Lab-Scale Electrodeposition Behaviors of Pr(III) with Use of Quartz Cell in Molten LiCl-KCl Eutectic

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1. Introduction

Pyroprocessing, the most promising back-end fuel cycle of the future for the reuse of used nuclear fuel, is under rapid development. Electrorefining, known as an important unit process, recovers most of uranium dissolved in molten LiCl-KCl electrochemically. As electrorefining is proceeded, all actinides and lanthanides in metallic form are electrochemically oxidized and dissolved into the salt, while UCl_3 in the salt is reduced and forms U-metal at solid cathodes[1]. Since this unit process includes diverse actinides and recovers most of uranium, information on stream of nuclear materials and electrochemical condition inside of electrorefiner must continuously be notified not only for its performance assessment and process prediction but also for its safeguards.

Currently, there are several computational models for electrorefiner (REFIN, ERAD, and etc.)[2]. However, the absence of model which reflects the change in surface area of cathode due to electrodeposition of UCl_3 critically disturbs the precision of simulation. The change in surface area leads the change in current density, diffusion layer, potential and current gradient, and thus changes the entire electrochemical conditions in electrorefiner. In this paper, as a beginning step of investigating electrodeposition behavior of lanthanides and actinides, lab-scale electrodeposition experiments and methodological evaluation on the use of quartz cell are performed.

2. Experimental

2.1. Sample Preparation

In order to reflect pyroprocessing condition, a glove box filled with high-purity argon gas (99.9999 % Ar, concentrations of H_2O and $O_2 < 1$ ppm) was prepared for overall experiments. Unintentional oxidation or hydrolysis were avoided. LiCl-KCl eutectic and PrCl3 (99.99 % anhydrous, Sigma-Aldrich), the target lanthanide, were inserted in quartz cuvette or cylindrical cell with two 1 mm tungsten electrodes as working and counter electrode. Silver wire was immersed in 1 wt. % AgCl-LiCl-KCl contained in pyrex guide tube as a reference electrode. Entire system was inserted in the furnace attached below the glove box, and it was used to maintain the temperature of whole system with 773 K. A potentiostat (Autolab, PGSTAT302N) was utilized for all electrochemical experiments, and a spectrophotometer (Carl Zeiss MCS 601 UV-NIR C with halogen lamp) was employed for simultaneous spectroscopic investigation.

2.2. Selection of Target Element

Among all lanthanides, cerium(Ce) was initially chosen for the target element because of its similar chemical characteristics to those of uranium[3] and electrochemical properties (reaction step: 1 step (+3 → 0), exchange current density U = 18.75 mA/cm^2, Ce = 17.61 mA/cm^2). However, an absorption spectrum of Ce for spectroscopic analysis showed high molar absorptivity(321 nm = 694.13 M^{-1}cm^{-1})[4] and yielded the sample with low concentration. This low-concentrated sample demonstrated unstable electrodeposition because of fast exhaustion of diffusion layer and ions in the bulk. Therefore, praseodymium(Pr) was chosen as the target element satisfying crucial characteristics: 1 step redox reaction and relatively low molar absorptivity (449 nm = 1.36 M^{-1}cm^{-1}).

3. Results and Discussions

3.1 Electrodeposition

At first, electrodeposition was carried out with providing fixed current using chronopotentiometry(CP) to imitate actual pyroprocessing. However, the interference of deposited material which was in contact with quartz cell caused unstable fluctuation of potential, and it led the diversion of the system from reduction condition. In order to force the system to be fixed in stable reduction condition, we controlled the potential by using chronoamperometry(CA) instead of CP.
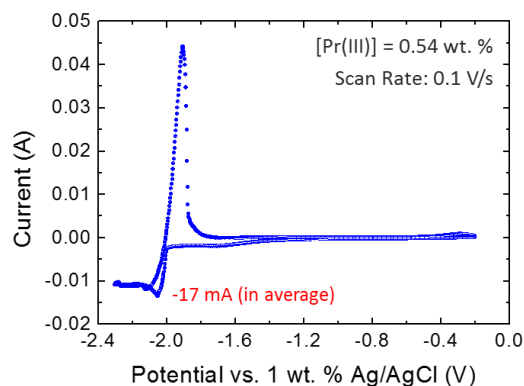

