

# Preliminary Study on Chlorination Reaction of Lithium Carbonate for Carbon-Anode-Based Oxide Reduction Applications

Min Ku Jeon<sup>1,2,\*</sup>, Sung-Wook Kim<sup>1</sup>, and Eun-Young Choi<sup>1,2</sup>

<sup>1</sup>Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon 34057, Republic of Korea

<sup>2</sup>University of Science and Technology, 217, Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea

(Received January 6, 2021 / Revised January 27, 2021 / Approved January 29, 2021)

---

The reaction between  $\text{Li}_2\text{CO}_3$  and  $\text{Cl}_2$  was investigated to verify its occurrence during a carbon-anode-based oxide reduction (OR) process. The reaction temperature was identified as a key factor that determines the reaction rate and maximum conversion ratio. It was found that the reaction should be conducted at or above  $500^\circ\text{C}$  to convert more than 90% of the  $\text{Li}_2\text{CO}_3$  to  $\text{LiCl}$ . Experiments conducted at various total flow rate ( $Q$ ) / initial sample weight ( $W_i$ ) ratios revealed that the reaction rate was controlled by the  $\text{Cl}_2$  mass transfer under the experimental conditions adopted in this work. A linear increase in the progress of reaction with an increase in  $\text{Cl}_2$  partial pressure ( $p_{\text{Cl}_2}$ ) was observed in the  $p_{\text{Cl}_2}$  region of 2.03–10.1 kPa for a constant  $Q$  of  $100 \text{ mL}\cdot\text{min}^{-1}$  and  $W_i$  of 1.00 g. The results of this study indicate that the reaction between  $\text{Li}_2\text{CO}_3$  and  $\text{Cl}_2$  is fast at  $650^\circ\text{C}$  and the reaction is feasible during the OR process.

Keywords: Lithium carbonate, Chlorination reaction, Oxide reduction, Pyroprocessing, Carbon anode

---

\*Corresponding Author.

Min Ku Jeon, Korea Atomic Energy Research Institute, E-mail: [minku@kaeri.re.kr](mailto:minku@kaeri.re.kr), Tel: +82-42-868-2435

## ORCID

Min Ku Jeon

<http://orcid.org/0000-0001-8115-3241>

Sung-Wook Kim

<http://orcid.org/0000-0002-5537-4793>

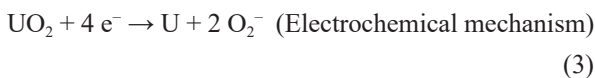
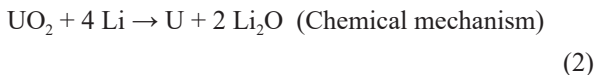
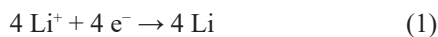
Eun-Young Choi

<http://orcid.org/0000-0003-1693-7642>

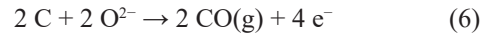
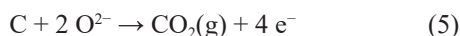
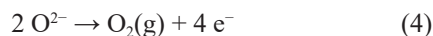
## 1. Introduction

The oxide reduction (OR) process has been the subject of much research aimed at applying the oxide fuels discharged from pressurized water reactors in the metallic fuel pyroprocessing. This metallic fuel pyroprocessing was successfully demonstrated through the Experimental Breeder Reactor-II project in the USA [1]. Once the oxide fuels are converted into their metallic forms by OR operation, U is selectively recovered via an electro-refining process and transuranic (TRU) nuclides are then recovered along with U via an electro-winning process [2]. The OR process normally employs LiCl as a molten salt and is operated at around 650°C [3-6]. Oxide fuels are loaded into a metallic cathode basket, with platinum normally employed as the anode owing to its high stability under the harsh condition of high temperatures and a corrosive environment (evolution of O<sub>2</sub> gas) [3-6]. However, a recent investigation claimed that repeated OR operations cause noticeable degradation of the platinum anode [7]. Previously, carbon was proposed as an alternative to platinum for the anode [8, 9]. In these reports, the operating voltage was maintained at less than 3.47 V to avoid decomposition of the LiCl salt and the consequent production of chlorine gas at the anode. The reactions employed in this carbon anode system can be summarized as follows:

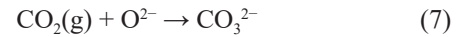
<Cathode>



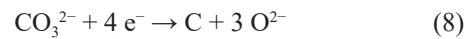
<Anode>



Although the carbon anode system showed some promise, the formation of carbonate ions through the following reaction (7) was pointed out as an issue [8, 9].

