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Lithium recovery from radioactive molten salt wastes by electrolysis

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In order to determine the operating conditions of an electrolyzer to recover lithium metal from molten salt wastes composed of LiCl, Li_2O, Cs_2O, and SrO, electrolytic reduction experiments have been carried out in a single compartment electrochemical reactor with a mono-polar connection. All the combinative experiments were conducted in an argon atmospheric glove box, and each applied potential-current value was synchronously measured and analyzed in aspects of the preferentially recovering probability of lithium in mixed phases. The effect of the electrode surface area on the current was also observed. Based on our experimental results compared with electrochemical thermodynamic evaluation, it is revealed that Li_2O can be preferentially reduced to lithium by controlled LiCl concentration and applied potential.

Introduction

The extension of a nuclear fuel-loading cycle in a nuclear power plant is being pursued to decrease the unit cost of electric power generation. As a result, the burn-up and radioactivity of spent fuel discharged from the nuclear reactor should be increased. Taking the decay heat and radioactivity account of the high burn-up spent fuel, the conventional storage concepts must be modified for increasing its storage efficiency. To make matters worse, the capacity limit of at-reactor storage facilities are revealed as the current and near future problems of most countries having nuclear power plants.

As a method to solve these problems, a new concept for the development of an advanced storage technology was suggested in 1994 and its technical feasibility is being analyzed at the Korea Atomic Energy Research Institute (KAERI). The advanced technology for spent PWR fuel storage is composed of the reduction of oxide fuel by lithium in a molten LiCl salt bath, the casting and encapsulation of reduced metal fuel, and the highly consolidated storage of an encapsulated metal fuel canister using conventional storage methods.[1]

It is known at a glance that the storage volume should be reduced by a quarter and the cooling load of spent fuel should be reduced by half, if the ceramic spent fuel is converted to a metallic state by lithium. In the course of this reduction the preferential removal of highly radioactive decay-heat elements, ^{137}Cs and ^{90}Sr is achieved.[2,3]

One of the important economical factors in the advanced technology is how to effectively recover lithium from radioactive molten salt wastes discharged from the reduction step of oxide fuels. Even if it is well known that lithium metal is produced from spodumene (lithium aluminum silicate) ore by the commercial process composed of leaching, precipitation, chlorination, and electrolysis, the recovery condition of lithium from the radioactive molten salt waste by electrolysis should be different from the electrolyzing condition of the commercial process because of the difference of composition and compound between two molten salts, such as Li_2O presence or absence.

This study is focused on the lithium recovery from the radioactive molten salt wastes. The composition of the molten salt waste to be discharged from the lithium reduction step is discussed and the reduction potentials of considerable reactions in the electrolyzer are estimated in electrochemical thermodynamic aspects. By the experimental method using the single compartment eletrolyzer with the mono-polar connection, the applicable potential to recover lithium in multi-component molten salt systems is observed and discussed.

Composition of molten salts and considerable reactions

As shown in previous papers, the molten salts to be discharged from the lithium reduction of simulated oxide fuels consisted of LiCl, Li_2O, Cs_2O and CsI, CsCl, SrO, $SrCl_2$, and other metal oxides.[3,4]

In the preferential recovery of lithium from the molten salt mixture by electrolysis, the information on the initial salt composition is very important to lay down a scheme for reasonable research work. Table 1 shows the composition of the molten salt mixture discharged from the lithium reduction of simulated oxide fuels at 1000 K. Even if lithium metal can be obtained from lithium oxide and lithium chloride in the molten salt mixture by electrolysis, it is necessary that the probability of the preferential lithium recovery from the mixture should be considered in the reduction potential aspects of various cell reactions.

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Table 1. Composition of molten salt mixture discharged from lithium reduction of simulated oxide fuel at 1000 K

Compound	Weight fraction, %
LiCl	78.79
Li_2O	19.70
CsCl+CsI	0.31
Cs_2O	0.15
$SrCl_2$	>0.19
SrO	<0.01
ZrO	0.11
Nd_2O_3	0.74

It is well known that alkali and alkali earth metal oxides can be dissolved into molten lithium chloride salt which has more "covalent character" than the analogous salts of the other alkali metals.[5] Neodymium oxide and zirconium oxide are insoluble in the lithium chloride melt. Even if neodymium oxide particles partially react with lithium oxide dissolved into the molten salt, and then change to lithium neodymium oxide ($LiNdO_2$) as this reaction product, the $LiNdO_2$ has limited solubility in the salt.[6]

