Thermodynamic Calculations on the Chemical Behavior of SrO During Electrolytic Oxide Reduction

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Strontium is known as a salt-soluble element during the electrolytic oxide reduction (EOR) process. The chemical behavior of SrO during EOR was investigated via thermodynamic calculations to provide quantitative data on the chemical status of Sr. To achieve this, thermodynamic calculations were conducted using HSC chemistry software for various EOR conditions. It was revealed that SrO reacts with LiCl salt to produce $SrCl_2$, even in the presence of Li_2O, and that the ratio of $SrCl_2$ depends on the initial concentration of Li_2O dissolved in LiCl. It was found that SrO reacts with Li to produce Sr during EOR and that the reduced Sr reacts with LiCl salt to produce $SrCl_2$. As a result, the proportions of metallic forms were lower in Sr than in La and Nd under various EOR conditions. The thermodynamic calculations indicated that the three chemical forms of SrO, $SrCl_2$, and Sr co-exist in the EOR system under an equilibrium with Li, Li_2O, and LiCl.

Keywords: Strontium oxide, Thermodynamic calculations, Electrolytic oxide reduction, Pyroprocessing, HSC chemistry

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Min Ku Jeon   http://orcid.org/0000-0001-8115-3241   Sung-Wook Kim   http://orcid.org/0000-0002-5537-4793
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1. Introduction

As a key process that enables the use of oxide-type used nuclear fuel (UNF) in electrochemical pyroprocessing, the electrolytic oxide reduction (EOR) process is unde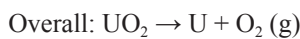r intensive research [1-3]. The EOR process normally employs Li_2O containing (1 - 3wt%) LiCl salt to produce Li metal at the cathode and oxygen gas at the anode. There are two mechanisms, chemical and electrochemical, that explain the EOR process. The latter, electrochemical direct reduction mechanism, propose that the following reactions occur during the EOR process [4-6].

Cathode: $UO_2 + 4e^- \rightarrow U + 2O^{2-}$
Anode: $2O^{2-} \rightarrow O_2 (g) + 4e^-$
Overall: $UO_2 \rightarrow U + O_2 (g)$
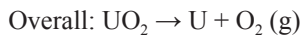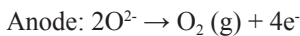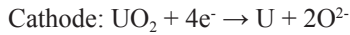
On the other hand, Li_2O is decomposed to produce Li metal and oxygen gas in the chemical reduction mechanism. The Li metal produced at the cathode reacts with UNF as follows.

Cathode: $4Li+ + 4e^- \rightarrow 4Li$ (Electrochemical reaction)
$UO_2 + 4Li \rightarrow U + 2Li_2O (= 4Li^+ + 2O^{2-})$
Anode: $2O^{2-} \rightarrow O_2 (g) + 4e^-$
Overall: $UO_2 \rightarrow U + O_2 (g)$
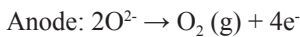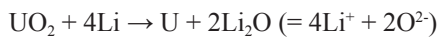
In either mechanism, the overall reaction can be simplified as a transfer of oxygen atoms from the UNF oxide to the anode to produce oxygen gas. And it is hard to distinguish between the two mechanisms as the standard potentials for UO_2 and Li_2O differ by around 0.07 V. In addition to its original role, the EOR process also works as a Sr removal step owing to the solubility of strontium in LiCl. Sr is an important element in pyroprocessing owing to the high decay heat of Sr-90. Park et al. [7] reported that around 67% of Sr was dissolved into LiCl salt after EOR runs of simulated fuel pellets. Herrmann and Li [8] also found 82% of Sr in the salt after several EOR runs

with light water reactor (LWR) oxide UNFs. The authors claimed that the incomplete dissolution of Sr came from a difference in the initial composition of the fuels. The diffusion of Sr in LiCl salt was investigated by Park et al. [9], who identified dissolution of SrO and slow diffusion of Sr^{2+}. The dissolution of SrO during EOR was observed even when the salt included 3wt% of Li_2O [10]. Choi and Kang reported that only around 3wt% of Sr remained in the simulated fuels after the EOR runs and subsequent distillation process [11]. Thanks to these efforts to reveal the behavior of Sr during the EOR operation, it is widely accepted that Sr is a salt-soluble element that can be removed during the EOR operation. However, the reactive behavior of Sr with salts, and with Li produced during the EOR, was not fully understood. For example, the effects of Li_2O and Li on the dissolution and their chemical interaction with Sr during EOR had not yet been quantitatively analyzed. In this study, theoretical approaches were taken by which to provide quantitative results on the reactive behavior of SrO during the EOR operation via thermodynamic calculations.

