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Preparation of metallic niobium from niobium pentoxide by an indirect electrochemical reduction in a LiCl-Li_2O molten salt

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Abstract

The indirect electrolytic reduction of Nb_2O_5 has been investigated to produce metallic niobium powder in an electrolysis cell with a unique cathode assembly which consists of an electric conductor, solid oxide and magnesia membrane. The metallic niobium powder has been prepared by the mechanism of an electrode reaction followed by a chemical reaction in a LiCl-Li_2O molten salt at 650 °C. The overall cathodic and the anodic reactions are the reduction of Nb_2O_5 and the formation of O_2 gas, respectively. The XRD analysis suggests that the lithium niobates are fully converted to the metallic niobium by supplying 1.5-fold charges to the theoretical charges. The obtained results demonstrate that the electrolytic reduction technology by using a LiCl-Li_2O molten salt is an efficient tool for preparing metallic niobium from Nb_2O_5.

Keywords: Nb_2O_5; Metallic niobium; $LiNbO_3$; Indirect electrolytic reduction; LiCl-Li_2O molten salt

1. Introduction

Metallic niobium is important in the production of high-temperature-resistant alloys and special stainless steels. Also, its most interesting applications are in the field of superconductivity. It is well known that niobium is a promising radio-frequency superconductor and niobium-based alloys, such as NbTi and Nb_3Sn, are superconducting materials [1,2].

The most widely used technique to prepare niobium is the aluminothermic process, where niobium in Nb_2O_5 is displaced by aluminum through a direct physical contact between the Nb_2O_5 feed and the metal reductant of Al to form niobium metal and alumina at a temperature above the melting point of niobium [3]. This conventional process for the production of niobium has several drawbacks from viewpoint of an energy saving, waste management and simplicity. Recently, an electrochemical reduction process has been focused on to prepare various metallic particles [2–9]. Various molten salt systems have been used for an electrolytic production of pure metal powders from their oxides. Yan and Fray [2] carried out an electro-deoxidation of Nb_2O_5 to niobium powder by applying a voltage, below the decomposition potential of a eutectic $CaCl_2$-NaCl molten salt. Chen et al. [4] proposed a direct electrochemical reduction of titanium oxide to titanium in a molten $CaCl_2$ salt. The novel electrochemical method, so called the FFC Cambridge process by using a eutectic $CaCl_2$-NaCl salt system, is a much easier, less expensive and more environmentally friendly process than the conventional metallurgical routes [4]. Park et al. [5] employed a $CaCl_2$ as an electrolyte for the preparation of metallic titanium from TiO_2. Grinevitch et al. [11] investigated the interaction between K_2NbF_7-KCl-NaCl melt and niobium oxides by an electrochemical method. NbTi and Nb_3Sn superconductors were prepared from their oxide precursors in a $CaCl_2$-based molten salt [12].

Our research group has investigated the indirect electrolytic reduction of metal oxides to prepare metallic particles in a LiCl-Li_2O molten salt [7–10]. The novel concept of the electrolytic reduction process is to reduce the metal oxides to their metallic forms by combining an electrode reaction and a chemical reaction. We have designed a unique cathode assembly with a porous magnesia membrane to realize a metallization of the oxides. By using a porous magnesia membrane, the fine metal oxide powder is used for a preparation of the metallic powder without a pelletizing process.

In this work, we have investigated the reduction of Nb_2O_5 to produce metallic niobium powder in an electrolysis cell. The chronopotentiometry method has been employed for the preparation of metallic niobium in a LiCl-3 wt% Li_2O molten salt

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system. This paper reports on the mechanism for the indirect electrolytic reduction of Nb_2O_5 and the behavior of the Li_2O concentration during the electrolytic run.

2. Experimental

2.1. Chemicals and reagents

The chemicals used as a molten salt were anhydrous lithium chloride (LiCl) and lithium oxide (Li_2O). All the chemicals were analytical grade and used as received without any further purification. LiCl and Li_2O were reserved in a glove box where an inert atmosphere was maintained by an Ar gas flow to prevent absorption of the water vapor. The niobium pentoxide (Nb_2O_5) used in this study was 99.97 % pure, with mean particle sizes of 7.5 μm.

