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► **To cite this version:**

C. Remazeilles, M. Gibilaro, Laurent Massot, Christelle Chiron, A.M. Martinez, et al.. In-situ electrochemical oxide monitoring in LiF-NdF₃-Nd₂O₃: Application to Nd₂O₃ solubility determination. Journal of Electroanalytical Chemistry, 2021, 893, pp.115334. 10.1016/j.jelechem.2021.115334 . hal-04142914

HAL Id: hal-04142914

<https://hal.science/hal-04142914v1>

Submitted on 22 Jul 2024

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In-situ electrochemical oxide monitoring in LiF-NdF₃-Nd₂O₃: application to Nd₂O₃ solubility determination

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Abstract

Neodymium oxide titration was investigated in the LiF-NdF₃-Nd₂O₃ melt on platinum electrode by square wave voltammetry (SWV) in order to develop an in-situ and fast technique for oxide amount monitoring during Nd or Nd-Fe production by electrolysis. The methodology was verified by elemental analyses in the 850-1050 °C temperature range and then applied to Nd₂O₃ solubility determination in LiF-NdF₃.

Keywords: Molten fluoride; Rare Earth Oxide; Neodymium; Oxide titration

1 Introduction:

Rare earths became strategic metals at the end of the last century and are used in many devices like computer memory, batteries, permanent magnets, *etc...* They represented 13% of the global trade in 2010 and keeps growing each year from 130 kilotons in 2010 to 210 kilotons in 2019 [1, 2]. Due to the absence of operational mining in Europe, rare earths are defined as critical raw resources by the European Commission [3]. According to a sustainable development politics, metallic rare earths recycling was investigated through different research programs [4]. In this context, part of the Rare Earth Recycling For Europe (REE4EU) H2020 project was dedicated to neodymium recycling from spent permanent magnets (Nd₂Fe₁₇B) [5].

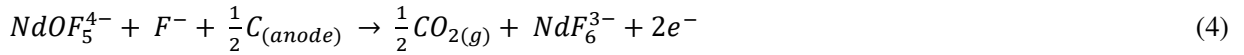
Metallic neodymium or Nd-Fe alloys are industrially produced by electrolysis in molten LiF-NdF₃-Nd₂O₃ at 825-1085 °C [6, 7]. Neodymium fluoride is reduced at a cathode composed either C, Mo or a Fe based alloy. When reduced, Nd is denser than the solvent and sinks to the bottom. Neodymium oxide is continuously added to ensure the oxidation of a consumable carbon anode into CO₂, this also regenerates NdF₃ (*cf.* Eq.4). The global reaction of the process is:



Stefanidaki *et al.* proposed in a LiF-NdF₃ mixture that NdF₃ and Nd₂O₃ are solubilized as NdF₆³⁻ and NdOF₅⁴⁻ respectively [8]:



The anodic reaction is then:

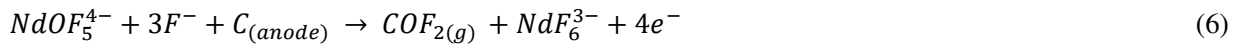
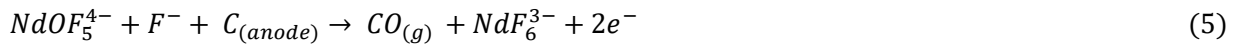


The neodymium oxide feeding is one of the key parameters of the process. Nd₂O₃ overfeeding leads to the formation of a dense sludge that remains at the bottom of the electrolysis cell and induces material loss, pollution and difficulties for sludge-metal separation. To prevent the oxide precipitation, several authors investigated the Nd₂O₃ solubility in LiF-NdF₃ at different temperatures, NdF₃/LiF ratio and additives; all those works were compiled by Guo *et al.* [9] and reported in *Table 1*.

Wu *et al.* measured the Nd₂O₃ solubility in LiF-NdF₃ for different NdF₃ content from 20 to 34 mol%, in a 750 - 900 °C temperature range and with or without BaF₂ addition (2/4/5 wt%) by an oxygen elemental analysis of crystalized sample. The results show a solubility of Nd₂O₃ of 7 - 10 wt% increasing with both temperature and BaF₂, with a stronger influence of the temperature [10]. Then Dysinger & Murphy examined the influence of NdF₃ content, from 5 to 20 mol%, in LiF-CaF₂ (80 - 20 mol%) and obtained

Nd₂O₃ solubility from 2.93 to 3.92 wt% at 1030 °C [11]. All other authors observed that an increase in temperature and NdF₃ content lead to a higher Nd₂O₃ solubility [8, 12].

