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RARE METAL EXTRACTION & PROCESSING  
RARE EARTH ELEMENTS II AND PLATINUM GROUP METALS

ELECTROCHEMICAL BEHAVIOR OF NEODYMIUM  
IN MOLTEN CHLORIDE SALTS

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DE LA RECHERCHE À L'INDUSTRIE  
**cea den**



Rare earth (RE) **metal** are commonly used in advanced technologies

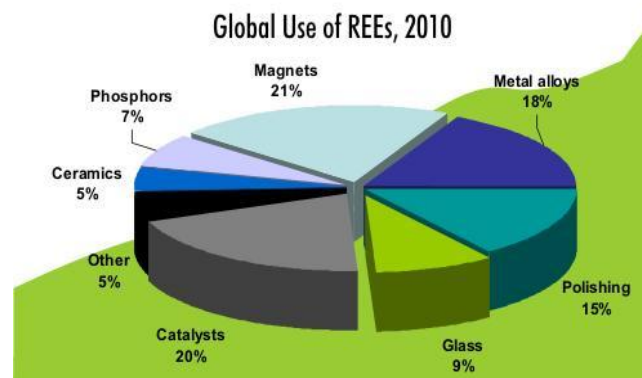
→ Uses:  $\approx$  40% of RE metal

RE metal:

- **Metallurgy**: reduction by Ca, Li, Na metal
- **Electrolysis** in molten salt

→ impossible in aqueous media

**Europe**: storage of waste containing rare earths



Rare earth recycling from **permanent magnets** NdFeB and **NiMH batteries** by:

- **Hydro/pyro** process (dissolution, selective extraction, electrolysis)
- **Pyrometallurgical** process ( $\text{FeCl}_2$  oxidation or chloration and electrolysis)



- Fluoride media:**

**Industrial process Nd-Fe alloy :** electrolysis of  $Nd^{3+}$  in  $LiF-NdF_3-Nd_2O_3$  molten salt on iron cathode at 1050 °C

→ **Liquid alloy Nd-Fe (80-20%)**

- Chloride media:**

Electrodeposition leads to **low recovery yields (<40%)**

→ Stability of  $Nd^{2+}$  in chloride salt

→ Comproportionation reaction:

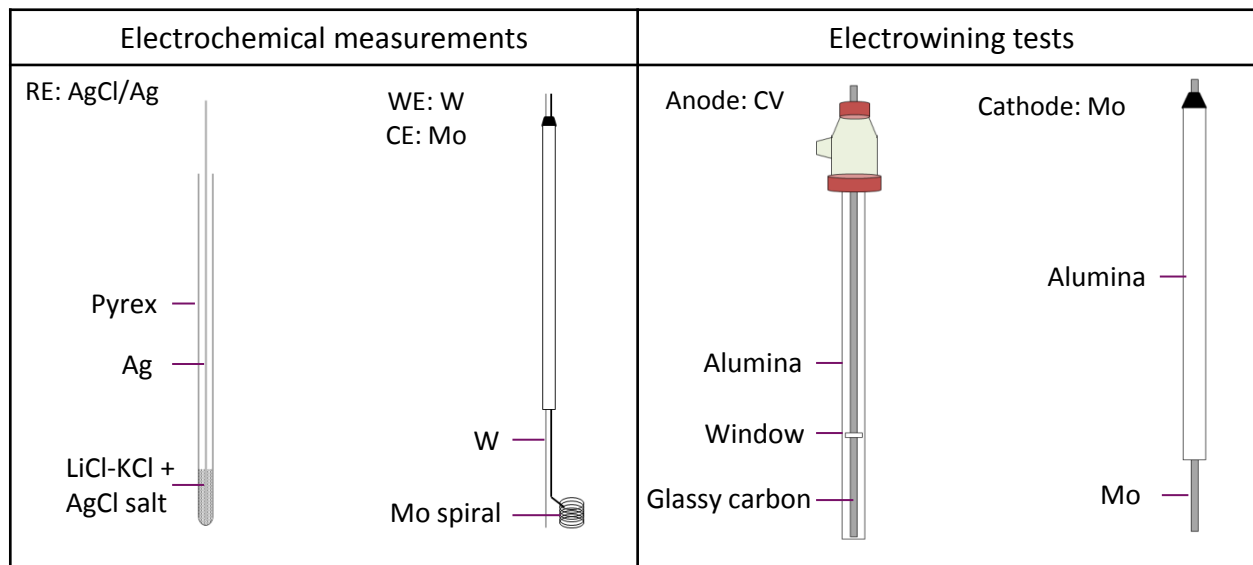
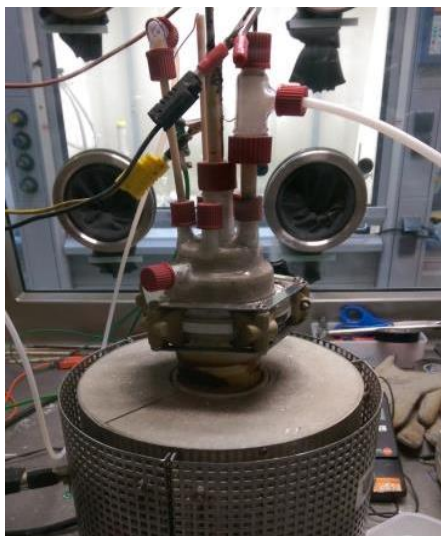


