

Active Electrode for Measuring Lanthanide Ion Concentrations in Molten Chloride Salt Reactors

Wonseok Yang¹, Taeho Jang², Changyoung Jung³, Sang-Eun Bae³, Sungyeol Choi^{2*}

¹Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea

² Department of Nuclear Engineering, Seoul National University, Seoul 08826, Republic of Korea

³ Korea Atomic Energy Research Institute, 111 Daedeok-daero 989, Yuseong-gu, Daejeon 34057, Republic of Korea

*Corresponding Author: choisys7@snu.ac.kr

Abstract

The concentration of Lanthanide ions needs to be monitored to successfully operate a molten salt reactor because of their high neutron absorption cross-section. One method for monitoring the concentration of lanthanide ions in molten salt is the electrochemical method which can be operated in high-temperature and high-radiation environments. However, in NaCl-MgCl₂-UCl₃ salt, the lanthanide elements cannot be electrochemically monitored by an inert working electrode due to the magnesium ion reduction potential being higher than that of the lanthanide ions. To measure lanthanide ions with the electrochemical method, an active electrode (aluminum) was used. Various voltammetry techniques and anodic stripping analysis were used to measure lanthanide ions in NaCl-MgCl₂ eutectic salt. Using an aluminum working electrode, we are able to measure lanthanide ions in a narrow electrochemical window of NaCl-MgCl₂ eutectic salt because lanthanide ions form intermetallic compounds with aluminum.

Keywords: Electrochemical sensor, Fission product, Molten salt reactor, Aluminum working electrode

1. Introduction

Molten salt reactors are advanced nuclear reactor systems that utilize high-temperature molten salts as both the fuel and the coolant. These reactors offer several advantages, such as improved fuel utilization, inherent safety features, and the potential for efficient power generation. However, the presence of lanthanide ions in the molten salt can pose challenges due to their high neutron absorption cross-section, affecting the overall reactor performance. Therefore, monitoring the concentration of lanthanide ions is crucial for the successful operation of a molten salt reactor.

Electrochemical methods have emerged as promising techniques for monitoring in molten salt systems. These methods offer the advantages of operability in high-temperature and high-radiation environments [1], making them well-suited for use in molten salt reactors. However, in certain salt compositions, such as NaCl-MgCl₂-UCl₃, the electrochemical monitoring of lanthanide ions using an inert working electrode is not feasible due to the higher reduction potential of magnesium ions compared to that of lanthanide ions. This limitation hinders the direct measurement of lanthanide ions using traditional electrochemical techniques.

To overcome this challenge, alternative electrode materials need to be explored. In this study, an active electrode material, aluminum, was utilized to enable the electrochemical monitoring of lanthanide ions in the NaCl-MgCl₂ eutectic salt. Aluminum is known to form intermetallic compounds with lanthanide ions, providing an opportunity for electrochemical measurement within a narrow electrochemical window.

In this context, various voltammetry techniques, including cyclic voltammetry and square wave voltammetry, along with anodic stripping analysis, were employed to measure the concentration of lanthanum ions in the NaCl-MgCl₂ eutectic salt. The combination of these electrochemical methods with the use of an aluminum working electrode allowed for the successful measurement of lanthanum ions.

2. Materials and Experimental Setup

Sodium chloride (NaCl), magnesium chloride (MgCl₂) and lanthanum trichloride (LaCl₃) (purity \geq 99.99%) were obtained from Sigma-Aldrich Co., Ltd. Silver chloride (99.998%, ultra-dry), silver wire (Ag, wire, 99.99%, 1 mm diameter), tungsten rod (W rod, 99.99%, 1.5 mm diameter), and aluminum wire (Al wire, 99.99%, 1 mm diameter) were purchased from Alfa Aesar. All chemicals and materials were used without further purification and handled in a glovebox with an argon atmosphere ([H₂O], [O₂] < 1 ppm).

