Electrochemical Recycling of NdFeB Magnet in Molten Salt

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Abstract

The high consumption of NdFeB magnets in different sectors demands future recycling action, as it accounts for around 21% of total rare earth element (REE) use. The NdFeB magnet contains neodymium, praseodymium and dysprosium as additional. This REE constitutes 20-30% of the magnet in which iron is the dominant element. A pyrometallurgical route to recycle this magnet has been developed using rare earth oxide (REO) with low impurity content. The final step of molten salt electrolysis (MSE) is needed to convert it into a reusable rare earth alloy for magnet production to obtain metallic REE. This work examines REO's electrochemical measurement and electrodeposition in fluoride-based molten salts. Experimental work was done in a graphite crucible placed in the electrochemical cell, which operates with a three-electrode system. The electrolyte, which consists of NdF_3-PrF_3-DyF_3-LiF, is mixed with REO, which contains Nd_2O_3-Pr_2O_3-Dy_2O_3. The REO used in this work was an experimentally prepared REO from an NdFeB magnet and an artificially mixed REO. Cyclic voltammetry shows different cathodic peaks, which could be caused by individual REE reduction and intermetallic compound formation. Moreover, it is also observed that the system can achieve a higher current range with lower potential compared to individual Nd/Pr/Dy electrolysis. A short-term electrodeposition test was shown to produce REE alloy on the molybdenum working electrode.

1. Introduction

The consumption of permanent magnets is inarguably one of the highest utilization of rare earth elements. This is because rare earth based permanent magnet, or NdFeB magnet possesses the highest magnetic performance in comparison to other magnet [1,2]. This performance is suitable for heavy duty equipments such as in electric vehicles and wind turbines [3]. The NdFeB permanent magnet was invented in 1984 by mixing neodymium (also a small amount of praseodymium), iron and boron [4,5]. The $Nd_2Fe_{14}B$ (sometimes with a slightly different ratio) as the main phase is surrounded by the Nd-rich phase, which acts as the grain boundary. This phase is formed during the vacuum melting process of the ingredients. The addition of other rare earth elements such as praseodymium and dysprosium will create a small portion of $RE_xFe_yB_z$ in the main phase[4,5]. The addition of Pr is known to reduce Nd need, while Dy could improve the magnet's resistivity at high temperatures [6,7].

The NdFeB magnet could be manufactured as a bonded or sintered magnet. However, sintered magnet is usually more preferable due to its higher magnetic performance. In making the sintered magnet, the compositions are melted in a vacuum furnace to produce an ingot. The ingot is then pulverized through hydrogen decrepitation and jet milling before the sintering, which is later continued by magnetization [8] . This sequence is the main production route to produce the NdFeB magnet. Different variations, for example, could occur during the formation of the raw material and steps to making the ingot.

The usage of NdFeB magnet through different applications varies with the lifespan of the equipment. It takes more than 10 years for the wind turbine, 5-10 years for electric vehicles and 2-5 years for small electrical devices (computer, loudspeaker, etc) [3,9]. Many efforts are now focused on developing recycle process for those end-of-life NdFeB magnets to secure sustainable rare earth elements supply in the future. Up to this point, there are different alternatives recycle routes that could be selected, which can be categorised into two groups: Direct magnet recycling and indirect magnet recycling (REE recycling) [8,10,11]. The first terminology implies that the magnet could be recovered from the scraps and used for new equipment without significant conditioning. However, it is often the case that the Eol magnets accumulate impurities or are too difficult to separate from the scrap. Furthermore, it is also possible that the magnet from the scrap equipments contain impurities that hinder direct recycling. In this case, technologies to recover high purity REE from the magnet plays important role. The obtained REE could either be use again as magnet ingredients or for other purposes.

As one of the widely used technologies for primary REE extraction, molten salt electrolysis (MSE) will be used instead to recover REE from the NdFeB magnet. Molten salt electrolysis was initially and widely developed to produce aluminium from Al_2O_3 (Hall-Heroult process). This is because there are many elements, including Al and REEs, that have lower reduction potential than hydrogen. This will not allow the reduction using electrolysis in aqueous-based electrolyte as hydrogen production will take place instead. The MSE process, especially for REEs, was usually performed using chloride or fluoride salt as the electrolyte with a temperature range from around 600 – 1100°C [12–15]. Particular advantages of choosing fluoride salts over chloride is the higher solubility of the rare earth oxides (REO) as the raw material for producing rare earth metals (REM) and avoidance of toxic gas formation (Cl_2) on the anode surface [16]. Furthermore, REO is also the common end-product of hydrometallurgical process that is used to extract REE from its mineral in primary production. From this standpoint, REO will also be used as the raw material in this study.

