Electrochemical and thermodynamic properties of neodymium in molten chlorides

A. Novoselova, V. Smolenski
Institute of High-Temperature Electrochemistry UD RAS, Russian Federation

Abstract

This work presents the electrochemical study of $NdCl_3$ solutions in fused LiCl-KCl-CsCl eutectic and individual CsCl in the temperature range 573–943 K using inert molybdenum electrodes. It has been shown that Nd^{3+} ions are reduced to metallic neodymium through two consecutive steps: $Nd^{3+} + \bar{e} \rightarrow Nd^{2+}$ and $Nd^{2+} + 2\bar{e} \rightarrow Nd^{0}$. The electroreduction of Nd^{3+} to Nd^{2+} ions was found to be reversible and the electroreduction of Nd^{2+} to Nd^{0} was found to be irreversible. The chemical stability of Nd^{2+} ions in fused neodymium solutions was investigated at different temperatures. It was determined that the compound $NdCl_2$ is not stable in molten salts at high temperatures (above 810-840 K). The results of a study of the Nd^{3+}/Nd^{2+} couple redox potentials vs. Cl^-/Cl_2 reference electrode in a wide temperature range in molten chlorides was carried out by direct potentiometric method. Apparent standard redox potentials of the couples $E^*_{Nd^{3+}/Nd^{2+}}$ were determined in fused LiCl-KCl-CsCl eutectic. Basic thermodynamic properties of the reaction $NdCl_{2(l)} + ½\ Cl_{2(g)} \Leftrightarrow NdCl_{3(l)}$ were calculated.

Introduction

Electrowinning processes in molten salt baths have been applied for the production of reactive metals such as lanthanides [1] [2]. The production of neodymium metal has been known as a problem in some cases because of its low current efficiency. It has been pointed out that the reaction of produced Nd metal with Nd^{3+} ions in the melt causes the low current efficiency [2-5]. Formation of Nd^{2+} in molten salts has been suspected. Studies on the equilibrium between Nd metal, Nd^{2+}, and Nd^{3+} ions in molten salts are necessary to improve the electrowinning process of neodymium metal.

They are also useful for developing the pyrochemical reprocessing of spent nuclear fuels, where Nd and other lanthanides (Ln) have to be removed from actinides (Ac). The aim of the separation techniques which are currently being investigated is to optimise the recovery efficiency of minor actinides, minimising at the same time the fission product content in the final product. Special attention is paid to lanthanides mainly due to their neutronic poison effect and the high content in the spent fuel. In addition, lanthanides have similar chemical properties hence separation between these groups of elements (Ln and Ac) is very difficult. For this reason, a good knowledge of the basic properties of Ac [6-17] and Ln [18-35] in the proposed separation media is very important.

The analyses of the literature data show that there has been no clear evidence for the existence of Nd^{2+} in molten salts. There is little information of spectra Nd^{2+} as solid compounds [36], in organic solvents [37] [38] and in molten salts [39] [40]. Also, the electrochemistry of Nd^{3+} ions was investigated in fused LiCl-KCl eutectic by transient electrochemical technique [41-44].

The present study analysed the electrochemical behaviour of Nd^{3+} ions, the chemical stability of Nd^{2+} ions and thermodynamic properties of neodymium compounds in fused CsCl and LiCl-KCl-CsCl eutectic in a large temperature range by transient electrochemical technique and potentiometric method.

Experimental

The solvents KCl (>99.5% certified purity), and CsCl (>99.9% certified purity) were cleaned under vacuum in the temperature range 293 to 773 K. Then the reagents were fused in an atmosphere of dry argon. The solvents were purified by the operation of direct crystallisation [45]. Solvent LiCl (99.99% certified purity) was used as purchased from Sigma-Aldrich. $NdCl_3$ (99.99% certified purity) was purchased from Sigma-Aldrich. The prepared reagents were saved in glass capsules in inert atmosphere in a dry glovebox.

Electrochemical measurements were carried out using an Autolab PGSTAT30 potentiostat-galvanostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9). Different transient electrochemical techniques were used such as cyclic and square wave voltammetry, as well as potentiometry at zero current. The experiments were carried out under inert argon atmosphere using an electrochemical quartz sealed cell with a three-electrode set-up. The inert working electrode was prepared using a 1 mm metallic Mo wire (Goodfellow, 99.9%). It was immersed into the molten bath between 3 – 7 mm. The active surface area was determined after each experiment by measuring the immersion depth of the electrode. The counter electrode consisted of a 3 mm vitreous carbon rod (SU - 2000) with a large surface. The Cl^-/Cl_2 electrode is the reference electrode. It can be used for the direct thermodynamic calculations [46].