All experiments were conducted in a glovebox environment. A tube furnace (Diameter 51 mm, Depth: 300 mm) was installed at the bottom of the glovebox (Fig. 1). A quartz crucible with a 1-mm wall thickness was placed in the furnace. The temperature of the molten salt was measured using a K-type thermocouple, which was inserted directly into the salt at an approximate depth of 10 mm. The electrochemical measurements were performed using a PARSTAT MC Multichannel

Potentiostat (Princeton Applied Research). Three electrode system was used for the whole measurement. We use Al wire as the working electrode 1 and W rod as the working electrode 2. We compared the result of the voltammetry measurement of both working electrodes.

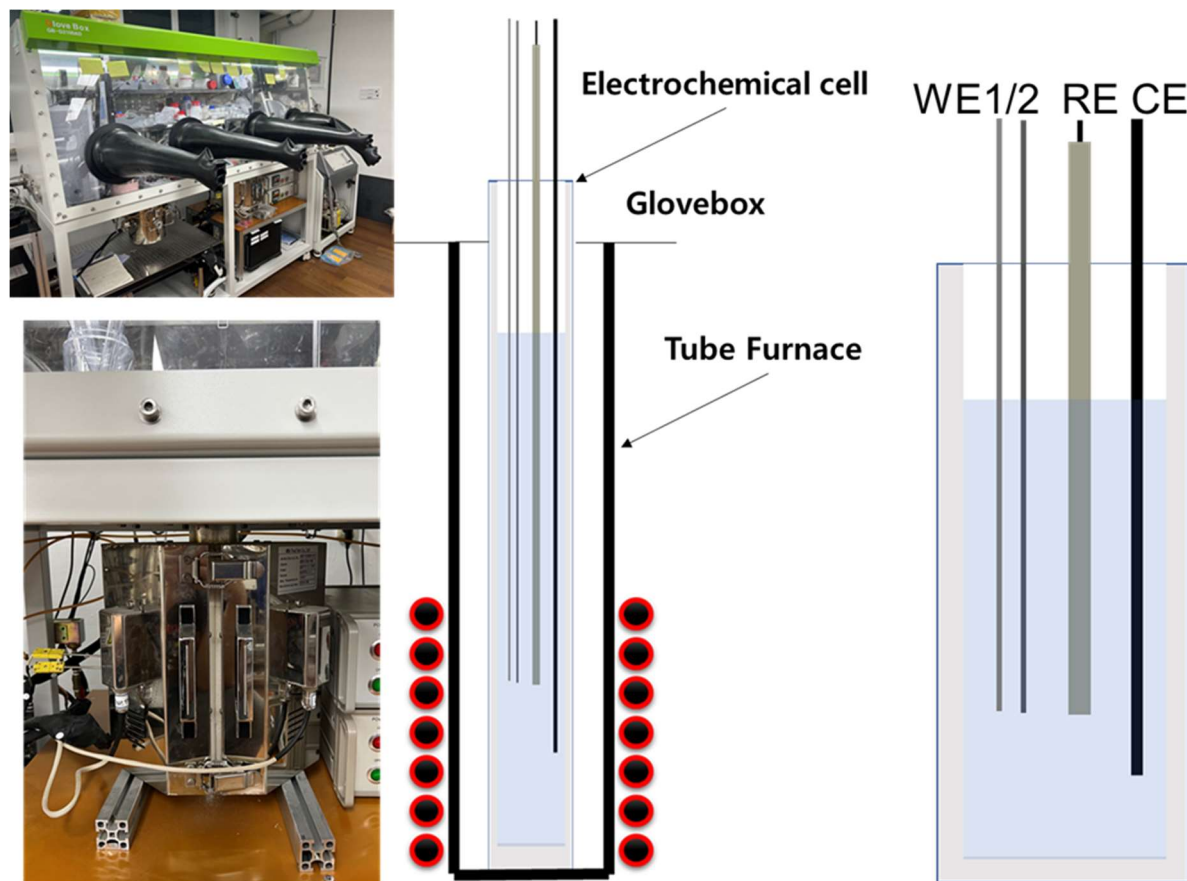


Fig 1. Glovebox, tube furnace, and electrochemical cell setup (WE1: aluminum wire, WE2: tungsten rod, RE: Ag|Ag⁺ reference electrode, and CE: glassy carbon rod)

3. Electrochemical measurements

In this study, the electrochemical behavior of La ions in NaCl-MgCl₂ eutectic salts was investigated using cyclic voltammetry (CV) and square wave voltammetry (SWV) as electrochemical measurement techniques at 773K. CV and SWV were employed as electrochemical measurement techniques to investigate the electrochemical reactions of La ions. These methods provide valuable information about the redox processes and kinetic behavior of the La species in solution.

