Electrodeposition of a Rare-Earth Iron Alloy from an Ionic-Liquid Electrolyte

Xuan Xu,[a, b] Saso Sturm,[a, b] Janez Zavasnik,[a, b] and Kristina Z. Rozman[a, b]

Rare earth element (REE)-based metals and alloys are generally synthesized by molten-salt electrolysis which is an energy-intensive approach. Previous attempts to deposit alloys of rare earths from solutions at mild temperatures have met with little success. Excitingly, in this investigation we were able to electrodeposit Nd–Fe from the 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]) ionic liquid (IL) at 110 °C. We observed that Nd³⁺ cannot be reduced independently, although it can be co-deposited inductively on a Cu substrate with the addition of Fe³⁺. The transmission electron microscopy (TEM) analysis combined with electron-energy-loss spectroscopy (EELS) verified that Nd³⁺ is reduced to Nd⁴⁺ during the electrodeposition process. The TEM/EELS was also able to confirm that the deposition of the Nd–Fe starts with the sole deposition of Fe, followed by the co-deposition of Nd–Fe. This is in agreement with transition-state theory, which has the iron initially reduced to an activated state (Fe⁷⁺), where it is able to catalyse the reduction of the rare earth from Nd⁴⁺ to Nd³⁺. This new insight into the electrodeposition process brings us a very important step closer to being able to recycle rare earths efficiently and even to realise electrodeposited rare-earth-based permanent-magnet thin films at a mild temperature, thus giving us a sustainable, green-chemistry approach that provides a genuine alternative to high-temperature molten-salt electrolysis.

1. Introduction

The rare earth elements (REEs) are vital components in permanent magnets, optical devices and catalytic convertors, making them critical to modern industry.[1] Neodymium, the primary REE for Nd–Fe–B permanent magnets, has seen tremendous price volatility and is one of the world's most critical raw materials, based on its availability and strategic importance.[2]2 As a result, recycling REE-containing magnets is an important route to guaranteeing access to this important resource.

Electrodeposition is an attractive process, as it possesses many advantages over other deposition technologies, e.g., less costly and easily maintained equipment, low energy and space requirements, and modest temperatures. The process also offers great flexibility, with the possibility to tailor properties to a specific application based on the composition of the solution and the operating conditions.[3] Therefore, the electrodeposition of REE-transition metal (TM) alloys can be considered as a green, sustainable and efficient approach to the recycling Nd–Fe–B permanent magnets. The conventional route for recycling Nd–Fe–B permanent magnets is a hydrometallurgical process that converts the magnets to REE oxides by the acid leaching, solvent extraction and a thermal treatment.[4] The obtained REE oxides are then conventionally reduced by molten-salt electrolysis at > 550 °C,[5] consuming great deal of energy to maintain the electrolytic bath in the liquid state, making it far from environmentally friendly. Therefore, being able to electrodeposit REE metals and REE-TM alloys at a mild temperature would mean we can dramatically reduce the environmental footprint for Nd–Fe–B magnets.

Neodymium has a reduction potential of −2.32 V vs. a standard hydrogen electrode (SHE),[6] making it very difficult to deposit in a metallic form. The electrodeposition of REEs and elements such as Fe, Ni or Co in the form of films from aqueous solutions has been reported.[7,8] However, the reduction potentials of REEs are so negative that the evolution of hydrogen is inevitable. This hydrogen then increases the pH of the solution, thereby favouring the formation of REE hydroxides and oxides.[9] However, this suggests that the electrodeposition of REEs from non-aqueous solvents might offer a promising alternative,[9] although it is recently reported that 0.4 wt.% of water in the electrolyte facilitate the deposition of Nd.[10] Indeed, there are literature reports about the electrodeposition of REE alloys using deep eutectic solvents (DESs) and organic solvents.[11] But here the organic chemicals are generally volatile, casting doubt on the environmental credentials of the process. Ionic liquids (ILs), with their high ionic conductivity, wide electrochemical window, lack of volatility and a very low vapour pressure, also look promising.[12] In fact, the electrodeposition of Nd using imidazolium and phosphonium-based ILs was reported,[13] but oxygen contents up to 50 at.% in the deposits make these materials of little practical value.

The origin of these Nd oxides formed during the electrodeposition (or after) is unresolved. To find an answer, it is necessary to determine the valence state of the Nd, i.e., Nd⁴⁺ or Nd³⁺ in the deposited materials. Although X-ray photo-

[a] X. Xu, Prof. Dr. S. Sturm, Dr. J. Zavasnik, Prof. Dr. K. Z. Rozman
Department for Nanostructured Materials
Jožef Stefan Institute
Jamova 39, SI-1000 Ljubljana, Slovenia
E-mail: xuan.xu@ijs.si
[b] X. Xu, Prof. Dr. S. Sturm, Dr. J. Zavasnik, Prof. Dr. K. Z. Rozman
Jožef Stefan International Postgraduate School
Jamova 39, SI-1000 Ljubljana, Slovenia
Supporting information for this article is available on the WWW under https://doi.org/10.1002/celc.201900286
electron spectroscopy (XPS) was used in these earlier studies,[10,14] the valence state of the Nd deposit was unclear. This is because the binding energies of metallic Nd (Nd⁰) and neodymium oxide (Nd₂O₃) are very close, i.e., 980.5–981.5 eV and 981.7–982.3 eV, respectively, making it almost impossible to differentiate between the two states.[15]

It is a fact that individual deposition of pure neodymium metal is extremely difficult due to its very negative reduction potential. However, Nd⁰, as well as many other rare-earth elements, can be deposited together with one or more metals from the TM group.[16] This electrodeposition phenomenon is called the “induced co-deposition”. The end-of-life Nd-Fe–B magnets, as an important secondary REEs resource, are generally recovered as REE–Fe alloys, REE oxides and REE chlorides/fluorides.[17] Electrochemical co-deposition of Nd–Fe alloys using a Nd-source (NdCl₃) made out of recycled Nd-Fe–B magnets would contribute to overcoming the REEs supply risk and contribute to a significant part in REEs circular economy loop. However, electrodeposition studies of Nd–Fe from ILs as well as the co-deposition mechanism are up to now scarce in the literature.

