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Electrochemical and spectroscopic investigations of Tb(III) in molten LiCl–KCl eutectic at high temperature

Bong Young Kim, Dong Hyoung Lee, Jun-Yeop Lee, Jong-Il Yun *

Department of Nuclear and Quantum Engineering, KAIST, 373-1 Guseong-dong Yuseong-gu, Daejeon 305-701, Republic of Korea

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ABSTRACT

Electrochemical and spectroscopic properties of Tb(III) in molten LiCl–KCl eutectic at high temperature were investigated by cyclic voltammetry and time-resolved laser-induced fluorescence spectroscopy (TRLFS). The diffusion coefficient of Tb(III) and the formal standard potential of Tb(III)/Tb^0 were determined to be $2.06 \pm 0.4 \times 10^{-5}\,\mathrm{cm}^2\ \mathrm{s}^{-1}$ and -2.83 ± 0.03 V vs. Cl_2/Cl^- at 887 K, respectively. Additionally, visible fluorescence of Tb(III) due to the electronic transitions from $^5D_3$ and $^5D_4$ to ^7F_J was observed and measured by TRLFS for the first time. These results provide the first fluorescence spectroscopic evidence for a direct *in situ* quantification of Tb(III) in the high temperature molten salt system.

1. Introduction

For recycling spent nuclear fuel and thus reducing the amount of high-level radioactive waste, different pyrochemical processes are under development. They are based primarily on electrochemical methods such as electrolysis or electrorefining, or electroreductive extraction in a molten salt solvent at high temperature. It enables to beneficially reuse uranium and plutonium by the recovery of group actinide (U, Pu, and minor actinide (Np, Am, and Cm)) from the fission products present in spent nuclear fuel according to the different standard free energy of formation of chloride [1].

Knowledge about the electrochemical behaviors of elements in the pyrochemical process of spent nuclear fuel is a major concern. For the purpose, electrochemical properties, such as the diffusion coefficient, the activity coefficient, and the formal standard potential, have been intensively investigated by conventional transient electrochemical techniques, such as cyclic voltammetry and chronopotentiometry. For the quantification and structural analysis, the absorption spectroscopic properties of the most of lanthanide elements were characterized in LiCl–KCl molten salt at high temperatures [2–6]. Raman spectroscopic studies for Sm(III), La(III), Nd(III), and Gd(III) were also performed in the lanthanide chloride–alkali chloride binary melt system [7,8]. Recently, the fluorescence measurements on the lanthanide elements in molten salt were reported at room temperature [9,10]. However, there is still no direct fluorescence measurement of elements dissolved in the high-temperature molten salt system.

This work focuses on the fluorescence spectroscopic behaviors of Tb (III) in the molten LiCl–KCl eutectic. For the first time, we demonstrate the direct *in situ* quantification of Tb(III) in the chloride molten salt at high temperature using TRLFS. Besides, the diffusion coefficient of Tb(III) and the formal potential of Tb(III)/Tb^0 were also determined by cyclic voltammetry.

2. Experimental

2.1. Apparatus

Electrochemical and fluorescence experiments were performed in a glove box under high-purity argon gas atmosphere (99.999% Ar, H_2O and $O_2 < 1$ ppm). A temperature controlled furnace system was installed leak-proof in the lower part of the glove box and designed for fluorescence measurements, as shown in Fig. 1. A 1 cm rectangular quartz cell with a long-necked cylindrical quartz tube was placed at the center of the electric furnace with optically accessible windows. The operating temperature was monitored by a thermocouple placed in contact with the sample quartz cell.

