Electrochemical Carbon Formation from a Graphite Anode in $\text{Li}_2\text{O}/\text{LiCl}$ Molten Salt†

HYO YEOL RYU¹, SANG MUN JEONG^{1,*}, YUN CHAN KANG² and JEONG-GUK KIM³

¹Department of Chemical Engineering, Chungbuk National University, Heungduk-gu, Cheongju-si, Chungbuk 361-763, Republic of Korea

²Department of Chemical Engineering, Konkuk University, Gwangjin-gu, Seoul 143-701, Republic of Korea

³Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, 305-353, Republic of Korea

*Corresponding author: Fax: +82 43 2692370; E-mail: smjeong@chungbuk.ac.kr

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Electrochemical carbon formation from a graphite anode has been investigated in an LiCl molten salt containing oxygen ions. Carbon can be formed *via* various chemical or electrochemical routes. The carbon dust produced during electrolysis probably contaminates the salt and it leads to a decrease of the current efficiency and the purity of the metal product. A possible reaction path for carbon formation during electrolysis has been proposed in this study.

Key Words: Carbon formation, Graphite anode, LiCl , Molten salt, Carbonate.

INTRODUCTION

Recently, the molten salt electrolysis for the metal production has been focused on due to its simplicity and economic and environmental advantages¹⁻⁵. Carbon based anodes such as those made of graphite or glassy carbon have been widely used in electrolysis or electrochemical reduction⁶. It has been reported that a problem in employing carbon as an anode is the accumulation of carbon dust in the salt, which may cause the electrical short circuit⁷. Therefore, the stability of anodes in the molten salt is an important factor because of the process economics and operability⁶.

It is important to understand the electrochemical behaviours of graphite anodes; these behaviours could allow us to prevent the unexpected formation of carbon dust during the electrochemical run. In the present work, possible chemical and electrochemical routes for carbon formation have been suggested by thermodynamic calculation and electrochemical experiment.

EXPERIMENTAL

Various concentrations of $\text{Li}_2\text{O}/\text{LiCl}$ salt were used as electrolyte in this work. The experimental apparatus can be installed according to previous publication⁵. In order to investigate the electrochemical behaviour of a graphite anode, a graphite rod (1 cm^2 of surface area) was used as a working electrode for cyclic voltammetry measurement. Also, an Ni/NiO electrode was employed as a reference electrode.

Constant voltage electrolysis was also conducted at 650 °C in 3 wt % $\text{Li}_2\text{O}/\text{LiCl}$ molten salt to observe the carbon formation in the salt. In the constant voltage electrolysis performed, a stainless steel rod of 3 mm diameter and a graphite rod 10 mm in diameter were used as cathode and anode, respectively. The cathode was separated from the anode by a porous MgO diaphragm in order to prevent any electrical short circuit by the extracted lithium metal. The standard state thermodynamic data related to the electrochemical formation of carbon was obtained by using the HSC chemistry 6.0 program.

RESULTS AND DISCUSSION

Electrochemical behaviour of a graphite anode by cyclic voltammetry: Fig. 1 shows cyclic voltammograms at various Li_2O concentrations in the LiCl molten salt. In Fig. 1(a), it might be possible to ascribe the anodic wave at 0.8 V to the decomposition of water or hydroxide ion as an impurity and the rising oxidation current at 1.5 V might be caused by the oxidation of Cl^- ion to Cl_2 gas. An anodic current peak appears near -0.4 V, assigned to the formation of CO or CO_2 gas, after the adding of Li_2O to the salt; this peak gradually increases with increase of the Li_2O concentration up to 5 wt %. It was reported that CO_2 is more actively produced than CO at 650 °C⁷. As the potential is swept to a more positive direction, an increase in the anodic current at 0.9 V might be related to the evolution of O_2 gas. The anodic reactions are as follows:

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Thermodynamic evaluation of the electrochemical carbon formation: The thermodynamic data were calculated to predict the carbon formation when the graphite anode was employed in $\text{Li}_2\text{O}/\text{LiCl}$ molten salt. Once CO or CO_2 gas is produced on the anode surface, the redox reaction of the chemical equilibrium mixture, the so called Boudouard reaction, probably takes place. This is the disproportionation of CO into CO_2 and C or its reverse.

