

Electrochemical Behavior of Li-B Alloy Anode - Liquid Cadmium Cathode (LCC) System for Electrodeposition of Nd in LiCl-KCl

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Abstract : The performance of Li-B alloy as anode for molten salt electrolysis was firstly investigated. The crystalline phase of the prepared Li-B alloy was identified as Li_7B_6 . The potential profile of Li-B alloy anode was monitored during the electrodeposition of Nd^{3+} onto an LCC (liquid cadmium cathode) in molten LiCl-KCl salt at 500°C. The potential of Li-B alloy was increased from -2.0 V to -1.4 V vs. Ag/AgCl by increasing the applied current from 10 to 50 $\text{mA}\cdot\text{cm}^{-2}$. It was found that not only the anodic dissolution of Li to Li^+ but also the dissolution of the atomic lithium (Li^0) into the LiCl-KCl eutectic salt was observed, following the concomitant reduction of Nd^{3+} by the Li^0 in Li-B alloy. It was expected that the direct reduction could be restrained by maintaining the anode potential higher than the deposition potential of neodymium.

Keywords : Li-B alloy, anodic dissolution, spontaneous reaction, LiCl-KCl molten salt

Introduction

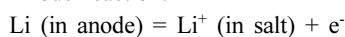
Despite the nuclear energy expected to meet the growing energy demand, the problem of accumulating spent fuel from nuclear power plants needs to be addressed. One of the ways is to recycle the spent fuel as a metal fuel for fast neutron reactors by employing pyroprocessing. Pyroprocessing, which involves the electrolysis in molten salt, enables to recover actinides, to reduce the amount of spent nuclear fuel with destroying toxic waste products, and to enhance the proliferation resistance significantly.¹⁻²⁾ The main step in the pyroprocessing is electrorefining, where uranium (U) is preferentially reduced on the solid cathode and other actinide elements (i.e., transuranic elements, TRUs) are recovered into the liquid cadmium cathode (LCC) together with U due to their small activity coefficients in liquid cadmium.³⁾ In the flow diagram of pyroprocessing in the Korea

Atomic Energy Research Institute (KAERI), two types of anode are used; first one is the spent fuel (i.e., used metal fuel), which is already reduced in the electrolytic reduction step, and second one is graphite. In the course of selective deposition of U on solid cathode, the spent fuel is anodically dissolved in molten salt electrolyte. Then, the anode (i.e., spent fuel) is changed with inert graphite to enhance the co-deposition of TRUs onto an LCC. Because U occupies the largest portion in the actinides transported from the used metal fuel, the use of spent fuel as an anode may reduce the recovery efficiency of TRUs. The use of inert anode (i.e., graphite) is advantageous to increase the co-deposition of TRUs, resulting in the increase of TRU recovery, but the chlorine gas evolution is occurred by electrochemical decomposition of the carrier salt. Thus, it accompanies the most important subject, that is, the maintenance of inert atmosphere to avoid corrosion problem. In this study, we specifically addressed the need for a new anode material having no influence on the salt composition as well as no corrosion problem for efficient recovery of TRUs.

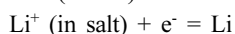
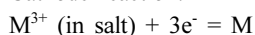
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Previously, ANL (Argonne National Laboratory) and CRIPI (Central Research Institute of Electric Power Industry) had presented the recovery of actinides from molten salt with the use of reductive material such as a Cd-Li alloy as an anode to avoid a corrosion problem.^{3,4)} At the Cd-Li alloy anode, the direct chemical reduction of metal (i.e., actinides and rare earths) ions in molten salt with Li as well as the anodic dissolution of Li is occurred. The metals are reduced preferentially at the cathode, and then the lithium can be reduced when the concentration of the metal ions is lowered.³⁾

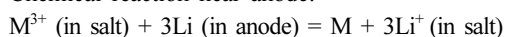
Anode reaction:



Cathode reaction:



Chemical reaction near anode:



Even though the reaction mechanism at the Cd-Li anode - cathode system where actinides are successfully reduced was identified in previous studies,^{3,4)} the use of Cd-Li anode may not be desirable in a scale-up process in terms of the design and compactness of equipment. Since the Cd-Li alloy is in liquid state at 500°C, which is the operation temperature of pyroprocessing (except electrolytic reduction), it needs to be contained in a ceramic crucible and it occupies a large volume in the reactor, resulting in the difficulty of electrode handling.

