Influence of LiF on the synthesis of the neodymium & praseodymium molten salt electrolysis

Dominic Feldhaus, Marie-Theres Tschauner, Prof. Dr. Ing. Dr. h.c. Bernd Friedrich

RWTH Aachen University
IME Process Metallurgy and Metal Recycling
Intzestraße 3
Aachen, Germany

Keywords: molten salt electrolysis, linear sweep voltammetry, neodymium, praseodymium, fluoride melts

Abstract

In the molten salt electrolysis, neodymium and praseodymium in their oxidic forms are fed into fused salt, the electrolyte, to be reduced by applying current to the system and be deposited as metal. The electrolyte consists of neodymium fluoride, praseodymium fluoride and lithium fluoride. An issue that makes the long-term electrolysis impracticable is the fact that the anode effect occurs more often after some time of processing if only oxides are fed to the system. One reason for this unstable condition seems to be an insufficient solubility of the oxides that is related to the depletion of lithium fluoride in the melt due to its evaporation over time, which, among other things, is important for the solubility of the oxides.

In the present study, several electrochemical measurements were conducted to examine this complex system. It was possible to reactivate already processed electrolytes by feeding different amounts of lithium fluoride. With this approach, the maximum reached current density could be raised significantly.

Introduction and Motivation

For more than ten years the electrolysis has been studied now at the IME. Beginning with the deposition of titanium [1, 2] to neodymium [3 – 5] and didymium the alloy of neodymium and praseodymium [6 – 8]. This research is now being continued by the investigation of the electrodeposition of neodymium and praseodymium metal on an inert anode in connection with the analysis and study of exhaust gases generated during the experiment. Therefor a melt acting as an electrolyte composed of a suitable combination of neodymium and praseodymium salts and solvents is required [9]. Chlorides, fluorides, oxides of alkali and alkaline earth metals combined with Nd are often investigated in the past [10 – 12]. Fluoride electrolytes are most suitable due to their high conductivity, low hygroscopy and high current efficiency of Nd deposition compared to chloride electrolytes [13, 14]. Commonly used fluoride electrolytes contain LiF (NaF or KF) and CaF_2, but for most investigations, only LiF is used as it positively influences the electrical conductivity, fluidity and oxide solubility of the electrolyte [11 – 19]. Nd sources in these melts are NdF_3 and Nd_2O_3 and Pr is supplied by PrF_3 and Pr_6O_{11}.

During the electrolysis process reactions on the anode cause the formation of CO and CO_2. However, if conditions in the system change for example the concentration of LiF is too low, unwanted side reactions produce perfluorocarbons (PFCs) like CF_4 and C_2F_6. The global warming potential for a 100-year time horizon is 6630 for CF_4 and 11100 for C_2F_6. This means CF_4 is a 6630 times and C_2F_6 a 11100 times more powerful greenhouse gas than CO_2. Both gases are broken down very slowly in the atmosphere and are estimated to have lifetimes of thousands of years [20].

For the goal of stable long term electrolysis without anode effects and therefore the formation of PFCs, it is important to have an electrolyte with stable composition. Experiments have shown that after about eight hours of electrolysis the anode effect, a phenomenon at which the anode is covered with a gas film that prevents the current flow, occurs more often if only oxides are fed to the system. Reasons for this seem to be the increasingly insufficient solubility of the oxides over time. This is due to the continuous evaporation of LiF which is an important component of the system that lowers the melting temperature, increases the conductivity of the electrolyte and acts as an F^- donor, which is required for the formation of oxyfluoride, an intermediate in the process from oxide to metal.

This LiF evaporation can be seen in figure 1. One part of the LiF settled on the lid of the electrolysis cell, while the remaining part was transported out of the cell via the exhaust system.

Figure 1: Lid of the electrolysis cell with white powdery condensate

Analysing the condensate on the lid with ICP-OES (Table 1) showed Nd contents of 8.96 wt.-% up to 13.6 wt.-%, Pr from 3.2 wt.-% to 4.6 wt.-% and 18.0 wt.-% up to 18.6 wt.-% of Li. The content of fluorine from LiF was determined to range from 63.8 wt.-% to 69.2 wt.-%. This results in LiF content ranging from 67.08 wt.-% to 69.32 wt.-%. The remaining fraction of the condensate was therefore made up of metal fluorides, 12.5 wt.-% to 19.0 wt.-% NdF_3 and 4.5 wt.-% to 6.5 wt.-% PrF_3. The high content of LiF in the condensate shows that a large amount of the LiF evaporated from the electrolyte and condensed on the lid over time, causing the actual concentration of LiF in the electrolyte to be lower than it is initially.

