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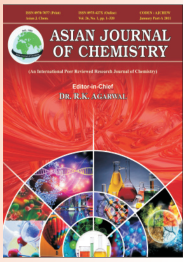

Quantitative Analysis of Lanthanide Ions in LiCl-KCl Molten Salt by Normal Pulse Voltammetry†

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An electrochemical approach to determine the lanthanide concentrations by normal pulse voltammetry was presented in the binary system of gadolinium (Gd) and lanthanum (La) as a part of the long-term goal to predict the total lanthanide concentrations in multi-component molten salt. The experimental conditions were optimized in terms of the pulse width and pulse period and a calibration curve was constructed in the molten salt with gadolinium ions. The limiting current of normal pulse voltammetry increased with gadolinium concentration with an excellent linearity in a concentration range of below 2 wt %. In addition, the total concentration of lanthanides in the binary solutions was estimated on the basis of the calibration curve. The maximum currents taken in the binary solutions of Gd and La were excellently fitted to the calibration curve, indicating that the total amount of lanthanides can be determined by normal pulse voltammetry technique.

Keywords: Lanthanides, Pyrochemical process, Normal pulse voltammetry.

INTRODUCTION

The pyrochemical processes have attracted much attention owing to their potential advantages such as the reuse of nuclear fuel, proliferation resistance and radioactive waste reduction[1-5]. One of main ideas for nuclear fuel recycling is to use the recovered actinides (*i.e.*, uranium and transuranium elements) as a fuel of next-generation nuclear plants such as a sodium-cooled fast reactor (SFR). The pyrochemical processes are composed of several distinctly different steps including electrolytic reduction, electrorefining and electrowinning process[4,5]. In the electrorefining process, most of the uranium in the spent fuel is recovered at a solid cathode[6]. The remaining uranium and transuranium elements (TRU) in a molten salt are moved to the electrowinning process where they are simultaneously recovered at a liquid cadmium electrode, which makes it impossible to separate pure plutonium[7-9]. During the electrolytic process, however, a small amount of lanthanide species with large neutron capture cross sections can be co-deposited onto the cadmium electrode, which leads to a significant decrease in the neutron flux of a reactor core. For practical application of the recovered actinides to SFR fuel, it is critical to reduce the amount of co-deposited lanthanide elements in the electrowinning step[4,5]. For this reason, it is necessary to conduct real-time measurements of lanthanide concentration in molten salt for an efficient process control of the electrowinning step.

In this study, *in situ* monitoring of lanthanides by normal pulse voltammetry (NPV) was investigated. The efficacy of the approach was evaluated in a binary system of gadolinium and lanthanum as a part of a long-term goal to measure the total amount of all lanthanides in molten salt.

EXPERIMENTAL

A LiCl-KCl eutectic mixture, silver chloride, gadolinium trichloride and lanthanum trichloride were used as received from Sigma-Aldrich. A conventional three-electrode system and quartz tube cell were used for electrochemical measurements. A tungsten wire of 1 mm diameter (Nilaco) and glassy carbon rod of 3 mm diameter (Alfa Aesar) served as the working and counter electrodes, respectively. The Ag/Ag^+ redox couple was used as the reference electrode system. The Ag/Ag^+ reference electrode contained in a one-end closed Pyrex tube consisted of an Ag wire with a diameter of 1 mm and a LiCl-KCl eutectic mixture with 1 mol % AgCl. The sample handling and all electrochemical measurements were carried out at 773 K in a glove box filled with a high purity argon gas (Fig. 1).

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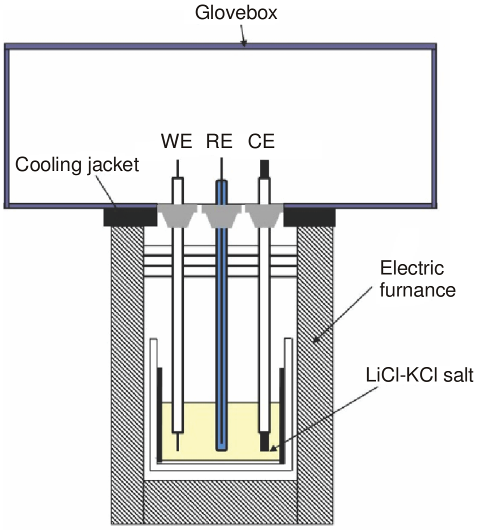

