Studies on Cerium Electrochemistry in High Temperature Ionic Liquids

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The cathodic behavior of Ce^{3+} ions in LiF-NaF-BaF_2, LiF-NaF-$NaCl$ and $NaCl$-KCl molten salts at 730° C has been studied using different electrochemical techniques. The decomposition potential (E_d) and the cathodic overvoltage were determined by introducing $NaCeF_4$ as electrochemical active species using steady-state potential-current curves recorded under galvanostatic conditions. The values of $|E_d|$ were 1.85 V in LiF-NaF-BaF_2, 2.114 V in LiF-NaF-$NaCl$ and 2.538 V in $NaCl$-KCl, respectively. It was also found that the ohmic drop potential in melt is not dependent on $NaCeF_4$ concentration and it rises as the current intensity increases. The Tafel slopes and other kinetic parameters were calculated on the assumption that the cathodic process consisted of direct discharge of Ce^{3+}, with no solvent-solute interaction. In order to elucidate the mechanisn of cathodic process the cyclic voltammetry technique was finally used. From the evolution of the voltammograms we conclude that the electrochemical reduction of Ce^{3+} ion is actually a reversible process on the molybdenum electrode and cathodic reduction of Ce^{3+} takes place in one single step involving three electron exchange. Our study adds to the accumulating data and confirms available results of electrodeposition of metalic cerium from molten salts using $NaCeF_4$ as solute.

Keywords: cerium deposition; molten salts; lanthanides; $NaCeF_4$; electrolysis

Cerium is the most abundant of the rare earth metals (lanthanides), as componentit in a number of minerals, the most important being monazite and bastnasite. Lanthanide metals of high purity are commonly prepared by metallothermic reduction, a process for which specific energy consumption is extraordinary high [1]. However, their electrodeposition from high temperature ionic liquids (HTILs) may be an alternative technique of preparation.

There are basically two methods of producing cerium by molten salt electrolysis. In a first method, the individual rare earth oxides, including cerium oxide, are separated from the ore (monasite, bastnasite) and purified. The oxides are then chlorinated and the molten rare earth chlorides are electrolysed. In the second method, purified cerium oxide is first obtained in a similar manner as above described and then it is electrochemically processed in a molten salt cell consisting of a mixture rare earth fluoride and alkali metal fluoride salts.

One of the most advantageous features of molten salts as aprotonic electrolytes is their wide electrochemical window that offers considerable merits in energy conversion and material synthesis applications. In many cases, the accessible potential range is as wide as that between alkali metal deposition (cathodic limit) and halogen gas evolution (anodic limit) [2-6].

Metallic cerium has been widely considered as a very important element because it has many applications in the fields of catalysis, electronics materials, applied alloys, glasses and magnetic materials. The reductive extraction of metallic cerium from HTILs such as LiF-NaF-BaF_2, LiF-NaF-$NaCl$ and $NaCl$-KCl with $NaCeF_4$ as electrochemical active species deserves an examination as a possible alternative to the present technique used. The objective of the present study is to investigate the preparation of high purity metallic cerium by electroreduction of $NaCeF_4$ (Ce^{3+}) in three eutectic molten systems: fluorides, chloro-fluorides and chlorides at 730° C.

Experimental part

The high purity salts of 99.9 % (LiF, BaF_2, KCl, $NaCl$, NaF, $NaCeF_4$) were supplied by Fluka, Merck and Johnson Matthey, respectively. The individual salts were dehydrated under vacuum heating. The $NaCeF_4$ solute was selected from all the complexes formed by CeF_3 with alkali fluorides because it was easily synthesized and was not hygroscopic as the compounds formed with potassium fluoride [7].