Fig. 1. Cyclic voltammetry (CV) diagram of 0.54 wt. % Pr(III) with a scan rate of 0.1 V/s

By running CV of Pr(III), the reduction potential was revealed to be -2.05 V with reference to Ag/AgCl, and its peak current was -17 mA. Therefore, CA was performed with the same system with a fixed potential of -2.05 V.
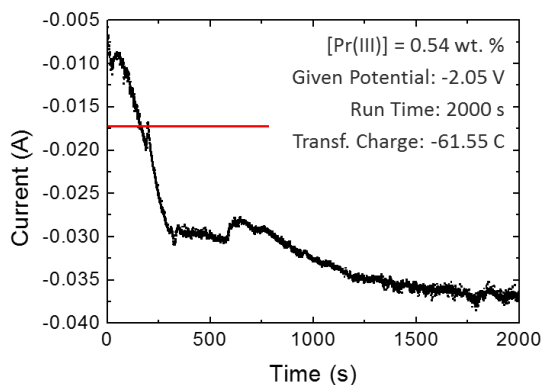

Fig. 2. CA diagram of 0.54 wt. % Pr(III) for 2000 s with fixed potential of -2.05 V

During 2000 s of electrodeposition, the current was increased to the twice value of the peak current at CV but was soon stabilized by forming a plateau at -36 mA. The increase in the magnitude of flowing current was caused by increase in surface area of the working electrode. The amount of transferred charge was calculated by integrating CA diagram and was -61.55 C. Considering one step reaction which required 3 electrons to reduce one Pr(III) ion, -61.55 C corresponded to -0.29 wt. % of Pr(III).

Fig. 3. Photograph of working and counter electrode with electrochemically deposited praseodymium.

This deposited material was definitely praseodymium metal for two reasons: vigorous dissolution in nitric acid with bubble generation (H_2 gas) and way higher concentration of Pr (~ 22 wt. %) than that in the bulk from ICP-OES result. Ideally deposited product must have 100 % Pr, but large portion of it was LiCl-KCl.

The concentration of bulk after electrodeposition was 0.239 wt. % according to ICP-OES data, and the concentration balance demonstrated that 0.301 wt. % of Pr(III) was deposited. This value was close to the amount of charge transferred.

3.2 Blackening Effect

A quartz cell had an unintended interference with deposited material during experiments. Compared to the previous CA diagram, Fig. 4 illustrates continuous and linear increase in the magnitude of current, instead of stabilized plateau.
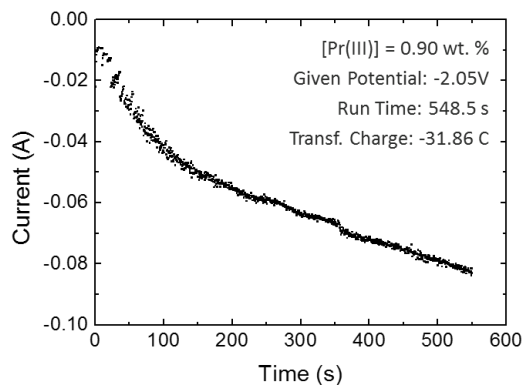

Fig. 4. CA diagram of 0.90 wt. % Pr(III) for 548.5 s with fixed potential of -2.05 V

During this experiment, UV-Vis spectroscopy was simultaneously performed for monitoring bulk concentration.
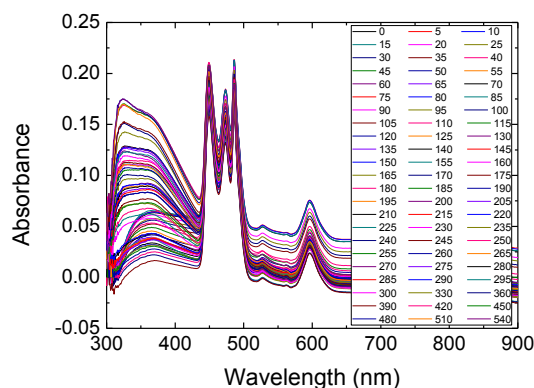

