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## Comparison of the electrochemical behavior of some Rare Earth Elements in butyl methylpyrrolidinium dicyanamide ionic liquid

M. Razo-Negrete<sup>1</sup>, R. Ortega-Borges<sup>1,\*</sup>, V. Zinovyeva<sup>2</sup>, C. Cannes<sup>2</sup>, C. Le Naour<sup>2</sup>,  
G. Trejo-Córdova<sup>1</sup>, Y. Meas<sup>1</sup>

<sup>1</sup> CIDETEQ. Parque Tecnológico Qro-Sanfadila, Mexico

<sup>2</sup> Institut de Physique Nucléaire d'Orsay-Université de Paris Sud. 15 rue Georges Clémenceau 91406 Paris CEDEX France

\*E-mail: [rortega@cideteq.mx](mailto:rortega@cideteq.mx)

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To evaluate the feasibility of developing an efficient electrochemical separation process for rare earth elements (REE) at room temperature, the electrochemical behavior of some representative REE was evaluated in butyl methylpyrrolidinium dicyanamide (BMPyr-DCA), a room temperature ionic liquid. Because of their chemical properties, their commercial availability and their technological applications, yttrium, lanthanum, neodymium and samarium were selected for this study. The differences in the electrochemical properties of these elements as trivalent salts in BMDCA solutions were evaluated by cyclic voltammetry using a Pt electrode under an Ar atmosphere. For the elements with chemical properties that predict only the reduction in one stage (Y, La and Nd), the results exhibited the simultaneous reduction of BMPyr-DCA and the REE cation and the corresponding oxidation of the reduced REE at anodic potentials that were dependent on the REE cation. For Sm, a two-step reduction process from Sm(III) to Sm(II) and from Sm(II) to Sm(0) was observed, and a clear cathodic peak was observed far from the cathodic electrochemical window limit (-1.38 and -2.25 V vs Fc/Fc<sup>+</sup>); only one anodic peak was observed at -0.93 V, a more negative potential than for the other studied REE. The results show the same behavior as observed in other media (aqueous and molecular media and molten salts) and allow for the evaluation of the possibility of selectively identifying the studied REE in the context of their differing electrochemical responses.

**Keywords:** dicyanamide ionic liquids, rare earth electrochemical behavior, rare earth element separation process, ionic liquids electrochemistry

### 1. INTRODUCTION

Rare earth elements (REE) are a group of chemical elements that include scandium (Sc), yttrium (Y) and the lanthanide series (Ce-Lu), and they have quite similar chemical properties [1-7]

because of their identical outermost electron configurations. Due to their nuclear, fluorescent, chemical, electrical, optical and magnetic properties, REE are recognized as one of the most important chemical elements for industrial and technological applications [8-14]. REE are broadly employed in electric and electronic devices, lighting phosphors, magnets, petroleum refining systems, wind power, electric vehicles, etc. [3, 8, 12]. The continuous technological advances, mainly in the electronic industry and the growing consumption of electronic products, have as a consequence increased the demand for REE of high purity [3, 15].

The production of REE is dominated by China, which generates approximately 97% of the global REE production and was the first exporter of these elements to the global market. However, a deficit in the supply of REE is foreseen due to the decrease of exports by China as it increases its consumption for national production [3, 15-16], and due to the increase of global demand, which presents an expected 8% annual growth until 2020. To solve this supply deficit, important efforts are being made in different countries to develop REE recovery processes from secondary sources, such as urban mines [3, 8, 17].

Interest in urban mines is associated with their volume and composition. According to the 2017 report of The Global e-Waste Monitor, published by the United Nations University (UNU) [18], 44,700,000 tons of electronic wastes were generated in 2016, including equipment and devices such as spotlights and lamps, screens, appliances, cell phones, electronic tablets and other personal devices. It is estimated that the volume of electronic waste will increase to more than 52 million tons in 2021. Concerning the composition of electronic wastes, the main components are halogenated compounds, heavy metals and various REE [3, 14, 18-19]. For this reason, electronic wastes are an important secondary source for the recovery of REE with the consequent interest that they present from both the economic and ecological points of view and for their partial contribution to cover the growing demand for REE in the coming years.

Despite the interest in electronic wastes, its valorization is not simple due to the diversity of parts that constitute it, such as electronic devices, cell phones, television screens, and hardware components, as well as the diversity of compounds that can be recovered. For the recovery of REE from electronic wastes, the main processes available are hydrometallurgical and pyrometallurgical processes [13, 20] despite having adequate efficiencies, these processes require operating conditions that are not necessarily simple, requiring several complex steps. Concerning the classical chemical process, due to the similar physicochemical properties of REE, the selective separation of these elements is a greatly important challenge to optimize for an efficient separation process [21-25].

Currently, several chemical processes for the separation of these elements have been developed. Among them, several extraction processes have been optimized and are currently used in the separation and purification processes of REE [14, 16, 23, 26-27]. However, like most chemical processes, extraction presents some difficulties and limitations, which complicates its use: its operation involves successive stages, poor selectivity and/or efficiency, high production costs and health and environmental risks due to the use of organic and volatile solvents [21, 28-30]. Thus, the current limitations of the available processes to recover REE from electronic wastes make it necessary to study, develop and optimize new alternative processes that allow us to design appropriate revalorization procedures.