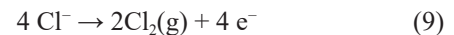


These carbonate ions are electrochemically decomposed to produce carbon dust at the cathode, according to the following reaction (8), leading to poor process efficiency.



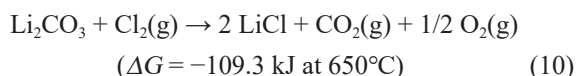
In order to address the carbonate issue, our group recently proposed the use of a carbon anode at a high potential to decompose the LiCl salt itself. Applying higher voltage results in the production of chlorine gas at the anode via the following equation (9):

<Anode>



Here, the reactions mentioned above to produce O<sub>2</sub>, CO, and CO<sub>2</sub> at the anode are still involved in the high-voltage operation due to oxygen ions which are liberated from oxide fuels. Hence, the carbonate formation reaction will proceed even during the high-voltage OR operation, while it was predicted that chlorine gas generated at the anode may react with Li<sub>2</sub>CO<sub>3</sub> or Li<sub>2</sub>O to produce LiCl [10, 11]. The previous work showed that the concentration of Li<sub>2</sub>CO<sub>3</sub> remained below 0.3wt% after repeated experiments at high cell voltage levels (above 10 V) [10]. This result can be explained by various chemical reactions that can take place between Li<sub>2</sub>CO<sub>3</sub> and Cl<sub>2</sub> along with other chemicals, such as Li, Li<sub>2</sub>O, and C [10]. The direct reaction between Li<sub>2</sub>CO<sub>3</sub> and Cl<sub>2</sub> (shown below as reaction (10)) was previously introduced by Nakamura et al. [12], in which the effects of

the reaction temperature and particle size were investigated. The authors could achieve high proportions of LiCl in the temperature range of 350–500°C with particle sizes smaller than 0.82 mm. However, detail information about the experimental conditions such as gas flow rate, the amount of reactant, and partial pressure of Cl<sub>2</sub> was not provided in that report [12].



In this work, the reaction above was investigated as functions of the reaction temperature, the total flow rate of Ar and Cl<sub>2</sub> (*Q*), and the chlorine partial pressure (*p*Cl<sub>2</sub>) to identify whether it is a reasonable explanation for the limited accumulation of Li<sub>2</sub>CO<sub>3</sub>.

## 2. Experimental

A quartz tube (4 cm diameter) equipped with an electrical furnace in the middle was employed as a reactor. Both ends of the tube were sealed with silicone stoppers connected to Teflon tubes to ensure the flow of gas. The flow rates of the Ar and Cl<sub>2</sub> gases were controlled independently using mass flow controllers (MFCs, Kofloc co., Japan). Li<sub>2</sub>CO<sub>3</sub> powder as a reactant was weighed (0.25–1.00 g for each experiment) and then positions in the middle of the quartz tube using an alumina boat. The reactor was purged using Ar gas before the furnace was heated to remove air inside the reactor. After the furnace reached the setting temperature with a ramping rate of 10°C·min<sup>-1</sup>, Cl<sub>2</sub> gas was fed into it by controlling the MFC. The Cl<sub>2</sub> gas flow and the heater were turned off at the end of reaction. The *p*Cl<sub>2</sub> value was derived from the inlet flow rate ratio of Cl<sub>2</sub> over sum of Ar and Cl<sub>2</sub>.