In the context of NdFeB magnet recycling, several options are available, which can be classified into two groups: Direct and Indirect recycling. Direct recycling implies the possibility to directly use the NdFeB magnet from end-of-life (EOL) in the same electronics or electrical devices manufacturing chain. Hydrogen decrepitation plays an important role in this recycling route as demagnetisation is the only prerequisite [8]. However, difficulties are common in the sorting process as the magnet might already be damaged, lost or contain impurities during the lifespan or disposal of the device. For this case, in which direct recycling is almost not practical, recovering the REE in the form of their individual element is more promising. These routes offer the possibility to take different NdFeB magnet compositions and the flexibility of resources and product usage. In the indirect recycling process, there are different options of hydrometallurgical processes that aim to produce REO [3,9,17]. The REO can then be used as valuable products or further purified with electrolysis to obtain high-purity metal.

In contrast to the hydrometallurgical route, the rare earth oxides for this study were obtained from the NdFeB magnet through pyrometallurgical processes that consist of oxidation and carbothermic reduction, which have been developed in the previous studies [18,19]. By this approach, iron as the major component in NdFeB magnet could be significantly separated, producing rare earth oxides containing neodymium, praseodymium and dysprosium with high concentration.

In order to obtain the rare earth metals back, MSE process utilizing that mixed oxides from magnet are studied. In this work, electrochemical measurements will be done to characterized the behaviour of this oxides in the melt. Most literature on REE recycling with MSE used single REO, which is obtained synthetically (contains very few impurities). Therefore, the aim of this study is to provide preliminary electrochemical measurement of MSE that contains multiple REO from NdFeB magnet recycling process. In this REO, iron and boron are considered as the impurities from the magnet-to-REO conversion. A comparison with a mixture of synthetic REO will be presented to emphasise different characteristics of the process. The results are expected to provide an understanding of the electrochemical behaviour for further measurements and optimisation.

2. Materials & Methods

Different fluoride-based rare earth salts and rare earth oxides were used to prepare several systems for these experiments. Electrolyte compositions consist of neodymium fluoride (NdF_3 - 99.5%), praseodymium fluoride (PrF_3 – 99.5%), dysprosium fluoride (DyF_3 – 99.5%) and lithium fluoride (LiF – 99.5%) that were supplied by Treibacher, Austria and Shanghai Xinglu Chemical Co., Ltd, China. The synthetic oxides, which are neodymium oxide (Nd_2O_3 - 99.5%), neodymium oxide (Pr_6O_{11} - 99.5%), neodymium oxide (Dy_2O_3 - 99.5%) were also from the same providers. The magnet-based mixture of REO were manufactured from the NdFeB magnet from Ljubljana Magneti, Slovenia. The electrochemical measurements were done by IviumStat potensiostat (Ivium technologies, Netherlands) with a 2 mm diameter molybdenum/tungsten working electrode (WE) and a 2 mm diameter tungsten quasi-reference electrode (RE) and a 4 mm diameter graphite as counter electrode (CE) (EWG and CTG GmbH, Germany). The experiments are done under an argon atmosphere that flows continuously during the experiment to carry out the produced gas. Two bottles that contained water and sodium hydroxide solution, and one empty bottle for melt protection from possible accidental liquid flowback were connected with effluent from the cell.

The mixture of electrolyte and oxides was fed into a graphite crucible (CTG GmbH, Germany), which was placed inside a custom-made stainless steel electrochemical cell. The ratio of electrolyte components were based on previous investigations [18]. For different electrolyte compositions, 1% of oxides were added. This mixture was melted in a heat-resistant furnace at a temperature of 1100°C. The electrochemical cell was provided with a water cooling system in the lid and neck part to allow electrodes to change and be evaluated. The complete setup schematic is shown in Fig. 1.