Among the processes that are considered to be adequate alternatives for the selective separation of REE, the processes that use ionic solvents as molten salts or ionic liquids as the reaction medium are considered to be suitable alternatives to processes taking place in water or conventional molecular solvents. Ionic liquids, particularly room temperature ionic liquids (RTILs), represent a good alternative for chemical and electrochemical processes because they can be operated in conditions similar to those involved in aqueous processes, such as operation temperatures above 100 °C.

RTILs are ionic solvents, and similar to high temperature molten salts (such as fused alkaline chlorides), they are mainly composed of ionic species formed when the original compounds are fused, commonly at temperatures lower than 100 °C.

In contrast to classical ionic solvents (molten salts), RTILs are formed by organic cations and organic or inorganic anions associated with ionic aggregates [31-36]. Owing to their physicochemical properties such as negligible vapor pressure, modifiable viscosity and density, low melting point, noncorrosive and nonflammable properties, high thermal stability and good solvent ability [37-40], RTILs have gained interest as a replacement for conventional solvents in the extraction processes of REE because they offer the advantages of operation safety, high efficiency, high selectivity, high chemical stability and decreased output of polluting effluents, among others. These advantages have allowed for the development of separation processes that separate lanthanide and actinide elements in the nuclear industry [41-47].

In recent times, interest in the use of RTILs as reaction media for the development of new processes has steadily increased. In the case of a process involving REE, continuous effort has been made to develop an efficient separation process in RTILs. In this context, electrochemical process [31,36] have allowed for the separation of REE in metallic form by electrodeposition [22, 48].

RTILs have the advantage of great electrochemical stability, as evidenced by a large electrochemical window that allows for electrodeposition, as in the case of REE, of several highly electropositive metals without the simultaneous hydrogen evolution reaction (HER) [49-51], which prevents the efficient electrodeposition of very reducing metals in aqueous media. Another great feature of RTILs is the capability of modulating their physicochemical properties such as viscosity, conductivity, and density by mixing them with other RTILs or other inert molecular solvents, which allows for the optimization of electrochemical processes by controlling the rates of charge transfer and mass transfer, thus controlling the rate of electrochemical reactions and the properties of the products (morphology, composition, etc.) [38, 52].

Among the very large number of RTILs that can be used for electrochemical applications, bis(trifluoromethanesulfonyl)imide (TFSI) anion-based RTILs have been shown to achieve the electrodeposition of single REE [36, 53-64]. An observed limitation of conventional TFSI anion-based RTILs, containing imidazolium or pyridinium cations, is the limited solubility of different metallic salts in them [65-69]. To solve this problem, a new group of RTILs based on the dicyanamide (DCA) anion has been developed by MacFarlane et al. [70]. The main characteristics of DCA anion-based RTILs are associated with a lower viscosity than that observed for TFSI-based ILs. This reduction in viscosity allows for better mass transport, higher conductivity, and higher solvation ability of metal ions due to the strong coordinating properties of DCA anions [67, 68, 70].

Based on these properties, the use of DCA anion-based RTILs has been evaluated for the electrodeposition of some transition metals such as Zn, Au, Sc, Ge, Cu, Co, Mg, Pd and Ni [65-68, 71-80]. Concerning the electrochemical study of REE in DCA anion-based RTILs, there are few studies, and only the electrodeposition of La has been achieved in BMIm-DCA [81]. In this work, the electrochemical behavior of different REE is studied in BMPyr-DCA ionic liquid in a controlled atmosphere to evaluate the feasibility of developing electrochemical processes for their efficient separation based on their selective electrodepositions.

## 2. EXPERIMENTAL

The studied REE were Y, La, Nd and Sm.  $\text{Y}(\text{TFSI})_3$ ,  $\text{La}(\text{TFSI})_3$ ,  $\text{Nd}(\text{TFSI})_3$  and  $\text{Sm}(\text{TFSI})_3$  anhydrous salts ( $\text{RE-TFSI})_3$  were purchased from Solvionic (purity 99%), stored in an argon-filled glove box (Jacomex) and used without further purification. The ionic liquid 1-butyl-1-methylpyrrolidinium dicyanamide (BMPyr-DCA) was from Solvionic (purity 99.5%). The water content of the as-purchased BMPyr-DCA was measured via Karl Fisher titrations (Mettler Toledo DL39 Karl Fischer coulometer). Before use in the electrochemical studies, BMPyr-DCA was dried at 80 °C under vacuum for 2 days using standard Schlenk-line techniques. After the drying process, the water content was re-evaluated, and the dried BMPyr-DCA was stored in the glove box.

To avoid any interference from water, humidity or oxygen in the electrochemical response of either the ionic liquid or the solutions of the studied REE, all working solutions of  $\text{RE}(\text{TFSI})_3$  were prepared with dried BMPyr-DCA. To keep a minimum content of water and to avoid any interference in the electrochemical response, all electrochemical tests were carried out in an argon-filled glove box at 25 °C. In these confined conditions, the water or humidity content in the glove box was controlled to a maximum of 10 ppm of  $\text{H}_2\text{O}$ .

