Technical Note

Cesium and strontium recovery from LiCl-KCl eutectic salt using electrolysis with liquid cathode

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ABSTRACT

Deposition behaviors of Sr and Cs in various liquid cathodes, such as Zn, Bi, Cd, and Pb, were examined to evaluate their recovery from LiCl—KCl eutectic salt. Cations in the salt were deposited on the liquid cathode, exhibiting potential of −1.8 to −2.1 V (vs. Ag/AgCl). Zn cathode had successful deposition of Sr and exhibited the highest recovery efficiency, up to 55%. Meanwhile, the other liquid cathodes showed low current efficiencies, below 18%, indicating LiCl—KCl salt decomposition. Sr was recovered from the Zn cathode as irregular rectangular $SrZn_{13}$ particles. A negligible amount of Cs was deposited on the entire liquid cathode, indicating that Cs was hardly deposited on liquid cathodes. Based on these results, we propose that liquid Zn cathode can be used for cleaning Sr in LiCl—KCl salt.

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1. Introduction

Pyroprocessing is one of the most attractive technologies for recycling used nuclear fuels from power plants, as spent nuclear fuel retains over 95% of its U and transuranic elements (TRU) [1,2]. During this process, spent fuel is dissolved in a molten LiCl—KCl eutectic salt via electrolysis and U and TRU are deposited onto the cathode [3—8]. Simultaneously, various radioactive fission products contained in the spent fuel dissolve in the molten salt.

Table 1 lists the fundamental properties of these dissolved radioactive fission products, of which Sr, Cs, and Te exhibit the highest radioactivity. The flowsheet shows that contents of the fission product, such as Te, are considered negligible, while considerable amounts of Sr and Cs accumulate in the salt during the process [9]. For example, approximately 1 kg of Sr and Cs can move to the molten salt after treatment of 10 tons of spent fuels. Thus, its accumulation in salt makes this process hazardous.

Chemical oxidation using oxidants, such as carbonate and phosphate, has been considered for the removal of radioactive materials from molten salts [10,11]; however, such chemical methods inevitably produce fine particles after reactions and require a subsequent particle collection process. Electrochemical deposition of Cs has also been considered for removal using conventional solid electrodes; however, the deposition of Cs^+ ions is hardly involved in the cathode reaction because of the low reduction potential (Table 1), and Li is dominant in the cathode [12].

Liquid cathodes have been used for the group recovery of U, TRU, and rare earth elements (RE) in nonproliferation pyroprocessing [8,13,14]. The liquid cathode co-deposits abundant fission products along with U and TRU, positively shifting the reduction potential due to the activity coefficient of the liquid metals, which differ from solid cathodes, such as stainless steel, tungsten, and graphite. This suggests that Sr and Cs can be deposited onto a liquid cathode [15—17], and that there is great need to study Sr and Cs removal from molten LiCl—KCl with liquid cathodes.

This study was aimed to examine the deposition behavior of Sr and Cs in various liquid cathodes. Table 2 lists the fundamental properties of potential liquid cathode candidates, such as Zn, Bi, Cd, and Pb. These metals possess lower melting temperatures than the operation temperature of 500 °C, and higher densities than that of LiCl—KCl salt (~1.6 g/cm^3), allowing them to settle down in the crucible. Simultaneously, these liquid metals can be distilled in a vacuum at approximately 1200 °C to separate the Sr and Cs from the liquid cathode for recycling. Zn, Bi, and Cd can evaporate under

Table 1
Fundamental properties of radioactive fission product.

Elements	Melting Temperature [°C]	Activity[a] [Bq/g]	Standard Potential at 500 °C [V vs. Ag/AgCl]
Sr	769	3.055E+16	$Sr^{2+} + 2e^{-} = Sr$ ($E_0 = -3.035$ V)
Cs	28.4	4.361E+14	$Cs^{+} + e^{-} = Cs$ ($E_0 = -3.701$ V)
Ba	725	9.108E+09	$Ba^{2+} + 2e^{-} = Ba$ ($E_0 = -3.066$ V)
Se	217	5.982E+09	$Se + 2e^{-} = Se^{2-}$ ($E_0 = -1.432$ V)
Te	449.5	2.478E+11	$Te + 2e^{-} = Te^{2-}$ ($E_0 = -1.881$ V)

[a] All isotopes in used nuclear fuels were considered.