Many studies on the anodic reaction showed that CO₂ is not the only gas produced during the electrolysis, some CO was detected. In case of underfeeding the CO/CO₂ ratio increased; under these conditions, the formation of COF₂ and perfluorocarbon compounds were also observed [13 - 16]:



Carbon monoxide is a toxic gas and its production leads to over consumption of anodes meanwhile perfluorocarbon compounds are well known to form an isolating gas layer adsorbed on the graphite anode surface, leading to power cuts (phenomenon called ‘anode effect’ in the aluminium industry) and are powerful greenhouse gases [17]. To fulfill the European regulation that impose to contain, prevent and thereby reduce emissions of fluorinated greenhouse gases [18], the oxide concentration during the electrolysis has to be controlled.

The oxygen content in samples is often determined by oxygen elemental analysis. This technique requires sampling (that could induce pollution), a special equipment and time to prepare sample for analysis. The main purpose of this work is to develop a fast and *in situ* technique for oxide monitoring.

Our methodology is based on previous work using square wave voltammetry (SWV), as previously reported for oxide titration in LiF-NaF-Li₂O [19]. However, gold was used as working electrode, and it is not suitable here due to its melting point (1064 °C) being too close from the operating temperature (1050 °C); platinum was then selected for its stability in molten fluoride media and its higher melting point (1768 °C).

This work deals with the determination of the upper limitation of the oxide feeding, meaning Nd_2O_3 solubility in the eutectic LiF-NdF_3 in the 850 - 1050 °C temperature range in order to prevent sludge formation during the process.

2 Experimental

The cell was a vitreous carbon crucible placed into a cylindrical vessel made of refractory steel and closed by a stainless lid cooled by water. The cell was protected against fluoride vapors by a graphite liner and all the experiments were performed under inert dry and deoxygenated atmosphere of Argon (99.995 vol.% from Linde). The cell was placed inside a furnace equipped with regulator and thermocouples (Eurotherm).

2.1 Chemicals

The solvent was the LiF-NdF_3 mixture (400g) at the eutectic composition (77-23 mol%). The solvent was pretreated under vacuum ($8 \cdot 10^{-2}$ mbar) by increasing temperature up to 600 °C for 6 days to dry the salts. Pure LiF , NdF_3 and Nd_2O_3 were provided by FoxChemical (99.99%).

2.2 Elemental Oxygen analysis

Oxygen analyzer (EGMA 820 Horiba) was used to measure the elemental oxygen content in a solid sample: 50-100 mg of sample were crushed into powder, loaded in a nickel capsule and then heated in a graphite crucible up to 3000 °C to form CO_2 . Gas extracted by a helium flux is quantified by IR spectrometry.

A pretreated matrix of LiF-NdF_3 was used to realize a blank, then a calibration curve was realized by Nd_2O_3 addition. Each samples were analyzed at least 5 times and the analyzer was calibrated for the $\text{LiF-NdF}_3\text{-Nd}_2\text{O}_3$ mixture in the 0.5 - 6 wt% range.

2.3 Electrodes

The working electrode was a 0.5 mm diameter platinum wire (Goodfellow 99.9%). The immersion depth was determined after measurement to determine the electroactive surface area.

A molybdenum rod (3 mm diameter) was used as auxiliary electrode with a large surface area (> 2 cm²) and a glassy carbon rod as quasi-reference electrode.

2.4 Electrochemical equipment

All electrochemical studies were performed using Autolab PGSTAT 30 potentiostat controlled with NOVA 2.1 software.

3 Results and discussion

3.1 Square wave voltammetry (SWV)

Figure 1 presents a typical SWV voltammogram performed in LiF-NdF₃-Nd₂O₃ (1.14 wt%) at 850 °C on a platinum electrode with a frequency of 100Hz. A single peak, observed at 1.4 V vs. ref, is associated to the oxidation of NdOF₅⁴⁻ into O_{2(g)} (*cf.* Eq.8). This assumption is confirmed by disturbance of signal characteristic of gas bubbling on the electrode. Then platinum oxidation is observed at potential higher than 2.1 V vs. ref. The insert on *figure 1* shows a linear relationship between the peak current density and the square root of the frequency in the 64-144 Hz frequency range, indicating a diffusion limitation of the reaction and proving that SWV is suitable for further analysis.



The number of exchanged electrons can be correlated to the half peak width $W_{1/2}$ by the following equation [20, 21]:

$$W_{1/2} = 3.52 \frac{RT}{nF} \quad (9)$$

where n is the number of exchanged electrons, F the Faraday constant ($C.mol^{-1}$), R the ideal gas constant ($J.K^{-1}.mol^{-1}$) and T the absolute temperature (K). At 850 °C, the $W_{1/2}$ average value is 156 mV, leading to a number of exchanged electrons of 2.2 ± 0.4 ; in agreement with $O_{2(g)}$ evolution (reaction 8).