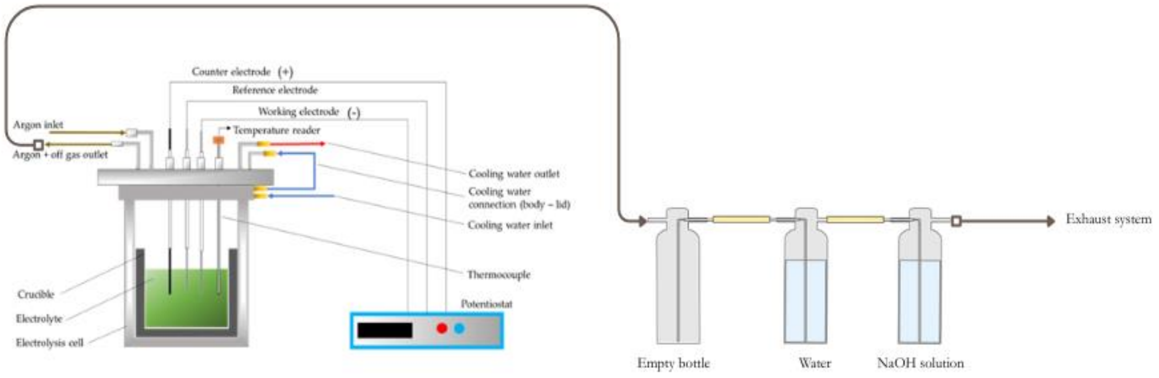


Figure 1: Experimental setup

The production of REO from NdFeb magnet was done by using methods developed in previous work by Kruse et al [17] and Chung, et al [18]. The process began with oxidation to fully oxidise the elements and destroying the main magnetic phase. Carbothermic reduction in vacuum induction furnace. This process produced separation between slag phase (REO-rich) and metallic phase (Fe-rich) (Figure 2). The NdFeB magnet and obtained REO was then characterized using ICP-OES (Spectro Arcos GmbH). The schematic representation of this method from our previous work shown in Fig 2 [20].

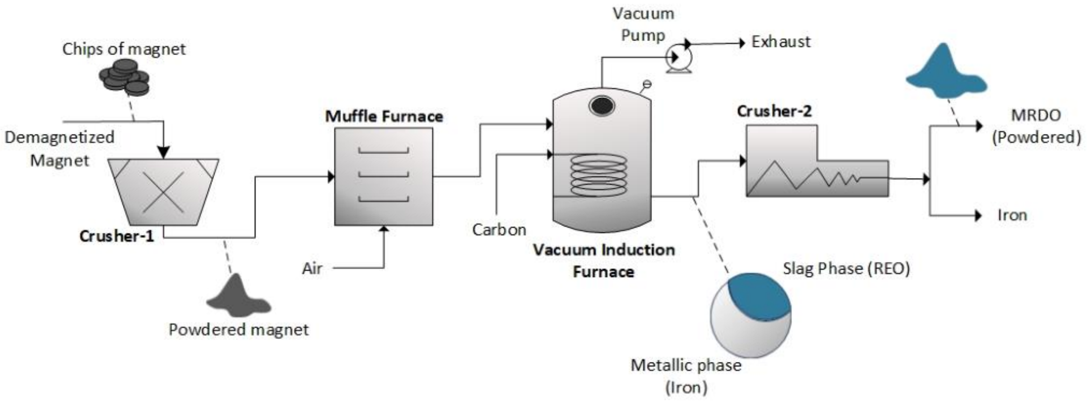
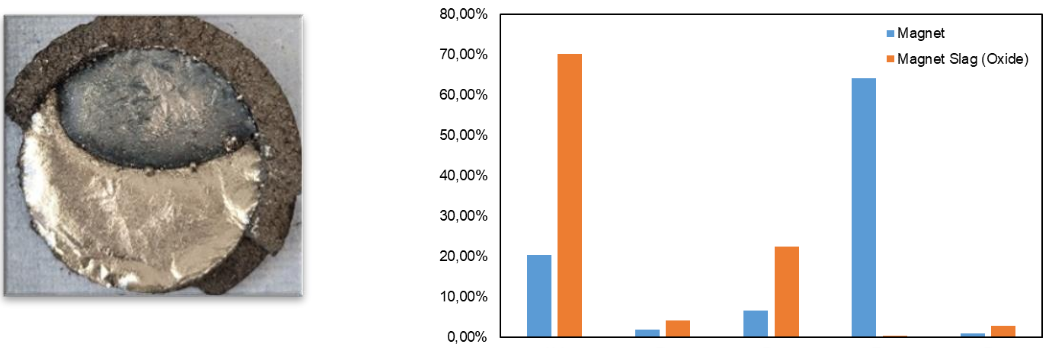