Table 2
Fundamental properties of possible candidates for liquid cathode materials.

Elements	Melting Temp. [°C]	Boiling Temp. [°C]	Density [g/cm³]
Pb	327.5	1740	11.34
Zn	419.6	907	7.14
Bi	271.3	1560	9.8
Cd	320.9	765	8.64

these conditions, leaving behind only Sr or Cs (Bi possesses high boiling temperature above 1500 °C, but evaporates around 730 °C in a vacuum [18]). Because Pb successfully deposits Sr [19], it was used for comparison. LiCl–KCl–$SrCl_2$ and LiCl–KCl–CsCl salt mixtures were prepared at 500 °C, and Sr or Cs were electrochemically deposited into a liquid cathode by a constant 100 mA current (approximately 20 mA/cm²). The anode and cathode potentials were monitored during the deposition, and cathode products were characterized after deposition. Possible cathode materials for the recovery of Sr and Cs are discussed in detail based on the experimental results.

2. Methods and materials

LiCl–KCl eutectic salt (Alfa Aesar, A Johnson Matthey Company, purity >99.9%) was dried at 300 °C in a vacuum before use, and $SrCl_2$ (Sigma-Aldrich Co. LLC., powder, purity >99.99%) or CsCl (Sigma-Aldrich Co. LLC., beads, purity >99.999%) were dissolved in the molten LiCl–KCl salt for electrochemical deposition. Pb (Sigma-Aldrich Co. LLC., shot, purity >99.9%), Zn (Sigma-Aldrich Co. LLC., shot, purity >99.9%), Bi (Sigma-Aldrich Co. LLC., beads, purity >99.999%), and Cd (Alfa Aesar, A Johnson Matthey Company, ingot, purity >99.999%)) were used as liquid cathodes.

Cell configuration is depicted in Fig. 1. Approximately 10 g of $SrCl_2$ or CsCl and approximately 110 g of LiCl–KCl were loaded into an alumina crucible (diameter: 70 mm, height: 55 mm). The crucible was heated up to 500 °C at a rate of 6 °C/min; for complete melting, the temperature was maintained for more than 2 h. Pb (~42 g), Te (~25 g), Zn (~28 g), Bi (~36 g), and Cd (~35 g) were loaded in an alumina crucible (inner diameter: 25 mm, height: 25 mm) and immersed in the molten salt mixture. A W wire (diameter: 1 mm; Nilaco Corp., Japan) and glassy carbon rod (diameter: 3 mm, Alfa Aesar, USA) were immersed in the molten metal and salt, respectively, and they were used as the working and counter electrodes. A Ag wire inserted into LiCl–KCl-1 mol% AgCl loaded in a Pyrex tube was used as the reference electrode. A constant current (galvanostatic) of 100 mA (~20 mA/cm², inner diameter of a crucible was considered as a surface area of liquid cathodes) was applied to the cathode for approximately 4 h, and two consecutive runs were performed (approximately 800 mAh of total charge passed). The resultant voltages in the anode and cathode were monitored during the deposition (chronopotentiometry). The entire electrochemical test was performed in a glove box filled with Ar gas (<1 ppm H_2O, < 10 ppm O_2).

The liquid metal compositions after electrochemical test were analyzed via inductively coupled plasma-mass spectrometry (ICP-MS) (iCAP Qc, Thermo Fisher Scientific, USA). The uncertainty of the ICP-MS measurements ranged from 1 to 10%, depending on the element. Morphologies and chemical compositions were observed using scanning electron microscopy (SEM) (S-8010, Hitachi Ltd., Japan) in conjunction with energy-dispersive X-ray spectroscopy (EDS) (EX-250 X-max, Horiba Ltd., Japan). The fundamental properties and standard potentials of the metals were calculated using HSC Chemistry (v. 9.3, 2018) (Outotec Oyj, Finland) [20].