The experimental setup used in electrochemical studies consists in a electrical furnace, an electrochemical cell with atmosphere control (vacuum and argon gas flushing system) and electronic equipment for electrochemical investigation. The overpotential was determined by potential-current 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^{-1}. These steps were higher than those usually applied for electrolysis of $NaCeF_4$ electrochemical species (ES) proceeds at 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 $V \cdot s^{-1}$. A SU-2000 type glassy carbon (GC) 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 H"1ppm). The melt temperature was maintained ±2°C with an Alcatel thermoregulator. The voltammograms were registered on a Mo wire electrode (Ö=2mm) 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 [7]. Experimental set-up is shown in figure 1.

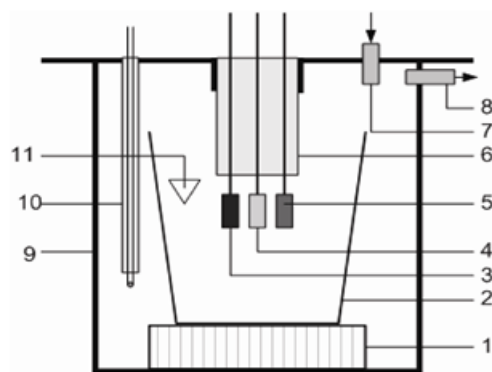* email: virgilconstantin@yahoo.com; Phone: (+40)02131885958

Fig. 1 Experimental set-up: 1-ceramic support; 2-GC crucible; 3-working electrode; 4-auxiliary electrode; 5-QRE(Pt); 6-alumina sheat; 7-Ar (in); 8-vacuum (out); 9-electrical furnace; 10-thermocouple (type S); 11-molten salts

Results and discussions

The selected electrolytes-HTILs, namely, LiF-NaF-BaF$_2$, LiF-NaF-NaCl and NaCl-KCl, have low eutectic temperature, good electrical conductivity and low hygroscopicity.

The ES was NaCeF$_4$ [8] and the working temperature was maintained constant, at 730° C.

The physico-chemical properties (molar composition, eutectic temperature (T$_e$), density (d), electrical conductivity (k), viscosity (ç) and decomposition potential (E$_d$) of the electrolytes selected for this study are presented in table 1.

Decomposition potential and ohmic drop

In order to know if the chosen HTIL electrolyte is adequate for the electrodeposition of the ES, the decomposition potential was determined in each individual eutectic system.

In figures 2-4 are depicted the voltage-current curves in the folowing electrolytes: LiF-NaF-BaF$_2$+5 wt.% NaCeF$_4$, LiF-NaF-NaCl+5 wt.% NaCeF$_4$ and NaCl-KCl-5 wt.% NaCeF$_4$ at 730° C working temperature. It may be observed that the shapes of the U-I curves are similar in all studied molten systems. The ohmic resistance of the electrolyte was measured with a B641-Wayne-Kerr auto-balance bridge (with a 0.1% precision) and its value are found to be 0.34 Ω for the first melt, 0.38 Ω for the second melt and 0.46 Ω for the third melt, respectively.

Starting from the classical relation:

$$E = U - IR \quad (1)$$

where: E(V) is electromotrice force, U(V) is the cell voltage, I(A) the current intensity and R(Ω) the cell ohmic resistance, the voltage-current curves (U-I) can be transformed into potential-current (E-I) curves. The decomposition potential (E$_d$) was evaluated from the extrapolation to zero current of the linear parts of these plots [7]. The mean values of the decomposition potential were found to be 1.85 V for the system LiF-NaF-BaF$_2$+5 wt.% NaCeF$_4$, 2.114V for LiF-NaF-NaCl+ 5 wt.% NaCeF$_4$ and 2.538 V for the system NaCl-KCl+5 wt.% NaCeF$_4$. The E$_d$ was also determined for 10 wt.% NaCeF$_4$ in all three studied electrolytes and, as expected, the concentration of the cerium complex does not influence the value of the decomposition potential.
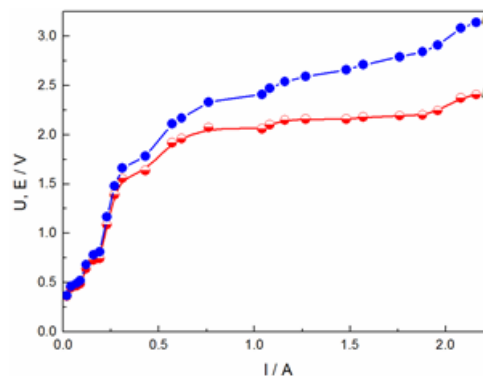