Fig. 1. A schematic of a high-temperature electrochemical cell in LiCl-KCl molten salts

Moisture and oxygen levels in the glove box were kept at less than 2 ppm. Determination of the lanthanide concentration by normal pulse voltammetry (NPV) was performed using an AutoLAB PGSTAT 302N (Metrohm). To find the practical measurement conditions, various normal pulse voltammetric responses were taken by varying the pulse width, pulse period and concentration of lanthanides. The current response was measured multiple times in 1 ms at the end of the pulse width where the pure faradaic current remains because the charging current decays exponentially.

RESULTS AND DISCUSSION

When the pulsed potentials are sufficiently negative *versus* the standard electrode potential that a charge transfer reaction occurs, a limiting current has been attained when an electrochemical system is governed only by diffusion and the electrode morphology is not changed during the electrochemical reaction. The sigmoidal shape typically observed for NPV is similar to the shape of the current-potential curve taken in a classical polarographic experiment. To obtain the optimal conditions for a stable sigmoidal shaped current-potential curve, the normal pulse voltammetric response was collected in a LiCl-KCl eutectic solution with 0.586 wt % gadolinium ions under various test conditions. Fig. 2 shows that the limiting current decreased with an increase in the pulse width. This result looks reasonable when considering that the diffusion-controlled faradaic current decays as a function of $1/t^{1/2}$. It was observed that the normal pulse voltammetric response was very sensitive to the pulse period, as shown in Fig. 2. Regardless of the pulse width, surprisingly, NPV curves with a sigmoidal shape were attained when the pulse period was 10-times longer than the pulse width. Interestingly when the pulse period was 5-fold longer than the pulse width, the reduction current was observed to gradually decrease with the pulsed potential after the current reached the limiting current. On the other hand, the reduction current increased with the pulsed potential when the pulse period was significantly longer. It is thought that this feature can be caused by an increase in the practical surface area of the working electrode owing to an irregular deposition of gadolinium. For the next quantitative analysis of lanthanides by NPV in the molten salt, the pulse width of 50 ms and the pulse period of 1000 ms were chosen in terms of the stability and sensitivity of an NPV analysis.

