

Research Article

Electrochemical Removal of Rare Earth Element in LiCl-KCl Molten Salt

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This study was carried out to examine the removal of rare earth (RE) elements by electrodeposition for the purification and reuse of LiCl-KCl salt after electrorefining and electrowinning. The electrochemical behavior of RE elements (Dy and Gd) in LiCl-KCl-DyCl₃-GdCl₃ at 500°C was investigated using the cyclic voltammetry (CV) technique using Mo and Mg electrodes. It was observed that the reduction potential of the RE elements shifted at the Mg electrode owing to the alloy formation with Mg (RE-Mg alloy). Subsequently, a series of potentiostatic electrolysis tests were conducted to remove the RE elements in the salt and check the formation of deposits at the Mg and Mo electrodes. The scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM/EDS) technique was used to confirm that the reduced RE metals were deposited on the surface of the Mg electrode. However, no significant deposit on the Mo electrode was observed, and a mud-like deposit was found on the bottom of the electrochemical cell. The salt analysis performed by employing the inductively coupled plasma-optical emission spectrometry (ICP-OES) indicated that the removal efficiency of Dy³⁺ and Gd³⁺ through electrodeposition was 83.5~95.2 and 91.6~95.2%, respectively.

1. Introduction

Pyroprocessing is an option which enables to recover the useful nuclear elements from spent fuel and to recycle them for fast reactors [1, 2]. Pyroprocessing consists of several unit processes to separate, recover, and store the radioactive elements in the spent fuels [3, 4]. After head-end process, the spent oxide fuel is immersed and reduced in 650°C LiCl at the electrolytic reduction process. Then, the reduced spent fuel is transferred into an electrorefiner which contains a eutectic LiCl-KCl melt with some portion of UCl₃ at 500°C. Uranium is recovered using solid cathode (i.e., electrorefining) [5–7] and uranium and transuranic elements are recovered using liquid cathode (i.e., electrowinning) [8–10]. After both of the recovery steps such as electrorefining and electrowinning, there are abundant amounts of rare earth (RE) elements in the salt. Consequently, the molten salt electrolyte containing RE elements should be properly treated to minimize salt waste, to fabricate a durable waste

form, and to reuse the purified salt electrolyte in electrorefining and electrowinning. Besides, RE elements are key elements in industries and often used as additives to improve properties of alloy such as thermal and mechanical properties and corrosion resistance [11].

To separate RE elements from the salt, various processes have been employed, such as ion-exchange [12], zone freezing method [13], and phosphate precipitation [14, 15]. However, these require a specific device for solid salt detachment and/or layer separation and an additional process such as distillation. Some researchers attempted to extract RE from the molten solvent via electrochemical methods. They have used an Al electrode in a chloride salt [16–19], Ni and Cu electrodes in a fluoride salt [20], W electrode in MgCl₂-containing salt [21], and Mg electrode [22–24]. Especially, Yang et al. reported that the selective extraction of Dy was carried out using Mg electrode [22]. We thought that the electrochemical removal of RE in salt enables to the purification and reuse without salt transfer step from

electrorefiner/electrowinner to another reactor. The objective of the present study was to examine the removal of RE elements by electrodeposition using Mo and Mg electrode. The use of Mg was considered as it is a reactive material that forms RE-Mg alloys and Mo is an inert electrode widely used in electrochemical experiments. Cyclic voltammetry (CV) measurements were obtained to observe the redox peaks of RE elements by using Mo and Mg electrodes in LiCl-KCl containing DyCl_3 and GdCl_3 at 500°C . Subsequently, a series of constant-potential electrolysis tests was performed to remove Dy^{3+} and Gd^{3+} in the salt and a cross-sectional analysis of deposit was carried out by SEM/EDS technique.