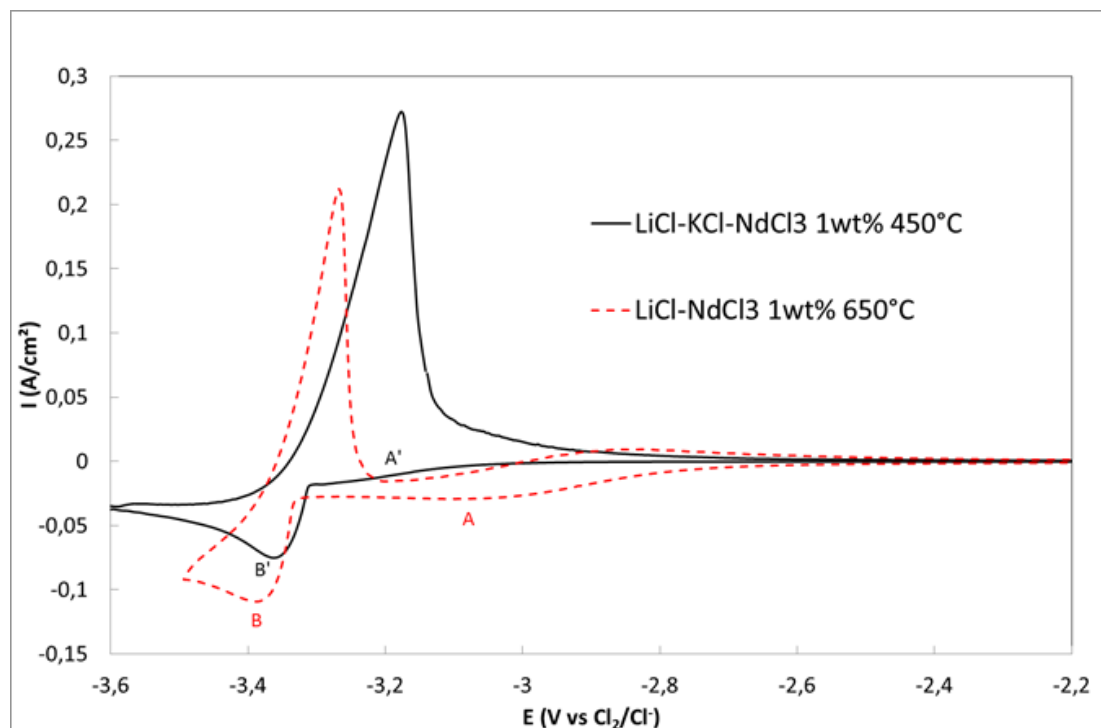
Lucas et al. 2015





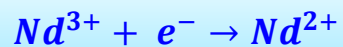
- Inactive pyrochemical lab in glove-boxes (< 10 ppm of H<sub>2</sub>O and O<sub>2</sub>)
- Cell: quartz
- Salt are stored at 150°C
- Salt fusion in an alumina crucible under Ar
- Working temperature:  
450 °C (LiCl-KCl) and 650°C (pure LiCl)