2.2. Experimental apparatus

The electrochemical reduction units consisted of Ar gas and reactant feeding systems, an electrolysis cell and a temperature controller. Fig. 1 shows the experimental apparatus for the electrolytic reduction of the Nb_2O_5 powder. The electrolysis cell was composed of a resistance furnace, a K-type thermocouple, alumina and magnesia crucibles, three anodes, a cathode assembly, and a reference electrode. The cathode assembly consisted of a stainless steel conductor, Nb_2O_5 powder and a non-conductive porous magnesia membrane. Nb_2O_5 powder was filled in between a stainless steel conductor and a magnesia membrane. 3 Pt rods were used as the anode electrode. Also, a Pt quasi-reference electrode was used for measuring the anode and cathode potentials during the experiments.

2.3. Experimental procedure

The electrolyte in this work was Li_2O-LiCl molten salt. The electrolysis cell was flushed with high purity argon gas while it was heated to the required temperature. The performance test of the electrochemical system was carried out at 650 °C under an Ar atmosphere. Inert Ar gas continuously conveyed the oxygen gas out of the reactor to maintain a constant oxygen partial pressure which can affect the anode potential. A line for cooling water was installed at an upper flange to prevent an evaporation of the molten salt. Nb_2O_5 powder of 7 g and LiCl of 270 g were introduced into the reactor at room temperature, respectively. The reactor was heated up and maintained at 650 °C. And then Li_2O was fed into the reactor to reach a concentration of *ca*. 3 wt% of the total molten salt. After a complete melting of the Li_2O in the LiCl molten salt, the electrolysis cell was operated by applying a desirable current with a potentiostat. During the run, the variation of the Li_2O concentration in the molten salt was checked by the titration method as follows: The molten salt sample of about 0.4 g was taken from the electrolysis cell by using a pipette and it was dissolved in distilled water. And then the dissolved alkali solution was titrated with 0.1 N HCl. After a completion of the reaction, the cathode part was separated from the cell. And then the reduced metallic niobium was taken out of the magnesia membrane. Thereafter, the product was washed with deionized water and dried in a vacuum oven to avoid a re-oxidation. The final sample was kept in a glove box under an inert Ar atmosphere.

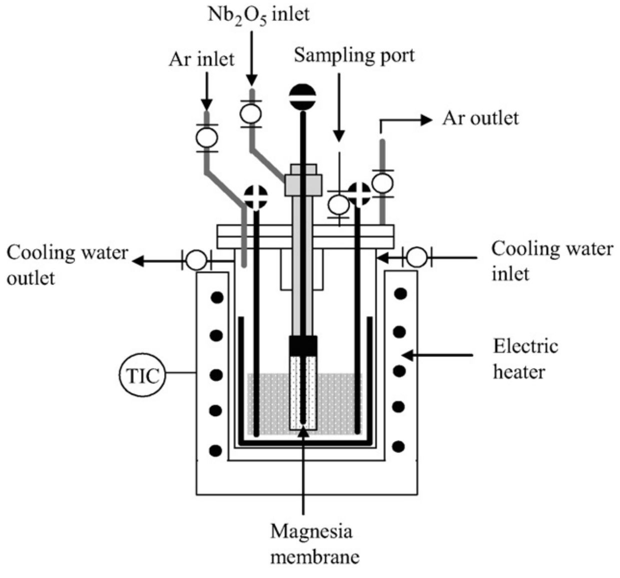

Fig. 1. Experimental setup for the electrolytic reduction of Nb_2O_5.

3. Results and discussion

Nb_2O_5 powder was maintained in the LiCl-Li_2O molten salt without applying a current at 650 °C to investigate a chemical change of Nb_2O_5 in the molten salt. The X-ray diffraction (XRD) method was used to analyze the crystalline structure of the fresh Nb_2O_5 and the other products with a variation of the treatment time in the molten salt, as can be seen in Fig. 2. The characteristic peaks of Nb_2O_5 gradually decrease with the treatment time and they disappear after a reaction time of 10 h. On the other hand, the characteristic peaks of $LiNbO_3$ and $LiNb_3O_8$ sharply increase with time, which is possibly due to the reaction between Nb_2O_5 and Li_2O. Also, the characteristic peak of NbO_2 is observed as minor peaks after a treatment time of 5 h. This result suggests that Nb_2O_5 is changed to $LiNbO_3$ or $LiNb_3O_8$ as intermediate reaction products in the molten salt phase during the electrochemical run. Yan and Fray [2] reported that $Ca(NbO_3)_2$ as an intermediate is formed by a reaction between CaO and Nb_2O_5 in the presence of CaO in the molten salt. It has also been reported that the $LiTaO_3$ phase is formed and it is eventually reduced to

