Recent advances in electrochemical recovery of rare earth elements from NdFeB magnets

L. Fu [a,*], H. Karimi-Maleh [b,c]

[a] College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou, 310018, PR. China
[b] School of Resources and Environment, University of Electronic Science and Technology of China, 611731, Chengdu, PR China
[c] School of Engineering, Lebanese American University, Byblos, Lebanon
Corresponding author: Li Fu (fuli@hdu.edu.cn; lifu.ac@gmail.com)

Abstract

Recent advances in electrochemical methods show promise for more sustainable recycling of rare earth elements (REEs) from end-of-life NdFeB permanent magnets. Demand for NdFeB magnets is rapidly growing for clean energy applications, motivating recycling efforts to diversify REE supplies. Core electrochemical steps involve selective dissolution of REE-rich phases at the anode and reduction of REE ions at the cathode. Pretreatment including demagnetization, mechanical size reduction, and leaching help liberate and concentrate the REEs. Thermal demagnetization and mechanical crushing make the magnets brittle and improve leachant penetration. Acid leaching dissolves REEs but co-dissolves iron. To facilitate high-temperature recovery of REEs, molten salt electrolytes such as chlorides are utilized, whereas ionic liquids enable recovery under milder conditions, albeit with a caveat of potential decomposition during the process. Aqueous solutions have been most thoroughly investigated for versatility and affordability. Fluoride-based molten salt electrolytes effectively dissolve RREs and provide stable environments for high-temperature electrodeposition, enhancing the efficiency and sustainability of rare earth element recovery. Additional purification is needed to isolate high purity REE oxides and metals, using techniques like solvent extraction, selective precipitation, and electroseparation. Key factors for optimal electrochemical recycling are maximizing selectivity for REEs, minimizing energy use and waste generation, and simplifying integration. While technical challenges remain, recent advances demonstrate electrochemical technologies can improve the sustainability of recycling critical REEs from permanent magnets.

Introduction

REEs comprise the fifteen lanthanides along with scandium and yttrium, which display similar chemical properties. REEs have become indispensable for many advanced technologies, including renewable energy, electronics, automotive, and defense applications [1,2]. This is due to their unique magnetic, optical, and catalytic properties which enable superior performance [3]. Permanent NdFeB magnets are a prime example, relying on REEs such as neodymium, praseodymium, dysprosium, and terbium to achieve the strongest magnetic properties of any commercial magnet material [4].

The global demand for REEs has expanded rapidly, currently estimated at over 120,000 tons annually and projected for continued growth [5]. However, REE reserves are geographically constrained, with China controlling the vast majority of mining and processing. Concerns over supply disruptions, cost fluctuations, and environmental impacts have motivated efforts to diversify and expand sustainable REE supplies through recycling of end-of-life products containing REEs [6]. NdFeB permanent magnets represent the largest potential source, with magnet production exceeding 30,000 tons annually [7]. Widely used in consumer electronics and clean energy technologies with 10-20 year lifespans, recycling of these magnets could satisfy a significant portion of REE demand [8].

REE recovery from end-of-life NdFeB magnets presents unique challenges. The REEs are alloyed with transition metals like iron and cobalt, comprising 20-35 wt% of the magnets [9]. Liberation and separation steps are first required to isolate the REE constituents. Hydrometallurgical processes based on acid dissolution have been extensively investigated for extracting and separating the REEs from other constituents [10]. However, these involve significant chemical reagents and generate large aqueous waste streams. Pyrometallurgical approaches based on high temperature treatment have also been explored, but have drawbacks in terms of REE losses and purification [11].

Electrochemical methods are promising for more sustainable REE recovery from waste NdFeB magnets [12]. Direct cathodic reduction can be applied for electrowinning metallic REEs without acid dissolution. Alternatively, leaching may still be utilized as a primary separation step, followed by electrorefining to recover high purity REE metals from the leach solutions [13,14]. The kinetics, electrolytes, cell configurations, and electrode materials can be tailored to maximize selectivity and efficiency in extracting REEs over the co-constituent transition metals [15].

This review aims to provide a comprehensive overview of recent advances in electrochemical technologies for recycling REEs from NdFeB permanent magnets. First, the fundamental principles including electrolyte properties, electrode reactions, cell designs, and process parameters will be outlined. Second, various pretreatment methods will be compared as initial steps to liberate and concentrate the REE

constituents from dismantled magnets. Third, electrochemical extraction and recovery processes will be assessed, evaluating current efficiency, energy use, complexity, and recovery purity. Finally, downstream separation and purification techniques will be examined to obtain individual rare earth oxides and metals. Table 1 provides a comprehensive overview of the different electrochemical processes investigated for recovering REEs from NdFeB magnets, highlighting their unique approaches and outcomes. These information can be used for better understand the content of each section. The goal is to critically review the current status in the field, analyze the advantages and limitations of different methods, and identify the most promising directions for further development of electrochemical recycling processes for REEs from end-of-life NdFeB permanent magnets.

**Electrochemical Principles for Rare Earth Recovery**

The core steps in electrochemical recycling of REEs from NdFeB magnets involve reduction and deposition processes at the cathode as well as dissolution at the anode [16]. Specifically, the NdFeB material is dissolved in an electrolyte solution, where a voltage is applied to reduce and deposit REEs on the cathode. Concurrently, at the anode, dissolution of other magnet materials occurs. The kinetics and mechanisms of these electrode reactions must be considered in designing an optimal process.

The cathode reaction involves the electrochemical reduction of dissolved RE^{3+} ions to deposit the rare earth metals:

$$RE^{3+} + 3e^- \rightarrow RE(s)$$
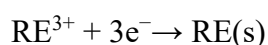
The cathodic current efficiency depends on many factors including the RE ion concentration, current density, temperature, pH, and cathode material. Too high overpotentials result in hydrogen evolution instead of RE deposition. Smooth cathode surfaces and basic pH favor higher current efficiencies [17]. Composite cathodes incorporating REs or intermetallics have shown promise for preferential nucleation.

For the anode reaction, oxidative dissolution of the magnet chunks or leachates occurs:

$$RE(s) \rightarrow RE^{3+} + 3e^-$$
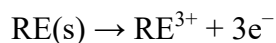
Co-dissolution of other metals like Fe is also possible depending on conditions. Anode materials are often chosen to be chemically inert, such as platinum, graphite, or lead dioxide. The extent of dissolution depends on electrolyte exposure and applied potential. Selective recovery of REEs over other co-constituents is a key aim. The NdFeB magnets utilized consist of multiple alloys, with the metals Nd/Nd^{3+} (-2.32 V vs. the standard hydrogen electrode), Fe/Fe^{2+} (-0.447 V), and B/H_3BO_3 (-0.89 V) displaying

relatively cathodic electrode potentials. In an acidic environment, however, O_2 precipitation (1.229 V) exhibits a more anodic electrode potential compared to the other constituent metals [18]. Kinetic factors also play a role, where particle size, agitation, temperature, and potential control can help tune selectivity [19]. Extraction from leachates can provide some initial separation if dissolution was selective. Figure 1 illustrates the typical techniques used in the electrochemistry of NdFeB magnets, detailing the processes and reactions at both the cathode and anode.

Aqueous electrolytes are most commonly employed, providing a conductive medium for ion transport as well as an environment in which metal ions remain soluble [20]. Molten salt electrolytes such as chlorides or fluorides are generally used for REE recovery to form soluble complexes. Ionic liquids (ILs) are also possible but less studied. The electrolyte pH is important for controlling speciation as well as hydrogen evolution side reactions at the cathode [21]. Under basic conditions, the propensity for hydroxide formation in electrolytic processes is generally reduced, rather than suppressed entirely. This occurs because in a basic environment, the increased concentration of hydroxide ions competes with metal ion hydroxide formation. This competition can reduce the likelihood or rate of metal hydroxide precipitation, which is advantageous in certain electrolytic processes. However, it's important to note that this effect is highly dependent on the specific metal ions involved and the exact conditions of the electrolyte, including its concentration and temperature. Therefore, while basic conditions can mitigate hydroxide formation to an extent, the term "suppress" might be too strong, and it would be more precise to say that these conditions can help to control or reduce hydroxide formation.