Table 1: Content of Li and Nd in the condensate of different measurements of the inhomogeneous sample from the cell lid

ICP-OES		
Li [wt.-%]	Nd [wt.-%]	Pr [wt.-%]
18,0	13,6	4,6
18,6	8,96	3,2

In the present study, the influence of the LiF content on the electrolyte for the molten salt electrolysis of didymium was investigated. This was done by incrementally adding LiF to the cell containing electrolyte that has been used previously in other investigations and conducting linear sweep voltammetry to study the changes in critical current density, the current density that is reached before the anode effect occurs. The results can be used for further investigation of the feasibility of long-term electrolysis for the production and recycling of didymium.

This work is part of the BMBF project REGINA project (Rare Earth Global Industry and New Applications), funded by the federal ministry of education and research. Grant agreement number 033R185D

Methods and Materials

To prepare the electrolyte components, they were dried for 24 hours at 523 K. Following this step, they were premixed and fed into a high purity graphite crucible in which the mixture was placed in a vacuum induction furnace under an argon atmosphere of 1800 mbar up to 1359 K to be melted and homogenised. The LiF and the oxides which were added during the experiments were prepared by drying them for 24 hours at 523 K as well. The initial electrolyte composition was 65.7 wt.-% NdF_3 (Treibacher ≥ 99.9 %), 21.8 wt.-% PrF_3 (Treibacher 99.9 %) and 12.5 wt.-% LiF (STREM chemicals 99.9 %). This ratio was chosen because it is the most suitable in terms of melting temperature and viscosity. Electrolytes of this composition were already used in previous electrolysis experiments, where they were heated up for about 12 hours while the electrolysis, the process of applying the current, took about 8 hours. During these experiments, the oxide content (Nd_2O_3 (Treibacher 99.8 %) and Pr_6O_{11} (Treibacher 99.5 %) in a 3 : 1 ratio was held at about 2 wt.-%. The exact electrolyte composition could not be determined due to those circumstances and insufficient possibilities for the analysis of the electrolyte. Only LiF was added to the previously used electrolytes in the here described experiments.

For the electrochemical measurements, a three electrode system has been used. The working electrode (WE) consists of a glassy carbon rod (EWG 99,95 %, 4 mm diameter), counter electrode (CE) and reference electrode (RE) are both made of molybdenum (HTW > 99,99 %, 2 mm diameter). The current of the WE was measured relative to the Mo RE in the melt under given conditions. Before the electrodes were placed into the cell using Swagelok connections in the lid and alumina tubes to isolate the sealing from the heat, they were polished to remove any contaminations. The immersion depth into the electrolyte was 1.5 cm. The cell, as seen in figure 2, was covered with a water-cooled gas tight lid with the Swagelok connections, to prevent harmful gases from escaping the cell during the experiments. The cell was placed into a resistance heated furnace and heated up to 1423 K to reach the process temperature of 1323 K in the electrolyte. The temperature was measured by a thermocouple Type B via a Swagelok connection. The system was flushed by a constant argon flow of 1.5 L/min to prevent the melt from having contact with air. The off gas was led into washing bottles that were filled with water and NaOH and afterwards treated by the exhaust system.