Here, we synthesized a Li-B alloy to be used as anode in molten salt electrolysis in molten chloride salt. The Li-B alloy can keep solid state above 650°C,⁵⁻⁸⁾ and it has a reductive characteristic like a Cd-Li alloy. As a preliminary study, neodymium (Nd) was used as a target metal instead of U, since its reduction potential is close to those of TRUs at an LCC and it exist abundantly in the spent fuel. For this purpose, we have carried out to investigate the anodic behaviour of the Li-B alloy in LiCl-KCl-NdCl₃ (1 wt%) at 500°C. The potential of the Li-B alloy anode was monitored during the electro-deposition of Nd³⁺ onto an LCC and the cyclic voltammetry (CV) was intermittently measured to check the concentration of Nd³⁺ in the salt.

In addition, the phase and morphology of the Li-B alloy used in this study was analysed by X-ray diffraction (XRD) and scanning electron microscope (SEM).

Experimental

The Li-B alloy was prepared from lithium and crystalline boron according to the procedure already described.⁵⁻⁷⁾ Briefly, the lithium (99% purity, Aldrich) and boron (99% purity, -60 mesh, Aldrich) were weighed into a nickel crucible and heated at 450°C. Then, the temperature was raised to 630°C and maintained that temperature for 1 h. Subsequently, the Li-B alloy ingot was removed from the crucible and allowed to cool. A piece of the Li-B alloy (0.22 g) was placed on a nickel grid to be used as an anode for the electrolysis. Cd (99.99% purity, Alfa Aesar) in alumina crucible with Mo (diameter of 1 mm, Alfa Aesar) as a lead wire was used as a cathode (surface area = 1.13 cm²). A silver-silver chloride (Ag wire, 1 wt% AgCl in LiCl-KCl) electrode incorporated in a thin Pyrex tube was used as a reference electrode. A 500°C LiCl-KCl eutectic salt (99.99 wt%, anhydrous, Sigma-Aldrich) with an addition of 1 wt% NdCl₃ (99.9% purity, Alfa Aesar) was used as the base electrolyte (200 g). Fig. 1 shows a schematic diagram of the electrochemical cell used in this study. All the preparations and the experiments were conducted in an argon-filled glove box, where both the oxygen and water contents were maintained at less than

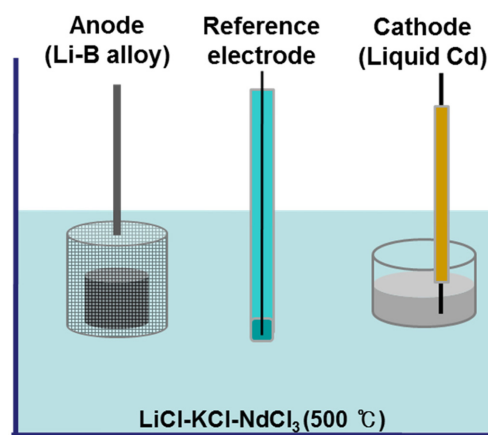


Fig. 1. Schematic of electrochemical cell used in this study.

2 ppm. Cyclic voltammetry was conducted to check the variation of the concentration of Nd^{3+} in the salt after electrolysis using a W wire (diameter of 1 mm, Alfa Aesar) and glassy carbon (diameter of 3 mm diameter, Alfa Aesar) as a working and counter electrode, respectively. The applied current density was calculated based on the surface area of cathode. All of the electrochemical measurements were carried out using an AutoLab (The Netherlands). The salt analysis was conducted by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The surface morphology of the prepared Li-B alloy was observed with a scanning electron microscope (SEM, Hitachi, SU-8010). The elements of the alloy were identified with an energy dispersive X-ray (EDX) spectrometer (Horiba, EX-250 X-max). In addition, X-ray diffraction (XRD, BRUKER, D8 ADVANCE) was employed to investigate the phase composition of the prepared Li-B alloy.

