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Short Communication

Determination of Lanthanide Ions in a LiCl-KCl Molten Salt by Square Wave Voltammetry

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Application of square wave voltammetry (SWV), a pulse technique without renewal of the diffusion layer between waves, was demonstrated for quantitative analysis of the lanthanide concentrations. The reproducible measurement conditions in a molten salt were investigated in terms of the principal parameters such as a pulse height and a wave frequency for getting a proper calibration curve. It was observed that peak current of SWV increased when gadolinium concentration was less than 1 wt%. In addition, the total amount of lanthanides in the binary solutions of gadolinium (Gd) and lanthanum (La) was determined by the peak deconvolution of SWV curves.

Keywords: Square wave voltammetry, Quantitative analysis, Lanthanides, Molten salt

1. INTRODUCTION

Numerous studies have focused on the research and development of the pyroprocessing technology for safe and proliferation resistance reprocessing of spent nuclear fuels. Over a few decades, it has been recognized that the pyroprocess has strong advantages such as low-cost and radioactive waste reduction[1-4]. One of major steps in the pyroprocess is electrowinning process, where the remaining elements in a molten salt after electrorefining process, that is, uranium and minor actinides such as neptunium, americium, and curium, are simultaneously recovered at the liquid cadmium cathode[5-8]. The concentration ratio between uranium and lanthanides in the molten salt significantly changes during the electrowinning process. During the electrolytic recovery with the liquid cadmium cathode, such a concentration change should be monitored in real time for minimizing lanthanide contamination within recovered metals[5]. Many years ago, real-time monitoring of lanthanide concentration in molten salt by normal pulse voltammetry (NPV) has been presented[1]. It has been known that NPV has a strong advantage in terms of detection limits and sensitivity, but a longer time is needed since the diffusion layer between cycles is renewed between cycles. To address this issue, in this work, we present in situ determination of lanthanides by square wave voltammetry (SWV), one of the most advanced pulse voltammetry. In SWV, there is no renewal of the diffusion layer between cycles, so that SWV provides a relatively faster analysis compared with competing other pulse techniques[9,10]. The efficacy of this approach is verified in binary systems composed of gadolinium (Gd) and lanthanum (La) in a LiCl-KCl eutectic salt.

2. EXPERIMENTAL SECTION

An anhydrous lithium chloride-potassium chloride (LiCl-KCl) eutectic mixture, silver chloride (AgCl), gadolinium trichloride ($GdCl_3$), and lanthanum trichloride ($LaCl_3$) were purchased from Sigma-Aldrich. They were used as received without additional treatment. The LiCl-KCl eutectic mixture was put in a high purity quartz cell that was placed in an alumina crucible. This crucible was moved to electric furnace installed at the bottom of glove box. After that, $GdCl_3$ was added to the eutectic solution. Practical concentration of Gd(III) in the solution was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The temperature of the eutectic salt was maintained at 773 K. Electrochemical measurements were carried out in a three-electrode high-temperature cell containing LiCl-KCl eutectic mixture with an AutoLAB PGSTAT 302N (Metrohm). A high purity tungsten wire of 1 mm diameter (99.99%, Nilaco) was used as a working electrode. A glassy carbon rod of 3 mm diameter (Alfa Aesar) served as a counter electrode. The Ag/Ag^+ redox system in a thin Pyrex glass tube of 6 mm diameter, composed of silver wire and 1 mol% silver chloride (AgCl) in the LiCl-KCl salt, was used as a reference electrode. To secure the practical implementation conditions of SWV, a number of SWV curves were obtained by varying the principle parameters of SWV, that is, a pulse height and a square wave frequency by which the square wave is characterized. But, the staircase shifted by ΔE_s (5 mV) at the beginning of each cycle in all experiments. After determining proper measurement conditions, a calibration curve was obtained in a wide range of Gd concentrations. The calibration curve was used to confirm the efficacy of SWV for in situ monitoring of binary systems consisting of Gd and La.