2. Materials and Methods

All the experiments were performed in a glove box with an Ar (g) atmosphere ($\text{H}_2\text{O} < 1$ ppm; $\text{O}_2 < 3$ ppm). A mixture of LiCl-KCl eutectic salt (99.99% purity, Sigma-Aldrich) and RECl_3 (RE: Dy and Gd, 99.99% purity, Alfa-Aesar) was prepared in an alumina crucible (30 mm inner diameter, 50 mm height). Three-electrode system was used for the experiment. A Mo wire (1 mm diameter, Nilaco) and Mg plate (2 mm \times 5 mm, Alfa-Aesar) was used as a working electrode. The electrode surface area was determined by width, thickness, and dipping height. A glassy carbon rod (3 mm diameter, Alfa-Aesar) and a Ag/AgCl (1 mol%) in the Pyrex tube was used as a counter electrode and a reference electrode, respectively. All the tests were conducted at 500°C . The electrochemical experiments were carried out by Bio Logic SP-300 potentiostat/galvanostat. The electrodeposition tests were carried out by applying a constant potential. The applied potential value for each electrodeposition run was adjusted with respect to be more slightly negative than EMP before run. Table 1 shows the detailed experimental conditions. The cross-sectional image and the elemental analysis of the RE deposit were observed with scanning electron microscopy (SEM; Hitachi, S-8010) in conjunction with energy-dispersive X-ray spectroscopy (EDS; Horiba, EX-250 X-max). The salt composition was analyzed via an inductively coupled plasma-optical emission spectrometer (ICP-OES; ACTIVA M, Horiba Jobin Yvon SAS).

3. Results and Discussion

The reduction potential of Dy^{3+} and Gd^{3+} in LiCl-KCl at 500°C was identified using a Mo and Mg electrode. Figure 1 shows the cyclic voltammogram using Mo electrode (surface area: 0.165 cm^2) with a scan rate of 100 mV/s . The cathodic peaks at about -1.92 V and -2.04 V , represent the reduction reactions of Dy^{3+} to Dy and Gd^{3+} to Gd, respectively. In case of Mg electrode (surface area: 0.502 cm^2), the reduction peaks were not clearly observed, as shown in Figure 2. It is because of the formation of RE-Mg alloy. At a scan rate of 3 mV/s , low height of two peaks were found at -1.88 and -1.94 V , which were assumed to be the formation of Dy-Mg alloy and Gd-Mg alloy, respectively [22]. The phase diagram shows that one Dy-Mg alloy (DyMg) and four Gd-Mg alloys (GdMg, GdMg₂, GdMg₃, and GdMg₅) can exist at 500°C

TABLE 1: Experimental conditions of the potentiostatic electrodeposition tests.

Run #	Cathode	Applied potential (V)	Time (h)
1	Mg strip	-1.90	12
2	Mo wire	-1.90	11
3	Mo coil	-1.90	21
4	Mo coil	-1.92	21
5	Mo coil	-1.94	5

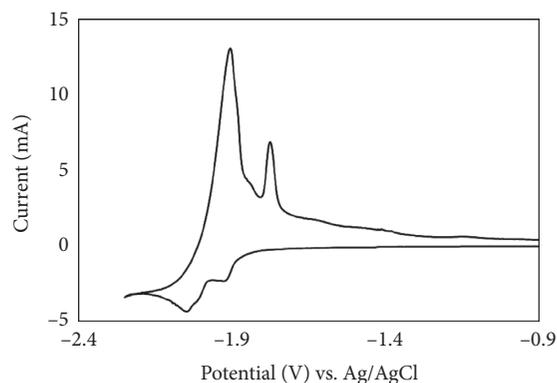


FIGURE 1: Cyclic voltammogram of Mo electrode in LiCl-KCl-0.2 wt% DyCl_3 -1 wt% GdCl_3 at 500°C with a scan rate of 100 mV/s .

[25], but one peak of Dy-Mg alloy and one peak of Gd-Mg alloy were observed in this study.