Several SWVs were performed for different Nd_2O_3 additions and the differential peak (δip) current densities obtained at 850 °C are reported in *figure 2* and exhibit a linear relationship with the Nd_2O_3 content. This result confirms that the solubilized form of Nd_2O_3 is the electroactive species observed and allows the Nd_2O_3 *in-situ* titration in the melt by measuring the SWV peak current density. The relationship between Nd_2O_3 content and δip at 850 °C is:

$$\delta ip (A.cm^{-2}) = 0.29 [Nd_2O_3] (wt. \%) \quad (10)$$

The experiment was repeated at several temperatures. The obtained values at 850, 900, 950 and 1050 °C are reported in *table 2*. It can be observed that the sensitivity of the measurement increases with the temperature.

3.2 Nd_2O_3 solubility determination

Nd_2O_3 solubility was determined by measuring the Nd_2O_3 content in the melt, using SWV titration at 850 °C. The results are presented in *figure 3*. This figure exhibits a plateau due to the precipitation of Nd_2O_3 and corresponds to its solubility value. The solubility measured equals to 1.4 ± 0.1 wt% at 850 °C and was confirmed by oxygen elemental analysis: 1.5 ± 0.3 wt%.

Solubility measurements were repeated at several temperatures. The obtained values by SWV and elemental analysis at 850, 900, 950 and 1050 °C are reported in *table 3*. The results obtained with both methods are similar, confirming that SWV is a reliable technique for oxide monitoring in LiF-NdF₃ melts.

The variation of solubility between 850 and 1050 °C can be plotted as logarithm of $NdOF_5^{4-}$ solubility vs. reciprocal of the absolute temperature (see *figure 4*), by the following equation:

$$\ln(S_{NdOF_5^{4-}}) = \frac{-8386}{T} + 5.5114 \quad (11)$$

Among the values available in literature, Nd_2O_3 solubility provided by Dysinger & Murphy in $\text{LiF-CaF}_2\text{-NdF}_3$ (20 mol% of NdF_3) at 1030 °C (3.92 wt%) is in the same order magnitude than the one interpolated at the same temperature using *Eq.11* (4.4 wt%). Differences between these values can be explained by the difference in NdF_3 content and CaF_2 addition.

4 Conclusion

In this study, an electrochemical technique (SWV) was investigated as a fast and *in situ* method for the oxide titration in the $\text{LiF-NdF}_3\text{-Nd}_2\text{O}_3$ system. The oxidation of the solubilized form of Nd_2O_3 into $\text{O}_{2(\text{g})}$ in one step exchanging 2 electrons was observed on Pt.

The peak current density of the SWV signal is linearly correlated with the Nd_2O_3 content in 850-1050 °C temperature range. This relationship can be directly used for oxide monitoring during the process and was applied to determine the Nd_2O_3 solubility in order to prevent overfeeding and sludge formation. The solubility measurements were verified by oxygen elemental analysis and the results obtained by these two techniques are similar, being 1.4 wt% at 850 °C and 4.4 wt% at 1050 °C.

SWV is then a reliable and fast technique that can be used *in situ* for the oxide monitoring in the $\text{LiF-NdF}_3\text{-Nd}_2\text{O}_3$ system and was successfully applied for obtaining the upper limitation of the oxide feeding. This technique will be applied in a future work to study the influence of oxide content in the fluoride electrolyte on the CO, COF_2 and perfluorocarbon compounds formation.

References

- [1] S. Massari and M. Ruberti, "Rare earth elements as critical raw materials: Focus on international markets and future strategies," *Resour. Policy*, vol. 38, no. 1, 2013.
- [2] M. Gowing, "Rare Earth Industry Update," Mackie Research Capital Corporation, 2011.
- [3] "Critical raw materials," *Internal Market, Industry, Entrepreneurship and SMEs - European Commission*, 2016:

https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en.