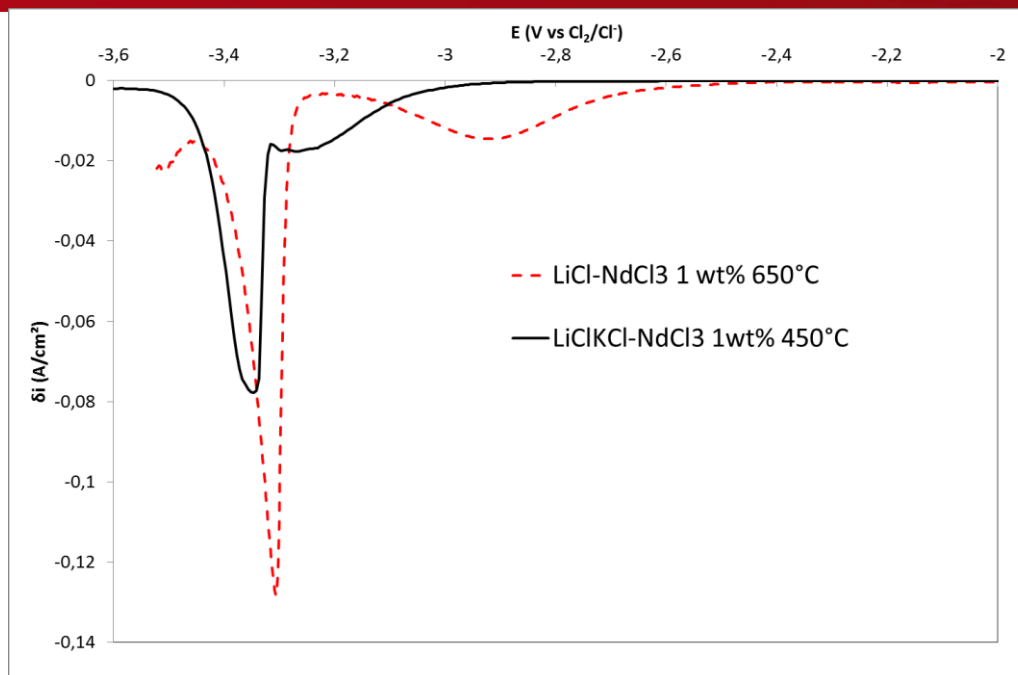
Cyclic voltammograms of  $\text{NdCl}_3$  (1 wt%) in LiCl-KCl and LiCl melts at  $v=100$  mV/s, working electrode: W

- Two step reduction:



→ The electrochemical behavior of  $\text{Nd}^{3+}$  depends on the melt composition (chloroacidity)





Square wave voltammograms for the reduction of 1 wt%  $\text{NdCl}_3$  at a W electrode in LiCl-KCl at 450 °C and LiCl at 650 °C