Understanding the mechanism for the co-deposition of neodymium and iron is critical if we are to successfully electrodeposit these elements. So far, a complete mechanism has not been reported. It was, however, found that in DESs, Nd⁰ cannot be reduced alone to metallic rare earth, but it can be inductively co-deposited with Fe⁰.[11a,20] These studies indicated that co-deposition is possible, using a potential that is much more positive than that for the individual deposition of REEs. However, an explanation for why REE⁰ could be reduced in the presence of Fe⁰ at a more positive potential was not presented in detail.

It is well known that some elements with negative electrochemical standard potentials cannot be electrodeposited in metallic form from aqueous solutions, but they can be co-deposited with transition metals (TMs), forming alloys.[18] For example, metallic tungsten cannot be deposited alone from an aqueous solution, but it does deposit in the presence of iron ions in solution, forming metallic alloys.[16] For Fe–W co-deposition, catalytic mechanisms induced by adsorbed species such as hydrogen (Hₐ) or the adsorbed TM (TMₐ) are proposed.[20] Here, we hypothesize that the mechanism for REE–TM co-deposition might be similar to that of TM–W co-deposition. Three possible co-deposition mechanisms have been proposed. A "catalytic reduction" theory was proposed by Holt and Vaaler[21] to explain the reduction of aqueous tungstate solutions in the presence of zero-valence TM elements (i.e., Ni, Co and Fe). In this process, the reduction of TM⁰ to TM⁰ occurs first; it then catalyses the tungsten deposition until the surface is covered with it, preventing any further tungsten deposition. This process continues until a new layer of the TM element forms. The observation of laminated structures was the basis for this concept by Younes and Gileadi,[22] although how the zero-valence state of an TM element catalyses tungsten deposition was not elaborated. Another mechanism, proposed by Clark and Lietzke,[18] emphasizes the role of hydrogen, where there is an initial deposition of a partially reduced tungstate film on the cathode, followed by the catalytic reduction of this film by hydrogen in the presence of freshly deposited iron, cobalt, or nickel. Without the inducing element, the tungstate ion is only partially reduced (WO₄²⁻ → WO₃),[24] and due to its low overpotential with respect to hydrogen evolution, it cannot be further reduced. The third mechanism is based on the formation of TM tungstate complexes that are precursors to tungsten alloys, as introduced by Younes-Metzler et al.[25] In this concept mixed-metal soluble complexes were used by adding a complexing regent of citrate[19a] or gluconate[26] as a prerequisite for the TM–W co-deposition. The latter two mechanisms rely on active hydrogen produced by the electrolysis of water and the formation of TM-tungstate coordination compounds with certain complexing regents that help to realize the co-deposition process.

In this study an induced co-deposition mechanism for REE–TM is proposed based on the transition-state theory, which assumes that the transition-state TM is the catalyst for the REE⁰ reduction to REE⁰. The electrodeposition of Nd–Fe involved the ionic-liquid-based electrolyte, 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]) as the electrolyte for the electrodeposition of the Nd and Fe. [EMIM][DCA] is an oxygen-free IL that exhibits a low viscosity (21 cP at 20 °C), which ensures a high mass-transfer efficiency and a high conductivity, both of which are beneficial for electrodeposition.[23] DCA-based ILs with a good coordination ability were already applied to REE metal electrodeposition,[28] as metal chlorides are found to dissolve well in the DCA-based ILs by forming complexed anions.[29] The electrochemical behaviours of the Nd⁰ and Fe⁰ were investigated, from which a co-deposition mechanism for REE–TM was proposed with a kinetic model. A detailed study using transmission electron microscopy (TEM) combined with electron-energy-loss spectroscopy (EELS) was performed in order to locally investigate the chemical composition of the deposit and the valence state of the deposited Nd. The proposed co-deposition mechanism proceeds via the transition state TM (TM⁺) that catalyses the reduction of REE⁰ to REE⁰.

2. Results and Discussion

2.1 Electrochemical Behaviour of Fe⁰ and Nd⁰ in [EMIM][DCA]

IL

Cyclic voltammetry (CV) was used to investigate the electrochemical behaviours of the Fe⁰ and Nd⁰ in [EMIM][DCA]. The black curve (curve 1) in Figure 1a shows the CV of the [EMIM][DCA] solution at a scan rate of 40 mVs⁻¹. The current starts to increase from −1.5 V vs. Pt and this can be attributed to the decomposition of the [EMIM]⁺ cation,[20] which indicates the cathodic limit potential of the [EMIM][DCA]. For this reason, the potential scan was stopped at −1.50 V in all the subsequent CVs. In the blue curve (curve 2) that represents the Nd⁰ solution, there is no significant current increase observed up to −1.50 V, which indicates that the Nd⁰ reduction is not induced on its own in this IL system, most probably due to the very negative reduction potential of Nd⁰.[6] It should be noted that the current
Figure 1. (a) CV of a Pt electrode in (1) [EMIM][DCA], (2) FeCl$_2$_{0.03 mol L$^{-1}$}-[EMIM][DCA], (3) NdCl$_2$ (0.1 mol L$^{-1}$)-[EMIM][DCA] and (4) FeCl$_2$ (0.03 mol L$^{-1}$)-NdCl$_2$ (0.1 mol L$^{-1}$) [EMIM][DCA], with scan rate from 10 – 100 mV s$^{-1}$ and c) Plot of $\nu^{1/2}$, 110 °C.