- [4] T. Dutta *et al.*, “Global demand for rare earth resources and strategies for green mining,” *Environ. Res.*, vol. 150, 2016.
- [5] “H2020 - REE4EU Project”:
<http://www.ree4eu.eu/>.
- [6] H. Tamamura, “Process for preparation of neodymium or neodymium-iron alloy,” US5091065A, 1992.
- [7] R. Keller and K. T. Larimer, “Electrolytic production of neodymium without perfluorinated carbon compounds on the offgases,” US5810993A, 1998.
- [8] E. Stefanidaki, G. M. Photiadis, C. G. Kontoyannis, A. F. Vik, and T. Østvold, “Oxide solubility and Raman spectra of $\text{NdF}_3\text{-LiF-KF-MgF}_2\text{-Nd}_2\text{O}_3$ melts,” *J. Chem. Soc. Dalton Trans.*, vol. 0, no. 11, 2002.
- [9] X. Guo, Z. Sun, J. Sietsma, and Y. Yang, “Semiempirical Model for the Solubility of Rare Earth Oxides in Molten Fluorides,” *Ind. Eng. Chem. Res.*, vol. 55, no. 16, 2016.
- [10] W. Wu, J. Sun, L. Hai, and H. Gao, “ Nd_2O_3 Solubility in Fluoride Melt,” *Chin Rare Earths*, vol. 12, no. 3, 1991.
- [11] D. K. Dysinger and J. E. Murphy, “Electrowinning of Neodymium, From a Molten Oxide-Fluoride Electrolyte,” 1994.
- [12] X. Hu *et al.*, “Research on form of Nd-F-O complex ions in $\text{NdF}_3\text{-LiF-Nd}_2\text{O}_3$ melts,” in *2009 World Non-Grid-Connected Wind Power and Energy Conference*, Nanjing, China, Sep. 2009.
- [13] S. Liu, L. Chen, B. Li, L. Wang, B. Yan, and M. Liu, “Anode processes for Nd electrowinning from $\text{LiF-NdF}_3\text{-Nd}_2\text{O}_3$ melt,” *Electrochimica Acta*, vol. 147, 2014.
- [14] L. Zhang, X. Wang, and B. Gong, “Perfluorocarbon emissions from electrolytic reduction of rare earth metals in fluoride/oxide system,” *Atmospheric Pollut. Res.*, vol. 9, no. 1, 2018.

- [15] H. Vogel and B. Friedrich, "Reducing Greenhouse Gas Emission from the Neodymium Oxide Electrolysis. Part II: Basics of a Process Control Avoiding PFC Emission," *Int. J. Nonferrous Metall.*, vol. 06, no. 03, 2017.
- [16] K. S. Osen *et al.*, "Perfluorocarbon Formation During Rare Earth Electrolysis," in *Light Metals 2018*, O. Martin, Ed. Springer International Publishing, 2018.
- [17] C. M. Roehl, D. Boglu, C. Brühl, and G. K. Moortgat, "Infrared band intensities and global warming potentials of CF₄, C₂F₆, C₃F₈, C₄F₁₀, C₅F₁₂, and C₆F₁₄," *Geophys. Res. Lett.*, vol. 22, no. 7, 1995.
- [18] *Regulation (EC) No 842/2006 of the European Parliament and of the Council of 17 May 2006 on certain fluorinated greenhouse gases*, vol. 161. 2006.
- [19] L. Massot, L. Cassayre, P. Chamelot, and P. Taxil, "On the use of electrochemical techniques to monitor free oxide content in molten fluoride media," *J. Electroanal. Chem.*, vol. 606, no. 1, 2007.
- [20] Louis. Ramaley and M. S. Krause, "Theory of square wave voltammetry," *Anal. Chem.*, vol. 41, no. 11, 1969.
- [21] M. S. Krause and Louis. Ramaley, "Analytical application of square wave voltammetry," *Anal. Chem.*, vol. 41, no. 11, 1969.

TABLES

T (°C)	NdF ₃ content and additives	Nd ₂ O ₃ solubility	Reference
750 - 900	20 - 34 mol% NdF ₃ ± BaF ₂	6.67 - 10.10 (wt%)	<i>Wu et al.</i> [10]
1030	5 - 20 mol% NdF ₃ + CaF ₂	2.95 - 3.92 (wt%)	<i>Dysinger & Murphy</i> [11]
750 - 900	15 - 30 mol% NdF ₃ ± MgF ₂	0.54 - 1.61 (wt%)	<i>Stefanidaki et al.</i> [8]
1050 - 1150	42 - 58 mol% NdF ₃	3.28 - 4.97 (wt%)	<i>Hu et al.</i> [12]

Table 1: Nd₂O₃ solubility data in LiF-NdF₃ melts of various composition at different temperature ranges with or without additives [9].

T(°C)	850	900	950	1050
Slope value (A.cm ⁻² / wt%)	0.29 ± 0.01	0.32 ± 0.01	0.34 ± 0.01	0.36 ± 0.01

Table 2: Coefficient of the linear relationship between δip (A.cm⁻²) of the SWVs (100 Hz, Pt electrode) and the Nd₂O₃ content in wt% in LiF-NdF₃-Nd₂O₃ at several temperatures.

T(°C)	S (wt%) - SWV	S (wt%) - El.An
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850	1.4 ± 0.1	1.5 ± 0.2
900	2.4 ± 0.1	2.6 ± 0.3
950	3.0 ± 0.1	3.2 ± 0.3
1050	4.4 ± 0.1	4.6 ± 0.6

Table 3: Nd₂O₃ solubility in LiF-NdF₃ for different temperatures obtained by SWV and Elemental Analysis.