3. RESULTS AND DISCUSSION

Fig. 1 shows a typical waveform and measurement scheme for SWV. The scan begins at an initial potential where a charge transfer reaction does not occur. Current samples are obtained twice at each cycle at the very end of each pulse. The forward current (i_F) and the reverse current (i_R) are taken from the first pulse in the direction of the staircase scan and from the second pulse in the opposite direction, respectively. In SWV, difference current (i = i_F - i_R) voltammograms are recorded with respect to the potential on the corresponding wave[9].

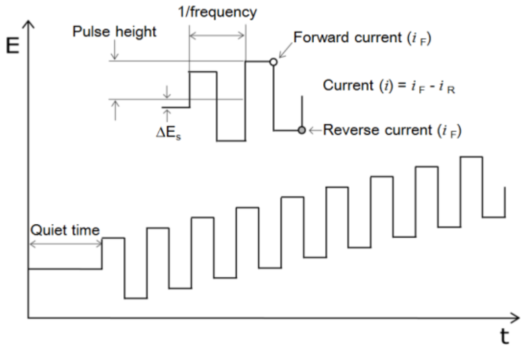

Figure 1. Waveform and measurement scheme for SWV

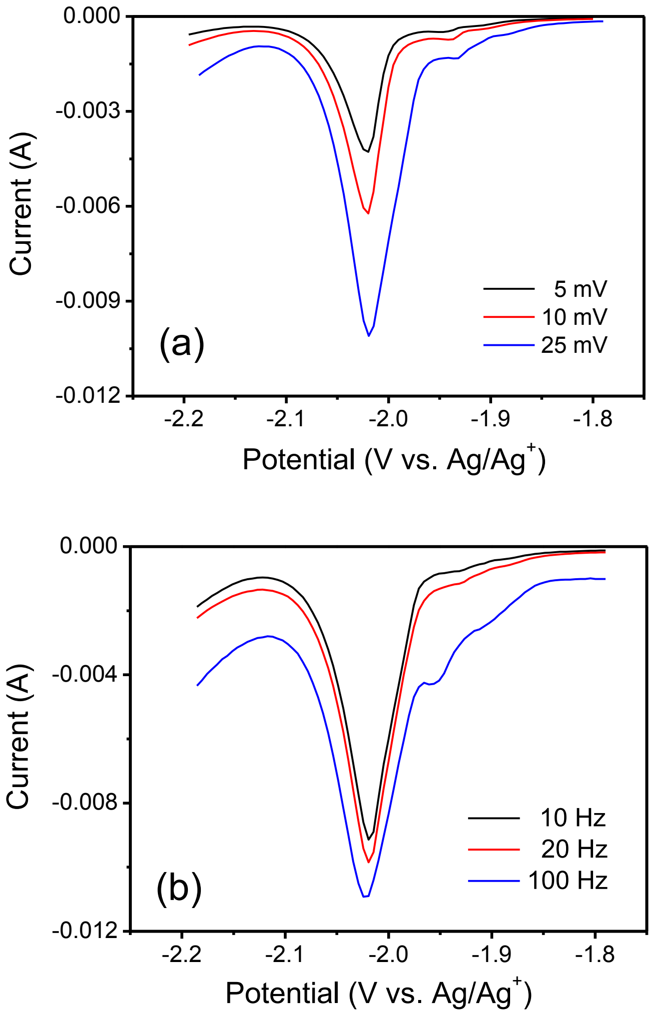

Figure 2. SWV curves for reduction of Gd(III) to Gd taken (a) under various pulse heights with a fixed frequency of 10 Hz and (b) under various wave frequencies with a fixed pulse height of 25 mV.

The peak current is directly proportional to sample concentration, which appears near standard electrode potential of the corresponding redox couple. To obtain the optimal conditions for getting a stable bell-shaped difference current-potential curve, the SWV curves were collected with 0.25 wt% gadolinium (Gd) under various measurement conditions.