Fig. 1. Cyclic voltammograms of a graphite rod at 650 °C in Li_2O - LiCl molten salt. The concentration of Li_2O was (a) 0 wt %, (b) 1 wt %, (c) 3 wt % and (d) 5 wt %, respectively

Fig. 2 shows the thermodynamic data for reaction (4). Since the Gibbs's free energy change for the Boudouard reaction exhibits a negative value at temperatures lower than 650 °C, the forward reaction takes place favourably in the standard state. The equilibrium constant (pK) is also plotted in Fig. 2(a). pK increases with an increase in the temperature. Fig. 2(b) shows the equilibrium partial pressure ratio between

Fig. 2. (a) Gibbs's free energy change and chemical equilibrium constant for Boudouard reaction. (b) Equilibrium partial pressure between CO and CO_2 at 650 °C for reaction (4)

CO and CO_2 . Fig. 2 suggests that an excessive formation of CO on the anode might lead to carbon dust in the salt according to reaction (4). Also, a concentration of CO_2 higher than the equilibrium concentration might consume the graphite anode to form CO . CO and CO_2 released can chemically react with Li_2O in the salt phase to form Li_2CO_3 , as follows:

The Gibb's free energy changes for reactions (5) and (6) exhibit negative values in a temperature window between 400° and 900 °C (Fig. 3). Thus, reactions (5) and (6) could take place spontaneously and reaction (6) would become another route for carbon formation from the graphite anode. Also, the ionized Li_2CO_3 (Li^+ ion and CO_3^{2-} ion) could be electrochemically decomposed during electrolysis to give carbon deposit on the cathode surface as according to the following reaction^{8,9}:

Fig. 3. Gibb's free energy change for reaction (5) and (6)

Fig. 4 shows the Gibb's free energy change and the standard decomposition voltage for decomposition of Li_2CO_3 were 494 kJ and 1.28 V at 650 °C, respectively. These results suggest that the carbon deposit is easily produced on the cathode surface. A possible reaction path-way for undesirable carbon formation can be proposed when the graphite anode is used for molten salt electrolysis in the presence of oxide ion

Fig. 4. Gibb's free energy change and standard decomposition voltage for Li_2CO_3 decomposition reaction; $\text{Li}_2\text{CO}_3 (2\text{Li}^+, \text{CO}_3^{2-}) \rightarrow \text{C} + \text{O}_2 (\text{g}) + \text{Li}_2\text{O}$

(Fig. 5). During electrolysis, the carbon anode is electrochemically reacted with the oxide ions and the evolution of CO or CO_2 gas as the anode reaction takes place. According to the Boudouard reaction, the concentration of CO and CO_2 gases reaches equilibrium. The CO_x gas might chemically react with Li_2O in the salt phase to form Li_2CO_3 and carbon dust. Thereafter, the ionized carbonate proceeds with the electrode reaction to give the carbon deposit on the cathode. Such carbon dust formed through various chemical or electrochemical reaction routes would eventually bring about a decrease in the current efficiency and lower the purity of metal product.

Fig. 5. Possible reaction path of electrochemical carbon formation

Visual observation of the carbon formation after electrolysis: To confirm carbon dust during electrolysis, constant voltage electrolysis was carried out in the 3wt% $\text{Li}_2\text{O}/\text{LiCl}$ molten salt. Fig. 6(a) shows the current-time graph during electrolysis of Li_2O from the salt. After applying 3.2 V, the response current decreases sharply due to the mass transfer effect during the initial stage. Then, the current gradually increases, which is probably due to the electrochemical carbon formation by reactions (6) and (7). The carbon dust electrochemically produced is dispersed in the salt phase: this dust is likely to contaminate the salt and to provide an electrical short circuit between the cathode and the anode^{6,7}. Fig. 6(b) shows the solidified salt contaminated by carbon dust. The used graphite anode is shown in Fig. 6(c), indicating that it can be consumed to form carbon dust in the $\text{Li}_2\text{O}/\text{LiCl}$ molten salt.

Fig. 6. (a) Current-time graph during electrolysis and photographs of (b) the solidified salt and (c) the used graphite anode after electrolysis

Conclusion

Electrochemical carbon formation from a graphite anode has been investigated in $\text{Li}_2\text{O}/\text{LiCl}$ molten salt. During electrolysis, the carbon particles from a graphite anode react with oxide ions to release CO or CO_2 gas as the anode reaction.

The concentrations of CO and CO₂ might reach chemical equilibrium via the Boudouard reaction. Also, CO and CO₂ gases are likely to proceed in a chemical reaction with Li₂O to form Li₂CO₃ and carbon dust in the salt. The ionized carbonate ion could be electrochemically decomposed to carbon and oxide ions at the cathode. The results obtained in this work indicate that carbon can be formed from several routes including chemical or electrochemical routes. The carbon dust produced during electrolysis probably contaminates the salt and leads to a decrease of the current efficiency and of the purity of the metal product.

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