Fig. 2 Experimental determination of E$_d$ for LiF-NaF-BaF$_2$ + 5 wt.% NaCeF$_4$ system at 730° C
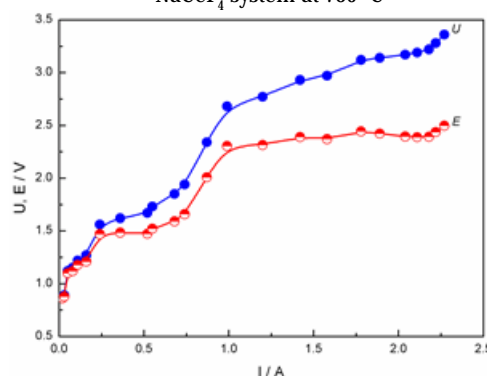

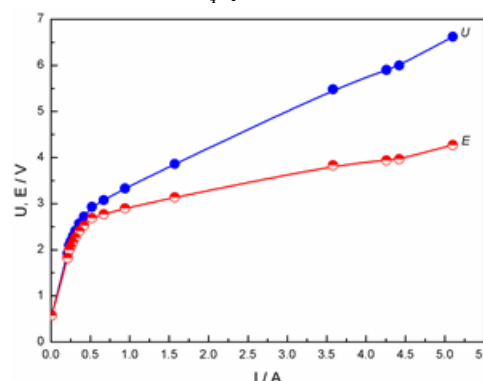Fig. 3 Experimental determination of E$_d$ for LiF-NaF-NaCl + 5 wt.% NaCeF$_4$ system at 730° C

Fig. 4 Experimental determination of E$_d$ for NaCl-KCl + 5 wt.% NaCeF$_4$ system at 730° C

Some complementary information was obtained from the ohmic drop potential (E$_\Omega$) and polarization curves. From the evolution of linear E$_\Omega$=f(I), presented in figure 5, where

No.	System	Composition	T$_e$	d	κ	η	E$_d$*
		mol %	K	kg·m^{-3}	Ω^{-1}·m^{-1}	mPa·s	V
1.	LiF-NaF-BaF$_2$	33.2-38-28.8	894	2780	501	4.50	4.28
2.	LiF-NaF-NaCl	26.3-38.2-35.5	855	1850	485	2.17	3.69
3.	NaCl-KCl	42.5-57.5	931	1550	262	1.23	3.20

Table 1
PHYSICO-CHEMICAL CONSTANTS OF THE HTILs [9]

*E$_d$ of melted systems was calculated theoretically from individual decomposition potentials of the components [10].
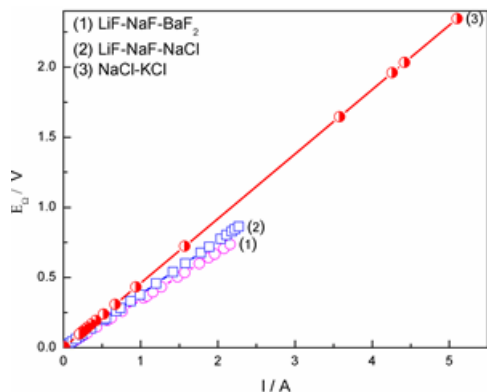
Fig. 5 Ohmic drop (E_Ω) as a function of current obtained for $NaCeF_4$ addition in molten solvents at 730° C

E_Ω represents the values of ohmic drop potential in the electrolytes with 5% ES, it was found that the ohmic drop potential is not dependent on ES concentration and it rises linearly as the current intensity increases.

