Electrochemical behavior of neodymium in molten chloride salts

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CONTEXT

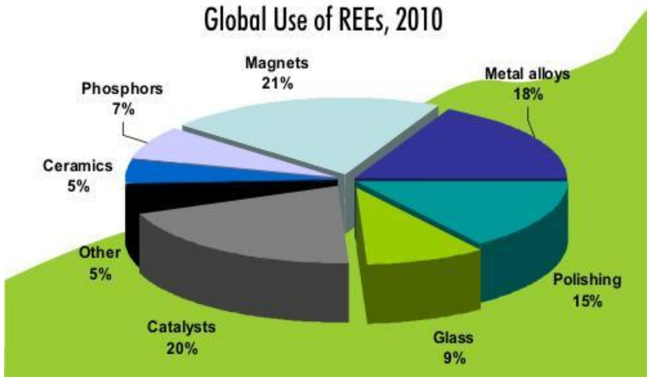
Rare earth (RE) **metal** are commonly used in advanced technologies

→Uses: ≈ 40% of RE metal

RE metal:

- **Metallothermy**: 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)

RARE EARTH 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

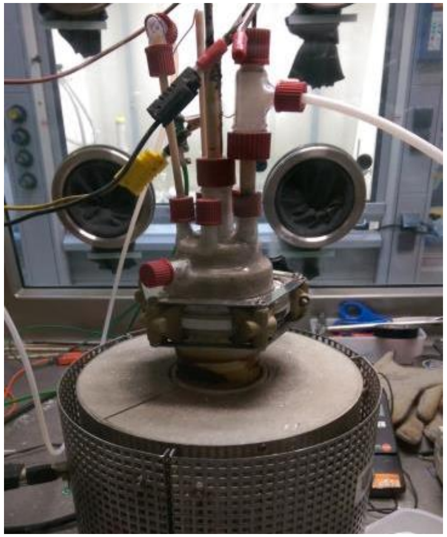
→ Comproportionation reaction:

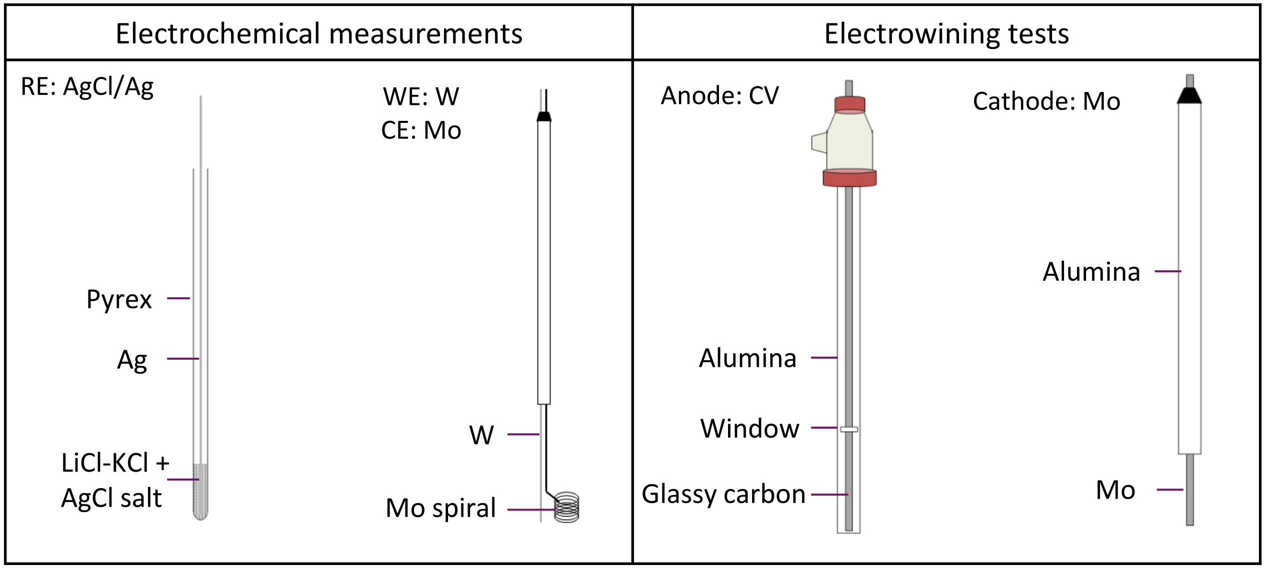
$$2Nd^{3+} + Nd^{0} \leftrightarrow 3Nd^{2+}$$

