

PERFLUOROCARBON FORMATION DURING RARE EARTH ELECTROLYSIS

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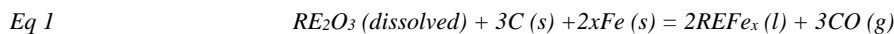
Abstract A challenge during rare earth (RE) electrolysis is to avoid emissions of perfluorocarbon (PFC) greenhouse gases. The objective of this work was to study how to operate the RE electrolysis process with neither PFC formation nor anode effect. Linear Sweep Voltammetry was carried out at 1050 and 1100 °C, and electrolysis was performed in REF₃-LiF melts at ca. 1050 °C during on-line off-gas analysis. To avoid anode effect, the current density values must be strictly less than 0.43 and 0.68 A cm⁻² at working temperatures of 1050 and 1100 °C, respectively. The optimal REO batch feed rate for avoiding PFC formation could be established by correlating the onset of PFC with the values and the changes that occurred in the anode potential.

1. Introduction

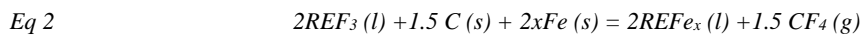
Many rare earth (RE) elements and alloys are today produced in its liquid form by electrolysis in molten fluorides using RE oxide (REO) as raw materials. A major challenge with this process is to avoid Perfluorocarbon (PFC) greenhouse gas evolution and at the same time uphold a good cell operation in terms of avoiding sludge formation due to over feeding of REO. China is the main RE metal producer in the world, but reliable information on the actual electrolysis technology used is scarce. However, it seems that the process releases large amounts of PFC gases, mainly CF₄ and some amounts of C₂F₆, almost continuously. This is alarming, as CF₄ and C₂F₆ have very high global warming potentials (GWP) due to their long life time in the atmosphere.

This work is done within the frame of the EU-financed project REE4EU. One of the project's main objectives is to achieve a direct production route for rare earth alloys through use of in-process and End-of-Life permanent magnets waste as raw materials in REF₃ electrolysis, RE being a mixture of dysprosium (Dy) and neodymium (Nd) in a ratio correlating with the ratio in the raw material.

The wanted anode reaction is the discharge of dissolved oxide (or oxyfluoride) species to CO (or CO₂) gas. The total cell reaction during CO evolution is shown in Eq 1:



In case of depletion of dissolved oxides at the anode interface, decomposition of the fluoride melt will take place and the anode product will be C₂F₆ or CF₄, see also Eq 2.



To avoid PFC evolution, an adequate supply of dissolved oxide raw material in the electrolyte that matches the operational amperage must be maintained continuously. The relatively low rare earth oxide solubility in many RE fluoride melts and slow oxide dissolution rates gives a narrow operational window in this respect. The critical current density (ccd) is defined as the maximum current density which can be obtained before the onset of anode effect (here defined as a total blockage of the anode surface accompanied by abrupt voltage rise and current drop towards zero) at a given oxide concentration. The ccd increases with oxide concentration and in aluminium electrolysis has been reported to be lower if the anode has undergone anode effect before [1].

The objective of this paper was to optimise the anode current density in terms of how to run the electrolysis process with no PFC formation. The bath composition in industrial REE electrowinning from fluoride melts usually has a RE/Li molar ratio of 50:50. The solubility of REO increases with increasing REF₃ concentration, however increasing REF₃ content also increases the solubility of RE metal and bath melting point. In this work, both eutectic and equimolar melts have been studied, the eutectic melt representing a "worse case" since the REO solubility is quite low. Linear sweep voltammetry was used to determine the onset of anode effect in eutectic NdF₃-

LiF (molar ratio 23:77) melt with addition of synthetic Nd_2O_3 at 1050 and 1100 °C. The behaviour of PFC formation was studied by on line gas analysis during electrolysis experiments in equimolar $\text{REF}_3\text{-LiF}$ melts at ca. 1050 °C.

