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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

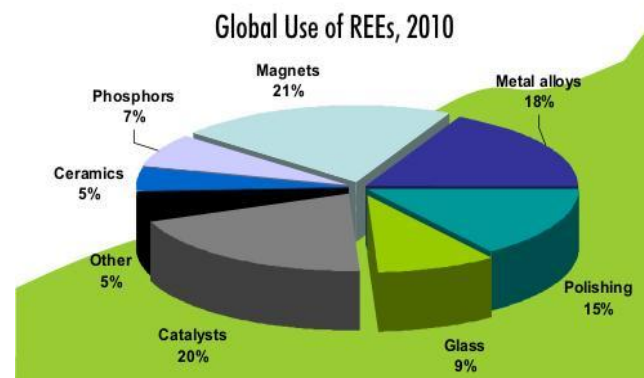
→ Uses: \approx 40% of RE metal

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 (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

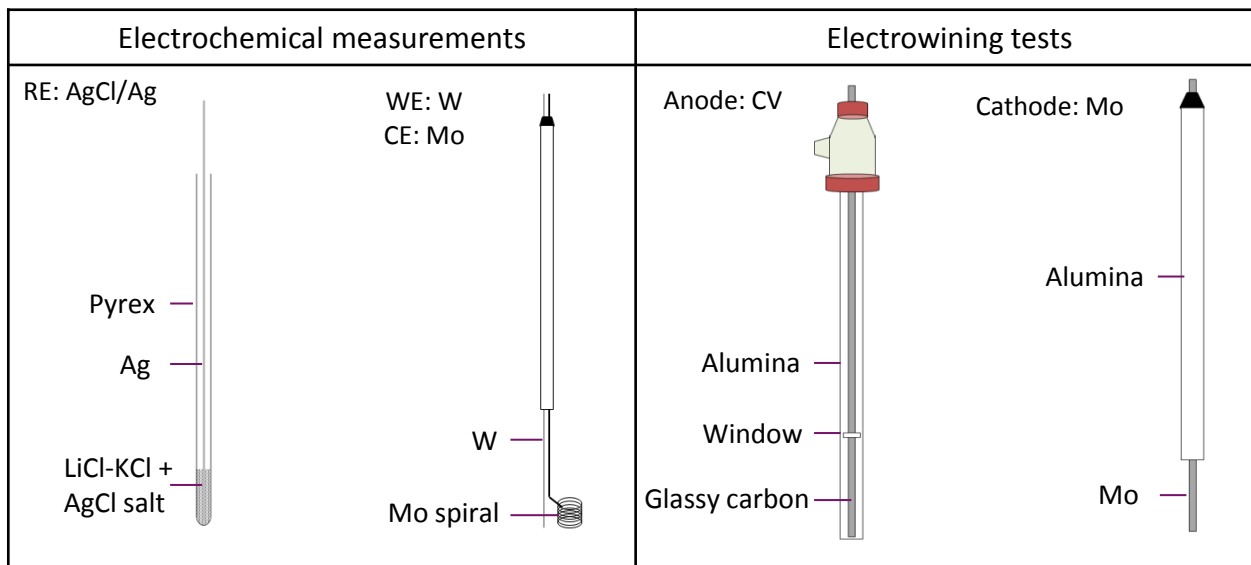
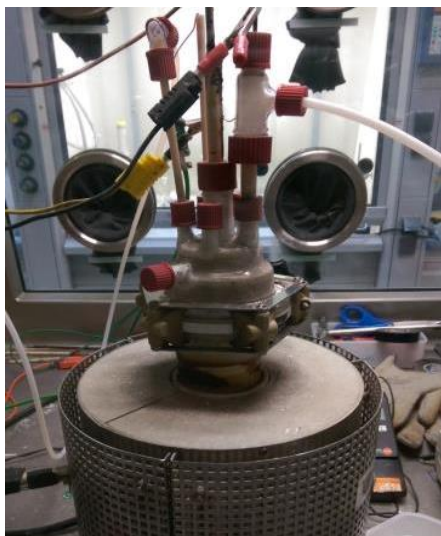
→ Comproportionation reaction:

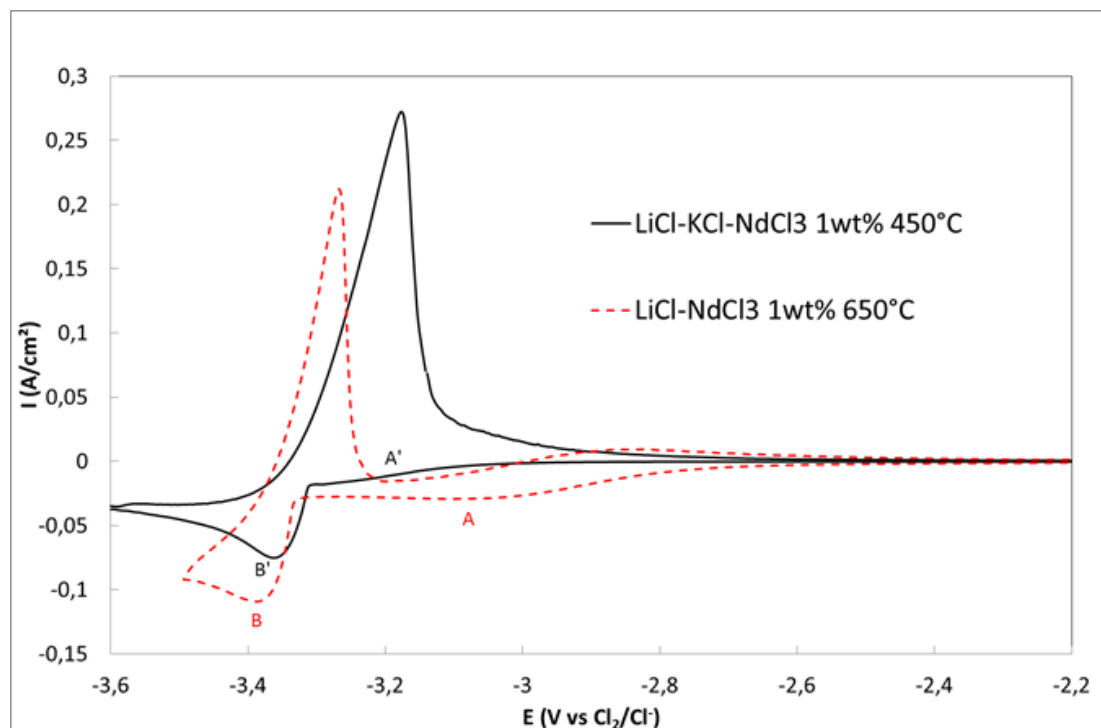


Lucas et al. 2015



- Inactive pyrochemical lab in glove-boxes (< 10 ppm of H₂O and O₂)
- 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)





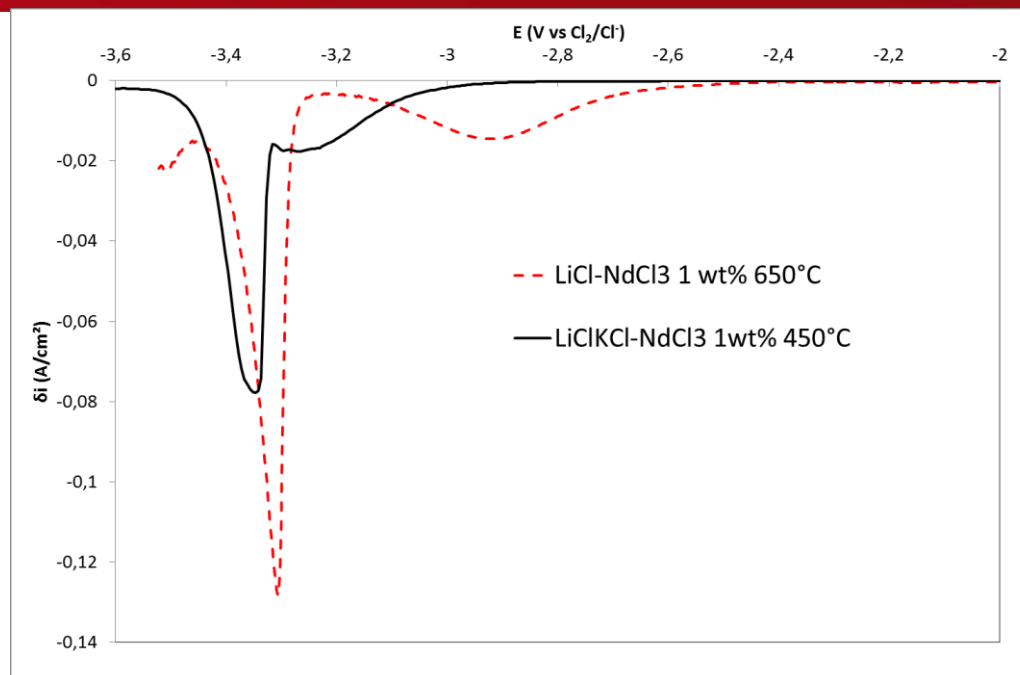
Cyclic voltammograms of NdCl_3 (1 wt%) in LiCl-KCl and LiCl melts at $v=100$ mV/s, working electrode: W

