Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF RARE EARTHS, Vol. 27, No. 6, Dec. 2009, p. 986
JOURNAL OF RARE EARTHS
www.re-journal.com/en/

Electrode process of La(III) in molten LiCl-KCl

GAO Fanxing (高繁星), WANG Changshui (王长水), LIU Lisheng (刘利生), GUO Jianhua (郭建华),
CHANG Shangwen (常尚文), CHANG Li (常 利), LI Ruixue (李瑞雪), OUYANG Yinggen (欧阳应根)

(Department of Radiochemistry, China Institute of Atomic Energy, Beijing 102413, China)

Received 21 October 2008; revised 15 December 2008

Abstract: The electrode process of La(III) at Mo electrode in the molten LiCl-KCl for temperatures ranging from 683 K to 773 K was studied by cyclic voltammetry and chronopotentiometry, respectively. The results showed that in the molten LiCl-KCl, reduction of La(III) occurred in a step with a global exchange of three electrons. Cyclic voltammetry studies indicated that at a sweep rate lower than 0.2 V/s, the electroreduction of La(III) to lanthanum metal was reversible and controlled by diffusion of La(III). However, the process became under a mixed control of both diffusion and electron transfer when sweep rate exceeded 0.2 V/s. And an empirical temperature dependence of the diffusion coefficient of La(III) was proposed: $\ln D_{La(III)}=7.742–1.441\times10^4/T$. And the relation between the formal potential of La(III)/La versus Ag/AgCl reference electrode and temperature was described in the following equation: $E^{\theta'}=–1.402–4.689\times10^2/T$.

Keywords: molten LiCl-KCl; electrochemistry; lanthanum chloride; diffusion coefficient; formal potential; rare earths

Electrolytic technology in the reaction media of molten salts has been considered as an important route to treat raw materials and to prepare metals and alloys. Moreover, dry process employing electrolytic technology in molten salts, adopted in spent nuclear fuel cycle, is considered as a promising method to deal with high-burn-up, short-cooled, high-plutonium-concentration spent fuels. The basic data, such as formal potential, diffusion coefficient, electrode mechanism and so on, are of importance in developing this technology[1,2]. There are several studies reported on the electrode process of La(III) in molten chlorides, but due to the varieties of the exact experimental conditions, such as salt composition, temperature, working electrode materials, occurring forms of the electroactive species in the molten salts, data reported by different institutes differ considerably. And some of the representative data are listed in Table 1[3–7].

In the present study, transient electrochemical techniques, such as cyclic voltammetry and chronopotentiometry were employed to investigate the electrode process of La(III) in molten LiCl-KCl in the temperature range of 683–723 K at Mo electrode. And diffusion coefficients of La(III) and formal potentials of La(III)/La versus Ag/AgCl reference electrode were obtained.

1 Experimental

1.1 Preparation of LiCl-KCl-LaCl$_3$ salt

The chloride mixture of 59 mol.% LiCl-41 mol.% KCl was treated by the following procedure: the mixture was firstly desiccated under a dynamic vacuum (less than 80 Pa) through step-by-step increased temperatures: 373 K (1 h)–400 K (1 h)–573 K (1 h); then the mixture was melted in purified argon atmosphere[8]. Certain amount of anhydrous LaCl$_3$ (99.9% purity, purchased from Alfa Aesar) was then dissolved into the treated LiCl-KCl melt, and LiCl-KCl-LaCl$_3$ salt was finally obtained. The total concentration of La(III) in the prepared salt was determined by ICP-AES method (IRIS-ADVANTAGE).

1.2 Experimental apparatus

A simple-structure, steady-performance Ag-AgCl (5 mol.%) reference electrode adopting Pyrex glass as ions conducting

Table 1 Diffusion coefficient and potential of La(III) at 723 K in the molten LiCl-KCl

Year	People	D/(10^{-5} cm^2/s)	*E*/V vs Cl$^-$/Cl$_2$
1986	Y.Mottot	0.72	–3.165
1999	Frederic Lantelme	1.47	–3.177
2003	Y.Castrillejo	1.17±0.13	–3.183±0.022
2005	Patrick Masset	0.8±0.1	–3.126

Foundation item: Project supported by the National Basic Research Program of China (2007CB209900)

Corresponding author: OUYANG Yinggen (**E-mail:** oyyg@263.net; **Tel.:** +86-10-69358113)

DOI: 10.1016/S1002-0721(08)60375-0

membrane was fabricated. A Mo wire of 1 mm diameter (99.95% purity, purchased from Alfa Aesar) was used as the working electrode. The Mo wire was carefully polished and desiccated in vacuum oven before every experiment. The active area of the working electrode was determined by measuring the immersed length of the electrode in the molten salts[1–4,9]. A 6 mm diameter graphite rod served as the auxiliary electrode. Connected with a potentiostat, a three-electrode electrochemical measuring system was set up. Cyclic voltammograms and chronopotentiograms were recorded by PAR 273A potentiostat with an EG&G M273A electrochemical software.