Electrochemical experiments were carried out by using a typical three-electrode system with a Pt disk as the working electrode (geometric area of  $0.03 \text{ cm}^2$ ), a Pt wire as a counter electrode and a silver wire immersed in a glass tube with a Vycor tip filled with 0.01 M  $\text{Ag}(\text{CF}_3\text{SO}_3)$  in dried BMPyr-DCA was used as the reference electrode. All measured potentials are referred to as  $\text{Fc}/\text{Fc}^+$  redox couples in BMPyr-DCA, used as an internal redox couple with an experimental formal potential of 0.54 V vs  $\text{Ag}/\text{Ag}^+$ .

The electrochemical behavior of BMPyr-DCA and  $\text{RE}(\text{TFSI})_3$  solutions was evaluated by cyclic voltammetry using an Autolab PGSTAT30 instrument controlled by NOVA software. Voltammetric studies were developed by applying a scan rate of  $100 \text{ mV s}^{-1}$ , unless mentioned otherwise. Scans were started towards the cathodic direction from the open circuit potential (OCP).

### 3. RESULTS AND DISCUSSION

#### 3.1 Determination of the water content in dried and undried BMPyr-DCA

As in many molecular or ionic solvents, the presence of water in BMPyr-DCA can modify both its chemical and electrochemical behaviors in several ways: by reaction between BMPyr-DCA and H<sub>2</sub>O, producing species that can later affect the stability of the solvent, or by modifying its response by acting as an electroactive species similar to an impurity or an added solute.

In addition, in the specific case of RTILs, the presence of water can strongly modify their physicochemical properties by reducing, for example, the conductivity and viscosity, thus facilitating transport by diffusion [18, 65-71]. Several authors [65-71] have identified and studied the effect of the presence of water on the electrochemical behavior of pure RTILs and of various chemical species dissolved in them. The results showed a decrease in the electrochemical window due to the competitive reduction of water versus direct reduction of the RTILs and an effect on the morphology of electrodeposits.

In our case, the presence of water is associated with the hygroscopic character of BMPyr-DCA; for this reason, pretreatment of BMPyr-DCA before use as a solvent was necessary to avoid the potential interference of water in the electrochemical response of BMPyr-DCA.

The drying process, detailed in section 2, allows for a decrease in the water content in BMPyr-DCA, as shown in Table 1.

**Table 1.** Effect of the drying process on the water content of BMPyr-DCA.

BMPyr-DCA	H <sub>2</sub> O concentration (ppm)
Before drying	445.68 ± 30.10
After drying	88.48 ± 15.05

**Table 2.** Content of water in 30 mM REE(TFSI)<sub>3</sub> solutions prepared with dried BMPyr-DCA.

Solution	H <sub>2</sub> O concentration (ppm)
Dried BMPyr-DCA	88.48 ± 15.05
Y(TFSI) <sub>3</sub>	217.96 ± 17.26
La(TFSI) <sub>3</sub>	169.34 ± 15.30
Nd(TFSI) <sub>3</sub>	139.97 ± 25.19
Sm(TFSI) <sub>3</sub>	196.4 ± 9.72

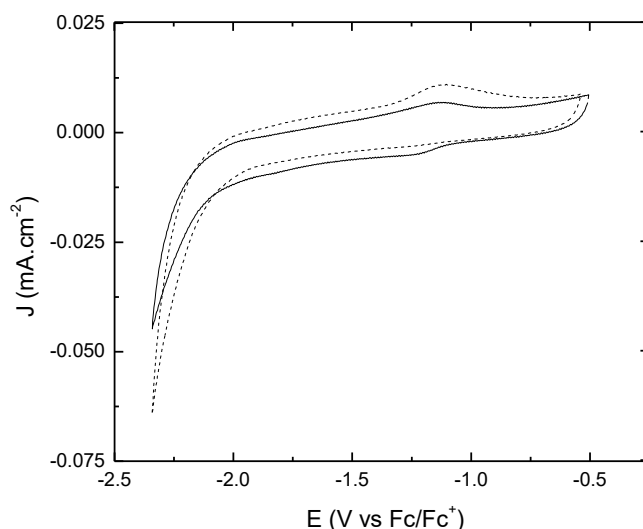
The results show that the water content decreased by 80%, from 445 ppm to 88 ppm, after the drying process. Given the hygroscopic character of BMPyr-DCA, after the drying process, BMPyr-DCA was stored under inert atmosphere to avoid the reincorporation of water/humidity.

Because of the importance of controlling the water content in pure BMPyr-DCA and in solutions prepared with it, the water content was also evaluated in solutions of REE prepared with previously dried BMPyr-DCA. The solutions were 30 mM REE(TFSI)<sub>3</sub> in BMPyr-DCA. The results obtained from the evaluation of the water content are shown in Table 2.

For all REE solutions, a higher concentration of water was observed when compared with dried BMPyr-DCA. These results show that even if anhydrous chemicals and dried BMPyr-DCA were employed to prepare the studied REE solutions, it is not possible to avoid the presence of water in the working solutions; the increase in water content in REE solutions is attributed to the absorption of water from the environment. For this reason, the maximal value of water content (217 ppm) was taken as our reference to control the effect of water in further electrochemical studies.

