Deposition behaviours of uranium and rare-earth element depending on the electrolytic deposition technique

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Abstract

The electrode reactions of Nd in LiCl-KCl-$NdCl_3$ and LiCl-KCl-$NdCl_3$-$CdCl_2$ solutions were observed on a solid W cathode using cyclic voltammetry, and the deposition behaviours of U and Nd in LiCl-KCl-UCl_3-$NdCl_3$ solution on a liquid Cd cathode were compared using constant current deposition and constant potential deposition. The soluble-soluble reduction of Nd(III) to Nd(II) ions, and the reduction of Nd(II) to Nd occurred serially when sweeping in the negative potential direction. Five oxidation peaks corresponding to the Cd-Nd intermetallic compounds appeared in the cyclic voltammograms of the LiCl-KCl-$NdCl_3$-$CdCl_2$ solution. The reduction and anodic peak potentials of Nd were -2.04 V and -1.94 V on the W electrode, respectively. In the case of the LiCl-KCl-UCl_3-$CdCl_2$ solution, one cathodic pre-peak and one cathodic peak of U were seen during the cathodic sweep. Constant potential deposition would be more effective for depositing U with fewer Nd elements on a Cd cathode.

Introduction

A key step in pyroprocessing technology is an electrorefining process, which can recover pure U using solid cathodes (W and graphite, *et al.*) or actinide elements such as U and Pu simultaneously using liquid cathodes (Cd and Bi, *et al.*) [1-3]. The potential difference between U and Pu is very different depending on the cathodes, for example, around 270 mV on a solid W cathode and 70 mV on a liquid Cd cathode [4]. Therefore it is nearly impossible to recover pure Pu from the spent fuels using a liquid Cd cathode (LCC). On the other hand, the potential difference between actinides and rare-earth elements is also not large when using a LCC, and so several kinds 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.

Two popular techniques in electrolytic deposition are constant current and constant potential deposition. In the area of pyroprocessing techniques, the constant current deposition method has been principally used because it is more powerful than the constant potential method in obtaining a high throughput. On the other hand, the constant potential method is more useful for selectively depositing a certain element among those elements having various potential differences. Therefore, it is necessary to compare the two methods for mitigating the amount of rare earths during the electro-deposition of actinide elements.

In this study, U and Nd were selected as an actinide and rare-earth element, respectively. First, the electrode reactions of Nd in LiCl-KCl-$NdCl_3$ and LiCl-KCl-$NdCl_3$-$CdCl_2$ were observed using cyclic voltammetry. Second, both constant current and constant potential deposition were carried out in order to compare the deposition behaviours of U and Nd in LiCl-KCl-UCl_3-$NdCl_3$.

Experimental procedures

Each of the electrochemical experiments was conducted at 773 K under a purified Ar atmosphere of less than 5 ppm oxygen and 1 ppm water. Cyclic voltammograms of a LiCl-KCl-1 wt.% $NdCl_3$ solution with or without $CdCl_2$ were obtained using a solid W wire of 1 mm in diameter and a glassy carbon of 3 mm in diameter. The apparent surface area of the W cathode and glassy carbon anode were 0.26 cm^2 and 1.48 cm^2, respectively. A silver-silver chloride (1 wt.% AgCl in LiCl-KCl) electrode contained in a thin Pyrex glass tube was used as a reference. About 0.1 g of $NdCl_3$ and 0.01 g of $CdCl_2$ were directly mixed with 10 g of the LiCl-KCl solution contained in a quartz tube cell with a diameter of 18 mm. The cyclic voltammetric measurements were performed using an Autolab equipped with a PGSTAT 302N potentiostat and GPES 4.9 version software. The scanning rate for the cyclic voltammetry varied between 20 mV/s and 500 mV/s in this study.