Increases from $-1.25$ V to $-1.50$ V in both curve 1 and curve 2 that is typically observed in the CV curves of the liquid electrolytes, called potential-dependent double layer charging current.$^{[31]}$ With the increasing potential, the charging current response of the double layer increases accordingly. The red curve (curve 3) and the green curve (curve 4) are the CVs of the FeCl$_2$-[EMIM][DCA] and FeCl$_2$-NdCl$_2$-[EMIM][DCA], respectively. The starting point for the Fe$^0$ reduction in curve 3 is $-1.19$ V, while the reduction peak (P$_{3b}$) appears at $-1.25$ V and the corresponding oxidation peak (P$_{3a}$) is present at $-0.60$ V. A small current shoulder appeared after P$_{3b}$ at around $-0.50$ V is observed. The similar reports could be found from other studies$^{[32]}$ which attributed the shoulder to a strong interaction, such as the desorption$^{[31]}$ of the Fe$^0$ complex on the electrode surface. In curve 4, the current increase that can be ascribed to the starting point for the Fe$^0$ and Nd$^{III}$ co-reduction is observed at $-1.25$ V, while the reduction peak (P$_{4a}$) appears at $-1.30$ V, with a much higher peak current, both of which are shifted negatively compared to curve 3. The reason for the more negative starting point for the Fe$^0$ and Nd$^{III}$ co-reduction (at $-1.20$ V) is probably due to the reduced coverage of Fe$^0$ on the cathode as a result of the addition of Nd$^{III}$, according to the Nernst equation$^{[33]}$ and the more negative reduction potential is due to the more negative reduction potential needed for the Nd$^{III}$. The peak current for Nd$^{III}$ and Fe$^0$ (6.5 mA cm$^{-2}$ at $-1.30$ V) that is higher than in the case of Fe$^0$ reduction (3.5 mA cm$^{-2}$ at $-1.25$ V) indicates that the reduction of Nd$^{III}$ contributed to the current increase. Because Nd$^{III}$ could not be reduced by itself as described in curve 2, the peak current increase of curve 4 can be only ascribed to the co-deposition of Nd and Fe, compared to that of curve 3. It should be noted that the peaks of P$_{3b}$ in curve c and P$_{4b}$ in curve d are ascribed to the electrochemical decomposition of the IL. Because it has been shown from the black curve which is for pure IL that the decomposition of the IL should start from $-1.50$ V. The decomposition potential for the IL shifted positively from $-1.50$ V to $-1.4$ V after the Fe$^0$ deposition peak. It has been already reported that zero-valent iron is able to catalyse the decomposition of imidazolium cations$^{[34]}$ and upon that P$_{3b}$ and P$_{4b}$ coming after the peak of Fe$^0$ deposition and Fe$^0$-Nd$^{III}$ co-deposition, respectively could be ascribed to the catalytic decomposition of the IL by Fe. The oxidation peak (P$_{4a}$) at $-0.33$ V in curve d is more positive and wider, with a higher peak current than those in curve 3, which can be attributed to the co-reduction of Nd and Fe. Figure 1b shows the CV of FeCl$_2$-NdCl$_2$-[EMIM][DCA] at different scan rates, ranging from 10 mV s$^{-1}$ to 100 mV s$^{-1}$. The reduction peaks shift from $-1.20$ V to $-1.30$ V with an increasing scan rate, where the peak current increases from 5.0 mA cm$^{-2}$ to 12.0 mA cm$^{-2}$. The oxidation peaks of the Nd and Fe deposits in the reversed scan are observed in the potential range $-0.81$ V to $-0.22$ V and show an increase in intensity and a shift towards a more negative potential at higher scan rates. This indicates that the oxidation of Nd and Fe is faster at a higher scan rate due to the faster electron-transfer rate. A broad shoulder and a secondary oxidation peak (where the arrow points in Figure 1b) in the oxidation zone are also developed at higher scan rates, as a result of the Nd and Fe compounds beginning to form, which can oxidize as separate phases at high scan rates.$^{[35]}$ The potential difference between the cathodic (P$_{4a}$) and the anodic (P$_{4b}$) peak of Nd–Fe is larger than 800 mV (Figure 1a, curve 4). A plot of $I_p \sim \nu^{1/2}$ is shown in Figure 1c, and can be described by the Randles-Sevcik equation,$^{[33,36]}$ which categorizes the Nd and Fe co-reduction process as irreversible and controlled by diffusion.

