# Electrodeposition of Nd and Pr onto W from fluoride based melts
## *Elektrohemijsko taloženje Nd i Pr na W iz fluoridnih rastopa*

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**Abstract**

*Electrodeposition of neodymium and praseodymium metal from molten $NdF_3$+$PrF_3$+LiF+ 0.5wt.%$Pr_6O_{11}$+0.5wt.%$Nd_2O_3$ electrolytes on W was investigated using voltammetry at 1050 °C. The square wave voltammetry confirmed that Nd electrodeposition is a two-step reduction process: first, involving one electron exchange (Nd(III)→Nd(II)) and second, involving two electrons exchange (Nd(II)→Nd(0)). However, praseodymium deposition proceeds as an one-step process involving exchange of three electrons (Pr(III)→Pr(0)). Nd and Pr metals were electrodeposited applying potentiostatic mode. The working electrode surface was analyzed by X-ray diffraction after Nd and Pr co-deposition.*
*Keywords: neodymium; praseodymium; fluoride melts; SWV; XRD*

**Izvod**

*Elektrohemijsko taloženje neodijuma i prazeodijuma iz fluoridnog $NdF_3$+$PrF_3$+LiF+ 0.5wt.%$Pr_6O_{11}$+0.5wt.%$Nd_2O_3$ rastopa na W radnoj elektrodi ispitivano je pomoću voltametrijskih tehnika na 1050 °C. Voltametrija sa pravougaonim talasima (SWV, square wave voltammetry) potvrdila je da je elektrohemijsko taloženje Nd proces koji se odvija u dva koraka: prvi, uključuje razmenu od jednog elektrona (Nd(III) → Nd(II)) i drugi korak, uključuje razmenu dva elektrona (Nd(II) → Nd(0)). Međutim, taloženje prazeodijuma uključuje izmenu tri elektrona (Pr(III) → Pr(0)) u jednom koraku. Nd i Pr su elektrohemijski taloženi primenom potenciostatskog režima. Nakon elektrohemijskog taloženja Nd i Pr površina radne elektrode analizirana je rengensko-difrakcionom tehnikom.*
*Ključne reči: neodijum; prazeodijum; fluoridni rastopi; SWV; XRD*

## Introduction

As the demand for Nd-Pr alloys had increased over time, the design and creation of the new processes for providing sufficient amount of these rare earth elements are required [1–3]. Neodymium–iron–boron permanent magnets ($Nd_2Fe_{14}B$, or NdFeB), depending on the application, contains about 31–32 wt.% of rare earth elements (REEs), mainly neodymium and praseodymium (Nd+Pr) [4]. Due to the complexity associated with the continuous growth of rare earth solid wastes, a simple, and environmentally friendly recycling process will play an important role for future sustainable primary supply of REEs. There are several approaches to the recovery of rare earth elements from the end-of-live (EOL) magnets: hydrometallurgical and pyrometallurgical processes, liquid metal extraction, molten salt electrolysis [5,6]. Among these processes, molten salt electrolysis offers an attractive solution in lights of its high purity of end product, low energy consumption, and high efficiency [5]. For electrolytic production of neodymium and praseodymium

via molten salt electrolysis, in terms of efficiency and environmental footprint, molten fluorides or chlorides are commonly used as electrolytes [5].

In the present investigation concerning the electroreduction processes of neodymium(III) and praseodymium(III) ions in fluoride molten salts system we demonstrate that metallic neodymium and praseodymium can be electrodeposited on a chosen inert electrode. More specifically, the reaction mechanism of neodymium and praseodymium deposition was studied in the fluoride based molten salts containing the rare earth oxides, in order to ensure appropriate potential for increase of Nd and Pr metal deposited on the tungsten cathode surface.

