

네오디뮴 재활용 공정 개발을 위한 LiCl-KCl-CdCl₂-NdCl₃의 전기화학적 거동 평가

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Electrochemical Investigation on LiCl-KCl-CdCl₂-NdCl₃ for Developing Nd Recycling Process

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1. Introduction

Neodymium-iron-boron (NdFeB) magnets, which has the strongest magnetic power among all the magnets currently available, are widely used in various industries including automobiles, electronics, and medical devices. The global demand of NdFeB has continuously increased as its applications are actively extended in the field of the clean energy as it is used in electric vehicle motors and wind turbine generators. However, more than 85 % of rare earth elements (REEs) which include Nd are produced in China and weaponization of REEs supply was evidently shown in 2010 and 2019 which results in dramatic price increase of REEs [1]. One of the highly-potential supply sources of Nd is end-of-life (EOL) NdFeB products. Two conventional methods which are currently employed for recycling of Nd from EOL NdFeB are hydrometallurgical methods and pyrometallurgical methods. the former is typically used to recycle REEs from highly contaminated and oxidized products. However, this process involves many operational steps and generates a lot of by-products (e.g., Cl₂, SO₂/SO₃) and liquid wastes which can cause environmental problems [2]. The later process includes high temperature melting, reacts with liquid magnesium, and electrolytic refining with molten salts [3]. However, recycled Nd is obtained as type of metal fog due to disproportionation reaction ($\text{Nd}^0 + 2\text{Nd}^{3+} \leftrightarrow 3\text{Nd}^{2+}$) [4]. These disadvantages restrict recycling of Nd which only takes lower than 5 % of EOL NdFeB magnets [1].

If the Nd recycling process can be progressed in lower temperature (~500 °C) and recycled Nd can be obtained as a form of ingot, economics of Nd recycling process will be guaranteed and recycling amount of Nd will be increased. In this study, selective oxidation of Nd from Nd metal by using CdCl₂ and calculating NdCl₃ concentration in NdCl₃-CdCl₂ mixtures from cyclic voltammetry of CdCl₂ redox scan range, reduction of Nd³⁺ on liquid cadmium cathode (LCC) are investigated.

2. Experimental Setup

2.1. Chemicals and Electrodes

Anhydrous LiCl-KCl (Alfa Aesar, 99.99 %) with a composition ratio of 58:42 mol%, anhydrous NdCl₃ (Alfa Aesar, 99.99 %), anhydrous CdCl₂ (Alfa Aesar, 99.998 %), metallic Nd plate (Lumi-M, Korea, 99.95 %) and metallic Cd wire (Alfa Aesar, 99.95 %) were used for the studies. LiCl-KCl eutectic mixture was dried for 36 hours at 200 °C, lower than melting point of 355 °C, to remove any residual moisture.

As shown in figure. 1, electrochemical cells are composed with 2 types; normal inert cathode system ((a) in figure. 1) and liquid cadmium cathode (LCC) system ((b) in figure. 1). Tungsten (W) wire (Alfa Aesar, 99.95 %) with the diameter of 1 mm was used as a working electrode and conductive wire for LCC, W rod (Alfa Aesar, 99.95%) with the diameter of 3.125 mm was used as a counter electrode.

All electrochemical experiments were performed in a glove box which is designed to limit oxygen and moisture concentrations to be less than 0.1 ppm under Ar gas (99.99 %) environment. The electrochemical cell for CV experiments was placed in the electric resistance furnace installed under the glovebox module as shown in Fig. 1. A Pyrex tube containing only the pure LiCl-KCl salt was additionally used as a dummy cell to measure the temperature of the cell for experiments, assuming that temperatures of salts between electrochemical cell and dummy cell were same after the sufficient time of 12 hours was passed. The temperature was measured by inserting K-type thermocouple into the dummy cell. By calibration of the temperature of the furnace wall, the cell temperature was maintained to the desired temperature within 1 °C by Proportional-Integral-Derivative (PID) controller of the furnace. Pyrex tubes with a diameter of 11 mm and

a height of 350 mm for CV experiments and temperature measurement were equipped at the same axial position in the furnace to minimize temperature difference.

