

Effect of Cd on the deposition behavior of U and Nd in LiCl-KCl-UCl₃-NdCl₃ solution

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1. Introduction

A key step in pyroprocessing technology is an electrorefining process, which can recover pure U using solid cathodes (W or Mo) or U and TRU simultaneously using liquid cathodes (Cd or Bi) [1-3]. This is because the reduction potential difference between U and TRU elements is so large at solid cathodes but very narrow at liquid cathodes [4, 5]. On the other hand, the potential difference between actinides and rare earth elements is not also large when using a LCC (liquid cadmium cathode), and so a lot of rare earth elements can be deposited with actinides. These rare earth elements should be deposited at rates as low as possible to produce nuclear fuels for a fast reactor. Therefore, the factors having an influence on the deposition of actinide and rare earth elements need to be studied. In this study, firstly, the electrode reaction of U-Cd and Nd-Cd was observed using a cyclic voltammetry. Secondly, constant current deposition was carried out in order to study the factor having an influence on the deposition behavior of U and Nd on liquid Cd.

2. Methods and Results

2.1 Experimental procedures

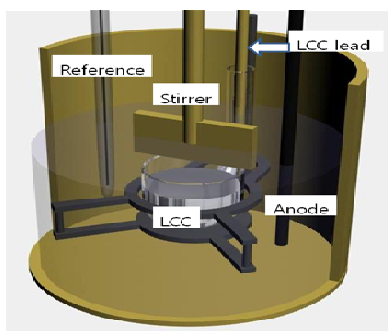


Fig. 1 Electrolytic cell used for the deposition experiments in LiCl-KCl-UCl₃-NdCl₃ solution on liquid cadmium cathode.

All the experiments were conducted at 773 K under a purified Ar atmosphere of less than 10 ppm oxygen and 10 ppm water. An electrolytic cell used for this experiment is shown in Fig. 1. A Mo of 1mm in diameter and a glassy carbon of 3 mm in diameter were used as a cathode and an anode for the cyclic voltammetry, respectively. For the deposition experiments, liquid cadmium was used as a cathode. An

Ag/Ag⁺ electrode (1wt%AgCl in LiCl-KCl) was used as a reference. Constant current (50, 100 mA/cm²) was applied to deposit U on LCC in LiCl-KCl-2wt%UCl₃-2wt%NdCl₃ solution.

2.2 Cyclic voltammetry of U and Nd on W electrode

According to the U-Cd phase diagram, the melting point of UCd₁₁ is 745 K, meaning that UCd₁₁ phase exist only below the temperature. Fig. 1 shows the cyclic voltammogram in the LiCl-KCl-2wt%UCl₃, where some amount of CdCl₂ was mixed with this solution. The U reduction peak potential in Fig. 2 is about -1.44 V which is analogous to the U potential reported in LiCl-KCl-UCl₃ solution without CdCl₂. So, it is confirmed that the U reduction potential was not nearly influenced by the Cd elements.

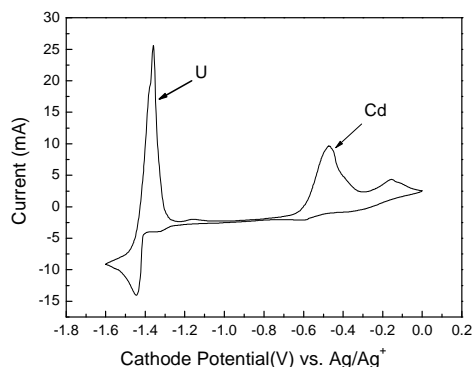


Fig. 2. Cyclic voltammograms of LiCl-KCl-2wt%UCl₃-CdCl₂ solution on solid W electrode.

Fig. 3 shows the cyclic voltammogram of LiCl-KCl-1wt%NdCl₃-0.1wt%CdCl₂ solution on the W electrode. As the potential increases in the negative direction, CdCl₂ first begins to reduce to Cd on the surface of W electrode and then Nd is deposited with the Cd element, and thus several peaks other than the Nd or Cd peak are created. Seven kinds of intermetallic compounds are present at 773 K according to the Cd-Nd phase diagram. It is therefore considered that the several peaks were Cd-Nd intermetallic compounds. Finally an Nd peak is formed around -2.0V as shown in Fig. 3. This result shows that the Nd could be deposited with Cd elements even below -1.6 V.

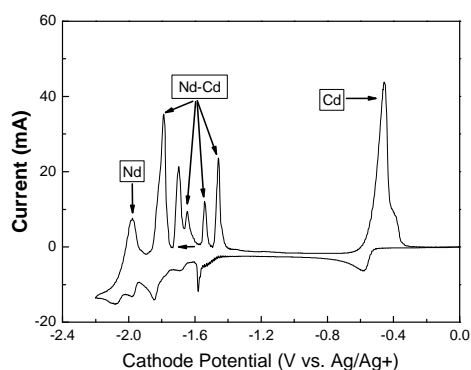


Fig. 3. Cyclic voltammogram of LiCl-KCl-1wt%NdCl₃-0.1wt%CdCl₂ solution on solid W electrode.

2.3 Deposition of U and Nd on LCC

Fig. 4 shows the deposition result of U on liquid Cd cathode at 50 and 100 mA/cm². Total passed current was the same as 270 mAh. The deposition potential stayed around -1.47 V throughout the deposition at 50 mA/cm². But, at 100 mA/cm², the potential first increased negatively to -1.8 V and then decreased to about -1.5V. As mentioned above, Nd elements could be deposited even below -1.6V due to the effect of Cd. So, this potential difference resulted in the different deposition behavior, that is, much more Nd elements were deposited with the U elements at 100 mA/cm² when compared with the result of 50 mA/cm². By the way, it took longer time at 50 mA/cm² than at 100 mA/cm². Therefore, proper current should be selected to deposit more U and less Nd in a short time.

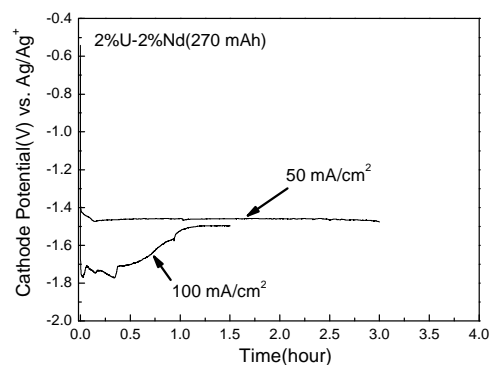


Fig. 4. Variation of the cathode potential at 50 and 100 mA/cm² on liquid Cd in LiCl-KCl-2wt%UCl₃-2wt%NdCl₃.

3. Conclusions

The deposition characteristics of U or Nd on W electrode was different when CdCl₂ was contained in the LiCl-KCl solution. U deposition potential did not nearly change whether Cd elements were in the LiCl-KCl solution or not. On the other hand, Nd could be deposited at lower potential in CdCl₂-containing

solution when compared with in the solution without CdCl₂. Because of that, some amount of Nd elements were deposited with U even if the cathode potential did not reach around -2.0V which was the analogous to the Nd standard potential on solid cathode. Therefore, proper current should be selected to deposit more U and less Nd on liquid Cd.

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