Overpotential measurement

A study of the electrode processes is useful as it provides information on the sequence of partial electrode reactions as well as electrode reaction rates, which, according to Faraday's law, are proportional to current density (i). The dependence of current density on both electrode potential and cerium concentration in melt allows to calculate the following important kinetic parameters: exchange current density (i_0), transfer coefficients (α) electrochemical reaction orders, limiting reaction currents, valence of the electrode reaction (n), etc. [7].

The potential of a polarized electrode differs from the equilibrium potential established when no current passes through the electrode. The difference between these potentials was defined as the cathodic overpotential (η) [11-15].

The electrode kinetic studies consist always in establishing the relationship between electrode overpotential (η) and current density (i). The study of the cathodic overvoltage at the electrolysis of ES dissolved in the fluoride and fluoride-chloride mixture melt aims at gathering some information about the mechanism of cerium electrodeposition process [7].

In figure 6 is depicted the evolution of the polarization potential $|E_p|$ with current density (i) after the correction with the E_Ω^p for the studied systems.

Taking in account the electrochemical point of view[11] and applying the Butler-Volmer equation for our systems, we can interpret the semi-logarithmic curves, presented in figure7 one can conclude that the two different slopes from figure 7 are caused by the change of the rate-determining step in the same time with the rise of the current density. Slow process of charge transfer at small cathodic overvoltage at $\eta < -0.150V$ controls the cathodic process and process and therefore the nucleation becomes rate determining step at $\eta \approx 0.600V$. Examination of table 2 shows that Tafel slopes from experimental data agree

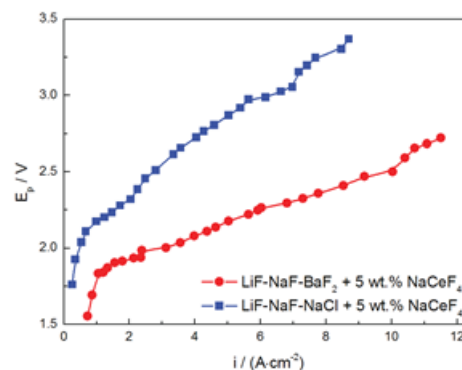Fig. 6 Cathodic steady-state polarization curves for LiF-NaF-BaF_2-$NaCeF_4$ and LiF-NaF-NaCl-$NaCeF_4$ at 730° C
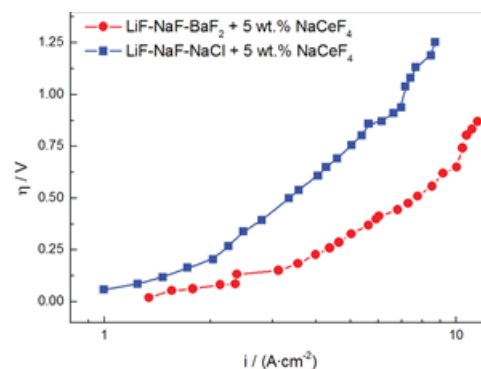

Fig.7 Cathodic overvoltage vs. current density (Tafel semi-logarithmic curves) obtained at 730° C in molten systems with 5 wt.% $NaCeF_4$

approximately with the calculated value (b=2.303RT/nF=0.473 for n=3), which proves the contribution of the overvoltage of charge transfer during cathodic polarization and, in the same time, a mechanism of direct discharge of Ce^{3+} ions with the change of three electrons in single step. The other part of the cathodic overvoltage represents a range where the crystallisation is very important, the process, being controlled by the nucleation rate. In figure 7 we can also see a remananced overvoltage, non-Tafel, which according to Vetter [10] was assigned to the diffusion overvoltage caused by the mass transfer from the melt bulk to the surface of the electrode.

We present in table 2 the kinetic parameter, values of cathodic Tafel slope, calculated from the Tafel line, exchange current density (i^o) and Tafel range of current density validity according to the Tafel equation (η=a+blog i).