Figure 2: Process schematic of MRDO production using pyrometallurgical process

The MRDO from the process is shown in Fig. 3(a). Elemental analysis reports that the REO has very low content of Fe, suggesting that the process was effective for separating iron as major magnet compositions. It is seen that the total rare earth contents could be enriched from less than 30% to about 95% in the MRDO (Fig. 3(b)). It implies that carbothermic reduction was able to reduce iron oxides into metallic iron, which later separated itself from the slag phase.The results also reported the relatively similar boron concentration between the metallic and slag phases. This implies that boron oxide compounds were not reduced during carbothermic reduction.



(a)

(b)

Figure 3: (a) Product from carbothermic reduction; (b) Elemental analysis comparison of NdFeB magnet and REO from the slag phase

Table 1 shows different sets of electrolyte systems. This study combined partial results from various experiments on MSE for REO. Some of the considerations in selecting the electrolyte in MSE are the solubility of oxides and conductivity. Oxide solubility is usually in line with the proportion of the corresponding oxide in the salts form; in this case, higher rare earth salt concentration will increase rare earth oxide solubility (Guo). Providing electrolytes with similar cations to the oxide will also reduce the number of available elements, thus keeping the limiting current high [21].

Except for the synthetic REO, the electrolyte in this study was adapted from the previous investigations [13,22]. Other literature, however, showed that more LiF could be used without disturbances in the electrochemical measurement. This concept was then adapted to incorporate multiple rare earth salts, the proportion of which is calculated based on rare earth elements contained in the NdFeB magnet in the study. However, the phenomena that would be discussed here are the electrochemical behaviours that are not bound by the electrolyte compositions.

Table 1: Different electrolyte composition for experiments

Electrolyte Composition, %	**Oxides, % from total electrolyte**
PrF_3 – LiF = 85 – 15	0 and 1% of Pr_6O_{11}
NdF_3 - PrF_3 – LiF = 61.10 – 26.30 -12.5	1% magnet-based REO
NdF_3 - PrF_3 - DyF_3– LiF = 17 – 1 – 5 - 77	1% synthetic REO (Nd_2O_3 – Pr_6O_{11} – Dy_2O_3)

Cyclic voltammetry with different cathodic ends and scan rate was used in this study for electrochemical measurements. Potentiostatic electrodeposition was also performed to validate possible metal formation based on the electrochemical measurements. X-Ray diffraction (XRD) analysis will also be performed on the working electrode after electrodeposition.

3. Results & Discussions

3.1. Effect of oxides addition

The cyclic voltammetry (CV) results for the PrF_3-LiF (85-15 mol%) system, with and without the addition of 1% Pr_6O_{11}, reveal significant differences in electrochemical behavior, particularly in the reduction and oxidation processes. In general, figure 4 shows no-oxide system exhibits unclear cathodic and anodic process which characteristic by very broad cathodic and anodic current density, without tendency of peak appearance. Moreover, it could be noted that the current density plot has more noise than oxide-containing system. This could be the indication of unstable electron transfer due to CF_4 bubble formation on the anode.

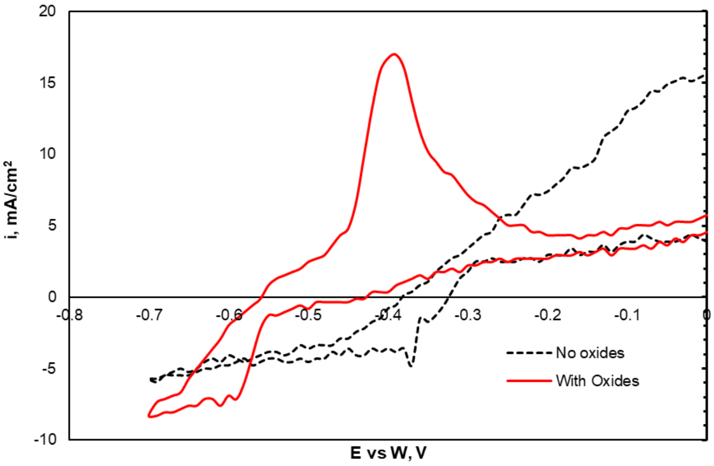


Figure 4: Cyclic voltammogram of PrF_3 – LiF = 85 – 15% (with and without oxides) with W WE at 1100°C at -1.3 V with scanrate 100 mV/s