The potentiometric study was carried out with an Autolab PGSTAT30 potentiostat-galvanostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9) using potentiometry (zero current) and coulometry methods. The electrochemical set-up for

potentiometric investigations has been described in detail in [35]. The inert working electrode was prepared using a molybdenum plate (S = 1.0 to 1.5 sm^2) which was located in the BeO crucible with the investigated melt. During the experiments Nd^{3+} ions were electrochemically reduced to Nd^{2+} ions up to the ratio Nd^{3+}/Nd^{2+} equals one using the galvanostatic method. The ratio of Nd^{3+}/Nd^{2+} in the experiments was controlled by coulometric method and by chemical analyses of solid samples after the experiments. The Cl^-/Cl_2 electrode was used as reference electrode.

The neodymium total concentration was determined by taking samples from the melt, which were dissolved in nitric acid solutions and then analysed by ICP-MS. The concentration of Nd^{2+} ions in the investigated melts was determined by volumetric method of analysis.

Results and discussion

Transient electrochemical methods

Cyclic voltammetry was carried out on inert molybdenum electrode in fused LiCl-KCl-CsCl-$NdCl_3$ solution in the temperature 773 K at different scan rates, (see Figure 1). The figure shows two cathodic waves at potentials of –3.223 V and –3.394 V and their corresponding anodic waves at –3.072 V and –2.861 V vs. the Cl^-/Cl_2.

The short polarisation of the molybdenum electrode at potentials of the 1st and the 2nd cathodic waves (Figure 1) shows the absence of any plateau on the dependence potential-time, Figure 2 (1, 2, 3) for the first wave and the existence of clear plateau for the second wave, Figure 2 (4, 5). It means that the cathodic process at the potentials of the 1st wave does not connect with the deposit of solid phase on the surface of inert working electrode whereas at the potentials of the 2nd wave the metallic neodymium was precipitated.

The reaction mechanism of the cathodic reduction of Nd^{3+} ions up to metal Nd was investigated by analysing the voltammetric curves obtained at several scan rates (Figure 1). The figure shows that for the reduction of Nd^{2+} to Nd^0 (E = –3.394 V) the cathodic potential peak shift to more negative side and the anodic potential peak shift to more positive side with the increase in sweep rate. Cathodic and anodic peak current is directly proportional to the square root of the polarisation rate. From these results and according to the theory of the linear sweep voltammetry technique [47] it is concluded that the redox system Nd^{2+}/Nd^0 is irreversible, controlled by the rate of charge transfer.

The number of electrons exchanged in the reduction of Nd^{3+} to Nd^{2+} ions for a reversible system was calculated from cyclic voltammograms for the redox couple Nd^{3+}/Nd^{2+} by expression [48]:

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d - i}{i} \tag{1}$$

where E is a cathodic potential (V), $E_{1/2}$ is a half-wave potential (V), R is the ideal gas constant (J K^{-1} mol^{-1}), T is the absolute temperature (K), n is the number of electrons exchanged, F is the Faraday constant (96 500 C mol^{-1}), i_d is the limit diffusion current density and i is the current density. The number of electrons exchanged determined by this way was 0.99 ± 0.02.

The electrochemical reduction process of Nd^{3+} ions in the eutectic has been identified to be a two-step process via Nd^{2+} ions:

$$Nd^{3+} + \bar{e} \leftrightarrow Nd^{2+} \tag{2}$$

$$Nd^{2+} + 2\bar{e} \leftrightarrow Nd^0 \tag{3}$$

Figure 1: Cyclic voltammograms of fused LiCl-KCl-CsCl-$NdCl_3$ (m($NdCl_3$) = $1.53 \cdot 10^{-1}$ mol kg^{-1}) solution at different scan rates on molybdenum electrode (S = 0.16 cm^2) at 773 K

