Dissolution of Ce from Cd Solution Containing U/Ce Elements by Electrolysis

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1. Introduction

SFR fuel composition is mainly composed of U-TRU-Zr elements. The U-TRU metal alloy can be supplied by the Pyroprocessing [1,2], specifically U-TRU recovery process using liquid cadmium cathode (LCC). In a certain case, a lot of rare earth (RE) element could be recovered on the LCC with the TRU element during the Pyroprocessing when the concentration of RE ions is higher than that of the TRU ions in the salt [3,4]. In this case, most of the RE element needs to be removed from the Cd solution containing U/TRU/RE elements. KAERI has already developed RAR (Residual Actinides Recovery) process for this purpose. RAR technique used the mixed electrolytic-chemical process. In this study, only electrolysis technique was utilized to remove Ce element from Cd solution containing U/Ce elements.

2. Methods and Results

2.1 Experimental procedures

LiCl-KCl-1.85wt%UCl_3-2.25wt%$CeCl_3$ salt and Cd ingot were used for this experiment. The purity of Cd was 99.999%, which is supplied by the Aldrich. The salt of 182g and Cd ingots of 210g were contained in an alumina crucible having an inner diameter of 5cm and a height of 10cm. The alumina crucible was heated at 500°C and both salt and Cd were melted at this temperature, where the salt and the Cd were located in the upper and lower part in the alumina crucible, respectively.

Glassy carbon rod and Ag/1mol%AgCl was used counter electrode and reference electrode for the cyclic voltammetry, respectively. Tungsten wire with a diameter of 1mm was used as a working electrode. Fig. 1 shows the cyclic voltammogram of the above salt at 500°C, where U ion corresponds to around -1.4V and Ce ion about -2.0V. Several peaks between -1.4 V and -2.0V show the Ce-Cd intermetallic compounds. All the experiments for this study were conducted in a glove box having an atmosphere of 1 ppm of moisture and 1 ppm of oxygen because the salt was very hygroscopic.
The dissolution process was carried out at 2 steps. At the 1st step, most of the U/Ce ions in the salt will be deposited to the LCC. At the 2nd step, most of the Ce elements in the Cd solution will be oxidized as the Ce ions to the salt.

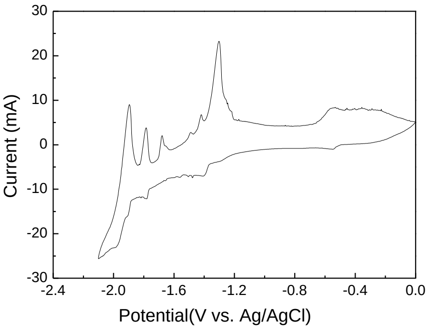

Fig. 1. Cyclic voltammogram of initial LiCl-KCl-UCl_3-$CeCl_3$ salt, where the peaks show the presence of U and Ce ions in the salt.

2.2 Deposition

Glassy carbon rod with the diameter of 3mm and Ag/1mol%AgCl were used counter electrode and reference electrode for the deposition experiment, respectively. Liquid cadmium was used as a working electrode, where STS wire having a diameter of 1mm was used as a Cd lead to pass the currents.

Fig. 2 shows the variation of cathode potential at the current density of 30 mA/cm^2. The potential was about -1.9V in an initial state and moved to around -2.0V in 1.5 hour. Beyond this time, the cathode potential rose to -1.9V and then moved to the negative direction. Around 3 hours in Fig. 2, most of the U ions and Ce ions in the salt were predicted to be deposited to the LCC because the theoretical deposition time for the consumption of U/Ce ions were near 3 hours.

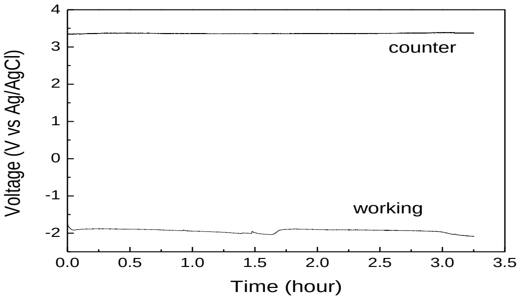

Fig. 2. Chronopotentiometry showing the deposition of U and Ce ions to the liquid Cd cathode.