Molten salt electrolysis, spanning both thermal and electrochemical methods, has been widely applied for the separation and extraction of REEs [22]. Compared to aqueous solutions, high-temperature molten salts offer superior media for electrochemical processing of REEs, owing to their heightened chemical stability, conductivity, reaction rates, broad applicable temperature range, and negligible vapor pressures. Jeon et al. [23] investigated a molten salt electrolysis method to selectively extract Nd from NdFeB magnets for recycling. The electrolysis used molten LiCl-KCl salts with $CdCl_2$ at 773K. The $CdCl_2$ ionized the Nd into Nd^{3+} while leaving the iron and boron intact. With sufficient $CdCl_2$, over 99% of the Nd was extracted from the magnets within 2 hours, and the magnets naturally fragmented and pulverized during the process. Cyclic voltammetry data correlated well with the $CdCl_2$ concentration, allowing for online monitoring of the Nd extraction reaction progress. The extracted Nd could then be electrodeposited using a liquid Cd cathode, avoiding issues with Nd comproportionation, and separated through Cd distillation. This molten salt electrolysis method enables efficient and selective Nd recovery from NdFeB magnets. Yang et al. [24] investigated a molten salt electrolysis method to REEs from waste NdFeB permanent magnets. The process uses a $LiF-CaF_2$ molten salt electrolyte at 1040°C. The NdFeB waste is used as the anode, where the REEs are selectively oxidized into ions and dissolved into the electrolyte. Channels form in the anode from the oxidation,

allowing penetration of the molten salts to continuously transport the REE ions. The REE ions are then reduced and electrodeposited as pure REE metals onto a cathode. The process achieved high separation rates of Nd and Pr from the magnets, up to 99% at optimal current densities. It avoids anode gas emissions, making it environmentally friendly. Venkatesan et al. [25] investigated an electrolysis process to selectively extract REEs from NdFeB magnet waste at room temperature. The pretreatment uses a dual anode system with the NdFeB magnet as the active metal anode and an inert platinum-coated titanium anode (Figure 2). The electrolyte used is NH_4Cl. During the electrolysis, the REEs and iron in the magnet dissolve and convert to hydroxides while Fe(II) generated from iron dissolution gets oxidized to Fe(III) by the inert anode. This results in a mixed hydroxide precipitate containing $REE(OH)_3$ and $Fe(OH)_3$. The electrolysis is performed at room temperature with high efficiency, avoiding the high temperatures used in roasting pretreatments. The effects of electrolyte concentration and inert anode current density were studied. Increasing NH_4Cl concentration from 1 M to 4 M improved anodic dissolution efficiency to 99.8% and decreased energy consumption to 2.9 kWh/kg magnet. Applying a current density of 0.2 A/cm^2 at the inert anode ensured efficient oxidation of Fe(II) to Fe(III), with over 94% of iron removed from the leachate. After electrolysis, the mixed hydroxide precipitate is selectively leached with dilute HCl to extract the REEs into solution while leaving iron in the solid residue. Over 97% of REEs and cobalt were extracted into the leachate while iron remained in the residue as FeOOH. The REEs were then recovered from the leachate by oxalic acid precipitation, regenerating the HCl and closing the loop. The process operates at mild room temperature conditions with an energy consumption of 3 kWh/kg magnet and provides an efficient hydrometallurgical route for recycling REEs from NdFeB magnets in a closed loop.

Fluxes play important role of the molten salt electrolysis. Abbasalizadeh et al. [26] tested four different fluorinating agents - AlF_3, ZnF_2, FeF_3, and Na_3AlF_6 (cryolite) - added to a LiF-NdFeB system at 1223K. The results showed that all four fluorinating agents successfully extracted neodymium and dysprosium from the magnets, converting them into rare earth fluorides like NdF_3 while leaving the iron and boron unreacted. AlF_3, ZnF_2, and FeF_3 in particular were very effective at selective extraction of the rare earths. The conversion to rare earth fluorides enables a one-step electrolytic process to recover high purity rare earth metals, which is important for recycling rare earth magnets.

Ionic liquids, as non-aqueous systems, present viable alternatives to high-temperature molten salts for NdFeB magnet recovery and metal ion processing under low-temperature conditions. Their non-aqueous nature renders ionic liquids suitable media for the mild conditions required in NdFeB magnet recycling. Xu et al. [27] studied on using an ionic liquid (1-ethyl-3-methylimidizolium dicyanamide) as a non-aqueous electrolyte to electrodeposit a neodymium-iron alloy at the mild temperature of 110°C. The study found that neodymium alone could not be reduced to its metallic form directly from the electrolyte, but it could be co-deposited along with iron. The proposed

mechanism is that ferrous ions are first reduced to form an activated transition state iron (Fe*), which then catalyzes the reduction of neodymium from +3 to 0 oxidation state, allowing the co-deposition. Experimental results matched well with a derived mathematical model that predicted neodymium content based on iron concentration and applied potential. Transmission electron microscopy combined with electron energy loss spectroscopy confirmed the co-deposition mechanism by showing that a thin layer of iron formed first before the alloying with neodymium occurred. After annealing, the majority of the deposited neodymium was present as Nd(0) either in metallic form or as neodymium carbide, indicating the trivalent neodymium was reduced during electrodeposition. The ionic liquid electrolyte enables electrodeposition of the neodymium-iron alloy at a much lower temperature compared to conventional molten salt electrolysis. Xu et al. [28] used a nonaqueous solution of dimethylformamide (DMF) containing 0.3 M $FeCl_2$. This ionic-liquid electrolyte enables the selective etching of the grain boundaries in the magnet, which contain rare earth oxides, while leaving the $Nd_2Fe_{14}B$ grains intact. By applying a current density below 5 mA/cm^2, the metallic Nd and Nd-rich grain boundary phases are preferentially etched away due to their lower electrode potential compared to the $Nd_2Fe_{14}B$ phase. After extended etching, the $Nd_2Fe_{14}B$ grains are disconnected from the grain boundaries and can be magnetically separated, with a recovery of 67.2% of the magnet's mass. The ionic-liquid electrolyte is crucial in enabling this selective etching process while avoiding the use of aqueous solutions. Molodkina et al. [29] reported on the induced electrochemical codeposition of Nd with the transition metal iron (Fe) from a fluorine-free IL electrolyte based on 1-butyl-1-methylpyrrolidinium dicyanamide ([BMP][DCA]) at room temperature. Using cyclic voltammetry, the authors demonstrate that Fe can reduce Nd(III) to Nd(0) at a more positive potential than Nd(III) alone, enabling codeposition of Nd-Fe alloys. The addition of water significantly promoted the electrodeposition of the individual metals, with shifts in reduction potentials up to 0.8 V, likely due to disordering of the IL interfacial structure. However, increasing water content strongly inhibited codeposition, hypothesized to be from formation of oxidized Nd species blocking further Fe reduction. Overall, the study provides new insights into induced codeposition of rare earth-transition metal alloys in ILs, revealing a complex dependence on water content that must be controlled to optimize Nd-Fe codeposition. The results suggest IL electrolytes could enable efficient electrochemical recycling of Nd from secondary sources. ILs hold great promise for applications in areas like metal electrowinning and recycling of NdFeB magnets [30]. However, an important consideration is that some ILs can decompose during electrodeposition, resulting in incorporation of IL breakdown products into cathode deposits as impurities [31]. While ILs enable electrodeposition of challenging metals, contamination must be minimized to obtain pure deposits. Strategies like selecting ILs with enhanced stability or operating at less extreme potentials could mitigate unwanted IL decomposition. Overall, realizing the full potential of ILs in metal recovery requires understanding decomposition pathways and developing approaches to curb contamination. With careful IL selection and electroplating conditions, their unique properties can be harnessed while avoiding pitfalls like deposit impurities.