2.2 Theoretical Mathematical Model of REE-TM Co-Deposition Based on the “Transition-State Theory”

The results obtained from the CV study presented in Figure 1 show the co-reduction of Nd (REE) together with the deposition of Fe (TM); however, the theoretical background to support the processes of how the REE$^{III}$ is reduced inductively with TM remains unclear. With this assumption, the influence of the substrate on the deposition of the REE-TM is neglected.
According to Henry Eyring,\textsuperscript{[37]} reactions proceed through a well-defined transition state or activated complex, as shown in Figure 2a. The standard free-energy change in the transition state or activated complex, as shown in Figure 2b), from which some of the energy can be transferred to the REE. This energy is transferred from one atom to another is still not clear yet, as the modern investigations of the validity of the transition-state theory are still going on.\textsuperscript{[38]} The most common postulate is called the strong-collision assumption that large enough amounts of energy are transferred in molecular (atomic in this case) collisions.\textsuperscript{[39]} Based on this theory, an assumption is made that the TM is reduced first to the zero valence state (TM\textsuperscript{0}, activated state or transition state, shown in Figure 2b), from which some of the energy can be transferred to the REE to reduce its energy barrier, which makes it ready to be reduced at a much more positive potential (\(\psi_{\text{REE}}\)) than its standard electrode potential (\(\phi_{\text{REE}}\)). Based on this mechanism, at the very beginning of the electrodeposition the first few atomic layers of the deposit have to be metallic TM with high energy (TM\textsuperscript{1}), which then subsequently catalyses the reduction of the REE\textsuperscript{II}.

The concentration of the activated TM (TM\textsuperscript{1}) formed by the electrodeposition proposed in the above-mentioned model directly influences the reduction of REE\textsuperscript{II}, as the formation of TM\textsuperscript{1} is controlled by the TM concentration in the electrolyte and the applied potential/current density. Based on this, the function relationship between the molar fraction of REE in the deposit and the concentration of TM\textsuperscript{1} in the bulk solution, as well as the applied potential/current density, can be established. The solvation behaviour and stable species of RE chlorides in DCA-based ILs still need to be elaborated in the future, although the [Fe(DCA)]\textsuperscript{2+} complex was confirmed as the main species in [EMIM][DCA] IL by S. Begel.\textsuperscript{[40]} According to the report from Q. B. Zhang\textsuperscript{[28]} who speculated the [La(DCA)]\textsuperscript{3+} complex as the stable species in 1-butyl-3-methylimidazolium dicyanamide ([BMIM][DCA]) IL, the [Nd(DCA)]\textsuperscript{3+} complex is to be expected as the main species due to the chemical similarity of Nd and La. In order to clearly present the induced co-deposition process, the speciation of the Nd\textsuperscript{II} and Fe\textsuperscript{II} in [EMIM][DCA] are simplified as Nd(DCA)\textsubscript{3} and Fe(DCA)\textsubscript{2}, which are illustrated in Figure 2c and d. Before the deposition (t = 0), both the TM\textsuperscript{0} and REE\textsuperscript{II} are adsorbed onto the cathode surface and are ready to be reduced. Once a potential or a current is applied (t = t\textsubscript{i}), TM\textsuperscript{0} is first reduced to TM\textsuperscript{1}, whereas the TM\textsuperscript{0} and REE\textsuperscript{II} in the vicinity will compete to alloy with it. During the alloying, the energy is transferred from TM\textsuperscript{1} to TM\textsuperscript{0} and REE\textsuperscript{II} (t = t\textsubscript{j}) to form the complexes of TM\textsuperscript{0} + TM\textsuperscript{1} and TM\textsuperscript{0} + REE\textsuperscript{II}, which are ready to be further reduced at t = t\textsubscript{o}. Since the specific amount of energy from TM\textsuperscript{1} can be absorbed by both REE\textsuperscript{II} and TM\textsuperscript{0}, at any instant of time t, all the involved reactions from t\textsubscript{i} to t\textsubscript{o} are happening at the same time, and can be expressed as follows:

\[
\begin{align*}
    i_1 & : \text{TM}^0 + 2e^- \rightarrow k_1 \text{TM}^1 \\
    \text{REE}^{\text{II}} + \text{TM}^1 & \rightarrow k_2 \text{TM}^1 \cdot \text{REE}^{\text{II}} \\
    \text{TM}^{\text{II}} + \text{TM}^1 & \rightarrow k_3 \text{TM}^1 \cdot \text{TM}^{\text{II}} \\
    \text{TM}^1 & \rightarrow \text{Energy} \\
    i_2 & : \text{TM}^1 \cdot \text{REE}^{\text{II}} + 3e^- \rightarrow k_4 \text{TM} \cdot \text{REE} \\
    \text{REE}^{\text{II}} + \text{TM}^1 & \rightarrow k_5 \text{TM}^{*} \cdot \text{TM}^{\text{II}} \\
    \text{TM}^{\text{II}} + \text{TM}^1 & \rightarrow k_6 \text{TM}^{*} \cdot \text{TM}^{\text{II}} \\
    \text{TM}^{*} + \text{TM} & \rightarrow 2 \text{TM}^{*} + \text{Energy} \\
    i_3 & : \text{TM}^{*} \cdot \text{TM} \cdot \text{REE}^{\text{II}} + 3e^- \rightarrow k_7 \text{TM} \cdot \text{TM} \cdot \text{REE} \\
    \text{TM}^{\text{II}} + \text{TM}^{*} + \text{TM} & \rightarrow k_8 \text{TM}^{*} \cdot \text{TM}^{\text{II}} \\
    \text{TM}^{*} & \rightarrow \text{TM} + \text{Energy} \\
    i_4 & : \text{TM}^{*} \cdot \text{TM} \cdot \text{REE}^{\text{II}} + 2e^- \rightarrow k_9 \text{TM}^{*} \cdot \text{TM} \\
    \text{TM}^{\text{II}} + \text{TM}^{*} + \text{TM} & \rightarrow k_10 \text{TM}^{*} \cdot \text{TM}^{\text{II}} \\
    \text{TM}^{*} \cdot \text{TM} & \rightarrow 2 \text{TM}^{*} \cdot \text{TM}^{*} + \text{Energy} \\
    i_5 & : \text{TM}^{*} \cdot \text{TM} \cdot \text{REE}^{\text{II}} + 2e^- \rightarrow k_11 \text{TM}^{*} \cdot \text{TM} \cdot \text{TM} \\
    \text{TM}^{\text{II}} + \text{TM}^{*} + \text{TM} & \rightarrow k_12 \text{TM}^{*} \cdot \text{TM}^{\text{II}} \\
    \text{TM}^{*} & \rightarrow \text{TM} + \text{Energy} \\
\end{align*}
\]