## Experimental

Neodymium fluoride ($NdF_3$, ≥99.9%), praseodymium fluoride ($PrF_3$, ≥99.9%), lithium fluoride (LiF, ≥99.5%), neodymium oxide ($Nd_2O_3$, ≥99.9%) and praseodymium oxide ($Pr_6O_{11}$, ≥99.9%) were purchased from Treibacher, Althofen, Austria. The electrolyte composition was: $45.5wt.\%NdF_3+45.5wt.\%PrF_3+9wt.\%LiF+0.5wt.\%Pr_6O_{11}+0.5wt.\%Nd_2O_3$. The graphite crucible, filled with the salt mixture, was placed into the steel electrochemical cell, the lid was closed and the cell was placed into a resistance furnace. A three electrode configuration was employed, in which as a working electrode was used a tungsten 2 mm diameter rod (EWG 99.95%), reference electrode was made from tungsten (1 mm diameter rod) and the counter electrode was glassy carbon rod (>99.99% HTW SIGRADUR® G). The details of the electrochemical cell set up and procedure of electrolyte preparation have already been reported elsewhere [7,8]. The measurements started after the molten salt was stable at the experimental temperature of 1050 °C. The electrochemical measurements: cyclic voltammetry (CV), square wave voltammetry (SWV) and open-circuit chronopotentiometry, were controlled by an IviumStat potentiostat (5 A/10V; Ivium Technologies). The deposition was carried out in a potentiostic mode, which was monitored as current density versus time. The structure analysis of the deposit was revealed by X-ray diffraction (XRD), Philips PW 1050 powder diffractometer.

## Results and Discussion

It was cyclic voltammetry to be employed first in the study of electrochemical reactions related to Nd(III) and Pr(III) ions redox transitions on W working electrode in molten $NdF_3+PrF_3+LiF+0.5wt.\%Pr_6O_{11}+0.5wt.\%Nd_2O_3$ salts. Fig. 1 shows typical CV obtained on a W working electrode when cathodic end potential, $E_C$, was gradually swept from the initial potential, $E_I$, towards more negative values.

Within the applied potential range, the voltammograms exhibited three current waves $C_1$, $C_2$ and $C_3$ in the cathodic sections and corresponding anodic counterparts $A_1$, $A_2$ and $A_3$ in the anodic sections of the scanned potential range.

In the cathodic run peak $C_1$ starting at ≈ -0.400 V vs. W and its anodic counterpart $A_1$ at ≈ -0.360 V vs. W should be attributed to the redox transition Nd(III) ↔ Nd(II). At potentials negative compared to -0.400 V vs. W a second reduction peak $C_2$ at ≈ -0.520 V vs. W was observed. This peak we associate with electrodeposition of Nd, (Nd(II) + 2e$^-$ → Nd(0)). During the anodic scan direction the electrochemical dissolution of Nd is manifested at potential around -0.500 V vs. W, as an anodic peak $A_2$. Third cathodic peak $C_3$ starting from about -0.720 V vs. W can be assigned to electrochemical reduction of Pr(III) to Pr(0), and the anodic peak $A_3$ at -0.620 V vs. W is associated with the dissolution of previously deposited Pr metal, in other words Pr(0) → Pr(III).
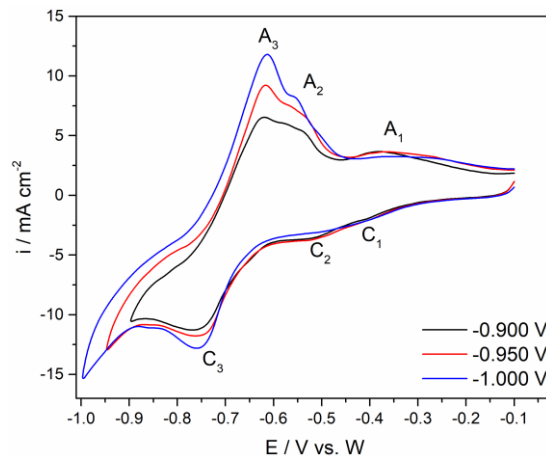
**Figure 1.** *CV recorded on W working electrode, $E_I$= -0.100 V vs. W to different cathodic end potential $E_C$, obtained with sweep rate of 100 mVs$^{-1}$ in NdF$_3$+PrF$_3$+LiF+0.5wt.%Pr$_6$O$_{11}$+0.5wt.%Nd$_2$O$_3$ electrolyte, T= 1050 °C.*