Unlike ionic liquids, aqueous solutions have been more thoroughly investigated and generate greater research enthusiasm for NdFeB magnet recovery owing to their versatility, integrability with other processes, low cost, and high safety. The aqueous processing pathway for NdFeB magnet recycling has a more extensive research foundation and interest versus ionic liquid systems, attributable to the compatibility, combinability, affordability, and benign nature of aqueous solutions. The study by Prakash et al. [32] on NdFeB magnet recycling primarily constitutes a theoretical analysis. The research theoretically examines the selective dissolution of REEs from NdFeB magnet scrap in an aqueous environment. This is based on the principle that REEs have more negative standard reduction potentials than iron, theoretically allowing for their selective dissolution. However, the paper also addresses the theoretical challenge of iron's co-dissolution, which can occur due to the mechanical degradation of the alloy during the dissolution process. To theoretically overcome this, it proposes a method where any co-dissolved iron could be redeposited onto the cathode, while REEs are dissolved into the solution. The research underscores the importance of controlling the electrochemical potential and maintaining a specific pH range (1-2) to facilitate this selective process and to minimize side reactions, such as hydrogen evolution. It's important to note that these findings and proposals are based on theoretical analysis and not on experimental data, which may not be immediately evident from the manuscript and could lead to misunderstandings about the nature of the research. Dupont and Binnemans [33] developed an innovative recycling process for NdFeB magnets, focusing on the sustainable recovery of REEs. This process utilized the carboxyl-functionalized ionic liquid [Hbet][Tf2N], leveraging its acidity and thermomorphic properties. The method involved a combined leaching and extraction step, where the ionic liquid facilitated the selective dissolution of valuable REEs from the magnet's matrix at high temperatures. Upon cooling, the system separated into two phases, enabling the efficient segregation of REEs from iron. The researchers achieved high separation factors for neodymium, dysprosium, and cobalt from iron, with the subsequent stripping process using oxalic acid to precipitate REE(III) and cobalt(II) ions. This step also transferred iron(III) from the ionic liquid to the water phase as a soluble oxalate complex. The process was further refined to remove cobalt by treating the mixed oxalate precipitate with aqueous ammonia, resulting in highly pure REE oxalates. These oxalates were then calcined to form REE oxides with over 99.9% purity.

Based on the efficiency and selectivity demonstrated in various studies, the use of molten salt electrolytes, particularly LiCl-KCl with $CdCl_2$ or $LiF-CaF_2$, appears to be highly effective for the selective extraction of REEs like Nd and Pr. These electrolytes, when coupled with inert anode materials such as platinum or graphite, provide a robust system for REE recovery. For pretreatment, processes that utilize selective dissolution or leaching, such as the dual anode system with NH_4Cl electrolyte, show great promise in enhancing the recovery efficiency. As for purification, the selective leaching with dilute HCl, followed by oxalic acid precipitation, offers an efficient route for separating REEs from other constituents. These methodologies, when integrated thoughtfully,

could form a cohesive and effective framework for the recycling of REEs from NdFeB magnets, aligning with both environmental sustainability and economic viability.

Selection and optimization of electrode

Creating an electrolyte environment that does not inhibit and actually promotes the free dissolution of REEs is crucial. While REEs can become passive in highly alkaline environments, their behavior in various solutions varies. For instance, Song et al. [34] found that NdFeB magnets develop passive hydroxide layers in sodium hydroxide and oxalic acid. Similarly, Zheng et al. [35] noted passive behavior in phosphoric acid, characterized by low corrosion current. However, in other acids like sulfuric acid, nitric acid, and hydrochloric acid, these alloys dissolve more readily, exhibiting high current density. Additionally, even in environments where they show passivity, REEs are still vulnerable to attacks by chloride and other ions. Overall, REEs tend to dissolve easily in acidic solutions. Other electrolyte system has been explored as well. For example, recent studies have demonstrated the effectiveness of fluoride-based molten salt electrolytes, such as NdF_3-LiF and NdF_3-PrF_3-LiF combinations, in the electrodeposition of REEs [36,37]. The cyclic voltammetry results showed reduction peaks indicating the stepwise deposition of Nd and Pr metals on the cathode (Figure 3). These fluoride salts offer high solubility for rare earth oxides and facilitate stable electrochemical environments for the reduction and recovery of REEs. The choice of fluoride salts is particularly advantageous in scenarios where high-temperature operations are feasible and where maximizing the recovery efficiency of REEs is critical. Research in this domain has shown promising results, indicating that fluoride molten salts could play a significant role in advancing the sustainability and efficiency of REE recovery processes.

Cathodes are often titanium plate [38], molybdenum [39,40], stainless [41] or graphite [42]. Potentiostatic electrolysis produced consistent deposition current densities, and analysis of the Mo cathode after lengthy deposition times confirmed the presence of metallic Nd and Pr on the surface [40]. SEM imaging displayed deposition buildup (Figure 4), while ICP-OES quantified up to 72.77% Nd and 23.92% Pr recovered on the cathode from the magnet recycling-derived oxide material. The molybdenum cathode facilitated the productive electrodeposition and recovery of reusable neodymium and praseodymium metals from spent NdFeB magnets dissolved in the fluorine melts. In the theoretical study conducted by Prakash et al. [32], they primarily selected inexpensive stainless steel as the cathode material across the various electrochemical recycling processes, without providing an in-depth justification. However, the choice of stainless steel cathodes seems to be driven by several factors. Firstly, stainless steel is widely used in industrial electrolysis due to its low cost, mechanical strength, and corrosion resistance. Using an inexpensive material helped reduce the operational costs for processes aimed at commercial viability. Secondly,

stainless steel is an inert material that promotes the desired hydrogen evolution reaction at the cathode. Generating hydrogen gas was favorable to avoid reducing Fe(III) back to Fe(II), which would interfere with the selective extraction of REEs. The large overpotential of stainless steel for hydrogen evolution kinetically hindered the back reaction of Fe(III) reduction. Thirdly, the author mentions using a cathode area much larger than the anode area in some reactors. The large cathode area minimized the side reaction of Fe(III) reduction by increasing the relative rate of the hydrogen evolution reaction. Fourthly, stainless steel prevented contamination of metal deposits at the cathode, such as the small amounts of iron and cobalt occasionally observed. The inert nature of stainless steel ensured high purity of cathode deposits by avoiding dissolution of the substrate. Lastly, while not explicitly stated by the author, stainless steel cathodes are easy to fabricate and install in various reactor configurations.

Liquid cadmium cathode (LCC) has been recently explored for the electrochemical recovery of Nd from NdFeB permanent magnets compared to using an inert solid cathode [43]. The key advantage is that Nd forms an intermetallic alloy with the molten Cd, which significantly reduces the activity of Nd and shifts its reduction potential to a more positive value. This enables the selective electrowinning of Nd from the magnet at a higher potential than possible on an inert cathode. In addition, the Nd can be electrodeposited in a single reduction step on the LCC rather than the two steps required on an inert cathode. The formation of the Nd-Cd intermetallic compounds also provides a route for separating the Nd from the Cd cathode. After electrowinning, the Nd-Cd alloy can in principle be separated by density differences from the lower density molten Cd and Li-Cd phases, allowing recovery of a Nd product. Overall, the LCC provides a more effective and selective route for recovering neodymium metal from NdFeB magnet scrap through molten salt electrorefining. Kato et al. [44] explored the electrorefining process in a molten LiCl–KCl eutectic salt containing actinide (An) and REEs to recover An elements into CCL. Aimed at enhancing the efficiency of nuclear fuel recycling, the research focused on separating actinides from rare-earths using a saturated liquid Cd cathode. Key findings included successfully recovering An elements up to 10 wt% in the Cd cathode, surpassing the solubility of An elements in liquid Cd at the experimental temperature of 773 K. This high recovery rate was significant as it exceeded the known solubility limits, indicating a more efficient separation process. The study also revealed that in the saturated Cd cathode, An and REEs formed a $PuCd_{11}$ type compound, MCd_{11} (M = An and RE elements), and the separation factors of various elements against Pu were calculated for this composition.

In light of the summarized data, the most effective approach for the electrochemical REEs from NdFeB magnets would involve using Mo cathodes in combination with a fluorine-based molten salt electrolyte, specifically NdF_3-LiF or NdF_3-PrF_3-LiF melts. This combination has demonstrated superior performance in the selective recovery of Nd and Pr, evidenced by high deposition rates and the purity of the recovered metals. The pretreatment and purification process that yielded the best results involved dissolving the magnet scrap to form the oxide material, followed by its dissolution in

the chosen fluorine melts. This method ensures a high recovery rate of REEs with minimal impurities, as indicated by the high percentage of Nd and Pr recovered during the process. The use of molybdenum cathodes is pivotal due to its high melting point and the ability to provide a suitable substrate for the electrodeposition of REEs, as demonstrated in the electrorefining process. This approach not only enhances the efficiency of the recovery process but also contributes to the sustainability and cost-effectiveness of recycling rare earth elements from electronic waste.