2. Thermodynamic calculations

HSC Chemistry 9.0 software [12] was employed in the thermodynamic calculations of this study. Gibbs free energy change (ΔG) values and equilibrium constants (K) at 650℃ were derived using the "Reaction Equations" module. The effects of Li_2O concentration and Li amount on the status of Sr during EOR were investigated using the "Equilibrium Compositions" module. In order to mimic the EOR process conditions in a simple manner, the composition of UNF used in the previous work [7] was employed, but only for La, Nd, and Sr in relation to U, as listed in Table 1. The lanthanide elements were incorporated as comparison indicators because it was experimentally and theoretically proved that these elements are hard to reduce during EOR and that they remain in partially reduced state even after

Table 1. Composition of UNF fuel employed for thermodynamic calculations

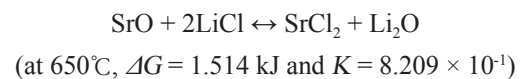| Elements	Weight ratio	No. of moles in 1 g UNF	Molar ratio
UO_2	98.939%	3.664×10^{-3}	98.912%
La_2O_3	0.210%	6.446×10^{-6}	0.174%
Nd_2O_3	0.723%	2.149×10^{-5}	0.580%
SrO	0.128%	1.236×10^{-5}	0.334%
Total	100.000%	3.704×10^{-3}	100.000%

UO_2 was fully reduced to U [7, 8, 13]. The activity coefficient of Li_2O was set to 8.4 according to the previous work [14], where the value was derived from measured Li_2O solubility of 11.9mol% (8.7wt%) in LiCl at 650℃ with pure solid Li_2O. The activity coefficient value of Li was previously studied by Liu and Poignet [15], and it was dependent on the molar fraction of Li. The activity coefficient of Li increases from 0.504 (at the molar fraction of 0.00238) to 13.7 (at the molar fraction of 0.01442), and is slightly less 12.4 at the molar fraction of 0.01837. In the present study, the value of 12.4 was adopted for thermodynamic calculations. This is because the initial molar fractions of Li employed in the present work were within 0.0314 - 0.188, significantly higher than the maximum value (0.01837) in the previous work [15]. The amounts of LiCl and UNF were set as 10 and 1 g, respectively, in all calculations. This ratio of 10:1 in LiCl:UNF was set-up based on KAERI's scale-up experiences.

3. Results and Discussion

The first question of this work to answer is whether SrO reacts with LiCl salt in the presence of Li_2O. As noted in the introduction, the EOR process normally employs LiCl salt containing around 1wt% Li_2O. The chemical reaction between SrO and LiCl can be expressed as follows:

Table 2. Molar quantity of each component at the initial and at the equilibrium conditions. The "y" term represents molar quantity of $SrCl_2$ at the equilibrium state

Chemicals	Initial amount (moles)	Amount at equilibrium (moles)
SrO	1.236×10^{-5}	1.236×10^{-5} - y
LiCl	2.358×10^{-1}	$2.358 \times 10^{-1} - 2y$ ($\fallingdotseq 2.358 \times 10^{-1}$)
$SrCl_2$	0	y
Li_2O	3.347×10^{-3}	$3.347 \times 10^{-3} + y$
Total	$\fallingdotseq 2.391 \times 10^{-1}$	$\fallingdotseq 2.391 \times 10^{-1}$

$$SrO + 2LiCl \leftrightarrow SrCl_2 + Li_2O$$
(at 650℃, ΔG = 1.514 kJ and K = 8.209×10^{-1})

At first glance, it is questionable whether the above reaction can proceed even though ΔG value is positive. A simple calculation was conducted prior to the HSC chemistry calculations in order to predict the direction of the above equation. According to the definition of K, it can be expressed as follows:

$$K = \{[a_{SrCl2}] \times [a_{Li2O}]\} / \{[a_{SrO}] \times [a_{LiCl}]^2\}$$
$$= \{[\gamma_{SrCl2} \times x_{SrCl2}] \times [\gamma_{Li2O} \times x_{Li2O}]\} / \{[\gamma_{SrO} \times x_{SrO}] \times [\gamma_{LiCl} \times x_{LiCl}]^2\}$$