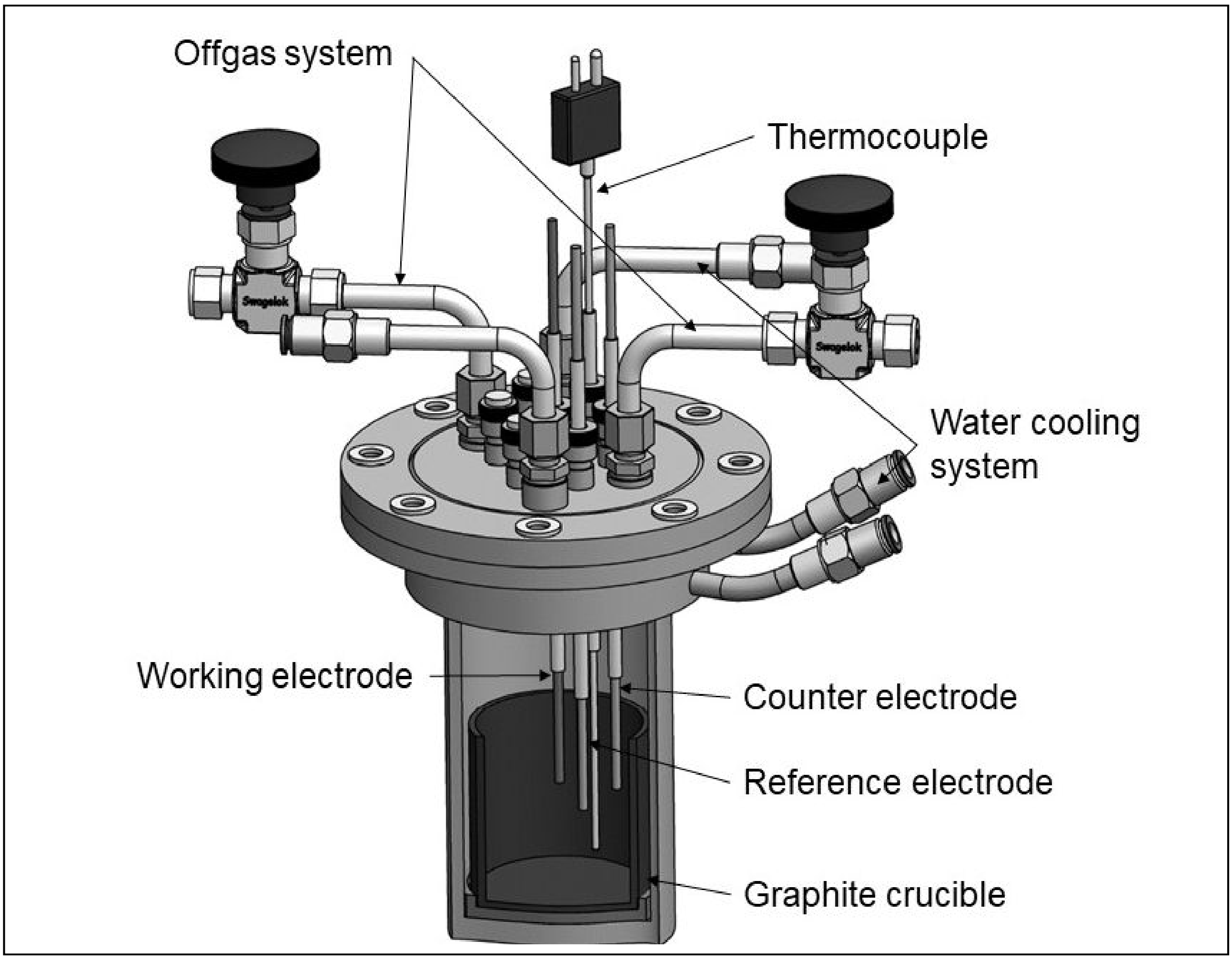

Figure 2: Experimental setup

The electrochemical measurements were conducted by an IviumStat potentiostat (5 A, 10 V, Ivium Technologies, Eindhoven, The Netherlands) and the results were recorded with IviumSoft by the same company. Linear voltammetry was used to investigate the anodic behaviour. The measurements were obtained on a glassy carbon working electrode against Mo reference electrode with sweep rates of 25 mV/s, 50 mV/s, 100 mV/s. A video of the preparation of the cell and the running experiment has already been published on YouTube. [21]

Results and Discussion

Linear sweep voltammograms were conducted by applying a rising potential to the electrolyte. In dependence on the electrolyte's composition and its resistance, the arising current is recorded, seen in figure 3. In general, the curve starts flat with small current densities at low potentials, after reaching the decomposition voltage the current density increases almost linear with rising potential as oxidation reactions take place until the current density drops to almost zero. At this point, the anode effect has occurred at the critical current density.