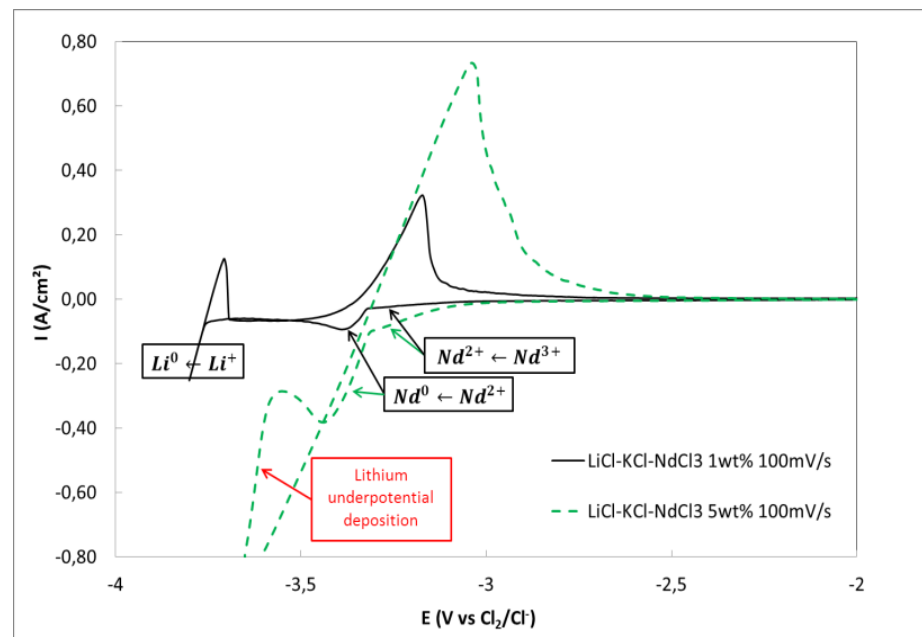
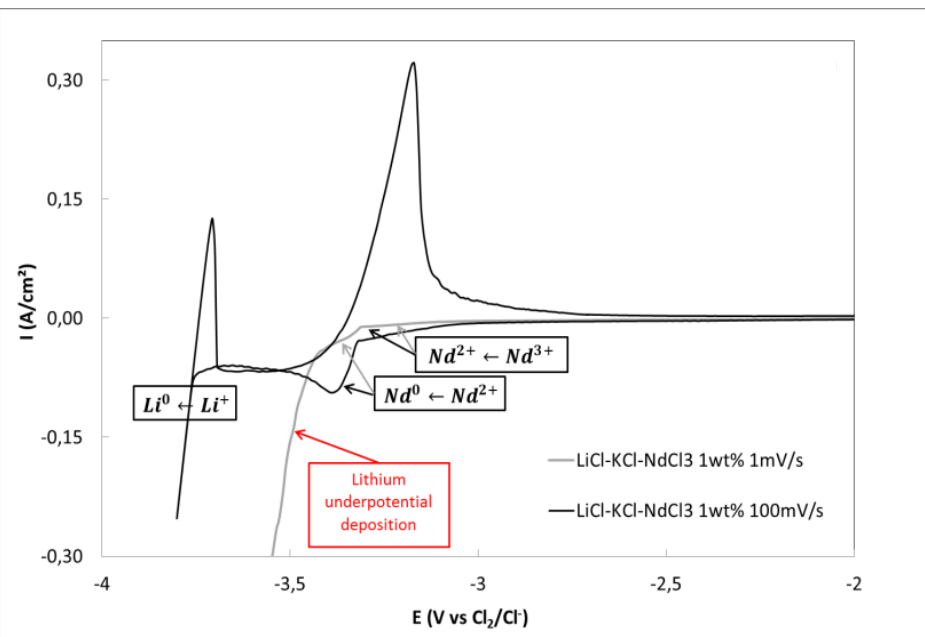
Square wave voltammetry :

- First step: 1 electron exchanged
- Second step: not well defined

$$W_{1/2} = 3,52 \frac{RT}{nF}$$

→ Effect of comproportionation reaction





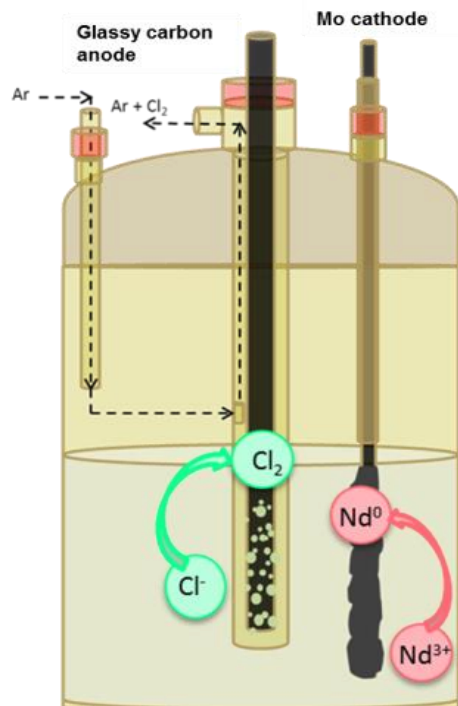
Lithium underpotential deposition when neodymium salt concentration is increased (*Martinez et al. 2012*)