A series of potentiostatic electrolysis tests were subsequently conducted to remove the RE elements (Dy^{3+} and Gd^{3+}) in LiCl-KCl-0.15 wt% DyCl_3 -0.59 wt% GdCl_3 at 500°C using Mg and Mo electrode. Figure 3 shows the results of CV measurements before and after each electrolysis run. In run 1, the Mg plate (surface area: 1.04 cm^2) was used as a working electrode to recover the RE elements in the form of RE-Mg alloy and to remove these elements from the salt by applying -1.9 V for approximately 12 h. As shown in Figure 3, the redox peak heights of Dy^{3+} and Gd^{3+} clearly decreased after the run 1. However, another anodic peak appeared at -1.82 V , likely, because of the presence of Mg^{2+} in the salt, which was contributed by the Mg electrode. In particular, owing to the small size of the employed experimental cell, the distance between the anode and cathode (10~15 mm) was not sufficient to ensure that the cathodic reaction was independent of the anodic reaction. Because the Cl_2 (g) generated on the graphite anode surface may affect the Mg cathode, it results in the producing of MgCl_2 in the salt [24]. This was confirmed by the salt analysis by ICP-OES technique, as shown in Figure 4. Initially, Mg^{2+} did not exist in the salt, but after run 1, the concentration of Mg^{2+} increased to 0.16 wt%. To prevent the dissolution of Mg electrode, the cathode was changed to inert Mo electrode in the subsequent electrolysis runs. In run 1, Dy^{3+} was decreased from 0.15 to 0.12 wt% and Gd^{3+} was decreased 0.59 to 0.40 wt%. Even though the applied potential was -1.9 V , which is slightly positive than the reduction peak potential of Gd^{3+} on Mg electrode, those two elements were reduced. This result was not consistent with the study of Yang et al. [22]. In their

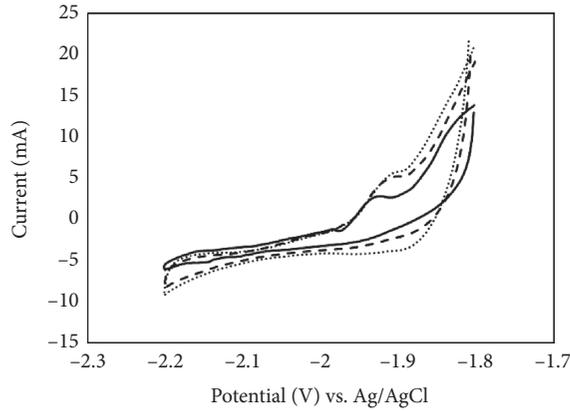


FIGURE 2: Cyclic voltammograms of Mg electrode in LiCl-KCl-0.2 wt% DyCl₃-1 wt% GdCl₃ at 500°C with various scan rates (— 1 mV/s, --- 3 mV/s, 5 mV/s).

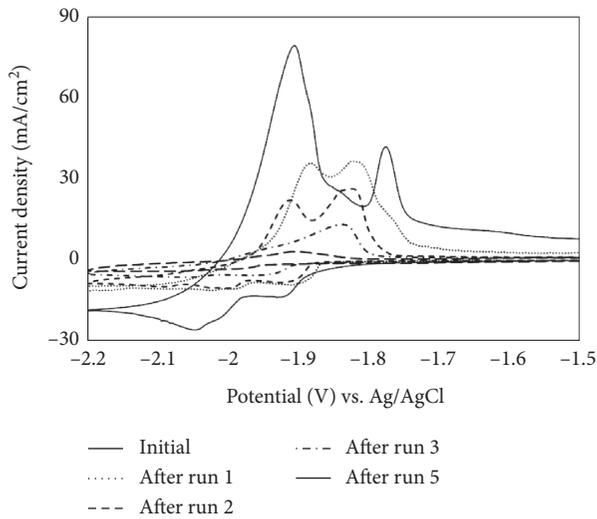


FIGURE 3: Cyclic voltammograms before and after each potentiostatic electrolysis run (scan rate = 100 mV/s).

report, they presented the extraction of Dy from LiCl-KCl melt containing DyCl₃ and GdCl₃ using Mg electrode. However, here, selective reduction of Dy was not examined.