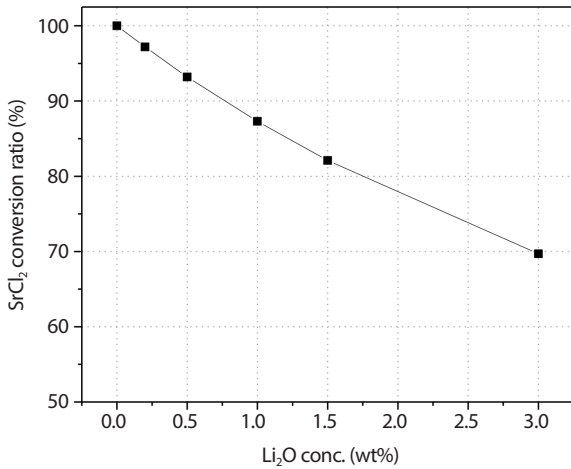Here, a_i, γ_i, and x_i respectively represent activity, activity

Fig. 1. Effect of the Li₂O concentration on the ratio of SrCl₂ in relation to the initial amount of SrO. The calculations were conducted based on the conditions 10 g LiCl, 1 g UNF, and 650℃.

coefficient, and molar ratio of species i. Because the activity coefficients of SrCl₂, SrO, and LiCl are unknown, they were set at "1", while that of Li₂O was set at 8.4 [14]. With this input, the above equation can be re-written as follows:

$$K = \{[x_{SrCl2}] \times [8.4 \times x_{Li2O}]\} / \{[x_{SrO}] \times [x_{LiCl}]^2\}$$
$$= 8.209 \times 10^{-1}$$

Molar quantity of each component at the initial and at the equilibrium state is listed in Table 2. Here it needs to mention that the maximum value of y, the molar quantity of SrCl₂ at the equilibrium state, is identical to the initial amount of SrO (= 1.236×10^{-5}). Thus, we can assume that the impact of y is negligible for the amount of LiCl and total number of moles as noted in the Table. The molar fraction of each chemical at an equilibrium state with 1wt% initial Li₂O concentration can be expressed as follows.

$$x_{SrCl2} = y / [\text{total}] = y / (2.391 \times 10^{-1})$$
$$x_{Li2O} = (3.347 \times 10^{-3} + y) / [\text{total}]$$
$$= (3.347 \times 10^{-3} + y) / (2.391 \times 10^{-1})$$
$$x_{SrO} = (1.236 \times 10^{-5} - y) / [\text{total}]$$
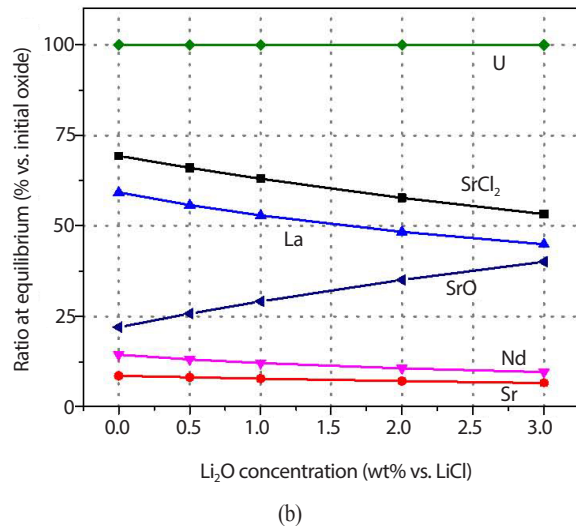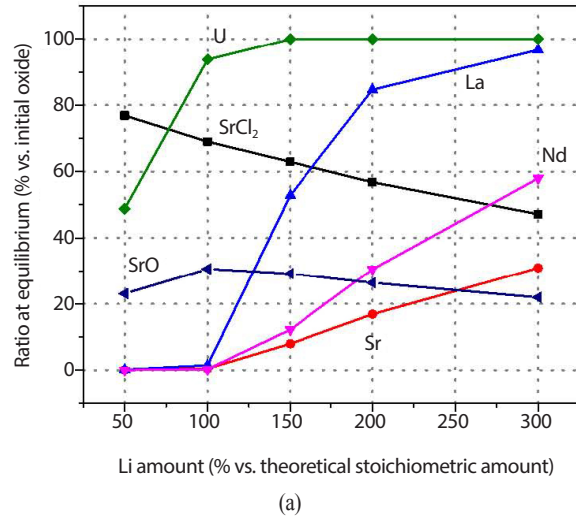$$= (1.236 \times 10^{-5} - y) / (2.391 \times 10^{-1})$$

(a)

(b)

Fig. 2. (a) Effect of the Li amount on the ratio of UNF constituents against the initial amount of oxide. The calculations were carried out under the conditions 10 g LiCl, 1 g UNF, and 1.5wt% Li₂O.
(b) Effect of the Li₂O concentration on the ratio of UNF constituents against initial oxide amount. The calculations were conducted under the conditions 10 g LiCl, 1 g UNF, and 1.5 times the theoretical stoichiometric amount of Li.

