Liquid Bi pool is a candidate electrode for an electrometallurgical process in the molten LiCl-KCl eutectic to treat the spent nuclear fuels from nuclear power plants. The electrochemical behavior of Bi$^{3+}$ ions and the electrode reaction on liquid Bi pool were investigated with the cyclic voltammetry in an environment with or without BiCl$_3$ in the molten LiCl-KCl eutectic. Experimental results showed that two redox reactions of Bi$^{3+}$ on inert W electrode and the shift of cathodic peak potentials of Li$^+$ and Bi$^{3+}$ on liquid Bi pool electrode in molten LiCl-KCl eutectic. It is confirmed that the redox reaction of lithium with respect to the liquid Bi pool electrode would occur in a wide range of potentials in molten LiCl-KCl eutectic. The obtained data will be used to design the electrometallurgical process for treating actinide and lanthanide from the spent nuclear fuels and to understand the electrochemical reactions of actinide and lanthanide at liquid Bi pool electrode in the molten LiCl-KCl eutectic.

Keywords: Molten salt, Liquid Bi pool electrode, Bismuth, Electrode reaction
1. Introduction

Molten salt has high radiation and thermal stability as well as high solubility of actinides, so it is used as a good medium of electrometallurgical processes to recover actinides from spent nuclear fuel in nuclear industry [1]. The electrometallurgical processes based on molten salt are divided into electrolytic reduction of oxides, electrorefining for recovery of uranium, electrowinning for recovery of uranium and transuranic elements, and purification of salt waste. Each process employed a specific electrode to obtain a desired product and efficiency such as solid metal electrode for electrorefining and electrolytic reduction processes, and liquid metal electrode for electrowinning and salt waste purification processes.

The electrode types in electrometallurgical processes can be divided into reactive solid electrode, inert solid electrode, and liquid metal electrode. Using reactive solid electrode, ions are reduced on the electrode and then become intermetallic with electrode. Liquid metal electrodes also allow reductant to be formed intermetallic and reduction potentials of ions to be shifted to more positive value than pure ones. Inert electrode can have similar effect on reduction potentials with supporting ions which are co-reduced with target ions [2]. Due to intermetallic formation between electrode material and actinide elements, the equilibrium potentials of actinides do not show a significant difference, making it difficult to extract alone. Group separation between actinides and lanthanides is preferred in nuclear industry due to proliferation issue. Intermetallic formation of actinides or lanthanides with electrode is potentially beneficial to separate into groups and has been studied with various electrodes, especially, liquid metal electrodes such as Cd, Bi, Al, Ga, Sn, In, and Zn. Decontamination factors of actinides from lanthanides is decreasing in the following order: Al > Ga > Bi > Sn > In > Zn > Cd [3]. Although Al and Ga showed high selectivity, Al has a high melting point and Ga is rather expensive. Bi is, therefore, a good candidate electrode for the electrolytically reductive extraction of dissolved species from molten salt. Although liquid Bi pool electrode has been adopted as an electrode for electrolytically reductive extraction in the development of electrometallurgical process of spent nuclear fuel, the results regarding the electrochemical behavior of the liquid Bi pool in the molten LiCl-KCl eutectic have not been investigated.

When Bi is used as an electrode in the molten LiCl-KCl eutectic, the electrode reaction of Bi ions may affect the electrode reaction of other chemical species. Especially, thermodynamic assessment of Bi-Li exhibits intermetallic compounds of LiBi and Li₂Bi [4] and it is necessary to understand Li-Bi alloy formation for using Bi electrode in molten LiCl-KCl eutectic. However, there is sparse information on electrode reaction of Bi in molten LiCl-KCl eutectic. In the study, an electrochemical behavior of Bi³⁺ ions was investigated on inert solid electrode and liquid Bi pool electrode as working or counter electrode. The paper describes the original data about electrode reactions of liquid Bi pool and Bi³⁺ ions in the molten LiCl-KCl eutectic.

2. Experimental

All storages, preparation, and experiments using all chemicals and electrolytes were performed under an inert argon atmosphere in a glove box. The concentration of oxygen and moisture were kept at 1 ppm or less. All electrochemical tests were performed in an electric furnace using a ceramic heater with a programmable temperature controller. An electrochemical cell was configured with three-electrodes system in a closed-end quartz tube (inner diameter: 11 mm), which was inserted into the electric furnace. The operating temperature was monitored with a K-type thermocouple sheathed with a closed-end Pyrex tube.