3. Results and discussion

3.1. Electrochemical deposition of Sr or Cs into liquid metal

Zn, Bi, Cd, and Pb, which possessed lower melting temperatures than the test temperature of 500 °C and higher densities than that of the molten LiCl–KCl salt, were used as liquid cathode materials. Fig. 2 shows the anode and cathode potentials as a function of time during the Cs and Sr deposition tests in the liquid Zn cathode. Approximately 100 mA (approximately 20 mA/cm²) of constant current was applied, passing ~800 mAh of charge during deposition. This charge theoretically correspond to approximately 3.97 and 1.31 g of the Cs and Sr, respectively. All liquid cathodes showed similar trends in the potential changes as those in when Cs deposited on liquid Zn as shown in Fig. 2(a); i.e., the cathode potentials decreased with the deposition time from approximately −1.8 to −2.1 V. As all of the cations (Li^+, K^+, Cs^+, and Sr^{2+}) in the salts had lower reduction potentials than −3.0 V, the decrease of the potentials indicate that deposition into the liquid cathode had occurred. The potential changes in the Zn cathode deposited with Sr were differed slightly (Fig. 2(b)); the cathode potential suddenly decreased below −2.0 V during the deposition and became stable after 250 min of deposition. The reason for this sudden change is not yet understood; however, we speculate that metals deposited on the surface of Zn acted as a solid cathode. The anode potential was above 1.7 V in all tests, indicating Cl_2 gas production.

3.2. Characterization of cathode products

Fig. 3(a) shows the Pb morphology after the Sr deposition test, which maintained the well-known button shape of the metallic ingot. All cathode metals had nearly identical shapes as that of Pb after the deposition of both Sr and Cs, only except for the Zn cathode after Sr deposition. Zn had a slightly rugged surface after the deposition test, as shown in Fig. 3(b). The different morphologies of the Zn cathode were attributed to the amount of Sr dissolved in the Zn cathode, as described below.