Fig. 2a shows that the difference current greatly increased as a pulse height increased. This trend is similar to that reported in the work of Iizuka et al. in which the effect of pulse height on SWV curves for reduction of Ce(III) to Ce was described[11]. It was observed that the SWV response due to reduction of Gd(III) to Gd was also sensitive to the square wave frequency, as shown in Fig. 2b. The influence of the square wave frequency on SWV curves was re-examined in this work. The peak width of SWV curve increased with an increase of the square wave frequency, which is very similar to the results of the previous work[11]. It was observed that SWV curves became distorted at high frequency like 100 Hz. After making this observation, the pulse height of 10 mV and the pulse frequency of 10 Hz were chosen for the subsequent quantitative analysis of lanthanides by SWV.

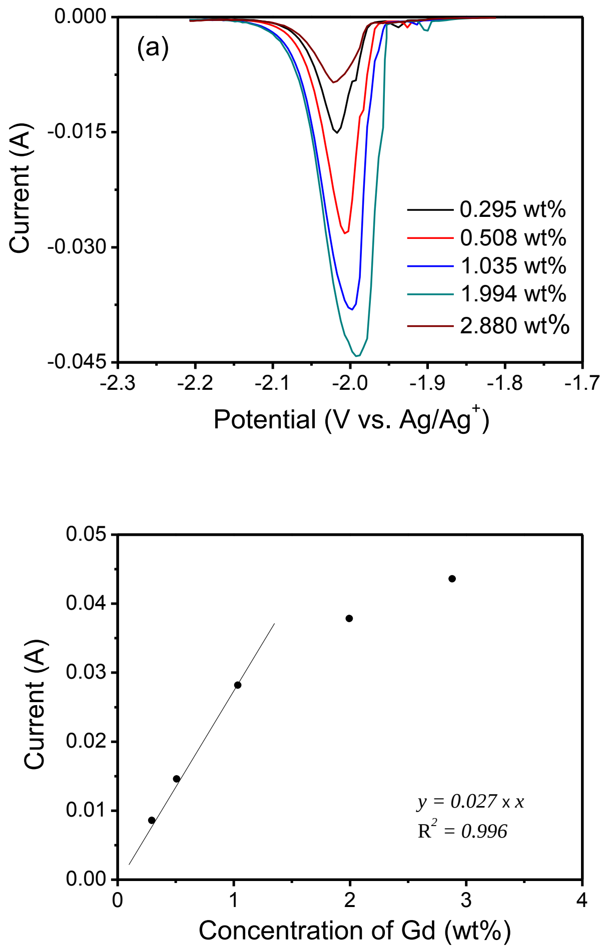

Figure 3. (a) SWV curves taken in various Gd(III) concentrations: a pulse height = 10 mV and a wave frequency = 10 Hz; and (b) the plot of peak currents versus Gd(III) concentration and the corresponding calibration curve below 1 wt% Gd(III).

To attain a calibration curve, a series of SWV curves were taken in various Gd concentrations. Fig. 3 shows that the peak current linearly increased with Gd concentration up to 1 wt%, implying that monitoring of lanthanides by SWV should be done less than 1 wt%. So, the calibration curve (solid regression line) was determined below 1 wt% (Fig. 3). A big deviation from the linear regression line was observed at higher concentrations above 1 wt% (Fig. 3). This feature is similar to that observed in the previous work in which a concentration dependence of peak height in SWV curves for reduction of Pu(III)[11].

Table 1. Binary solutions composed of $GdCl_3$ and $LaCl_3$ in a LiCl-KCl eutectic salt.