Potentiometric stripping analysis (PSA) was utilized to assess the variations in signal response corresponding to the concentration of La ions. This technique allows for the determination of trace amounts of La ions in solution by applying a stripping potential, which induces the electrochemical reduction of the La ions on the electrode surface. The resulting current response can be correlated to the concentration of La ions in the solution, providing insights into the sensitivity and detection limits of the analytical system.

4. Results and discussion

4.1. Comparison with inert W electrode

The measurement of lanthanum ions using an inert (W) electrode was unsuccessful. However, it was found that the electrodeposition of lanthanum ions could be effectively measured using an Al electrode, particularly prior to the electrodeposition of Mg ions (Fig 2).

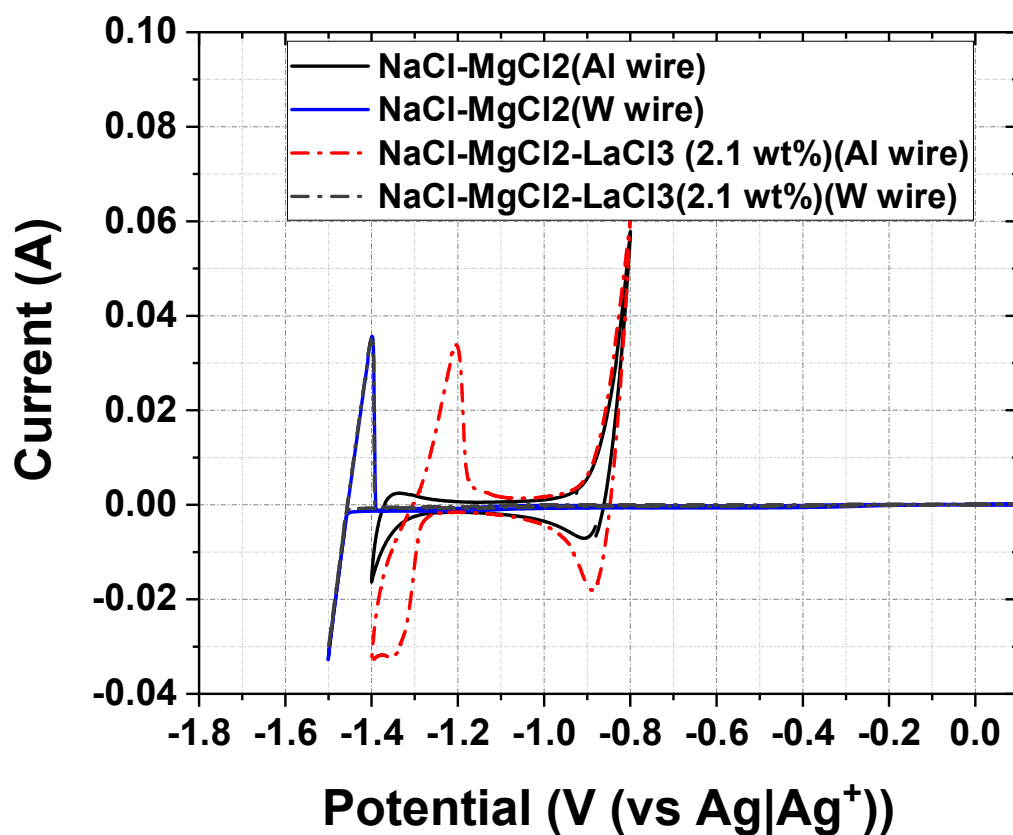


Fig 2. Cyclic voltammogram of NaCl-MgCl₂ and NaCl-MgCl₂-LaCl₃ (2.1 wt%) (WE1: aluminum wire, WE2: tungsten rod, RE: Ag|Ag⁺ reference electrode, CE: glassy carbon rod, Scan rate: 0.1 V/s, Temperature 773 K)

As can be seen in Fig 3, there are three electrochemical reactions in NaCl-MgCl₂-LaCl₃. Reduction 1 is magnesium ion deposition [2]; Reduction 2 is a reduction of lanthanum ions; Reduction 3 is aluminum ion deposition [3]. The number of electrons transferred in reduction 2 need to be investigated.