2. Experimental

2.a. Optimization of the anodic current density - Linear sweep voltammetry (LSV)

The cell consisted of a vitreous carbon crucible (7 cm diameter and 7 cm height or 10 cm diameter and 18 cm height) placed in a cylindrical vessel made of refractory steel and closed by a stainless steel lid cooled by circulating water. The inside part of the walls was protected against fluoride vapors by a graphite liner, and the experiments were performed under inert argon atmosphere. The cell was heated using a programmable furnace and the temperatures were measured using a chromel-alumel thermocouple.

Linear sweep voltammetry (LSV) was performed in eutectic $\text{NdF}_3\text{-LiF}$ (23-77 mol%) with synthetic Nd_2O_3 added at saturation levels at 1050 and 1100 °C with an Autolab PGSTAT30 potentiostat, using glassy carbon and graphite as a working and counter electrodes, respectively, and platinum as a "quasi" reference electrode.

2.b. Lab-scale electrolysis with on-line FTIR gas analysis

The experimental cell consisted of a programmable vertical gas tight furnace with a mullite liner that housed a glassy carbon crucible containing the $\text{NdF}_3\text{-DyF}_3\text{-LiF}$ (50 mol% LiF) electrolyte. A vertical electrode set up with a cylindrical graphite anode surrounding an alloying iron cathode rod was utilised. RE-Fe alloy was the cathode product. Typical anode to cathode distances in the small lab-scale were in the order of 2-3 cm. The experiments were run at ca. 1050 °C under Ar 5.0 atmosphere. The REO-mix feed was dried, weighed out and stored hot and/or in a desiccator prior to and during the experiment as not to add H_2O and thus induce HF formation, and added to the melt through a tube of sintered alumina.

Electrolysis experiments were performed by applying constant current using an HP 6031A System Power Supply. The cell voltage and current as well as the temperature were logged during the course of the experiment by means of a multichannel Keithley 2000 Multimeter. The temperature was monitored continuously using a thermocouple type S (Pt-Pt 10%Rh) situated above the melt. In addition, the glassy carbon crucible was used as a "quasi reference electrode" so that the anode and cathode voltages could be monitored.

Ca. 700 grams of equimolar $\text{REF}_3\text{-LiF}$ had been mixed with 2 wt% REO, pre-melted and cooled in a graphite crucible. The obtained chunk of salt was then placed in the glassy carbon crucible, and the furnace was sealed off with the electrode set up in place and heated to the working temperature the day before the experiment and left molten overnight. To verify that all the oxide had dissolved, a melt sample was taken next morning and analyzed with respect to oxide content by carbothermal method, using LECO TC-436 DR (Leco Corp., USA). The electrolysis experiment was run at anodic current densities around 0.15 A cm^{-2} , and initial cathodic current density of around 1.5 A cm^{-2} . Subsequent amounts of oxide were fed batch-wise during the course of the electrolysis. The oxide additions could be carried out without opening the cell to the atmosphere, so the gas analysis could take place during the entire experiment without disturbance. A melt sample was taken at the end of the experiments and analysed with respect to oxide content.

After typically 5-6 hours of electrolysis, the furnace was cooled down under argon atmosphere to room temperature. The next day the cell was opened, the salt crushed, and any metal produced recovered.

A Fourier Transform Infrared Spectrometer (FTIR) apparatus (Protea ProtIR 204m) was used for online analysis of the off-gases (CO , CO_2 , C_2F_6 , CF_4) from the cell. Existing models were used in order to transform the FTIR readings to actual gas concentrations, upon calibration of the apparatus. The argon flow through the furnace was kept constant during the whole experiment to 700 mL/minute, and the out gas was led through the FTIR via an 8-mm alumina or nickel out gas tube situated above the melt "inside" the anode. For safety reasons, a pressure gauge was placed on the gas inlet side of the cell to monitor the pressure build up that often occurs during gas analysis due to high resistance on the outlet side caused by filters, high gas flows, condensation of bath etc.

3. Results and Discussion

3.a. LSV studies of anode effect

Figure 1 shows the curves for the linear sweep voltammetry (LSV) at 1050 and 1100 °C in the eutectic NdF₃-LiF composition with synthetic Nd₂O₃ added at saturation levels.