Test solution	Concentration of Gd(III) (wt%)	Concentration of La(III) (wt%)	Total concentration (wt%)
1	0.62	0.15	0.77
2	0.38	0.08	0.46
3	0.10	0.13	0.23

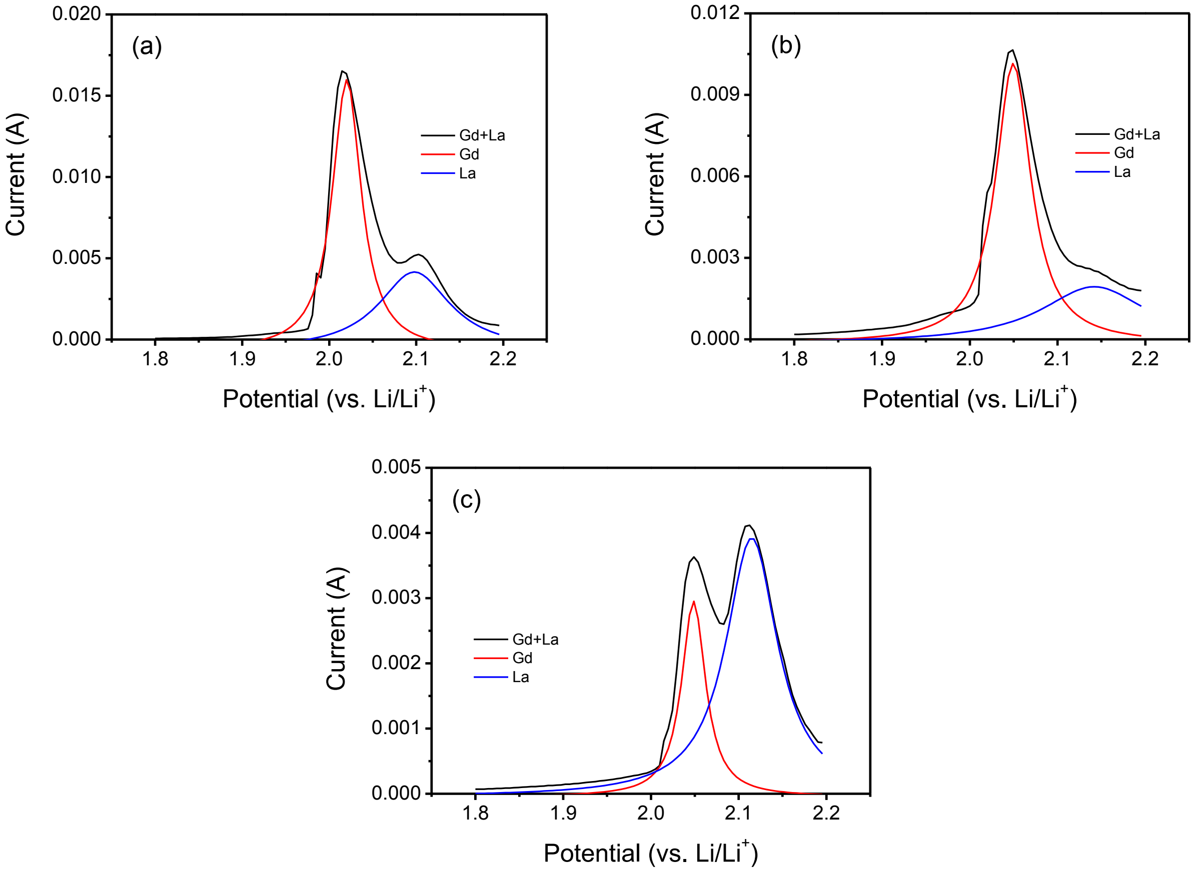

Figure 4. SWV curves (black) in various binary systems of Gd(III) and La(III) and the corresponding deconvoluted curves (blue and red).

Interestingly, at high concentrations, the difference peak current moved toward positive potential direction, indicating that a significant portion of Gd took part in electrodeposition at relatively higher potentials. This can be attributed to the increased surface area of the working electrode, which arose from more irregular deposition of Gd at higher concentrations. Indeed, it is hardly to separately determine the concentration of each individual lanthanide element in mixture solutions with general electrochemical techniques due to their similar standard electrode potentials. In this context, for a efficient control of the electrowinning process, estimating of total concentration of lanthanide species is considered as a practically meaningful task.

