

Electrochemical Behavior of Er Ion and Bi Ion in LiCl-KCl Molten Salt

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1. Introduction

The pyro separation process using molten salts is one of the most promising options for extracting lanthanides (Lns) and actinides from the fission products. The pyro separation process using chlorides or fluorides as solvent, having some advantageous properties, such as high level radiation resistances of the process, are considered as a promising technique for the resolution of the problem of actinide and fission product partitioning. The most developed pyroprocess techniques include electrorefining, electroextraction with reactive cathodes, liquid-liquid metal reductive extraction. The electrochemical extraction of lanthanides was investigated in molten chlorides using reactive working electrode, Bismuth electrode.[1-3]

Since there are many advantages (No change of the electrode surface, easier aggregation and moving) using liquid metal as working electrode, the electrochemical extracting Lns on liquid bismuth electrode from molten salts have a strong point for pyrochemical reprocessing of spent nuclear fuels. For liquid Bi as cathodic material, the electrochemical behavior of Ln(III) La, Ce and Pr was studied in the LiCl-KCl system. However, the concentration changes of Erbium ions in the melts of electrochemical extraction process was not explored on liquid Bi electrode.

This study is to establish therefore, we focused on the electrochemical behavior of Bismuth ions and Erbium ions. The technique is applied to investigate electrode reactions of erbium ion and Bismuth ion in the molten salt LiCl-KCl. Finally, we analyze the effect of Bi ion concentration on the electrochemical reduction of Er.

2. Experimental

Electrochemical tests were conducted in a glove box and the electrochemical cell was set up inside a steel furnace connected under the glove box. The cell was fabricated to accommodate both working electrode(tungsten wire), counter electrode(tungsten wire), reference electrode(silver wire) and

thermocouple. All the electrodes and chlorides were contained in a quartz cell. The electrochemical measuring instrument was Versa State from Princeton Applied Research Inc. and the software used was Versa studio. The electrochemical methods involved were cyclic voltammetry, square wave voltammetry, and open circuit chrono-potentiometry.

3. Results and Discussion

As a first result, the behavior of Er was confirmed by electrochemical measurement of Cyclic Voltammetry. At a temperature of 773K, the standard potential of Er is about -2.05V. The results confirm the current and potential through various scan rates. The Value of the potential and Current are shown in Table 1.

The cyclic voltammogram of LiCl-KCl+ErCl₃(1wt%) at 773 K showed a single redox peak corresponding to the Er³⁺/Er couple under potential window between -2.3V and -1.5V (vs. Ag/AgCl reference electrode). Analysis of voltammogram exhibited that a formal standard potential of Er³⁺/Er redox couple was obtained to -1.8V/-2.03V (vs. reference electrode). As a result of adding BiCl₃(1wt%), various intermetallic compounds redox peaks were observed in Fig. 2.

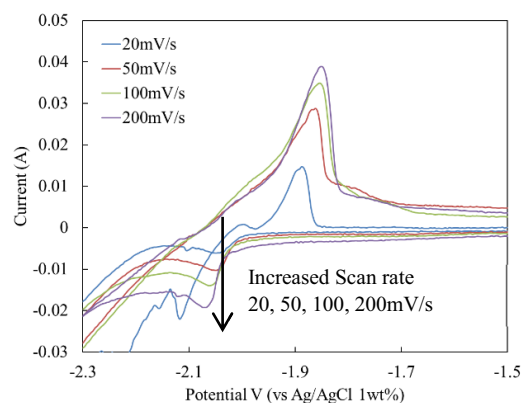


Fig. 1. Cyclic voltammogram obtained for Er³⁺ in LiCl-KCl melt using the tungsten electrode (A=0.332 cm²) at 773K, 1wt%, scan rate: 20, 50, 100, 200mV/s.