The electrolytic cell used for the deposition experiments is shown in Figure 1. Approximately 105 g of LiCl-KCl-2%UCl_3-2%$NdCl_3$ solution was contained in an alumina crucible with a diameter of 50 mm, and a Pyrex crucible containing around 22 g of Cd was dipped into the alumina crucible as a cathode for the deposition experiments, where 1 mm diameter Mo lead wire was electrically connected into the Cd through a guide tube attached to the lower side of the Pyrex crucible, as shown in Figure 1. Another 1 mm diameter Mo wire was used as a cathode to obtain the cyclic voltammograms in the LiCl-KCl-2%UCl_3-2%$NdCl_3$. A glassy carbon of 3 mm in diameter and a silver-silver chloride (1 wt.% AgCl in LiCl-KCl) electrode were used as an anode and reference, respectively. A rectangular type stirrer (20 mm × 20 mm) was rotated at a speed of 40 rpm during the deposition, and was positioned above the LCC Pyrex crucible. Electro-deposition experiments were conducted at a constant current with a cathodic current density of 50 mA/cm^2 and at a constant potential of -1.45 V, respectively. The total electric charge used in each experiment corresponds to about 140 mAh. The cyclic voltammetry and deposition experiment in the LiCl-KCl-UCl_3-$NdCl_3$ solutions were conducted using a Bio-logic VMP-3 potentiostat and EC-Lab 9.98 version software.

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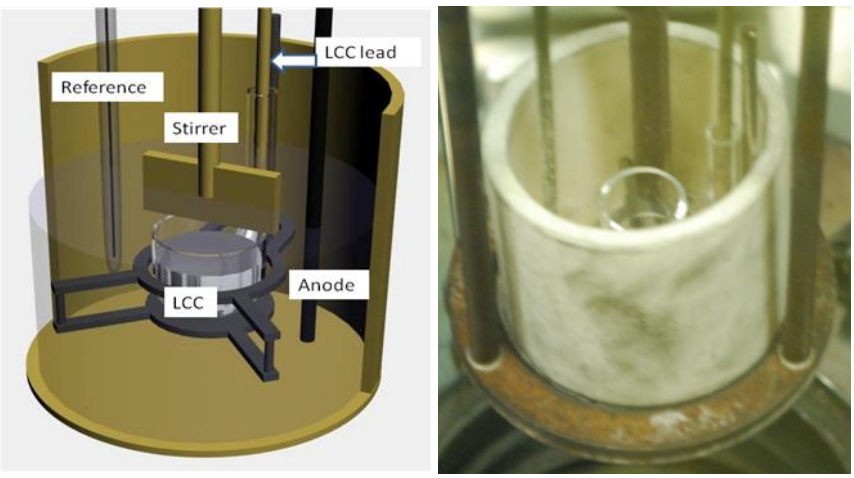
Figure 1: Electrolytic cell used for the deposition experiments in a LiCl-KCl-UCl_3-$NdCl_3$ solution on a Cd electrode at 773 K



Results and discussion

Figure 2 shows the cyclic voltammograms in the LiCl-KCl-1 wt.% $NdCl_3$ solution on a W electrode as a function of scan rate. As the scan rate increased, the cathodic peak currents continuously increased but the peak potentials did not nearly change. The cathodic peak current (i_{pc}) was linearly proportional to the scan rate up to 0.2 V/s as shown in Figure 3, which indicates that the process is reversible and controlled by the diffusion of the electroactive species. For the 0.5 V scan rates, the cathodic peak potential had a slight shift, which indicates that the system becomes quasi-reversible beyond 0.2 V/s.

In many cases, only one reaction proceeds in LiCl-KCl solution during the anodic or cathodic sweep. For example, Gd [5] or Ce [6] exists as $GdCl_3$ or $CeCl_3$ in the solution, respectively. Therefore, during a cathodic sweep, only a reduction reaction of Gd(III) to Gd or Ce(III) to Ce is produced. On the other hand, as shown in Figure 2, the reduction reaction of Nd was composed of two stages. That is, the soluble-soluble reduction of Nd(III) to Nd(II) ions and the reduction of Nd(II) to Nd occurred serially when sweeping in the negative potential direction. Among them, the reduction peaks of Nd(III) to Nd(II) were not clearly observed in this study. Castrillejo, *et al.* [7]

Figure 2: Cyclic voltammogram of a LiCl-KCl-1 wt.% $NdCl_3$ solution at 773 K on a W electrode