Table 2. Standard Gibbs free energy and reduction potential of pure substances

Reaction	Temperature, K	ΔG_f,kJ/mol	log K	$E°$, V
$LiCl(l)^* \rightarrow Li + 1/2Cl_2$	923	333.782	−18.968	−3.459
	1023	328.252	−16.893	−3.402
$Li_2O(s)^{**} \rightarrow 2Li + 1/2O_2$	923	477.097	−27.462	−2.472
	1023	463.257	−23.879	−2.401
$2Li_2O(s) + C \rightarrow 4Li + CO_2$	923	558.525	−32.230	−1.447
	1023	530.685	−27.400	−1.375
$2Li_2O(l) + C \rightarrow 4Li + CO_2$	923	502.493	−28.434	−1.302
	1023	480.195	−24.516	−1.244
$CsCl(l) \rightarrow Cs + 1/2Cl_2$	923	354.332	−20.003	−3.672
	1023	341.620	−17.556	−3.541
$CsI(l) \rightarrow Cs + 1/2I_2$	923	290.023	−16.453	−3.006
	1023	279.358	−14.296	−2.895
$Cs_2O(s) \rightarrow 2Cs + 1/2O_2$	923	221.834	−12.552	−1.150
	1023	208.054	−10.622	−1.078
$2Cs_2O(s) + C \rightarrow 4Cs + CO_2$	923	47.969	−2.410	−0.124
	1023	20.279	−0.886	−0.053
$SrCl_2(s) \rightarrow Sr + Cl_2$	923	683.820	−39.324	−3.544
	1023	669.101	−34.469	−3.468
$SrO(s) \rightarrow Sr + 1/2O_2$	923	498.829	−28.681	−2.585
	1023	488.763	−25.177	−2.533
$2SrO(s) + C \rightarrow 2Sr + CO_2$	923	601.989	−34.668	−1.560
	1023	581.697	−29.996	−1.507
$2SrO(l) + C \rightarrow 2Sr + CO_2$	923	503.869	−28.511	−1.306
	1023	487.537	−24.891	−1.263

* (l) – liquid state.
** (s) – solid state.

In accordance with the expected chemical composition and phase of the salt, the standard reaction Gibbs free energy and reduction potential for each possible electrolytic cell reaction have been estimated by Kirchoff's law and Gibbs function and are tabulated in Table 2.

When considering the preferential recovery of lithium based on Tables 1 and 2, it is expected that the preferential reduction of lithium chloride to recover lithium by electrolysis is very difficult because the reduction potential of lithium chloride is similar to those of cesium chloride and strontium chloride. Otherwise the preferential reduction of lithium oxide seems to be possible in the molten salt mixture if the lowest concentrations of cesium and strontium oxides maintain in the molten salt mixture. Fortunately the concentrations of cesium and strontium oxides in the mixture should be controllable due to the equilibrium values in the following chemical reactions.

$$Cs_2O + 2LiCl \rightarrow 2CsCl + Li_2O \quad (1)$$

$$SrO + 2LiCl \rightarrow SrCl_2 + Li_2O \quad (2)$$

In Eqs (1) and (2), equilibrium constants, $K(T)$ are about 0.1 to 0.5 at the temperature range of 900~1200 K and the ratios of $[CsCl]/[Cs_2O]$ and $[SrCl_2]/[SrO]$ are increased with increasing the concentration of lithium chloride by Le Chatelier's principle. In the reduction step of oxide fuels in a molten lithium chloride salt bath by lithium, the concentrations of cesium and strontium oxides are unchangeable values which depend on the composition of oxide fuels related to burn-up and the concentration of lithium chloride is an operating variable.

In aspects of the corrosion of anode (oxidation electrode) and application of cell potential, carbon electrode as anode is more suitable than metal electrode to prevent the formation of metal oxide film on the anode surface.

Experimental

The electrolytic cell was made of stainless steel and placed in a stainless steel housing that was placed in the furnace as shown in Fig. 1. A 6.4 mm diameter graphite rod of electrode grade was used for the anode and the cathode was a stainless steel rod 3.0 mm in diameter. The anode was placed in an alumina cylinder for flushing evolved chlorine and carbon dioxide with argon gas. The cylinder prevents the reduced metal from contacting the cell wall. The temperature probe sheathed by an alumina tube was also placed in the cell. A sampling tube made of borosilicate glass was dipped when necessary.