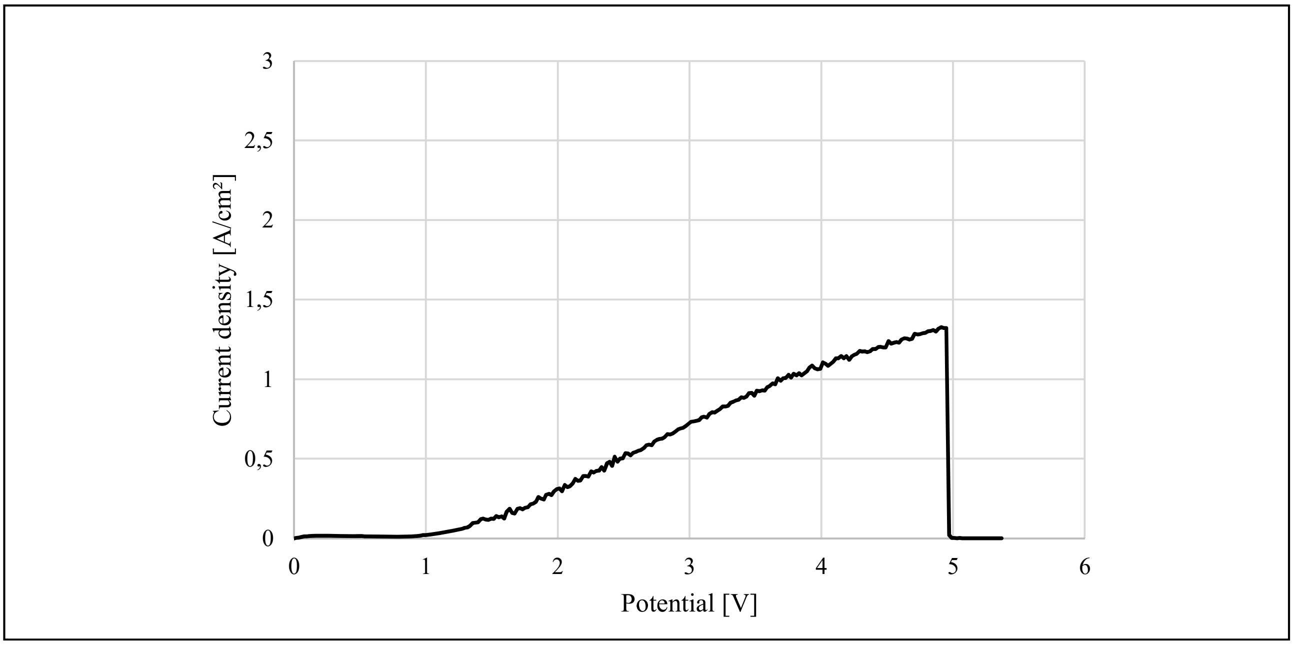

Figure 3: Linear sweep voltammogram recorded at 100 mV/s

Previous investigations [7] have shown that when neodymium oxide is fed to the electrolyte oxyfluorides are formed, which is shown in equation (1):

$$Nd_2O_3 + [NdF_6]^{3-} + 9\,F^- = 3\,[NdOF_5]^{4-} \quad (1)$$

The moment the decomposition potential is reached, these oxyfluorides react further (2):

$$3\,[NdOF_5]^{4-} - 6\,e^- \rightarrow 3\,Nd^{3+} + {}^3\!/_2\,O_2 + 15\,F^- \quad (2)$$

The neodymium ions are then electrochemically reduced to Nd(0) at the cathode in two steps (3) & (4):

$$\text{Step 1: } Nd^{3+} + e^- \rightarrow Nd^{2+} \quad (3)$$

$$\text{Step 2: } Nd^{2+} + 2e^- \rightarrow Nd(0) \quad (4)$$

At higher potential values, right before the anode effect, the electrochemical reaction shifts from oxyfluorides to neodymium fluoride; thus NdF_6^{3-} takes part in the reaction. The theoretical decomposition voltage of this reaction is 1.4 V higher than the reaction of oxyfluorides [4]. This difference becomes noticeable in the change of the reaction gases. Instead of CO / CO_2, which emerges at the reaction of neodymium oxide, CF_4 / C_2F_6 (PFC Gases) are formed shortly before the anode effect when neodymium fluoride is electrochemically decomposed. The PFCs have a much higher wettability at the anode and thus cause a gas layer that interrupts the current and induce the anode effect. [22]

So far, unpublished results show that these reaction steps, which apply to neodymium, can also be applied to the simultaneous deposition of neodymium and praseodymium. In addition to neodymium oxyfluorides, the electrolyte also contains praseodymium oxyfluorides, which are also reduced in two steps at the cathode.

In figure 4, linear sweep curves with different amounts of LiF added are shown, beginning by adding none LiF until an amount of 5 wt.-%.