A schematic diagram of the electrolytic cell is shown in Fig. 1. Connected with gas station, vacuum system and a medium frequency induction heating oven, this apparatus can be used to purify chloride salts and conduct electrochemical experiments in molten salts. After connected with the three-electrode system electrochemical experiments in molten salts can be conducted with this apparatus.

2 Results and discussion

2.1 Results obtained by cyclic voltammetry technique

Fig. 2 shows a representative cyclic voltammogram obtained at 723 K with 7.70×10^{-5} mol/cm^3 $LaCl_3$ in LiCl-KCl at Mo electrode. Two cathodic peaks (a1, a2) and two anodic peaks (b1, b2) can be observed clearly. The shape of cathodic peak a1 and the corresponding anodic peak b1 are typical of the formation of a new phase, and followed by the stripping process of the phase. Cathodic peak a2 indicates the cathodic limit of the media electrolyte due to production of liquid lithium, and anodic peak b2 represents oxidation of lithium.

2.1.1 Diffusion coefficient Fig. 3 shows the peak current of peak a1 which is directly proportional to the square root of the sweep rate, which indicates that this process is controlled by diffusion of La(III) towards the surface of Mo electrode. For a diffusion-controlled reversible electrochemical process with an insoluble product, the peak current and the diffusion coefficient of La(III) obey Berzins and Delahay equation[10]:

$$\frac{i_p}{\sqrt{v}}=0.61(nF)^{3/2}(RT)^{-1/2}AD^{1/2}C \qquad (1)$$

where i_p is cathodic peak current (A), A is electrode area (cm^2), C is bulk concentration of the electroactive species (mol/cm^3), D is diffusion coefficient (cm^2/s), n is number of electrons involved in the reaction which is assumed to be 3 in this reaction, F is Faraday constant, R is gas constant, T is temperature in Kelvin. And $D_{La(III)}$ was calculated to be 4.27×10^{-6} cm^2/s.

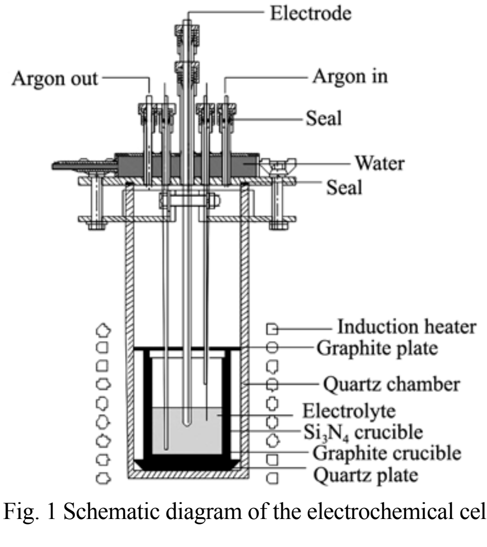

Fig. 1 Schematic diagram of the electrochemical cell

2.1.2 Number of electrons For an electrochemical reaction with insoluble product, the peak potential E_p and half peak potential $E_{p/2}$ obey a relation expressed by the following equation[11]:

$$E_{p/2}=E_p+0.7725(RT+nF) \qquad (2)$$

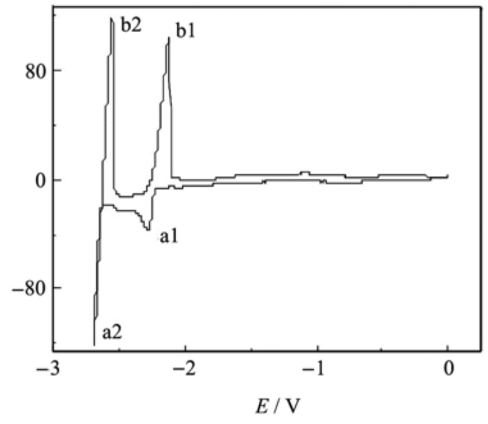

Fig. 2 Cyclic voltammogram of LiCl-KCl-$LaCl_3$
A_{Mo}=0.30 cm^2, 723 K, v: 100 mV/s, $C_{La(III)}$: 7.70×10^{-5} mol/cm^3, RE: Ag/AgCl (5 mol.%)

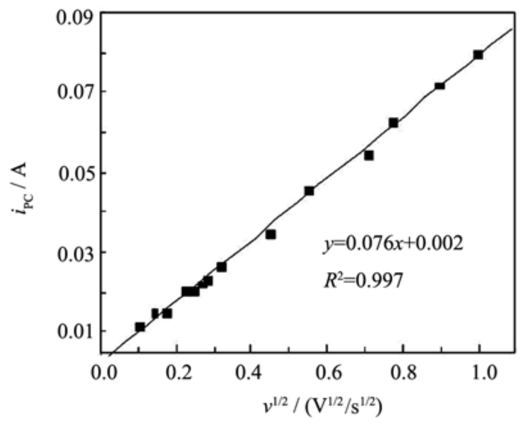

Fig. 3 Dependence of peak current on square root of sweep rate
A_{Mo}=0.46 cm^2, 723 K, $C_{La(III)}$: 7.70×10^{-5} mol/cm^3, RE:Ag/AgCl (5 mol.%)