The cell and the cell housing were placed in a glove box that maintained argon atmosphere. All alumina materials were dried at 573 K for 48 hours before use. Argon gas was introduced into the glove box through the molecular sieve column to remove residual moisture in argon gas.

All the chemicals used as the composition of molten salt mixture were weighed inside the glove box and put into the cell. 99.99% lithium chloride from Aldrich, 99.5% lithium oxide from CERAC, 99% cesium oxide from Rare Metallic, and 99.5% strontium oxide from Alfa were used. The combinative molten salt systems for experiment consisted of 3 cases; single system of LiCl and binary system of 95 mol% LiCl–5 mol% Li_2O and four component system of 94.22 mol% LiCl-4.96 mol% Li_2O-0.58 mol% Cs_2O-0.24 mol% SrO. All the experiments were carried out at 923 K.

WENKING PGS 95 potentiostat/galvanostat from Bank was employed to supply current to the cell. The potential was programmed to vary linearly from zero to designed values and then was maintained at the value. Current was measured using a A/D converter and synchronously acquired with potential value.

Results and discussion

Electrolytic reduction of LiCl

When the applied potential increased from 0 to 5 V, the current response in the electrolytic reduction system of LiCl is shown in Fig. 2. The reduction potential of lithium chloride of 3.5 V is observed by the asymptote method and the reduction current is monotonously increased with increasing the applied potential. The reduction potential of 3.5 V closely agrees with the calculated value in Table 2. From this result, it is expected that ohmic drop by the formation of chlorine gas should be almost negligible in the electrolytic reduction system of pure lithium chloride using a steel cathode and graphite anode.

Electrolytic reduction of LiCl-Li_2O

In the reduction experiment of the LiCl-Li_2O binary system, the 3 kinds of reduction currents are observed at the applied potentials of 0.55, 1.73 and 3.55 V as shown in Fig. 3. The first current break-through between 0.55 and 1.73 V seems to be related with the reduction of the unknown impurities in 99.5% Li_2O that is more easily reduced than Li_2O. And the second current break-through between 1.73 and 3.55 V seems to be due to the electrolytic reduction of lithium oxide. In the second current break-through, the limiting current is observed in the range of 2.55 to 3.55 V of the applied potential. In order to achieve preferential reduction of lithium oxide in the binary system, the applied potential of 2.55 to 3.55 V is demanded. On the other hand the reduction potentials of lithium oxide and lithium chloride are slightly higher than the calculated values in Table 2.

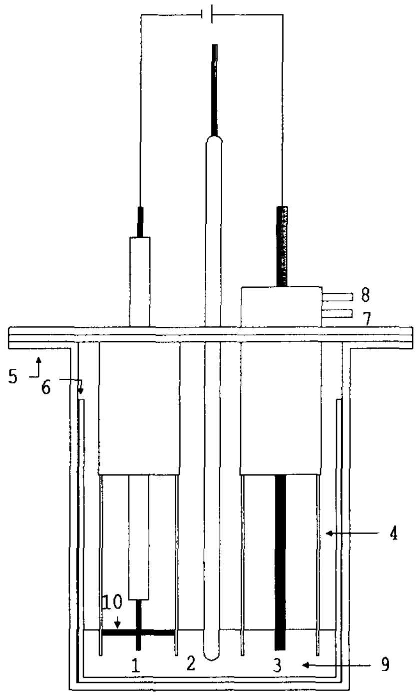

Fig. 1. Configuration of electrolytic cell for lithium recovery experiment; 1–steel cathode, 2–thermocouple, 3–graphite anode, 4–alumina tube, 5–steel case, 6–stainless steel cell, 7–purging gas inlet, 8–puring gas outlet, 9–molten salt phase, 10–molten metal phase