where \(k_1\) and \(k_2\) are the electrochemical rate constants, and \(k_3\) and \(k_4\) are the equilibrium constants.

Since the lifetimes for the activated species are very short (a mean life of \(10^{-14}\) to \(10^{-13}\) s\textsuperscript{[37]}), the complex reactions of TM\textsuperscript{0} with REE\textsuperscript{II} and TM\textsuperscript{0} are considered to be in equilibrium at all times and the corresponding reverse reaction rates are neglected compared to the forward reaction rates. Therefore, the Tafel kinetics is assumed to be valid for these reactions, the partial current densities, \(i_j\), can thus be expressed as a function of the kinetic constants, \(k_j\):

\[
i_j = n_j A F k_j (1 - \theta) e^{-n_j F \psi_j / RT}
\]

where \(n_j\) is the number of electrons transferred in the electrochemical reaction \(j\), where \(n_1 = n_3 = n_5 = 2\), \(n_2 = n_4 = n_6 = n_7 = n_8 = 3\), \(n_9 = n_10 = n_11 = 2\), and \(n_12 = 3\)
small; therefore, we make the term 1 - \( \theta \) constant as 1 - \( \theta \) and let \( f = F/RT \). The corresponding equations are as follows:

\[
i_1 = 2AFk_i(1 - \theta)\eta_0c(TM^*)e^{-\alpha_0\eta_0f} \\
c(TM^* \cdot REE^*) = k_0c(TM^*)c(REE^*) \\
c(TM^* \cdot TM^I) = k_0c(TM^*)c(TM^0) \\
c(TM) = k_0c(TM^*) \\
i_2 = 3AFk_i(1 - \theta)c(TM^* \cdot REE^*)e^{-\alpha_0\eta_0f} \\
\dot{i}_1 = 2AFk_i(1 - \theta)c(TM^* \cdot TM^*)e^{-\alpha_0\eta_0f} \\
c(TM^* \cdot TM^* \cdot REE^*) = k_0c(TM^* \cdot TM^0)c(REE^*) \\
c(TM^* \cdot TM^0) = k_0c(TM^* \cdot TM^0)c(TM^0) \\
i_2 = 3AFk_i(1 - \theta)c(TM^* \cdot TM^0)e^{-\alpha_0\eta_0f} \\
i_1 = 2AFk_i(1 - \theta)c(TM^* \cdot TM^0)e^{-\alpha_0\eta_0f}
\]

Clearly,

\[
\frac{\dot{i}_1}{i_1} = \frac{\dot{i}_2}{i_2} = \cdots = \frac{\dot{i}_n}{i_n} = k_0c(TM^0) = \frac{\dot{i}_2}{i_2} = \cdots = \frac{\dot{i}_n}{i_n}
\]

Therefore, for simplicity, the current efficiency is assumed as 100\%, and the total current density \( i \) can be expressed as:

\[
i = i_1 + i_2 + \cdots + i_n = \frac{1 - k_0c(TM^0)}{1 - k_0c(TM^0)}(i_1 + i_2)
\]

Since the reactions (1), (a), (b), (c) and (2) are considered as a unit that are repeated by the reaction (1)', (a)', (b)', (c)' and (2)' (second unit) and the reactions afterwards (the rest units). In terms of the calculation of the molar fraction of REE \( X_{REE} \) in the deposit, i.e., the alloy, \( X_{REE} \) should always be the same in all units. Thus, only one unit can be considered for the calculation. At any time interval, \( \Delta t \), the number of electrons resulting from the total concentration change of the reduced TM \( (\Delta c(TM))_n \) is equal to the electrons flowing through \( i_1 \), while the number of electrons for the REE\(^{\text{III}} \) reduction is equal to the electrons flowing through \( i_2 \). Therefore,

\[
i_1\Delta t = \frac{\Delta c(TM^0)}{n_1FV} + \frac{\Delta c(TM^0 \cdot REE^\text{III})}{n_2FV} + \\
\Delta c(TM^0 \cdot TM^I) + \Delta c(TM) + \Delta c(TM \cdot REE) \tag{10}
\]

\[
i_2\Delta t = \Delta c(TM \cdot REE) \tag{11}
\]

where \( V \) is the effective volume covering all the electro-active species involved in all the reactions happening near/on the cathode surface.