Cyclic voltammetry was carried out in an electrochemical cell having a three-electrode system with a Princeton Applied Research VersaSTAT3-200 potentiostat. The molybdenum (Sigma-Aldrich 99.99% purity) wire with a diameter of 1 mm served as both working electrode (WE) and counter electrode (CE). The Ag/AgCl electrode (99.99% Ag wire with 1 mm in diameter) used as reference electrode (RE) was encased in a thin-end pyrex glass tube, in which the LiCl–KCl eutectic salt contains 1.0 wt.% AgCl (Sigma-Aldrich 99.998% purity). Prior to measurements, all electrodes were polished with a sand paper and cleaned with nitric acid

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* Corresponding author. Tel.: +82 42 350 3825; fax: +82 42 350 3810.
E-mail address: jiyun@kaist.ac.kr (J.-I. Yun).

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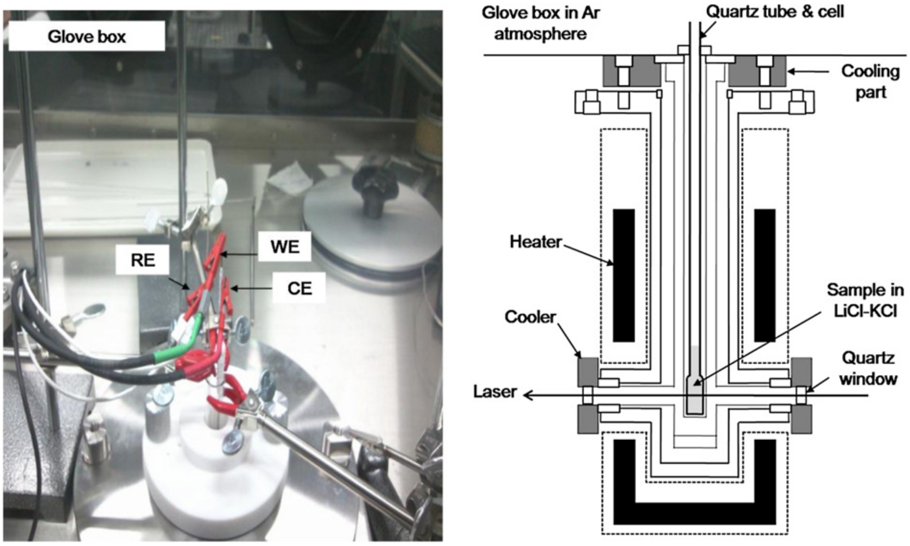

Fig. 1. Electrochemical equipments in the argon atmosphere glove box and the temperature controlled furnace system for fluorescence measurements of Tb(III).

(25% dilution), ultrapure water using ultrasonic bath, and ethanol sequentially.

To measure the fluorescence of Tb(III) ions in molten LiCl–KCl eutectic, a quadrupled wavelength (266 nm) of a Nd:YAG laser (Continuum, Surelite-20) was used as an excitation source. The laser energy was monitored by a low energy detector (Gentec, XLE4). Fluorescence spectra were recorded with an intensified charge coupled device (ICCD, Andor Technology, iStar) coupled with a Czerny-Turner spectrometer (Andor Technology, shamrock sr-303i). Fluorescence was transferred into the entrance slit of the spectrometer through optic fiber bundle perpendicular to the laser beam direction. All fluorescence spectra were measured at 813 K.

2.2. Chemicals

The concentration of Tb(III) ions in the chloride form (Sigma-Aldrich 99.99% $TbCl_3$ powder) varied from 0.05 wt.% to 0.48 wt.% by dissolution in polarographic-grade anhydrous LiCl–KCl eutectic salt (Sigma-Aldrich 99.99% purity, 44 wt.% LiCl). The amount of Tb(III) ion concentrations was determined by inductively coupled plasma-atomic emission spectrometer (ICP-AES).