Fig. 3 shows the concentration differences of U ions and Ce ions in the salt before and after the deposition. The concentration of ions can be qualitatively compared by the peak height of the voltammogram. The concentration of U, Ce and Cd ions were remarkably decreased after the deposition, showing most of the ions such as U and Ce in the salt were deposited to the LCC during the deposition of 3 hours.

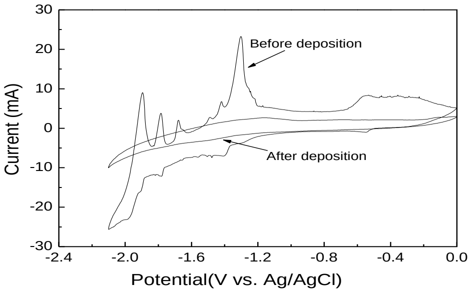

Fig. 3. Cyclic voltammogram showing the concentrations of U and Ce ions largely decreased after the deposition

2.3 Dissolution

This step is to oxidize the Ce element in LCC to the Ce ions in the salt. For this process, STS wire having a diameter of 3mm and the deposited liquid Cd were used as a counter and working electrode, respectively. Open-circuit potential (OCP) of the deposited LCC was -1.515V. To oxidize the Ce element in the LCC, 0.1V was applied to the LCC in the positive direction based on the OCP of the LCC, making the LCC potential -1.417V. This potential was chosen from the result that dissolution potential of U was normally between -1.45 and -1.35V at 500^{o}C.

Fig. 4 shows the variation of the current and cathodic potential when 0.1V was applied to the LCC in the positive direction based on the OCP of LCC. The cathode potential was below -2.4V until the dissolution time was 4 hours and beyond this time the potential changed positively to -2.17V. It is explained from this potential that Li ions was deposited to the solid STS cathode for about 4 hours because Li deposition potential is around -2.4V and then Ce ions began to deposit to the STS cathode because Ce deposition potential between -2.0 and -2.1V. It is predicted that Ce ions would be present in the salt after this process. Of course, the Ce ions were dissolved from the Cd solution containing U and Ce element.

After the 1st dissolution experiment in Fig. 4, the 2nd dissolution was tried to dissolve more Ce elements from the Cd solution. The OCP of LCC after the 1st dissolution was -1.513V. Also in this dissolution experiment, 0.1V was applied to the LCC in the positive direction based on the OCP of LCC. Fig. 5 shows the chronoamperometry result, where the cathode potential shifted from -2.1V to -1.6V during the dissolution reaction, showing some change occurred in the salt concentration. It is judged that Cd-U solution having less Ce element can be prepared through this dissolution process.

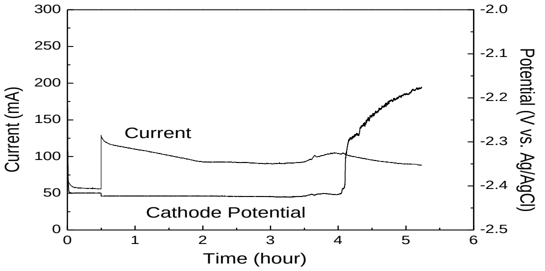

Fig.4. Variation of current and cathodic potential during the chronoamperommetry, showing the oxidation of Li and Ce elements

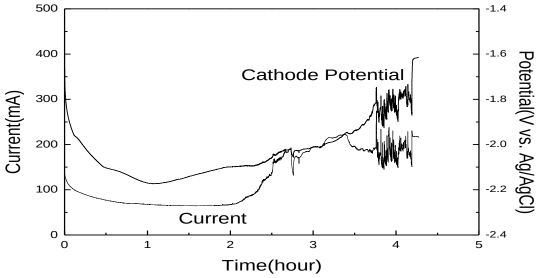

Fig.5. Variation of current and cathodic potential during chronoamperommetry, showing the oxidation of Ce element

3. Conclusions

U-TRU alloy having less impurity is necessary for the fabrication of SFR fuel and these U-TRU elements can be prepared by Pyroprocessing. But, in a certain case, a lot of RE elements could be recovered with the TRU element during the Pyroprocessing. Electrolytic method was used to reduce the amount of Ce elements from the Cd solution containing U/Ce elements. It is judged from this study that electrolytic dissolution can be one of the methods to reduce RE elements from the Cd solution containing U-TRU-RE elements.

Acknowledgement

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