It is observed that Tafel plots for both fluoride and chloro-fluoride melts have the same evolution, but for LiF-NaF-BaF_2-$NaCeF_4$ system the obtained values for kinetic parameters are more favorable.

Cyclic voltammetry

Cyclic voltammetry was selected also as the experimental method for this study because observation

Table 2
DETERMINED FROM POLARIZATION CURVES: KINETIC PARAMETERS, TAFEL SLOPES EXCHANGE CURRENT DENSITY AND TAFEL RANGES OF CURRENT DENSITY

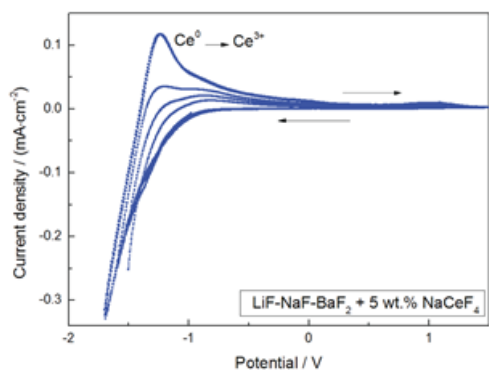| System	Cathodic Tafel slope V/dec	i_0 A·cm^{-2}	Tafel range of current A·cm^{-2}
LiF-NaF-BaF_2-$NaCeF_4$	0.30	1.50	2.2-6.7
LiF-NaF-NaCl-$NaCeF_4$	0.60	1.20	1.5-4.5

Fig. 8. Cyclic voltammograms of cerium deposition/dissolutionin molten (LiF-NaF-BaF$_2$) + 5 wt.% NaCeF$_4$;WE=Mo, RE=Pt (quasi reference), AE=GC, t=730° C, different scan rates:10; 30; 50; and 100 mV·s^{-1}
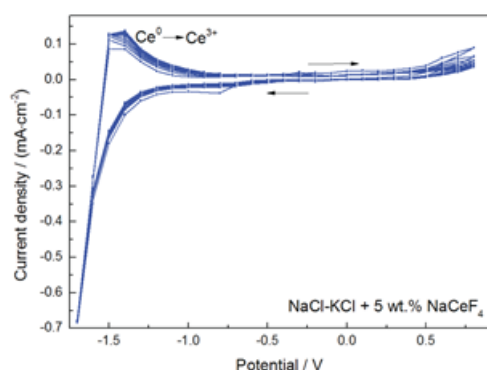

Fig. 9. Cyclic voltammograms of cerium deposition/dissolutionin molten (NaCl-KCl) + 5 wt.% NaCeF$_4$;WE=Mo, RE=Pt (quasi reference), AE=GC, t=730° C, different scan rates:10; 30; 50; and 100 mV·s^{-1}

of the electrochemical redox reactions can be made rapidly over a a wide potential range. Moreover, this tehnique provides information on the kinetics and reversibility of electrode reaction and the stability of the products of these reactions. Typical cyclic voltammograms obtained for electrochemical reduction of Ce^{3+} ion at molybdenum electrode are shown in figure 8 and 9.

The proposed mechanism for cerium deposition, is shown in figure 10, for the fluorinated systems containing CeF$_4^-$ complex ions, reduction of Ce^{3+} occurs according to one stage with a charge transfer of three electrons:

Fig. 10 Proposed mecanism for electroreduction of NaCeF$_4$ in HTILs and anodic evolution of fluorine gas
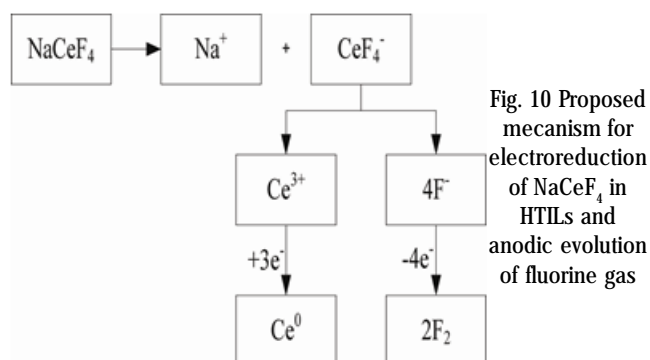
Conclusions