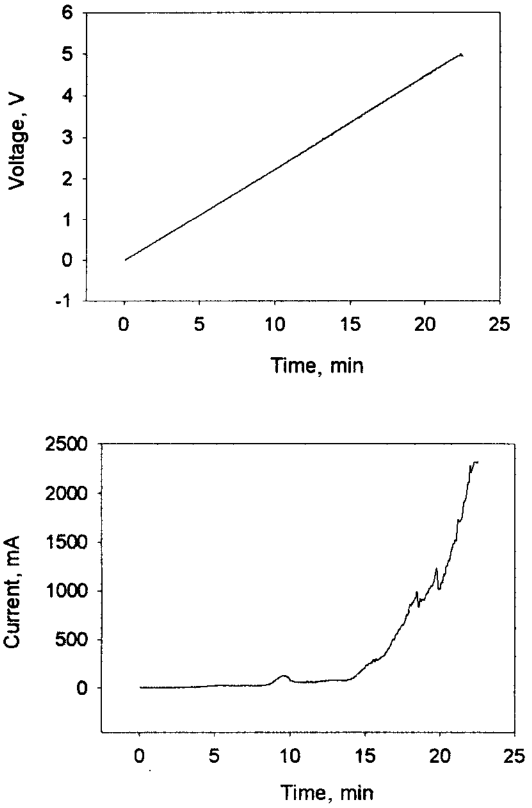

Fig. 2. Electrolytic reduction of LiCl at 923 K and 0.225 V/min

This may be due to the ohmic drop according to the carbon dioxide formation on the anode surface. As contrasted with the single component system of LiCl, chlorine gas formed on the graphite anode escapes more easily from the anode surface than the carbon dioxide in the binary system because of the chemical reaction ($\Delta G_f = -395.699$ kJ/mol at 923 K) between carbon and oxygen. The third current break-through beyond the applied potential of 3.55 V results from the electrolytic reduction of lithium chloride. For the binary system the cell current beyond 3.55 V is somewhat larger than the current of the single component system of LiCl. This may be due to the co-reduction of lithium chloride and residual lithium oxide.

Electrolytic reduction of LiCl-Li_2O-Cs_2O-SrO

Figure 4 shows the synchronized current-potential relation in the electrolytic reduction of the LiCl/Li_2O/Cs_2O/SrO mixed salt. When the applied potential increases from 0 to 4 V, the current break-through points are observed at 0.45, 1.95, and 3.6 V, respectively. If taking into account the ohmic drop according to the carbon dioxide formation on the anode surface, each observed reduction potential may be higher than the calculated reduction potential as shown in Table 2. It is therefore expected that the first, second, and third points are related to the reduction of cesium oxide, lithium and strontium mixed oxides, and lithium chloride, respectively.

Consequently the preferential recovery of lithium from the LiCl/Li_2O/Cs_2O/SrO mixed salt is very difficult because of almost the same reduction potentials of lithium oxide and strontium oxide, even if the cesium oxide is prior removed by the adoption of polarography. In order to recover preferentially the lithium from the radioactive molten salt wastes, cesium and strontium oxides must be converted into chloride compounds by controlling of lithium chloride concentration in the reduction of oxide fuel by lithium.

Effect of electrode surface area on reduction current

The effect of electrode surface area on the reduction current was observed in the LiCl–Li_2O binary system. This information is important to decide the effective ratio of cathode and anode areas, especially in the case that the supporting material of anode is participated in the reaction.