Lucas et al. 2015

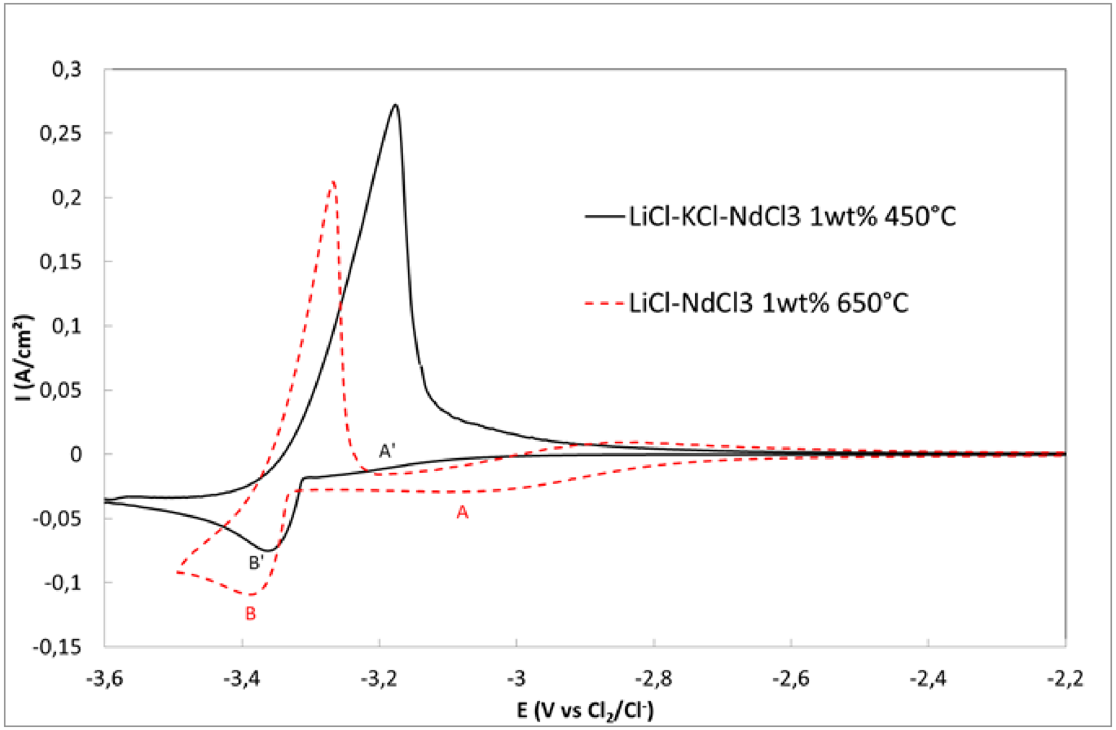
EXPERIMENTAL CONDITIONS

- Inactive pyrochemical lab in glove-boxes (< 10 ppm of H_2O and O_2)
- 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)