Pretreatment Methods

Pretreatment steps are crucial prior to electrochemical processing to liberate the REE-rich phases from the magnet matrix and concentrate them in a form amenable to dissolution and recovery. Common pretreatment methods utilize thermal, mechanical, and/or chemical processes.

Thermal demagnetization involves heating the magnets above their Curie temperature of 312°C to remove the hard magnetic properties. This makes the materials brittle and easier to mechanically crush. Partial roasting at 500-1000°C in air can selectively oxidize the rare earth phases for subsequent leaching while keeping iron unoxidized. However, uncontrolled oxidation results in REE losses. Mild hydrogen decrepitation at 600-800°C causes embrittlement and fracturing as hydrogen is absorbed but avoids oxidation. For a typical demagnetization process [38], the magnets are heated to 150°C for 2 hours in a muffle furnace, followed by rapid water quenching and cooling. This heating and quenching helps demagnetize the magnets by randomizing the magnetic domains. Residual magnetism can interfere with the electrolysis, so removing it is an important first step. Next, the demagnetized magnets undergo additional circulating operations, repeating the heating and cooling cycle 2-4 times. This further eliminates any remaining traces of magnetism. In another work [40], to transform the REE in the spent magnets into a form suitable for molten salt electrolysis, the magnets underwent an extensive pretreatment process. First, the magnets were oxidized in air at an elevated temperature of 1000°C for 3 hours. This oxidation roast converted the REE alloys in the magnets into mixed rare earth oxides. Next, the oxidized material underwent smelting via carbothermic reduction in an argon atmosphere at low pressure. This reduction smelting step used a carbon crucible to remove substantial iron content from the oxidized magnets. The result was a magnet recycling-derived oxide powder enriched in rare earth oxides like Nd and Pr oxides. Specifically, the magnet recycling-derived oxide contained approximately 33 wt% Nd and 10 wt% Pr oxides, increasing the concentration from the original magnet composition. These sequential oxidation and smelting pretreatments were crucial to transform the solid metal alloy magnets into a composition of rare earth oxides dissolved in the molten salt suitable for efficient electrolytic recovery of Nd and Pr. The magnet recycling-derived oxide enabled selective electrodeposition of purified Nd and Pr metals on the cathode during the later

electrolysis.

Mechanical size reduction by crushing, grinding, and milling is universally employed as the simplest approach to liberate the ~5-20 μm REE-rich grains. However, excessive mechanical processing can lead to oxidation losses. Coarse grinding to 0.3-3 mm is suitable to enable leachant penetration while minimizing surface area for oxidation. Cryomilling at liquid nitrogen temperatures can make materials very brittle for size reduction. Magnetic separation after mechanical treatment can remove some iron.

After pretreatment size reduction, chemical leaching steps are employed to dissolve the REEs into aqueous solutions or concentrates for electrorefining. Inorganic acids like H_2SO_4, HCl, and HNO_3 effectively dissolve REEs but co-dissolve significant amounts of Fe and Co. For example, the magnet waste can be first partially leached with a 3.5 M HCl [45]. This partial leaching step selectively extracts around 20-30% of the metals present in the magnet waste, including 20-30% of the REEs along with 20-30% of the iron. Importantly, 98% of the iron extracted into the leachate is in the Fe(II) oxidation state. The advantage of this partial leaching is that it avoids the need for complete acid dissolution of the entire magnet waste, which would consume large amounts of acid. For example, complete acid dissolution of industrial magnet waste requires around 15 M HCl of REEs, whereas this partial leaching requires less than 4 M HCl of REEs. The partial leaching is also relatively fast, being complete within 60 minutes. Following this partial leaching step, the Fe(II) present in the leachate can then be selectively oxidized to Fe(III) and precipitated, while leaving the REEs in solution. This allows selective separation of the REEs from the major iron component of the magnet waste. Overall, the partial leaching step with HCl provides a more sustainable and selective initial dissolution of the magnet waste, avoiding excessive acid consumption and enabling subsequent oxidative precipitation of iron for REE purification.

Prakash et al. [32] theoretically explored various pretreatment methods as initial steps in the electrochemical recycling processes for NdFeB magnet waste. In the electro-oxidative approach, the magnet waste was first completely dissolved in HCl to extract all the metals into solution. This unselective dissolution simplified the subsequent selective electro-oxidation of Fe(II), but consumed excess acid. To avoid complete acid dissolution, a room temperature electrolysis pretreatment was developed using the magnet waste itself as an active anode and an inert titanium anode. This converted the metals in the magnet to hydroxides while oxidizing Fe(II), enabling selective acid leaching of REE later. Though more selective, this electrolysis pretreatment required higher energy consumption. In the two-chamber membrane reactor process, the pretreatment consisted of a partial acid leach using just enough HCl to dissolve the REEs. This minimized acid consumption but still extracted some Fe(II). For the three-chamber reactor, no acid pretreatment was used at all. Instead, the magnet waste was directly treated in the electrochemical system. The pretreatments became progressively more selective and sustainable from full dissolution, to electrolysis, to partial leaching, to a completely integrated electrochemical process avoiding separate steps. The

tradeoffs were in complexity, kinetics, energy, and waste. Full dissolution simplified selective oxidation but required excess acid. Electrolysis avoided acid but had higher energy needs. Partial leaching reduced acid consumption but co-extracted iron. The integrated reactor eliminated pretreatment altogether while efficiently extracting REEs. The progression indicates the author's aim of developing an optimal methodology balancing targets like selectivity, waste reduction, energy use, and process intensity. While effective REE extraction was demonstrated with each method, the ultimate goal was a selective, closed-loop, room temperature process integrated into a single electrochemical reactor, avoiding pretreatments. The exploration of different pretreatment strategies reflects both the complexity of NdFeB recycling and the author's systematic efforts to address these challenges.

The ideal approach for the electrochemical recovery of REEs from magnet waste would involve a combination of optimized pretreatment and purification methodologies. For the electrolyte, a molten salt system appears most suitable, given its efficacy in dissolving the transformed rare earth oxides. As for the electrode, a robust material capable of withstanding the harsh conditions of molten salt electrolysis, such as titanium or graphite, could be proposed. Among the pretreatment methods, the combination of mild hydrogen decrepitation and controlled partial roasting offers an effective balance between REE liberation and minimal loss due to oxidation. The subsequent purification step could optimally involve a partial leaching process with HCl, which selectively extracts a significant percentage of REEs while enabling the oxidative precipitation of iron, thus providing a more concentrated and purified REE solution for the electrochemical process. This integrated approach, involving selective thermal treatment, controlled leaching, and suitable electrochemical setup, is projected to yield the most efficient and sustainable recovery of REEs.

Product Purification and Separation

After electrochemical extraction and recovery processes, additional separation and purification steps are required to isolate high purity individual rare earth elements and oxides. The electrochemical approaches yield REE concentrates or alloys containing mixtures of light rare earths (LREEs) like Nd and Pr as well as heavy rare earths (HREEs) like Dy and Tb.

Solvent extraction involves mixing the REE solution with an immiscible organic phase containing chelating extractants that preferentially complex certain REEs. The Nd^{3+} was separated from Fe^{2+} in the electrolyte using solvent extraction with P507 extractant [38]. Two stages of cross-current extraction achieved >99% extraction of Nd into the organic phase. The P350-N235 synergistic extraction system is a novel solvent extraction approach that uses a mixture of two extractants - P350 (di-(1-methyl-heptyl) methyl phosphonate) and N235 (a tertiary amine) - to efficiently recover Nd from

aqueous nitric acid solutions [46]. This system was developed to overcome issues with conventional saponified solvent extraction systems that produce wastewater. The P350 extractant provides the main extraction capability, while N235 enhances the extraction through synergistic interaction with P350. When mixed at an optimal ratio of 0.3 molar fraction P350, the system achieved near complete ~100% Nd extraction, with a 60-fold enhancement over extraction by P350 alone. The extraction was fast, reaching equilibrium within 3 minutes, and worked across a wide pH range. Addition of a salting agent further improved extraction efficiency to 98.76%. The system selectively extracted Nd over other rare earths present in typical leach solutions from NdFeB magnet waste. The extraction was exothermic and thermodynamically favorable. Kinetic studies showed the rate-limiting step was chemical reactions at the extractant-metal interface. After stripping with oxalate, the extractant system maintained high 96.96% extraction efficiency over 5 cycles.