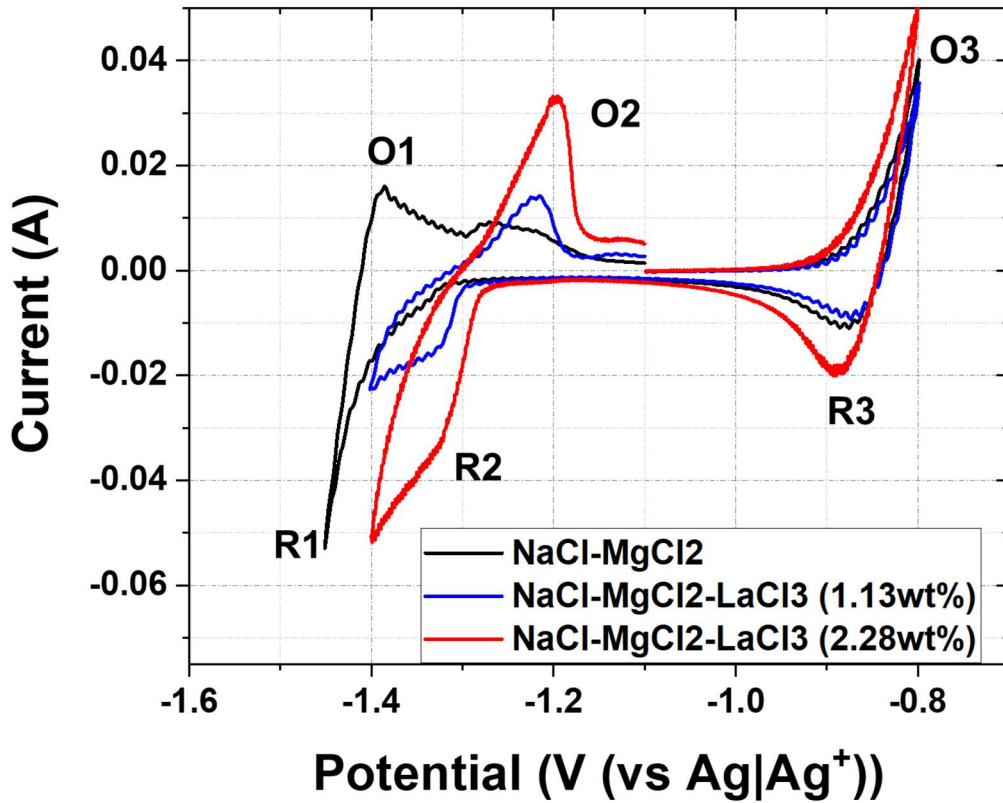


Fig 3. Cyclic voltammogram of NaCl-MgCl₂ and NaCl-MgCl₂-LaCl₃ (1.13 and 2.28 wt%) (WE: aluminum wire, RE: Ag|Ag⁺ reference electrode, CE: glassy carbon rod, Scan rate: 0.1 V/s, Temperature 773 K)

4.2. Number of electrons transferred

To investigate the number of electrons involved in the reduction of lanthanum ions, square wave voltammetry was employed, and the full width at half maximum (FWHM) of the peaks in the square wave voltammogram was analyzed. The relationship between the FWHM and the number of electrons involved was determined to be

$$\text{FWHM} = 3.52RT/nF$$

Where R is the gas constant; T is temperature; n is the number of electrons transferred; F is Faraday constant [4].

Consequently, based on the analysis of Figure 4, the calculated number of electrons participating in the reaction was determined to be 2.97, which was found to be close to 3. Therefore, it can be concluded that the reduction reaction of lanthanum ions involves the formation of La-Al alloy through an electrodeposition process [5]. The participation of three electrons in the reduction reaction indicates the transfer of three electrons from the electrode to each lanthanum ion during the electrochemical process.

