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# PROCEEDINGS

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## Electrochemical co-deposition of neodymium and praseodymium from oxyfluoride molten salts

### *Elektrohemijsko taloženje neodijuma i prazeodijuma iz oksifluoridnih rastopa*

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#### **Abstract**

*The demand for rare earth elements (REE) have become extremely high following their increased application in high-tech products. It is particularly pronounced in fabrication of powerful magnets used in green technology. To secure long term sustainable use of REE, recycling and recovery of these materials became of significant importance. The REE are mostly extracted via electrolysis from their oxides, and therefore the efficiency of the electrolytic process became dependent on the degree of the rare earth metal oxides dissolution in an appropriate electrolyte combination. The combinations often include rare earth fluorides, alkali metal fluoride, usually LiF, or alkali earth metals fluorides. Besides reducing the liquidus temperature, LiF also functions as a dilution agent for the rare earth oxides. In the present study we aim to provide an understanding of the electrochemical behaviour of neodymium and praseodymium in the fluoride based melts composition containing different LiF concentration. Comparison of the experimental results obtained from chosen electrolyte systems, should enable to precisely incorporate adjustable parameters which could favor more deposited neodymium and praseodymium metal remaining on an inert working substrate. Based on the data collected from the electrochemical techniques, in molten fluoride systems enriched with rare earth oxides, it was concluded that the reduction process of Nd(III) ions proceeds via two-steps, and Pr(III) ions in one step, e.g. Nd(III)/Nd(II), Nd(II)/Nd(0) and Pr(III)/Pr(0). The values of the peak potentials attributed to the Nd(III) and Pr(III) ions reduction processes presented by the cyclic voltammograms in both electrolyte systems were very similar. Experimentally measured current densities recorded during Nd and Pr metals electrodeposited applying potentiostic mode from the 65.5wt%NdF<sub>3</sub>+21.75wt%PrF<sub>3</sub>+12.5wt%LiF+1wt.%Pr<sub>6</sub>O<sub>11</sub>+1wt.%Nd<sub>2</sub>O<sub>3</sub> electrolyte were substantially lower than (almost three times) those obtained under the same conditions from 45.5wt%NdF<sub>3</sub>+45.5wt%PrF<sub>3</sub>+9wt%LiF+1wt.%Pr<sub>6</sub>O<sub>11</sub>+1wt.%Nd<sub>2</sub>O<sub>3</sub> electrolyte. The XRD analysis confirmed better Nd/Pr deposition efficiency in the electrolyte with lower LiF content.*

**Keywords:** neodymium; praseodymium, LiF, fluoride molten salt

#### **Izvod**

*Metali retkih zemalja (REE) postali su veoma traženi zbog njihove sve veće primene u visokotehnološkim proizvodima. Pretežno se koriste u proizvodnji permanentnih magneta koji se najviše upotrebljavaju u tehnologijama održivog razvoja. Da bi se obezbedila dugoročna i održiva upotreba REE reciklaža ovih metala je postala imperativ. REE se uglavnom dobijaju elektrolizom iz svojih oksida, pa je stoga efikasnost procesa elektrolize zavisna od stepena rastvaranja oksida metala retkih zemalja u elektrolitu odgovarajućeg sastava. Elektroliti se uglavnom sastoje od fluorida retkih zemalja, fluorida alkalnih metala, najčešće LiF, ili fluorida zemnoalkalnih metala. Pored smanjenja temperature topljenja elektrolita LiF se koristi i kao rastvarač oksida retkih zemalja. U ovom radu*

*ispitali smo elektrohemijsko ponašanje neodijuma i prazeodijuma u elektrolitima na bazi fluorida sa različitim koncentracijama LiF. Poređenje dobijenih eksperimentalnih rezultata iz izabranih elektrolita, trebalo bi da nam omogući optimizaciju parametara koji bi favorizovali veći prinos neodijuma i prazeodijuma na inertnoj radnoj elektrodi. Na osnovu rezultata dobijenih primenom elektrohemijskih tehnika iz fluoridnih elektrolita obogaćenih oksidima metala retkih zemalja, zaključili smo da se preces redukcije Nd(III) jona odvija u dva koraka, a Pr(III) jona u jednom koraku, odnosno, Nd(III)/Nd(II), Nd(II)/Nd(0) i Pr(III)/Pr(0). Potencijali vrhova talasa pripisani procesima redukcije jona Nd(III) i Pr(III), predstavljeni cikličnim voltamogramima dobijenih u oba ispitivana elektrolita, imali su veoma približne vrednosti. Eksperimentalno merene gustine struje dobijene tokom elektrohemijskog taloženja Nd i Pr primenom potenciostatskog režima iz 65.5wt%NdF<sub>3</sub>+21.75wt%PrF<sub>3</sub>+12.5wt%LiF+1wt.%Pr<sub>6</sub>O<sub>11</sub>+1wt.%Nd<sub>2</sub>O<sub>3</sub> elektrolita bile su višestruko manje (tri puta) od vrednosti dobijenih pod istim uslovima iz 45.5wt%NdF<sub>3</sub>+45.5wt%PrF<sub>3</sub>+9wt%LiF+1wt.%Pr<sub>6</sub>O<sub>11</sub>+1wt.%Nd<sub>2</sub>O<sub>3</sub> elektrolita. XRD analiza potvrdila je veću količinu taloga Nd/Pr iz elektrolita sa nižom koncentracijom LiF.*

**Ključne reči:** neodijum; prazeodijum; LiF; fluoridni rastop

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