

## A Study on Electrochemical Reduction of Rare Earth Oxides in Molten LiCl-Li<sub>2</sub>O Salt

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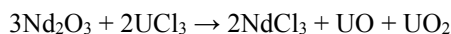
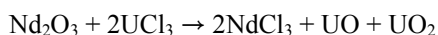
### 1. Introduction

Pyroprocessing is a technology for recycling the spent oxide fuel into metal fuel for sodium-cooled fast reactor [1]. In the electrochemical reduction process, oxide fuels are converted to the metal form to supply metal feed to the electrorefining process. The electrode reactions in the reduction process are as follows [1]:

Cathodic reaction:  
 $M_xO_y + 2ye^- \rightarrow xM + yO^{2-}$

Anodic reaction:  
 $O^{2-} \rightarrow 1/2O_2 + 2e^-$

While actinide oxides including uranium, plutonium and so on, noble metal oxides are easily reduced in the electrochemical reduction step, reduction of rare earth oxides (Nd<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> and so on) is considerably difficult due to their thermodynamic stability [2,3]. In the previous literatures, the reduction degree of rare earth oxides is reported to be ~ 50% and it is affected by the physico-chemical properties of the oxide feed [4-6]. When the unreduced rare earth oxides are transferred to the electrorefining process, they are chemically reacted with UCl<sub>3</sub> to produce the insoluble uranium oxides and rare earth oxychlorides [1,7]:



Such reactions can cause the salt contamination and a decrease in purity of the recovered uranium in the electrorefining process. Thus, it is important to increase the reduction degree of rare earth oxides in the electrochemical reduction process [1,7].

In this study, the electrochemical reduction of RE<sub>2</sub>O<sub>3</sub> (RE = Nd or Ce) has been conducted via co-reduction NiO to increase the reduction degree of the rare earth oxides in molten molten LiCl containing 1wt% Li<sub>2</sub>O. The electrochemical reduction behavior of the mixed RE<sub>2</sub>O<sub>3</sub>-NiO oxide has been investigated and the reduction path of RE<sub>2</sub>O<sub>3</sub> has been proposed

### 2. Experimental

The mixture of oxide powder (atomic ratio of rare earth to nickel = 1:5) and zinc stearate (as a binder) were mixed in a mortar. Nd<sub>2</sub>O<sub>3</sub> (99% purity, Alfa

Aesar), NiO (99% purity, Alfa Aesar) powder and zinc stearate (technical grade, Aldrich) were used for fabrication of the mixed oxide pellet. Approximately 0.2 g of the mixed powder was die-pressed at 200 bar into cylindrical pellet by using hydraulic press, and the pellet was sintered at 1100 °C for 3h.

An electrolysis cell was assembled in a high-purity argon (H<sub>2</sub>O < 0.1 ppm) atmosphere glove box. As shown in Fig. 1, the sintered pellets were wrapped with Ni gauze, and the pellets were attached to a stainless steel rod to be used as the cathode. A Pt plate and a Ni/NiO electrode were selected as the anode and reference electrode, respectively. [8]. Anhydrous LiCl (thermally dehydrated at 450 °C) and Li<sub>2</sub>O (99.5 purity, Alfa Aesar) were used as electrolyte.

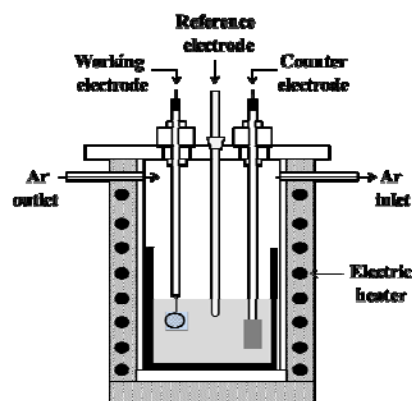
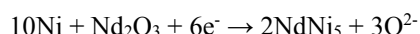
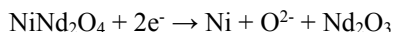
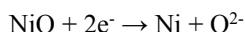


Fig. 1. Experimental set-up used for electrochemical reduction of mixed oxide pellet.