In contrast, the presence of oxides creates a noticeable change of cathodic and anodic peaks to be more well-defined. Both cathodic and anodic scan show single peak that correspond to one-step, 3 electron transfer, which was also proven from previous studies [14]. This shift suggests that the presence of oxygen species from Pr_6O_{11} alters the electrochemical reduction process, likely due to the formation of Pr oxyfluoride species (PrOF) or the stabilisation of intermediate oxidation states, which modify Pr^{3+} activity in the melt. Other studies that focused on the environmental impact pointed that anode effect can be prevented also when oxides were used as the input material in fluoride based melts [13,23].

3.2. Molten Salt Electrolysis of Magnet-based REO

Figure 3 shows cyclic voltammogram with different cathodic ends. Distinct redox peak is relatively difficult to observe except for pairs of C2-A2 for lithium reduction and oxidation. Point C1 indicates cathodic peak that is followed by limiting current type curve. Experimental work using similar system reported 2 steps Nd^{3+} reduction steps that started at -0.4 V and continued at -0.55 V. In the study, the potential where Pr^{3+} was reduced to Pr(0) (around -0.65 V), was found to be after the reduction of Nd^{2+} to Nd(0) [14,24]. Other investigation of Lanthanides in chloride melts by Liu et al generally shows that the reduction potential of lanthanides were close to each other, including neodymium, praseodymium and dysprosium [15]. Previous studies by Cvetkovic et al [14,24] with same electrolyte but synthetic oxides revealed 2 steps Nd^{3+}-reduction which was followed by 1 step Pr^{3+} reduction. In the study, these cathodic peaks were also coupled with 3 anodic peaks.

The cyclic voltammetry (CV) results for the NdF_3-PrF_3-LiF (61.10-26.30-12.60 mol%) system with 1% oxides show a distinct CV shape compared with Fig 3. A cathodic current was observed in the early scan (deviation from 0 mA as the baseline). This current could be initiated by the reduction of oxides related to iron and boron, which have a more positive reduction potential than Nd, Pr, and Dy. Since Fe and B can form compounds with multiple stoichiometric coefficients, a wide range of potential where faradaic current are theoretically expected, which as also the case for the shape of the CV at the early scan.

The reverse scan at different cathodic ends showed similar broad anodic current, in which peak determination is difficult. Point A1 is assigned to indicate anodic phenomena that could correspond to oxidation of the deposited rare earth metals in the cathodic run. Small anodic peak (A3) could be also belong to rare earth metal oxidation. However, this could indicate low rate oxidation process. as the curve shows limiting current-like pattern. As this pattern does not present in Fig. 3, it could be that the deposit was more difficult to be oxidised. Moreover this also suggests that oxidation is not dominated by the dissolution of deposited Nd and Pr metals, but also involves the oxidation of additional metal deposited.

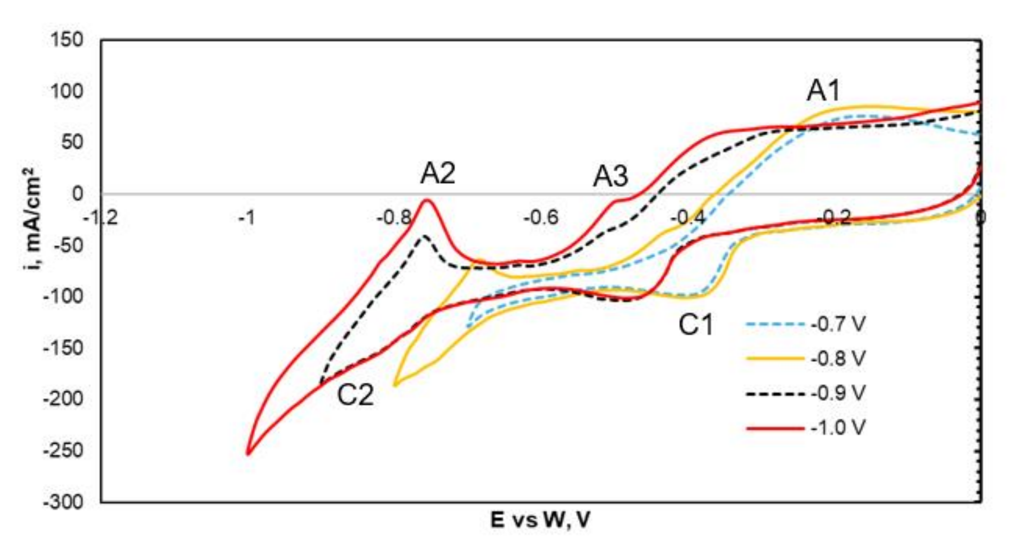


Figure 4: Cyclic voltammogram of NdF_3 - PrF_3 – LiF = 85 – 15% (1% MRDO) with W WE at 1100°C with scan rate 100 mV/s with different cathodic ends