The effect of the reaction temperature was investigated by repeating experiments at 300, 400, 500, and 650°C with 100 mL·min<sup>-1</sup> of *Q* and 5.07 kPa of *p*Cl<sub>2</sub> for various

durations. The experiments were conducted at 650°C for 30 min with *p*Cl<sub>2</sub> of 5.07 kPa and various *Q* (100–300 mL·min<sup>-1</sup>) and initial weight of sample (*W*<sub>i</sub>, 0.25–1.00 g) to study the effect of *Q*/*W*<sub>i</sub> ratio. The effect of *p*Cl<sub>2</sub> was investigated for various *p*Cl<sub>2</sub> conditions of 2.03, 3.04, 5.07, and 10.1 kPa at 650°C with 100 mL·min<sup>-1</sup> of *Q* and 1.00 g of *W*<sub>i</sub>. The experiments were also conducted for 20 min with 200 mL·min<sup>-1</sup> of *Q* and 0.25 g of *W*<sub>i</sub>.

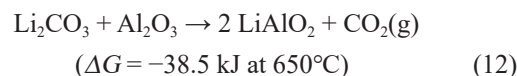
The progress of the chlorination reaction was calculated by measuring the weight change in the sample before and after the reaction. A structural analysis of the reaction products was conducted by means of the X-ray diffraction (XRD, Bruker D8 Advance).

## 3. Results and discussion

In order to quantify the progress of the reaction, the conversion ratio of Li<sub>2</sub>CO<sub>3</sub> to LiCl, *α*, was defined as follows,

$$\alpha = (W_f - W_i) / (W_i) / ((2 \times M.W_{\text{LiCl}} / M.W_{\text{Li}_2\text{CO}_3}) - 1) \quad (11)$$

where *W*<sub>f</sub> and *W*<sub>i</sub> represent the final and initial weight of the samples, respectively, and *M.W.*<sub>LiCl</sub> and *M.W.*<sub>Li<sub>2</sub>CO<sub>3</sub></sub> correspondingly indicate the molecular weight of LiCl (= 42.39 g·mol<sup>-1</sup>) and of Li<sub>2</sub>CO<sub>3</sub> (= 73.89 g·mol<sup>-1</sup>). Before getting started with chlorination reaction, the stability of Li<sub>2</sub>CO<sub>3</sub> under the gas flow and reaction temperature was verified. This was done to confirm that 1) Li<sub>2</sub>CO<sub>3</sub> is not blown away by the gas flow and 2) Li<sub>2</sub>CO<sub>3</sub> does not react with alumina boat via the following reaction.



After heating Li<sub>2</sub>CO<sub>3</sub> under a 300 mL·min<sup>-1</sup> Ar flow at 650°C for 2 h, no changes were found in the weight of

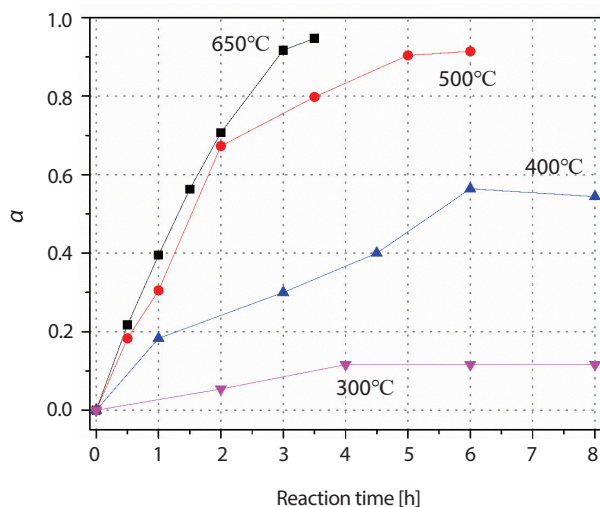


Fig. 1. Experimental results measured at reaction temperatures of 300, 400, 500, and 650°C when the  $p_{\text{Cl}_2}$  condition is 5.07 kPa and  $Q$  is 100 mL·min<sup>-1</sup>.

$\text{Li}_2\text{CO}_3$  indicating that the above issues can be ruled out in this study. This outcome is supported by previous works, in which thermal decomposition temperature of  $\text{Li}_2\text{CO}_3$  was reported to be 1,300°C [13] and beginning of the decomposition reaction was found at 720°C [14].