Results and Discussion

The crystalline phase of the prepared Li-B alloy was determined as mainly Li_7B_6 from the X-ray diffractogram (Fig. 2). In order to examine the behavior of the Li-B alloy anode in the molten salt, a constant-current electrolysis was conducted in LiCl-KCl-NdCl_3 (1 wt%) at 500°C . Before the electrolysis runs, 0.22 g of Li-B alloy was immersed in the LiCl-KCl-NdCl_3 (1 wt%) electrolyte for 100 min to check the direct chemical reduction of Nd^{3+} with Li in the alloy. Then, the electroreduction test

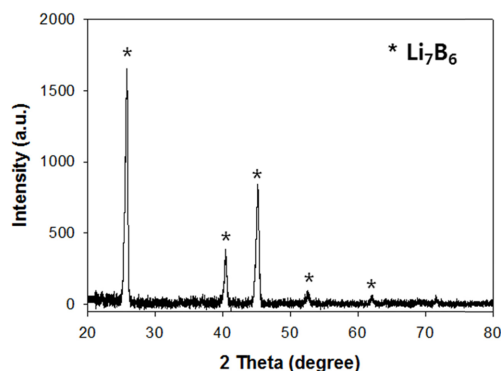


Fig. 2. X-ray diffraction spectra for the synthesized Li-B alloy.

divided into three runs were conducted using the alloy as an anode and liquid cadmium (11 g) as a cathode. Each runs were carried out serially for 30 min in the same system but the applied current density was increased as 10, 25, and $50 \text{ mA}\cdot\text{cm}^{-2}$.

Figs. 3a-c shows the cyclic voltammograms of the LiCl-KCl-NdCl_3 molten salt measured at appropriate intervals during the immersing of the Li-B alloy in the salt. The redox peaks corresponding to $\text{Nd}^{3+/0}$ was observed at -2.13 and -2.00 V vs. Ag/AgCl. The cathodic peak current, related to the concentration of Nd^{3+} in salt, was decreased as the immersing time increased. After immersing of the Li-B alloy in salt for 100 min, the height of cathodic peak was about 41.2% of initial height (Fig. 3c). This represents that the spontaneous reduction of Nd^{3+} in salt by Li in the Li-B alloy. Using the same alloy as an anode, the electrolysis in the same salt was conducted for 90 min with a liquid cadmium cathode. Fig. 4 shows the anode potential profile during the electrochemical reduction runs. In the first electrolysis run (applying current density = $10 \text{ mA}\cdot\text{cm}^{-2}$), the initial potential of Li-B alloy anode was about -2.0 V and it slightly increased to -1.95 V. Afterwards, it stepped to and maintained as -1.88 V for the first 10 min of second run (current density as $20 \text{ mA}\cdot\text{cm}^{-2}$) and sharply increased to -1.69 V. It was maintained until the end of second electrolysis run, even though the anodic potential fluctuation appeared. In run 3, the anode potential begins about -1.63 V and slightly

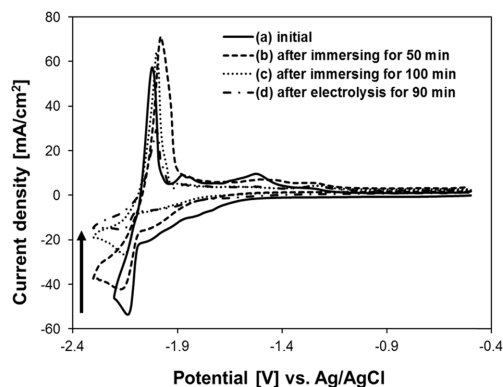


Fig. 3. Cyclic voltammograms for LiCl-KCl-NdCl_3 at 500°C : (a) initial, after immersing of Li-B alloy for (b) 50 min and (c) 100 min, and (d) after electrolysis with Li-B alloy anode for 90 min.

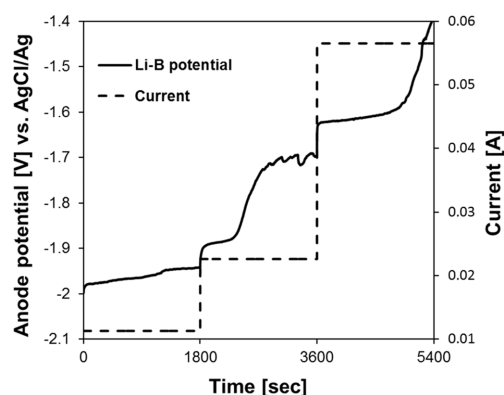
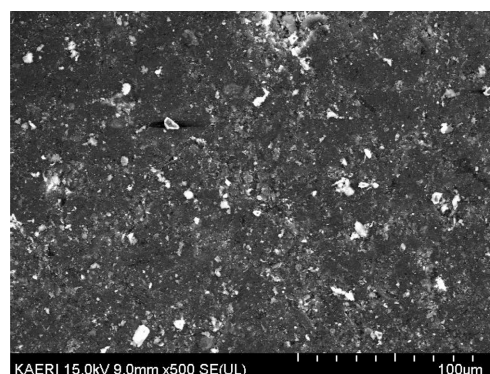