The Cs and Sr contents in cathode products were characterized by ICP-MS after the deposition test and are listed in Table 3. The recovery current efficiency was calculated based on a ratio of the weight of deposited elements to the theoretical weight. The weight of the deposited target element was obtained from the contents (in Table 3) and the amount of the loaded liquid cathode. The theoretical weight was calculated from the amount of current passed
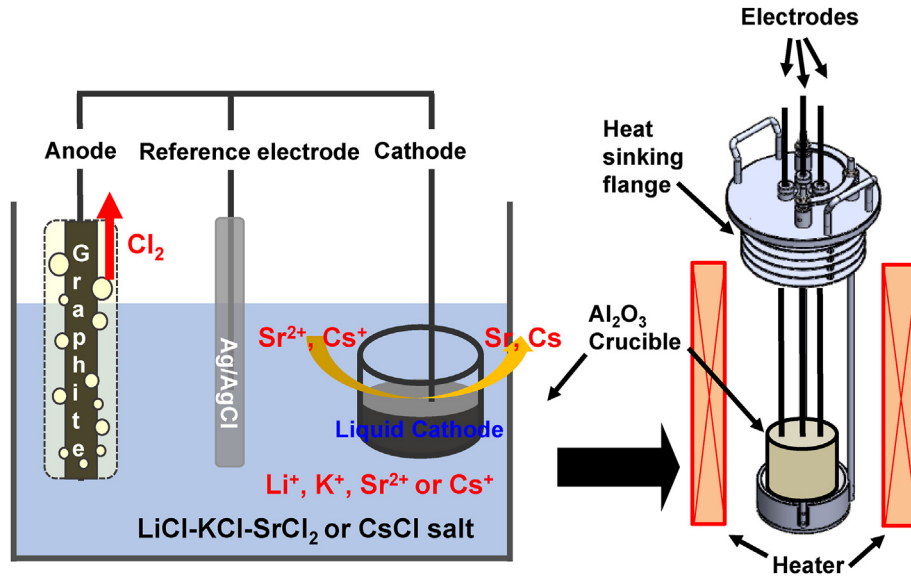
Fig. 1. A schematic for cell configuration and experimental apparatus.
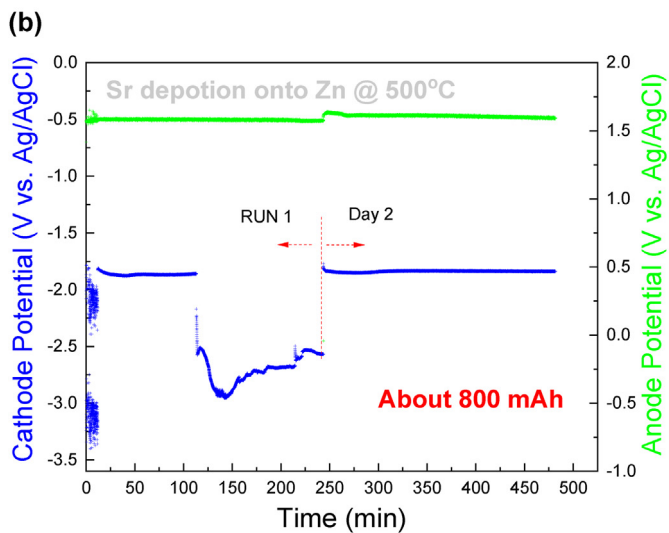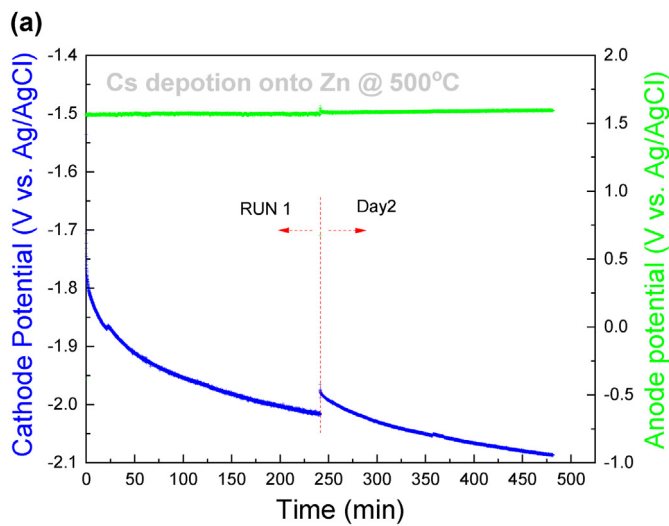

Fig. 2. Anode and cathode potentials as a function of time during the deposition of (a) Cs and (b) Sr into the liquid Zn cathode.
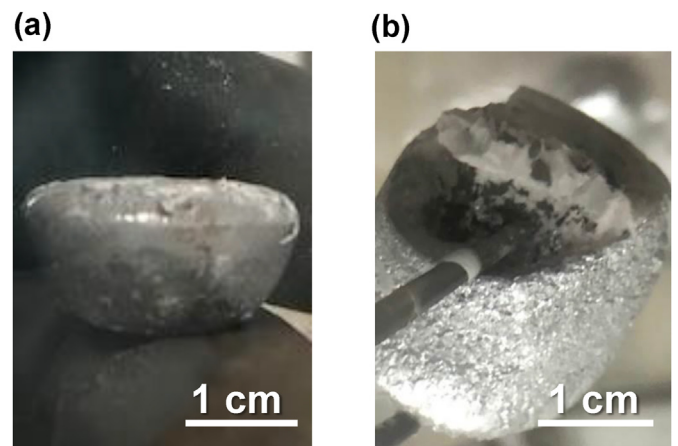

Fig. 3. Morphologies of the liquid (a) Pb and (b) Zn after Sr deposition test.

during deposition (~800 mAh). According to these calculations, both Sr and Cs were deposited onto the liquid cathode. The deposited quantity of Sr was more on the Zn and Bi cathodes than that on the Pb cathode. The Zn cathode exhibited the highest recovery, reaching a current efficiency of 55%. We consider that the depositions of Li and K (decomposition of LiCl−KCl salts (Eq. (1)) were attributed to the decrease in current efficiency.