- Low  $\text{Nd}^{3+}$  concentration (1 wt. %) at low scan rate ( $< 10\text{mV/s}$ )
- High  $\text{Nd}^{3+}$  concentration ( $> 3$  wt. %) at any scan rate

This characteristic was also observed for several lanthanide elements (La, Ce)







Reduction of  $\text{NdCl}_3$  at  $450^\circ\text{C}$  in  $\text{LiCl-KCl}$  with a high argon flow (10 L/h) by **electrolysis** under constant current ( $0.15\text{A}/\text{cm}^2 < J < 0.3\text{A}/\text{cm}^2$ )

**Low recovery yield**  $< 45\%$  in  $\text{LiCl-KCl}$

Significant impact of chemical reaction: dissolution of metal despite polarization



$E_{\text{OCP}}$  is progressively shifted after several electrolysis to the  $\text{Nd(III)/Nd(II)}$  redox potential: presence of  $\text{Nd(II)}$  in solution according to Nernst's law

Neodymium: metallic **powder**

Lanthanum and cerium: **dendritic** structure

Neodymium



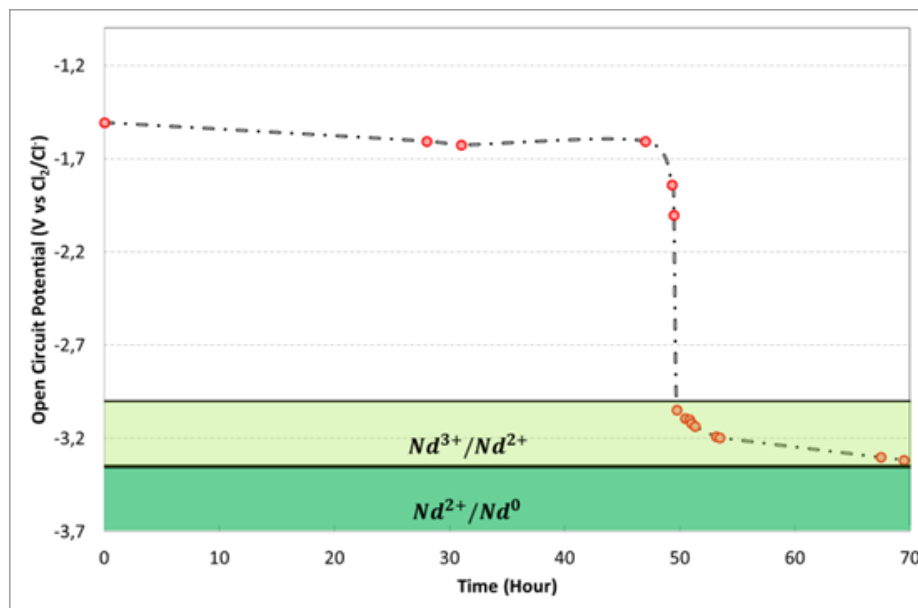
Lanthanum

Cerium



S. GERAN, CEA 2016

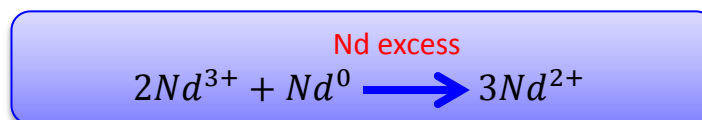




Open circuit potential variation during presence of Nd metal in salt

Addition Nd metallic ingot in a BN basket to a fresh LiCl-KCl-NdCl<sub>3</sub> salt: similar changes of E<sub>OCP</sub> are observed