- Two step reduction:



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





Square wave voltammograms for the reduction of 1 wt% NdCl_3 at a W electrode in LiCl-KCl at 450 °C and LiCl at 650 °C

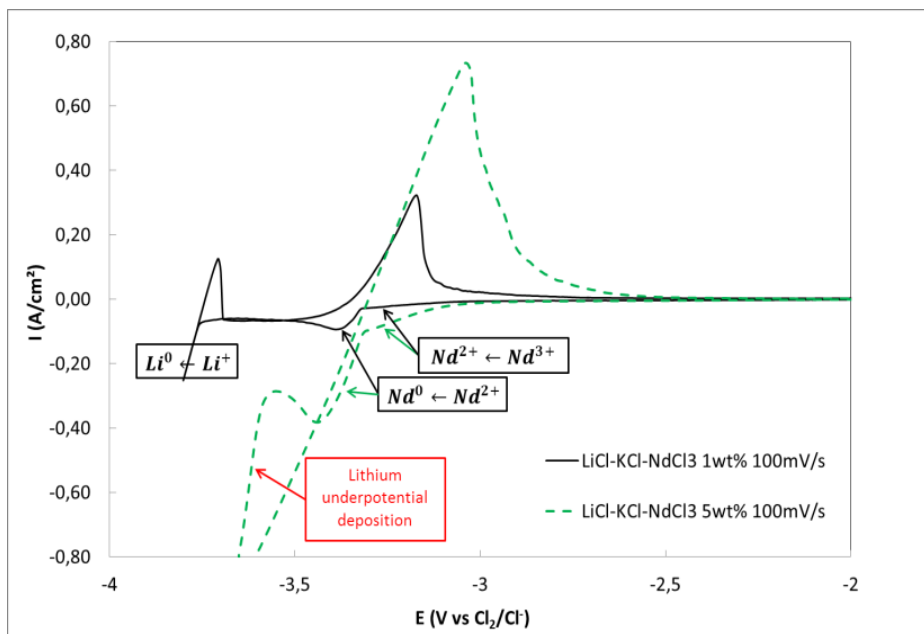
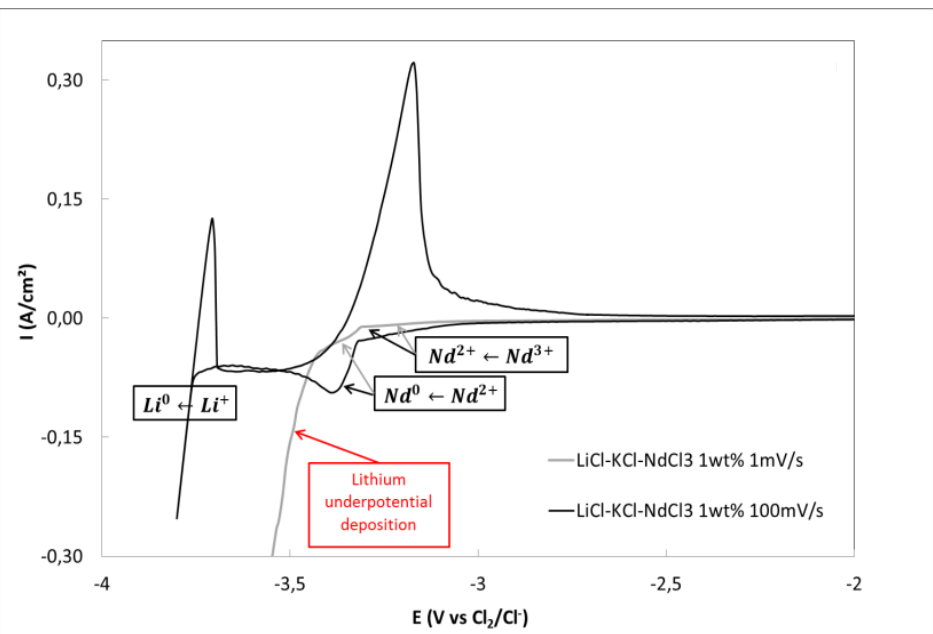
Square wave voltammetry :