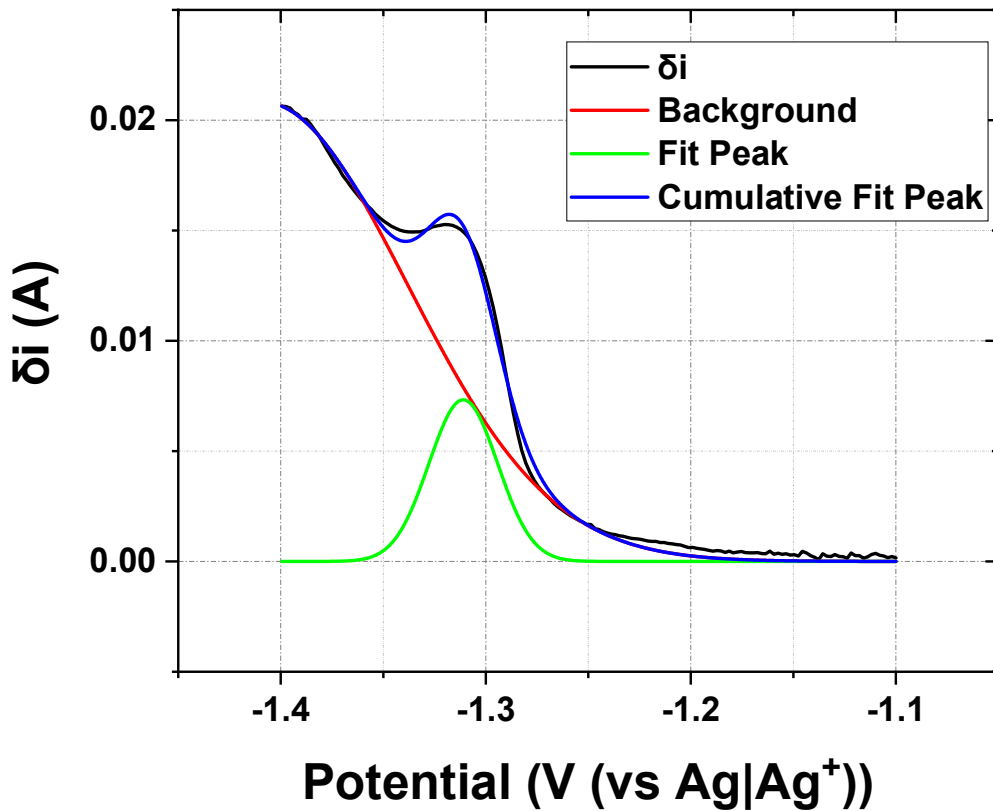


Fig 4. Square wave voltammogram of NaCl-MgCl₂-LaCl₃ (2.28 wt%) (WE: aluminum wire, RE: Ag|Ag⁺ reference electrode, CE: glassy carbon rod, Temperature 773 K, Pulse height: 10 mV, potential step: 2 mV, Frequency: 20 Hz)

4.3. Potentiometric stripping analysis for measuring lanthanide ion concentration

Fig 5 represents the results of the PSA (Potentiostatic Stripping Analysis) measurements. In Fig 5 (a), a flat region can be observed between -1.25 V and -1.2 V, which corresponds to the potential range where lanthanum (La) dissolves from the La-Al alloy. PSA is characterized by the relationship between dt/dE (time derivative of current with respect to potential) and concentration, which is depicted in Fig 5 (b). Fig 5 (c) demonstrates the relationship between the peak values of dt/dE from Fig 5 (b) and concentration.

As depicted in Fig 5 (d), a linear relationship is observed at low concentrations (below 1.5 wt%), while at higher concentrations, the peak values increase with concentration, but a linear relationship cannot be discerned. This suggests the possibility of the formation of different alloy phases as the concentration of La ions increases. The linear relationship observed at low concentrations indicates the feasibility of quantitative analysis using an Al electrode. This implies that at lower concentrations, where a linear relationship exists, the concentration of La ions can be accurately determined using

the Al electrode.

