

A Study on Electrochemical Behaviors of Samarium Ions in the Molten LiCl-KCl Eutectic Using Optically Transparent Electrode

LiCl-KCl 용융염에서 광학적으로 투명한 전극을 이용한 사마륨 이온의 전기화학적 거동에 관한 연구

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A spectroelectrochemical method has been applied to investigate the electrochemical behaviors and identify the kinds of samarium ions dissolved in high temperature molten LiCl-KCl eutectic. An optically transparent electrode (OTE) fabricated with a tungsten gauze as a working electrode has been used to conduct cyclic voltammetry and potential step chronoabsorptometry. Based on the reversibility of the redox reaction of $\text{Sm}^{3+}/\text{Sm}^{2+}$, which was determined from the cyclic voltammograms, the formal potential and the diffusion coefficient were calculated to be $-1.99 \text{ V vs. Cl}_2/\text{Cl}^-$ and $2.53 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, respectively. From the chronoabsorptometry results at the applied potential of $-1.5 \text{ V vs. Ag/AgCl (1 wt\%)}$, the characteristic peaks of absorption for samarium ions were determined to be 408.08 nm for Sm^{3+} and 545.62 nm for Sm^{2+} . Potential step chronoabsorptometry was conducted using the anodic and the cathodic peak potentials from the voltammograms. Absorbance analysis at 545.63 nm shows that the diffusion coefficient of Sm^{3+} is $2.15 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, which is comparable to the value determined by cyclic voltammetry at the same temperature.

Keywords: Samarium, Molten LiCl-KCl eutectic, Spectroelectrochemical, Cyclic voltammetry, Potential step chronoabsorptometry

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LiCl-KCl 용융염에서 광학적으로 투명한 텅스텐 망으로 제작된 작업전극에 대해 사마륨의 전기화학적 거동을 Cyclic voltammetry와 Potential step chronoabsorptometry의 전기화학적 및 분광전기화학적 방법으로 조사하였다. Cyclic voltammogram으로 결정된 $\text{Sm}^{3+}/\text{Sm}^{2+}$ 의 산화환원 반응의 가역성을 기반으로 형식전위와 확산계수를 계산하여 각각 $-1.99 \text{ V vs. Cl}_2/\text{Cl}^-$ 와 $2.53 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ 를 얻었다. 작업 전극에 $-1.5 \text{ V vs. Ag/AgCl (wt\%)}$ 로 전압을 인가하여 측정된 Chronoabsorptometry를 통해 사마륨 이온의 특성 파장으로 Sm^{3+} 에 대해 408.08 nm , Sm^{2+} 에 대해 545.62 nm 를 확인하였다. Voltammogram에서 얻은 환원 피크 전압과 산화 피크 전압을 이용하여 Potential step chronoabsorptometry를 수행하였다. 545.63 nm 의 흡광 피크 값을 분석하여 $2.15 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ 의 확산계수를 얻었으며 이 값은 동일한 온도에서 Cyclic voltammtry 분석으로 얻은 값과 큰 차이를 보이지 않았다. 실험결과로부터 고온 용융염에서 광학적으로 투명한 작업전극을 이용한 분광전기화학적 방법이 용융염에 용해된 이온의 종류를 확인하며 전기화학적 거동을 조사하는데 유용한 도구로 활용될 수 있음을 확인하였다.

중심단어: 사마륨, LiCl-KCl 용융염, 분광전기학, Cyclic voltammetry, Potential step chronoabsorptometry

1. Introduction

Used nuclear fuels (UNFs) generated from nuclear power plants have characterized to have very high radiotoxicity but contain energy-producing materials such as uranium and transuranic elements. A recovery of energy producing materials in the UNFs with a pyroprocess is one of the options to manage the UNFs in the nations with nuclear power plants. The pyroprocess is an electrometallurgical process to recover uranium and transuranic elements from the UNFs. In Korea, Korea Atomic Energy Research Institute (KAERI) has developed the pyroprocess based on the molten LiCl-KCl eutectic to reduce radiotoxicity of the UNFs and to minimize a volume of the final radioactive wastes [1]. The major parts of KAERI pyroprocess are composed of electrolytic reduction in a molten LiCl to reduce oxide into metallic form, electrorefining and electrowinning in a molten LiCl-KCl eutectic to recover uranium and transuranic elements, salt purification and recycle of molten LiCl and LiCl-KCl eutectic, and waste treatment process to generate waste package for disposal.