A 1-mm diameter W wire (99.95%, Alfa Aesar) was used as working or counter electrode. Liquid Bi metal (99.999%, 1–15 mm beads, Sigma-Aldrich) was also used as working or counter electrode. The reference electrode was fabricated by adding 1 wt% AgCl (99.998%, anhydrous,
Sigma-Aldrich) to LiCl-KCl eutectic (99.99%, 56:44mol%, anhydrous, Sigma-Aldrich) and inserting a 1-mm diameter Ag wire (99.999%, Alfa Aesar) in the mixture within a thin-walled Pyrex tube. All wires were polished with 2000-grit silicon carbide papers and then washed sequentially cleaned with ethanol, acetone, and ultrapure water respectively in an ultrasonic washing machine.

All electrochemical experiments were conducted with three-electrodes system in the high temperature quartz cell using Solatron 1470E. In the experiments, all potentials were referred to the Ag/AgCl (1wt%) reference electrode. The experiments were carried out with two configurations of electrodes for the purpose of characterizing electrochemical behaviors of Bi in LiCl-KCl eutectic. One is that W wire was used as working and counter electrodes. The other is that liquid Bi pool is used as alternative of the electrodes. For the former experiment, the cell shown in Fig. 1 was prepared as follows:

1-1) A LiCl-KCl eutectic salt (99.99%, 56:44mol%, anhydrous, Sigma-Aldrich) was first dried at 523 K for 5 h to remove excess moisture in the salt and then was melted in the closed-end quartz tube inside the electric furnace.

1-2) BiCl₃ (99.99%, anhydrous, Sigma-Aldrich) was weighed and added into the molten LiCl-KCl eutectic. The melt was maintained at 773 K for 3 h and then the electrodes were inserted into the melt.

1-3) Solatron 1470E was connected to the three electrodes of the cell and cyclic voltammetry was carried out with scan rate of 0.05–0.2 V/s in potential window between −2.5 V and 1.5 V.

For the latter experiment, the cell shown in Fig. 2 was prepared as follows:

2-1) Bi beads were inserted into the cell and then melted at higher temperature than melting point to make a liquid Bi pool.

2-2) W wire exposed about 1 mm from the Pyrex tube was inserted so as to be immersed in the liquid Bi pool. W wire plays a role of electric connection to liquid Bi pool and the Pyrex tube plays a role of electric insulation against the molten salt.

2-3) The cell was cooled to room temperature and then the prepared LiCl-KCl or LiCl-KCl+BiCl₃ is poured into the cell.

2-4) The cell temperature was increased to 523 K and was kept for 5 h to remove excess moisture in the salt.

2-5) The cell was kept during 3 h after increasing temperature to 723 K. Visual inspection of the cell is shown in Fig. 2.
Electrochemical experiments were carried out repeating (2-3).

Experiments were carried out with a combination of working electrode (WE) and counter electrode (CE) in an environment with or without BiCl$_3$ in the molten LiCl-KCl eutectic, as follow:

- Case I: WE (solid W wire) vs CE (solid W wire)
- Case II: WE (solid W wire) vs CE (liquid Cd pool)
- Case III: WE (liquid Cd pool) vs CE (solid W wire)

Electrode surface area of liquid Bi pool is approximately 95 mm$^2$. Electrode surface area of W is approximately 48 mm$^2$.

3. Results and Discussion

3.1 Case I: WE (solid W wire) vs CE (solid W wire)

Fig. 3 shows the cyclic voltammograms of LiCl-KCl+BiCl$_3$ (1wt%) on an inert W electrode at 723 K. The scan range of electrode potential is from −2.5 V to +1.5 V. The scan starts from 0 V to −2.5 V, and reversely scans to +1.5 V, and then returns to 0 V. The scan rates vary at 50–200 mV·s$^{-1}$. Cathodic peak A, observed at around −2.49 V, is attributed to the deposition of lithium ion, and the corresponding anodic peak A’ at around −2.33 V is ascribed to the oxidation of lithium. Anodic peak B appearing to the end of positive potential is attributed to the evolution of chlorine gas due to oxidation of chlorine ions. Except of peaks at both sides, two redox couples of R$_1$/O$_1$ and R$_2$/O$_2$ are observed, which are related to the redox reactions of Bi$^{3+}$ ions.

