective salts or oxides

- Our process separates and converts the rare earth salts and oxides in one low temperature environmentally benign processing step.

- Our process makes use of the unique properties of ionic liquids in electrochemical processing.

- Builds on recent advances using ionic liquid media to extract, dissolve, and electrodeposit metals from salts and oxide precursors

Rare Earth Processing in Ionic Liquids

- Solubility of Rare Earth precursors in ionic liquids?
  - Published solubility data[1,2] indicates low solubility of rare earth precursors

  - Work ongoing to increase solubility by tailoring ionic liquids and/or adding modifiers

- Electrodeposition of Rare Earths using Ionic Liquids
  - Ionic liquids are not limited by the water "window"
  - Not all ionic liquids are the same: cathodic stability can still be a problem

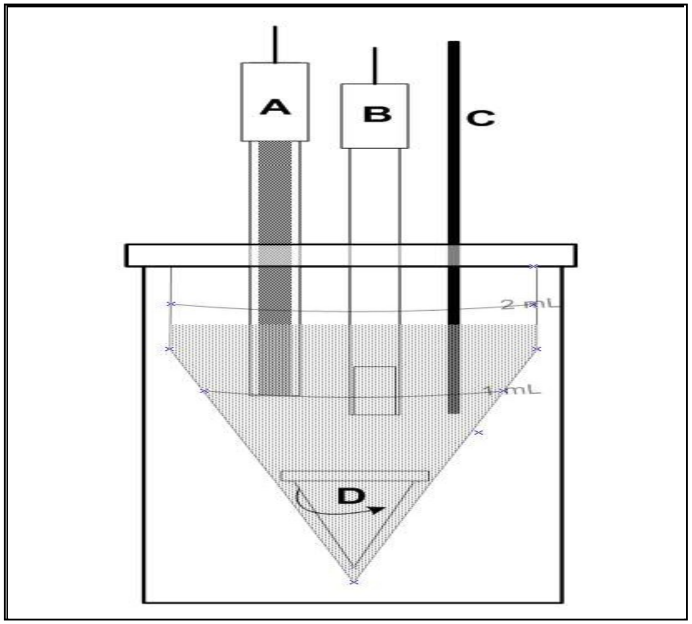
Proper selection of anion/cation pairs and pretreatments can lead to tailored properties to improve solubility and cathodic stability.

[1]Binnemans, K. *Chem. ReV.* 2007, *107*, 2592-2614.

[2]Mehdi, H.; Bodor, A.; Lantos, D.; Horvath, I. T.; De Vos, D. E.; Binnemans, K. *J. Org. Chem.* 2007, *72*, 517-524.

Research Methodology

- Achieve metal oxide solubility in ionic liquids
- Identify individual reduction peaks using cyclic voltammetry
- Electrodeposit rare earth metal at constant potential



