Electrochemical studies on cerium(III) in molten fluoride mixtures

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Abstract: This study aims to determine the principal electrochemical characteristics of the electrodeposition of cerium metal from molten fluoride systems. The cathodic process of Ce^{3+} ions in LiF-NaF and LiF-NaF-CaF$_2$ molten salts was studied using electrochemical techniques as steady state and cyclic voltammetry methods. The decomposition potential (E_d) and the overvoltage(η) were determined for NaCeF$_4$ using current-potential curves under galvanostatic conditions. The E_d was found to be 2.025 V in LiF-NaF and 2.045 V in LiF-NaF-CaF$_2$. It was also found that the ohmic drop potential (E_Ω) was not dependent on NaCeF$_4$ concentration and it rose as the current intensity increased. The overvoltage (η) was determined from the polarization curves and the Tafel coefficients and kinetic parameters were calculated on the assumption that the process constitutes of direct discharge of Ce^{3+}, with no solvent-solute interaction. In order to elucidate the cathodic process the investigation by cyclic voltammetry technique was finally used. From the evolution of the voltammograms we concluded that the electrochemical reduction of Ce^{3+} ion was actually a reversible process on the molybdenum electrode and cathodic reduction of Ce^{3+} took place in one single step involving three electron exchanges.

Keywords: cerium; molten salts; lanthanides; NaCeF$_4$; electrolysis; cyclic voltammetry

Cerium is the most abundant and the most widely used one of the rare earth metals (RE), making up about 0.0046% of the Earth's crust by weight. It is found in a number of minerals and its commercial applications are numerous. They include catalysts, additives to fuel to reduce emissions and to glass and enamels to change their color. The relatively high prices of the RE elements results not from their rarity but from the extreme difficulty of extracting them from their ores and, more significantly, purifying them.

From the late 1950's a considerable volume of work has been expended on the issue of obtaining higher purity lanthanide metals.

Molten salts have been used in industrial metallurgical processes for many years and in the last ~15 years many attempt was made in order to obtain purity refractory and rare earth metal by electrolysis in molten salts[1].

The most efficient method for the production of high purity rare earth metals was found to be the electrowinning in molten salts and there are many reports on the electrochemical studies on rare earth ions and some of them are presented in the references[2–7].

A molten fluoride bath has a great advantage compared with the chloride bath as high purity metal is obtained with improved current efficiency[8]. However, the molten fluoride bath has the disadvantage of higher melting point and aggressive corrosion. Cerium is the most abundant one of the rare earth metals. Rare earth metals are the elements in row 6 of the periodic table. The rare earth elements are not really rare. In fact, cerium ranks about number 26 in abundance among elements found in the Earth's crust. Cerium was the first rare earth element to be discovered and is an iron-gray metal with a melting point of 1068.15 K that easily reacts with other elements.

This study is a part of a systematic investigation on the alternative method for obtaining metallic cerium by using molten fluorides (in this case eutectic compositions of LiF-NaF and LiF-NaF-CaF$_2$) as a solvent while the solute was the complex of cerium(III) fluoride and sodium fluoride, NaCeF$_4$ (50 mol.% NaF and 50 mol.% CeF$_3$, T_e=999.15 K). Previous papers described the synthesis of this complex and its crystallographic parameters[9,10].

The purpose of this study was to determine the principal electrochemical characteristics of the electrodeposition of cerium metal from molten fluoride systems.

1 Experimental

1.1 Reagents

The used fluorides (NaF, LiF, CaF$_2$ and CeF$_3$) were p.a. grade reagents from Merck and Flucka. Every fluorinated compound was dehydrated under vacuum heating. The NaCeF$_4$ solute was selected from all the compounds formed by CeF$_3$ with alkali fluorides because it was easily synthesized and was not as hygroscopic as the compounds formed with potassium.

1.2 Apparatus and procedure

The experimental setup used in our electrochemical studies consists of three parts: reaction system (electrical furnace-electrochemical cell), atmosphere control (vacuum and argon gas flushing system) and electronic equipment for electrochemical investigation. The details for the assembly and working procedure were described previously[11,12].

The overpotential was determined by current-potential measurements in a stationary regime under galvanostatic conditions. Variable current steps between 20–50 mA were applied at a rate of 2–3 steps/min. These steps were higher than those usually applied for this type of determinations as $NaCeF_4$ electrolysis proceeds of very high current densities and potentials (specific for lanthanide compound electrolysis).

The cyclic voltammetry was performed by using a Volta-Lab 050-Radiometer potentiostat with Volta Master-4 packaged software. The potential scan rate was between 0.05–0.3 V/s. A SU-2000 type glassy carbon crucible served both as a container for the melt and counter electrode. This was placed in a hermetically sealed retort which could be filled with purified argon (produced by Air Liquid-France with impurities ≈1 ppm). The melt temperature was maintained ±2 ºC with an Alcatel thermoregulator. The voltammograms were registered on a Mo electrode (ϕ=2 mm) by a Pt quasi-reference electrode (QRE). In order to accurately delimit the surface area exposed to the melt the cathode was fastened in a boron nitride sheath.