Cathodic peak of R$_1$ at around +0.18 V is attributed to the reduction of Bi$^{3+}$ ions, and the corresponding anodic peak of O$_1$ at around +0.38 V is ascribed to the oxidation of Bi metal. Another redox couple of R$_2$/O$_2$ is related to redox reaction involving Bi$^{3+}$ ions. Its reaction is inferred by co-reduction of Bi$^{3+}$ and other ions in the melt. There are K$^+$ and Li$^+$ ions in the melt that can be co-reduced with Bi$^{3+}$ ions. Co-reduction occurs when the equilibrium potential of each ion is similar. Theoretical electromotive forces of K/KCl and Li/LiCl are 3.805 V (vs Cl$^-$/Cl$_2$) and 3.684 V (vs Cl$^-$/Cl$_2$), respectively, [4]. K$^+$ ions is more active than Li$^+$ ions and co-reduction of K$^+$ and Bi$^{3+}$ may be not possible at the potential region. However, it is possible to reduce Li$^+$ ions by the co-reduction of Li$^+$ and Bi$^{3+}$ ions. The binary phase diagram of Bi-Li shows two intermetallic compounds of LiBi and Li$_3$Bi [4]. A stable intermetallic compound of Li-Bi is Li$_3$Bi because LiBi compound dissociates to Li$_3$Bi plus liquid above ~688 K and is not relevant to the experimental condition of 723 K [6]. Co-reduction of reactive ions, Li$^+$, and non-reactive ions, Bi$^{3+}$, occurs when the equilibrium potentials of two ions are similar. The activity of each component in Bi-Li intermetallic changes dramatically at around 75 at.% Li so that the activity of Li sharply increases to about less than 10$^{-1}$ and the activity of Bi sharply decreases to about 10$^{-4}$ [7]. The activity change of each component allows the equilibrium potential of Li$^+$/Li to shift toward positive direction and the equilibrium potential of Bi$^{3+}$/Bi to shift toward negative direction.

![Fig. 3. Cyclic voltammograms of LiCl-KCl+BiCl$_3$ (1wt%) on an inert W electrode at 723 K. Tungsten wires were used for working and counter electrodes.](image-url)
potential of Bi³⁺/Bi to shift toward negative direction. Considering the degree of the activity change, the equilibrium potential of each ion is expected to be shifted toward the reduction potential of Li⁺ ions. Han et al. showed that the reduction peak on liquid Bi film electrode at 773 K was observed at −1.76 V and was suggested the reduction reaction to be $\text{Li}^+ + e^- \rightarrow \text{LiBi}_x [8]$. The cathodic peak of $R_2$ observed at around −1.8 V, thus, is attributed to intermetallic formation of Li₃Bi by co-reduction of Li⁺ and Bi³⁺ ions. The corresponding anodic peak of $O_2$ at around −1.55 V is related to phase transformation of Li₃Bi to Bi and oxidation of Li to Li⁺ ions. Bi metal remaining on the electrode is oxidized at oxidation potential of $O_1$. As a result, redox reactions of Bi³⁺ ions on the inert solid electrode in molten LiCl-KCl eutectic are as follow:

Redox couple $R_1/O_1$: $\text{Bi}^{3+} + 3e^- \leftrightarrow \text{Bi}$

Redox couple $R_2/O_2$: $\text{Bi}^{3+} + 3\text{Li}^+ + 6e^- \rightarrow \text{Li}_3\text{Bi}$

$$\text{Li}_3\text{Bi} \rightarrow \text{Bi} + 3\text{Li}^+ + 3e^-$$

As shown in Fig. 4, the cathodic peak current of $R_2$ is linearly dependent on the square root of the scan rate and the cathodic peak potential of $R_2$ slightly shifts toward negative value with increasing the scan rate. It indicates that the reduction reaction of $R_2$ on the inert solid electrode is quasi-reversible involving soluble-insoluble species.

3.2 Case II: WE (solid W wire) vs CE (liquid Bi pool)

Fig. 5 shows the cyclic voltammograms of LiCl-KCl+BiCl₃ (1 wt%) on W electrode against counter electrode of liquid Bi pool at 723 K with different scan rates from 50 mV·s⁻¹ to 200 mV·s⁻¹. Comparing with Fig. 3, liquid Bi pool as counter electrode has no effect on redox couples of $R_1/O_1$ and $R_2/O_2$, while redox couple of $A'/A'$ has different behavior. Anodic reaction of $A'$ is almost disappeared except scan rate of 50 mV·s⁻¹ and another anodic reaction of
A" is appeared. Cathodic reaction of A is also distorted and starts early at the positively shifted potential. It is investigated with comparing the voltammograms of LiCl-KCl (solid black line) and LiCl-KCl+BiCl$_3$ (1wt%) (solid blue line) on W electrode against counter electrode of liquid Bi pool and LiCl-KCl+BiCl$_3$ (1wt%) (dashed red line) on W electrode against counter electrode of solid W wire, as shown in Fig. 6.