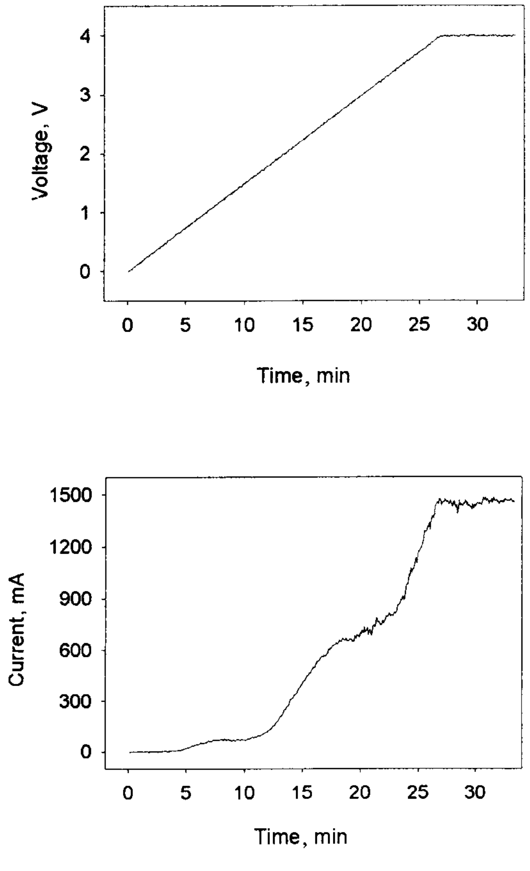

Fig. 3. Electrolytic reduction of LiCl-Li_2O at 923 K and 0.15 V/min

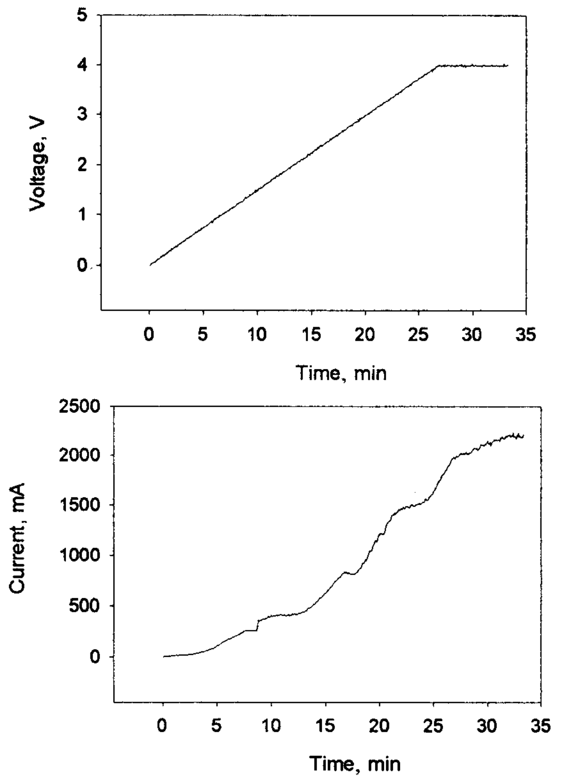

Fig. 4. Electrolytic reduction of $LiCl-Li_2O-Cs_2O-SrO$ at 923 K and 0.15 V/min

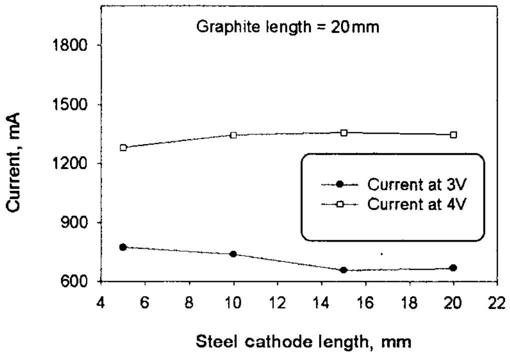

Fig. 5. Effects of cathode area on current of $LiCl-Li_2O$ electrolytic reduction; graphite length = 20 mm, ● current at 3 V, ☐ current at 4 V

Figure 5 shows the effect of cathode area on the reduction current. Controlling the dipped length of stainless steel into the molten salt phase changed the cathode area in this experiment. As shown in Fig. 5, the enlarged cathode area has little effect on the reduction currents. On the other hand, the reduction current is increased with an increase in the anode area as shown in Fig. 6.

As a result of this experiment, it is expected that the determination of the anode area when the electrolyzer is designed should consider a ratio of more than 1 in the anode area to cathode area.

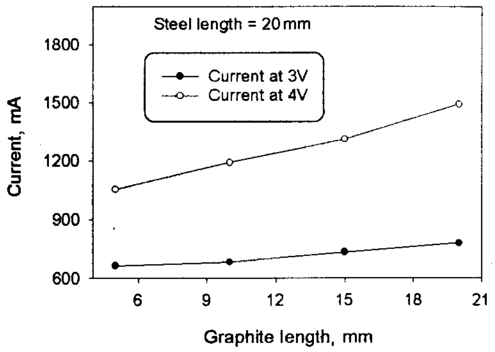

Fig. 6. Effects of anode area on current of $LiCl-Li_2O$ electrolytic reduction; steel length = 20 mm, ● current at 3 V, ○ current at 4 V

Conclusions

Through the thermodynamic analysis and experimental study on the preferential recovery of lithium metal from the simulated radioactive salt wastes embedding lithium chloride and oxide, the followings are concluded.

If possible, all cesium and strontium oxides dissolved in the mixed salts must be converted into chloride compounds to recover preferentially lithium metal by electrochemical reduction.

The preferential recovery of lithium metal is limited to the reduction of lithium oxide, except lithium chloride.

The proper potential in the reduction of lithium oxide for the preferential recovery is 2.55 to 3.55 V.

The effect of the anode area on the reduction current is more severe than that of the cathode area.

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