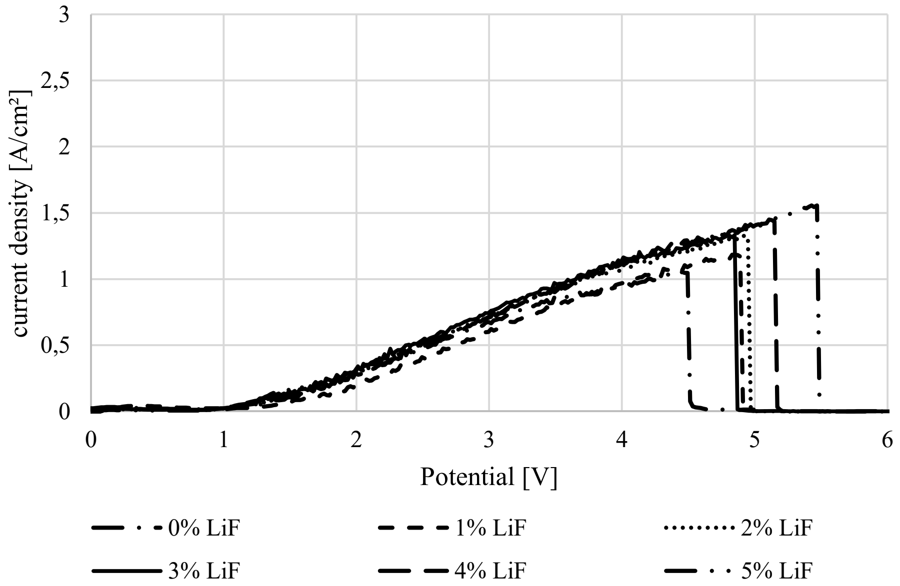

Figure 4: Comparison of the current density in the system NdF_3-PrF_3-LiF with a 2 wt.-% addition of Nd_2O_3 and Pr_6O_{11} (3 : 1 ratio) at different LiF contents at 1323 K vs Mo at 100 mV/s

Higher current density values imply that more metal is deposited at the cathode per time. Generally, the current density increases at a very similar rate for the different LiF contents, the values of the maximum current density and potential at which the anode effect occurs increase with higher LiF content.

Figure 5 shows the increase of the maximum current densities before the anode effect with increasing LiF content for different trails. Each line represents an electrolyte that was used before to synthesis Nd/Pr metal. The lines can be compared well since the experiments to which the electrolyte has been exposed have taken place under the same conditions. However, the oxide contents may vary slightly. Regression analysis is used to derive linear equations for the maximum current density vs total LiF content added and resulted in slopes of these lines ranging from 0.0381 to 0.2477.

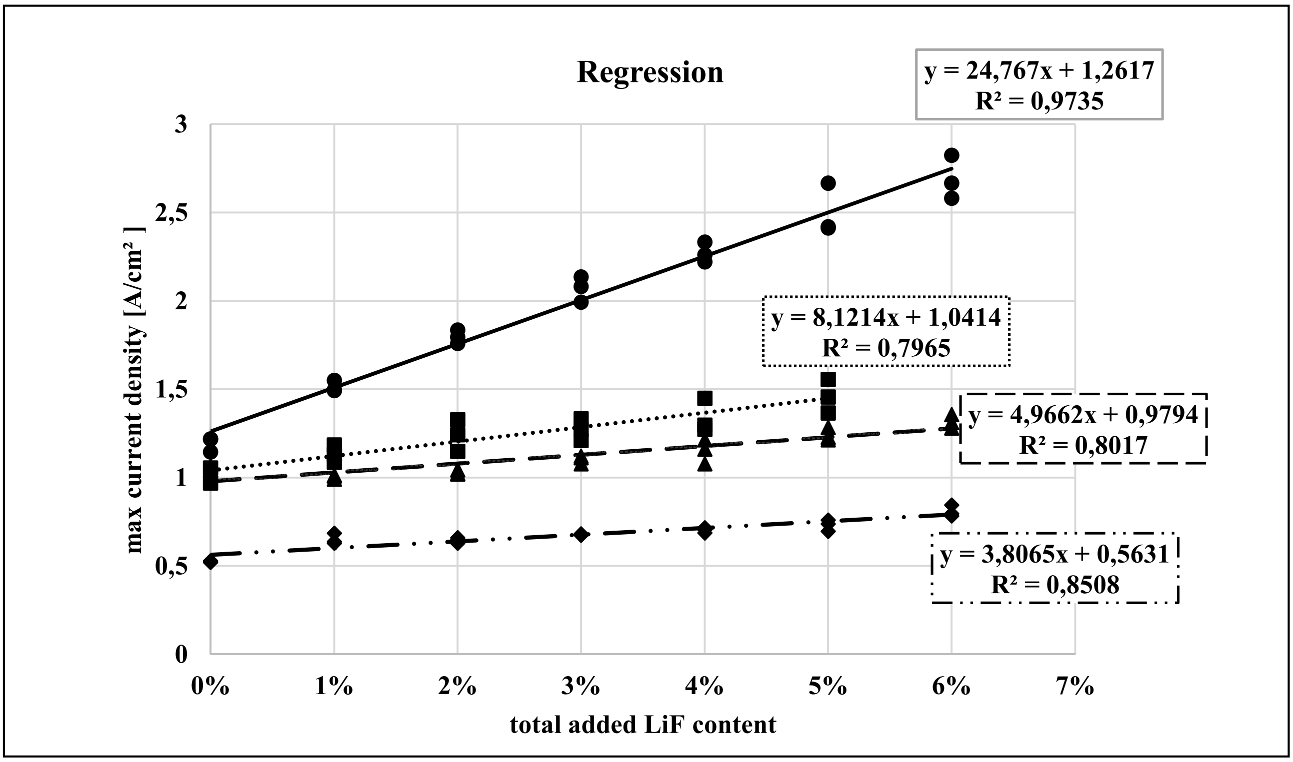

Figure 5: Graphs for the linear relationship between maximum current density and the total LiF content derived by linear regression with linear equation and coefficient of determination, R^2