ELECTROCHEMICAL MEASUREMENTS



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

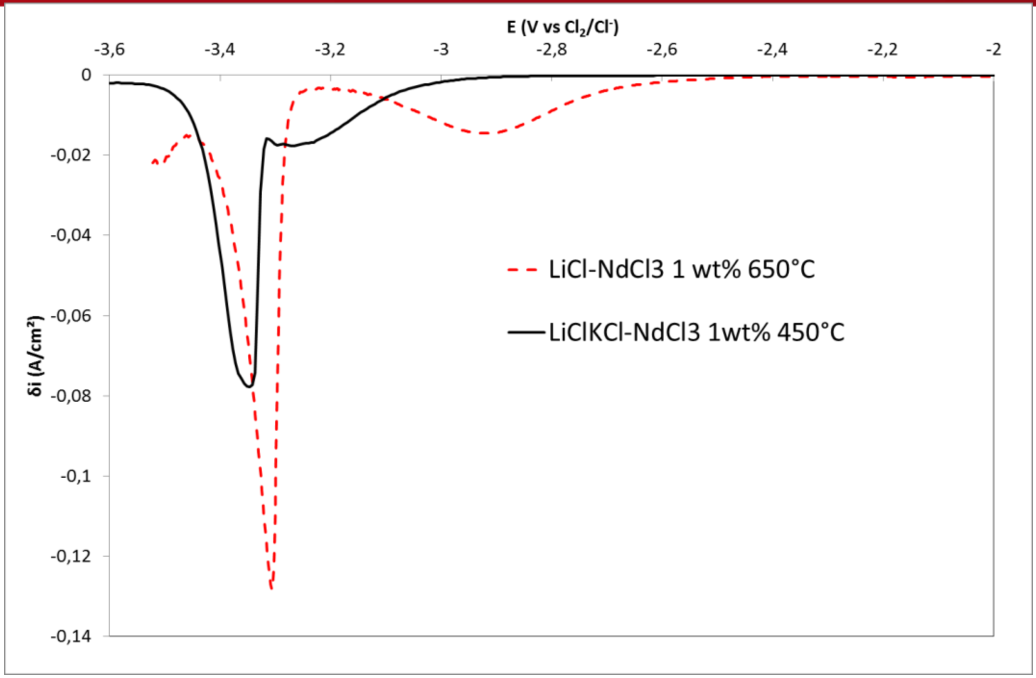
- **Two step reduction:**

$$Nd^{3+} + e^{-} \rightarrow Nd^{2+}$$

$$Nd^{2+} + 2e^{-} \rightarrow Nd^{0}$$

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

ELECTROCHEMICAL MEASUREMENTS



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 :

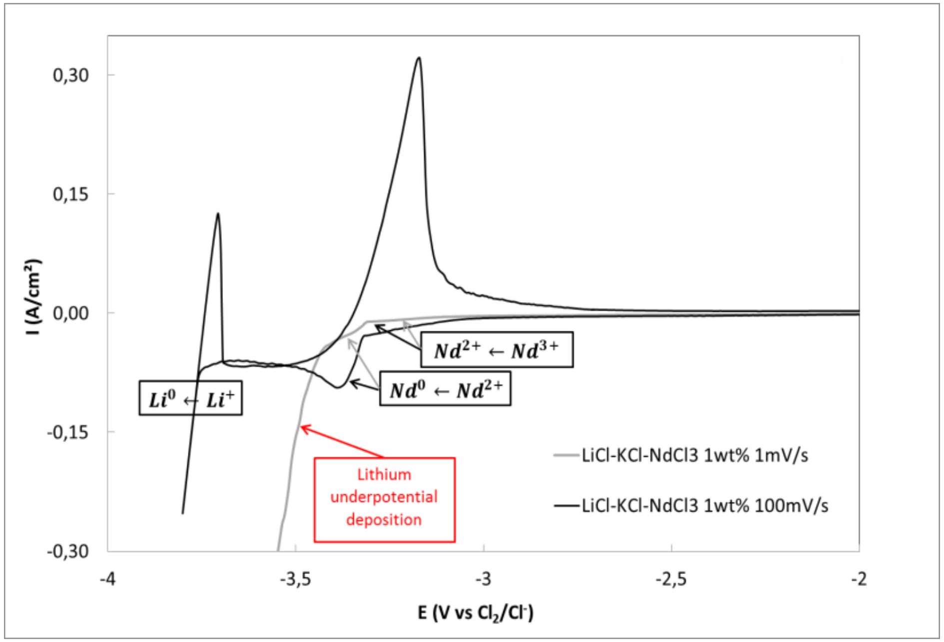
- First step: 1 electron exchanged
- Second step: not well defined