The mixture of LiCl and 1wt% Li<sub>2</sub>O was contained in a dense MgO crucible and heated to 650 °C to melt the salt. The electrolysis of the oxide pellet was performed by applying a constant cell voltage of 3.0V, which was controlled by using a DC power supply (E3633A, Agilent). The cathodic potential (vs. Ni/NiO) was measured by using a digital multimeter (34401A, Agilent) during the electrolysis. After the electrolysis, the cathode product was taken out of the electrolysis cell and washed by distilled water. The washed sample was dried in a vacuum oven. The reduced samples were characterized by X-ray diffraction (XRD), thermogravimetric analyzer (TGA) and scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS).

### 3. Results and Discussion

Fig. 2 shows the X-ray diffraction patterns of the reduced  $\text{Nd}_2\text{O}_3$ -NiO pellets with various electrolysis times. Before electrolysis, XRD pattern of the sintered pellet indicates that NiO and  $\text{Nd}_2\text{O}_3$  form  $\text{NiNd}_2\text{O}_4$  when the mixed oxides were calcined. NiO disappeared quickly and the characteristic peak of Nd metal appeared as an intermetallic compound after only 5 min of electrolysis. These results indicate that NiO and  $\text{NiNd}_2\text{O}_4$  can be easily reduced and form  $\text{NdNi}_5$  [9]. The corresponding reactions are as follows:



$\text{LiNdO}_2$  was also observed due to chemical reaction between  $\text{Nd}_2\text{O}_3$  and  $\text{Li}_2\text{O}$  in molten salt [10]. After 30 min of electrolysis, the characteristic peak of  $\text{LiNdO}_2$  disappeared and the mixed oxides were completely reduced to the  $\text{NdNi}_5$ . These results demonstrate that the mixed oxides can be reduced through co-reduction with NiO in molten  $\text{LiCl-Li}_2\text{O}$  salt [3,11].

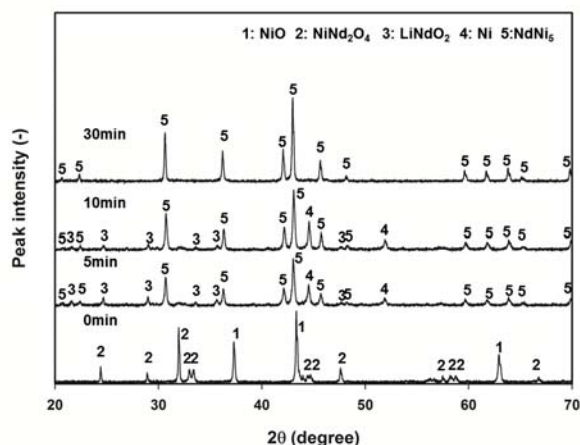


Fig. 2. X-ray diffraction patterns of the reduced  $\text{Nd}_2\text{O}_3$ -NiO mixed oxides with various electrolysis times at a cell voltage of 3.0V in 1wt%  $\text{Li}_2\text{O-LiCl}$  at 650 °C

#### 4. Conclusion

An electrochemical spent fuel processing technology, pyroprocessing, has been developed for recycling of spent fuel to be applied to a sodium-cooled fast reactor. The spent fuel is reduced in the oxide reduction process. It is well known that the rare earth oxides are hardly reduced due to their electrochemical and thermodynamic stability. The rare earth oxides unreduced in the reduction process can cause problems via reaction with  $\text{UCl}_3$  in the electrorefiner. To tackle those problems, the electrochemical reduction of rare

earth oxide has been conducted via co-reduction of NiO in  $\text{LiCl}$  molten salt containing 1 wt%  $\text{Li}_2\text{O}$ . The reduction of the oxide mixture starts from the reduction of NiO to Ni, followed by that of  $\text{RE}_2\text{O}_3$  on the produced Ni to form intermetallic  $\text{RENi}_5$ . The mixed oxide pellets were successfully reduced to the  $\text{RENi}_5$  alloy by constant electrolysis at 3.0 V at 650 °C. The crucial aspect to these results is that the thermodynamically stable rare-earth oxide,  $\text{Nd}_2\text{O}_3$  was successfully converted to the metal in the presence of NiO. By using this technique, it could be expected that the integration between the electrochemical reduction and electro-refining steps would be enhanced and some problems caused by fine uranium oxide powder (e.g., salt contamination, electrical short circuit, and a decrease in the uranium metal purity in the electrochemical refining step) would be solved.

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