The results showed that, for the two temperatures investigated, the current density increased with the potential until falling to almost zero at 3.4 V and 4.9 V respectively. For the curve performed at 1050 °C, the current increases again after this passivation and might correspond to what is termed partial anode effect. Similar results were reported by Vogel et al. [2]. For both temperatures, a wave around 2-2.5 V represents the limiting current density (0.12-0.2 A cm⁻²) for electrochemical discharge of oxide ion species to CO or CO₂. The results indicate that the current density values when using a carbon anode must be strictly less than the ccd values of 0.43 and 0.68 A cm⁻² at working temperatures of 1050 and 1100 °C, respectively. The melt was saturated with Nd₂O₃, i.e. > 3 wt%, however in a real process the oxide concentration will probably be 2 wt% or below in order to avoid sludge formation, so the real current density limitations will probably be lower.

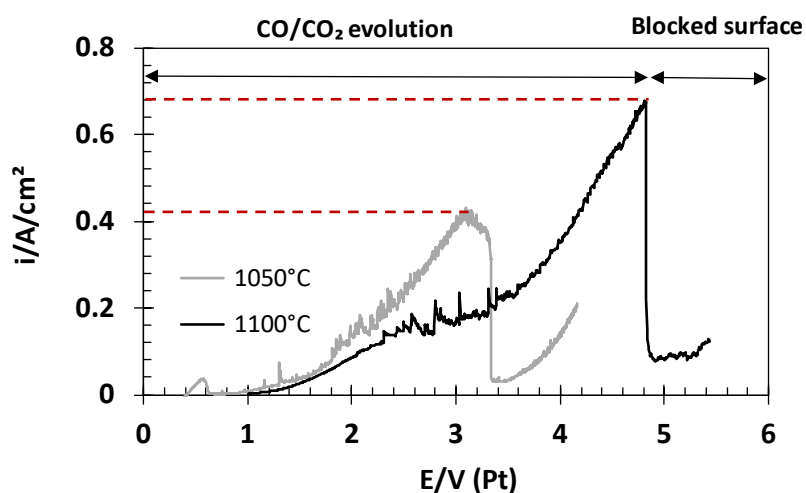


Figure 1. LSV curves obtained on a glassy carbon electrode in the eutectic NdF₃-LiF melt containing 4 wt% Nd₂O₃. Working temperatures 1050 (black line) and 1100 °C (grey line). Scan rate 10 mV s⁻¹.

3.b. Lab-scale electrolysis with on-line FTIR gas analysis

Figure 2 shows electrolysis data, and Figure 3 the results from the gas analysis plotted together with the anode voltage for a typical experiment in a NdF₃-DyF₃-LiF melt at ca. 1050 °C and using a Nd/Dy oxide mixture as feed. Note that the change and path crossing of the anode and cathode potentials during the first 50 minutes that can be seen from Figure 2, is probably due to a change in the "glassy carbon reference" potential, possibly caused by deposits of RE and subsequent RE-carbide formation when getting in contact with the glassy carbon crucible.