3. Results and discussion

3.1. Electrochemical behavior

Fig. 2 shows typical cyclic voltammogram of $TbCl_3$ in the molten LiCl–KCl eutectic on the molybdenum electrode at 887 K. The electrochemical window corresponds to the reduction of Li(I) and the oxidation of Cl (−I). The potential was applied beginning from 0.8 V to −2.65 V and in a reverse way from −2.65 V to 0.8 V with a scan rate of 0.1 V s^{-1}. The cathodic and anodic peaks observed in the electrochemical window range indicate the reduction of Tb(III) to Tb^0 and re-oxidation of Tb^0 to Tb (III), respectively. The absence of crossover between the cathodic and anodic parts implies that no complication occurs during the metal nucleation onto the working electrode [11,12]. The reversibility of the Tb (III)/Tb^0 redox system was examined at different scan rates of 0.05–0.3 V s^{-1}. A good linearity of the dependence of $I_{p,c}$ on the square root of the scan rate was confirmed up to 0.15 V s^{-1}. The diffusion coefficient was calculated using the Randles–Sevcik equation for a reversible soluble/insoluble system [12,13]:

$$\frac{I_{p,c}}{\sqrt{v}} = 0.61\frac{(nF)^{3/2}}{\sqrt{RT}}C_{Tb(III)}S\sqrt{D_{Tb(III)}} \tag{1}$$

where $I_{p,c}$ is the cathodic peak current (A), S is the surface area of the working electrode exposed to the molten eutectic (cm^2), $C_{Tb(III)}$ is the solute concentration of Tb(III) (mol cm^{-3}), $D_{Tb(III)}$ is the diffusion coefficient of Tb(III) (cm^2 s^{-1}), v is the potential scan rate (V s^{-1}), R is the gas constant (8.3145 J mol^{-1} K^{-1}), F is the Faraday constant (96,485 C), and n is the number of electrons involved in the reaction. According to Eq. (1), the diffusion coefficient of Tb(III) was determined to be $2.06 \pm 0.4 \times 10^{-5}$ cm^2 s^{-1}, which agrees well with literature [14]. The formal standard potential, E^{0*}, for Tb(III)/Tb^0 is defined as

$$E^{0*}_{Tb(III)/Tb^0} = E^{0}_{Tb(III)/Tb^0} + \frac{RT}{nF}\ln\gamma_{Tb(III)} \tag{2}$$

and calculated from the peak potential for a reversible soluble/insoluble system using the following equation [12,15,16]:

$$E_{p,c} = E^{0}_{Tb(III)/Tb^0} + \frac{RT}{nF}\ln\left(\frac{a_{Tb(III)}}{a_{Tb(0)}}\right) - 0.854\frac{RT}{nF}. \tag{3}$$

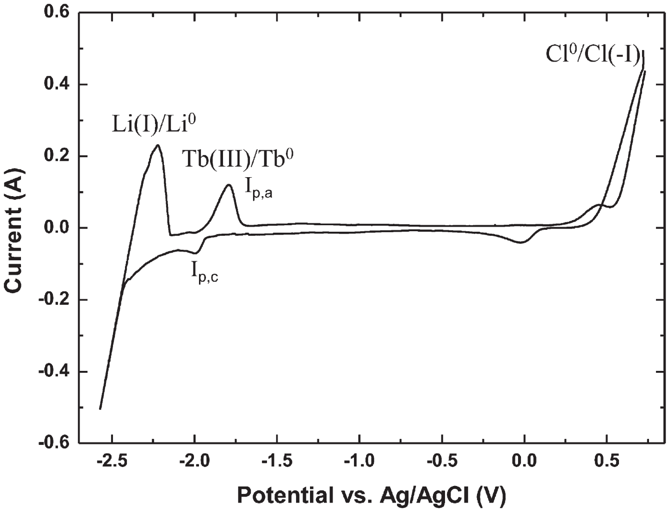

Fig. 2. Cyclic voltammogram of $TbCl_3$ in molten LiCl–KCl eutectic at 887 K. Working electrode: Mo, counter electrode: Mo, reference electrode: Ag/AgCl (1 wt.% in LiCl–KCl), $S = 0.322$ cm^2, $v = 0.1$ V s^{-1}, $C_{Tb(III)} = 8.1 \times 10^{-5}$ mol cm^{-3}.