

## An Electrochemical Study of Lanthanide Elements in LiCl-KCl Eutectic Molten Salt to Convert All The Spent Nuclear Fuel into Low and Intermediate Level Waste

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### 1. Introduction

Pyrochemical process is one of the key technologies to recover actinide elements and long-lived fission products from the spent nuclear fuel for the reduction of radioactive waste toxicity. An additional unit step for the residual actinide recovery, designated as "Pyro-RedSox (Pyrochemical Reduction and Selective Oxidation)", was proposed to convert all the spent nuclear waste into low and intermediate level waste by achieving high decontamination factor (DF) for TRU elements [1]. The measurement of basic material properties of lanthanide elements in LiCl-KCl eutectic molten salt is necessary to evaluate the performance of the step. Thus, standard potential, activity coefficient, and diffusion coefficient of lanthanide elements is being tried to determine using conventional electrochemical methods.

### 2. An Electrochemical Study of Lanthanide Elements in LiCl-KCl eutectic salt

#### 2.1 Pyro-RedSox Step for Residual Actinide Recovery

After electrorefining and electrowinning step to recover actinide elements, residual actinide elements and unrecovered elements are remained in the molten salt. As the first stage of Pyro-RedSox step, both actinide and rare earth elements are reduced into liquid metal (Cd or Bi) by applying controlled current or potential. And only rare earth elements can be selectively oxidized(chlorinized) into molten salt by adding oxidant ( $\text{CdCl}_2$  or  $\text{BiCl}_3$ ). The co-extraction of actinide elements into molten salt is prevented by controlling the oxidant amount [1].

#### 2.2 Experimental

Preparation of reagents and main experiment was carried out in a glove box under the inert atmosphere (concentration of both  $\text{O}_2$  and  $\text{H}_2\text{O}$  < 1 ppm). LiCl-KCl eutectic molten salt (59 mol% LiCl, anhydrous, >99.99% purity) was procured from Sigma Aldrich, melted at about  $600^\circ\text{C}$  for over 1 day to remove adsorbed oxygen and moisture. Lanthanide chlorides are also procured from Sigma Aldrich, and prepared as mixture with LiCl-KCl salt before the experiment.

For the electrochemical measurement, tungsten wire (Sigma Aldrich,  $D=1\text{mm}$ , >99.99% purity) was applied as working and counter electrode. as a reference electrode, a silver wire was immersed into a pyrex tube containing LiCl-KCl-AgCl(1wt%) mixture. A quartz tube (ID = 11mm) was carefully cleaned and dried for the experimental cell.

#### 2.3 Results and Discussion

##### 2.3.1 Cyclic Voltammetry Measurement of Samarium

Cyclic voltammetry was measured for LiCl-KCl-SmCl<sub>3</sub>(1 wt%, 0.039 mol/kg) mixture at  $500^\circ\text{C}$  as shown in Fig. 1. The perforated line is the cyclic voltammogram of LiCl-KCl only and the solid line is the cyclic voltammogram of LiCl-KCl-SmCl<sub>3</sub> mixture. From the measurement for LiCl-KCl salt, electroactivity domain, which is positively limited by the  $\text{Cl}^-/\text{Cl}_2$  oxidation and negatively limited by the  $\text{Li}^+/\text{Li}$  reduction, was determined as 3.51 V.

The wave of the cyclic voltammogram for LiCl-KCl-SmCl<sub>3</sub> mixture is characteristic of a soluble-soluble system related to  $\text{Sm}^{3+}/\text{Sm}^{2+}$  redox couple [2]. The peak potentials are approximately -0.86 V (cathodic) and -0.70 V (anodic) versus

Ag/AgCl reference electrode, respectively.

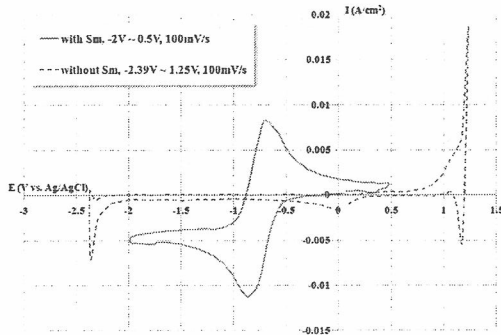


Fig. 1. Cyclic voltammogram for the reduction of samarium trivalent ion (1wt%, 0.039 mol/kg) on a tungsten electrode (S=0.45cm<sup>2</sup>) in LiCl-KCl eutectic salt with scan rate of 100 mV/sec at 773K.

### 2.3.2 Standard potential of the redox couple Sm<sup>3+</sup>/Sm<sup>2+</sup> and activity coefficient, diffusion coefficient of samarium

The standard potential of the Sm<sup>3+</sup>/Sm<sup>2+</sup> redox system was determined from cathodic and anodic peak potential. The determined standard potential was about -1.97 V versus Cl<sub>2</sub>/Cl<sup>-</sup>. The difference between the data of this study and reference data was about 0.3 V versus Cl<sub>2</sub>/Cl<sup>-</sup> at 773K as shown in Table 1.

Table 1. Standard potential of the Sm<sup>3+</sup>/Sm<sup>2+</sup> redox system in LiCl-KCl

	T(K)	E <sup>0</sup> (V vs. Ag/AgCl)	E <sup>0</sup> (V vs. Cl <sub>2</sub> /Cl <sup>-</sup> )
This study	773	-0.78	-1.97
Reference [3]	773	-0.97	-2.00
	823	-0.95	-1.98

The activity coefficient of samarium was also determined from the cathodic peak potential compared with reference data as shown in Table 2. The determined data was agreed well with reference.

Table 2. Activity coefficient of samarium in LiCl-KCl salt using the redox standard potential

	T(K)	10 <sup>4</sup> ×γ
This study	773	5.79
Reference [3]	773	3.58
	823	4.49

The diffusion coefficient of samarium trivalent ion in LiCl-KCl was determined from the peak current data of cyclic voltammogram using Randles-Sevcick equation.[2]. The determined data was well-agreed with reference data as shown in Table 3.

Table 3. Diffusion coefficient of samarium trivalent ion in LiCl-KCl calculated from the peak current data

	T(K)	× 10 <sup>5</sup> cm <sup>2</sup> /s
This study	773	1.08
Reference [3]	723	0.76
	773	1.30

### 3. Conclusion

The cyclic voltammetry was measured for LiCl-KCl-SmCl<sub>3</sub> mixture and the standard potential, activity coefficient, and diffusion coefficient of this system was determined from the voltammogram data. The calculated data was well-agreed with reference. Based on this results, another techniques for other lanthanide elements will be applied for better understanding of LiCl-KCl-LnCl<sub>n</sub> system.

### 4. Acknowledgement

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### 5. References

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