### 3.2 Electrochemical response of BMPyr-DCA

The electrochemical study of BMPyr-DCA was carried out by cyclic voltammetry. To identify the effect of the presence of water, the electrochemical response of BMPyr-DCA as a solvent was evaluated before and after the drying process. Figure 1 shows the obtained cyclic voltammograms, showing only the responses involving the electrochemical reduction limits; the anodic electrochemical limits are not shown given the almost null effect of the presence of water on the oxidation window limit.



**Figure 1** Cyclic voltammograms of pure BMPyr-DCA before (dotted line) and after (solid line) drying process on a Pt electrode. T= 25 °C. Scan rate: 100 mV s<sup>-1</sup>.

As shown in Figure 1, even if before the drying process the water content was five times higher than after it, only a small effect on the electrochemical response of BMPyr-DCA was observed. In fact,

in the range of potential values between -0.5 and -2.0 V vs  $\text{Fc}/\text{Fc}^+$ , the shape of the voltammograms is unchanged by the presence of water, and only minor changes in the measured current are observed. Because these currents are observed in the absence of electroactive species, they are assumed to be capacitive currents. In the selected potential range, lower values of current are observed in the presence of water, which is attributed to a decrease in the electrical resistance of BMPyr-DCA. This is due to the effect of water on the viscosity of BMPyr-DCA: water acts as a diluent, producing a decrease in viscosity and, consequently, an increase in conductivity and a decrease in capacitive currents.

For cathodic potentials higher than -2.25 V, the behavior of the observed current is typical of the electrochemical reduction limit imposed by the reduction of the solvent. The presence of water in the undried BMPyr-DCA does not have a significant influence on the cathodic limit. According to these results, a reduction electrochemical window of 1.75 V (from -0.5 to -2.25 V vs  $\text{Fc}/\text{Fc}^+$ ) is defined for dried and undried BMPyr-DCA as a solvent.

Concerning the anodic behavior of BMPyr-DCA, in previous experiments (not reported here), it was observed that for potential values higher than 0.0 V vs  $\text{Fc}/\text{Fc}^+$ , a rise in the anodic current occurs due to the oxidation of the DCA anion. It has been reported [50, 53-54] that this oxidation process involves the irreversible polymerization of DCA with the formation of an isolating film on the working electrode, independent of the associated cation and the nature of the working electrode. Based on this result, it is assumed that the anodic electrochemical limit of BMPyr-DCA is situated at 0.0 V vs  $\text{Fc}/\text{Fc}^+$ .

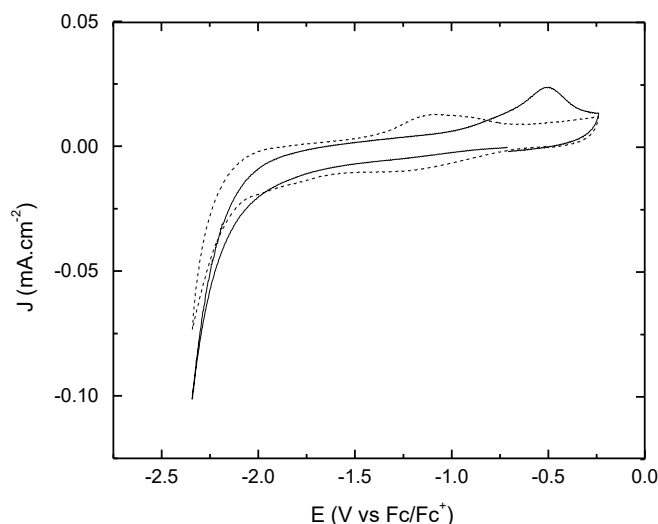
Combining the results of both the cathodic and anodic behavior of BMPyr-DCA, it is established that the electrochemical window of BMPyr-DCA is 2.25 V, with a minor influence of the presence of water. This value is between those reported for dried BMPyr-DCA [51, 52, 54, 69] on Pt.

### 3.3. Electrochemical response of REE solutions in BMPyr-DCA

#### 3.3.1 Electrochemical behavior of yttrium

Figure 2 shows the voltammetric response of 30 mM  $\text{Y}(\text{TFSI})_3$  in BMPyr-DCA (solid line). Comparing it with the corresponding pure BMPyr-DCA (dotted line), no well-defined peaks associated with yttrium are observed in the cathodic scan, but the reduction limit associated with BMPyr-DCA reduction is shifted to more anodic potentials.





**Figure 2.** Cyclic voltammograms of neat BMPyr-DCA (dotted line) and BMPyr-DCA + 30 mM Y(TFSI)<sub>3</sub> (solid line). Recorded at 25 °C on a Pt electrode. Scan rate: 100 mV.s<sup>-1</sup>.

For the Y(TFSI)<sub>3</sub> solution, the electrochemical reduction limit is observed at -1.95 V vs Fc/Fc<sup>+</sup>, while for pure BMPyr-DCA, it is observed at -2.1 V vs Fc/Fc<sup>+</sup>.