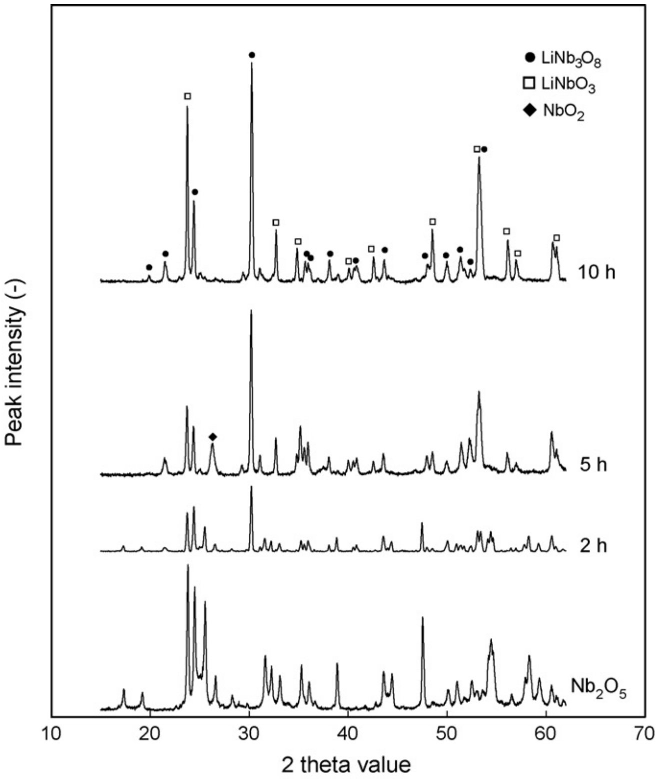

Fig. 2. X-ray diffraction patterns of Nb_2O_5 with a variation of the treatment time in the LiCl-Li_2O molten salt at 650 °C.

Ta metal during an electrolytic reduction of Ta_2O_5 in a LiCl-Li_2O molten salt [9]. Jiang et al. [13] reported the formation of $CaTiO_3$ during an electrochemical reduction of TiO_2 in a $CaCl_2$ melt.

The chronopotentiometric technique, where the potential is measured as a function of the time at a constant current, has been employed to electrochemically reduce Nb_2O_5 to Nb metal. The standard decomposition potentials of pure LiCl, Li_2O, Nb_2O_5 and $LiNbO_3$ at 650 °C can be calculated to 3.46, 2.47, 1.55 and 1.90 V, respectively [7]. The cell voltage (2.47–3.46 V) for a selective decomposition of Li_2O to produce Li metal without a decomposition of LiCl was suggested in our previous work [7–9]. In this cell voltage, Li metal and O_2 gas are produced by the electrolysis of Li_2O at the cathode and the anode, respectively. Fig. 3 shows the chronopotentiometric curves obtained with constant currents of 0.8 and 2.0 A. The anode and cathode potentials sharply decrease at the initial stage of a run and exhibit a pseudo-steady state, where they vary slowly with the reaction time. An initial transition stage in Fig. 3 is much longer than that in the electrolytic reduction of Ta_2O_5 reported in our previous work [7]. In this work, the cell voltage at a pseudo-steady state was somewhat lower than the theoretical operating window (2.47–3.46 V) for a selective decomposition of Li_2O in the electrolysis cell. Li_2O may be decomposed at a lower potential due to the EC mechanism in this work, where the cathode potential for the reduction of Li^+ shifts toward positive potentials [14]. It is noticeable that a sharp drop in the cathode potentials takes place at the latter part of the electrolytic run. Such a drop probably represents the transition of the reaction mechanism in the cathode. In the initial stage of the electrolytic run, the Li metal produced by the electrolysis of Li_2O is consumed by the chemical reaction with metal oxides such as Nb_2O_5 and $LiNbO_3$ to form metallic niobium and Li_2O in the inside of the cathode assembly. The resultant Li_2O is ionized to Li^+ and O^{2-}. This mechanism can be classified with a well-known EC mechanism, which includes an electrode reaction followed by a chemical reaction [14]. As the reaction proceeds, the niobium oxides as a reactant are gradually reduced to a metallic form and the amount of the niobium oxides becomes much smaller than that of the metallic niobium at the latter part of the run. In this case, the rate of Li generation exceeds the rate of Li consumption by a reaction with the niobium oxides. This result brings about the deposition of Li metal in the inside of the cathode, which probably leads to a sharp drop in the cathode potential. It has been reported that a similar drop in the cathode potential is due to a transition to a cathode potential which is representative of a lithium deposition potential in an electrochemical reduction of uranium oxides [15]. Also, the O^{2-} ion formed in the cathode moves to the anode across the solid oxide layer and the magnesia wall, and the bulk electrolyte. And then, the O^{2-} ion is eventually evolved as oxygen gas from the anode surface [7]. The anode potential gradually increases due to not only a decrease in the Li_2O concentration of the electrolyte bulk by Li_2O electrolysis, but also an oxidation of the Pt electrode surface [9].