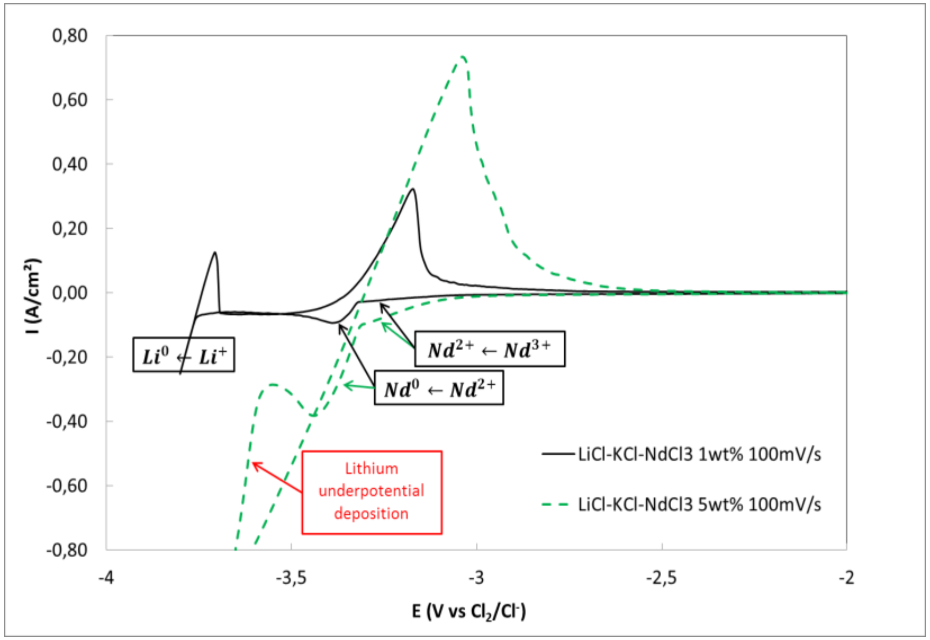
$$W_{1/2} = 3{,}52\frac{RT}{nF}$$

→ Effect of comproportionation reaction

$$2Nd^{3+} + Nd^{0} \leftrightarrow 3Nd^{2+}$$

ELECTROCHEMICAL MEASUREMENTS



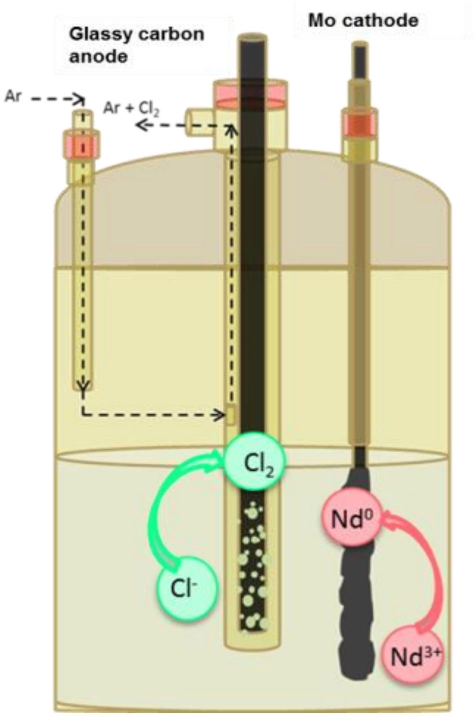


Lithium underpotential deposition when neodymium salt concentration is increased *(Martinez et al. 2012)*

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

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

ELECTROWINING TESTS



Reduction of $NdCl_3$ at 450°C in LiCl-KCl with a high argon flow (10 L/h) by **electrolysis** under constant current (0.15A/cm²<J<0.3A/cm²)

Low recovery yield < 45% in LiCl-KCl

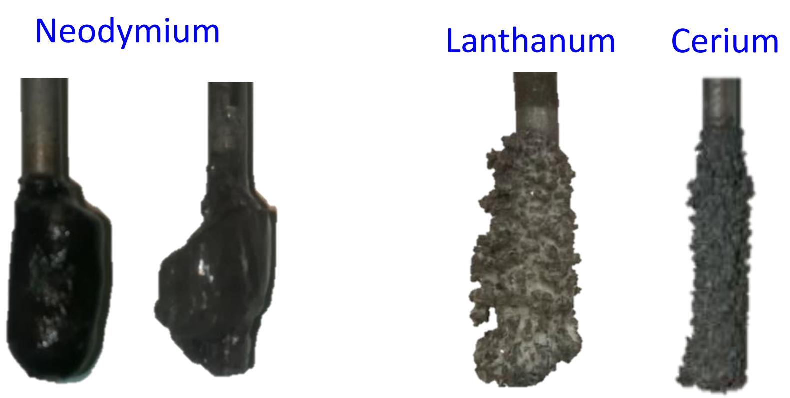
Significant impact of chemical reaction: dissolution of metal despite polarization

$$2Nd^{3+} + Nd^0 \leftrightarrow 3Nd^{2+}$$

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



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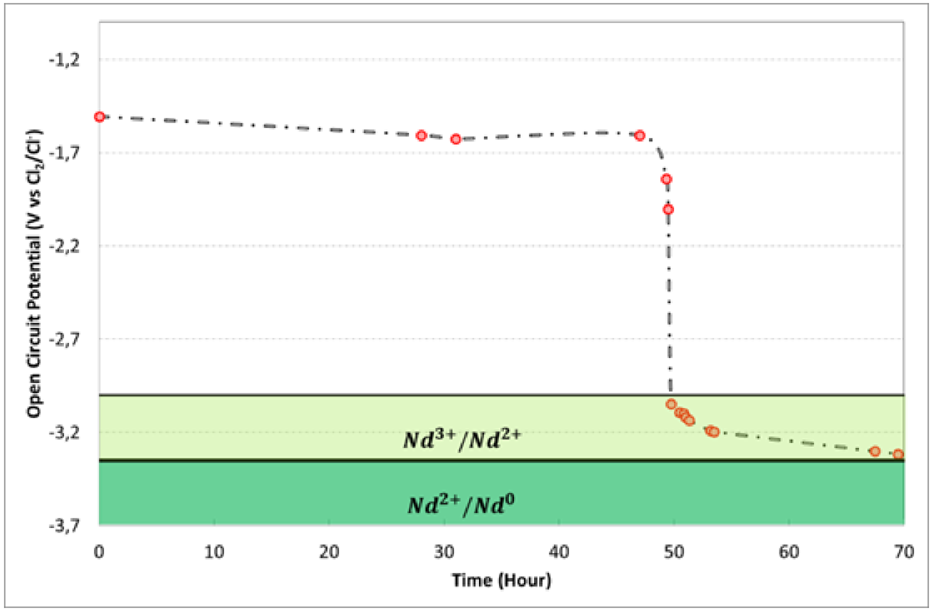
Nd metal addition: Stability of Nd(II)