When the potential scan is reversed, a new anodic peak appears with a peak potential of -0.5 V vs Fc/Fc<sup>+</sup> when Y(TFSI)<sub>3</sub> is present. This peak is clearly different from that observed when Y(TFSI)<sub>3</sub> is absent, and it is only observed when the potential scan is reversed for potential values more cathodic than -2.0 V. It is also observed that the peak current is dependent on the potential at which the scan is reversed. This observed behavior for the anodic peak allows us to propose that it is associated with the oxidation of the yttrium-reduced species formed during the cathodic scan. Because no evident reduction signals associated with yttrium are observed during the cathodic scan, it is proposed that the formation of these yttrium-reduced species is carried out at potential values very close to the values at which the reduction of pure BMPyr-DCA is also observed. Thus, because two reduction processes occur simultaneously at sufficiently negative potentials near -1.95 V vs Fc/Fc<sup>+</sup>, a well-defined peak of yttrium reduction cannot be observed, and as a global result, the cathodic reduction limit is shifted to less cathodic potentials.

This result is in accordance with previous results reported in the literature related to the electrochemical reduction of yttrium in ionic liquids. Glukhov et al. [77] reported the voltammetric study of yttrium in triflate-based ionic liquids. From studies carried out of Y(OTf)<sub>3</sub> in BMN-OTf on working Pt and Cu electrodes, no reduction peaks associated with yttrium reduction were observed, similar to the results obtained in this work. When solutions of Y(OTf)<sub>3</sub> in BMPyr-OTf were studied by using a Pt electrode, a reduction peak was observed at -2.6 V vs Ag|0.1 M Cl<sup>-</sup>, associated with the reduction process of Y<sup>3+</sup>/Y<sup>0</sup>. For this combination of Y(OTf)<sub>3</sub> and BMPyr-OTf, a black precipitate, assumed to be metallic yttrium, is obtained on Cu electrodes. According to these results, it can be assumed that from ionic liquids containing BMPyr as a cation, the reduction of yttrium is carried out at lower reduction potentials than those required to reduce the BMPyr cation. Based on this result, it could be expected that because they have the same common cation and because it is assumed that the cation defines the cathodic electrochemical limit [17, 18, 78-81] in the ionic liquid studied in this

work (BMPyr-DCA), the reduction of yttrium would be observed independent of the reduction process of the ionic liquid.

However, the obtained results show that in BMPyr-DCA, it is not possible to distinguish the reduction of yttrium from the reduction of BMPyr because both occur simultaneously. This is because the potential reduction of BMPyr is not only imposed by the chemical nature of BMPyr but also depends on the electrode arrangement, the water content and the physicochemical interactions between BMPyr and the associated anion forming the ionic liquid, as reported previously [76, 82-85]. In our case, it is proposed that under the studied conditions, the reduction of BMPyr-DCA is carried out at lower potentials than for other BMPyr-based liquids, which makes it impossible to distinguish the electrochemical response of yttrium. It is important to emphasize that in the working conditions used, there is no evidence of the formation of a deposit corresponding to the reduced form of yttrium. Therefore, it is assumed that Y(III) is reduced to a soluble species with an oxidation state between Y(III) and Y(0). The complexity of the electrochemistry of yttrium and the difficulty of obtaining metallic deposits from ionic liquids is evidenced by previous works. For example, in [86], the feasibility of electrodepositing Y from ionic liquids to develop Pt-REE alloys has been studied in two ionic liquids, 1-octyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (OcMePyr-TFSI) and N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium tetrafluoroborate ( $N_{122,201}\text{-BF}_4$ ), by adding Y(III) as  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and with HOPG (*highly oriented pyrolytic graphite*) as the working electrode. From these ionic liquids, voltammetric studies showed that in OcMPyr-TFSI, only the passivation of the electrode without formation of a deposit of metallic yttrium occurred, whereas in  $N_{122,201}\text{-BF}_4$ , three cathodic peaks related to the reduction of Y(III) to Y(0) in a three-step process was observed. In this last case, studies by EQCM did not show the formation of an yttrium deposit.

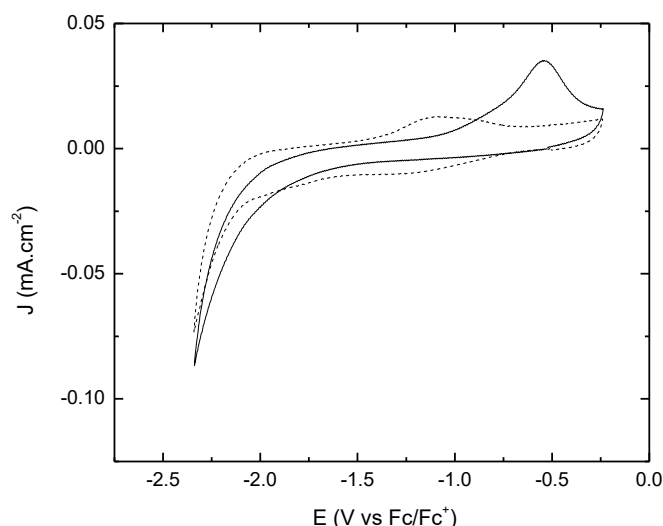
### 3.3.2 Electrochemical behavior of lanthanum

As in the previous case for yttrium, La(III) solutions were studied by cyclic voltammetry. Figure 3 shows the comparison between the electrochemical responses of 30 mM  $\text{La}(\text{TFSI})_3$  in BMPyr-DCA (solid line) and pure BMPyr-DCA (dotted line).