The coefficient of determination, R^2, is given for each equation in figure 5. R^2 describes the "goodness of fit", namely, how well the measurements are predicted by the model. It ranges from 0 to 1, with a value of 1 indicating a perfect fit. In this case, R^2 ranges from 0.7965 to 0.9735, which are relatively high values meaning that the linear equations predict the measurements very well, leading to the conclusion that up to a LiF content of about 15 wt.-%, assuming an initial content of 9 wt.-%, the maximum current density that is reached before the anode effect occurs, increases linearly. The differences in the slope can be attributed to the differences in electrolyte composition. The increased maximum current density through the addition of LiF is caused by the different properties and functions of the lithium and fluoride ions in the electrolyte. The comparatively small radius, the low resistance of movement and the high mobility of the Li^+ cation improve the electrical conductivity of the melt. [16, 23, 24]

Using the equation for determining the gradient in the max current density for each LiF addition and each trial is presented in table 2. The total average of all trials is a rise of 7.72 % in the current density value per 1 wt.-% fed LiF. The total increase, i.e. the current value after the addition of 6 wt.-% LiF compared to the current value at 0 wt.-%, is also presented in this table. On average, the max current density reached could be extended by 58.91 % to the initial value.

Table 2: Increase of the current density per added LiF and in total

Trial	Current density increase per 1 wt.-% LiF added [%]	Total current density increase from 0 wt.-% to 6 wt.-% LiF added [%]
1	13.90	117.79
2	6.61	46.78
3	5.84	40.60
4	4.53	30.45
Average	7.72	58.91

The lack of LiF in the melt due to evaporation results in several phenomena, which are listed in the following. First, the already elucidated conductivity of the melt decreases.

Second, fewer oxyfluoride complexes are formed because of the lack of fluorides and because the missing LiF has a negative influence on the solubility of neodymium and praseodymium oxides.

Third, the melting point of the electrolyte increases with the result of an increasing electrolyte's viscosity and thus a hindered movement of the oxyfluoride complexes in the melt.

Fourth, the content of LiF has an influence on the wettability of the anode by the electrolyte. Gases thus accumulate more easily at the anode which leads to an inferiority efficiency of the process. [16, 24, 25, 26]

For the fluoridic electrolysis producing neodymium, studies have considered the electrolyte composition with changing values of the oxide and LiF content. Liu, Chen et al. [25] has discovered that the anodic overvoltage was reduced with an increasing concentration of LiF in an NdF_3-LiF-Nd_2O_3 melt caused by improved wettability of the anode by the melt and reduced electrical resistance. The reduced overvoltage caused by improved wettability of the anode and reduced electrical resistance is in accordance with the increasing critical current density with increasing LiF content. As the overpotential increases slower with increasing current density, the reactions can continue to take place at relatively high current densities because a smaller potential difference is required for the reactions to happen. The influence of LiF on metal synthesis with the phenomena described are summarised below in figure 6.