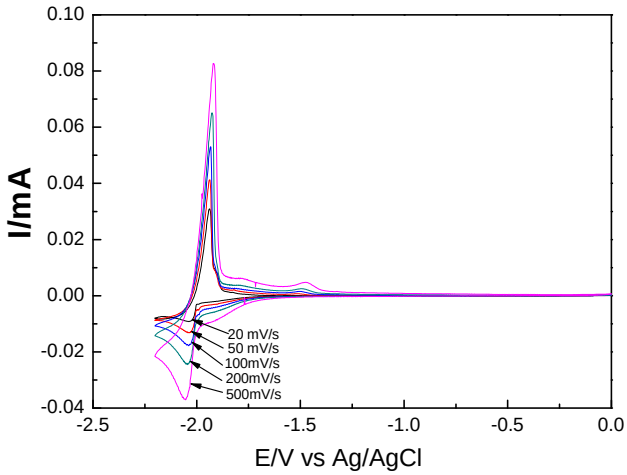
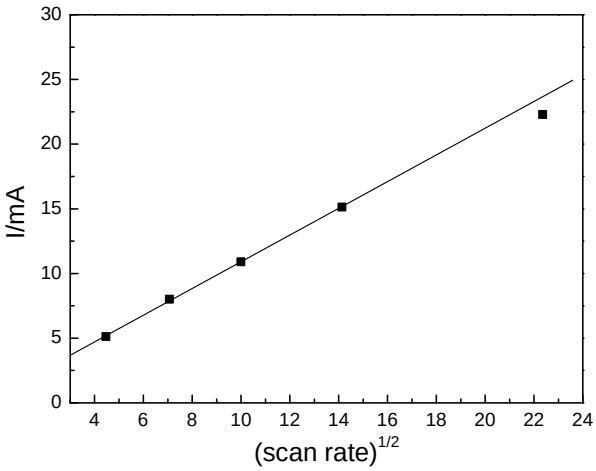


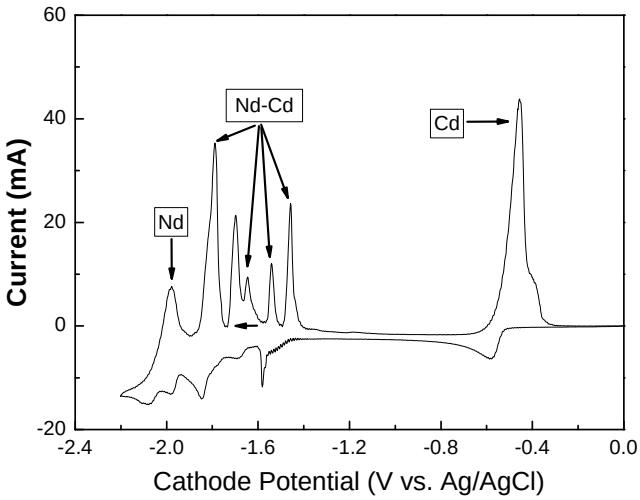
Figure 3: Cathodic peak current plotted against the square root of the scan rate



also showed that the reaction peaks of Nd(III) to Nd(II), or vice versa, were not observed in an LiCl-KCl solution, but that such reaction peaks were seen in a $CaCl_2$-NaCl solution. The shapes of the reduction peaks and corresponding anodic peaks are typical of those expected for the reduction of a cation to the corresponding metal, followed by re-oxidation of the deposited metal during the anodic sweep. The reduction and anodic peak potential of Nd were -2.04 V and -1.94 V on the W electrode, respectively.

Figure 4 shows the cyclic voltammogram of LiCl-KCl-1 wt.% $NdCl_3$-0.1 wt.% $CdCl_2$ solution on the W electrode. $CdCl_2$ begins to reduce to Cd in the potential range of -0.4 to -0.6 V during a cathodic sweep, and the surface of W electrode becomes coated by the Cd element. As the potential increases further in the negative direction, Nd is also deposited with the Cd element, and thus five peaks other than the Nd or Cd peaks, were further created compared with the voltammogram of the LiCl-KCl-$NdCl_3$. The peaks were better separated in the anodic sweep than in the cathodic sweep. According to the Cd-Nd phase diagram [8], seven kinds of intermetallic compounds from $Cd_{91}Nd$ to CdNd were present in the Cd-Nd phase. It is therefore considered that the extra five peaks were Cd-Nd intermetallic compounds. However, other than the Cd and Nd peaks, at most five anodic peaks were seen in Figure 4. This suggests that certain Cd-Nd intermetallic compounds form relatively quickly, but other phases form very slowly.