A salt waste generated from the pyroprocess after recovery of uranium and transuranic elements is classified to a high-level waste because it contains a residual actinide. The residual actinide recovery process such as reductive

extraction can be employed to reduce radiotoxicity of the salt wastes. As a candidate process, a sequential process of electrolytic reductive extraction and selective oxidative extraction in molten salt-liquid metal system was proposed to recover the residual actinide from the salt waste [2]. The performance prediction of the residual actinide recovery process requires the thermodynamic and kinetic data of lanthanide and actinide dissolved in the salt waste. Among the dissolved species in the salt waste, samarium may have either oxidation state of divalent ion or trivalent ion according to electrochemical conditions. The oxidation state of samarium ion may have an effect on the electrolytic reduction into liquid metal by disproportionate reaction.

Some work has been performed to determine redox potentials, electron transfer stoichiometry, and diffusion coefficient of samarium in the molten LiCl-KCl eutectic using conventional electroanalytical techniques. However, conventional electroanalytical techniques can rarely unequivocally identify electroactive species. In addition, the electroanalytical techniques provide only limited and indirect information on structural changes accompanying redox events. On the other hand, spectroscopic techniques could characterize the dissolved species in the molten salt. A spectroelectrochemical technique that is a combination of electroanalytical techniques with spectroscopic measure-

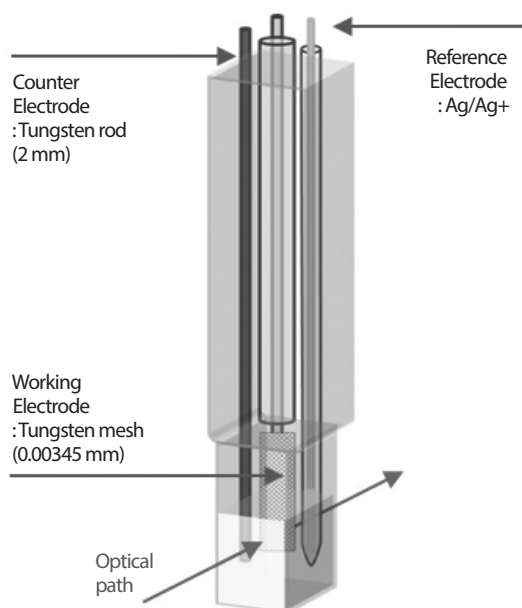


Fig. 1. The cell configuration for the spectroelectrochemical experiment in LiCl-KCl.

ment technique could provide a useful information to gain a knowledge on mechanism of the electron transfer reaction and the ionic state at the interface between electrode and solution. This technique has employed to investigate the electrochemical behaviors of the europium in the molten salt [3, 4].

In the study, the spectroelectrochemical technique under high temperature environments has been developed based on a concept of an optically transparent electrode [4] as a working electrode and employed to investigate an electrochemical behavior of samarium ion in the molten LiCl-KCl eutectic. Special electrochemical cell with optically transparent working electrode was designed to conduct the electrochemical experiment. Cyclic voltammetry was used to characterize the electrochemical conditions of samarium ions in the molten LiCl-KCl eutectic and then chronoabsorptometry at fixed potential and potential step chronoabsorptometry was used to characterize the redox reaction between trivalent and divalent samarium ions. Thermochemical data for samarium ion dissolved in the molten LiCl-KCl eutectic was estimated on the basis of the experimental results.

2. Materials and Methods

2.1 Chemicals and Materials

Anhydrous SmCl_3 and LiCl-KCl eutectic mixture (molar ratio of lithium to potassium = 59/41) were products of Sigma Aldrich and used without further purification. The appropriate amount of LiCl-KCl eutectic mixture poured into the quartz cell and then melted by raising the temperature of 773 K. Then, SmCl_3 was added and dissolved in the molten salt. Prior to the any measurement, the cell was thoroughly shaken to eliminate any bubbles present in the molten salt.