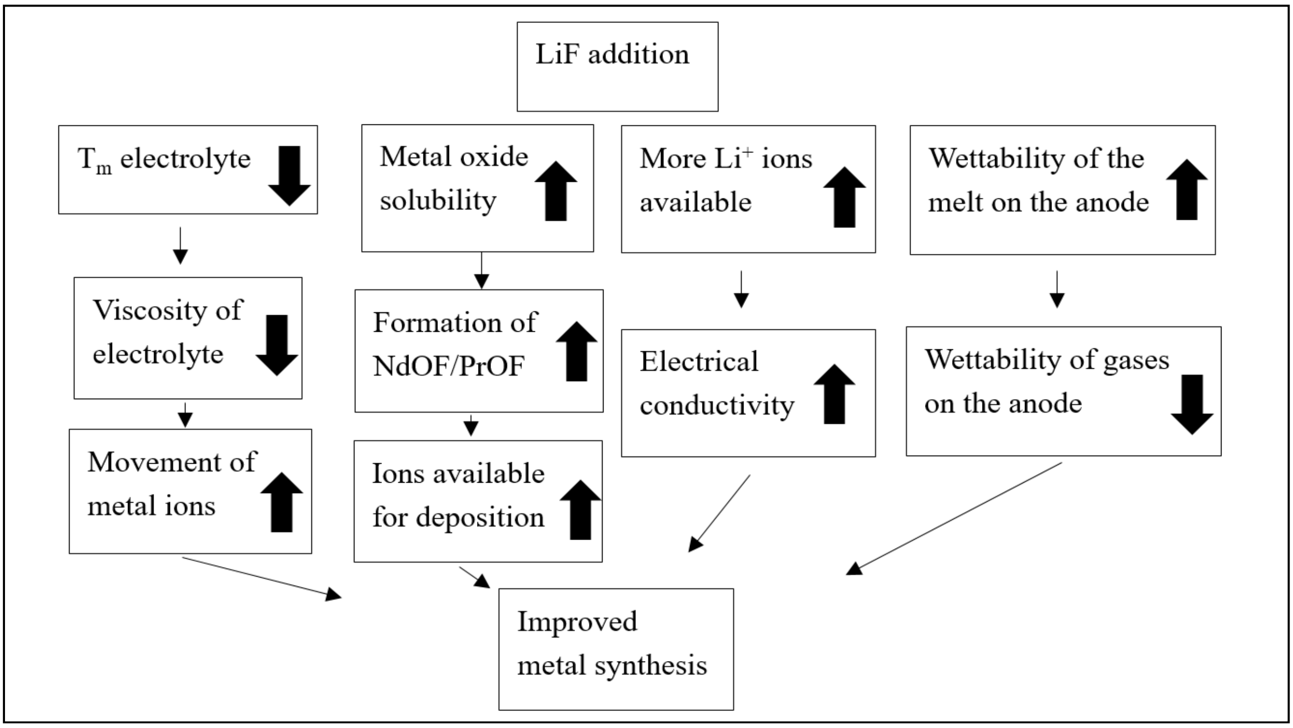

Figure 6: The influence of LiF on the metal synthesis

At the end of a trial, a piece of the cathode was analysed by XRD. During the electrochemical measurements, neodymium and praseodymium metal were deposited on the cathode, proving the combined reduction of both metal oxides.

Conclusion

In the present work, the influence of the LiF content on the electrochemical reactions of the combined deposition of neodymium and praseodymium and the anode effect was investigated. Linear sweep voltammetry was used to record current density vs potential voltammograms. The results showed that the critical current density, the current value at which the anode effect occurs, could be shifted to higher values with the addition of LiF to the electrolyte. Reasons for this are the improved conductivity and mass transport by the small Li$^+$ ions, decreased viscosity, and better solubility as the decrease of LiF concentration through evaporation is counteracted and the comparatively slower increase in overpotential at higher LiF contents as the current density increases. The increase in critical current density differed in each trial with the different electrolytes. On average, the increase of current density per 1 wt.-% LiF added 7.72 % and about 58.91 % in total.

The results showed that it is possible to reactivate previously used electrolyte to deposit didymium by solely adding LiF. This allows for further investigation of long-term electrolysis. Especially the relative constant increased maximum reached current density per fed LiF could allow a provided predictability of the amount and mixture of the feeding strategy. This strategy is a further step towards a more environmentally friendly production method of didymium, avoiding the generation of greenhouse gases such as CF_4 and C_2F_6.

References

[1] Aybars Güven, M.Sc, Prof. Dr.-Ing. Bernd Friedrich Electrochemical titanium diboride (TiB_2) synthesis from fluoride melts. Proceedings of EMC 2009 2009, 1313–1324.

[2] Claudia A. Oosterhof, Bernd Friedrich Molten salt electrolysis of titanium using a TiO_2-C composite anode in halide electrolytes. Titanium 2009.

[3] Dipl.-Ing. H. Vogel and Prof. Dr.-Ing. Dr. h.c. B. Friedrich Development and Research Trends of the Neodymium Electrolysis – A Literature Review. Proceedings of EMC 2015.

[4] Vogel, H., Flerus, B., Stoffner, F. and Friedrich, B. (2017) Reducing Greenhouse Gas Emission from the Neodymium Oxide Electrolysis. Part I. J. Sustain. Metall. 3, 99–107.

[5] Vogel, H. and Friedrich, B. (2017) Reducing Greenhouse Gas Emission from the Neodymium Oxide Electrolysis. Part II. IJNM 06, 27–46.

[6] Ksenija Milicevic, Dominic Feldhaus, Bernd Friedrich Conditions and Mechanisms of Gas Emissions from Didymium Electrolysis and Its Process Control. Light Metals 2018, 1435–1441.