Figure 4: Cyclic voltammograms of a LiCl-KCl-$NdCl_3$-$CdCl_2$ solution at 773 K on a solid W electrode



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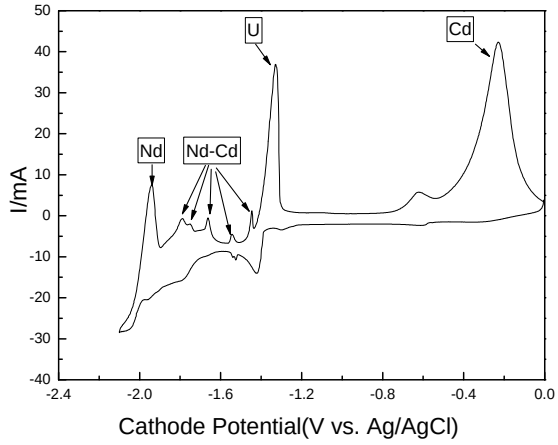
A small amount of Cd coated on the surface of a W electrode forms several kinds of Cd-Nd alloys. On the contrary, it is difficult to make many types of intermetallic compounds on a Cd pool electrode because there is too much liquid Cd in the pool, and many corresponding Nd elements are required to make Cd-Nd intermetallic compounds. Because of this, anodic or cathodic peaks were not well separated on the Cd pool electrode [6].

A cyclic voltammogram of U and Nd in LiCl-KCl-UCl_3-$NdCl_3$-$CdCl_2$ solution at 773 K on a Mo electrode is shown in Figure 5. A certain amount of Cd was added to this solution. During a cathodic sweep of up to -1.5 V, one cathodic pre-peak and one cathodic peak of U were seen in the voltammogram. According to Serrano and Taxil [9], the pre-peak and peak were associated with the adsorption of monovalent U and the deposition of U metal, respectively. No Cd-U alloy peaks are seen in Figure 5, because only a pure U phase is stable at 773 K in a U-Cd composition. If the temperature goes below 745 K, a peak corresponding to a UCd_{11} intermetallic compound may be observed in a LiCl-KCl-UCl_3-$CdCl_2$ solution.

Figure 5: Cyclic voltammograms of a LiCl-KCl-UCl_3-$NdCl_3$-$CdCl_2$ solution at 773 K on a solid Mo electrode



As the cathodic sweep proceeds further in the negative direction, Cd-Nd cathodic peaks and a Nd peak are serially observed in the voltammogram. The Nd cathodic peak in Figure 5 shifted to the lower part in the negative current direction, compared with Figure 4, which was probably due to moisture unexpectedly contained in the LiCl-KCl-UCl_3-$NdCl_3$-$CdCl_2$ solution. A small oxidative peak at around -0.6 V was not yet identified.

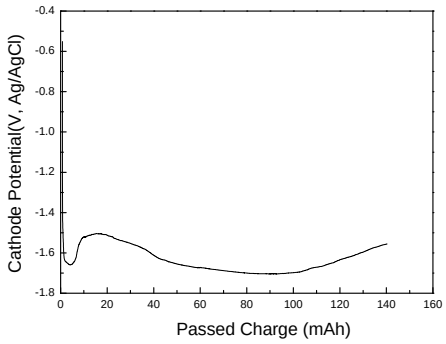
Figure 6 shows the variation of deposition behaviour of U and Nd in an LiCl-KCl-UCl_3-$NdCl_3$-$CdCl_2$ solution depending on the deposition time. The horizontal axis in the figure indicates the electric charge. These deposition experiments were conducted under constant current (50 mA/cm^2) and constant potential (-1.45 V) condition, respectively. Of course, the two deposition experiments were conducted at up to the same electric charge, which was about -140 mAh.

In the case of constant current deposition, the cathode potential varied from -1.505 V to -1.704 V throughout the deposition. Prior to this experiment in the same system, the deposition potential of U in LiCl-KCl-4 wt.% UCl_3 was recorded as -1.40 V at the same cathode current density. Therefore, a large amount of Nd would probably also be deposited under this constant current condition. In the final stage, the cathode potential continuously decreased in the positive direction, and therefore we stopped the deposition experiment.