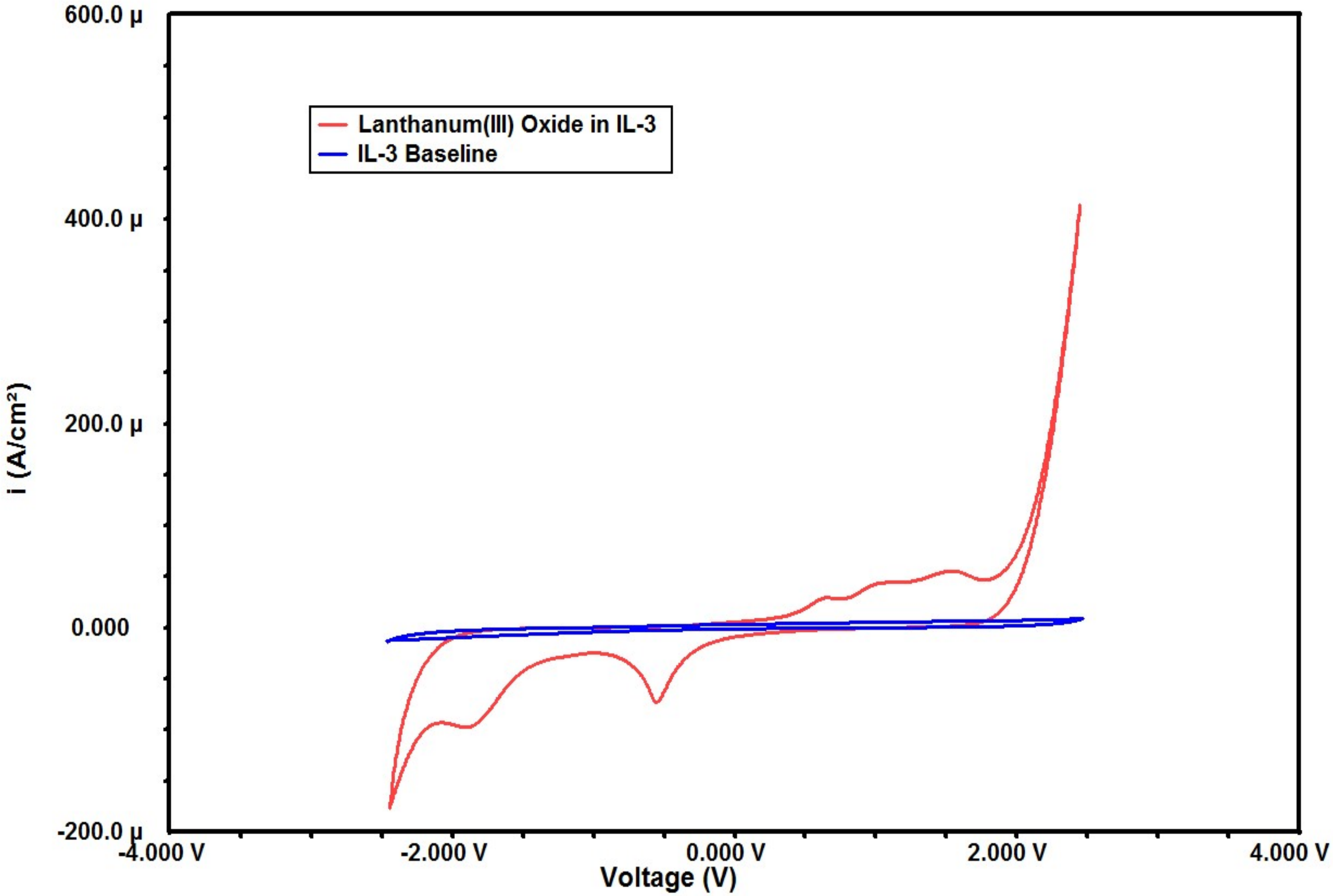
Standard 3-electrode cell used for cyclic voltammetry studies and bulk electrodeposition