Table 1. The Value of the Potential and Current at 773K

Scan Rate	Reaction	Potential(V)	Current(A)
20mV/s	$\text{Er} \rightarrow \text{Er}^{3+} + 3\text{e}^-$	-1.88	0.014
	$\text{Er}^{3+} + 3\text{e}^- \rightarrow \text{Er}$	-2.03	-0.007
50mV/s	$\text{Er} \rightarrow \text{Er}^{3+} + 3\text{e}^-$	-1.86	0.028
	$\text{Er}^{3+} + 3\text{e}^- \rightarrow \text{Er}$	-2.04	-0.01
100mV/s	$\text{Er} \rightarrow \text{Er}^{3+} + 3\text{e}^-$	-1.84	0.033
	$\text{Er}^{3+} + 3\text{e}^- \rightarrow \text{Er}$	-2.06	-0.014
200mV/s	$\text{Er} \rightarrow \text{Er}^{3+} + 3\text{e}^-$	-1.84	0.038
	$\text{Er}^{3+} + 3\text{e}^- \rightarrow \text{Er}$	-2.07	-0.019

The -1.8/-2.0V are the redox peak of Er and 0.3/0.5V is the peak of Bi metal. Except the B peak in the CV shown, the R1/O1, R2/O2 and R3/O3 are an intermetallic compounds and it can be seen that was also confirmed at the peak of oxidation-reduction behavior. According to the Phase Diagram, five intermetallic compounds Bi₂Er and BiEr are observed in the Er-Bi system at 773K. [4]

But we various Lu-Bi intermetallic compounds were formed in LiCl-KCl and the corresponding potentials were observed using CV. We applied Semi-Reduction Cyclic Voltammogram (concentration of Bi/Er ratio 0.7) to software Fityk 0.9.8 and searched for reduction peaks. The reduction peak of R₃/O₃ was not observed at Bi/Er molar ratio 0.7, but it was confirmed at Bi/Er molar ratio 1.14.

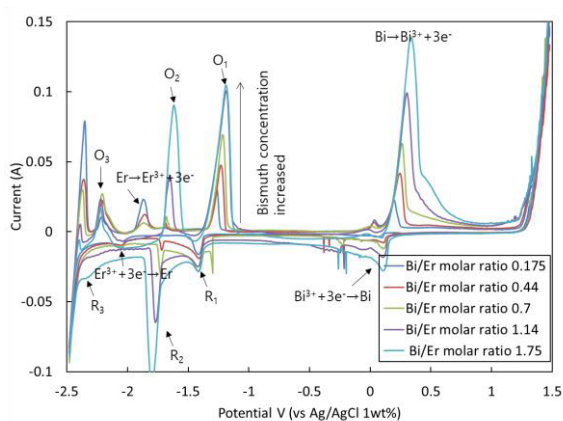


Fig. 2. Cyclic voltammogram obtained for ErCl₃(1wt%) add BiCl₃(0~2wt%) in LiCl-KCl melt using the tungsten electrode (A=0.332 cm²) at 773K, Scan Rate 0.1V/s.

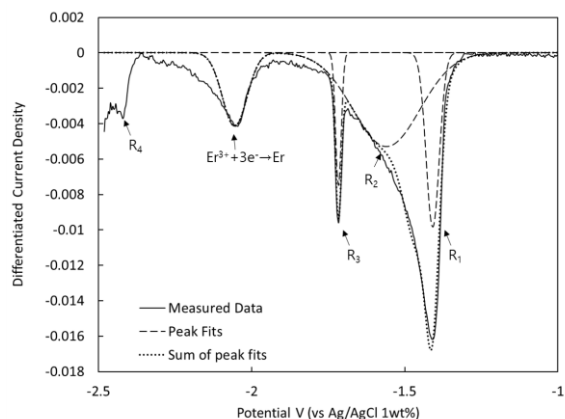


Fig. 3. Fitting of semi-differentiated cyclic voltammograms curve for reduction potential of concentration Bi/Er molar ratio 0.44.

4. Conclusion

The electrochemical behavior of bismuth ion and erbium ion was carried out by CV, and various intermetallic compound were confirmed. The -2.4V(O₃/R₃) redox potential is expected to be an unidentified IMC and will be closely monitored.

REFERENCES

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