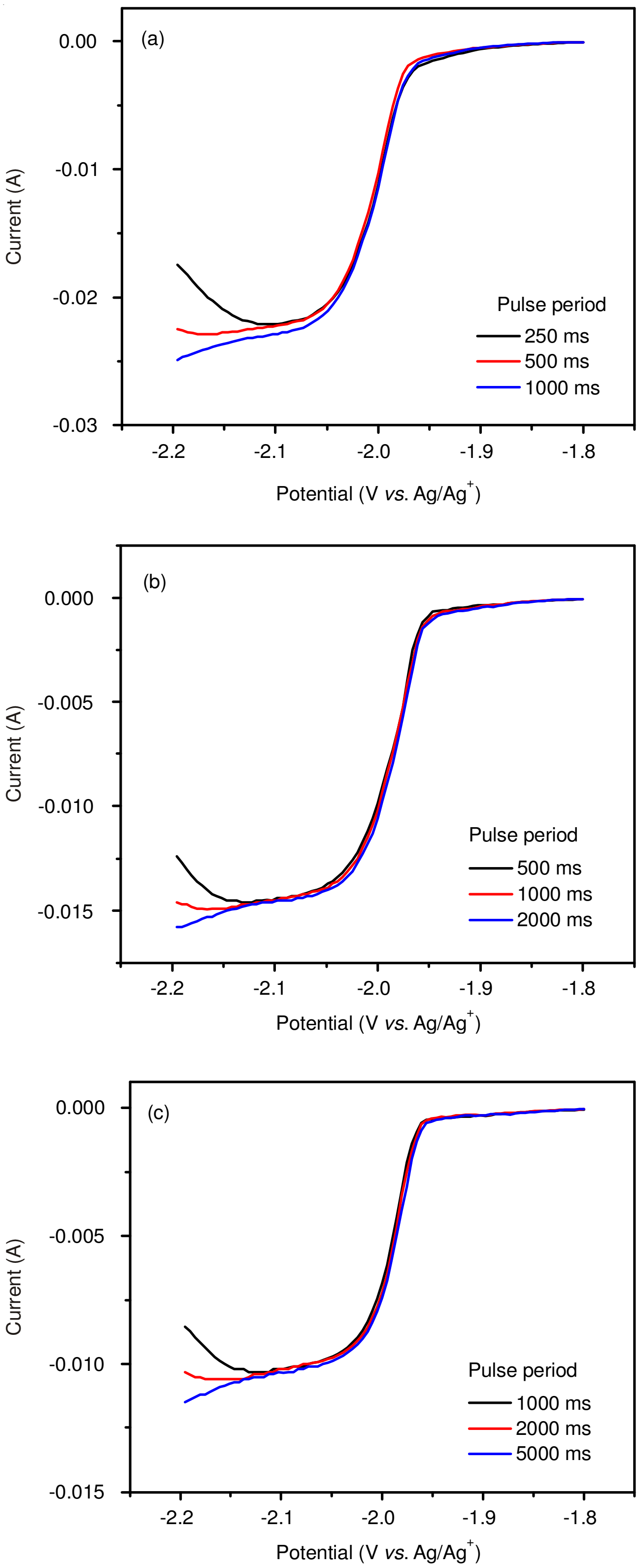

Fig. 2. NPV current-potential curves of Gd(III) ions taken under various measurement parameter conditions: (a) pulse width = 50 ms; (b) pulse width = 100 ms; (c) pulse width = 200 ms

To establish a calibration curve, a series of NPV responses were collected in various Gd concentrations. Fig. 3 shows that the limiting current linearly increased with Gd concentration up to 2 wt %, indicating that the quantitative analysis by NPV can be applied in a concentration range of below 2 wt %. For this reason, the calibration curve (solid regression line) was constructed in a low concentration range of below 2 wt % (Fig. 3). On the other hand, a slight deviation from the linear regression line occurred at higher concentrations above 2 wt % (Fig. 3). In general, an uneven deposition of Gd became more severe at such high concentrations, leading to an increased surface area of the working electrode. It seems that the increase in the reduction current with a pulsed potential was mainly attributed to changes in the practical surface area of the working electrode, where a charge transfer reaction takes place. It is not possible to separately measure the concentration of each individual element in lanthanide mixtures with electrochemical techniques because their standard electrode potentials are similar to one another. For this reason, it is practically important to determine the total concentration of lanthanide species for an efficient process control of the electrowinning step at a liquid cadmium cathode.

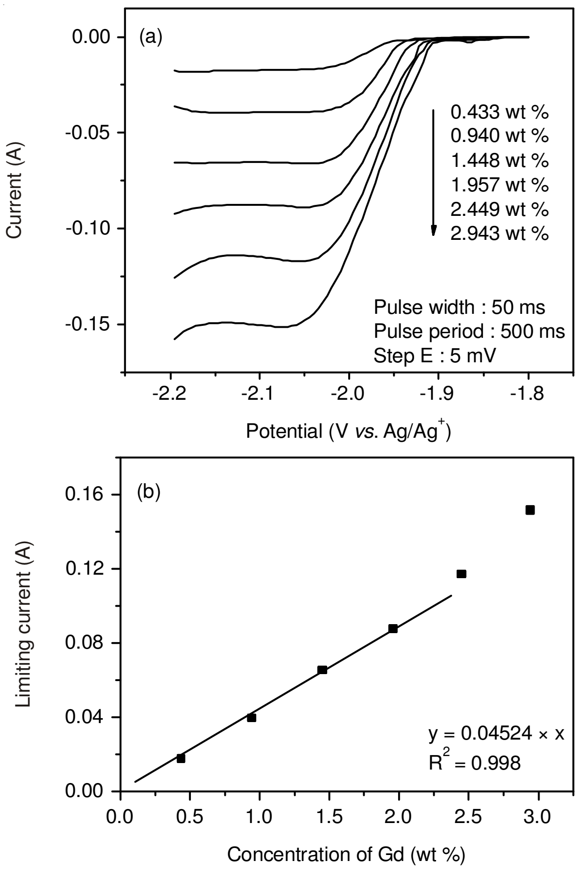

Fig. 3. (a) NPV curves obtained in various Gd(III) concentrations and (b) the plot of limiting current *versus* Gd(III) concentration and the calibration curve in the linear region

As a part of the final goal to measure the total lanthanide concentration in molten salt with a series of lanthanides, a preliminary study to assess the possibility of quantitative analysis by NPV was performed in various binary systems composed of Gd(III) and La(III), as shown Table-1. The two lanthanides, Gd(III) and La(III) ions, were selected since the standard electrode potentials of Gd(III)/Gd and La(III)/La redox couples are different from each other and are evenly deposited onto the surface of the tungsten working electrode.