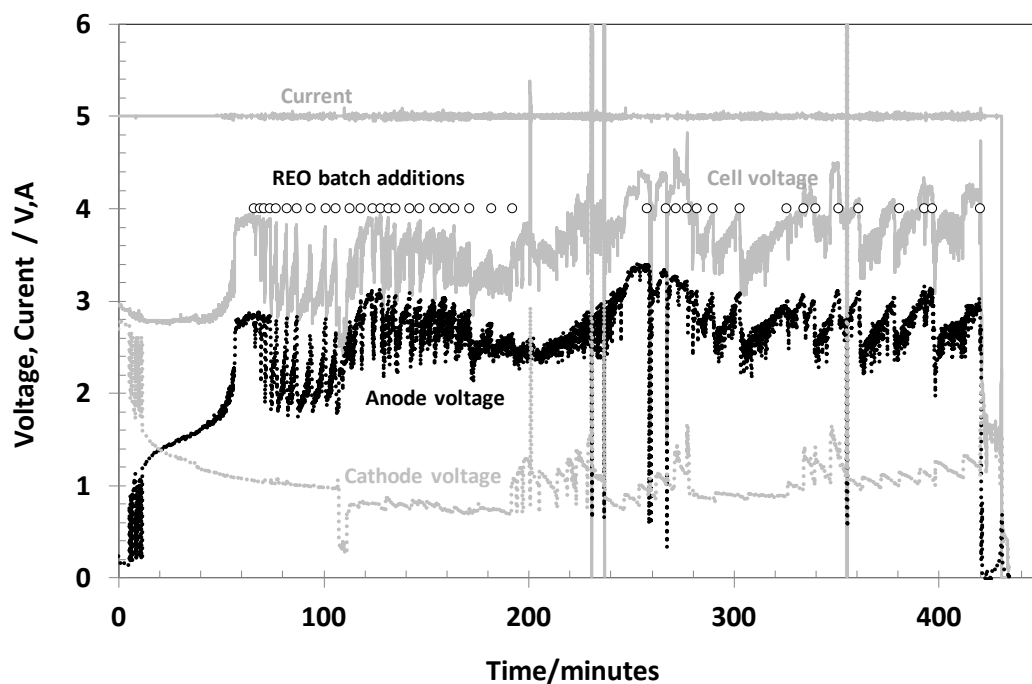


Figure 2 Example of cell voltage, anode and cathode voltages, current and temperature recorded during the course of one of the experiments carried out in $\text{DyF}_3\text{-NdF}_3\text{-LiF}$ at ca. 1050°C . The dots indicate the point in time for the oxide feedings.

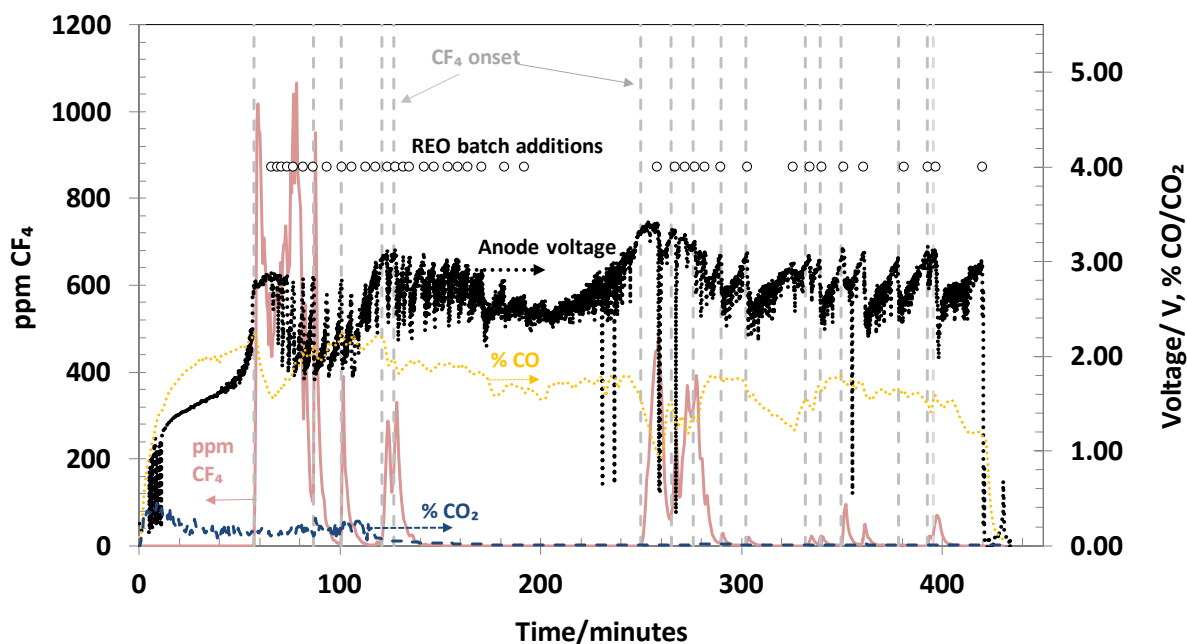


Figure 3 Anode voltage and concentrations of CO (g), CO_2 (g) and CF_4 (g) in the off gas recorded during the electrolysis experiment shown in Figure 2.