Similar to yttrium, no cathodic signals associated with its reduction are observed for La(III), and the cathodic electrochemical window is decreased in the presence of La(III) because the reduction of BMPyr-DCA is shifted. An anodic peak at -0.54 V vs  $\text{Fc}/\text{Fc}^+$  is observed when the potential scan is reversed.

According to these results, it is proposed that the electrochemical behavior of La(III) solutions in BMPyr-DCA is very similar to that observed for Y(III): in this case, La(III) is simultaneously reduced with the BMPyr cation, and the formed reduced species are further oxidized during the anodic scan.

Similar results were obtained by Asen et al.[86], who reported the simultaneous reduction of La(III) with the cathodic decomposition of OcMePyr-TFSI. This phenomenon is attributed to the slow kinetics of the electrochemical reduction of La, thus involving very high overpotentials for the reduction of  $\text{La}(\text{TFSI})_3$ .



**Figure 3.** Cyclic voltammograms on a Pt electrode of pure BMPyr-DCA (dotted line) and 30 mM  $\text{La}(\text{TFSI})_3$  in BMPyr-DCA (solid line).  $T = 25^\circ\text{C}$ . Scan rate:  $100\text{ mV}\cdot\text{s}^{-1}$ .

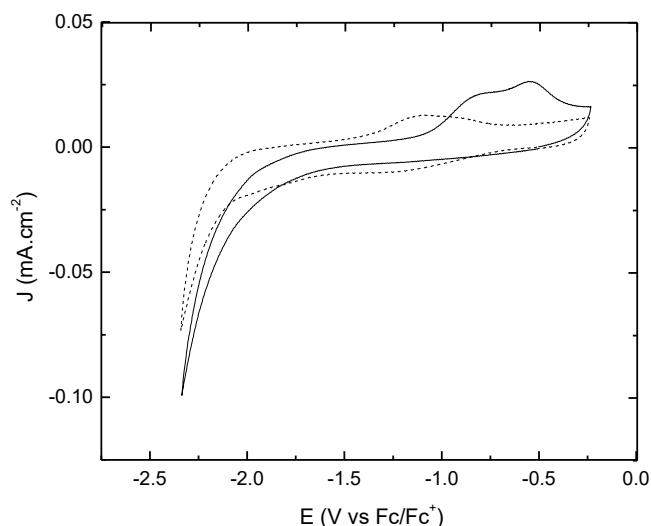
Despite the difficulty of observing the reduction of  $\text{La}(\text{III})$  independently of the reduction of the ionic liquid in our studied ionic liquid BMPyr-DCA and in pure OcMePyr-TFSI, other authors have reported the electrodeposition of La from ionic liquids. For example, Zhang et al. [64] studied the electrochemical response of  $\text{LaCl}_3$  in BMIm-DCA at  $60^\circ\text{C}$  on Pt. In this case, well-defined reduction peaks corresponding to the  $\text{La}^{3+}/\text{La}^0$  reduction process were observed, and nanostructured deposits of La were obtained. Similarly, Bhatt et al. [40] found a single reduction peak associated with the  $\text{La}^{3+}/\text{La}^0$  system when studying the electrochemical behavior of  $(\text{TFSI})_3(\text{H}_2\text{O})_3$  in  $\text{M}_3\text{NB-TFSI}$ . Bourbos et al. [20] also obtained an electrodeposit of Al on Cu from solutions of  $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  in BMPyr-TFSI. In contrast, with OcMePyr-TFSI, different results were obtained when the studied solutions were prepared with  $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  [38]. In this case, under atmospheric conditions with undried ionic liquid ( $[\text{H}_2\text{O}] > 1000\text{ ppm}$ ), the voltammetric study on Pt showed a reduction peak for lanthanum at  $-1.6\text{ V}$  vs Ag/AgCl, and electrodeposits of lanthanum were obtained.

According to these reported results and our experimental results, it is possible to conclude that, similar to the results observed for Y(III), the feasibility of reducing  $\text{La}(\text{III})$  to  $\text{La}(0)$  is dependent not only on the nature and purity of the ionic liquid but also on the nature of the cation and the associated anion forming in the studied ionic liquid.

### 3.3.3 Electrochemical behavior of neodymium

As with the previous elements, the electrochemical behavior of neodymium was studied from 30 mM  $\text{Nd}(\text{TFSI})_3$  solutions in BMPyr-DCA. When comparing the electrochemical responses of Nd(III) and pure BMPyr-DCA (Figure 4, solid and dotted lines, respectively), the anodic shifting of

the cathodic limit is observed in the presence of Nd(III). As in the previous cases, this result is associated with the simultaneous reduction of Nd(III) and BMPyr-DCA. Concerning the anodic behavior of the studied solutions, two oxidation peaks are observed when the potential scan is reversed, with potential peaks of -0.78 and -0.54 V vs Fc/Fc<sup>+</sup>. It is assumed that these peaks are associated with the oxidation processes of reduced species of Nd(III) formed during the cathodic scan.