3.3. Molten Salt Electrolysis of Synthetic REO

In addition to the magnet-based REO, similar measurements were done in the system containin synthetic REO. Cyclic voltammogram in Fig. 5 revealed different curve in comparison to Fig. 4, especially on the anodic current. At several cathodic ends, clearer anodic peak are observed (A1). This difference from Fig. 4 indicates that the deposition product from cathodic ends was easily oxidised. The potential where anodic process begins are more negative, which are also the case for cathodic peaks (C1).

The use of synthetic oxide does not produce a more distinctive individual reduction peak for Nd, Pr, and Dy. This suggests that multiple rare earth ions could influence each other during reduction. The absence of Fe and B in the system also contributes to the lower current at the potential sweep prior to the reduction potential. Therefore, it could strengthen the indication of possible various compounds in a wide range of potential due to Fe and B. Other remarks is that the addition of DyF_3 as electrolyte compositions, no additional peak is produced, in comparison with the system without DyF_3 discussed in subchapter 3.2. At this point, it is also presumed that the certain REO can dissolve in other rare earth salt

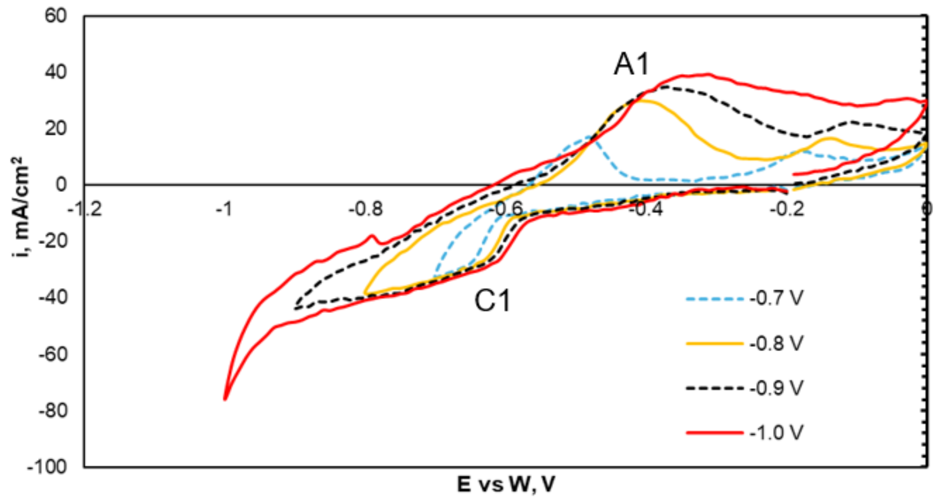


Figure 5: Cyclic voltammogram of NdF_3 - PrF_3 - DyF_3– LiF = 17 – 1 – 5 - 77% (1% synthetic REO) with W WE at 1100°C with scan rate 100 mV/s with different cathodic ends

3.4. Electrodeposition test of Magnet-based REO

To examine whether REM could be recovered, potentiostatic electrolysis was done using the second electrolyte system from Table 1, which uses 2% MRDO. The difference in amount from the other system prevents an anode effect that could destabilise or stop the process. The electrolysis was then done on the molybdenum working electrode as presented in Fig. 6 at -0.9 V. The current – potential monitoring is shown in Fig. 5. This potential was selected based on CV results in Fig. 4, between the observed REE and Li reduction potential. Figure 5 shows that current keeps increasing with time while potential could be maintained constantly. The process ended at around 3000 s (50 minutes) due to a constant increase in current. Another electrolysis study with similar systems reported a slight current increase over a longer period. The process was stopped as this unusual pattern could indicate deposition of lithium.