Inserting equations (3)–(7) into (10) and (11), we obtain,

\[
c(TM^*) = \frac{A_k(1 - \theta)c(TM^*)e^{-\alpha_0\eta_0f}}{k_0V + Ak_i(1 - \theta)k_0c(REE^\text{III})e^{-\alpha_0\eta_0f}} (1 - e^{-\frac{\Delta V}{k_0V + Ak_i(1 - \theta)k_0c(REE^\text{III})e^{-\alpha_0\eta_0f}}}) \tag{12}
\]

Based on these kinetic equations, the molar fraction of REE, \( X_{REE} \), in the deposit is calculated from the partial current densities according to the following equation:

\[
X_{REE} = \frac{\dot{i}V}{\dot{i}_1V + \dot{i}_2V} = \frac{\dot{i}_1V + \dot{i}_2V}{\dot{i}_1V + \dot{i}_2V} \tag{13}
\]

Insert equations (3) and (7) and combine with equation (12), equation (13) is rewritten as follows:

\[
X_{REE} = \frac{\dot{i}_1}{\dot{i}_1 + \dot{i}_2} = \frac{k_0c(TM^0)c(REE^\text{III})e^{-\alpha_0\eta_0f}}{1 + \frac{k_0c(TM^0)c(REE^\text{III})e^{-\alpha_0\eta_0f}}{1 - k_0c(TM^0)}} \tag{14}
\]

Equation (14) indicates that the REE content in the deposit depends on the applied overpotential and the concentration of TM\(^0 \) in the bulk solution. A higher applied overpotential or a lower TM\(^0 \) concentration results in a higher REE content in the deposit. Theoretically, this kinetic model can be generally applied to describe the induced co-deposition phenomenon for all REE-TM systems.

### 2.3 Validation of the Theoretical Mathematical Model

Experiments for the Nd–Fe electrodeposition were performed by chronocamperometry at \(-1.40 \text{ V vs. Pt}\), which is slightly higher than the peak potential for Nd–Fe co-deposition \( (P_{\text{Nd}}) \), shown in Figure 1a. Figure 3 shows the experimental and simulated Nd contents for different Fe\(^{\text{III}} \) concentrations from 0.01 mol L\(^{-1} \) to 0.04 mol L\(^{-1} \). The Nd content decreases from 22.5 at.% to 5.7 at.% when the Fe\(^{\text{III}} \) concentration increases from 0.01 mol L\(^{-1} \) to 0.04 mol L\(^{-1} \). The experimental data fits the kinetic model with a high correlation coefficient \( R^2 \) of 0.946, validating the proposed co-deposition mechanism that describes the catalytic role of Fe\(^{\text{III}} \) in the co-deposition behaviour.
of Nd–Fe. The rate constants of $k_0$ and $k_i$ derived from the simulated parameters $D$ and $E$ show that $k_i$ is significantly smaller than $k_0$, thus it can be concluded that Fe$^{3+}$ is preferentially combined with Fe$^{3+}$ instead of Nd$^{3+}$, resulting in a relatively low Nd content in the deposit.

### 2.4 Electrodeposition of Nd–Fe Films Using the Pulse-Current Technique

In order to achieve a homogenous deposition and to avoid any concentration polarization, the pulse-current technique$^{[40]}$ was applied. An example of the current-pulse waveform with the corresponding potential response during current-pulse polarization is shown in Figure 4a. During the resting period, $t_{\text{off}}$ (1 s), the potential remained at around $-0.78$ V ($E_0$). When a cathodic current of $-16$ mA cm$^{-2}$ was applied during $t_{\text{on}}$ (0.1 s) the potential shifted suddenly to a less-noble value of $-1.16$ V ($E_1$), at the end of $t_{\text{on}}$. An increase in the electrodeposited potential during $t_{\text{on}}$ corresponds to the growth of a concentration polarization layer on the surface during each cycle and the introduction of $t_{\text{off}}$ after $t_{\text{on}}$ recovered the surface concentration of the Nd$^{3+}$ and Fe$^{3+}$ ions.$^{[41]}$ According to the Nernst equation, a lower deposition potential is needed for Nd and Fe deposition at higher concentrations of Nd$^{3+}$ and Fe$^{3+}$ ions, which helps to reduce the possibility of [EMIM]$^+$ decomposition. Figure 4b shows the relative atomic ratio of Nd $\text{[Nd/(Nd + Fe)]}$ in the Nd–Fe thin film as a function of pulse duration (10–100 ms). No obvious increase in Nd $\text{[Nd/(Nd + Fe)]}$ for both the applied concentration ratios of Fe$^{3+}$/Nd$^{3+}$ 3:10 and 1.5:10, where the Nd content was almost constant at $\sim 9$ at.% and $\sim 13$ at.%, respectively, with an increase in the pulse duration. This is because $t_{\text{on}}$ (10–100 ms) was short, while the average corresponding potentials stayed at almost the same value with the same applied current density.

Figure 5a shows a secondary-electron SEM image of the as-deposited Nd–Fe film on a Cu substrate with a pulse current density of $-16$ mA cm$^{-2}$. The current efficiency of the deposition process was calculated as 69.8% which is lower than the other report on transition metal deposition from [EMIM][DCA] IL (97%–99%).$^{[42]}$ The loss of current efficiency for Nd–Fe deposition may be attributed to the decomposition of the IL, that is in correspondence with the EDXS analysis that detected the presence of carbon and nitrogen in the deposits. The granular structure (diameter, $d \leq 5$ μm) without cracks is visible. The grain size increases with the increasing current density due to the larger total charge consumed at the same deposition time of 300 s. (Figure 5b). The granular structure ($d \leq 5$ μm) without cracks is visible. Figure 5b shows the relative atomic ratio of Nd $\text{[Nd/(Nd + Fe)]}$ in the Nd–Fe thin film as a function of the pulse current ($-4$ to $-32$ mA cm$^{-2}$). The Nd content increases from 7.5 at.% to 9.9 at.% at the concentration ratio of
1.5 : 10. Therefore, in order to remove the unstable organic compounds, the deposited film was annealed at 350 °C under argon for 30 min. The sample with the same initial composition was annealed at 750 °C under argon for 30 min, which is the temperature to obtain the Nd–Fe crystalline phase.\cite{44}