Selective precipitation with oxalic acid has been extensively investigated to directly produce REE oxalates of high purity from electrorefining solutions or leachates [47]. This simplifies separation but high purity oxalic acid is required. Thermal treatment converts the oxalates to oxides. Leaching experiments showed sulfuric acid effectively dissolves the REEs, and addition of oxalic acid improved selectivity by forming insoluble REE-oxalate precipitates [48]. The precipitates contained mainly Nd, Pr and Ce oxalates. Electrochemical leaching increased leaching rate 3-5 times compared to chemical leaching alone. Applied current density and acid concentration strongly affected dissolution rate and energy consumption. The proposed leaching mechanism involves preferential dissolution of Nd-rich phases, leaving the iron-rich matrix intact. Overall, the study demonstrated efficient REE recovery from magnet waste is possible using electrochemically-assisted leaching with oxalic acid to form REE-oxalate precipitates. In another work [49], the magnets were dissolved using sulfuric acid and oxalic acid electrolyte solution. Under optimized conditions, the rare earth elements selectively precipitated as positively charged oxalate particles on the cathode, while iron remained in solution. After 2 hours of electrolysis, the REE purity in the cathode deposit reached 86-88%, with a yield around 60%. The process only requires demagnetization, etching, and electro-leaching steps to recover high purity REEs. Key factors enabling REE deposition on the cathode were the low solubility of REE oxalates and electrostatic attraction of the positively charged particles.

Prakash [32] investigated several approaches to obtain purified REE products from the recycling processes. A key purification step was precipitating REE selectively over iron using oxalic acid, taking advantage of the large difference in solubility between rare earth and iron oxalates. Oxalic acid precipitation was used in the electro-oxidative approach and dual anode electrolysis pretreatment to recover REE from solution as oxalates. The REE oxalates were then calcined to obtain high purity REE oxides. An alternative strategy explored was removing iron by increasing the pH to precipitate iron hydroxides, leaving REE in solution. Ammonia neutralization was used in the electro-oxidative method and membrane reactor process for iron removal. The iron-free

solution still contained cobalt, which could be separated by electrowinning to recover metallic cobalt. After iron removal, REE were again precipitated with oxalic acid and calcined to oxides. To avoid using oxalic acid and calcination, the three-chamber membrane reactor demonstrated direct electroseparation of REE from nitrates to hydroxides at the cathode. The REE hydroxides were purified by removing co-precipitated iron hydroxides at a higher pH. This elegantly avoided oxalic acid, calcination, and associated carbon emissions. The products were ultimately REE oxides or metallic cobalt of high purity. The separation steps evolved from chemical precipitation to electroseparation, reducing waste and chemicals.

A comprehensive conclusion can be drawn regarding the most effective electrolyte, electrode, and pretreatment and purification methodologies for the electrochemical recovery of REEs. For electrolyte selection, the use of aqueous nitric acid solutions has shown significant promise, especially when combined with advanced solvent extraction techniques like the P350-N235 synergistic system. This combination not only enhances extraction efficiency but also offers environmental benefits by reducing wastewater production. The choice of electrode material, while not explicitly detailed, should ideally be one that facilitates efficient electrochemical reactions without corroding or degrading in the chosen electrolyte. As for pretreatment and purification, the method combining solvent extraction with selective precipitation using oxalic acid stands out. This approach not only ensures high purity of the recovered REEs, particularly Nd, but also allows for a more controlled and efficient separation process. It also benefits from the additional step of thermal treatment of the oxalates to obtain oxides, further refining the purity of the final product. Thus, incorporating these methodologies could potentially lead to more effective and environmentally sustainable recovery of REEs from various sources.

Conclusions

The review of electrochemical processes for the recovery of REEs from NdFeB magnets has identified several promising approaches, informed by a synthesis of current literature. This revised conclusion incorporates insights from the newly added table, which encapsulates critical parameters such as resource sources, pretreatments, electrolytes, electrodes, purification methods, and results.

Optimal Electrolyte and Electrode Selection: Based on the summarized data, the most effective electrolytes for REE recovery are aqueous solutions, molten salt electrolytes, and ionic liquids, each suited to different processing conditions. For electrodes, materials like titanium, molybdenum, and stainless steel have emerged as preferred choices due to their efficacy in REE deposition and minimal co-reduction of other metals.

Effective Pretreatment and Purification Methodologies: The review highlights that a combination of mechanical and chemical pretreatment methods, such as thermal demagnetization, mechanical size reduction, and selective acid leaching, effectively liberates and concentrates REEs. In terms of purification, techniques like solvent extraction and selective precipitation with oxalic acid are identified as the most efficient in producing high-purity REE oxides and metals.

Future Directions and Challenges: The future of electrochemical REE recovery lies in further optimizing these processes for efficiency, selectivity, and environmental sustainability. The integration of these processes into existing recycling infrastructure, minimizing energy usage, and the development of closed-loop operations remain key areas for ongoing research and development.

In conclusion, the electrochemical recycling of NdFeB magnets for REE recovery is a rapidly evolving field with significant potential for sustainable resource management. The outlined methodologies and identified best practices provide a roadmap for future advancements in this domain, aiming to mitigate supply risks and contribute to a circular economy for critical materials.

Competing interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Author Contributions

Conceptualization, L.F. and H.K-M.; writing—original draft preparation, L.F.; writing—review and editing, H.K-M.; project administration, L.F. All authors have read and agreed to the published version of the manuscript.

Data availability

Data sharing not applicable – no new data generated.

Reference

[1] V. Balaram, Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact, Geosci. Front. 10 (2019) 1285–1303. https://doi.org/10.1016/j.gsf.2018.12.005.

[2] T. Liu, J. Chen, Extraction and separation of heavy rare earth elements: A review, Sep. Purif. Technol. 276 (2021) 119263. https://doi.org/10.1016/j.seppur.2021.119263.

[3] R.K. Jyothi, T. Thenepalli, J.W. Ahn, P.K. Parhi, K.W. Chung, J.-Y. Lee, Review of rare earth elements recovery from secondary resources for clean energy technologies: Grand opportunities to create wealth from waste, J. Clean. Prod. 267 (2020) 122048. https://doi.org/10.1016/j.jclepro.2020.122048.

[4] N.A. Chowdhury, S. Deng, H. Jin, D. Prodius, J.W. Sutherland, I.C. Nlebedim, Sustainable Recycling of Rare-Earth Elements from NdFeB Magnet Swarf: Techno-Economic and Environmental Perspectives, ACS Sustain. Chem. Eng. 9 (2021) 15915–15924. https://doi.org/10.1021/acssuschemeng.1c05965.

[5] P.K. Sarswat, M. Leake, L. Allen, M.L. Free, X. Hu, D. Kim, A. Noble, G.H. Luttrell, Efficient recovery of rare earth elements from coal based resources: a bioleaching approach, Mater. Today Chem. 16 (2020) 100246. https://doi.org/10.1016/j.mtchem.2020.100246.

[6] W. Zhang, A. Noble, X. Yang, R. Honaker, A Comprehensive Review of Rare Earth Elements Recovery from Coal-Related Materials, Minerals. 10 (2020) 451. https://doi.org/10.3390/min10050451.

[7] A. Amato, A. Becci, I. Birloaga, I. De Michelis, F. Ferella, V. Innocenzi, N.M. Ippolito, C. Pillar Jimenez Gomez, F. Vegliò, F. Beolchini, Sustainability analysis of innovative technologies for the rare earth elements recovery, Renew. Sustain. Energy Rev. 106 (2019) 41–53. https://doi.org/10.1016/j.rser.2019.02.029.

[8] A. Rybak, A. Rybak, Characteristics of Some Selected Methods of Rare Earth Elements Recovery from Coal Fly Ashes, Metals. 11 (2021) 142. https://doi.org/10.3390/met11010142.