In run 2, the applied potential was -1.90 V, which is the same potential value with run 1, using Mo wire electrode (surface area: 0.32 cm²). After 11 h, the cyclic voltammetry was measured to check the removal of rare earth elements in the salt. As shown in Figure 3, the cathodic peaks decreased slightly, while the anodic peaks distinctly decreased. After the electrolysis for 11 h, the salt composition of Dy³⁺, Gd³⁺, and Mg²⁺ was decreased as 0.08, 0.22, and 0.08 wt%, respectively. In the runs 3~5, the cathode was replaced from Mo wire to Mo coil to increase the electrode surface area (3.37 cm²) and to remove the elements in the salt as much as possible. The applied potentials of run 3~5 were negatively increased from -1.90 to -1.94 V because the EMP value before each run was shifted. For example, the EMP values before run 3~5 were -1.88, -1.91, and -1.93 V vs. Ag/AgCl. During the run 5, much higher current flowed so the

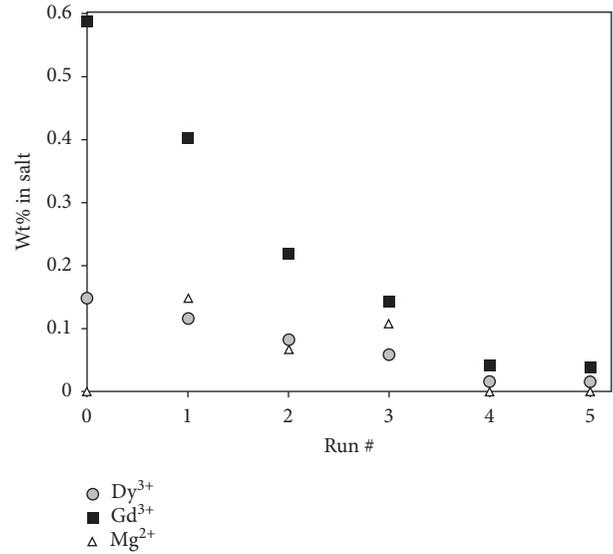


FIGURE 4: Composition of Dy³⁺, Gd³⁺, and Mg²⁺ in the salt before and after each electrolysis run.

electrolysis was stopped at 5 h of operation. After the electrodeposition runs, the redox peaks of the rare Earth elements in the salt were clearly diminished (Figure 3). Through the electrodeposition runs 3~5, the concentration of Dy³⁺ and Gd³⁺ was decreased to 0.016 and 0.040 wt%, respectively, and the Mg²⁺ was not detected. The removal efficiency of Dy³⁺ and Gd³⁺ was calculated to be about 83.5~95.2 and 91.6~95.2%, respectively, even though the current efficiency was very low. To overcome the low current efficiency, the anodic reaction such as the chlorine gas evolution needs to be separated from the cathodic reaction such as the electrodeposition of metal ions in the salt. Also, an addition of Cl₂ (g) capturing unit may work to prevent the rechlorination of the metal deposits and to protect the Mg electrode.

The photographs of Mg electrode before and after the electrodeposition run 1 were presented in Figure 5. As shown in Figure 5(b), the RE deposit on Mg electrode was visually examined. The cross-sectional area of the RE deposit on Mg electrode was analyzed by SEM-EDS. Figure 6 is the cross-sectional SEM image of RE deposited Mg electrode, as shown in Figure 5(b). Two layers were observed in the cross-sectional image by SEM (Figure 6(a)) and the layer consists of Dy, Gd, and Mg confirmed by EDS. It indicates the RE deposits were formed on the Mg surface (Figure 6(b)). The outer layer had slightly higher amount of RE, but it was not significant. It may be due to the interdiffusion of RE elements through Mg bulk phase. Also, there was no big difference in the concentration profiles of Dy and Gd in the cross-sectional area in Figure 6(b), which is expected from the salt analysis result. In case of Mo electrode, a distinguishable deposit on the electrode surface was not found, but black-mud like compound was observed on the bottom of the cell and it was difficult to collect as mentioned in the previous study [26]. Therefore, it needs to be consider to use of the alloy forming material and its ion for the attainment of RE recovery.