Iizuka et al. presented the possibility of on-line monitoring of actinide concentrations in the molten salt containing various fission products by normal pulse voltammetry[11]. To date, there have been no studies on the determination of total amount of lanthanide species in a mixture solution by SWV. As a preliminary work of the determination of total amount of lanthanide species in molten salt with numerous lanthanides, applicability of SWV was investigated in three binary systems composed of Gd(III) and La(III), as shown Table 1. The two representative lanthanides, Gd(III) and La(III) ions, were selected since their standard electrode potentials are slightly different from each other.

Fig. 4 shows the SWV curves and the results of peak deconvolution for three binary solutions of Gd and La. It was clearly observed that the SWV curves contained two waves due to a difference in the standard electrode potentials of Gd(III)/Gd and La(III)/La. Two resolved SWV curves were created from the SWV curves of binary solutions by using peak deconvolution technique. Total peak currents ($i_{p,total}$) calculated as the sum of two peak currents ($i_{p,Gd} + i_{p,La}$) were plotted versus the total concentrations of Gd(III) and La(III). The plot was compared with the calibration curve established with Gd(III) ions. The total peak currents of the binary solutions showed an excellent fitting result against the calibration curve (solid line) as shown in Fig. 5, implying that the total amount of lanthanides in a multi-component molten salt system can be estimated by SWV.

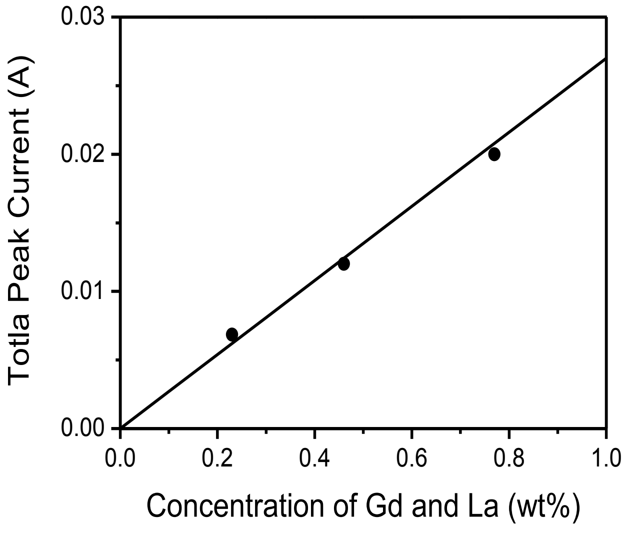

Figure 5. The plot of total peak currents ($i_{p,Gd} + i_{p,La}$) versus total concentration of Gd(III) and La(III). Solid line (–) is the calibration curve obtained in the linear region of Fig. 3.

4. CONCLUSION

In this work, we demonstrated applicability of quantitative analysis of lanthanides by square wave voltammetry (SWV) in single component and binary mixture solutions. To obtain a stable bell-shaped SWV curves, a number of measurements were performed by varying the principal parameters such as a pulse height and wave frequency. After finding proper measurement conditions, the calibration curve was obtained in molten salt with gadolinium ions. Moreover, SWV curves for the binary solutions of gadolinium (Gd) and lanthanum (La) were obtained, which were resolved to two SWV curves by peak deconvolution. Total peak currents, the sum of peak currents of two deconvoluted curves, were plotted with respect to the total concentration of Gd and La. It was found that the total peak currents of the binary solutions were excellent fitted to the calibration curve, suggesting that the quantitative analysis by SWV may be applied to the in situ monitoring of molten salt solution containing various lanthanide ions during the electrowinning process

ACKNOWLEDGMENTS
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