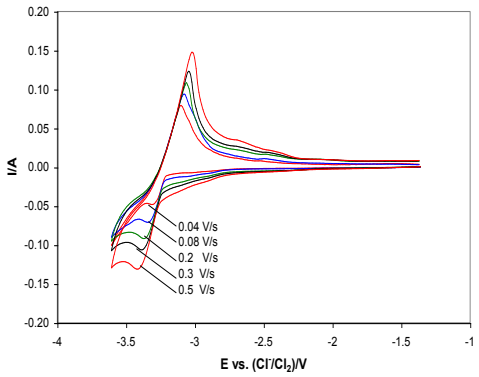
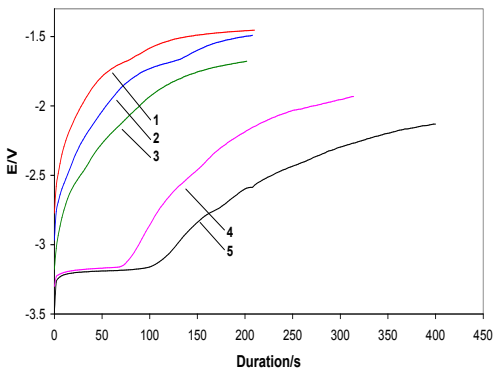


Figure 2: The dependence potential–time, obtained after short polarisation of Mo electrode at different potentials in LiCl-KCl-CsCl-$NdCl_3$ solution at 773 K, m($NdCl_3$) = $1.53 \cdot 10^{-1}$ mol kg^{-1}



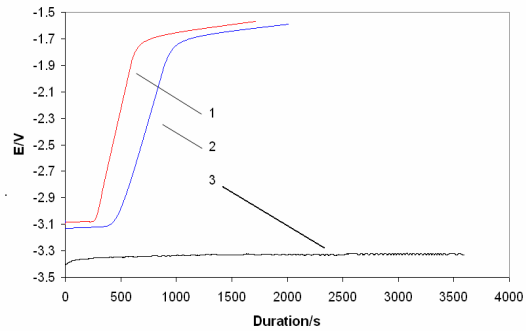
1 – $E_{dep.}$ = −2.8 V, t = 10 s; 2 – $E_{dep.}$ = −3.0 V, t = 8 s; 3 – $E_{dep.}$ = −3.2 V, t = 6 s; 4 – $E_{dep.}$ = −3.4 V, t = 6 s; 5 – $E_{dep.}$ = −3.6 V, t = 4 s.

It is known that the compound $NdCl_2$ is not chemically stable at temperatures higher than 810 K [49] and the following disproportionate reaction takes place:

$$3\ NdCl_2 \leftrightarrow 2\ NdCl_3 + Nd \tag{4}$$

It has been shown that the reaction (4) shifts to the right and is completed within several minutes at high temperatures, Figure 3 (1, 2). At low temperatures the reaction (4) shifts to the left, Figure 3 (3). The analysis confirms literature data [40] [44] [49] that the compound $NdCl_2$ is not stable in molten salts at high temperatures. The conclusion of this study is that it is possible to use *emf* method for the potentiometric investigation of neodymium compounds only at temperatures below 798 K in fused chloride solvents.

Figure 3: Equilibrium potentials of $E_{Nd^{3+}/Nd^{2+}}$ *vs.* the concentration ratio of [Nd^{3+}]/[Nd^{2+}] in molten CsCl (1, 2) and LiCl-KCl-CsCl (3). 1 - Q = 25.7 A·c, T = 943 K, [Nd^{3+}]/[Nd^{2+}] = 2.344; 2 - Q = 77.0 A·c, T = 943 K, [Nd^{3+}]/[Nd^{2+}] = 1.098; 3 - Q = 105.0 A·c, T = 558 K, [Nd^{3+}]/[Nd^{2+}] = 1.098



Potentiometric measurements

Variation of the equilibrium potential of the couple Nd^{3+}/Nd^{2+} as a function of the natural logarithm ratio of concentrations [Nd^{3+}] and [Nd^{2+}] in fused LiCl-KCl-CsCl eutectic at 668 K obtained by *emf* method on molybdenum indicated electrode obeys the Nernst's law, taking into account the value of thermo-*emf* between molybdenum and carbon electrodes (exp. 5) [46]:

$$E_T^{Mo-C} = -0.0076 + 1.74 \cdot 10^{-5} T \pm 0.0008 \ V \tag{5}$$

$$E_{Nd(III)/Nd(II)} = -(3.291 \pm 0.001) + (0.056 \pm 0.001) \times \ln([Nd^{3+}]/[Nd^{2+}] \pm 0.001 \quad V \tag{6}$$

The number of exchanged electrons (n) taking part in the process of the electrochemical reduction was determined from the slope of the straight line. From Equations (6) the number of exchanged electrons for the reaction (2) was 1.02 ± 0.01.