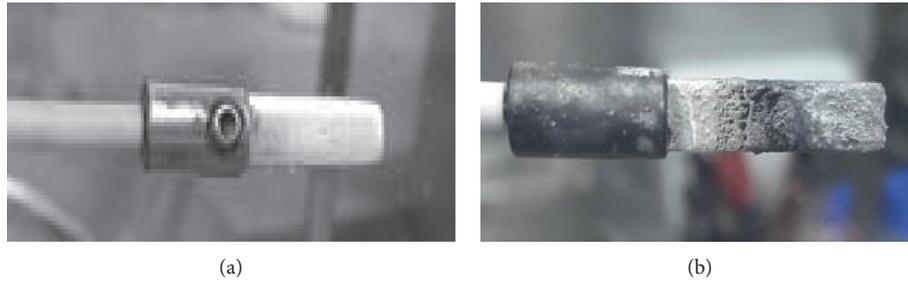


FIGURE 5: Photographs of Mg electrode (a) before and (b) after the electrodeposition run 1.

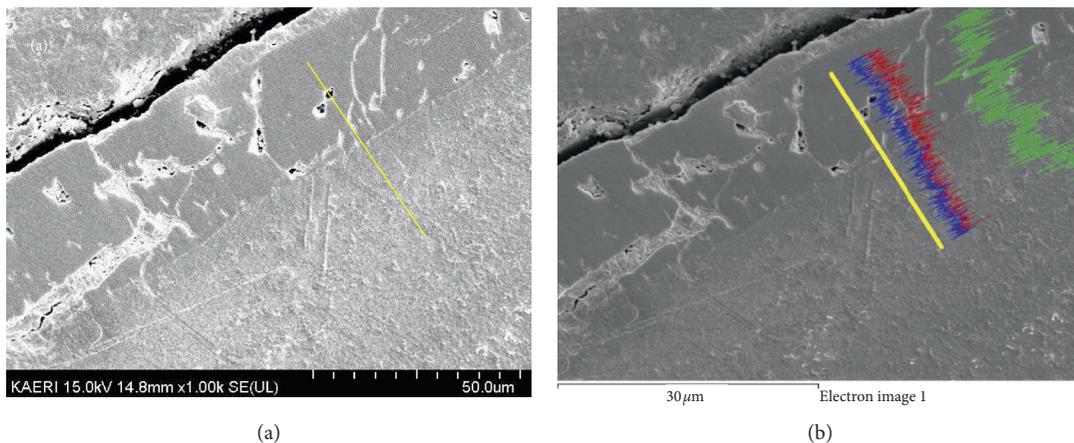


FIGURE 6: SEM (a) and EDS (b) analysis results for the cross-sectional area of RE deposited Mg electrode (green line: Mg, red line: Gd, blue line: Dy).

4. Conclusions

In this work, the electrochemical behavior of DyCl_3 and GdCl_3 in a LiCl-KCl eutectic melt at 500°C was examined by performing CV and electrodeposition tests using Mo and Mg electrodes. The CV results exhibited a shift in the reduction potentials of Dy^{3+} and Gd^{3+} when using the Mg electrode, owing to the formation of RE-Mg alloys. Furthermore, potentiostatic electrolysis tests were performed to remove Dy and Gd from the salt. The ICP-OES analysis of the salt samples indicated that Dy^{3+} and Gd^{3+} in the salt is removed using both of the Mg and Mo electrode with the removal efficiency of Dy^{3+} and Gd^{3+} was obtained as 83.5~95.2 and 91.6~95.2%, respectively. The low current efficiency could be improved by adopting a Cl_2 (g) venting system to prevent the rechlorination, protect the cathode material, and separate the electrodeposition reaction from the anodic reaction. The SEM-EDS analysis of the deposited RE layer on the Mg electrode clarified that the reduced Dy and Gd existed in the form of RE-Mg alloy.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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References