[7] Cvetković, V.S., Feldhaus, D., Vukićević, N.M., Barudžija, T.S., Friedrich, B. and Jovićević, J.N. (2020) Investigation on the Electrochemical Behaviour and Deposition Mechanism of Neodymium in NdF_3–LiF–Nd_2O_3 Melt on Mo Electrode. Metals 10, 576.

[8] Cvetković, V.S., Vukićević, N.M., Feldhaus, D., Milicevic-Neumann, K., Barudžija, T.S., Friedrich, B. and Jovićević, J.N. (2021) Electrodeposition of Aluminium-Vanadium Alloys from Chloroaluminate Based Molten Salt Containing Vanadium Ions. Metals 11, 123.

[9] Zang, Q., Hua, Y., Xu, C., Li, Y., Li, J. and Dong, P. (2015) Non-haloaluminate ionic liquids for low-temperature electrodeposition of rare-earth metals – A review. Journal of Rare Earths 33, 1017–1025.

[10] Diaz, L., Chamelot, P., Gibilaro, M., Massot, L., Serp, J. Electrochemical Behavior of Neodymium in Molten Chloride Salts. Rare Metal Technology 2017, 77–86.

[11] Taxil, P., Chamelot, P., Massot, L. and Hamel, C. (2003) Electrodeposition of alloys or compounds in molten salts and applications. J min metall B Metall 39, 177–200.

[12] Yang, Y., Lan, C., Guo, L., An, Z., Zhao, Z. and Li, B. (2020) Recovery of rare-earth element from rare-earth permanent magnet waste by electro-refining in molten fluorides. Separation and Purification Technology 233, 116030.

[13] Huang, C., Liu, X., Gao, Y., Liu, S. and Li, B. (2016) Cathodic processes of neodymium(iii) in LiF-NdF_3-Nd_2O_3 melts. Faraday discussions 190, 339–349.

[14] Stefanidaki, E., Hasiotis, C. and Kontoyannis, C. (2001) Electrodeposition of neodymium from LiF–NdF_3–Nd_2O_3 melts. Electrochimica Acta 46, 2665–2670.

[15] Chen, Z. et al. (2018) Electrochemical deposition of neodymium in LiF-CaF_2 from Nd_2O_3 assisted by AlF3. Electrochimica Acta 261, 289–295.

[16] Guo, X., Sun, Z., Sietsma, J., Blanpain, B., Guo, M. and Yang, Y. (2018) Quantitative Study on Dissolution Behavior of Nd_2O_3 in Fluoride Melts. Industrial & engineering chemistry research 57, 1380–1388.

[17] Lee G-G, Jo S-K, Lee C-K et al Study on electrolysis for neodymium metal production. Rare metal technology 2015, 249–252.

[18] Liu, X., Huang, C. and Li, B. (2017) The Effects of NdF2 on Current Efficiency of Nd Extraction from NdF_3-LiF-Nd_2O_3 Melts. Materials Translation 58, 395–399.

[19] Thudum, R., Srivastava, A., Nandi, S., Nagaraj, A. and Shekhar, R. (2013) Molten salt electrolysis of neodymium. Mineral Processing and Extractive Metallurgy 119, 88–92.

[20] Stocker, T.F., Ed (2013) Climate change 2013. The physical science basis; summary for policymakers, a report of Working Group I of the IPCC, technical summary, a report accepted by Working Group I of the IPCC but not approved in detail and frequently asked questions; part of the Working Group I contribution to the fifth assessment report of the Intergovernmental Panel on Climate Change. Intergovernmental Panel on Climate Change. New York.

[21] IME-RWTH Process Metallurgy and Metal Recycling (2021) Molten salt electrolysis of rare earth elements (IME-RWTH University). https://youtu.be/SXlevENsILw.

[22] Liu, S., Chen, L., Li, B., Wang, L., Yan, B. and Liu, M. (2014) Anode processes for Nd electrowinning from LiF-NdF3-Nd2O3 melt. Electrochimica Acta 147, 82–86.

[23] Danielik, V., Fellner, P. and Thonstad, J. (1998) Content of sodium and lithium in aluminium during electrolysis of cryolitbased melts. Journal of Applied Electrochemistry 28, 1265–1268.

[24] Hu, X., Wang, ZW., Shi, Z., et al Electrical conductivity and Nd solubility of NdF_3-LiF-Nd_2O_3 melts. Characterization of minerals metals and materials 2007, 77–80.

[25] Liu, K.R., Chen, J.S., Wei, X.J. Study of anodic overvoltage in neodymium electrolysis. Acta Metallurgica Sinica 2003, 355–359.

[26] Zheng T., Ren Y. and Mao Y Study on the Viscosity ofNdF_3-LiF-Nd_2O_3 System. Chinese Rare Earth 2000, 33–36.