Experimental Design for Recovery of Nd from NdFeB Magnet by using Molten Salt Technique and Liquid Cd Cathode

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1. Introduction

Neodymium-iron-boron (NdFeB) is the most widely used type of permanent magnet. The global demand of Nd exceed 5,500 tons in the last year and its consumption rate is continuously increasing by 3 – 5 % [1]. The most of Nd is recycled by hydrometallurgical processes which causes production of massive liquid waste. Also, the recovered Nd products include Nd oxide which is not desirable. In the current status, the recycling Nd from the used NdFeB is considered as uneconomic. However, under the global circumstances where the supply of rare-earth metals (REMs) has become constrained, the development of recycling process Nd from the used NdFeB is timely indispensable.

Molten salt techniques with liquid cadmium cathode (LCC) system have been intensively used in the pyroprocessing for the last three decades to recycle fissile materials from the spent nuclear fuel (SNF). By using the same principle employed in the pyroprocessing, it is possible to recover Nd with achievement of waste reduction as well as high purity of Nd.

Among molten salts used in the pyroprocessing, LiCl-KCl eutectic is promising salt that can be used in the Nd recycling process thanks to its low operable temperature, corrosivity and wide electrochemical window.

The electrochemical behaviors of Nd in LiCl-KCl have been studied for pyroprocess for SNF due to that it is one of fission products belonging REMs [2]. However, only few data for fundamental electrochemical properties of Nd in LCC are available. More specifically, the intermetallic formation of Nd-Cd during Nd recovery by LCC should be elucidated for the successful Nd recycling.

In this paper, electrochemical behaviors of Nd in the solid cathode system and LCC system have been reviewed to clarify the current understanding of electrochemical reactions of Nd in molten LiCl-KCl and suggest future experiments for areas of unknown.

2. Review on electrochemical behaviors of $NdCl_3$ in molten LiCl-KCl eutectic

Electrochemical behaviors of Nd with an inert solid cathode in molten LiCl-KCl eutectic salt have been intensively studied due to the simpler behaviors compared to those with LCC system. Fig. 1 shows a comparison of voltammograms obtained by cyclic voltammetry (CV) with the solid tungsten and LCC electrode in the same molten salt condition. As shown in Fig. 1, the reduction and oxidation of Nd^{3+} to Nd metal on the inert solid cathode (solid purple line) proceeds through two step indisputably; Nd^{3+}/Nd^{2+}(I_a, I_c) and Nd^{2+}/Nd^0(II_a, II_c). The electrochemical behaviors of Nd are distinguished with other lanthanides, such as La, Ce because of the disproportionation reaction which is described as follows:

$$Nd^0 + 2Nd^{3+} \rightarrow 3Nd^{2+} \qquad (1)$$

It is reported that the Gibbs free energy of this disproportionation reaction by Eq. (1) is -20.8 ± 3.2 kJ/mol at 500 ℃, indicating that this reaction is thermodynamically spontaneous under the presence of the Nd metal [3].

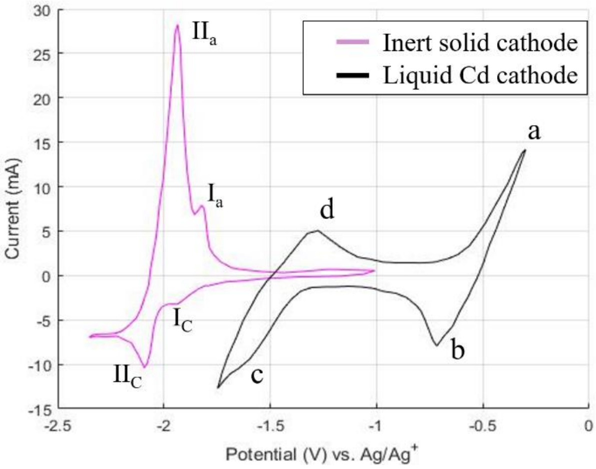

Fig. 1 Comparison of cyclic voltammograms in LiCl-KCl-1 wt.% $NdCl_3$ at 698K with different cathodes (scan rate = 10 mV/sec) (This figure is re-plotted from [4]).

CV with LCC (solid black line) showed totally different electrochemical behaviors of Nd which can be noted in Fig. 1 as follows:

a: Dissolution of Cd
b: Cd^{2+}/Cd^0 reaction
c: Formation of Nd-Cd and Li-Cd alloys
d: Dissolution of $Cd_{11}Nd$

The formation of intermetallic Nd-Cd alloy was found, which resulted from the decrease of activity of Nd on the LCC. Hence, Nd ions can be reduced on LCC at the more positive potential, compared to the case with the inert electrode. In addition, the reduction of Nd on the LCC occurs via a single step whereas it does by two steps on the inert electrode. Although Nd-Cd alloy formed on the LCC has various ratio of Nd to Cd, Cd-rich Nd-Cd intermetallic compound was preferably formed due to enough amount of Cd that can participate in the intermetallic formation in the LCC.

As shown in Fig. 2, by comparison of three voltammograms, it can be noticed that the reduction of Li occurred at the potential much less negative than the typical reduction potential of Li (-2.5 V vs. Ag/AgCl). It is also reported that the formation of Li-Cd alloy can occur because of very small activity coefficient of Li in Cd [5]. In the previous studies, this under-potential deposition of Li was observed when LCC was used to extract lanthanides [6]. Thus, it is expected that Li-Cd and Nd-Cd alloys are co-deposited, and their local distribution in LCC might affect the performance of the recycling process for Nd.