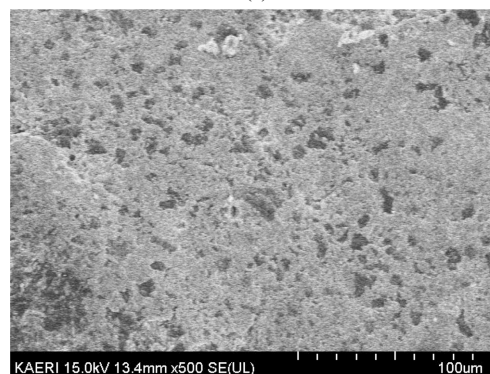
Fig. 4. The potential change of Li-B alloy anode with various applied current during the electrolysis in LiCl-KCl-NdCl₃ molten salt at 500°C.

increased. Then it rose suddenly about 20 min after the start of run 3. It is expected that the Li-B anode was polarized due to the exhaustion of Li. At a lower current density ($10 \text{ mA}\cdot\text{cm}^{-2}$), the anode potential was close to the reduction potential of Nd^{3+} , indicating that the direct chemical reduction of neodymium at the anode was likely to occur. On the other hand, the anode potential was higher than that at a higher current density ($25, 50 \text{ mA}\cdot\text{cm}^{-2}$). Thus, the spontaneous reduction of Nd at the Li-B alloy anode in the electrolysis could be avoided by maintaining it higher than the deposition potential of neodymium. After the electrochemical reduction runs for 90 min, the cathodic peak current was significantly decreased (Fig. 3d). Finally, about 76.2% of Nd^{3+} in the salt was reduced for about 3 h by both direct chemical and electrochemical reaction with the Li-B alloy (Fig. 3a to 3d). The applied charge was about 162.8 C, which is consistent with $1.04 \times 10^{-3} \text{ mol}$ of Nd^{3+} . But, the reduced amount of Nd^{3+} in salt was determined to be $1.92 \times 10^{-3} \text{ mol}$ which is higher than the theoretical value (i.e., the passed current). Among the total reduced amount of Nd^{3+} , 46% is due to the spontaneous reaction between Nd^{3+} and Li-B alloy in the salt, and 54% is induced by the electrochemical reaction. The Li-B alloy was maintained as a solid state after the tests at 500°C, representing the feasibility of the Li-B alloy anode in high temperature molten salt with easy handling.

Fig. 5 shows the SEM images on the surface of



(a)



(b)

Fig. 5. SEM images of the surfaces of Li-B alloy (a) before and (b) after the chemical and electro-reduction test for 3 hrs in LiCl-KCl-1 wt% NdCl₃ molten salt at 500 °C.

Li-B alloy before and after the chemical and electrochemical reduction. The original surface of Li-B alloy is not very smooth, which is due to the breaking it into small species. The surface morphology the Li-B alloy was changed to be porous structure after the electroreduction test. It was reported that Li-B alloy is two-phase system which consists of metallic lithium contained in a solid matrix (Li_7B_6).^{5,6)} This observation of the surface change of the Li-B alloy revealed that the Li confined in the matrix of Li-B alloy is spontaneously and electrochemically extracted to be involved in the reduction of Nd^{3+} in the salt.

Conclusions

This study shows that the preliminary results on the use of Li-B alloy as an anode in high-temperature molten salt electrolysis. The prepared Li-B

alloy was determined to have a main Li_7B_6 matrix in which Li is absorbed. The behavior of Li-B alloy was investigated in a LiCl-KCl-NdCl_3 molten salt by cyclic voltammetric measurements and by monitoring the anode potential with various applied currents. A spontaneous chemical reaction between Nd^{3+} in the salt and Li metal at the alloy as well as the electrochemical reduction of Nd^{3+} on LCC was observed. It was determined that, among the total amount of neodymium reduction, 46% is due to the direct chemical reaction and 54% is induced by the electroreduction at the LCC. The potential profiles of the anode with various current densities suggest that the direct chemical reduction at the Li-B alloy anode can be avoided by keeping the anode potential higher than the deposition potential of neodymium. Because of the reductive characteristics of Li-B alloy, it is thought that the Li-B alloy has advantages in being used in drawdown process. Further researches on the restraining the chemical reduction and recovering the directly reduced fine metal particles are critically needed.

Acknowledgements

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