$$x_{LiCl} = [\text{LiCl}] / [\text{total}]$$
$$= (2.358 \times 10^{-1} - 2y) / (2.391 \times 10^{-1}) \doteqdot 9.862 \times 10^{-1}$$

Solving the equilibrium constant equation using the above numbers results in $y = 1.077 \times 10^{-5}$, meaning that 87.1% of initial SrO was converted into SrCl₂. Thus, de-

spite the positive ΔG value, the relatively large amount of LiCl pushed the reaction to the right to produce $SrCl_2$ even in the presence of 1wt% Li_2O. Further calculations were conducted using the HSC chemistry code. The calculation results are summarized in Fig. 1 for various Li_2O concentrations (0.0 - 3.0wt%) while other conditions were fixed at 10 g of LiCl and 1 g of UNF. It is clear in the figure that an increase in the initial Li_2O concentration significantly reduces the ratio of $SrCl_2$ at equilibrium, as expected. However, around 70% of SrO was still converted into $SrCl_2$ in the presence of 3wt% Li_2O.

The second question of this work to be answered was whether SrO reacts with Li, produced via the chemical reduction mechanism, during the EOR. The reaction for SrO reduction is as below:

$$SrO + 2Li \leftrightarrow Sr + Li_2O$$
$$(\text{at } 650℃, \Delta G = 26.596 \text{ kJ and } K = 3.126 \times 10^{-2})$$
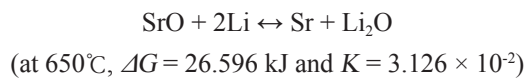
A set of thermodynamic calculations was conducted for various amounts of Li while the other conditions were kept constant at 1wt% Li_2O, 10 g of LiCl, and 1 g of UNF. The calculation results are summarized in Fig. 2(a). Clearly, U reached complete reduction when 1.5 times the theoretical amount of Li was supplied. In the case of Sr, $SrCl_2$ was the major chemical form of Sr (with 23 - 30% of SrO) when 50 and 100% the theoretical amount of Li was supplied. Metallic Sr began to appear at 1.5 times the theoretical amount of Li, while the ratio of both $SrCl_2$ and SrO decreased with increase in the Li amount. Compared to the ratios of metallic La and Nd, which were included in the calculations for comparison against Sr, the proportions of metallic forms were lower in Sr than in La and Nd. Another set of calculations was carried out for various concentrations of Li_2O while keeping the amount of Li at 1.5 times the theoretical amount, with 10 g of LiCl and 1 g of UNF. The calculation results are shown in Fig. 2(b). It was revealed that an increase in the Li_2O concentration resulted in a higher SrO ratio while the ratios of $SrCl_2$ and Sr decreased. The ratios

of metallic La and Nd decreased with an increase in the Li_2O concentration. The low ratio of metallic Sr (compared to La and Nd) under the conditions used in all the calculations needs discussion. According to our previous work [13], La_2O_3 and Nd_2O_3 have K values of 1.41×10^{-6} and 1.82×10^{-7} for their reaction with Li to produce metallic La and Nd. These values are not comparable to 3.126×10^{-2} in the reduction reaction of SrO. This means that the ratio of metallic Sr should be higher than that of La and Nd under identical conditions. The following reaction equation could explain this discrepancy.

$$Sr + 2LiCl \leftrightarrow SrCl_2 + 2Li$$
$$(\text{at } 650℃, \Delta G = -25.08 \text{ kJ and } K = 2.626 \times 10^{1})$$
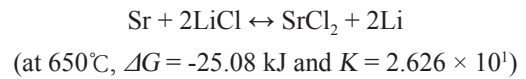
The above reaction suggests that metallic Sr will be converted to $SrCl_2$ by reacting with LiCl salt to a significant extent based on the negative ΔG value, K value ≥ 1, and relatively large amount of LiCl under the conditions of the EOR. Thus, the low ratio of metallic Sr in the reduction condition came from the conversion of Sr to $SrCl_2$. These results show that, under the conditions of an actual EOR, all three of the chemical forms $SrCl_2$, SrO, and Sr will co-exist in the EOR system, and their ratio will depend on the concentrations of Li_2O and Li in the LiCl salt.

4. Conclusions

The findings that were revealed through this work can be summarized as follows.
1) SrO in UNF might react with LiCl salt even in the presence of Li_2O during the EOR.
2) SrO might be reduced to Sr by Li during the EOR.
3) Reduced Sr might react with LiCl salt to produce $SrCl_2$.

The calculation results suggest that three chemical forms (SrO, $SrCl_2$, and Sr) will co-exist in the EOR system, and that their ratio will vary substantially depending on the

concentration of Li_2O and Li in the LiCl salt.

Acknowledgement

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