Solubility Investigated to Dissolve Rare Earths

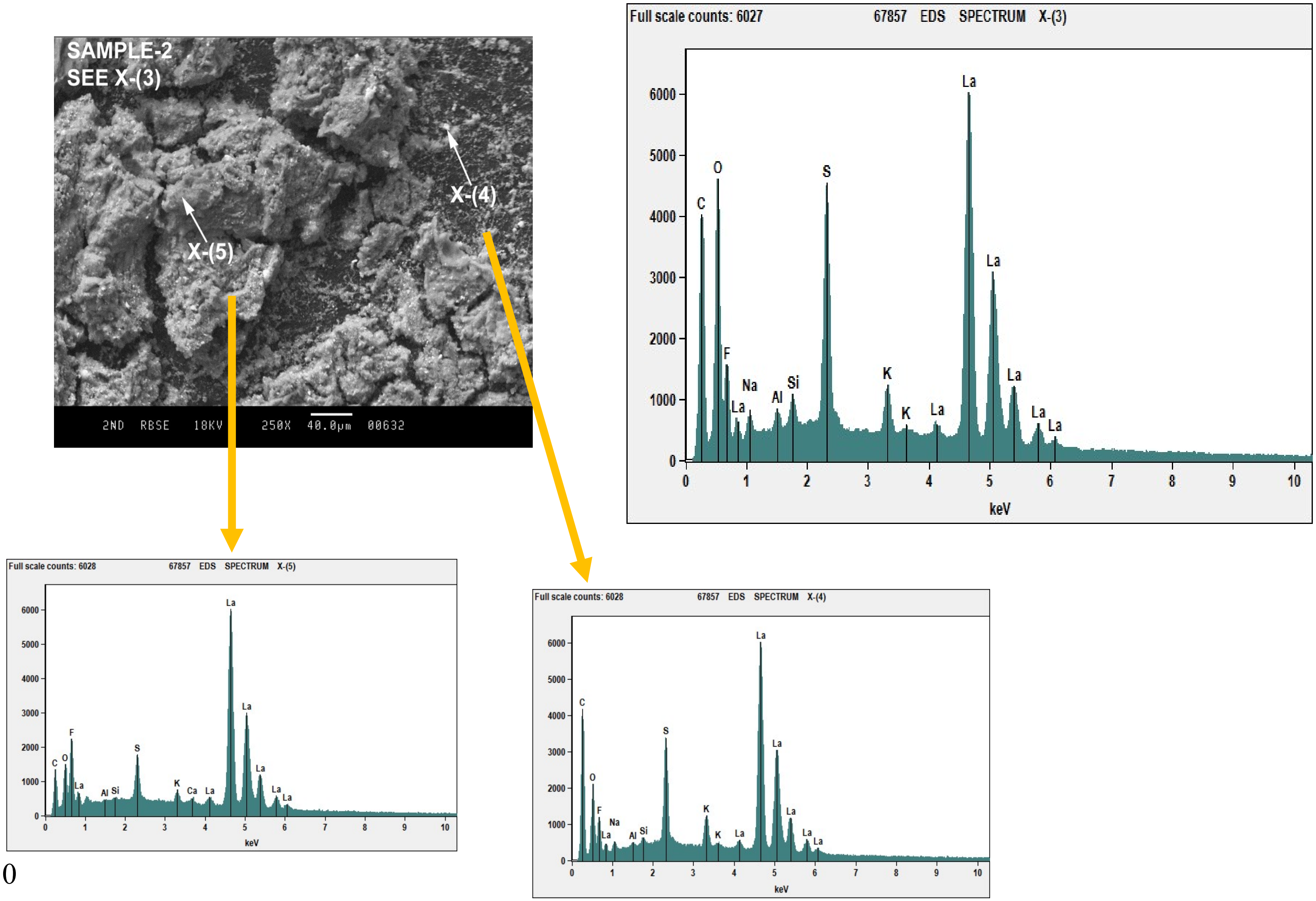
- Investigated several ionic liquids
  - Wide electrochemical window
  - Solubilize rare earth precursors

- Found one ionic liquid able to dissolve stoichiometric amounts of rare earth
  - A stoichiometric amount of metal oxide M_xO_y is dissolved if for every mole of M_xO_y, the amount of ionic liquid required equals *x* times the oxidation state of the metal. In other words, if 1 mole of M_2O_3 can dissolve in 6 moles of ionic liquid, it is a stoichiometric solution.
  - Work ongoing to improve cathodic stability
- Other select ionic liquids achieved significant dissolution of rare earth precursors
  - Developed proprietary pretreatments of electrolyte to improve cathodic stability and solubility
  - Rare earth oxide/ionic liquid approximate concentration greater than 0.1 M

