ELECTROCHEMICAL AND THERMODYNAMIC PROPERTIES OF THULIUM IN MOLTEN CHLORIDES

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Abstract

Actinides (An) recycling by separation and transmutation are considered worldwide as one of the most promising strategies for more efficient use of the nuclear fuel as well as for nuclear waste minimization, thus contributing to make nuclear energy sustainable. Pyrochemical separation techniques offer some potential advantages compared to the hydrometallurgical processes to separate An from lanthanides (Ln) contained in the irradiated fuel.

The goal of these investigations is to determine the electrochemical and thermodynamic properties of thulium compounds in molten alkali metal chlorides at large temperature region by transient electrochemical technique and *emf* method.

It was established that on an inert electrode Tm^{3+} ions are reduced to metallic thulium through two consecutive steps:

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

$$Tm^{2+} + 2\,\bar{e} \rightarrow Tm \quad (2)$$

The electroreduction of Tm^{3+} to Tm^{2+} ions was found to be reversible at low scan rates being controlled by the rate of the mass transfer and irreversible at high scan range (> 0.1 V s^{-1}) being controlled by the rate of charge transfer.

The diffusion coefficient of *Tm(III)* complex ions was determined at different temperatures. Arrhenius law was verified by plotting the variation of the logarithm of the diffusion coefficient *vs*. reverse temperature.

The results of a study of the Tm^{3+}/Tm^{2+} couple redox potentials *vs*. Cl^-/Cl_2 reference electrode at wide temperature range in molten chlorides was carried out by direct potentiometric and cyclic voltammetry methods. Apparent standard redox potentials of the couples $E^*_{Tm^{3+}/Tm^{2+}}$ were determined in different solvents. Basic thermodynamic properties of the reaction (3) were calculated

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

The comparison of the base thermodynamic properties of Tm compounds in molten alkali metal chlorides at 973 K. Apparent standard redox potentials Tm^{3+}/Tm^{2+} are given in the molar fraction scale.

Thermodynamic properties	NaCl-KCl	NaCl-KCl-CsCl	NaCl-2CsCl	CsCl
E^*/V	– 2.529	– 2.721	– 2.733	– 2.822
$\Delta G^*/(kJ\cdot mol^{-1})$	– 244.1	– 262.6	– 263.6	– 272.3
$\Delta H^*/(kJ\cdot mol^{-1})$	– 340.0	– 354.1	– 364.2	– 388.8
$\Delta S^*/(J\cdot K^{-1}\cdot mol^{-1})$	98.5	94.5	103.2	119.7
$K^*_{eq.}$	$7.76\cdot10^{14}$	$1.31\cdot10^{14}$	$1.44\cdot10^{14}$	$4.40\cdot10^{14}$
P_{Cl_2} / P_0	$6.11\cdot10^{-27}$	$5.86\cdot10^{-29}$	$3.50\cdot10^{-29}$	$5.61\cdot10^{-30}$