2.2 Instrumentation

The spectroelectrochemical measurement system under high temperature environments was designed and was fabricated to investigate electrochemical characteristics of the dissolved species in the molten LiCl-KCl eutectic. A measurement cell was made of 1.2 cm rectangular quartz cell with a long-necked cylindrical quartz tube as shown in Fig. 1. It was placed at the center of the electric furnace with optically accessible windows that was attached at the bottom of glove box filled with high purity argon gas (99.99%) continuously purified to remove oxygen and humidity. The content of O_2 and H_2O in the inside atmosphere of the glove box was maintained less than 1 ppm, respectively. To conduct electroanalytical and spectroscopic measurements at the same time, the three quartz windows in a 90° angle were installed to the lower part of the apparatus. The quartz windows were cooled by circulating water in order to prevent the thermal damage.

The cell is equipped with three electrodes that are composed of an optically transparent working electrode, a reference electrode, and a counter electrode. The optical transparency of working electrode was achieved with use of a tungsten gauze of 100 mesh (99.9%, Alfa Aesar) which is commercially available. The upper end of the

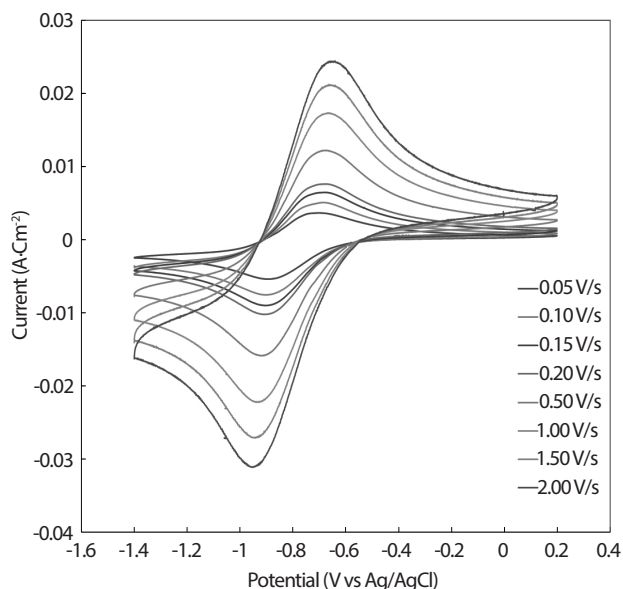


Fig. 2. Cyclic voltammograms for the redox reaction of $\text{Sm}^{3+}/\text{Sm}^{2+}$ at different scan rates at 723 K on an optically transparent electrode of tungsten gauze in $\text{LiCl-KCl}+\text{SmCl}_3$ (1wt%) solution.

tungsten gauze was pressed with silver wire for electrical connection. The silver wire was guided with Quartz tube for avoiding contact with the other electrode. The fabricated working electrode has 81% transmittance to light. The counter electrode was a tungsten rod (99.95% with 2mm in diameter, Sigma Aldrich). The reference electrode was Ag (99.99% Ag wire with 1.0 mm in diameter)/AgCl (1.0 wt% in LiCl-KCl) system. A solution of 1.0 wt% of AgCl in the molten LiCl-KCl eutectic was encapsulated in a thin-end Pyrex glass tube. A silver wire was inserted into the Pyrex tube to be immersed in the solution. All reported potentials were referenced versus the Ag/AgCl (1.0 wt%) reference electrode.

The spectroscopy measurement system was composed of light source (DH-2000-BAL, Ocean Optics), optical fiber (GH4001, Mitsubishi Rayon), collimating lens (84-UV-25, Ocean Optics) and UV-Vis spectrometer (multichannel spectrometer, Avantes) with Avasoft software (Avantes). The light beam travels out from a light source through an optical fiber that were connected to a collimating lens that

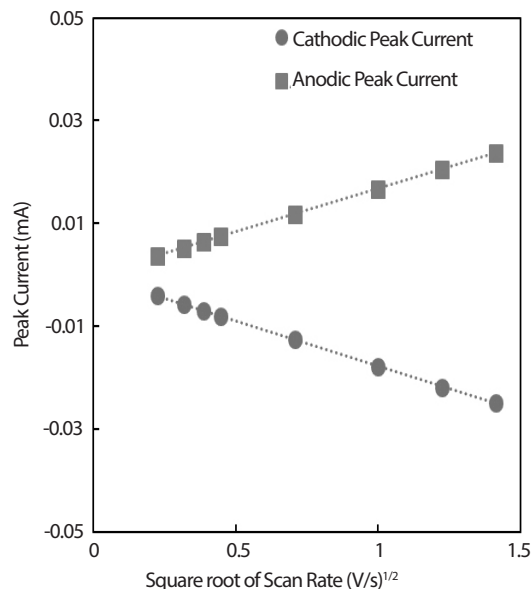


Fig. 3. Variation of cathodic and anodic peak current as a function of the square root of scan rate at 723 K on an optically transparent electrode of tungsten gauze in the molten LiCl-KCl eutectic.