The TEM images of the cross-section of the deposit annealed at 350 °C and 750 °C are shown in Figure 6a and Figure 6b, respectively. Figure 6a shows a homogeneous layer of the deposit annealed at 350 °C on the Cu substrate. The sample annealed at 350 °C remained amorphous, as confirmed by the absence of diffraction spots in the selected-area electron-diffraction pattern (SAED). Figure 6b shows the same layer after the annealing at 750 °C, which resulted in the formation of the porous nanocrystalline structure (as confirmed by the sharp diffraction reflections in the corresponding SAED pattern).

Figure 7a shows a high-angle annular dark-field scanning TEM (HAADF-STEM) image of a representative example of the cross-section of the deposit (12 at.% of Nd) annealed at 350 °C. A porous structure of the deposit formed on the Cu substrate is observed. A thin layer (labelled by two white dashed lines in Figure 7a), located between the Cu substrate and the porous deposit is shown along with the Cu substrate. Figure 7b shows the compositional change with the deposition depth (the red

\[ \text{Fe}^{2+}/\text{Nd}^{3+} : 3 : 10 \] with the increasing pulse current, and it increases at a higher rate in the electrolyte with a lower Fe\(^{2+}\)/Nd\(^{3+}\) concentration (Fe\(^{2+}\)/Nd\(^{3+}\)) 1.5 : 10.

2.5 TEM Analysis of Nd–Fe Deposits

In order to reveal the deposition mechanism, the chemistry and phase composition of the deposit were investigated by means of transmission electron microscopy (TEM), combined with energy-dispersive X-ray spectroscopy (EDXS) and electron-energy-loss spectroscopy (EELS). The amorphous nature of as-deposited Nd–Fe films was confirmed by the XRD analysis (Figure S3), as already described in the literature.\cite{11b} Therefore, a thermal treatment of the deposit is necessary to form the crystalline alloy phases, e.g., the Nd\(_2\)Fe\(_{17}\) phase. Based on the phase diagram for Nd–Fe,\cite{43} the deposit with a Nd content of 12 at.% that would correspond to the Nd\(_2\)Fe\(_{17}\) phase stoichiometry after annealing, was selected for a thermal treatment. According to the results of the TGA, the IL starts to decompose above 250 °C (Figure S4). Therefore, in order to remove the unstable organic compounds, the deposited film was annealed at 350 °C under argon for 30 min. The sample with the same initial composition was annealed at 750 °C under argon for 30 min, which is the temperature to obtain the Nd–Fe crystalline phase.\cite{44}

Figure 6. TEM images of the cross-section of the deposit (12 at.% of Nd) (a) annealed at 350 °C with a corresponding SAED pattern and (b) (same initial composition deposit) annealed at 750 °C with a corresponding SAED pattern. 

Figure 7. (a) HAADF-STEM image of a representative example of the cross-section of the deposit (12 at.% of Nd) annealed at 350 °C and (b) the compositional change with the deposition depth (the red...
The dark-grey part of Figure 7c is the pores formed by the nanoparticles that formed during the annealing at 750 °C. Therefore, thermodynamically the Nd⁰ cannot be reduced by C or H₂ at 750 °C, not even at 1500 °C, since all the ΔG are above 0 (Table S1). Therefore the Nd⁰ can only be obtained by the electro-reduction of Nd⁴⁺. The electrodeposition of Nd–Fe from the [EMIM][DCA] electrolyte at a mild temperature contributes to the green character of this process which can be considered as a sustainable and green alternative to high-temperature molten-salt electrolysis.

3. Conclusions

The induced co-deposition of Nd, a rare-earth element (REE) and iron, a transition metal (TM), was investigated in the [EMIM][DCA] electrolyte using electrochemical measurements and SEM- and TEM-based analysis. An induced co-deposition mechanism for REE (Nd) and TM (Fe) is derived and supported by a mathematical model that considers the effect of the Fe concentration on the Nd content in the deposit, in which the transition state iron (Fe⁰) is formed during the electrodeposition, catalysing the co-deposition of Nd and Fe. Upon annealing, NdC₂ is formed through the reaction of the electrodeposited Nd⁴⁺ with C as the Gibbs free energy (ΔG) of the reaction is negative. The developed REE–TM co-deposition mechanism is valid for the Nd⁴⁺-Fe⁰[EMIM][DCA] IL system creates tremendous opportunities for REE-TM permanent-magnet recycling and thin film production with a low environmental impact. A development of longer alkyl chains ILs would be a direction to follow in the future in order to increase the ILs stability[12] and the current efficiency.