- [1] J. J. Laidler, J. E. Battles, W. E. Miller, J. P. Ackerman, and E. L. Carls, "Development of pyroprocessing technology," *Progress in Nuclear Energy*, vol. 31, no. 1-2, pp. 131-140, 1997.
- [2] C. E. Till and Y. I. Chang, *Plentiful Energy: The Story of the Integral Fast Reactor*, Create Space Independent, Scotts Valley, CA, USA, 2011.
- [3] H.-S. Lee, G.-I. Park, K.-H. Kang et al., "Pyroprocessing technology development at KAERI," *Nuclear Engineering and Technology*, vol. 43, no. 4, pp. 317-328, 2011.
- [4] T. Inoue and L. Koch, "Development of pyroprocessing and its future direction," *Nuclear Engineering and Technology*, vol. 40, no. 3, pp. 183-190, 2008.
- [5] S. D. Herrmann and S. X. Li, "Separation and recovery of uranium metal from spent light water reactor fuel via

- electrolytic reduction and electrorefining,” *Nuclear Technology*, vol. 171, no. 3, pp. 247–265, 2010.
- [6] J.-H. Lee, Y.-H. Kang, S.-C. Hwang et al., “Electrodeposition characteristics of uranium in molten LiCl-KCl eutectic and its salt distillation behavior,” *Journal of Nuclear Science and Technology*, vol. 43, no. 3, pp. 263–269, 2006.
- [7] J. H. Lee, Y. H. Kang, S. C. Hwang, E. H. Kim, J. H. Yoo, and H. S. Park, “Separation characteristics of a spent fuel surrogate in the molten salt electrorefining process,” *Journal of Materials Processing Technology*, vol. 189, no. 1-3, pp. 268–272, 2007.
- [8] F. Simpson, “Developments of Spent Nuclear Fuel Pyroprocessing Technology,” Report No. INL/EXT-12-25124, Idaho National Laboratory, Idaho Falls, ID, USA, 2012.
- [9] D. Vaden, S. X. Li, B. R. Westphal, K. B. Davies, T. A. Johnson, and D. M. Pace, “Engineering-scale liquid cadmium cathode experiments,” *Nuclear Technology*, vol. 162, no. 2, pp. 124–128, 2008.
- [10] S. X. Li, S. D. Herrmann, K. M. Goff, M. F. Simpson, and R. W. Benedict, “Actinide recovery experiments with bench-scale liquid cadmium cathode in real fission product-laden molten salt,” *Nuclear Technology*, vol. 165, no. 2, pp. 190–199, 2009.
- [11] A.-r. Wu and C.-q. Xia, “Study of the microstructure and mechanical properties of Mg-rare earth alloys,” *Materials & Design*, vol. 28, no. 6, pp. 1963–1967, 2007.
- [12] M. T. Harrison, H. E. Simms, A. Jackson, and R. G. Lewin, “Salt waste treatment from a LiCl-KCl based pyrochemical spent fuel treatment process,” *Radiochimica Acta*, vol. 96, pp. 295–301, 2008.
- [13] Y.-Z. Cho, T.-K. Lee, J.-H. Choi, H.-C. Eun, H.-S. Park, and G.-I. Park, “Eutectic (LiCl-KCl) waste salt treatment by sequential separation process,” *Nuclear Engineering and Technology*, vol. 45, no. 5, pp. 675–682, 2013.
- [14] H. C. Eun, J. H. Kim, Y. Z. Cho et al., “An optimal method for phosphorylation of rare earth chlorides in LiCl-KCl eutectic based waste salt,” *Journal of Nuclear Materials*, vol. 442, no. 1-3, pp. 175–178, 2013.