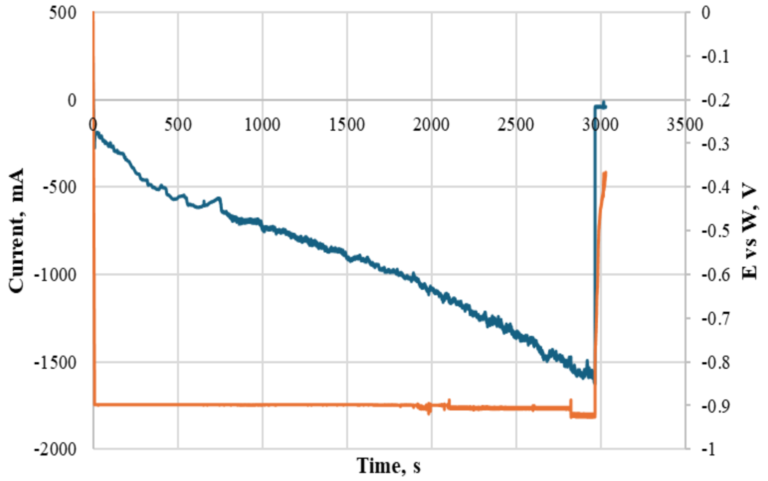


Figure 6: Potentiostatic deposition of NdF_3 - PrF_3 – LiF = NdF_3 - PrF_3 – LiF = 61.10 – 26.30 -12.5 With 2% of MRDO at -0.9 V

After the electrolysis, XRD analysis of the cathode revealed that metallic phase of Nd, Pr and Dy were detected on the Mo working electrode, while Fe and B related compound was not detected (Fig. 7), even though it was present in the initial oxides. For B, it is possible that it stays in the complex form or it reacted with F-ions to form volatile BF-compounds that left the system. The presence of Fe-related current in the CV (Figure 4) suggest that iron oxide was dissolved in the melt. However, during the electrolysis, it could be that the mass transfer of Fe ions were slower compared to the REE ions, which at the end hinder its heterogeneous reaction with the electrode.

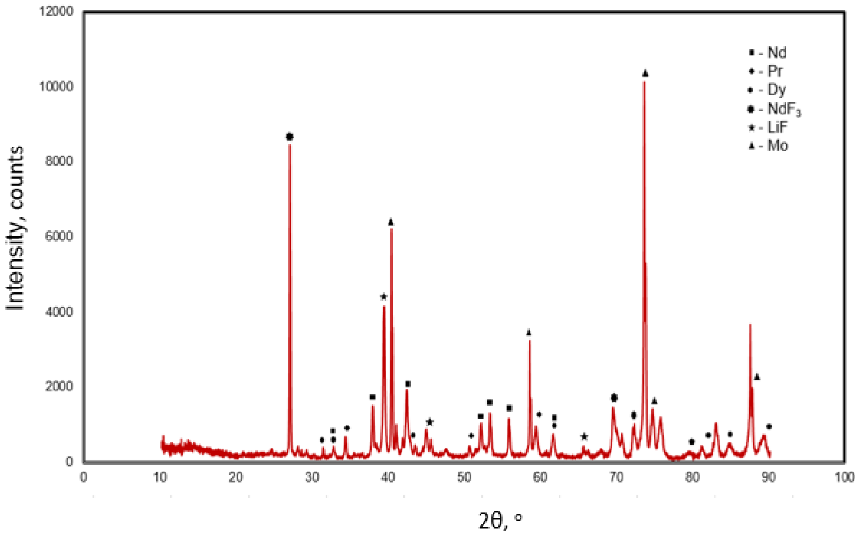


Figure 7: X-Ray Diffraction Spectra of the Working Electrode After Deposition

4. Conclusions & Outlook

The study discussed the comparison of MRDO and synthetic oxides in fluoride-based molten salt electrolysis. The MRDO is shown to contain very high concentrations of REE (Nd, Pr, Dy) with a slight amount of Fe and B. Using cyclic voltammetry, it was revealed that both system has electrochemical behaviour, such as differences in redox potential range, the magnitude of background current and anodic behaviour. This information could be further used for determining suitable potential or current density range for bulk electrolysis experiment for Nd, Pr, Dy metal synthesis. Moreover, these results lies the foundation for more comprehensive measurements to determine reaction kinetics and mass transfer, such as square wave voltammetry and chrono-potentio/amperometery. Further experiments are needed to validate the underlying phenomena for both processes and possibility to optimize the electrolysis process, especially from MRDO-based raw material in fluoride electrolytes.

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