The effects of the reaction temperature on the reaction kinetics were investigated by repeating the experiments at 300, 400, 500, and 650°C, and these results are shown in Fig. 1. It is obvious in the figure that lowering the reaction temperature profoundly diminishes the reaction rate. One interesting outcome was that the reactions did not complete at low temperatures of 300 and 400°C. This result suggests that the diffusion of chlorine atoms within the  $\text{Li}_2\text{CO}_3$  particle is too slow to achieve complete conversion at this temperature range. According to this result, it is beneficial to operate the OR process at 650°C with regard to the removal of  $\text{Li}_2\text{CO}_3$  in the salt. However, the trend was a little bit different in previous work done by Nakamura et al. [12]. The authors could achieve high conversion ratio even at 350°C and proposed a temperature range 400–506°C for high conversion ratio. It is interesting that the authors reported an abrupt decrease in the conversion ratio at 550°C. This

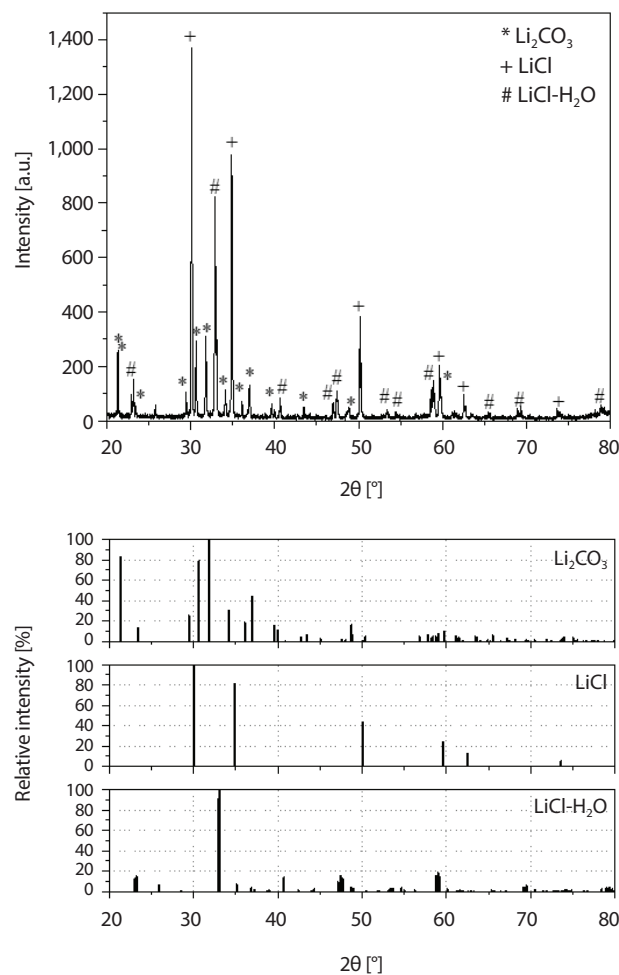


Fig. 2. XRD measurement results of  $\text{Li}_2\text{CO}_3$  reacted at 500°C for 2 h under a 5.07 kPa of  $p_{\text{Cl}_2}$  and 100 mL·min<sup>-1</sup> of  $Q$  condition. Peaks of the pertinent reference materials are also shown below.

discrepancy might have come from the different reaction conditions such as reactor design, gas flow rate, and chlorine partial pressure.

An XRD measurement was taken to confirm the reaction product, and the result is shown in Fig. 2. The peaks could be assigned using the three phases of  $\text{Li}_2\text{CO}_3$  (JCPDF no. 01-087-0729),  $\text{LiCl}$  (JCPDF no. 01-074-1972), and  $\text{LiCl}\cdot\text{H}_2\text{O}$  (JCPDF no. 01-070-9971). Here, it would be reasonable to assume that the  $\text{LiCl}\cdot\text{H}_2\text{O}$  phase was formed during the handling and measurement of the reaction product in air. This result confirms that the reaction between  $\text{Li}_2\text{CO}_3$

