Direct Formation of Lanthanide Trichloride From Lanthanide Oxide

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1. Introduction

In a pyrochemical process, uranium dioxide, actinide dioxide, and lanthanide oxide have been converted to their trichloride forms for their dissolutions and electrodepositions. However, we reported that the lanthanide oxides such as Nd_2O_3, Gd_2O_3, etc. are not fully reduced to their metallic form during an electro-reduction process so that the lanthanide elements may not be dissolved during an electro-refining process. In this work, in order to fully dissolve the lanthanide oxide into molten salt, we studied its direct dissolving method as the form of the lanthanide trichloride and report the results in the conference.

2. Experimental

All the experiments were carried out in a glove box under Ar where O_2 and H_2O level were maintained to be less than 1 ppm. Lithium chloride (LiCl)/potassium chloride (KCl) eutectic salts (anhydrous beads), and silver chloride (AgCl) were obtained from Sigma Aldrich. Neodymium oxide (Nd_2O_3) and gadolinium oxide (Gd_2O_3) were purchased from Alfa Aesar (purity ≥ 99.99%).

Electrochemical measurements were performed in a quartz tube (20 mm in outer diameter and 2 mm in wall thickness). W wire (Alfa Aesar, dia. 0.2 mm) and glassy carbon (Alfa Aesar, dia. 2 mm) electrodes were used as the working and counter electrodes, respectively. The W wire electrode was mechanically polished with sand paper prior to use. The reference electrode was Ag wire immersed in 1 mol% AgCl-LiCl-KCl melt. The Electrochemical measurements were performed using a Gamry Reference 3000.

3. Results and Discussion

In order to test the conversion of the lanthanide oxide to the lanthanide trichloride in LiCl-KCl melt, we chose Nd_2O_3 and Gd_2O_3 as the representatives of lanthanide oxides. Fig. 1 shows a picture of Nd_2O_3 dissolved LiCl-KCl melt. We added Nd_2O_3 powder in transparent LiCl-KCl melt and shook the cell. The Nd_2O_3 were not dissolved and existed as a form of colloids. The white blue of the picture is typical color of the Nd_2O_3 colloids. In order to dissolve Nd_2O_3 and get rid of the oxygen from the oxide, here we introduced ammonium chloride (NH_4Cl) in the melt. We expected that NH_4Cl may supply HCl in the melt. The HCl is very acidic molecule so that it can absorb the oxygen anion of the lanthanide oxides. Because the NH_4Cl is very volatile, we also expected that residuals of NH_4Cl after the reactions can be easily removed as a gas. The mechanism of the reaction can be described as shown below.

$$Nd_2O_3\,(s) + 6NH_4Cl\,(l) \rightarrow 2NdCl_3(l) + 3H_2O\,(g) + 6NH_3\,(g)$$

The products of the reaction are all gas phases except for the $NdCl_3$, which means that the by-

product of the reaction can be easily evaporated from the melt.

Fig. 1b and 1c show the pictures of LiCl-KCl melt containing Nd_2O_3 after NH_4Cl was added into the LiCl-KCl melt. As soon as the addition of the NH_4Cl, there was a vigorous formation of gas bubbles and then the bubbles gradually disappeared in 5 minutes. After the reaction was completed, the melt turned into transparent and clean sky blue color (Fig.1c).

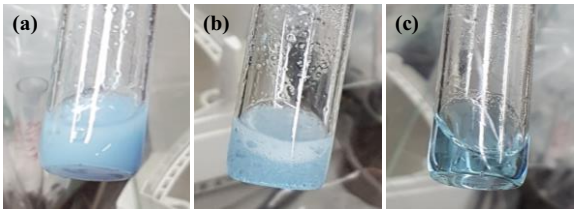

Fig. 1. Pictures of Nd_2O_3 dissolved LiCl-KCl melt at 450℃. (a) Before and (b, c) after the addition of NH_4Cl.

Fig. 2 shows a cyclic voltammogram obtained from a W wire immersed in LiCl-KCl melt containing Nd_2O_3 after addition of NH_4Cl. It is obvious that cathodic and anodic currents around -2.0 V occurred. The current can be attributed to the electrodeposition and dissolution of Nd in LiCl-KCl melt. This result indicates that the $NdCl_3$ were directly formed from Nd_2O_3 with addition of NH_4Cl in the LiCl-KCl melt.

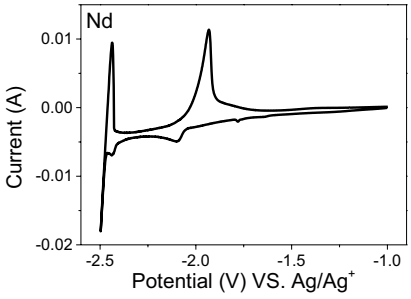

Fig. 2. A cyclic voltammogram obtained from a W wire immersed in LiCl-KCl melt containing Nd_2O_3 after addition of NH_4Cl.

4. Conclusion

In this work, we reported that lanthanide trichlorides can be directly formed from lanthanide oxide by the addition of NH_4Cl. The color of the transparent sky blue of the melt and CV results indicated that the $NdCl_3$ was successfully formed in the LiCl-KCl. In the conference, we report the results that are concerning the other lanthanide elements as well.

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