2 Results and discussion

The electrolytes were selected to have low eutectic temperature and good conductivity.

The physico-chemical and thermodynamic properties of the electrolytes selected for this study are presented in Tables 1 and 2[13,14].

2.1 Decomposition potential and ohmic drop

In order to know if the chosen electrolytes (LiF-NaF and LiF-NaF-CaF$_2$) are adequate for the electrodeposition of the electroactive species ($NaCeF_4$), the decomposition potential

Table 1 Thermodynamic properties of the employed fluorides[13]

Compound (solid state)	$-\Delta G_{f, 1000}/$ (kJ/mol)	$-\Delta G_{f,298}/$ (kJ/mol)	E^0_{298} [Me | F$_2$]/ V
LiF	523	585.76	6.06
NaF	468.608	543.92	5.60
CaF$_2$	1058.552	1163.152	6.03
CeF$_3$	1443.48	1615.024	5.58

Table 2 Physico-chemical constants of the solvents

No.	System	Composition/ mol.%	$T_e/$ K	$d/$ (kg/m^3)	$K/$ (Ω/m)	$\eta/$ (mPa·s)	$E_d^*/$ V
1	LiF-NaF	49.2–50.8	923	1980	494	2.90	3.97
2	LiF-NaF-CaF$_2$	28.9–64.5–6.6	888	3730	508	1.98	4.02

*E_d of those systems was additively calculated from individual decomposition potentials of the components[12]

of $NaCeF_4$ in both electrolytes was determined.

Figs. 1 and 2 represent the current-potential curves in the systems LiF-NaF-5% NaCeF$_4$ and LiF-NaF-CaF$_2$-5% NaCeF$_4$ when working temperature was 1003.15 K; the shapes of the U-I and E-I curves are similar in both systems. The resistance of the electrolyte was measured with a B641-Wayne-Kerr auto-balance bridge (with a 0.1% precision) and found to be 0.28 Ω for the first solvent and 0.36 Ω for the second one, respectively.

Starting from the classical relation:
$$E=U–IR \tag{1}$$
where: E(V) is counter electro-motive force, U(V) cell voltage, I(A) current intensity and R(Ω) cell resistance, current-voltage curves (I-U) were transformed into I-E curves.

The decomposition potential (E_d) was evaluated from the extrapolation to zero current of the linear parts of these plots.

The mean value of the decomposition potential was found to be E_d=2.025 V for the system LiF-NaF-5% NaCeF$_4$ and E_d=2.045 V for LiF-NaF-CaF$_2$-5% NaCeF$_4$, respectively where E_d is an absolute value. The E_d was also determined for 10%NaCeF$_4$ in both studied electrolytes and, as we expected, concentration of the cerium complex does not influence the value of the decomposition potential.

Some complementary information was obtained from the ohmic drop and polarization curves. From the evolution E_Ω=f(I), presented in Fig. 3, where E_Ω represents the sum of the values E_Ω in the electrolytes with 5% and 10% NaCeF$_4$, it was found that the ohmic drop potential (E_Ω=IR) is not
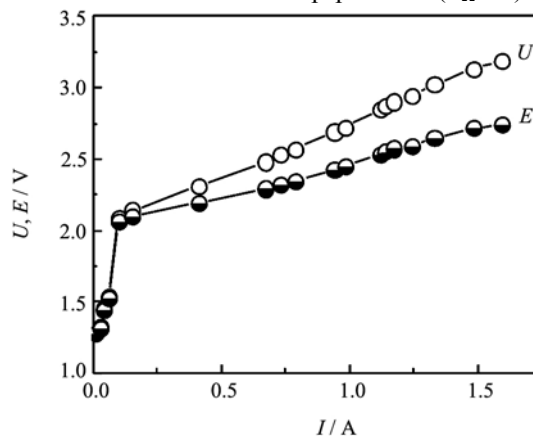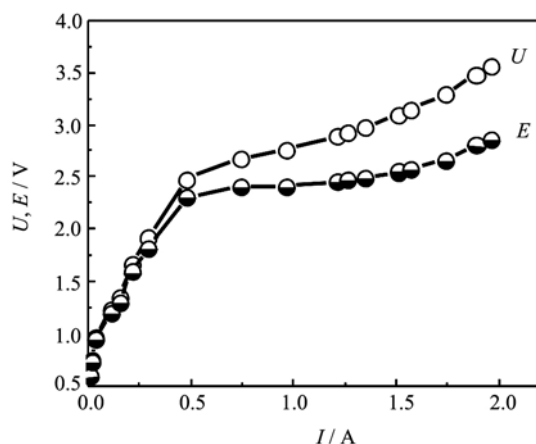

Fig. 1 Experimental E_d for LiF-NaF-5% NaCeF$_4$ system

Fig. 2 Experimental E_d for system LiF-NaF-CaF$_2$-5% NaCeF$_4$ system