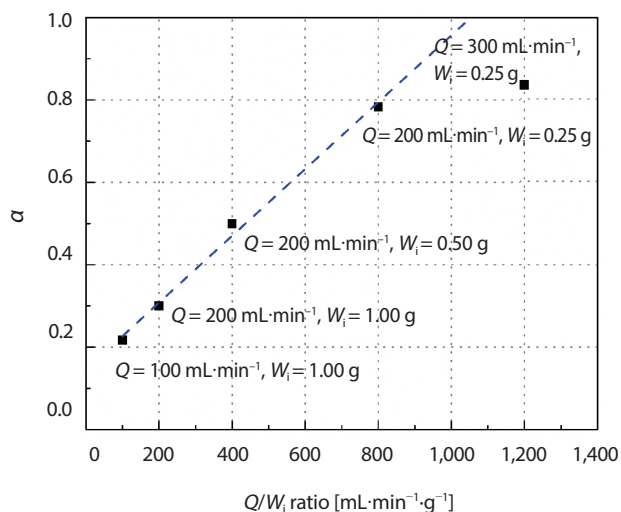
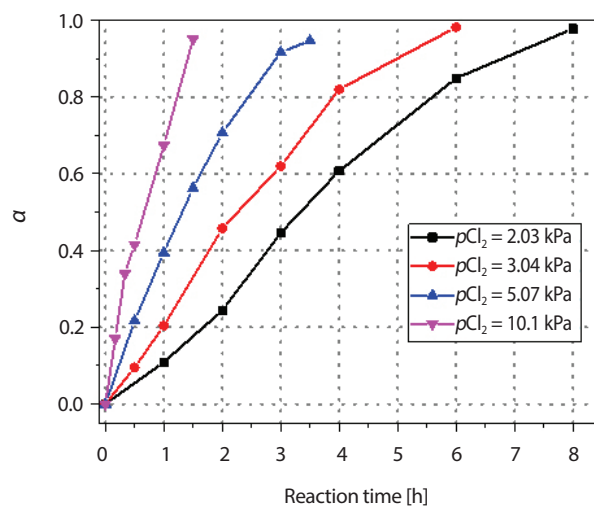


Fig. 3. Experimental results obtained after reaction for 30 min. at  $p_{Cl_2} = 5.07$  kPa and  $650^\circ\text{C}$  for various  $W_i$  and  $Q$  values.

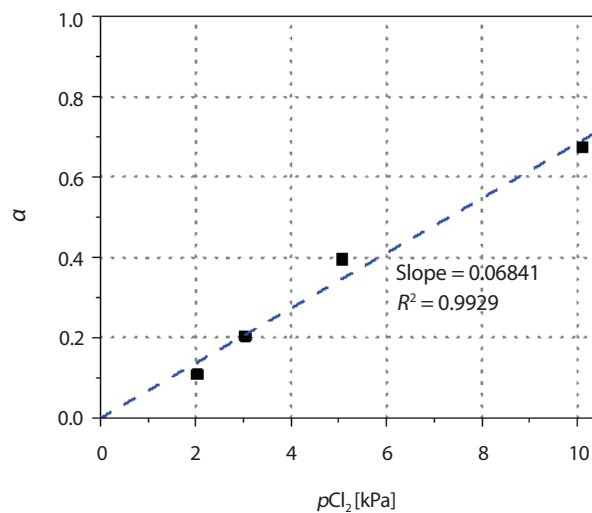
and  $Cl_2$  proceeded without any unexpected by-products and that the assumptions employed during the calculation of  $\alpha$  are reasonable. In addition, the results also propose that the direct chlorination reaction using  $Li_2CO_3$  and  $Cl_2$  is a viable means of synthesizing high-purity LiCl.

The effects of  $Q/W_i$  ratio were investigated by repeating identical experiments for various  $W_i$  (0.25, 0.50, and 1.00 g) and  $Q$  (100, 200, and 300  $\text{mL}\cdot\text{min}^{-1}$ ) values, and the results are shown in Fig. 3. The experimental runs were conducted for 30 min while  $p_{Cl_2}$  and the reaction temperature were held constant at 5.07 kPa and  $650^\circ\text{C}$ , respectively. It is clear in the figure that an increase in the  $Q/W_i$  ratio leads to an increase in  $\alpha$ , which proves that the chlorination reaction is under control of  $Cl_2$  mass transfer in the gas phase. A change in the  $Q/W_i$  ratio should not affect the reaction rate when the reaction is under control of chemical reaction. In other words, under the experimental conditions of this work, the consumption rate of  $Cl_2$  via the reaction with  $Li_2CO_3$  is faster than the transfer rate of  $Cl_2$  at the surface of  $Li_2CO_3$ .