In order to try to identify the onset potential for CF_4 formation, the strategy was to wait with the feeding until CF_4 evolution had occurred, so the first batch was fed after ca. one hour of electrolysis. Neither was any feeding conducted in the first ten minutes after PFC was observed, however no full anode effect (blockage of anode surface accompanied by very high voltages) took place. To stop the PFC evolution, oxide was added frequently in the time frame between 60 and 192 minutes. After a period of probably over feeding, no oxides were added for more than

an hour (from 192 to 267 minutes). PFC appeared not until almost one hour had passed, this time at a higher anode potential than the first onset. The characteristic recurrence of abrupt increase in the anode voltage from around 2-2.5 to 3-3.2 V that can be seen in the figures, often correlates with the onset of or sudden increase in CF_4 gas formation, indicated by the dotted lines. When oxide was fed, the anode potential decreased to around 2-2.5 V, and started to increase slowly again until the sudden jump to 3-3.2 V, accompanied by CF_4 evolution. As the experiment proceeded, this behaviour was utilized to decide on the REO feed rate. The optimal feed rate in terms of batch addition frequency that would prevent or mitigate CF_4 formation could then be established by feeding just before or at the same time the sudden anode potential rise occurred. This feature could perhaps be utilised for process control in industrial scale electrolysis. The feeding rate could be governed by monitoring the anode potential and automatically feed when the potential exceeds a certain value as also suggested by Vogel et al [3]. A similar behaviour has also been observed in the electrolysis of Dy-Fe alloy from the binary DyF_3 -LiF mixture [4].

Depletion of dissolved oxides at the anode interface, due to insufficient replenishment probably caused by slow dissolution rate, leads to discharge of fluoride ions from the electrolyte and subsequent potential increase. These reoccurring potential jumps accompanied by CF_4 formation probably represent beginning or partial anode effects that would eventually end in a massive rise in potential and drop of current if no action had been taken (oxide addition). However, it seems possible to sustain a stable operation at higher anode potentials and lower oxide contents, with co-evolution of CF_4 , also observed by Vogel et al. during Nd electrolysis [3]. Co-evolution of PFC, not necessarily being followed by a full anode effect has also been observed during aluminium electrolysis, as so called "low voltage" or "non-propagating" anode effects, representing "continuous background emissions" [5]. The mechanism is probably different however, since in aluminium electrolysis, the PFC occurring before a full anode effect is related to the large number of anodes run in parallel.

The average gas composition was found to be 96.2 % CO , 3.37 % CO_2 and 0.43 % CF_4 . Thus, the main off gas component was found to be CO . This may be due to: i) CO being the primary electrochemical anode reaction product, ii) CO is formed as a consequence of a back reaction from the anode product CO_2 and dissolved metal, or iii) CO it is formed due to a shift in the Boudouard equilibrium. Moreover, some of the current is used for fluoride ion discharge and thus subsequent CF_4 evolution, the CO rate of formation decreases (see Figure 3). This was also observed in the binary DyF_3 -LiF mixture [4].



Upon opening the cell and inspecting the salt after slow cool-down under inert atmosphere, sludge formation was observed in all the experiments conducted. The sludge formation is unwanted since it represents a significant oxide loss and operational disturbances. It is also believed to be harmful for the metal produced, and may somehow have contributed to rare earth metal losses from the rare earth alloy lying at the bottom of the cell. The grey layer seen in Figure 4 is believed to consist of such an "oxide-metal mix" sludge.

The average REO-mix feeding rate was usually kept at 40-70 % of the total charge imposed. In the experiment represented by Figure 4, the average batch size was 0.17 % of the electrolyte mass, and a current of 5 A corresponds to a depletion rate of around 0.026 wt% per minute.

Figure 4 Picture of the salt after one of the electrolysis experiment

Even though the point of time for feeding was governed by the anode potential/PFC formation, i.e. in a situation where the oxide concentration at the anode must have been quite low, the single batch sizes seemed to have been too large for all the REO to have time to dissolve before it settled in the cell bottom. Continuous feeding in small batch-sizes would probably help to utilize more of the oxide added.

