

Application of square wave voltammetry to on-line monitoring of lanthanide ions in LiCl-KCl molten salt at 773K

Tack-Jin Kim*, Dae-Yeob Park, Joon-Bo Shim, Si-Hyung Kim, Seungwoo Paek,
Kwang-Rag Kim, Gha-Young Kim, Jae-Hoo Jung, Do-Hee Ahn

Nuclear Fuel Cycle Process Development Division, Korea Atomic Energy Research Institute, 150 Deokjin-dong,
Yuseong-gu, Daejeon 305-353, Republic of Korea

*Corresponding author: ktj@kaeri.re.kr

1. Introduction

Molten salt based pyrochemical process has received attention as a possible future separation technique for reprocessing [1-2]. Recently, the technology has attracted much attention due to a possibility to be able to prepare metallic nuclear fuels for sodium-cooled fast breeder reactor [3].

In general, pyroprocess consists of three subsequent steps. First, uranium oxide is electrochemically reduced at the cathode to create a metal ingot containing uranium and oxygen gas is generated at the anode in electrolytic reduction process. Next, the metal ingot is transferred to an electrochemical cell of a LiCl-KCl molten salt at 773K for electrorefining process, where pure uranium metal is recovered through an electrochemical reduction route. Finally, uranium and TRU remained after the electrorefining process is completely recovered in electrowinning process, where uranium and TRU are co-deposited at liquid cadmium electrode to make cadmium-based alloy for nuclear non-proliferation.

In order to practically use the recovered actinides as a fuel of SFR, it is necessary to protect co-deposition of lanthanide elements. In case of a lanthanide-contaminated fuel, the neutron flux for transmutation of the actinides is significantly decreased due to the some lanthanide elements with large neutron capture cross sections. So, it is quite needed to measure the concentration of lanthanides in the molten salt to efficiently avoid the co-deposition of lanthanide elements and further to improve the efficiency of the electrowinning process.

2. Experimental and Results

2.1 Apparatus and Chemicals

All the sample preparations and electrochemistry experiments were carried out in an argon-filled glove box where concentrations of O₂ and H₂O were controlled less than 1 ppm. The experiment cell was a one end-closed pyrex tube placed in a furnace. Temperature fluctuation of the sample during the spectrometry was about \pm 1 K. Anhydrous LiCl-KCl and CeCl₃ (99.99% purity) were purchased from Aldrich-APL LLC and used without further purification.

The electrochemical measurements were carried out using an Autolab PGSTAT302 potentiostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9).

A conventional three-electrode cell with one compartment pyrex cell was used for all measurements. The cell temperature was maintained at 773 \pm 2 K. The experiment cell equipped with a three electrodes setup. The working electrode was made of tungsten rod of 1 mm diameter (Nilaco Co.). And counter electrode were prepared using a glassy carbon rod (3 mm in diameter, Alfa Aesar Co.). The active surface area was measured after each experiment by measuring the immersion depth of the electrode. Ag/Ag⁺ electrode systems, which consisted of a one end-closed pyrex glass tube where Ag wire (0.5 mm in diameter) is dipped in LiCl-KCl solution with 1 mol% AgCl, were used as a reference electrode. For the cyclic voltammetry and square wave voltammetry, Autolab PGSTAT302 potentiostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9) was used. Cyclic voltammetry was recorded over a potential range -0.2 ~ -2.2 V versus reference electrode at scan rates 100 mV/s. Square wave voltammetry were recorded over a potential range -1.8 ~ -2.2 V versus reference electrode.

2.2 Results

Fig. 1. shows a representative example of cyclic voltammogram of a solution of Ce(III) in the LiCl-KCl eutectic melt at 773K. The electroreduction takes place in a single electrochemical step A with the characteristic shape of the formation of a new phase, Ce(0).

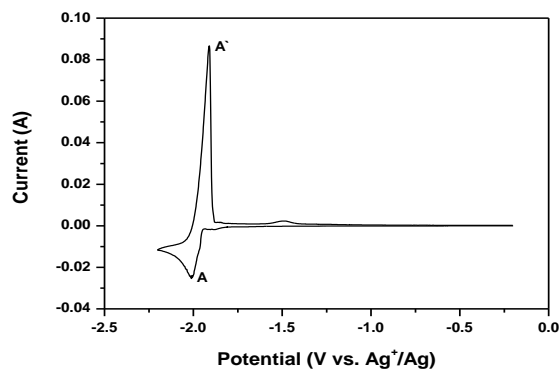


Fig. 1. Cyclic voltammogram for the reduction of a LiCl-KCl-CeCl₃ solution (1 wt%) at 773K.

In the reverse scan direction a peak A' is observed, with the expected characteristics for a stripping peak, decay steeper than rise due to the depletion of the metal, Ce(0), deposited during the forward scan.

The effect of the half height and the frequency of the square wave on the SWV result were examined with cerium. The peak current for cerium reduction increased approximately in proportion to the half height of the square wave except for the cases of 50 mV and 100mV. Sharpe peaks are preferable from the viewpoint of peak separation in a multi-component system and the peak height at the small square wave half height was considered large enough for detection and the succeeding data processing. Then a square wave half height of 5 – 10 mV was selected for the SWV measurement in this study.

The increase of the square wave frequency also brought growth in the current peak width to the negative direction. At low frequency, the sharp current peaks are observed which can be more easily separated from each other although the required time for measurement becomes longer.

The result of SWV for LiCl-KCl-CeCl₃ in a relatively higher concentration range (0.3 – 2.9 wt%). The current peaks by reduction of cerium were observed at around -2.0. However, the height of the peak current did not show a linear relation to the actual concentration of cerium over this concentration range (Fig. 2).

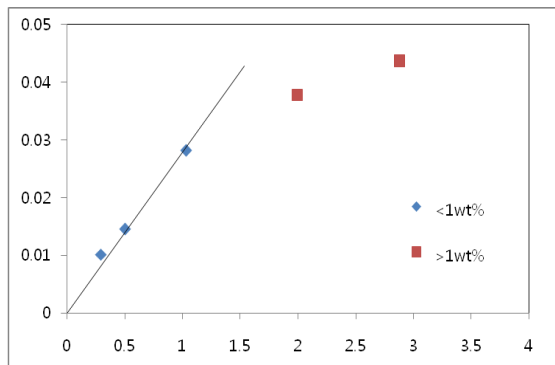


Fig. 2. Cocentration dependence of peak height in SWV curves for LiCl-KCl-CeCl₃.

3. Conclusions

From the above results, it was considered to be difficult to apply SWV to the process where the concentration of lanthanide in the molten salt electrolyte is higher than a few 1wt%. However, SWV has many advantages when it is applied at low concentrations of less than 0.1 wt% because of its high sensitivity and easy separation among the current peaks. It is still a candidate as an on-line monitoring method in the pyroprocess, where the concentrations of lanthanides are decreased to a low level.

Acknowledgement

This study was supported by the Mid- and Long-Term Atomic Energy R&D Fund of Korean Ministry of Science and Technology.

REFERENCES

- [1] H.P. Nawada, K. Fukuda, J. Phys. Chem. Solids 66 (2005) 647
- [2] K. Uozomi, M. Iizuka, T. Kato, T. Inoue, O. Shirai, T. Iwai, Y. Arai, J. Nucl. Mater. 325 (2004) 34
- [3] Cassayre L, Caravaca C, Jardin R, Malmbeck R, Masset P, Mendes E, Serp J, Soucek P, Glatz JP (2008) On the formation of U-Al alloys in the molten LiCl-KCl eutectic. J Nucl Mater 378 : 79-85