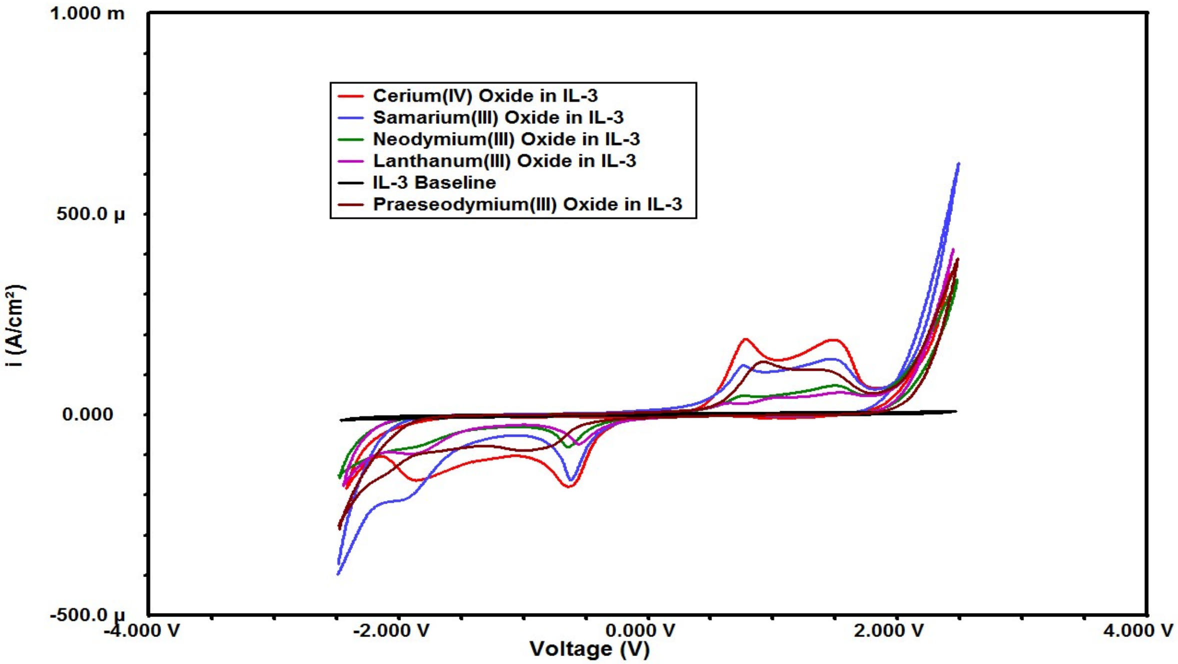
Cyclic Voltammetry Examination of Lanthanum oxide in ionic liquid (IL-3)

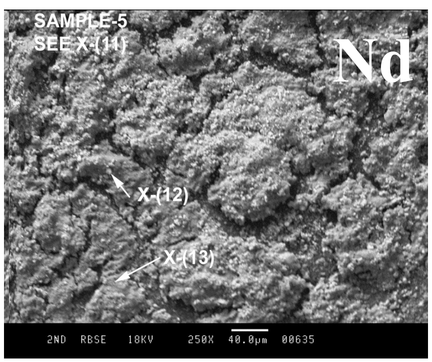


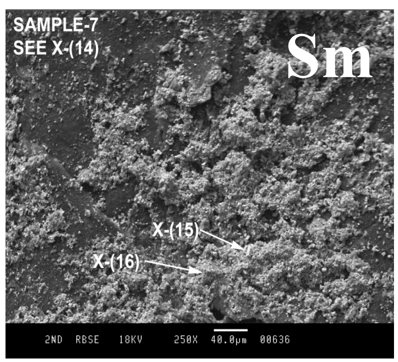
Bulk Electrodeposition and EDAX Results

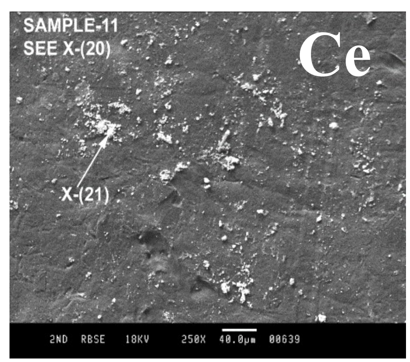


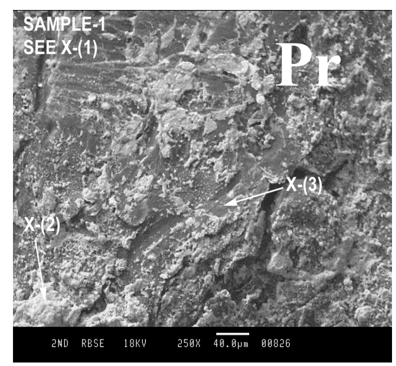
Cyclic Voltammetry Results Show Successful Deposition of La, Ce, Nd, Sm, Pr