Fig. 4(a) shows the experimental results for various  $p_{Cl_2}$  conditions with a constant  $Q$  of  $100 \text{ mL}\cdot\text{min}^{-1}$  and  $W_i$  of 1.00 g ( $Q/W_i$  ratio  $100 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$ ). It is clear in the figure that a higher  $p_{Cl_2}$  leads to a higher reaction rate as



(a)



(b)

Fig. 4. (a) Experimental results obtained at  $650^\circ\text{C}$  for various  $p_{Cl_2}$  conditions with  $Q$  of  $100 \text{ mL}\cdot\text{min}^{-1}$  and  $W_i$  of 1.00 g. (b) Linear fitting results derived from the 1 h reaction results of (a).

expected from the above results. A linear relationship between  $p_{Cl_2}$  and  $\alpha$  was found as shown in Fig. 4(b). As discussed above, these results are not available for analysis of reaction kinetics due to dominant influence of  $Cl_2$  mass transfer rate. However, this data is very promising in terms of high-voltage OR operation, as it proves fast chemical reaction between  $Li_2CO_3$  and  $Cl_2$  at the OR operation temperature. In addition, an average utilization value of 37.9% was

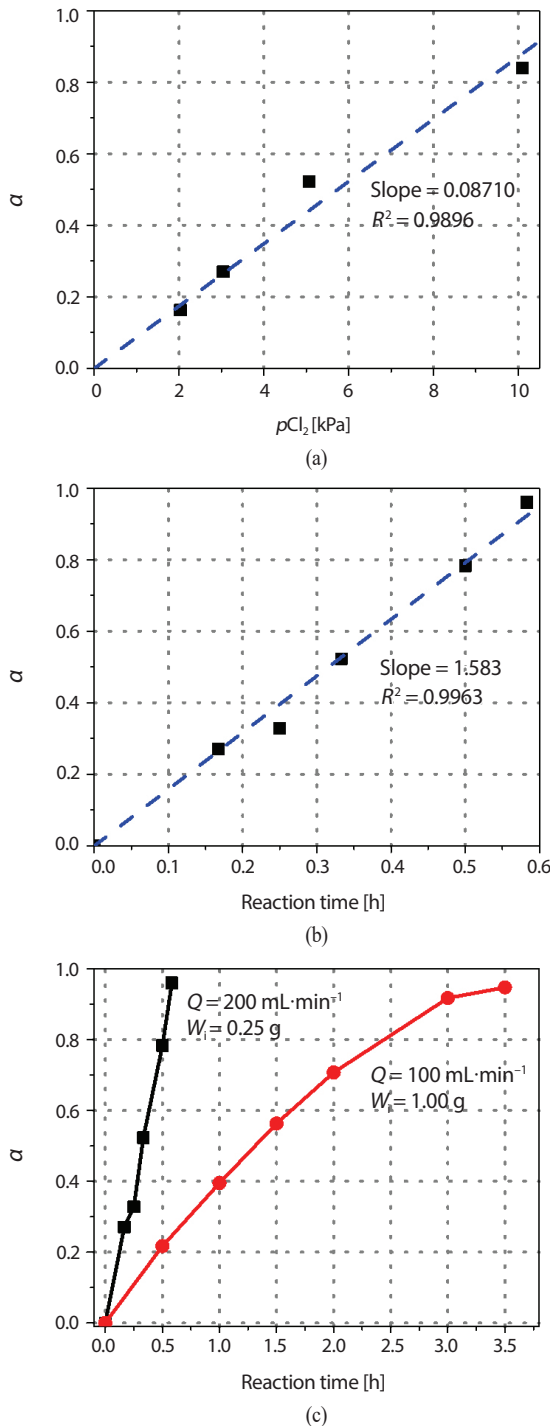


Fig. 5. (a) Linear fitting results derived from the 20 min reaction results at 650°C with  $Q$  of 200 mL·min<sup>-1</sup> and  $W_i$  of 0.25 g. (b) Experimental results obtained as a function of reaction time at 650°C with  $Q$  of 200 mL·min<sup>-1</sup> and  $W_i$  of 0.25 g. (c) Comparison of (b) with the results in Fig. 4(a) at an identical  $p\text{Cl}_2$  of 5.07 kPa.

derived at  $\alpha = 0.5$  proving that  $\text{Cl}_2$  is an efficient reactant for this reaction. The utilization ratio of  $\text{Cl}_2$  was calculated by dividing the amount of  $\text{Cl}_2$  consumed during the reaction by the supplied amount of  $\text{Cl}_2$ .