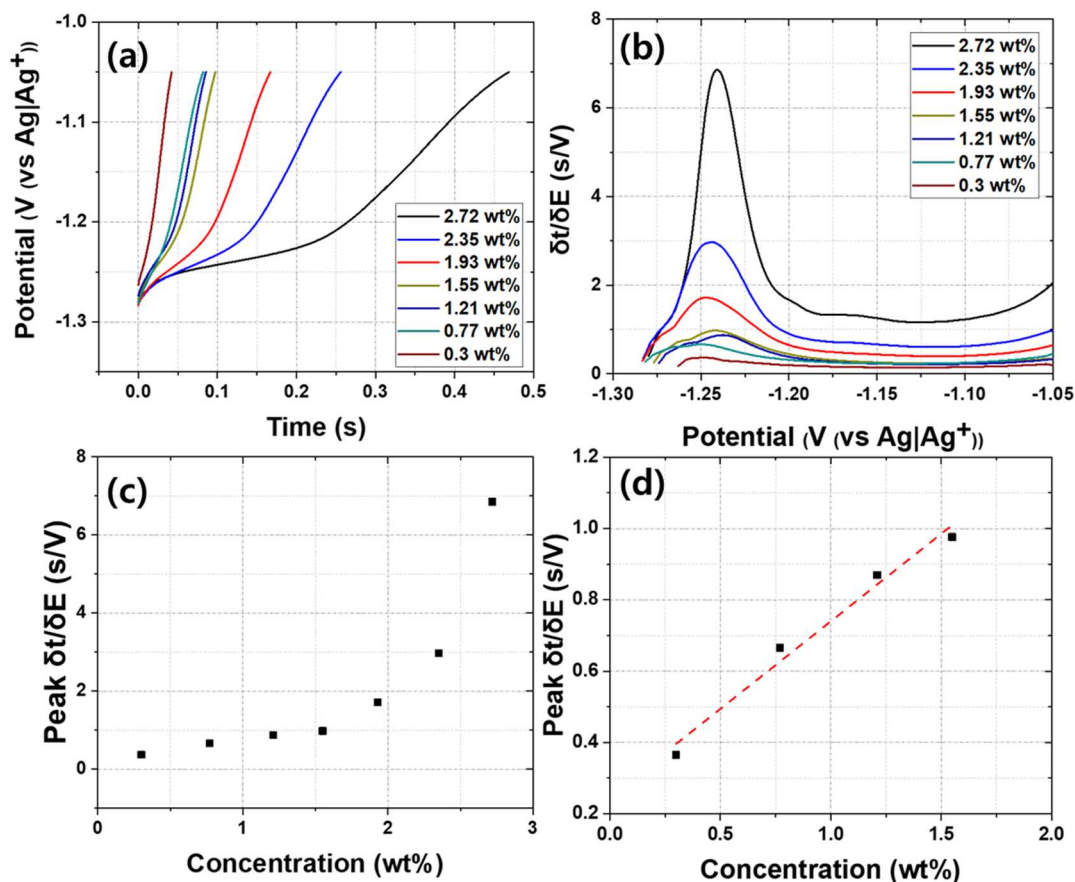


Fig 4. (a) and (b) are potentiometric stripping analysis (PSA) of NaCl-MgCl₂-LaCl₃ (various concentrations). (c) and (d) are graphs of peak dt/dE from PSA and concentration (WE: aluminum wire, RE: Ag|Ag⁺ reference electrode, CE: glassy carbon rod, Temperature 773 K, deposition potential: -1.35 V (vs. Ag|Ag⁺), deposition time: 0.01 s, Stripping current: 0.1 μA)

4.4. Limitations of aluminum sensor

To ensure the suitability of lanthanide ion concentration measurements in a molten salt reactor, an assessment of long-term stability is essential. Fig 5 illustrates the changes in the electrode and the salt solution before and after long-term evaluations. As observed in Fig 5, when an aluminum electrode is immersed in the molten salt for an extended period (5 day), a black film forms on the surface of the aluminum electrode. The salt solution also shows contamination by the presence of darkened material. Therefore, it is evident that a long-term stability issue exists.

The impact of the formation of a black film on the electrode surface highlights the need for further investigation into the changes in electrochemical signals associated with this phenomenon. Understanding the variations in electrochemical signals when the black film forms on the electrode surface is crucial for addressing long-term stability concerns.