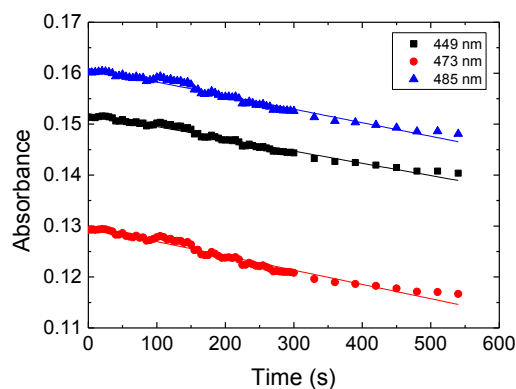Fig. 5. Absorption spectrum of Pr(III) during CA

Fig. 6. Decrease of absorption peaks of Pr(III) during CA

According to the charge balance from CA, -31.86 C of charge was flowed to the bulk, and this was 30 % of the bulk concentration; however, the absorption spectrum showed the reduction of 8 %. The cell was interrupted with blackened parts as shown in Fig. 7 and large amount of charge was leaked.
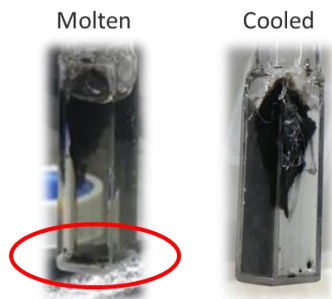

Fig. 7. Photographs of cuvette cell after the experiment

Highly possible candidates for this blackened part was praseodymium, tungsten, and silicon. By the use of LIBS and ICP-OES, this blackened part was turned out to be a compound of Si, which was the consisting material of quartz cell. No signal of tungsten was measured by LIBS.

Table 1. LIBS measurement of blackened part

Pr II		Si I	
Database	Measured	Database	Measured
414.311 (1000)	414.174	250.617 (400)	250.659
417.939 (500)	417.807	251.353 (400)	251.432
418.948 (500)	418.808	251.532 (500)	251.611
		251.833 (400)	251.920
		252.326 (400)	252.411
		252.774 (400)	252.851

The formation of blackened part of quartz cell was then tested with open circuit condition. After electrodeposition, the working electrode with deposited material was inserted into a quartz cell with blank LiCl-KCl. After 1500 s, the bottom part of cell became black again, and deposited material was cleaned. This process was visualized in Fig. 8.
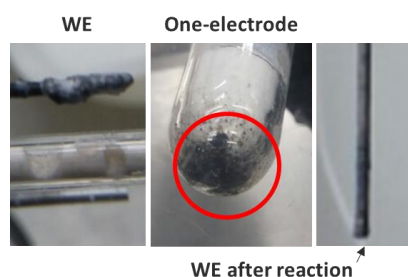

Fig. 8. Photographs of initial working electrode, cell after the reaction, and cleaned working electrode

These results showed that even the stable form of SiO_2 which consisted quartz cell spontaneously reacted with electrochemically deposited praseodymium in molten LiCl-KCl eutectic. This spontaneous reaction was accelerated by extra charge provision and was the main source of charge consumption (also known as charge waste/leakage).

4. Conclusions

In the lab-scale electrodeposition, sizes of quartz cell and deposited material became crucial factors for precise analysis of experiments. In a typical stabilized electrodeposition, CA diagram showed large plateau with reasonably increased magnitude of current due to the increase in surface area of working electrode. The amount of charge transferred (-61.55 C) can be utilized for concentration balance. According to ICP-OES, the decreased amount of bulk was 0.301 wt. % which was close to the expected decrease from the information of charge flow (0.29 wt. %). However, deposited material in contact with quartz wall in molten LiCl-KCl eutectic led a spontaneous reaction between each other. As an indicator of this undesired reaction, the cell became black, and enormous amount of charge was consumed. In other words, this blackening effect might disrupt overall electrochemical analysis and mass balance after the electrodeposition. Therefore, the contact of deposited material to quartz cell must be avoided. For stable lab-scale electrodeposition experiments, the use of small quartz cell should be rejected. Instead, use of alumina cell or larger cell to prevent deposited materials touching quartz wall is preferred.

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