- [15] Y.-Z. Cho, T.-K. Lee, H.-C. Eun, J.-H. Choi, I.-T. Kim, and G.-I. Park, “Purification of used eutectic (LiCl-KCl) salt electrolyte from pyroprocessing,” *Journal of Nuclear Materials*, vol. 437, no. 1-3, pp. 47–54, 2013.
- [16] Y. Castrillejo, M. R. Bermejo, E. Barrado, and A. M. Martínez, “Electrochemical behaviour of erbium in the eutectic LiCl-KCl at W and Al electrodes,” *Electrochimica Acta*, vol. 51, no. 10, pp. 1941–1951, 2006.
- [17] M. R. Bermejo, F. de la Rosa, E. Barrado, and Y. Castrillejo, “Cathodic behaviour of europium (III) on glassy carbon, electrochemical formation of Al₄Eu, and oxoacidity reactions in the eutectic LiCl-KCl,” *Journal of Electroanalytical Chemistry*, vol. 603, no. 1, pp. 81–95, 2007.
- [18] M. R. Bermej, E. Barrado, A. M. Martíneb, and Y. Castrillejo, “Electrodeposition of Lu on W and Al electrodes: electrochemical formation of Lu-Al alloys and oxoacidity reactions of Lu(III) in the eutectic LiCl-KCl,” *Journal of Electroanalytical Chemistry*, vol. 617, pp. 85–100, 2008.
- [19] Y. Castrillejo, P. Fernández, J. Medina, P. Hernández, and E. Barrado, “Electrochemical extraction of samarium from molten chlorides in pyrochemical processes,” *Electrochimica Acta*, vol. 56, no. 24, pp. 8638–8644, 2011.
- [20] A. Saïla, M. Gibilaro, L. Massot, P. Chamelot, P. Taxil, and A. M. Affoune, “Electrochemical behaviour of dysprosium(III) in LiF-CaF₂ on Mo, Ni and Cu electrodes,” *Journal of Electroanalytical Chemistry*, vol. 642, no. 2, pp. 150–156, 2010.
- [21] H. Tang, Y.-D. Yan, M.-L. Zhang et al., “Fabrication of Mg-Pr and Mg-Li-Pr alloys by electrochemical co-reduction from their molten chlorides,” *Electrochimica Acta*, vol. 107, pp. 209–215, 2013.
- [22] Y.-S. Yang, M.-L. Zhang, W. Han et al., “Selective electrodeposition of dysprosium in LiCl-KCl-GdCl₃-DyCl₃ melts at magnesium electrodes: application to separation of nuclear wastes,” *Electrochimica Acta*, vol. 118, pp. 150–156, 2014.
- [23] M. Zhang, Y. Yang, W. Han, M. Li, Y. Sun, and Y. Yan, “Separation of SmCl₃ from SmCl₃-DyCl₃ system by electrolysis in KCl-LiCl-MgCl₂ molten salts,” *Energy Procedia*, vol. 39, pp. 375–381, 2013.
- [24] W. Shidong, L. Quan, Y. Xiushen, S. Qingguo, and W. Zhijian, “Electrolytic Preparation of Mg-La alloy in chloride molten salt: effect of electrolyte composition,” *Rare Metal Materials and Engineering*, vol. 44, no. 7, pp. 1623–1628, 2015.
- [25] T. B. Massalski, *Binary Alloy Phase Diagrams*, ASM International, Cleveland, OH, USA, 1986.
- [26] T. Jiang, N. Wang, S.-M. Peng, M. Li, W. Han, and M.-L. Zhang, “Electrochemical formation of Mg-Lu alloy and alloy layer in molten LiCl-KCl,” *Journal of Alloys and Compounds*, vol. 658, pp. 198–209, 2016.