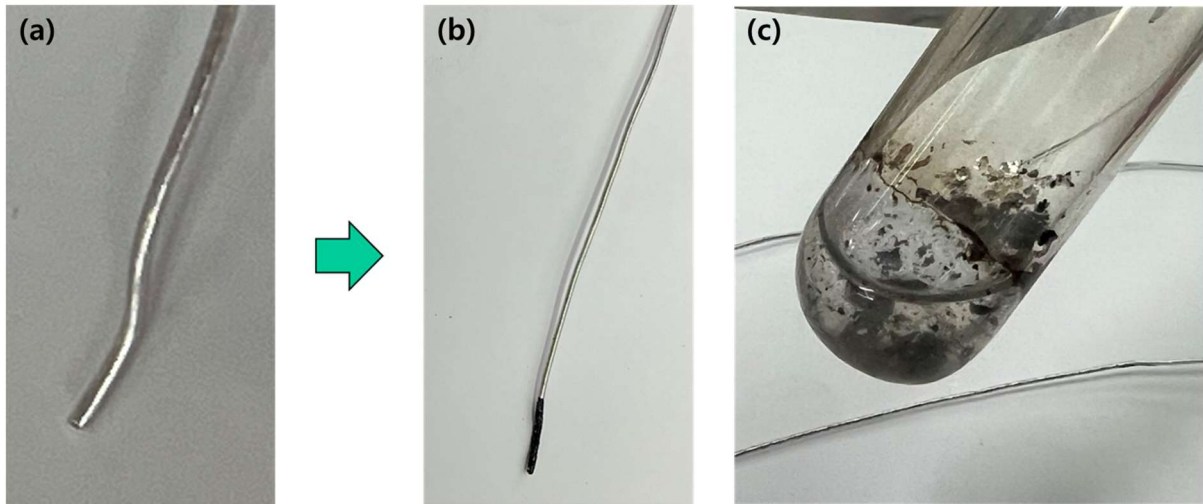


Fig 5. Changes in the Al electrode and the salt solution before and after long-term evaluations

5. Conclusion

In this study, the electrochemical method utilizing an active aluminum electrode has demonstrated its efficacy in measuring lanthanide ions in the NaCl-MgCl₂ eutectic salt. Various voltammetry techniques and anodic stripping analysis were successfully employed for this purpose. The formation of intermetallic compounds allowed for the deposition of lanthanum ions onto the aluminum electrode, facilitating their electrochemical measurement. At low concentrations, a linear relationship between the peak dt/dE values and the lanthanum ion concentration was observed through constant-current stripping analysis. However, the aluminum electrode encountered corrosion issues during long-term measurements, raising concerns regarding its stability. Future research should focus on addressing these corrosion issues, exploring alternative electrode materials, and surface modifications to enhance the electrode's long-term stability and improve the accuracy of electrochemical measurements. Nonetheless, this study highlights the potential of the electrochemical method with an aluminum electrode for monitoring lanthanide ion concentrations in NaCl-MgCl₂.

Reference

- [1] Rappleye, Devin, Kevin Teaford, and Michael F. Simpson. "Investigation of the effects of uranium (III)-chloride concentration on voltammetry in molten LiCl-KCl eutectic with a glass sealed tungsten electrode." *Electrochimica Acta* 219 (2016): 721-733.
- [2] Ding, Wenjin, et al. "Electrochemical measurement of corrosive impurities in molten chlorides for thermal energy storage." *Journal of Energy Storage* 15 (2018): 408-414.
- [3] Yan, Yong-De, et al. "Electrochemical extraction of neodymium by co-reduction with aluminum

in LiCl-KCl molten salt." *Journal of nuclear materials* 433.1-3 (2013): 152-159.

[4] Ramaley, Louis, and Matthew S. Krause. "Theory of square wave voltammetry." *Analytical chemistry* 41.11 (1969): 1362-1365.

[5] Liu, Ya-Lan, et al. "Co-reduction behaviors of lanthanum and aluminium ions in LiCl-KCl eutectic." *Electrochimica Acta* 147 (2014): 104-113.