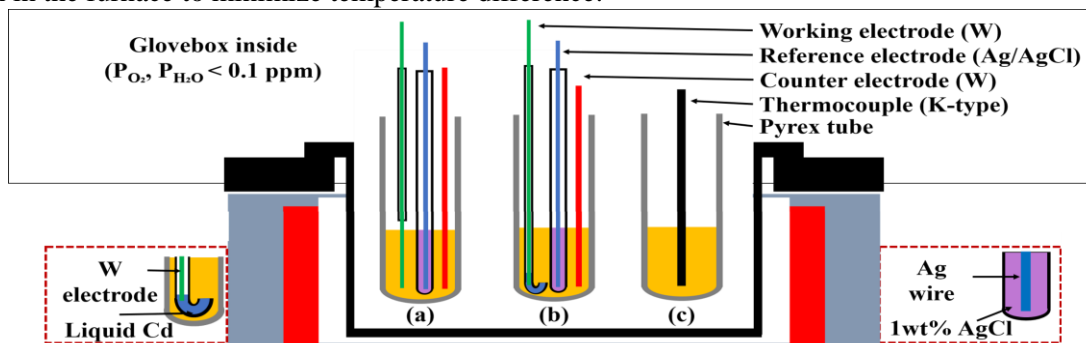


Figure 1. Schematics of electrochemical cell with inert cathode (a), electrochemical cell with LCC (b) and temperature measuring cells (c) in the glove box.

2.2. Experimental procedures

Test ID	Electrolyte Concentration	Working electrode type	Scan range (V vs. Ag/AgCl)	Scan rate (mV·sec ⁻¹)
CV-1	0.1 to 2.5 wt% CdCl ₂	Inert	-1.0 to 0.5	20, 50, 70, 100, 300, 500, 700, 1000, 1500
CV-2	2.0 wt% NdCl ₃		-2.2 to -0.5	
CV-3	0.1 to 1.5 wt% CdCl ₂ + 0.5 to 1.9 wt% NdCl ₃		-2.2 to 0.5	
CV-4	2.0 wt% CdCl ₂ + Nd metal		-2.2 to 0.5 and -1.0 to 0.5	
CV-5	1.0 wt% NdCl ₃	LCC	-1.6 to -0.4	20, 50, 70, 100, 300, 500, 700, 1000, 1500
CV-6	Pure LiCl-KCl			

Table 1. Electrochemical test matrix of this study.

Whole electrochemical experiments measurement was obtained using VersaSTAT3 potentiostat and Versastudio software from AMETEK SI. Whole experiments were done at 500 °C ± 1 °C. Every CV was performed at least 7 multiple cycles and converged data was obtained. Immersed depth of working electrode was measured after whole electrochemical experiments were done.

3. Results and Discussions

3.1. Selective oxidation monitoring of Nd by using CdCl₂.

Electrochemical behaviors of CdCl₂ and NdCl₃ were researched from CV-1 and CV-2. As is well known in previous studies, Nd is much more oxidative than Cd [5]. Thus, metallic Nd can be oxidized by CdCl₂ and its chemical reaction equation can be written as 3CdCl₂ + 2Nd → 2NdCl₃ + 3Cd. CV-3 is cyclic voltammetry of NdCl₃ at film electrode. Figure 2 shows Nd-Cd intermetallics formation potential is lower than redox potential of Cd at least 0.85 V. From this result, scan range of -1.0 to 0.5 V of CV-1 is independent with formation of Nd-Cd intermetallics and concentration of dissolved CdCl₂ can be measured by cyclic voltammetry in this scan range.