TABLE-1
COMPOSITION OF BINARY TEST SOLUTIONS COMPOSED OF $GdCl_3$ AND $LaCl_3$ IN A LiCl-KCl EUTECTIC SALT

Sample	Concentration of Gd(III) (wt %)	Concentration of La(III) (wt %)	Total conc. (wt %)
1	0.147	0.075	0.222
2	0.497	0.075	0.572
3	1.062	0.075	1.167
4	1.062	0.325	1.375

Fig. 4(a) shows the NPV curves for several mixture solutions of Gd and La. It is clearly shown that the reduction proceeded in two steps owing to a difference in the standard electrode potentials of Gd(III)/Gd and La(III)/La. The maximum currents were plotted *versus* the total concentration of Gd(III) and La(III) and compared with the calibration curve constructed in molten salt solutions with only Gd(III) ions. Fig. 4(b) shows that the maximum currents of the binary solutions were excellently fitted to the calibration curve (dotted line), suggesting that the total amount of lanthanides in a multi-component molten salt system can be estimated by NPV and further, this analytical approach may be applied to the *in situ* monitoring of lanthanides in the electrowinning process.

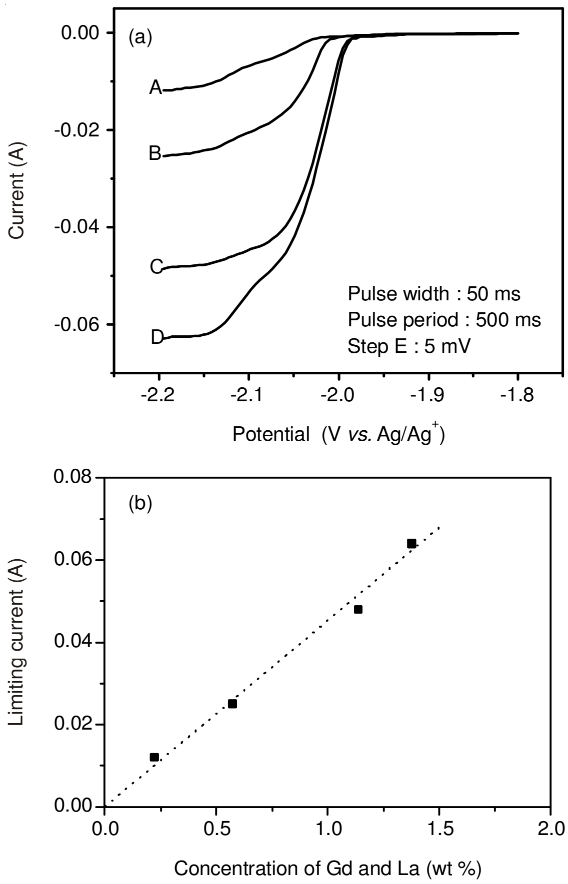

Fig. 4. (a) NPV curves in the various binary systems of Gd(III) and La(III) and (b) the plot of maximum current *versus* total concentration of Gd(III) and La(III). Dotted line (·······) is the calibration curve obtained in the single solution of Gd in the molten salts

Conclusion

As a preliminary study for the determination of total lanthanide concentrations in multi-component molten salt, the use of normal pulse voltammetry (NPV) for quantitative analysis of lanthanides was examined. To obtain a reproducible curve with a stable sigmoidal shape, measurement conditions were optimized in terms of the pulse width and pulse period. The efficacy of the approach was verified in a binary system of gadolinium and lanthanum on the basis of the calibration curve obtained in molten salt with gadolinium ions. The maximum currents of the binary solutions showed excellent fitting to the calibration curve. This fact suggests that the analytical approach can be applied to the *in situ* monitoring of a series of lanthanides during the electrowinning process.

ACKNOWLEDGEMENTS

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