To further investigate the electrochemical co-deposition of neodymium and praseodymium from NdF$_3$+PrF$_3$+LiF+0.5wt.%Pr$_6$O$_{11}$+0.5wt.%Nd$_2$O$_3$ electrolyte, a set of square wave voltammograms (SWV) at different frequencies was obtained on W electrode. The results are shown in Fig. 2. The potentials of all three reduction current peaks recorded by SWV at: $C_1 \approx$ -0.450 V vs. W, $C_2 \approx$ -0.650 V vs. W, and $C_3 \approx$ -0.720 V vs. W correspond very well to $C_1$, $C_2$ and $C_3$ recorded in the voltammograms presented in Fig. 1 obtained within the same potential range under the same conditions. In the case of a reversible reaction, the electron transfer number can be expressed by Eq. (1) which is a mathematical analysis based on the half-peak width recorded by SWV:

$$W_{1/2} = 3.52RT/nF \tag{1}$$

where $W_{1/2}$ is the half-peak width (V), $T$ is the temperature (K), $R$ represents the universal gas constant (J mol$^{-1}$ K$^{-1}$), $n$ is the number of exchanged electrons, and $F$ is the Faraday constant (96485 C mol$^{-1}$).



a)



b)
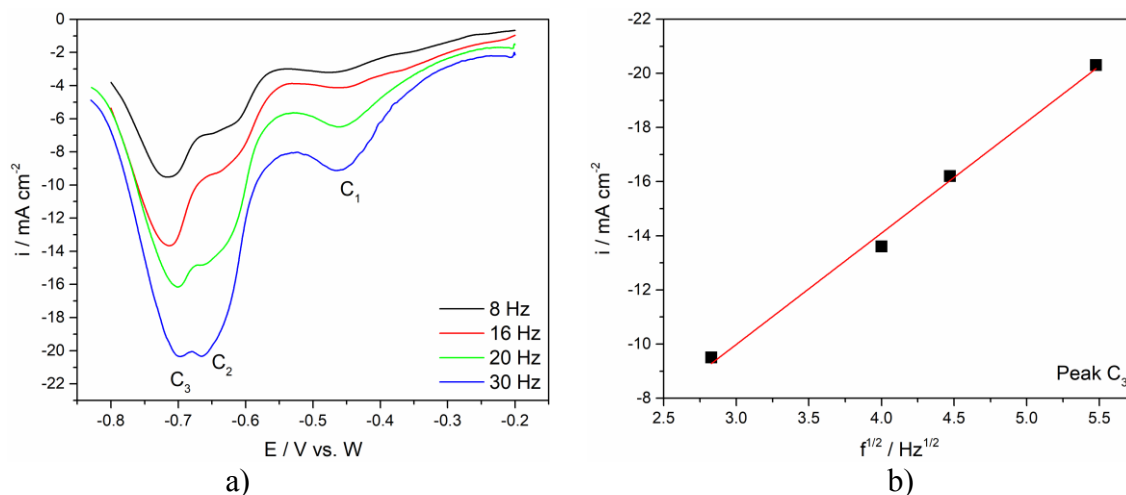
**Figure 2.** *(a) SWV obtained with different frequencies on W WE; pulse height: 25 mV; potential step: 1 mV; electrolyte NdF$_3$+PrF$_3$+LiF+0.5wt.%Pr$_6$O$_{11}$+0.5wt.%Nd$_2$O$_3$; (b) Variation of the peak current density vs. the square root of the frequency in the Fig. 2a) for peak C$_3$.*