Open circuit potential variation during presence of Nd metal in salt

Addition Nd metallic ingot in a BN basket to a fresh LiCl-KCl-$NdCl_3$ 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*)

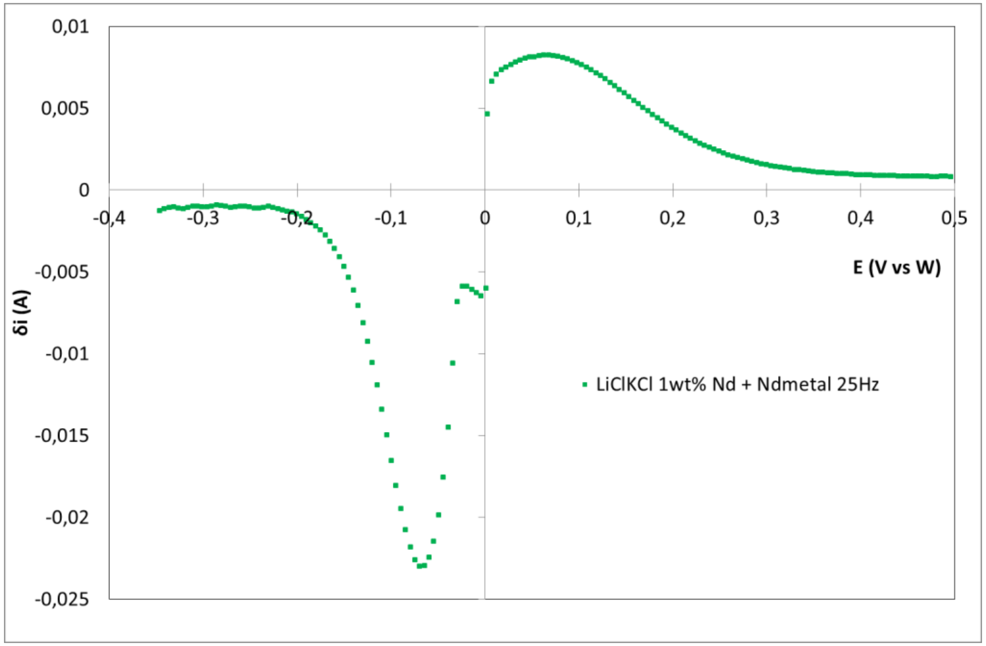
Nd excess

$$2Nd^{3+} + Nd^0 \rightarrow 3Nd^{2+}$$

E_{OCP} is stable for several weeks

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

Nd metal addition: Stability of Nd(II)



Square wave voltammograms at 25 Hz for the reduction of LiCl-KCl-$NdCl_3$ (1 wt%) after metal addition at a W electrode.

Anodic SWV: 1 electron exchanged

$$Nd^{2+} \leftrightarrow Nd^{3+} + 1e^{-}$$

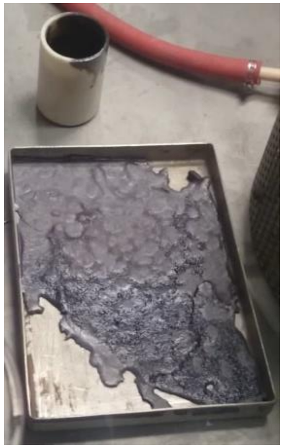
Cathodic SWV: residual Nd(III) reduction + Nd(II) reduction with an exchange of 2 electrons

$$Nd^{2+} + 2e^{-} \leftrightarrow Nd^{0}$$

Number of electrons is well defined in these conditions

Dark-purple salt → $NdCl_3$ and $NdCl_2$ in solution

Hayashi et al. 2004: $NdCl_2$: dark-red; $NdCl_3$: violet-blue



Conclusions and Prospects

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

Electrowining 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 $LiCl\text{-}KCl\text{-}NdCl_3$ and $LiCl\text{-}NdCl_3$ (chemical analysis and potential follow-up)
- Stability Nd(II) without excess of metal

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Acknowledgments:

Guillaume SERVE (technician)

Sylvain GERAN (intern)