**Figure 4.** Cyclic voltammograms on a Pt electrode of pure BMPyr-DCA (dotted line) and 30 mM Nd(TFSI)<sub>3</sub> in BMPyr-DCA (solid line). T= 25 °C. Scan rate: 100 mV.s<sup>-1</sup>.

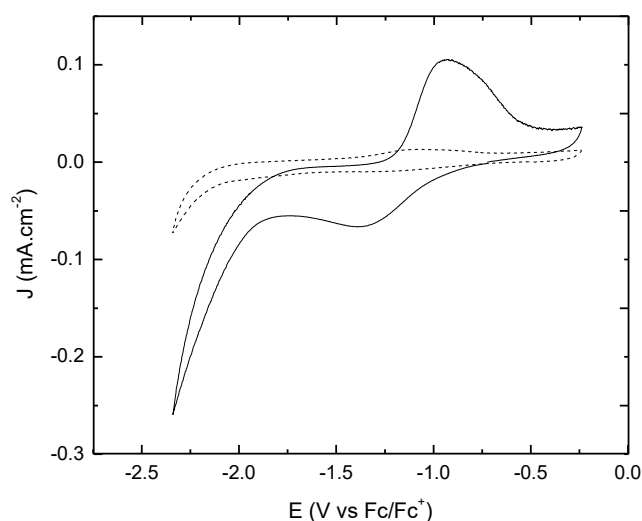
The electrochemistry of neodymium in ionic liquids has been studied by several authors [41, 84, 87-90]. Ota et al. [90] studied the electrochemical behavior of Nd(TFSI)<sub>3</sub> in triethyl-pentyl-phosphonium bis(trifluoromethyl-sulfonyl) amide ([P<sub>225</sub>][TfSA]) on Pt at 100 °C. Under these conditions, a reduction peak due to the reduction process of Nd<sup>3+</sup> to Nd<sup>0</sup> was observed at -2.79 V vs Fc/Fc<sup>+</sup>, and at more cathodic potentials, the cathodic reduction of the ionic liquid was immediately observed. Other studies in the same ionic liquid[87] have shown that the potential of the reduction peak associated with neodymium was dependent on the temperature, which shifted when the temperature of electrodeposition was increased. Therefore, at 150 °C, a black uniform deposit of Nd was obtained on Cu. On the other hand, Chou et al. [84] studied Nd(III) solutions in BMPyr-TFSI. Nd(III) ions were introduced in solution by electrochemical oxidation of metallic Pd. Cyclic voltammetry results showed a cathodic peak at -1.3 V vs Ag/Ag<sup>+</sup> and two anodic peaks at -1 V and 0.5 V vs Ag/Ag<sup>+</sup>. The cathodic peak was associated with Nd(III) reduction, while the anodic peaks were attributed to the successive oxidation of Nd(0) to Nd(II) and Nd(II) to Nd(III).

Given these results, we propose the electrochemical reduction of Nd(III) simultaneously occurs with the reduction of the ionic liquid, and the reduced species of Nd are later oxidized in two independent steps.

#### 3.3.4 Electrochemical behavior of samarium

In Figure 5, the electrochemical response by cyclic voltammetry of 30 mM Sm(TFSI)<sub>3</sub> in BMPyr-DCA (solid line) is compared with that corresponding to pure BMPyr-DCA (dotted line). A

well-defined reduction peak is observed at -1.38 V vs Fc/Fc<sup>+</sup> during the cathodic scan, and an associated anodic peak is observed with a potential peak of -0.93 V vs Fc/Fc<sup>+</sup> when the scan is reversed.



**Figure 5.** Cyclic voltammograms on a Pt electrode of pure BMPyr-DCA (dotted line) and 30 mM Sm(TFSI)<sub>3</sub> in BMPyr-DCA (solid line). T= 25 °C. Scan rate: 100 mV.s<sup>-1</sup>.

Independent experiments (not reported here) have shown the correlation between the observed cathodic and anodic peaks. The cathodic peak is associated with the reduction of Sm<sup>3+</sup> to Sm<sup>2+</sup>, while the anodic peak is associated with the oxidation of Sm<sup>2+</sup> to Sm<sup>3+</sup>. The reduction process from Sm<sup>2+</sup> to Sm<sup>0</sup> is not evidenced because it is assumed that it is carried out simultaneously with the cathodic reduction of BMPyr-DCA, as observed for the other REE studied. The observed peaks are in accordance with the results obtained by Bhatt et al. [40], who studied solutions of Sm(TFSI)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> in trimethyl-butylammonium bis(trifluoromethanesulfonyl)amide on Pt and found a reduction peak for Sm<sup>3+</sup> to Sm<sup>2+</sup> at -1.05 V vs Fc/Fc<sup>+</sup> and the corresponding oxidation process of Sm<sup>2+</sup> to Sm<sup>3+</sup> at -0.8 V. A second reduction peak, attributed to the reduction of Sm<sup>2+</sup> to Sm<sup>0</sup>, is observed at -2.85 V vs Fc/Fc<sup>+</sup>, but the corresponding oxidation peak of metallic samarium was not observed. Similarly, Pan et al.[37] and Yamagata et al. [42] have shown that in BMPyr-TFSI, the reduction and oxidation are carried out with very well-defined signals, as observed in this work.