[9] S. Pavón, A. Fortuny, M.T. Coll, A.M. Sastre, Improved rare earth elements recovery from fluorescent lamp wastes applying supported liquid membranes to the leaching solutions, Sep. Purif. Technol. 224 (2019) 332–339. https://doi.org/10.1016/j.seppur.2019.05.015.

[10] A.T. Brown, K.J.Jr. Balkus, Critical Rare Earth Element Recovery from Coal Ash Using Microsphere Flower Carbon, ACS Appl. Mater. Interfaces. 13 (2021) 48492–48499. https://doi.org/10.1021/acsami.1c09298.

[11] J.P. Laurino, J. Mustacato, Z.J. Huba, Rare Earth Element Recovery from Acidic Extracts of Florida Phosphate Mining Materials Using Chelating Polymer 1-Octadecene, Polymer with 2,5-Furandione, Sodium Salt, Minerals. 9 (2019) 477. https://doi.org/10.3390/min9080477.

[12] K. Zhang, E. Fan, J. He, X. Li, Y. Huang, Long-term effects of electrochemical corrosion on magnetic properties of sintered NdFeB magnets, J. Magn. Magn. Mater. 538 (2021) 168309. https://doi.org/10.1016/j.jmmm.2021.168309.

[13] X. Li, J. Ni, Z. Wang, J. Li, Y. Xu, S. Zhou, K. Xu, X. Hao, C. Hu, X. Na, L. Luo, Electrochemical corrosion behavior of hot-deformed NdFeB magnet with

different content of nano-TiC, J. Alloys Compd. 917 (2022) 165518. https://doi.org/10.1016/j.jallcom.2022.165518.

[14] Q. Zhou, S. Liu, Fabrication of Magnesium Phosphate Coating by Electrochemical Cathodic Method for Corrosion Protection of Sintered NdFeB Magnets, J. Mater. Eng. Perform. 30 (2021) 1200–1206. https://doi.org/10.1007/s11665-020-05421-5.

[15] K. Zhang, Z. Wang, J. He, X. Li, W. Gong, Y. Huang, Coupling effects of hydrogen and Dy/Nb on magnetic properties of sintered NdFeB magnets, Int. J. Hydrog. Energy. 47 (2022) 14027–14038. https://doi.org/10.1016/j.ijhydene.2022.02.154.

[16] X. Su, Electrochemical separations for metal recycling, Electrochem. Soc. Interface. 29 (2020) 55.

[17] A.V. Oladeji, J.M. Courtney, N.V. Rees, Copper deposition on metallic and non-metallic single particles via impact electrochemistry, Electrochimica Acta. 405 (2022) 139838. https://doi.org/10.1016/j.electacta.2022.139838.

[18] E. Uysal, S. Al, E. Emil-Kaya, S. Stopic, S. Gürmen, B. Friedrich, Hydrometallurgical recycling of waste NdFeB magnets: design of experiment, optimisation of low concentrations of sulphuric acid leaching and process analysis, Can. Metall. Q. 62 (2023) 107–118. https://doi.org/10.1080/00084433.2022.2058152.

[19] M. Chandra, D. Yu, Q. Tian, X. Guo, Recovery of Cobalt from Secondary Resources: A Comprehensive Review, Miner. Process. Extr. Metall. Rev. 43 (2022) 679–700. https://doi.org/10.1080/08827508.2021.1916927.

[20] J. Porcayo-Calderon, J.J. Ramos-Hernandez, E. Porcayo-Palafox, L.M. Martínez de la Escalera, J. Canto, J.G. Gonzalez-Rodriguez, L. Martinez-Gomez, Sustainable Development of Corrosion Inhibitors from Electronic Scrap: Synthesis and Electrochemical Performance, Adv. Mater. Sci. Eng. 2019 (2019) e6753658. https://doi.org/10.1155/2019/6753658.

[21] O. Dudarko, N. Kobylinska, V. Kessler, G. Seisenbaeva, Recovery of rare earth elements from NdFeB magnet by mono- and bifunctional mesoporous silica: Waste recycling strategies and perspectives, Hydrometallurgy. 210 (2022) 105855. https://doi.org/10.1016/j.hydromet.2022.105855.

[22] M. Case, R. Fox, D. Baek, C. Wai, Extraction of Rare Earth Elements from Chloride Media with Tetrabutyl Diglycolamide in 1-Octanol Modified Carbon Dioxide, Metals. 9 (2019) 429. https://doi.org/10.3390/met9040429.

[23] Y. Jeon, J. Hur, G.Y. Jeong, S. Sohn, J. Park, Selective and efficient extraction of Nd from NdFeB magnets via ionization in LiCl-KCl-CdCl$_2$ melt, J. Alloys Compd. 860 (2021) 158424. https://doi.org/10.1016/j.jallcom.2020.158424.

[24] Y. Yang, C. Lan, L. Guo, Z. An, Z. Zhao, B. Li, Recovery of rare-earth element from rare-earth permanent magnet waste by electro-refining in molten fluorides, Sep. Purif. Technol. 233 (2020) 116030. https://doi.org/10.1016/j.seppur.2019.116030.

[25] P. Venkatesan, T. Vander Hoogerstraete, K. Binnemans, Z. Sun, J. Sietsma, Y. Yang, Selective Extraction of Rare-Earth Elements from NdFeB Magnets by a Room-Temperature Electrolysis Pretreatment Step, ACS Sustain. Chem. Eng. 6 (2018)

9375–9382. https://doi.org/10.1021/acssuschemeng.8b01707.

[26] A. Abbasalizadeh, A. Malfliet, S. Seetharaman, J. Sietsma, Y. Yang, Electrochemical Recovery of Rare Earth Elements from Magnets: Conversion of Rare Earth Based Metals into Rare Earth Fluorides in Molten Salts, Mater. Trans. 58 (2017) 400–405. https://doi.org/10.2320/matertrans.MK201617.

[27] X. Xu, S. Sturm, J. Zavasnik, K.Z. Rozman, Electrodeposition of a Rare-Earth Iron Alloy from an Ionic-Liquid Electrolyte, ChemElectroChem. 6 (2019) 2860–2869. https://doi.org/10.1002/celc.201900286.

[28] X. Xu, S. Sturm, Z. Samardzija, J. Vidmar, J. Scancar, K.Z. Rozman, Direct Recycling of Nd–Fe–B Magnets Based on the Recovery of $Nd_2Fe_{14}B$ Grains by Acid-free Electrochemical Etching, ChemSusChem. 12 (2019) 4754–4758. https://doi.org/10.1002/cssc.201902342.

[29] E.B. Molodkina, M.R. Ehrenburg, I.A. Arkhipushkin, A.V. Rudnev, Interfacial effects in the electro(co)deposition of Nd, Fe, and Nd-Fe from an ionic liquid with controlled amount of water, Electrochimica Acta. 398 (2021) 139342. https://doi.org/10.1016/j.electacta.2021.139342.

[30] F. Xiao, W. Hu, J. Zhao, H. Zhu, Technologies of Recycling REEs and Iron from NdFeB Scrap, Metals. 13 (2023) 779. https://doi.org/10.3390/met13040779.

[31] R. Al-Salman, M. Al Zoubi, F. Endres, Evidence for an influence of anodic decomposition products of ionic liquids on the electrodeposition of $SixGe_{1-x}$ semiconductor, J. Mol. Liq. 160 (2011) 114–118.

[32] V. Prakash, Z.H.I. Sun, J. Sietsma, Y. Yang, Chapter 22 - Simultaneous Electrochemical Recovery of Rare Earth Elements and Iron from Magnet Scrap: A Theoretical Analysis, in: I. Borges De Lima, W. Leal Filho (Eds.), Rare Earths Ind., Elsevier, Boston, 2016: pp. 335–346. https://doi.org/10.1016/B978-0-12-802328-0.00022-X.

[33] D. Dupont, K. Binnemans, Recycling of rare earths from NdFeB magnets using a combined leaching/extraction system based on the acidity and thermomorphism of the ionic liquid [Hbet][Tf2N], Green Chem. 17 (2015) 2150–2163. https://doi.org/10.1039/C5GC00155B.