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

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

→ Effect of comproportionation reaction



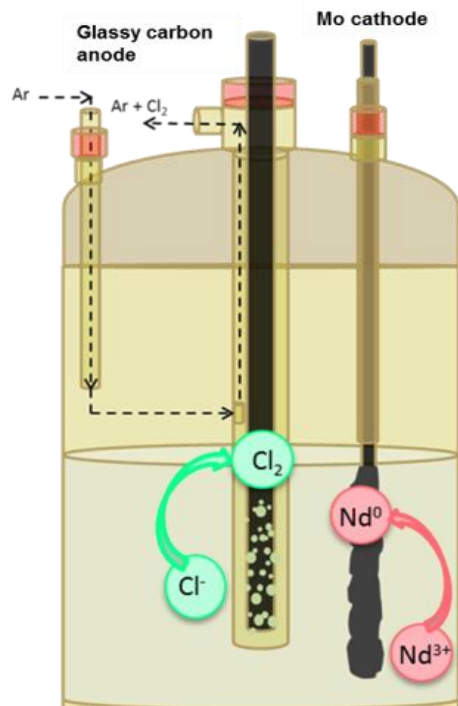


Lithium underpotential deposition when neodymium salt concentration is increased (*Martinez et al. 2012*)

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

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





Reduction of NdCl_3 at 450°C in 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 LiCl-KCl

Significant impact of chemical reaction: dissolution of metal despite polarization