Experimental Section

Chemicals and Reagents

The [EMIM][DCA] ionic liquid (> 98%) was purchased from Sigma-Aldrich, Germany. Prior to use, 10 wt.% molecular sieves (4 Å, Sigma-Aldrich) that were dried under vacuum at 160 °C for 24 hours were added to the IL to remove the water. FeCl₃·6H₂O and NdCl₃·6H₂O (Sigma-Aldrich) were dehydrated under vacuum at 140 °C for 24 hours and were used due to their good solubility in [EMIM][DCA]. All the dried chemicals were stored inside a closed bottle in an argon-filled glove box with water and oxygen contents below 1 ppm. The water concentration, which was determined by Karl Fischer titration (C20 S, Mettler-Toledo, Switzerland), in the electrolyte was less than 50 ppm.
Electrodeposition of Nd-Fe-based Films

A three-electrode cell with a potentiostat (Reference 600, Gamry Instruments, USA) was used for all the electrochemical measurements. The electrochemical behaviours of the Fe and Nd in 10 mL of [EMIM][DCA] containing 0.03 mol L⁻¹ FeCl₂ and 0.1 mol L⁻¹ NdCl₃ at 110 °C were evaluated using cyclic voltammetry (CV). Pt wires (ρ = 0.5 mm) were used as the working electrode and the quasi-reference electrode (QRE), because the potential obtained using a Pt QRE was stable and reproducible at a mid-range temperature. A Pt plate (30 mm × 10 mm) was selected as the counter electrode. The areas of the working electrode and the counter electrode immersed in the electrolyte were 4.71 mm² and 80 mm², respectively. For the electrodeposition experiments, a Cu substrate (5 mm × 5 mm) was employed as the anode. The Cu substrate was used instead of Pt because the cathodic parts of the CVs on the Pt and Cu electrode are similar (See supplementary information, Figure S1). Before use, they were degreased with acetone, followed by an acid treatment (1 mol L⁻¹ HCl) to remove the surface oxides and finally dried. All the experimental procedures were carried out in an Ar-filled atmosphere at 110 °C. The deposition process was realized by using a constant potential of −1.4 V and a pulsed current of iₚ = −4 to −24 mA cm⁻² for different times. The as-deposited samples were washed with dried dimethylformamide (DMF, Sigma-Aldrich, Germany) to remove any electrolyte adhered to the surface.

Characterization Techniques

The morphologies of deposits were characterized with a scanning electron microscope (SEM, JSM-5800, JEOL) operated at 20 kV and equipped with an energy-dispersive X-ray spectrometer (EDXS, SiLi detector from Oxford Instruments, using internal standards with a sensitivity of 10 mm) that was used to investigate the chemical composition of the samples. Thermogravimetric analysis (TGA) of the [EMIM][DCA] IL was conducted using a STA1500 (Rheometric Scientific) in a nitrogen atmosphere between 30 and 800 °C with a temperature ramp of 10 °C min⁻¹. Using the TGA, annealing experiments the deposits with the 12 at % of Nd was performed under Ar (99.999%) at 350 and 750 °C for 30 min (Carbolite, MTF 12, England). The ratio of Nd/(Nd + Fe) in the deposit is expected to remain the same after annealing at 350 °C and 750 °C, as the phase changes of the deposits with the 12 at % of Nd, that would correspond to Nd₅Fe₂, composition would not happen until the temperature ~1100 °C, where the Nd₅Fe₂ phase would transform to Fe (bcc) and Liquid phase via peritectic reaction, according to the phase diagram of Fe–Nd. A focused ion beam (FIB, FEI HeliosNanolab 650) was used to prepare the electron-transparent lamellae (the conditions: accelerating voltage ~30 kV down to 1 kV, probe current 9.3 nA down to 73 pA with the incidence angles from 2° to 7°, were carefully monitored throughout the whole etching process in order not to alter the samples structure and composition). The lamellae were investigated with the transmission electron microscope (TEM, JEM-ARM200F, JEOL) equipped with a cold field-emission gun, a scanning unit (STEM), and high-angle annular dark-field (STEM-HAADF) and annular bright-field (STEM-ABF) detectors. Low beam currents of 16 nA and low accelerating voltage of 80 kV were used to reduce the knock-on-damage to the sample. The phase composition and the crystal structures of the deposits were determined with an X-ray diffractometer (XRD, PANalytical, Netherlands) using Cu–Kα radiation (λ = 1.5406 Å).

Acknowledgements

This work was supported by the European Union’s EU Framework Programme for Research and Innovation Horizon 2020 under Grant Agreement No 674973 (DEMETER). The authors thank Bojan Ambrozic for his help on FIB lamella preparation, Dr. Marjeta Macke Krzmanc for TGA analysis, Monika Kuster for the help on XRD and FFT analysis and the COST Action e-MINDs community for sharing the knowledge.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: induced co-deposition mechanism · ionic liquids · molten-salt electrolysis · pulse plating · transition state theory


Induced co-deposition mechanism of rare earth element (REE) -transition metal (TM) describes the role of the activated state of TM which catalyzes the reduction of REE$^{III}$ to REE$^0$. The results highlight the theoretical model for REE-TM co-deposition and provide a novel mechanistic insight. The realization of electrodeposited Nd–Fe-based thin films at a mild temperature exhibits a sustainable, green-chemistry approach compared to molten-salt electrolysis.

X. Xu*, Prof. Dr. S. Sturm, Dr. J. Zavasnik, Prof. Dr. K. Z. Rozman

1 – 11

Electrodeposition of a Rare-Earth Iron Alloy from an Ionic-Liquid Electrolyte

---

**ORCID** (Open Researcher and Contributor ID)

Please check that the ORCID identifiers listed below are correct. We encourage all authors to provide an ORCID identifier for each coauthor. ORCID is a registry that provides researchers with a unique digital identifier. Some funding agencies recommend or even require the inclusion of ORCID IDs in all published articles, and authors should consult their funding agency guidelines for details. Registration is easy and free; for further information, see http://orcid.org/.

Prof. Dr. Saso Sturm
Prof. Dr. Kristina Z. Rozman
Xuan Xu http://orcid.org/0000-0001-7804-0369
Dr. Janez Zavasnik