An Effect of Bismuth Ion on the Reduction of Samarium Ion in Molten LiCl-KCl Eutectic Salt

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This study is a basic study on the co-reduction and confirmed the IMC of Sm and Bi in LiCl-KCl molten salt through electrochemical measurement method CV and SWV at 773K. It can be seen that many reduction potentials and oxidation potentials were generated via CV, the potentials of Bi and Sm are similar to the results seen in existing ones. In addition, Intermetallic compound potential was confirmed through SWV. Sm-Bi Intermetallic compound was deduced through the potential of CV and SWV.

I. INTRODUCTION

The Korea Atomic Energy Research Institute (KAERI) has developed Residual Actinides Recovery (RAR) by introducing Liquid Cadmium Cathode (LCC) to increase the recovery rate of TRU contained in the waste molten salt generated in the Pyro process [1]. However, since TRU still remains and can be classified as high - level waste, PyroRedSox process of PyroGreen using Liquid Bismuth was introduced to recover residual TRU [2].

PyroRedSox is a two-step process that involves electrochemical and chemical separation processes. First, electrolytic reduction is using Liquid Metal Bi to recover both actinide and lanthanide to Liquid Metal Bi. Next, selective oxidation is a process of separating and extracting Ln using an oxidizing agent (ex, $BiCl_3$) from liquid Bi to salt. When the liquid metal Bi is used a media for the Reductive Extraction in PyroRedSox process, the molten salt is likely to contain Bi ions. Then, the Bi ion will be combined with the Lanthanide ion to form an intermetallic compound. It affects the Lanthanide and cause the electrochemical property change of the Lanthanide in molten salt.

The purpose of this study is to establish therefore, we focused on the electrochemical behavior of Bismuth ions and Lanthanide ions. Samarium in Lanthanide was firstly selected because it has two oxidation states of di-valence and tri-valence in the molten salt LiCl-KCl. The technique is applied to investigate electrode reactions of samarium ion and Bismuth ion in the molten salt LiCl-KCl. Finally, we analyze the effect of Bi ion concentration on the electrochemical reduction of Ce.

I.A. Experiments

The electrochemical measurement system under high temperature environments was designed and fabricated to investigate electrochemical behaviors of the dissolved species in the molten salt LiCl-KCl. The electrochemical cell was composed of long-necked cylindrical quartz tube and three electrodes. The working electrode and counter electrode for the cell was fabricated with tungsten wire. Ag/AgCl(1.0 wt%) was used to the reference electrode. The experiments were carried out in a glove box filled with high purity argon gas.

The electrochemical measuring device was Versastat3 from Princeton Applied Research and Versa studio from software. Cyclic voltammetry(CV), Square Wave Voltammetry(SWV) experiments were performed to confirm co-reduction of Sm and Bi and intermetallic compound formation in LiCl-KCl-$CeCl_3$-$BiCl_3$ molten salt.

I.B. Results and Discussion

The cyclic voltammogram of LiCl-KCl+$SmCl_3$(1wt%) at 723 K showed a single redox peak corresponding to the Sm^{3+}/Sm^{2+} couple under potential window between -2 V and 0.5 V (vs. Ag/AgCl reference electrode). Analysis of voltammogram exhibited that a formal standard potential of Sm^{3+}/Sm^{2+} redox couple was obtained to -0.87V/-0.73 (vs. reference electrode). As a result of adding $BiCl_3$(1wt%), various intermetallic compounds redox peaks were observed in Fig 1. B'/B are the redox peak of Sm and A is the peak of Bi metal. Except the B peak in the SWV shown, the C, F, G is an intermetallic compound, and it can be seen that the SWV was also confirmed at the peak of oxidation-reduction behavior when compared with CV. According to the Phase Diagram, five intermetallic compounds Bi2Sm, BiSm, Bi3Sm4, Bi3Sm5 and $BiSm_2$ are observed in the Sm-Bi system at 773K. Various methods have been used to identify IMC, among which confirmed the IMC by measuring the XRD and SEM by applying a reduction potential at the generated potential. Through the literature [3], it can be seen that the amount of Sm increases with increasing negative potential. Therefore, the C, D, E, F, G reduction potential is inferred to be Bi_2Sm, BiSm, Bi_3Sm_4, Bi_3Sm_5 and $BiSm_2$.