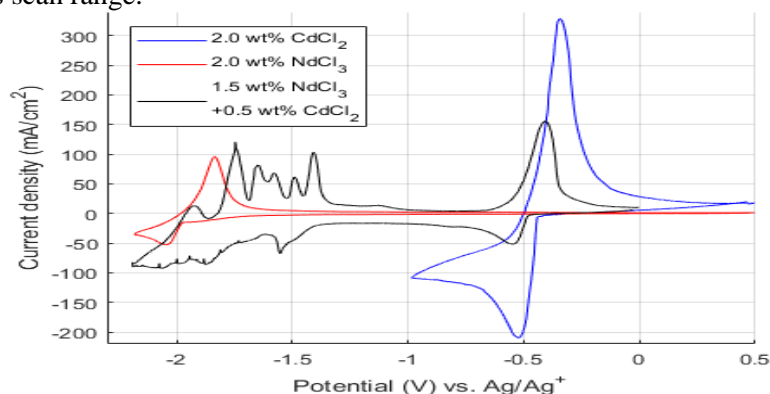


Figure 2. Comparison of cyclic voltammogram of 2 wt% CdCl₂ (blue line), 2 wt% NdCl₃ (red line), 0.5 wt% CdCl₂ + 1.5 wt% NdCl₃ mixture (black line) on inert cathode at 500 °C. (scan rate = 300 mV/sec)

Figure 3 shows cathodic peak potential and peak current density of CV-1 (black dots) and them of CdCl_2 in CV-3 (red stars). From this data, peak potential and current density of CdCl_2 of CV-3 is coincidence with peak data of CV-1. Although it is hard to measure NdCl_3 concentration data directly from cyclic voltammetry of $\text{NdCl}_3\text{-CdCl}_2$ mixture in scan range of -1.2 to -2.2 V although it includes redox potential of pure NdCl_3 because Nd-Cd alloy formation process makes complex data. However, concentration of CdCl_2 can be measured easily and directly. Thus, by using chemical reaction equation which was already mentioned, concentration of Nd^{3+} ion can be calculated from concentration of CdCl_2 . In CV-4, Nd metal whose amount can be oxidized by 2/3 of existing CdCl_2 in electrochemical cell was inserted into the cell. After 12 hours, cyclic voltammetry of this cell shows it is possible to calculate quantity of oxidized Nd metal from cyclic voltammetry in scan range of CdCl_2 (blue star).

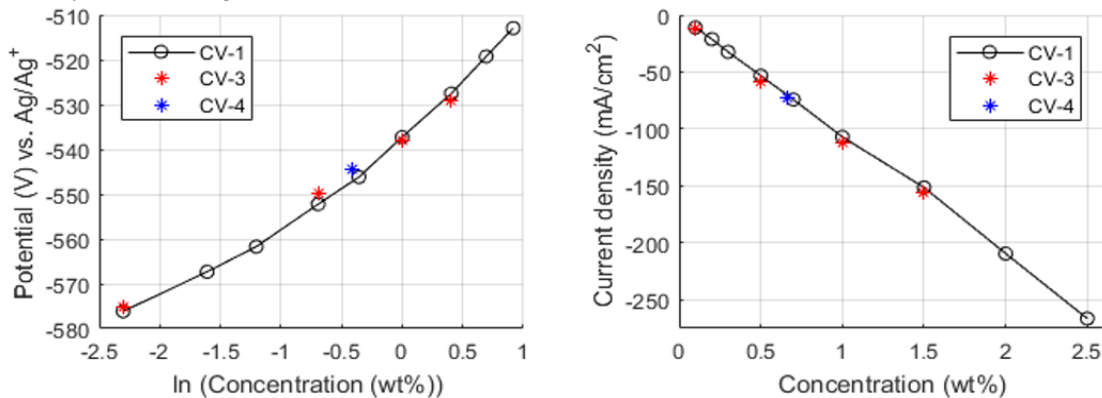


Figure 3. Cathodic peak potential and peak current density of CdCl_2 in CV-1 (black dots), them of CdCl_2 in CV-3 (red stars) and them of CdCl_2 in CV-4 (blue star) at 500 °C (scan rate = 300 mV/sec)

3.2. Cyclic voltammetry of NdCl_3 at LCC

CV-5 and CV-6 shows cyclic voltammetry of NdCl_3 LiCl-KCl (Figure 4, red line) and pure (Figure 4, black line) in LiCl-KCl at LCC. In Figure 4, blue line is obtained by subtracting CV-6 data from CV-5 and this graph shows clear electrochemical behavior whereas CV-5 data shows ambiguous behavior. From this data, redox reaction NdCl_3 on LCC takes place in one-step. Compare with data of CV-3, this reaction is concluded as formation of Cd_{11}Nd intermetallics which has the most abundant Cd concentration among the Nd-Cd intermetallics. Meanwhile, during the CV-2 experiment, small amount of metal fog which can be seen with the unassisted eye was generated by disproportionation reaction and it sink down at the bottom of cell after sufficient time had passed. However, CV-5 which used LCC do not shows any precipitates after whole cyclic voltammetry has done. From this results, disproportionation reaction of Nd which was the main disturbance factor of Nd recovery process in molten salts was effectively suppressed by locking Nd in Nd-Cd intermetallics.