The temperature dependences of apparent standard redox potentials of Nd^{3+}/Nd^{2+} couple in fused LiCl-KCl-CsCl eutectic was linear in the whole temperature range studied, Figure 4. The experiment data were fitted to the following equation:

$$E^*_{Nd(III)/Nd(II)} = -(3.855 \pm 0.016) + (8.7 \pm 0.2) \times 10^{-4} T \pm 0.003 \quad V \qquad [603\text{-}723\ K] \tag{7}$$

Using the values of the apparent standard redox potentials, the formal free Gibbs energy changes and the apparent equilibrium constants of the redox reaction (8):

$$NdCl_{2(1)} + ½\ Cl_{2(g)} \leftrightarrow NdCl_{3(1)} \tag{8}$$

can be calculated using the well-known expressions:

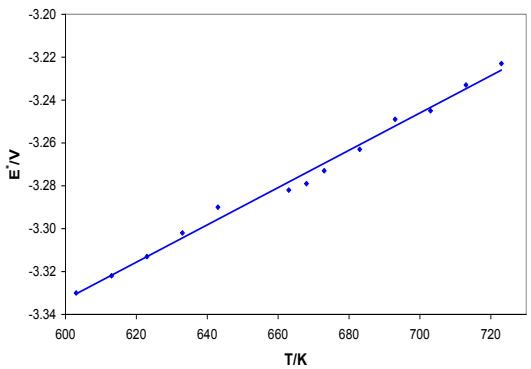
$$\Delta G^* = nFE^*_{Nd(III)/Nd(II)} \tag{9}$$

$$\Delta G^* = -RT \ln K^*_{eq.} \tag{10}$$

The temperature dependence of the Gibbs free energy change can be described by the following equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{11}$$

Figure 4: Apparent standard redox potentials of the couple Nd^{3+}/Nd^{2+} in fused LiCl-KCl-CsCl eutectic as a function of the temperature



The experimental data were fitted to the following equation:

$$\Delta G^{*} = -(372.0 \pm 1.5) + (84.0 \pm 1.9) \cdot 10^{-3} T \pm 0.3 \quad kJmol^{-1} \tag{12}$$

By the expression (10) one can calculate the apparent equilibrium constants for the redox reaction (8) in molten solution. The temperature dependence is the following:

$$\ln K^{*}_{eq.} = -10.11 + \frac{(44769 \pm 7)}{T} \pm 0.01 \tag{13}$$

It is also possible to estimate the equilibrium chlorine gas pressure above an alkali metal chloride melt containing neodymium tri- and dichlorides for the reaction (14):

$$NdCl_{3(l)} \leftrightarrow NdCl_{2(l)} + ½\ Cl_{2(g)} \tag{14}$$

by the well-known Equation (15) [46]. Such calculations were performed for the concentration ratio of $[Nd^{3+}]/Nd^{2+}]$ equals one.

$$\frac{RT}{2F}\ln(P_{Cl_2}) = E^{*}_{Nd^{3+}/Nd^{2+}} + \frac{RT}{F}\ln\left(\frac{[Nd^{3+}]}{[Nd^{2+}]}\right) \tag{15}$$

The calculated values are summarised in Table 1. It is obvious that with the increase in the temperature the apparent standard redox potentials and the formal free Gibbs energy change are shifted to more positive side, and the equilibrium constant of the reaction (8) is decreased. The value of an initial chlorine gas pressure above the neodymium solution melts are also increased with the temperature. It depends on the decrease in the stability of chloride complexes with the increase in the temperature [43].

Table 1: Data of apparent standard redox potentials, formal free Gibbs energy change, and equilibrium gas pressure of chlorine above the melt for neodymium compounds in fused LiCl-KCl-CsCl eutectic at different temperatures

Thermodynamic properties	573 K	623 K	673 K	723 K
E^*/V	–3.356	–3.313	–3.269	–3.226
ΔG^*/(kJ·mol^{-1})	–323.9	–319.7	–315.5	–311.3
ΔH^*/(kJ·mol^{-1})	–372.0			
ΔS^*/(J·K^{-1}·mol^{-1})	84.0			
$K^*_{eq.}$	$3.46 \cdot 10^{29}$	$6.54 \cdot 10^{26}$	$3.14 \cdot 10^{24}$	$3.16 \cdot 10^{22}$
P_{Cl_2} / P_0	$8.35 \cdot 10^{-60}$	$2.33 \cdot 10^{-54}$	$1.01 \cdot 10^{-49}$	$9.98 \cdot 10^{-46}$

Note: Apparent standard redox potentials are given in the molar fraction scale.

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