In order to compare the deposition behaviour of U and Nd based on the deposition techniques, constant potential deposition was conducted at -1.45 V, which was near the cathodic deposition potential of U in the LiCl-KCl-4 wt. %UCl_3 solution stated above. As the deposition time increased, the cathodic current increased to -100 mA and finally decreased around at -91 mA in the final stage.

Figure 6: Deposition behaviours of U and Nd in LiCl-KCl-2wt.%UCl_3-2 wt.% $NdCl_3$ on a liquid Cd electrode using different deposition techniques

(a) Constant current deposition at 50 mA/cm^2



(b) Constant potential deposition at -1.45 V

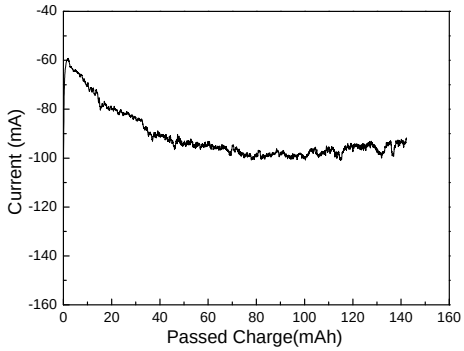
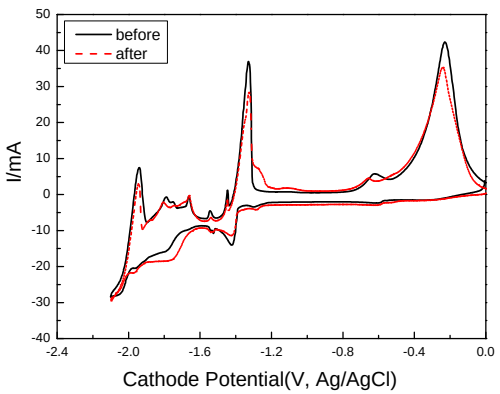


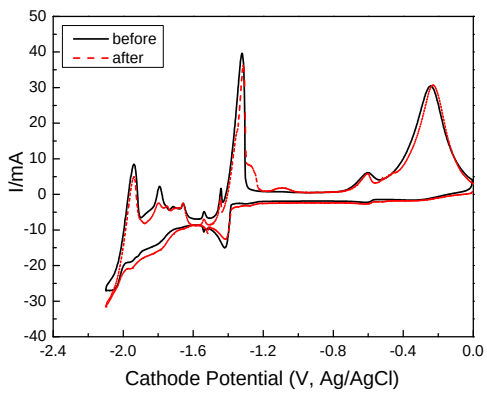
Figure 7 shows the change in the cyclic voltammograms before and after deposition, where the solid and the dotted lines correspond to the results before and after deposition, respectively. In the constant current deposition shown in Figure 7(a), the cathodic peak currents of U and Nd decreased together after the deposition, which means the two elements were co-deposited. In addition, in the constant potential deposition shown in Figure 7(b), the current magnitude of the U cathodic peak decreased but that of the Nd cathodic peak did not greatly change after the constant potential deposition. Chemical analysis result is needed to more precisely compare the deposition behaviours.

Figure 7: Changes in the cyclic voltammograms of U and Nd in LiCl-KCl-2 wt.% UCl_3-2 wt.% $NdCl_3$ before and after deposition on a liquid Cd electrode using constant current and constant potential deposition, respectively

(a) Constant current deposition at 50 mA/cm^2



(b) Constant potential deposition at -1.45 V



Conclusions

The electrode reaction of Nd in LiCl-KCl-$NdCl_3$ or LiCl-KCl-$NdCl_3$-$CdCl_2$ solution was observed on a solid W cathode, and the deposition behaviour of LiCl-KCl-UCl-$NdCl_3$ solution on the liquid Cd cathode was compared for constant current and constant potential deposition methods. The soluble-soluble reduction of Nd(III) to Nd(II) ions, and the reduction of Nd(II) to Nd, occurred serially when sweeping in the negative potential direction. The reduction peak potential and anodic peak potential of Nd were -2.04 V and -1.94 V on the W electrode, respectively. In addition, one cathodic pre-peak and one cathodic peak of U in the LiCl-KCl-UCl_3 solution were seen during the cathodic sweep. Constant potential deposition techniques are more useful for depositing U with fewer Nd elements in an LiCl-KCl-UCl_3-$NdCl_3$ solution.

Acknowledgements

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