The effect of  $p\text{Cl}_2$  was also investigated with a constant  $Q$  of 200 mL·min<sup>-1</sup> and  $W_i$  of 0.25 g ( $Q/W_i$  ratio 800 mL·min<sup>-1</sup>·g<sup>-1</sup>). Fig. 5(a) shows the experimental results with a corresponding linear fitting result. This result indicates that the reaction rate is still under control of chlorine mass transfer. Here, it should be noted that the slope of the linear fitting increased by 27% when the  $Q/W_i$  ratio increased 8 times from 100 to 800 mL·min<sup>-1</sup>·g<sup>-1</sup>. This outcome reveals that an increase in the  $Q/W_i$  ratio does not result in a proportional increase in  $\alpha$ , and it means lower  $\text{Cl}_2$  utilization at higher  $Q/W_i$  ratio. The reaction time– $\alpha$  relationship at  $Q$  of 200 mL·min<sup>-1</sup> and  $W_i$  of 0.25 g ( $Q/W_i$  ratio 800 mL·min<sup>-1</sup>·g<sup>-1</sup>) is shown in Fig. 5(b), which was conducted at 5.07 kPa of  $p\text{Cl}_2$  and 650°C. It is interesting to observe a linear relationship between the  $\alpha$  value and the reaction time over the entire range, because the reaction rate decreased with increasing reaction time at  $Q/W_i$  ratio of 100 mL·min<sup>-1</sup>·g<sup>-1</sup> (in Fig. 4(a)). The effect of  $Q/W_i$  ratio on  $\alpha$  is well displayed in Fig. 5(c), in which the results in 5(b) are shown along with the results of Fig. 4(a) with  $p\text{Cl}_2$  of 5.07 kPa. This result suggests that the slowing down of the reaction rate at  $Q/W_i$  ratio of 100 mL·min<sup>-1</sup>·g<sup>-1</sup> came from insufficient supply of  $\text{Cl}_2$  owing to its slow mass transfer rate, whereas this phenomenon was eliminated by increasing the  $Q/W_i$  ratio to 800 mL·min<sup>-1</sup>·g<sup>-1</sup>. The utilization ratio of  $\text{Cl}_2$  at  $\alpha = 0.5$  was 20.0% with  $Q/W_i$  ratio of 800 mL·min<sup>-1</sup>·g<sup>-1</sup>, which was significantly lower than 37.9% with  $Q/W_i$  ratio of 100 mL·min<sup>-1</sup>·g<sup>-1</sup>.

## 4. Conclusions

The chemical reaction between  $\text{Li}_2\text{CO}_3$  and  $\text{Cl}_2$  was investigated for various reaction temperatures,  $Q/W_i$  ratios, and  $p\text{Cl}_2$  values. The reaction temperature was identified

as a key parameter that determines the maximum  $\alpha$  value, and at least 500°C was required for complete conversion of  $\text{Li}_2\text{CO}_3$  into  $\text{LiCl}$ . The relationship between the  $Q/W_i$  ratio and  $\alpha$  value revealed that the overall reaction rate is under control of  $\text{Cl}_2$  mass transfer in the gas at 650°C. The key outcomes of this work show that the reaction between  $\text{Li}_2\text{CO}_3$  and  $\text{Cl}_2$  is fast at 650°C, and this reaction is strongly suggested as a mechanism which takes place at the anode during the high-voltage OR operation to limit the accumulation of  $\text{Li}_2\text{CO}_3$  in the salt.

## Acknowledgements

This work was sponsored by the Nuclear R&D program of the Korean Ministry of Science and ICT (2017M2A8 A5015077).