The REO content dissolved in the electrolyte right after termination of the experiment was analysed to be 1.37 wt %. The total amount of oxide fed corresponded to 70 % of the charge imposed. The total amount of oxygen exiting with the off-gas correlates with the net amount of REO reduced, and the oxide yield could be calculated to be 48 %. A low current efficiency due to parasitic reactions or electronic conduction because of dissolved metal will necessitate a decrease in the oxide replenishment rate. Attempts were made to increase the bath surface area and decrease the batch size, but sludge still seemed unavoidable. The problem may be alleviated in a full-scale cell, due to deeper bath, higher ACD, and more turbulence created by the gas evolution. A cell with a larger electrolyte amount to amperage ratio might render the operation dynamics less vulnerable for the slow oxide dissolution rate since the changes in oxide concentration due to consumption and replenishment will be slower. Dysinger and Murphy also reported challenges with sludge formation in Nd electrolysis, and commented that once settled in the cell bottom the oxide/oxyfluoride species will not dissolve in an appreciable rate [6].

In the experiment whose data are shown in Figure 2 and Figure 3, the starting oxide concentration was analysed to be 1.72 wt %. By assuming a faradaic efficiency between 50 and 80 % for the oxide reduction reaction in the first hour of electrolysis during which no new oxide was fed, the oxide concentration at the time of the first occurrence of CF_4 can be calculated to be 1.2-1.4 wt %. This will represent the oxide concentration corresponding to a limiting current density value for CO/CO_2 evolution of 0.15 A cm^{-2} which was the imposed anodic current density during the whole experiment. The value is also in the same range as the limiting current density values obtained in the LSV curves for the oxide oxidation reaction in the carbonaceous anode (see Figure 1). There seems to be an anodic current density range between 0.15-0.40 ($0.6 \text{ at } 1100 \text{ }^\circ\text{C}$) A cm^{-2} where co evolution of CF_4 takes place without entering into anode effect.

4. Summary and concluding remarks

The objectives of this paper were to optimise the anode current density and to understand how to run the electrolysis process with no PFC formation in RE electrolysis from fluoride melts using oxide as raw material. Linear sweep voltammetry was used to determine the onset of anode effect in eutectic $\text{NdF}_3\text{-LiF}$ melt with addition of synthetic Nd_2O_3 at 1050 and 1100 $^\circ\text{C}$. The behaviour of PFC formation was studied by on line gas analysis during electrolysis experiments in equimolar $\text{REF}_3(\text{DyF}_3\text{-NdF}_3)\text{-LiF}$ melts at ca. 1050 $^\circ\text{C}$.

It was found that in saturated eutectic $\text{NdF}_3\text{-LiF}$, the current density values when using a carbonaceous anode must be strictly less than 0.43 and 0.68 A cm^{-2} to avoid anode effect at working temperatures of 1050 and 1100 $^\circ\text{C}$, respectively.

In the equimolar $\text{REF}_3\text{-LiF}$ at 1050 $^\circ\text{C}$, at REO contents in the range 1.2-1.4 wt%, the limiting current density for CO/CO_2 evolution was found to be 0.15 A cm^{-2} .

Stable operation at higher anode potentials above the limiting current density for CO/CO_2 and co evolution of CF_4 without entering into anode effect seems possible.

The optimal REO batch feed rate for avoiding or mitigate PFC formation could be established by following the cell/anode voltage and gas analysis and correlating the onset of PFC with the values and the changes that occurred in the anode potential. However, the batch-wise feeding cell operation gave too high instantaneous feeding rate and sludge formation seemed unavoidable.

On-line analysis of the cell off-gas by FTIR showed that the main component is CO, but significant amounts of CO_2 were often observed in the beginning of the electrolysis. The overweight of CO is probably a combined consequence of i) back reaction; ii) Boudouard equilibrium shifted towards CO rich composition; and iii) CO being a primary anode reaction.

Acknowledgements

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5. References

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