$$(Li, K){-}Cl_{(in\ salt)} \rightarrow Li_{(in\ liquid\ cathode)} + K_{(in\ liquid\ cathode)} + 1/2Cl_{2(gas)}, \qquad (1)$$
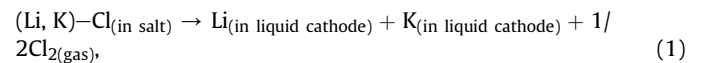
The other liquid cathodes showed a current efficiency below 18%, indicating that the salt decompositions were more favorable. The Bi cathode revealed a current efficiency of 18%, which was slightly lower than 29% obtained by Lichtenstein and coworkers [16].

In the case of Cs, a negligible amount of Cs was deposited over the entire liquid cathode. The Bi cathode exhibited the highest Cs content, but the extent was low, at 0.12 wt%. The current efficiency was calculated as low as 1.1%. Because the boiling temperature of Cs is low, at 671 °C [20], some Cs may have possibly evaporated during

Table 3
Contents of Cs or Sr in cathode products.

Elements	Pb		Zn		Bi		Cd	
	Content [wt%]	Efficiency [%]	Content [wt%]	Efficiency [%]	Content [wt%]	Efficiency [%]	Content [wt%]	Efficiency [%]
Sr	0.31	10.2	2.4	55.2	0.64	18.0	0.12	3.23
Cs	0.022	0.24	0.0072	0.052	0.12	1.11	0.011	0.098

Table 4
Contents of Cs in the Bi cathode after the deposition at 400, 450, and 500 °C.

Elements	400 °C	450 °C	500 °C
	[wt%]		
Cs	0.16	0.13	0.12

the deposition test; thus, we examined the effect of deposition temperature on Cs deposition in the Bi cathode. The Cs contents in the Bi cathode after the 400, 450, and 500 °C depositions are listed in Table 4. The extent of Cs was very low regardless of the temperature, but it decreased slightly as the temperature increased. These results confirm that Cs was hardly deposited on liquid cathodes, and the decomposition of LiCl−KCl was favorable. These results were well consistent with the previous work reported by Woods and Phongikaroon [17], and revealed that Cs was difficult to recover using the electrochemical method.

Cathode products obtained after the deposition test were cut

and sampled for SEM observations in an Ar glove box. Fig. 4 shows microscopic morphologies of the Zn cathode after Sr deposition. Fine particles with an irregular rectangular shape precipitated in the Zn matrix (Fig. 4(a)). These particles were considered $SrZn_{13}$ from the SEM-EDS (Fig. 4(b)), which showed 92.9% Zn and 7.1% Sr. Sr dissolved in the liquid Zn at an operating temperature of 500 °C and then precipitated as $SrZn_{13}$ during cooling. We believe that the unstable potential at the cathode (Fig. 2(b)) was attributed to precipitated $SrZn_{13}$ during deposition.

Fig. 5 shows the microscopic morphology of the Bi cathode after Cs deposition. Granular particles were formed, but no Cs was detected by SEM-EDS. Because SEM-EDS cannot observe Li, only K was detected along with Bi (not shown here). The results confirmed that the decomposition of LiCl−KCl occurred rather than Cs deposition.

These results revealed that Sr could be recovered from LiCl−KCl molten salt using a liquid cathode and that Zn was a suitable element to use for the cathode, with a >50% current efficiency. However, selectively recovering Cs from the molten salt using an electrochemical method is difficult, as it encourages salt decomposition.

