ELECTROCHEMICAL AND THERMODYNAMIC PROPERTIES OF NEODIMIUM IN MOLTEN CHLORIDES

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Abstract

Pyrochemical separation processes in molten salts, particularly molten chlorides, have more recently been proposed as a promising option in the nuclear fuel cycle for the future, mainly due to progress in the assessment of new concepts for transmutation and the corresponding fuel cycles and several processes have already been developed for the recovery of minor actinides from spent nuclear fuels and high level radioactive liquid wastes. Nd is one of major fission product elements having larger neutron capture cross sections, and hence its removal in the pyrochemical reprocessing is desired.

The goal of these investigations is to determine the electrochemical properties of neodymium (III) and the stability of neodymium (II) ions in fused CsCl and LiCl-KCl-CsCl eutectic at large temperature range by transient electrochemical technique and *emf* method.

It was established by transient electrochemical technique that on an inert electrode Nd^{3+} ions are reduced to metallic neodymium through two consecutive steps:

$Nd^{3+} + \bar{e} \rightarrow Nd^{2+}$ (1)

$Nd^{2+} + 2\,\bar{e} \rightarrow Nd^{0}_{(metal)}$ .. (2)

The following disproportionate reaction of Nd^{2+} takes place in molten salts at high temperatures:

$3\,NdCl_{2(l)} = 2\,NdCl_{3(l)} + Nd^{0}_{(metal)}$ ..... (3)

It has been shown that the reaction (3) is shift to the right and completed within several minutes in both solvents. So the compound $NdCl_2$ is not stable in investigated melts at temperatures above 798 K.

The value of an apparent standard redox potential of $E^{*}_{Nd^{3+}/Nd^{2+}}$ *vs.* Cl^{-}/Cl_2 reference electrode was calculated at the temperature range 573-723 K in fused LiCl-KCl-CsCl eutectic by *emf* method:

$$E^{*}_{Nd^{3+}/Nd^{2+}} = -(3.855\pm0.016)+(8.7\pm0.2)\cdot10^{-4}\cdot T\pm0.003,\ V \quad (4)$$

Basic thermodynamic properties of the reaction (5) were calculated and presented in Table:

$NdCl_{2(l)} + ½\,Cl_{2(g)} \Leftrightarrow NdCl_{3(l)}$. (5)

Basic thermodynamic properties of neodymium compounds in fused LiCl-KCl-CsCl eutectic at the temperature range 573-723 K. Apparent standard redox potentials Nd^{3+}/Nd^{2+} are given in the molar fraction scale.

Table

Thermodynamic properties	573 K	623 K	673 K	723 K
E^*/V	–3.356	–3.313	–3.269	–3.226
$\Delta G^*/(kJ\cdot mol^{-1})$	–323.9	–319.7	–315.5	–311.3
$\Delta H^*/(kJ\cdot mol^{-1})$	–372.0			
$\Delta S^*/(J\cdot K^{-1}\cdot mol^{-1})$	84.0			
$K^*_{eq.}$	$3.46\cdot10^{29}$	$6.54\cdot10^{26}$	$3.14\cdot10^{24}$	$3.16\cdot10^{22}$
P_{Cl_2} / P_0	$8.35\cdot10^{-60}$	$2.33\cdot10^{-54}$	$1.01\cdot10^{-49}$	$9.98\cdot10^{-46}$