[34] Y.W. Song, H. Zhang, H.X. Yang, Z.L. Song, A comparative study on the corrosion behavior of NdFeB magnets in different electrolyte solutions, Mater. Corros. 59 (2008) 794–801. https://doi.org/10.1002/maco.200804175.

[35] J. Zheng, L. Jiang, Q. Chen, Electrochemical Corrosion Behavior of Nd-Fe-B Sintered Magnets in Different Acid Solutions, J. Rare Earths. 24 (2006) 218–222. https://doi.org/10.1016/S1002-0721(06)60097-5.

[36] V.S. Cvetković, D. Feldhaus, N.M. Vukićević, K. Milicevic-Neumann, T.S. Barudžija, B. Friedrich, J.N. Jovićević, Influence of Rare Earth Oxide Concentration on Electrochemical Co-Deposition of Nd and Pr from NdF_3-PrF_3-LiF Based Melts, Metals. 12 (2022) 1204. https://doi.org/10.3390/met12071204.

[37] V.S. Cvetković, D. Feldhaus, N.M. Vukićević, T.S. Barudžija, B. Friedrich, J.N. Jovićević, Investigation on the Electrochemical Behaviour and Deposition Mechanism of Neodymium in NdF_3–LiF–Nd_2O_3 Melt on Mo Electrode, Metals. 10 (2020) 576. https://doi.org/10.3390/met10050576.

[38] W. Hu, F. Xiao, D. Wang, J. Zhao, J. Wang, H. Zhu, Recovery of Neodymium and Iron from Spent Ndfeb by Combined Electrochemical-Hydrometallurgical Process, (2023). https://doi.org/10.2139/ssrn.4326277.

[39] R. Schulze, A. Abbasalizadeh, W. Bulach, L. Schebek, M. Buchert, An Ex-ante LCA Study of Rare Earth Extraction from NdFeB Magnet Scrap Using Molten Salt Electrolysis, J. Sustain. Metall. 4 (2018) 493–505. https://doi.org/10.1007/s40831-018-0198-9.

[40] H. Chung, L. Prasakti, S.R. Stopic, D. Feldhaus, V.S. Cvetković, B. Friedrich, Recovery of Rare Earth Elements from Spent NdFeB Magnets: Metal Extraction by Molten Salt Electrolysis (Third Part), Metals. 13 (2023) 559. https://doi.org/10.3390/met13030559.

[41] P. Venkatesan, Electrochemical recycling of rare earth elements from NdFeB magnet waste, Delft Univ. Technol. Institutional Repos. (2019).

[42] A. Abbasalizadeh, L. Teng, S. Seetharaman, J. Sietsma, Y. Yang, Chapter 24 - Rare Earth Extraction from NdFeB Magnets and Rare Earth Oxides Using Aluminum Chloride/Fluoride Molten Salts, in: I. Borges De Lima, W. Leal Filho (Eds.), Rare Earths Ind., Elsevier, Boston, 2016: pp. 357–373. https://doi.org/10.1016/B978-0-12-802328-0.00024-3.

[43] Y. Jeon, G.Y. Jeong, J. Hur, J. Park, Experimental Design for Recovery of Nd from NdFeB Magnet by using Molten Salt Technique and Liquid Cd Cathode, in: Jeju, 2019: pp. 23–24.

[44] T. Kato, T. Inoue, T. Iwai, Y. Arai, Separation behaviors of actinides from rare-earths in molten salt electrorefining using saturated liquid cadmium cathode, J. Nucl. Mater. 357 (2006) 105–114. https://doi.org/10.1016/j.jnucmat.2006.06.003.

[45] P. Venkatesan, T.V. Hoogerstraete, T. Hennebel, K. Binnemans, J. Sietsma, Y. Yang, Selective electrochemical extraction of REEs from NdFeB magnet waste at room temperature, Green Chem. 20 (2018) 1065–1073. https://doi.org/10.1039/C7GC03296J.

[46] R. Wu, R. Liu, X. Liu, J. Zhang, W. Xue, Y. Yang, P350-N235 synergistic extraction system used for the recovery of Nd(III) from waste NdFeB magnets, Sep. Purif. Technol. 319 (2023) 124042. https://doi.org/10.1016/j.seppur.2023.124042.

[47] P. Venkatesan, Z.H.I. Sun, J. Sietsma, Y. Yang, An environmentally friendly electro-oxidative approach to recover valuable elements from NdFeB magnet waste, Sep. Purif. Technol. 191 (2018) 384–391. https://doi.org/10.1016/j.seppur.2017.09.053.

[48] I. Makarova, E. Soboleva, M. Osipenko, I. Kurilo, M. Laatikainen, E. Repo, Electrochemical leaching of rare-earth elements from spent NdFeB magnets, Hydrometallurgy. 192 (2020) 105264. https://doi.org/10.1016/j.hydromet.2020.105264.