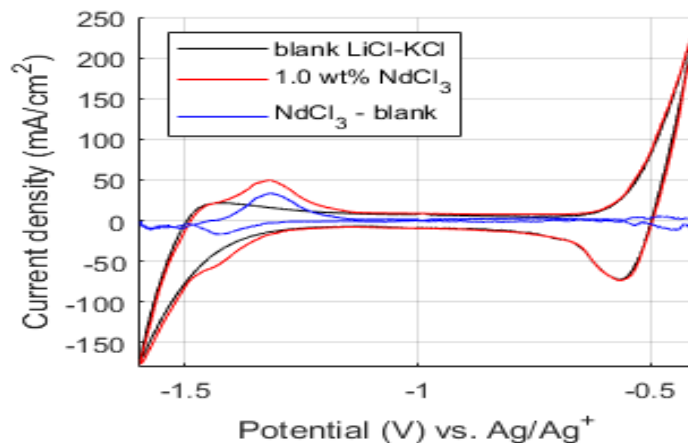


Figure 4. Cyclic voltammogram of 1 wt% NdCl_3 (red line), pure LiCl-KCl (black line) and subtracted result (blue line) on LCC at 500 °C (scan rate = 300 mV/sec)

From Figure 4, co-deposition of Li and Nd at LCC is inevitable. Since density of Cd metal (liquid, 500 °C, 7.75 g/cm³), Nd-Cd intermetallics (Cd₁₁Nd, solid, 8.57 g/cm³) and Li-Cd intermetallics (Cd₃Li, solid, 6.84 g/cm³) are different [6, 7], expected schematics of cross-section is predicted as Figure 5. further study by using SEM and EDS must be needed to obtain detail reduction mechanism of Nd on LCC.

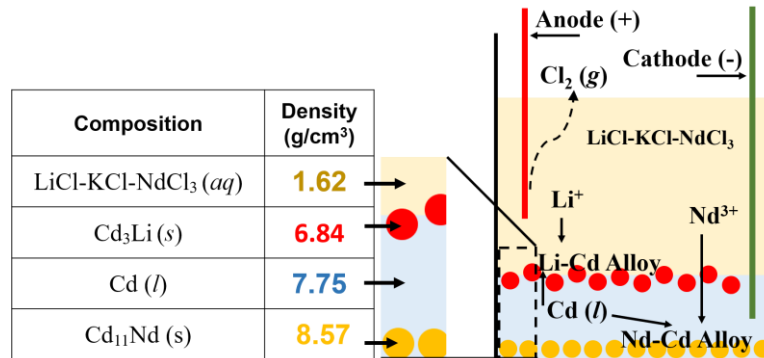


Figure 5. Expected distribution schematics of deposited elements in LCC and their density.

4. Conclusion

In this study, selective oxidation of Nd metal by using CdCl₂ in LiCl-KCl eutectic salts at 500 °C and recovery process which adopts LCC was investigated. Oxidized amount of Nd metal which can't be measured directly in NdCl₃ + CdCl₂ mixture was calculated by cyclic voltammetry data of CdCl₂. Also, with LCC, efficient recovery process of Nd can be achieved by suppressing disproportionation reaction of Nd.

Although co-deposition of Li on LCC is performed during Nd reduction process, deposited Li seems not a big concern. Because solubility of Li in liquid Cd is large, LCC will not change dramatically although it contains some amount of Li. Additionally, boiling temperature of Li (1,330 °C; 1 atm, 720 °C; 10⁻³ atm) takes middle position and large gap with Cd (767 °C; 1 atm, 380 °C; 10⁻³ atm) and Nd (3,074 °C; 1 atm, 1,725 °C; 10⁻³ atm). Thus, metallic mixture of Nd-Cd-Li can be separated by simple distillation and this process will be studied on later research. Additionally, eutectic breaking process because of Li co-deposition will be studied.

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