Decomposition potentials values for NaCeF$_4$ in the HTILs: LiF-NaF-BaF$_2$, LiF-NaF-NaCl and NaCl-KCl at 730° C were found to be 1.85 V, 2.114 V and 2.538 V, respectively. The constant value of ohmic drop in melt for various NaCeF$_4$ concentration proves that no solvent-solute interaction takes place during electrolysis. The polarization curves show that the electrode potentials become rapidly stationary and the current rises noticeable, but for the system LiF-NaF-BaF$_2$-NaCeF$_4$ the stationary stage is not reached. The cathodic overvoltage is high and Tafel range is large in this case. The studied process is a cathodic reduction of Ce^{3+} with n=3 (electrons) and using the classically formula for calculating Tafel slope, the experimental Tafel slope values are in good agreement with the calculated ones. The Tafel equation is verified on a large current density range; applying the Butler-Volmer equation one can conclude that the two different values Tafel slopes are caused by the control of charge-transfer at low overvoltage and by the crystallization of high overvolatge. The major influence is the control of the nucleation rate, so that Ce metal will be deposited as a microcrystalline powder. The shape of the voltammograms is characteristic for formation of the product that remains adherent to the electrode, confirmed by the visual examination of the Mo electrode.

References

1. SPEEDING, F.H., DAANE, A.H., (Eds.), The Rare Earth, John Willey & Sons Inc., New York, 1961.
2. GAO, F., WANG, CH., LIU, L., GUO, J., CHANG, S., CHANG, LI., LI, R., OUYANG, Y., J. Rare Earth, **27**, 2009, p. 986.
3. LIN, R., YE, G., HE, H., TANG, H., OUYANG, Y., J. Rare Earths, **30**, 2012, p. 151.
4. QI, X., ZHU, H.M., Rare Metals, **24**, 2005, p. 8.
5. KANEKO, A., YAMAMOTO, Y., OKADA, C., J. Alloys Comp., **193**, 1993, p. 44.
6. CASTRILLEJO, Y., BERMEJO, M.R., BARRADO, E., MARTINEZ, A.M., DIAZ, AROCAS, P., J. Electroanal. Chem., **545**, 2003, p. 141.
7. CONSTANTIN, V., POPESCU, A.M., OLTEANU, M., J. Rare Earth, **28**, 2010, p. 428.
8. CONSTANTIN, V., POPESCU, A.M., J. Rare Earths, **31**, 2013, p. 911.
9. JANZ, G.J., Molten Salts Handbook, Academic Press, New York, N.Y., 1967.
10. POPESCU, A.M., CONSTANTIN, V., Rev. Chim. (Bucharest), **58**, 2007, p. 1198.
11. VETTER, K.J., Electrochemical Kinetics-Theoretical and Experimental Aspects, Academic Press, New York, N.Y., 1967.
12. POPESCU, A.M., CONSTANTIN, V., Chem. Res. Chin. Univ., **31** no. 5, 2015, p. 858.
13. MALYSHEV, V., SHAKHNIN, D., GAB, A., ASTRELIN, I., MOLOTOVSKA, L., SOARE, V., DONATH, C., NEACSU, E.I., CONSTANTIN, V., POPESCU, A.M., Rev. Chim. (Bucharest), **67** no. 12, 2016, p. 2490.
14. MALYSHEV, V., GAB, A., SHAKHNIN, D., POPESCU, A.M., CONSTANTIN, V., OLTEANU, M., Rev. Roum. Chim., **55** no. 4, 2010, p. 233.
15. POPESCU, A.M., CONSTANTIN, V., Rev. Chim. (Bucharest), **48**, no. 8, 1997, p. 691.