The plot of the peak $C_3$ current density on SWV from Fig. 2a) *vs.* the square root of frequency is presented in Fig. 2b). It was found to be a linear relationship. Since the criterion of linearity for the peak $C_3$ was established Gaussian fitting model was applied and the exchange electron number was calculated using Eq. (1) [6,9]. It was found that the exchanged electron number for peak $C_3$ is 2.87, close to 3. Accordingly it was concluded that the reduction of praseodymium(III): namely Pr(III) → Pr(0), on W in this electrolyte is only one electrochemical three electron exchange step. This conclusion confirmed that the electrode reactions reflected by the current waves $C_2/A_2$ and $C_1/A_1$ can be assigned to the redox transition of Nd(III) ions to Nd metal in two steps: Nd(III) ↔ Nd(II) and Nd(II) ↔ Nd(0). This is in accordance with previous literature reports [7–9].

In order to establish Nd and Pr co-deposition a potentiostatic deposition at the potential negative to the $C_3$ peak potentials recorded in Fig. 1 and 2a) was performed, and W working electrode surface was analyzed afterwards by the XRD, Fg. 3.
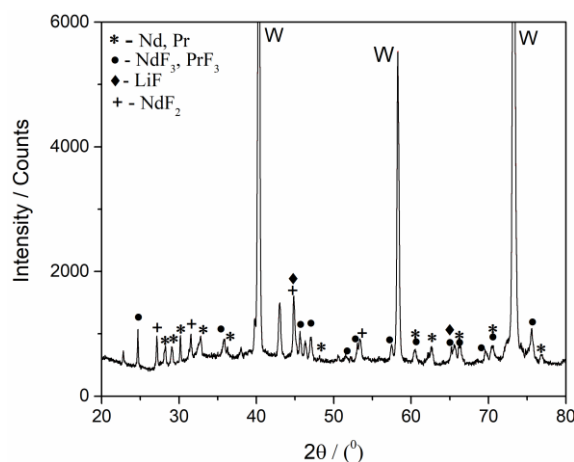


**Figure 3.** *XRD pattern of the W working electrode after deposition at -0.900 V vs. W for 240 min, from molten $NdF_3+PrF_3+LiF+0.5wt.\%Pr_6O_{11}+0.5wt.\%Nd_2O_3$ electrolyte, at 1050 °C, (the solidified electrolyte was removed from the electrode).*

The diffraction peaks at around $2\theta$ values: 28.1°, 29.1°, 30.2°, 32.8°, 36.3°, 48.1°, 60.5°, 62.6°, 67.0°, 70.4°, 76.8°, 77.3°, have to be attributed to both metals, Nd and Pr [JCPDS No. 03-065-3424 and JCPDS No. 01-089-2921]. Actually, both metals exhibit similar chemical properties, hexagonal crystal lattice and very similar lattice parameters. The presence of melt residue, $NdF_3$, $PrF_3$, LiF in the difractogram could not be avoided. However, $NdF_2$ was also detected and it seems that it was formed through disproportionation reaction between Nd metal electrodeposited and Nd(III) ions in the electrolyte: Nd(0) + 2Nd(III) → 3Nd(II). This is in accordance with previous literature reports by some other authors describing neodymium electrodeposition from neodymium oxyfluoride melts, at temperatures close to or above 1323 K [7–9].

**Conclusion**

In order to investigate electrochemical co-deposition of Nd and Pr, the electrochemical behaviour of Nd(III) and Pr(III) ions in molten $NdF_3+PrF_3+LiF+0.5wt.\%Pr_6O_{11}+0.5wt.\%Nd_2O_3$ were first studied on W electrode. Cyclic voltammetry and square wave voltammetry indicated that the reduction of Nd(III) ions to the metal proceeds as a two-step reduction process: Nd(III) → Nd(II) and Nd(II) → Nd(0), whilst the reduction of Pr(III) ions to the metal is a one-step reduction process: Pr(III) → Pr(0). Neodymium and praseodymium were successfully electrodeposited on W cathode by applying constant potential, from fluoride based Nd, Pr and Li molten salts containing rare earth oxides ($Nd_2O_3$ and $Pr_6O_{11}$). The findings of this study could be a promising final link towards intended integral recycling process for used NdFeB magnet scraps.

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