makes a 3 mm ϕ straight beam. The light beam that travels through the cell is caught by another collimating lens at the opposite side of the furnace and is lead to the spectrometer by another optical fiber. Electroanalytical measurements were carried out with Solatron Potentiostat controlled with CorrWare software (Scribner Assoc.)

3. Results and Discussion

3.1 Cyclic Voltammetry

Cyclic voltammetry was conducted to investigate electrochemical characteristics of samarium ion in the molten LiCl-KCl eutectic. Fig. 2 shows cyclic voltammograms for scan rates ranging from 0.05 to 2.00 V/s with the potential window from -1.4 V to 0.2 V at the temperature of 723 K on the optically transparent electrode of tungsten gauze. The voltammograms have single well-defined peaks for cathodic reaction at about -0.92 V and for

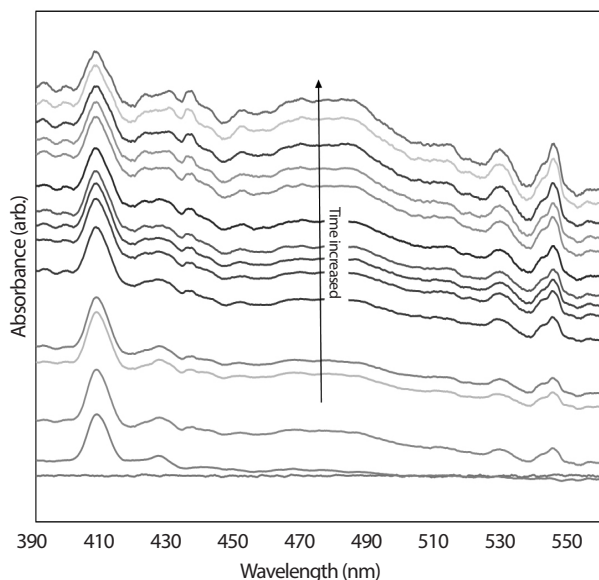


Fig. 4. Variation of absorbance spectra of LiCl-KCl-SmCl₃ (1wt%) melt during chronoabsorptometry at fixed potential of -1.5 V vs Ag/AgCl(1wt%) as a function of time at 723 K.

anodic reaction at about -0.67 V, respectively and exhibits a soluble-soluble system presumably related to Sm³⁺/Sm²⁺ redox system. The reversibility test was performed with a dependency of peak current versus square root of the potential scan rate and a slope of the log of the peak current versus log of the potential scan rate [6, 8]. The plots of the peak currents versus the square root of the potential scan rate, as shown in Fig. 3, show that the peaks of cathodic current and anodic current are linearly proportional to the square root of the scan rates, respectively. The slope of the log of the peak current versus the log of the potential scan rate is equal to approximately 0.5 by the regression analysis.

The reversibility of the redox reaction of Sm³⁺/Sm²⁺ allows us to determine the formal potential with the voltammograms. The formal potential, E^0 , of the redox reaction of Sm³⁺/Sm²⁺ was estimated from the data of the anodic and cathodic peak potentials obtained from the cyclic voltammograms using the following equations [6]:

$$E^0 = (E_{pc} + E_{pa}) / 2 \quad (1)$$

where E_{pc} is a peak potential of cathodic reaction, and E_{pa} is a peak potential of anodic reaction. The peak potentials measured against the Ag/AgCl reference electrode were transformed into the Cl₂/Cl⁻ reference electrode scale using correlation of $E_{Ag^+/Ag} = -1.0659 - 0.0001805 \times T$ (V vs. Cl₂/Cl⁻). Analysis of voltammograms exhibited that the formal potential of Sm³⁺/Sm²⁺ redox couple was -1.99 V vs. Cl₂/Cl⁻.