Even though liquid Bi pool is used as counter electrode of three-electrodes system in the molten LiCl-KCl eutectic, there are no reaction except redox reaction involving Li$^+$ ions and reaction of chlorine evolution without adding BiCl$_3$. The voltammogram (solid blue line) obtained with adding BiCl$_3$ exhibits two redox reactions involving Bi$^{3+}$ ions, which are analogous to that (dashed red line) against counter electrode of solid W wire, but the signal of redox couple of Li$^+$ ions are distorted. The reduction of Li$^+$ ions after cathodic signal of R$_2$ for intermetallic formation of Li$_3$Bi starts at more positive value than on solid W electrode and exhibits crossover, which occurs because the formation of stable lithium nuclei on electrode surface covered with Li$_3$Bi requires a more negative potential than the deposition of lithium on a lithium surface [9]. When the scan direction is reversed for detecting oxidation reaction, potential shift toward positive direction is observed for oxidation reaction of Li (anodic signal of A")).

It is noted that the potential scan for detecting reduction reaction allows Bi$^{3+}$ ions to be continuously supplied by the oxidation of Bi in counter electrode of liquid Bi pool corresponding to the reduction reaction. As Bi$^{3+}$ ions are sufficient in the melt, Bi$^{3+}$ and Li$^+$ ions are presumed to be continuously co-reduced after Li$_3$Bi formation of R$_2$, which is appeared as reduction signal of A1. The electrode surface plays a role of liquid Bi electrode in the potentials lower than about $-2$ V and the reduction of Li$^+$ ions resulted in the almost linear increase of the reduction current due to the increase in activity of Li in Li-Bi alloy. Electrode surface is covered with Li-rich Li-Bi alloy during reduction signal. Oxidation signal of A" corresponds to oxidation of excess Li without forming Li$_3$Bi in Li-Bi alloy. After consuming excess Li in Li-Bi alloy, oxidation of Li$_3$Bi begins, corresponding to oxidation peak of O$_2$. Oxidation reactions are distinguished according to the state of lithium as follows:

Oxidation reaction of A":

$$\text{Li} (\text{Li} + \text{Li}_3\text{Bi}) \rightarrow \text{Li}^+ + e^- + \text{Li}_3\text{Bi}$$

Oxidation reaction of O$_2$:

$$\text{Li} (\text{Li}_3\text{Bi}) \rightarrow \text{Li}^+ + e^- + \text{Bi}$$

The activity of Li is abruptly changed at 75mol% Li in Li-Bi alloy [7] and resulted in different oxidation signals. The oxidation signal of A" exhibits that the excess Li without forming Li$_3$Bi intermetallic exists as Li-Bi alloy on the electrode surface. Liquid Bi pool as counter electrode, therefore, only affects the reduction/oxidation behavior of Li$^+$ ions on solid W electrode and has little effect on other redox reactions.

3.3 Case III: WE (liquid Bi pool) vs CE (solid W wire)

Fig. 7 shows the cyclic voltammogram of LiCl-KCl...
on liquid Bi pool electrode at 723 K. Counter electrode is solid W wire. In 1\textsuperscript{st} cycle of the voltammogram, very small amount of anodic current is observed from 0 V to about −1.06 V and then cathodic current is rapidly increased to −2.5 V. Even though potential scan is reversed at −2.5 V, cathodic reaction occurs continuously until about −1.5 V. 2\textsuperscript{nd} and 3\textsuperscript{rd} cycles exhibit similar behavior except initial oxidation reaction. The cathodic reaction of D at potential lower than −1.06 V is considered to reduce Li\textsuperscript{+} ions on liquid Bi pool due to the decrease in activity of Li in liquid Bi pool, and the corresponding anodic reaction of D’ is ascribed to oxidation of Li from Li-Bi alloy. There is not any cathodic peak that can specify the intermetallic formation of Bi-Li. Another cathodic peak of C is observed at approximately −0.1 V and is ascribed to reduction of Bi\textsuperscript{3+} ions, while redox couple of Bi\textsuperscript{3+}/Bi on solid W electrode is observed at cathodic/anodic peaks of +0.14/+0.38 V, as shown in Fig. 3. Liquid Bi pool electrode shifts the reduction peak potential of Bi\textsuperscript{3+} ions toward the lower potential, resulting from complex phenomena of the increase in activity of Bi in the electrode and decrease mole fraction of Bi\textsuperscript{3+} ions near the electrode until limiting current condition. Therefore, the reduction and oxidation reactions corresponding to the signal of the voltammetry are expressed as follow:

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\text{Reduction signal of C: } \text{Bi}^{3+} + 3e^- \rightarrow \text{Bi (in Li,Bi)} \\
\text{Oxidation signal of C’: } \text{Bi} \rightarrow \text{Bi}^{3+} + 3e^- \\
\text{Reduction signal of D: } \text{Li}^+ + e^- \rightarrow \text{Li (in Li,Bi)} \\
\text{Oxidation signal of D’: } \text{Li (in Li,Bi)} \rightarrow \text{Li}^+ + e^- 
\]

Fig. 8 shows the cyclic voltammogram of LiCl-KCl on liquid Bi pool electrode at 723 K with different scan rates from 50 mV·s\textsuperscript{−1} to 200 mV·s\textsuperscript{−1}. The shape of the voltammogram is not greatly changed. As the scan rate increases, the anodic peak currents of D’ decrease and cathodic current of C tends to rapidly decrease after reaching the peak. For oxidation signal of D’, it is inferred that the increase of the scan rate causes the lithium content on the electrode surface to be diminished faster than supplied by diffusion from the bulk of Bi pool and allows the limiting current condition to be easily reached. As a result, anodic peak potentials of D’ shift toward negative values and anodic peak currents tend to decrease.

Fig. 9 shows the cyclic voltammogram of LiCl-KCl+BiCl\textsubscript{3} (1 wt\%) on liquid Bi pool electrode at 723 K. The overall shape of the voltammogram is analogous to Fig. 7.
besides of starting interval of 1st cycle. A large amount of cathodic current of C is observed in the 1st cycle but cathodic current of C decreases with increasing number of cycles. Cathodic current of C decreases sharply after reaching cathodic current peak. It is presumed that the cathodic peak potential is more negatively biased due to the greater amount of Bi$^{3+}$ ions in LiCl-KCl+BiCl$_3$ than LiCl-KCl, and cathodic current after passing through the peak potential decreases sharply due to the limitation of diffusion.

Fig. 10 shows the cyclic voltammogram of LiCl-KCl+BiCl$_3$ (1wt%) on liquid Bi pool electrode at 723 K with different scan rates from 50 mV·s$^{-1}$ to 200 mV·s$^{-1}$. The overall trend of the voltammogram of Fig. 10 is analogous to Fig. 8. However, comparing two voltammograms as shown in Fig. 11, the current profile with adding BiCl$_3$ is thicker than that without adding BiCl$_3$.

4. Conclusions

Electrochemical behaviors of Bi$^{3+}$ ions and liquid Bi pool electrode in the molten LiCl-KCl eutectic were investigated with cyclic voltammetry at 723 K. Two redox reactions involving with Bi$^{3+}$ ions in the molten LiCl-KCl eutectic were observed on the inert solid electrode, regardless of the type of counter electrodes. One is the reduction of only Bi$^{3+}$ ions at cathodic peak potential of approximately +0.18 V and the other is the co-reduction of Bi$^{3+}$ and Li$^+$ ions at cathodic peak potential of approximately −1.8 V and intermetallic formation of Bi-Li, which is Li$_3$Bi identified in the binary phase diagram of Bi-Li. Liquid Bi pool electrode, however, exhibits reduction of Li$^+$ ions due to the
decrease in the activity of Li in liquid Bi pool, regardless of Bi\textsuperscript{3+} ions in the molten LiCl-KCl eutectic. Reduction of Bi\textsuperscript{3+} ions is affected on the dissolved Li in liquid Bi pool and cathodic peak potential of Bi\textsuperscript{3+} ions on liquid Bi pool shifts more negative value than on inert solid electrode. Experimental results show that the use of Bi, which is relatively non-reactive in the molten LiCl-KCl eutectic, has the potential to extract Li\textsuperscript{+} ions from the molten LiCl-KCl eutectic by co-reduction on inert solid electrode and reduction on liquid Bi pool due to the reduced activity in intermetallic formation of Bi-Li.

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