4. Conclusions

We examined the deposition behaviors of Sr and Cs in various liquid cathodes, with Zn, Bi, Cd, and Pb chosen as possible liquid cathode materials. The following results were obtained:

Potential of cathode decreased with the deposition time from −1.8 to −2.1 V, indicating that the LiCl−KCl−CsCl and LiCl−KCl−$SrCl_2$ cations were deposited on the liquid cathode. Sr was successfully deposited on the Zn cathode and exhibited the highest recovery efficiency of up to 55%. The other liquid cathodes showed low current efficiencies below 18%, indicating that LiCl−KCl salt decomposition had occurred.
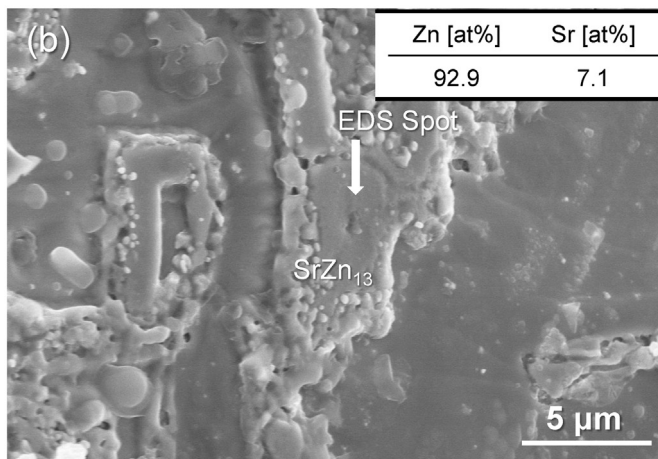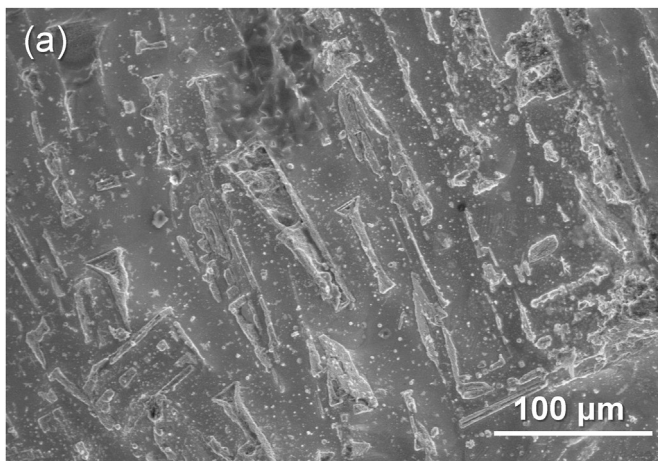
Fig. 4. (a) Microscopic morphologies and (b) energy-dispersive X-ray spectroscopy (EDS) analysis of the Zn cathode after deposition of the Sr.
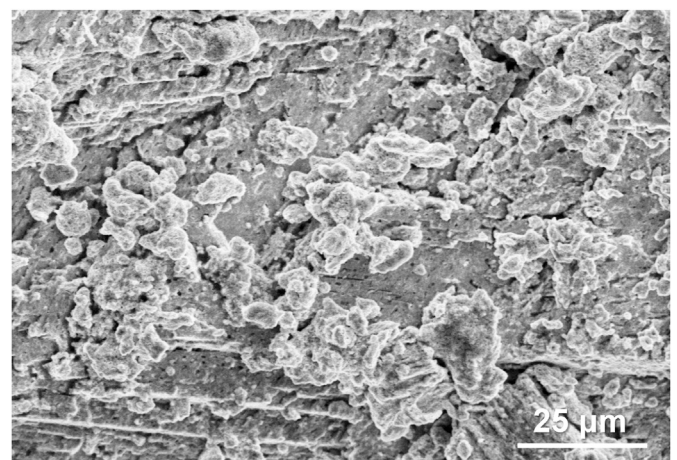
Fig. 5. Microscopic morphology of the Bi cathode after the deposition of Cs.

Sr was recovered in the Zn cathode as SrZn$_{13}$ as irregular rectangular particles from the Zn matrix.

A negligible amount of Cs was deposited on the entire liquid cathode, indicating that Cs was hardly deposited on liquid cathodes and that the decomposition of the salt was favorable.

Based on these results, we suggest a Zn liquid cathode for the Sr cleaning from LiCl−KCl salts during pyroprocessing. However, Cs is difficult to remove from salts using electrochemical methods.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Acknowledgements

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