The diffusion coefficient of Sm³⁺ ions in molten LiCl-KCl eutectic was determined using the cathodic peak current, according to the Randles-Sevcik equation for reversible soluble-soluble system:

$$I_{pc} = 0.4463 \times nFSC_0 \left(\frac{nF}{RT} \right)^{1/2} \nu^{1/2} D^{1/2} \quad (2)$$

where D is the diffusion coefficient [cm²·s⁻¹], S is the electrode surface area [cm²], C_0 is the solute concentration [mol·cm⁻³], F is the Faraday constant [C·mol⁻¹], R is the ideal gas constant [J·K mol⁻¹], n is the number of exchanged electrons, ν is the potential scan rate [V·s⁻¹] and T is the absolute temperature [K]. Analysis of voltammograms exhibited that the diffusion coefficient of Sm³⁺ was 2.53×10^{-6} cm²·s⁻¹.

3.2 Chronoabsorptometry at fixed potential

The absorption spectra of samarium ion in molten LiCl-KCl eutectic was measured under an applied potential of -1.5 V for cathodic reduction at 723 K during 120 seconds. Fig. 4 shows the absorption spectra of samarium in the molten LiCl-KCl eutectic. Initially, absorption of LiCl-KCl-SmCl₃ melt was appeared at 390 ~ 440 nm without the applied potential. After the potential was applied at -1.5 V, the reduction of Sm³⁺ to Sm²⁺ resulted in the color change from pale yellow to red-brown and a broad band at 520 ~ 560 nm appeared in the spectra. Peak findings of absorption spectra show that characteristic peaks are 408.08 nm and 545.62 nm that correspond to Sm³⁺ and Sm²⁺, respectively [7]. Absorp-

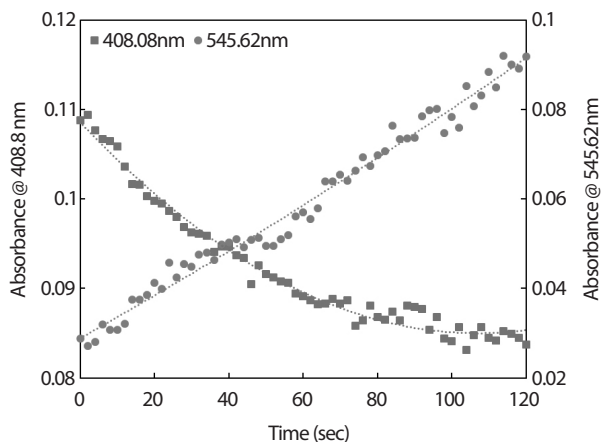


Fig. 5. Absorbance changes of LiCl-KCl-SmCl₃ (1wt%) melt at 408.08 nm and 545.62 nm during chronoabsorptometry at fixed potential of -1.5V vs Ag/AgCl (1wt%).

tion intensities at 408.08 nm and 545.62 nm were analyzed after baseline correction of spectra. Fig. 5 shows the change of absorption intensities at 408.08 nm and 545.62 nm. When the cathodic reduction at -1.5 V is progressed, absorbance at 408.08 nm is gradually decreased and absorbance at 545.62 nm is gradually increased. After turn off the applied potential, broad band at 520~560 nm gradually diminished indicating that the product of reduction of Sm³⁺ is stable in the melt only under the cathodic potential. Absorption intensities at each wavelength are proportional to the square root of time.

3.3 Potential Step Chronoabsorptometry

The double potential step chronoabsorptometry was conducted in LiCl-KCl-SmCl₃ at 723K. The potential step from -0.67 V to -0.92 V were selected from the voltammograms, which correspond to anodic and cathodic peak potentials, respectively. An initial potential was set to -0.67 V to ensure that the entire samarium concentration in the salt was in the fully oxidized. The potential was subsequently changed to -0.92 V during 50 seconds to reduce Sm³⁺ to Sm²⁺ at a diffusion controlled rate, which was followed by