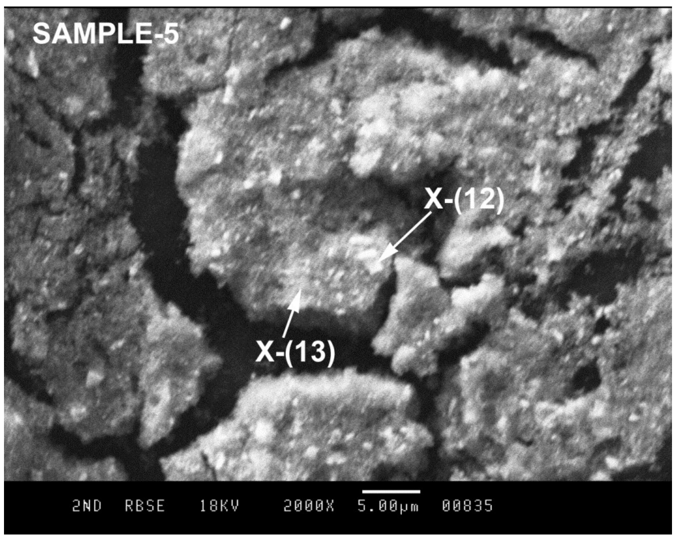


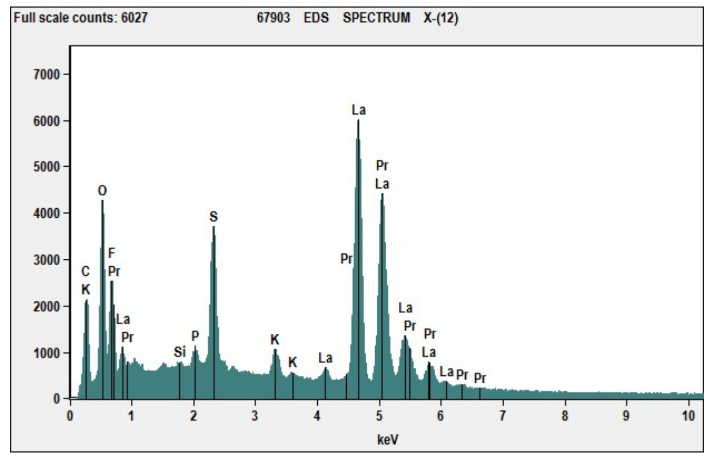




Selective Deposition of Rare Earth Metals

- Equimolar La/Pr binary solution
- Electrodeposit at constant potential
- EDAX analysis on deposit show significant La enrichment.

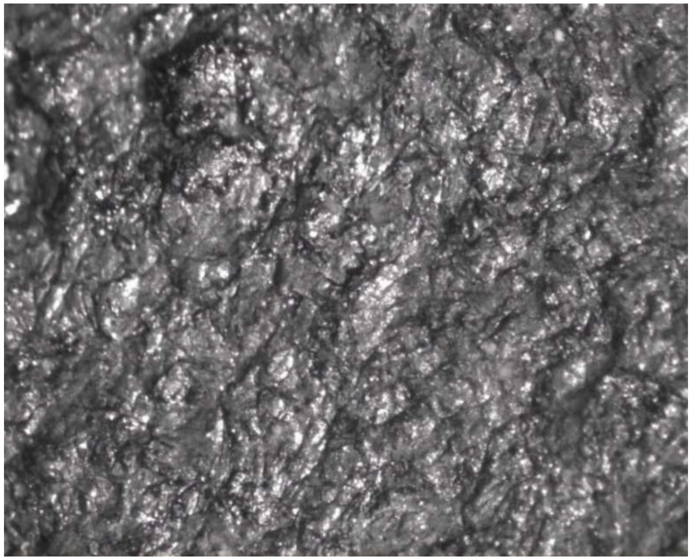




Element	*Atom %*	*Rel. Ratio*	*Rel. %*
Lanthanum (La)	15.9	0.807	80.7
Praseodymium (Pr)	3.8	0.193	19.3
Total	19.7	1.000	100.0

Electrodeposition Waveform Affects Deposit Morphology

- Constant potential versus pulse deposition
- Limited experiments with Praseodymium highlight the possibilities of this technique



Constant potential deposition of Pr on grafoil

Pulsed deposition of Pr of grafoil

Summary

- Successfully dissolved rare earth precursors in ionic liquids
- Demonstrated bulk electrodeposition of five rare earths (La, Ce, Nd, Sm, Pr) from ionic liquid electrolytes
- Developed proprietary techniques to improve solubility and electrodeposition
- Demonstrated selective deposition of rare earths from a binary mixture
- Next steps involve
  - Scale-up of the bulk electrodeposition of individual rare earths
  - Further study and optimization of selective deposition

Acknowledgments

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