## REFERENCES

- [1] C.E. Stevenson, *The EBR-II Fuel Cycle Story*, 53-198, La Grange park, Illinois (1987).
- [2] H. Lee, G.I. Park, K.H. Kang, J.M. Hur, J.G. Kim, D.H. Ahn, Y.Z. Cho, and E.H. Kim, "Pyroprocessing Technology Development at KAERI", *Nucl. Eng. Technol.*, 43(4), 317-328 (2011).
- [3] S.D. Herrmann, S.X. Li, M.F. Simpson, and S. Phongikaroon, "Electrolytic Reduction of Spent Nuclear Oxide Fuels as Part of an Integral Process to Separate and Recover Actinides From Fission Products", *Sep. Sci. Technol.*, 41(10), 1965-1983 (2006).
- [4] Y. Sakamura and T. Omori, "Electrolytic Reduction and Electrowinning of Uranium to Develop Pyrochemical Reprocessing of Oxide Fuels", *Nucl. Technol.*, 171(3), 266-275 (2010).
- [5] E.Y. Choi, J. Lee, D.H. Heo, S.K. Lee, M.K. Jeon, S.S. Hong, S.W. Kim, H.W. Kang, S.C. Jeon, and J.M. Hur, "Electrolytic Reduction Runs of 0.6 kg Scale-Simulated Oxide Fuel in a  $\text{Li}_2\text{O}$ - $\text{LiCl}$  Molten Salt Using Metal Anode Shrouds", *J. Nucl. Mater.*, 489, 1-8 (2017).
- [6] W. Park, E.Y. Choi, S.W. Kim, S.C. Jeon, Y.H. Cho, and J.M. Hur, "Electrolytic Reduction of a Simulated Oxide Spent Fuel and the Fates of Representative Elements in a  $\text{Li}_2\text{O}$ - $\text{LiCl}$  Molten Salt", *J. Nucl. Mater.*, 477, 59-66 (2016).
- [7] S.K. Lee, M.K. Jeon, S.W. Kim, E.Y. Choi, J. Lee, S.S. Hong, S.C. Oh, and J.M. Hur, "Evaluation of Pt Anode Stability in Repeated Electrochemical Oxide Reduction Reactions for Pyroprocessing", *J. Radioanal. Nucl. Chem.*, 316(3), 1053-1058 (2018).
- [8] J.M. Hur, J.S. Cha, and E.Y. Choi, "Can Carbon be an Anode for Electrochemical Reduction in a  $\text{LiCl}$ - $\text{Li}_2\text{O}$  Molten Salt?", *ECS Electrochem. Lett.*, 3(10), E5-E7 (2014).
- [9] H.Y. Ryu, S.M. Jeong, Y.C. Kang, and J.G. Kim, "Electrochemical Carbon Formation From a Graphite Anode in  $\text{Li}_2\text{O}/\text{LiCl}$  Molten Salt", *Asian J. Chem.*, 25(12), 7019-7022 (2013).
- [10] S.W. Kim, M.K. Jeon, H.W. Kang, S.K. Lee, E.Y. Choi, W. Park, S.S. Hong, S.C. Oh, and J.M. Hur, "Carbon Anode With Repeatable Use of  $\text{LiCl}$  Molten Salt for Electrolytic Reduction in Pyroprocessing", *J. Radioanal. Nucl. Chem.*, 310(1), 463-467 (2016).
- [11] S.W. Kim, D.H. Heo, S.K. Lee, M.K. Jeon, W. Park, J.M. Hur, S.S. Hong, S.C. Oh, and E.Y. Choi, "A Preliminary Study of Pilot-Scale Electrolytic Reduction of  $\text{UO}_2$  Using a Graphite Anode", *Nucl. Eng. Technol.*, 49(7), 1451-1456 (2017).
- [12] E. Nakamura, H. Takata, Y. Yokoyama, and H. Miyamoto, Process for producing metallic lithium, US patent No. 8,911,610 B2 (2014).
- [13] D.R. Lide, *CRC Handbook of Chemistry and Physics*, Internet version 2006, 4-70, Taylor and Francis, Boca Raton, FL (2006).
- [14] J.W. Kim and H.G. Lee, "Thermal and Carbothermic Decomposition of  $\text{Na}_2\text{CO}_3$  and  $\text{Li}_2\text{CO}_3$ ", *Metall. Mater. Trans. B*, 32(1), 17-24 (2001).