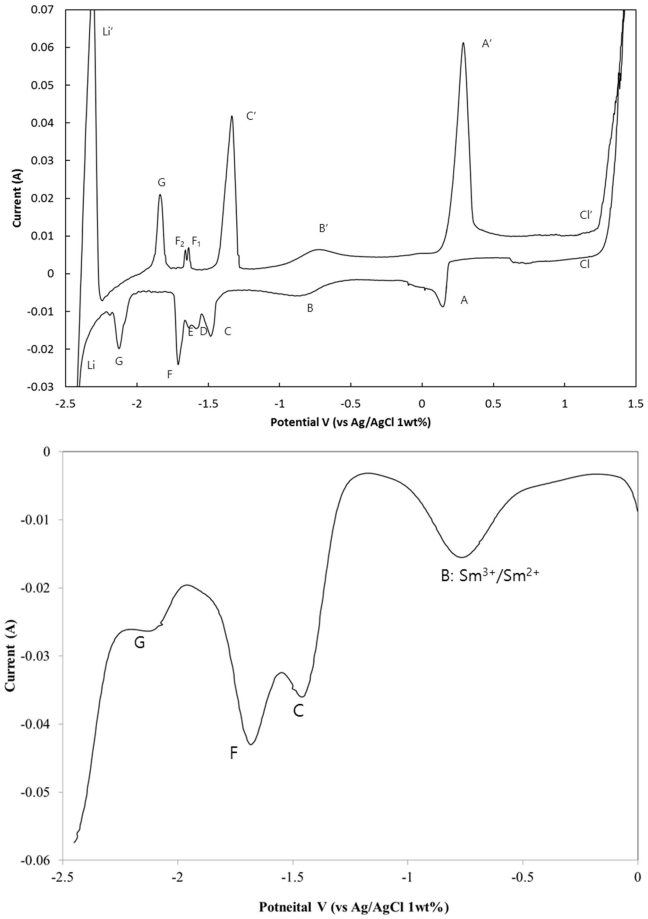

Fig.1. Cyclic Voltammograms obtained in molten salt LiCl-KCl with $CeCl_3$(1wt%) add $BiCl_3$(1wt%) on a tungsten electrode 0.62cm^2 at 773K. Scan rate 100mV/s, Scan direction: 0→-2.5 →1.5 →0V. And Square Wave Voltammograms obtained in molten salt LiCl-KCl with $SmCl_3$(1wt%)add $BiCl_3$(1wt%), Frequency: 20Hz, Pulse Height: 25mV, potential stap: 2mV.

II. CONCLUSIONS

In this study, electrochemical behavior of tungsten electrode in LiCl-KCl molten salt was performed at 773K.

Various electrochemical measurements CV, SWV were performed to confirm the formation of an intermetallic compounds Sm-Bi. Through the CV and SWV results, reduction / oxidation peaks were observed that were formed in the formation of various Sm-Bi intermetallic compound of $Bi^{3+}+3e^- \leftrightarrow Bi$ and Sm. Based on these results, we were able to know the formation of Bi_2Sm, BiSm, Bi_3Sm_4, Bi_3Sm_5 and $BiSm_2$. In the future, our research will carry out a study for Co-reduction by applying a selective potential on Sm-Bi. And SEM and EDX, XRD will be executed to directly observe the intermetallic compounds formed.

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REFERENCES

1. J.B.Shim, K.S.Han, S.H.Kim, et al., “Effects of CdCl2 on the residual actinides recovery(RAR) system of a spent LiCl-KCl salt”, in Proceedings of Global, Paris, France, September (2009).
2. Hyo sook Jung, et al., Environmental assessment of advanced partitioning, transmutation, and disposal based on long-term risk-informed regulation: PyroGreen, Progress in Nuclear Energy 58, 27-38 (2012)
3. Ya-Lan Liu, et al., Electrochemical extraction of samarium from LiCl-KCl melt by forming Sm-Zn alloys, Electrochimica Acta, 120, 369–378 (2014)