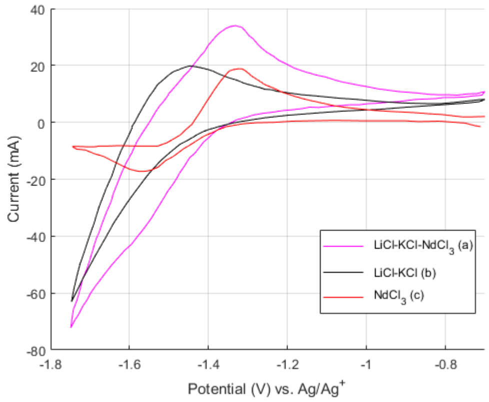

Fig. 2 Comparison of cyclic voltammograms by using LCC with different electrolyte compositions at 733K; (a) a mixture of LiCl-KCl-1 wt% $NdCl_3$, (b) a pure LiCl-KCl, and (c) a pure $NdCl_3$ (scan rate = 50 mV/sec) (This figure is re-plotted from [7]).

3. Experimental design for understanding Nd behaviors on LCC

As mentioned, the key in the analysis of electrochemical behaviors of Nd in LCC is the examination of the Nd-Cd intermetallic alloy formation during electrolytic refining process. Different Nd-Cd intermetallic compounds can form depending on Nd concentration in the electrolyte and applied potential on the LCC.

At the first stage of the electrowinning process, Nd in NdFeB magnet at the anode is selectively dissolved by using $CdCl_2$ by the fact that Cd is nobler than Nd. The dissolution of Nd is believed to be controlled by applied potential and the Cd concentration, which requires parametric studies to enhance dissolution kinetics of Nd.

In the experiment with LCC as the next stage as shown in Fig. 3, the electrochemical behaviors of Nd on the LCC will examined. Basic electrochemical properties related to not only Nd reduction, but also Nd-Cd alloy formation can be clarified.

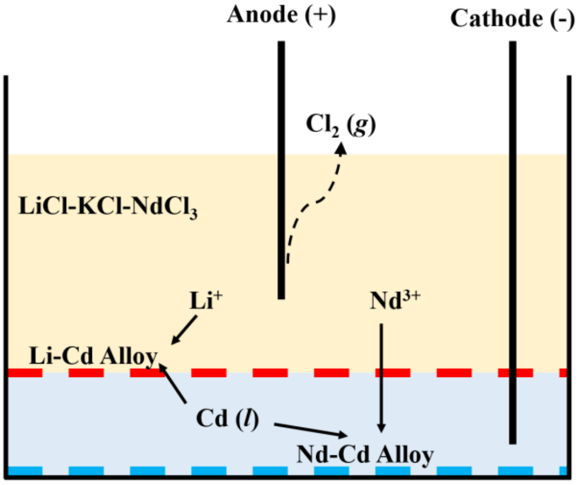

Fig. 3 A schematic showing electrolytic refining of Nd on the LCC.

Particularly, it is believed that Li-Cd and Nd-Cd intermetallic compounds are dispersed in LCC depending on their densities; Li-Cd alloys (6.84 g/cm^3) < liquid Cd (7.75 g/cm^3) < Nd-Cd (8.57 g/cm^3) [8, 9]. Also, previous study about Nd recovery with LCC shows similar data; the concentration of Nd-Cd alloy is highest at the floor region [10]. The solubility of Li in liquified Cd is high (27.5 wt%) [8] while Nd in Cd is relatively low (~2 wt%) at 500 °C ., Thus, the most of Li-Cd alloys exist as a liquid phase, but Nd-Cd intermetallic compounds remain as distinct precipitates Thus, by means of the density-based separation, Li-Cd (float at red-dot line) and Nd-Cd (sink at blue-dot line) alloys might be separable in the LCC shown in Fig. 3, and it can be examined in the experiment.

Recovered Nd-Cd intermetallic compound from the LCC can be converted into Nd by high-temperature distillation, since the maximum temperature of solidus line of Nd-Cd alloy is 1,040 °C at 1 atm and it will be lowered at the lower pressure condition. To check process applicability, compositions of Nd-Cd alloy before distillation and purity of final Nd product after distillation will be measured by ICP-OES and XRD.

4. Conclusions and Future Work

In this paper, electrochemical behaviors of Nd at inert solid cathode system and LCC system in molten LiCl-KCl eutectic are reviewed. The reduction of Nd at the inert solid cathode occurred via two steps, whereas that of Nd at the LCC takes one step. Also, the apparent reduction potential of Nd in the LCC is more positive than that in the inert solid cathode by the formation of Nd-Cd intermetallics. However, co-deposition of Li in LCC with Nd deposition is not unrevealed yet, which should be fully understood for the successful Nd recycling.

Through electrochemical experiment of LiCl-KCl-$NdCl_3$ with LCC, the possibility of electrowinning process of Nd from NdFeB can be examined by using $CdCl_2$ to understand the kinetics of selective oxidation of Nd from NdFeB magnet. To clarify electrochemical properties and behaviors of Nd, various electrochemical experiment techniques, such as cyclic voltammetry, chronopotentiometry, square wave voltammetry, and differential pulse voltammetry would be conducted. In addition, the co-deposition of Li with Nd in LCC will be investigated in the future work for the optimization of Nd recycling process by the combination of chemical and crystallographic analysis.

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