[49] I. Makarova, J. Ryl, Z. Sun, I. Kurilo, K. Górnicka, M. Laatikainen, E. Repo, One-step recovery of REE oxalates in electro-leaching of spent NdFeB magnets, Sep. Purif. Technol. 251 (2020) 117362. https://doi.org/10.1016/j.seppur.2020.117362.
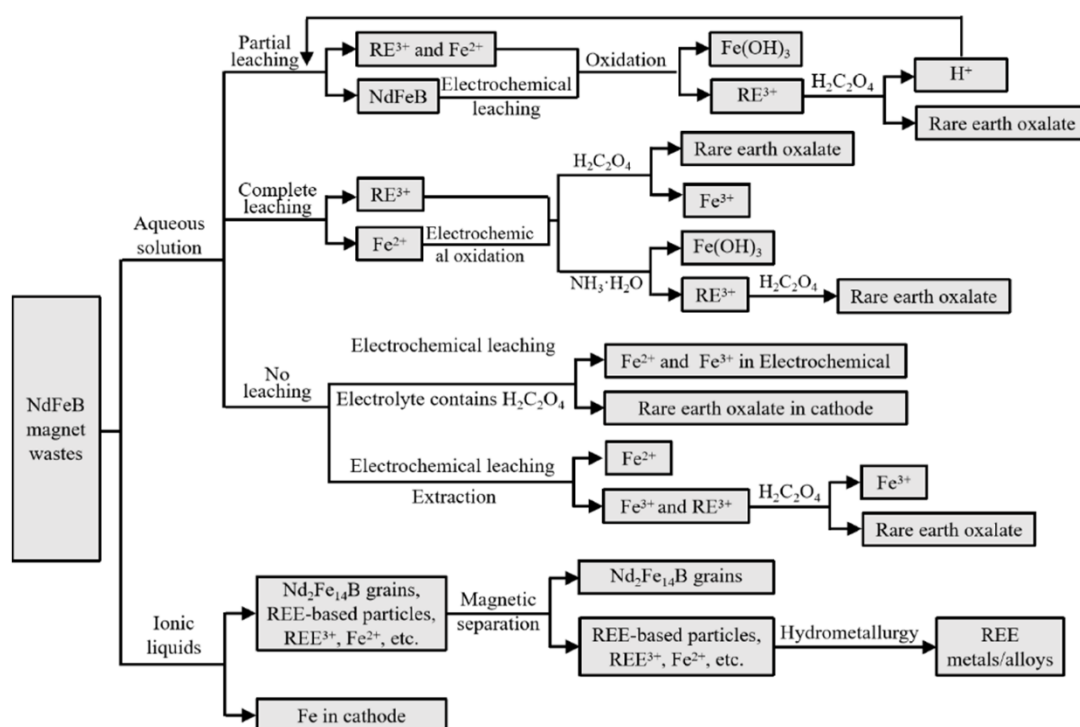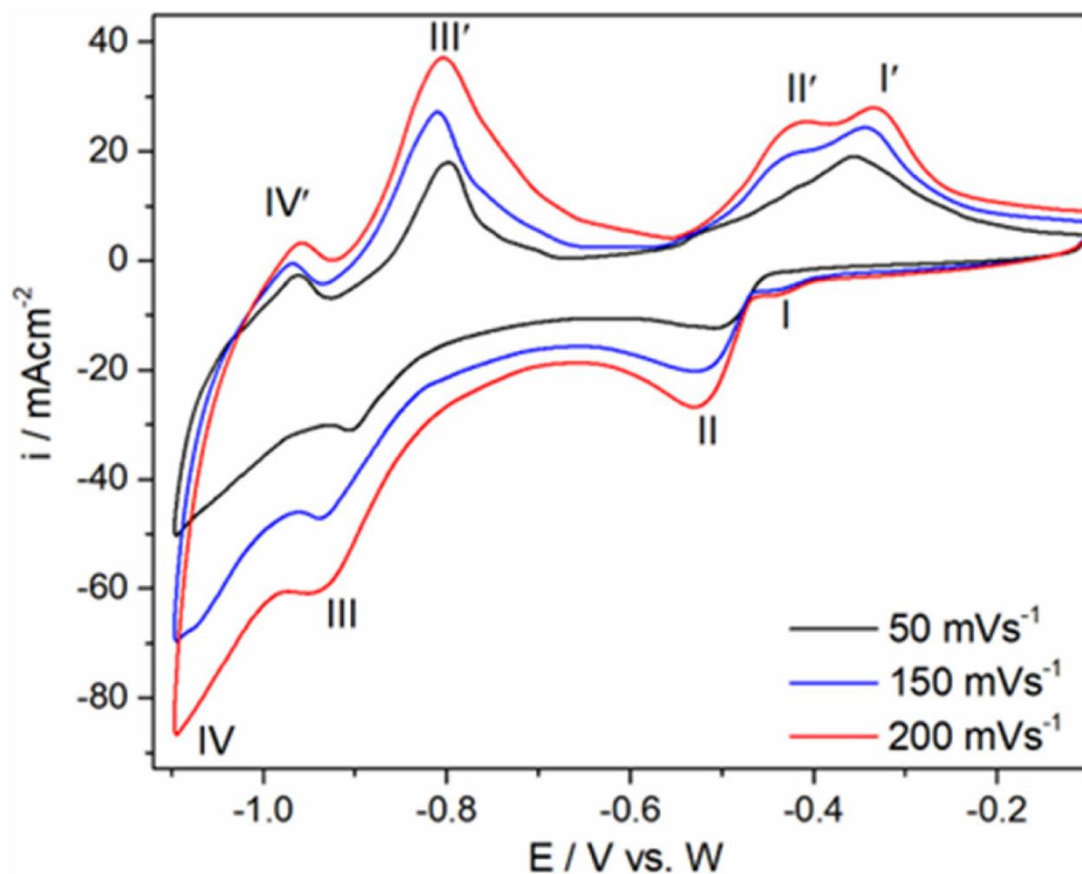
Figure 1. Flow chart of typical techniques for the electrochemistry of NdFeB magnet [30].
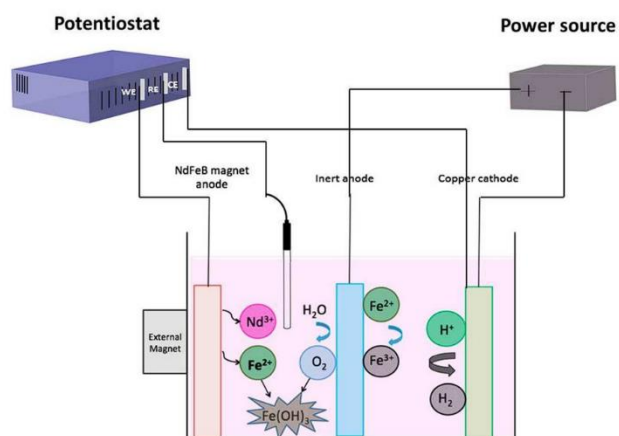
Figure 2. Schematic representation of dual anode electrolysis reactor to recycle NdFeB magnet waste [25].

Figure 3. CVs recorded on W working electrode in $NdF_3 + PrF_3 + LiF$ electrolyte with initial potential $(E_i) = -0.100$ V to cathodic end potential $(E_c) = -1.100$ V vs. W obtained with different sweep rates at 1050 °C [36].
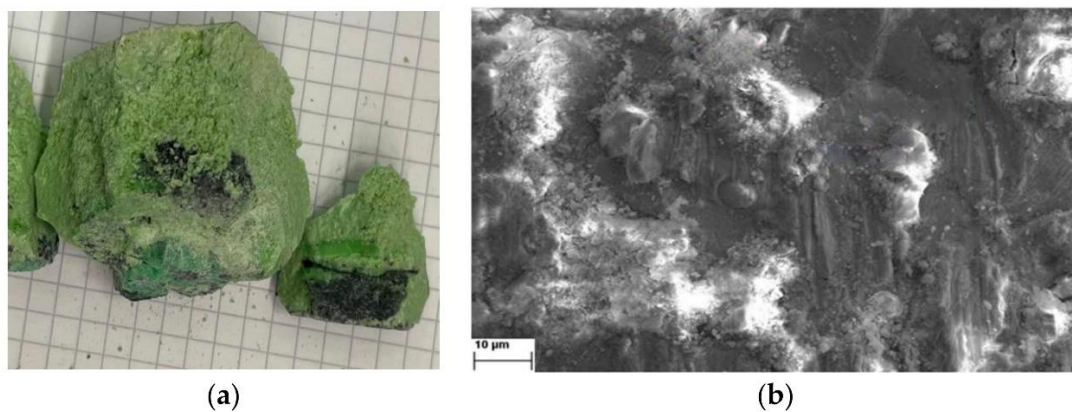
Figure 4. Post-experimental observation of the (a) electrolyte and (b) SEM image of the working electrode [40].

Table 1. Comparative summary of electrochemical processes for REE recovery from NdFeB magnets.

Study Reference	Method	Temperature	Electrolyte	Anode Material	Cathode Material	Key Findings
Jeon et al. [23]	Selective Ionization in Molten Salt	773K	LiCl-KCl with CdCl$_2$	NdFeB Magnet	Tungsten (W) and Silver (Ag/AgCl)	Over 99% Nd extraction within 2 hours; natural fragmentation and pulverization of magnets; effective online monitoring of reaction progress.
Yang et al. [24]	Electro-refining in molten fluorides	1123K	LiF-CaF$_2$	REPM Waste (Rare Earth Permanent Magnet Waste)	Platinum and Tungsten Wires	Nd and Pr were selectively dissolved into the molten LiF-CaF2 salts and directly prepared as rare-earth metals at the cathode, leaving a porous Fe$_2$B alloy and metallic Fe.
Venkatesan et al. [25]	Room-Temperature Electrolysis	Room Temperature	Not Specified	NdFeB Magnet	Inert Anode	Over 97% of REEs and cobalt leached.
Abbasalizadeh et al. [26]	Molten Salt Fluorination and Electrolysis	1223 K	LiF-NdFeB system with AlF3, ZnF$_2$, FeF$_3$, Na$_3$AlF$_6$	NdFeB Magnet	Not specified	Complete extraction of Nd (and Dy) from NdFeB magnets; formation of rare earth fluorides.

Xu et al. [27]	Electrodeposition from Ionic Liquid	383K (110°C)	1-Ethyl-3-methylimidizolium dicyanamide ([EMIM][DCA])	Not specified	Copper (Cu)	Successful electrodeposition of Nd–Fe from [EMIM][DCA] at mild temperatures. NdIII cannot be independently reduced but can be co-deposited with FeII. The process aligns with the transition-state theory, indicating an activated state of Fe catalyzes the reduction of NdIII to Nd0. This provides a sustainable and green approach for rare-earth recycling and thin film production.
Xu et al. [28]	Electrochemical Etching	Room Temperature	DMF/0.3 M $FeCl_2$	Sintered Nd–Fe–B Magnet	Pt Wire	Successful selective extraction of $Nd_2Fe_{14}B$ grains; estimated energy consumption of 2.99 kWh/kg; supports circular economy with low energy footprint.
Molodkina et al. [29]	Electrochemical Deposition	Room Temperature	[BMP][DCA] Ionic Liquid with controlled water content	Not specified	Pt(111) Single Crystal	Nd, Fe, and Nd-Fe electrodeposition can be realized in a dicyanamide IL. Water addition promotes Nd and Fe electrodeposition in single-component IL solutions but significantly decelerates Nd-Fe

						codeposition. The deceleration is attributed to the formation of surface Nd(III) oxides/hydroxides.