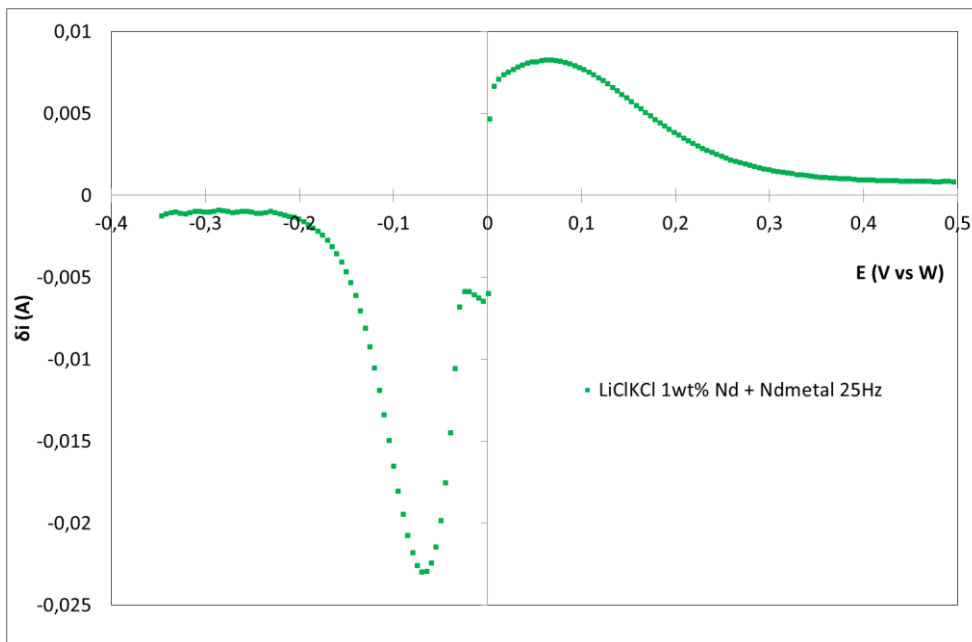
E<sub>OCP WE</sub> is shifted to Nd(III)/Nd(II) system (spectrophotometric studies: *Hayashi et al. 2004*)



E<sub>OCP</sub> is stable for several weeks

Nd(III) signal doesn't completely disappear: equilibrium between E<sub>Nd(III)/Nd(II)</sub> and E<sub>Nd(II)/Nd(0)</sub>





Square wave voltammograms at 25 Hz for the reduction of LiCl-KCl-NdCl<sub>3</sub> (1 wt%) after metal addition at a W electrode.

**Anodic SWV:** 1 electron exchanged



**Cathodic SWV:** residual Nd(III) reduction + Nd(II) reduction with an exchange of 2 electrons



Number of electrons is well defined in these conditions

**Dark-purple salt** → NdCl<sub>3</sub> and NdCl<sub>2</sub> in solution

*Hayashi et al. 2004:* NdCl<sub>2</sub>: dark-red; NdCl<sub>3</sub>: violet-blue



## Conclusions

Electrochemical behaviour:

- $\text{Nd}^{3+}$  reduction in a two step mechanism with an intermediary  $\text{Nd}^{2+}$
- $\text{Nd}^{2+}$  is stable under reducing conditions (presence of Nd metal)
- Lithium underpotential deposition is observed at high concentration of Nd(III)
- $\Delta E$  between Nd(III)/Nd(II) and Nd(II)/Nd(0) influences species stability

Electrowinning tests:

- Nd metal is deposited as a powder metal
- Nd recovery by electrolysis is difficult in chloride media: low faradic yield

## Prospects

- Neodymium electrolysis with anodic and cathodic compartments (diaphragms)
- Kinetics studies of the chemical reaction with addition of an excess Nd metal in  $\text{LiCl-KCl-NdCl}_3$  and  $\text{LiCl-NdCl}_3$  (chemical analysis and potential follow-up)
- Stability Nd(II) without excess of metal



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