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

Neodymium: metallic **powder**

Lanthanum and cerium: **dendritic** structure

Neodymium



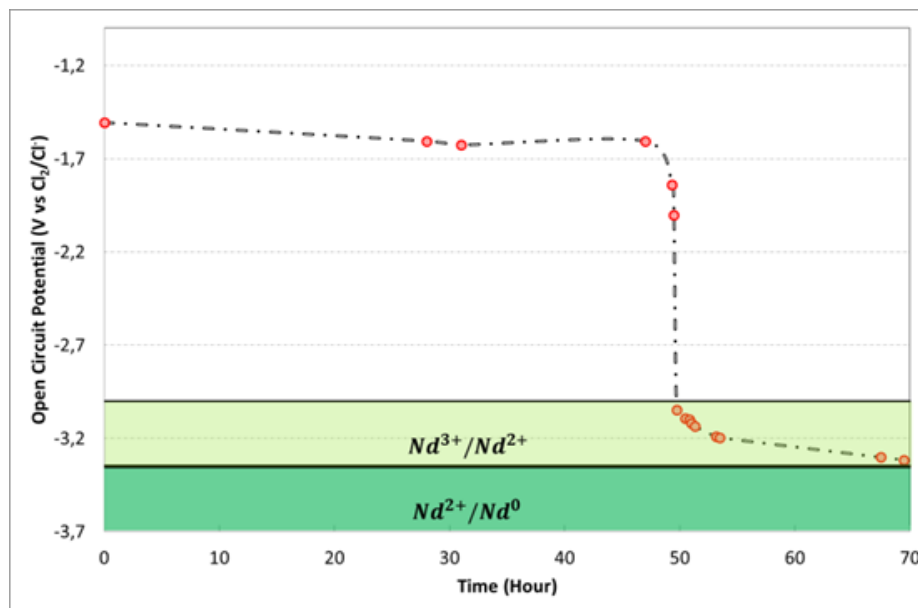
Lanthanum

Cerium



S. GERAN, CEA 2016

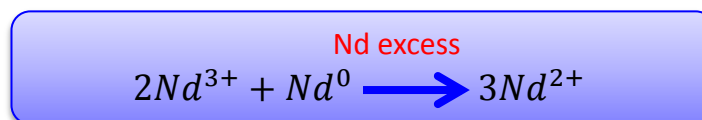




Open circuit potential variation during presence of Nd metal in salt

Addition Nd metallic ingot in a BN basket to a fresh LiCl-KCl-NdCl₃ salt: similar changes of E_{OCP} are observed

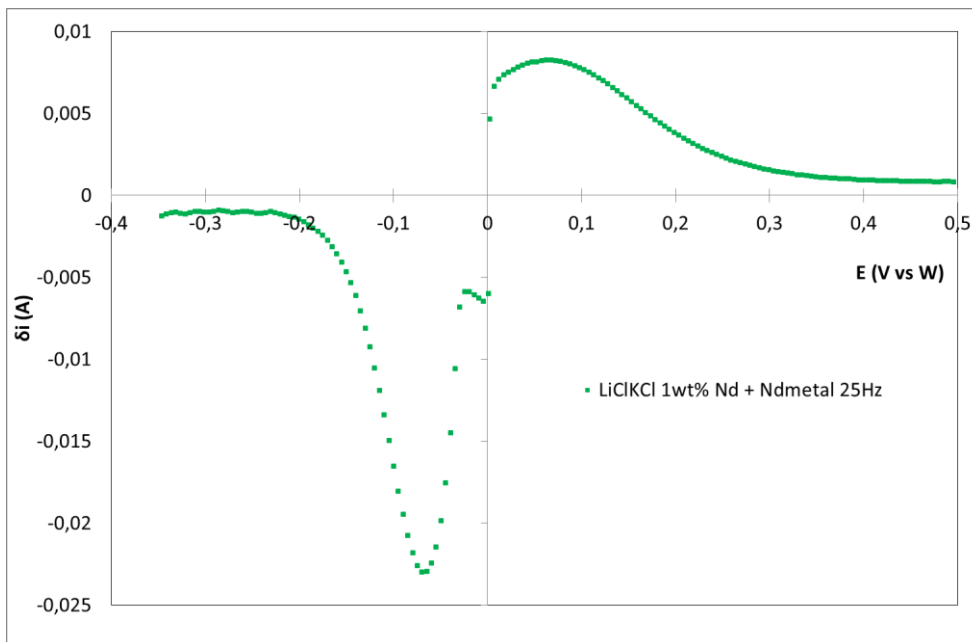
E_{OCP WE} is shifted to Nd(III)/Nd(II) system (spectrophotometric studies: *Hayashi et al. 2004*)



E_{OCP} is stable for several weeks

Nd(III) signal doesn't completely disappear: equilibrium between E_{Nd(III)/Nd(II)} and E_{Nd(II)/Nd(0)}





Square wave voltammograms at 25 Hz for the reduction of LiCl-KCl-NdCl₃ (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 → NdCl₃ and NdCl₂ in solution

Hayashi et al. 2004: NdCl₂: dark-red; NdCl₃: violet-blue



Conclusions

Electrochemical behaviour:

- Nd^{3+} reduction in a two step mechanism with an intermediary Nd^{2+}
- Nd^{2+} is stable under reducing conditions (presence of Nd metal)
- Lithium underpotential deposition is observed at high concentration of Nd(III)
- ΔE 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 LiCl-KCl-NdCl_3 and LiCl-NdCl_3 (chemical analysis and potential follow-up)
- Stability Nd(II) without excess of metal



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