### 3.4 Comparison of the electrochemical behavior of REE in BMPyr-DCA

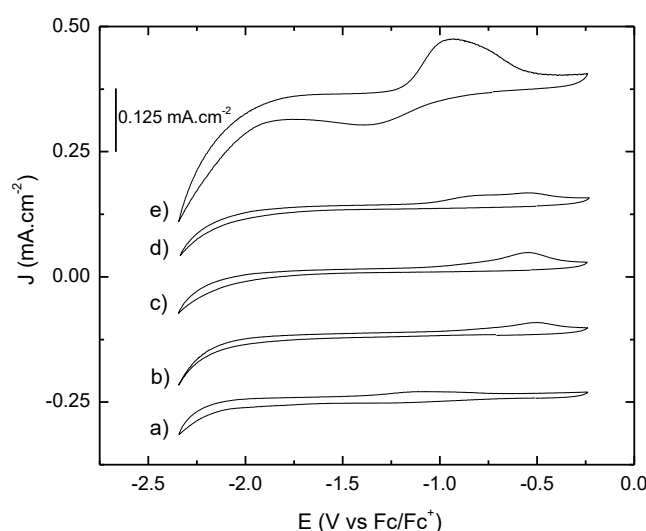
Figure 6 shows the cyclic voltammograms obtained for the studied REE in the ionic liquid BMPyr-DCA. According to the observed responses, it is possible to propose that for yttrium, lanthanum and neodymium, the reduction process involves the process of REE(III) to REE(0). However, a clear reduction peak was not observed for any of these REE, and it is assumed that their

reduction process was carried out simultaneously with the cathodic decomposition of BMPyr-DCA. For these REE, the observed oxidation peak when the scan was reversed is associated with the reduced species of REE(III) formed during the cathodic scan because the oxidation peak was observed only when REE(III) was present in solution.

Concerning the effect of REE(III) on the electrochemical cathodic limit, in all cases, a slight shift of the limit to more anodic potentials was observed because of the simultaneous reduction of REE(III) with the cation forming the ionic liquid BMPyr-DCA.

Samarium, in contrast to the other studied REE, shows a well-defined cathodic peak associated with the reduction process of  $\text{Sm}^{3+}$  to  $\text{Sm}^{2+}$  and the corresponding oxidation process of  $\text{Sm}^{2+}$  to  $\text{Sm}^{3+}$ .

Similar to the findings for the other REE, the reduction involving the formation of  $\text{Sm}(0)$  was not evidenced as a well-defined peak.



**Figure 6.** Cyclic voltammograms on a Pt electrode of: (a) pure BMPyr-DCA (b) 30 mM  $\text{Y}(\text{TFSI})_3$  in BMPyr-DCA (c) 30 mM  $\text{La}(\text{TFSI})_3$  in BMPyr-DCA (d) 30 mM  $\text{Nd}(\text{TFSI})_3$  in BMPyr-DCA (e) 30 mM  $\text{La}(\text{TFSI})_3$  in BMPyr-DCA  $T = 25^\circ\text{C}$ . Scan rate:  $100 \text{ mV.s}^{-1}$ .

**Table 3.** Comparison between the cathodic peak potentials ( $E_{cp}$ ) and the anodic peak potentials of the studied REE in BMPyr-DCA.

System	$E_{cp}$	$E_{ap}$
	(V vs $\text{Fc}/\text{Fc}^+$ )	(V vs $\text{Fc}/\text{Fc}^+$ )
$\text{Y}^{3+}/\text{Y}^0$	--	-0.50
$\text{La}^{3+}/\text{La}^0$	--	-0.54
$\text{Nd}^{3+}/\text{Nd}^0$	--	-0.78 (first anodic peak)/ -0.54 (second anodic peak)
$\text{Sm}^{3+}/\text{Sm}^{2+}$	-1.38	-0.93
$\text{Sm}^{2+}/\text{Sm}^0$	--	--

In Table 3, the cathodic and anodic peak potentials obtained from Figure 6 for the studied REE are presented. From these results and in account of the voltammetric behavior, it is possible to conclude that the studied REE are reduced and oxidized at very similar potentials as in aqueous media.

The obtained results of the comparison of the electrochemical behavior of the studied REE allow us to propose the possibility of identifying REE by their cyclic voltammetry responses. Thus, Sm can be identified and quantified by its cathodic response or its anodic response and Nd by using the first anodic observed peak. For La and Y, no selective electrochemical response is observed.

#### 4. CONCLUSIONS

The voltammetric study of REE in BMPyr-DCA shows that for yttrium, lanthanum and neodymium, the reduction process involves the reduction of REE(III) to REE(0) that is carried out simultaneously with the cathodic decomposition of BMPyr-DCA. For samarium, a more complex reduction process is observed, involving first a reduction process from  $\text{Sm}^{3+}$  to  $\text{Sm}^{2+}$  and a second reduction involving, as for the other studied elements, the simultaneous reduction of samarium species with the reduction of BMPyr-DCA.

Concerning the anodic response of the formed reduced species of the REE, the observed behavior is similar for Y and La but quite different for Sm and Nd.

These differences allow for the proposal of electrochemical conditions associated with the peak potentials observed for the studied REE to identify and quantify these REE.

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