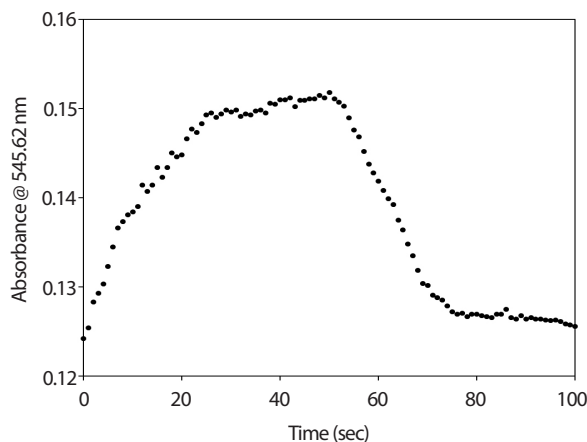


Fig. 6. Absorbance change of LiCl-KCl-SmCl₃ (1wt%) melt at 545.62 nm during potential step chronoabsorptometry, which the potential was stepped from -0.92 V to -0.67 V vs Ag/AgCl (1wt%) at 50 seconds.

changing the potential back to -0.67 V to reoxidize the sample to Sm³⁺. Absorption spectra were recorded during both reduction and oxidation steps. Fig. 6 shows the increase in absorbance at 545.62 nm upon lowering the potential to -0.92 V, indicating a reduction of Sm³⁺ to Sm²⁺. The magnitude of absorbance reaches a maximum after 25 seconds, indicating complete electrolysis of Sm³⁺ within the optical path of the cell. After 50 seconds the applied potential was stepped-up from -0.92 V to -0.67 V. This resulted in the oxidation of the electro-generated Sm²⁺ back to parent Sm³⁺. It is confirmed by the decrease in the absorbance at 545.62 nm and subsequent leveling off after 25 seconds.

Absorbance is related to diffusion coefficient of the dissolved ion in the solution under the double potential step chronoabsorptometry. Diffusion-limited current in potential step method is expressed using Cottrell equation and Absorbance is related to concentration by Beer's law. Combining two relations, the diffusion coefficient for Sm³⁺ was determined from the slope of the plot of absorbance vs t^{1/2}. Initially the variation of absorbance is diffusion controlled (up to t = 25s), which can be used to calculate the diffusion coefficient in accordance with the following equation [5]:

$$A = \frac{2\epsilon_r D^{1/2} C t^{1/2}}{\pi^{1/2}} \quad (3)$$

where A is the absorbance, ϵ_r is the molar absorptivity of Sm^{2+} , D is the diffusion coefficient of Sm^{3+} , C is the concentration of Sm^{3+} , and t is time. The molar absorptivity of Sm^{2+} in LiCl-KCl was calculated to be $5385 \text{ M}^{-1}\cdot\text{cm}^{-1}$ using the maximum absorbance of a fully reduced Sm^{2+} solution and Beer's law. Applying this equation to slope of the linear portion of the graph gives a diffusion coefficient of $2.15 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$ for Sm^{3+} , which is comparable to the value determined by cyclic voltammetry at the same temperature ($2.53 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$).

4. Conclusions

The spectroelectrochemical technique under high temperature has been developed with the optically transparent working electrode of tungsten gauze in order to investigate the electrochemical behavior in the electrolytic reduction process for actinide recovery process from the salt waste. It was first applied to samarium ion dissolved in the molten LiCl-KCl eutectic. In the study, the electrochemical characteristics of samarium ion dissolved in the molten LiCl-KCl eutectic were obtained with cyclic voltammetry, chronoabsorptometry at fixed potential, and potential step chronoabsorptometry. Based on the reversibility of the redox reaction of $\text{Sm}^{3+}/\text{Sm}^{2+}$ to be determined from the cyclic voltammograms, the formal potential and diffusion coefficient were calculated to be $-1.99 \text{ V vs. Cl}^2/\text{Cl}^-$ and $2.53 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$, respectively. The characteristic peaks of absorption for samarium ions were determined to be 408.08 nm for Sm^{3+} and 545.62 nm for Sm^{2+} from chronoabsorptometry at the applied potential of $-1.5 \text{ V vs. Ag/AgCl (1wt\%)}$. Potential step chronoabsorptometry was conducted using the anodic and cathodic peak potentials from the voltammograms. Absorbance analysis at 545.63 nm exhibits that diffusion coefficient of Sm^{3+} is $2.15 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$, which is comparable to the value determined by cyclic voltammetry at the same temperature. Experimental results show that the spectroelectrochemical technique with the

optically transparent working electrode is a useful tool to investigate the electrochemical behaviors of lanthanides dissolved in the molten LiCl-KCl eutectic.

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