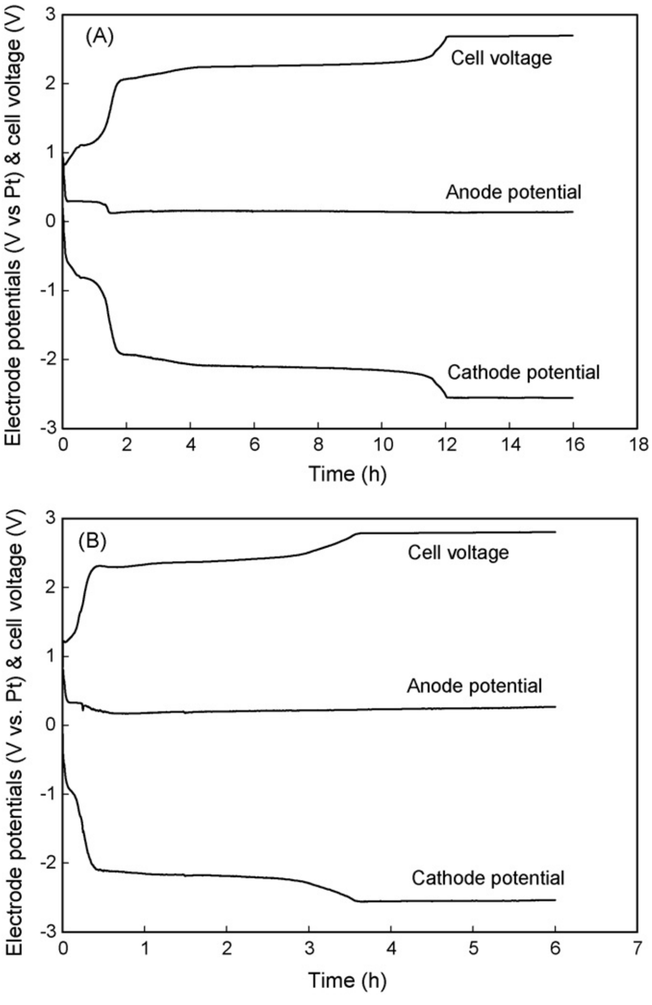

Fig. 3. Chronopotentiogram of the electrolytic reduction of Nb_2O_5 in the LiCl-3 wt% Li_2O molten salt at 650 °C. The applied current was (A) 0.8 A and (B) 2.0 A.

The reaction at the cathode part can be summarized as follows:

$$\text{Electrode reaction}: \quad Li^+ + e^- \rightarrow Li \tag{1}$$

$$\text{Chemical reactions}: \quad Nb_2O_5 + 10Li \rightarrow 2Nb + 10Li^+ + 5O^{2-} \tag{2}$$

$$LiNbO_3 + 5Li \rightarrow Nb + 6Li^+ + 3O^{2-} \tag{3}$$

$$LiNb_3O_8 + 15Li \rightarrow 3Nb + 16Li^+ + 8O^{2-} \tag{4}$$

The lithium niobates such as $LiNbO_3$ and $LiNb_3O_8$ are formed by the chemical reactions between Nb_2O_5 and Li_2O at the cathode assembly as described previously. The overall reaction at the cathode is as follows:

$$Nb_2O_5 + 10e^- \rightarrow 2Nb + 5O^{2-} \tag{5}$$

Also, at the anode;

$$O^{2-} \rightarrow 1/2O_2 \quad (g) + 2e^- \tag{6}$$

Fig. 4 shows the reaction scheme of an indirect electrolytic reduction of Nb_2O_5 in the LiCl-Li_2O molten salt.

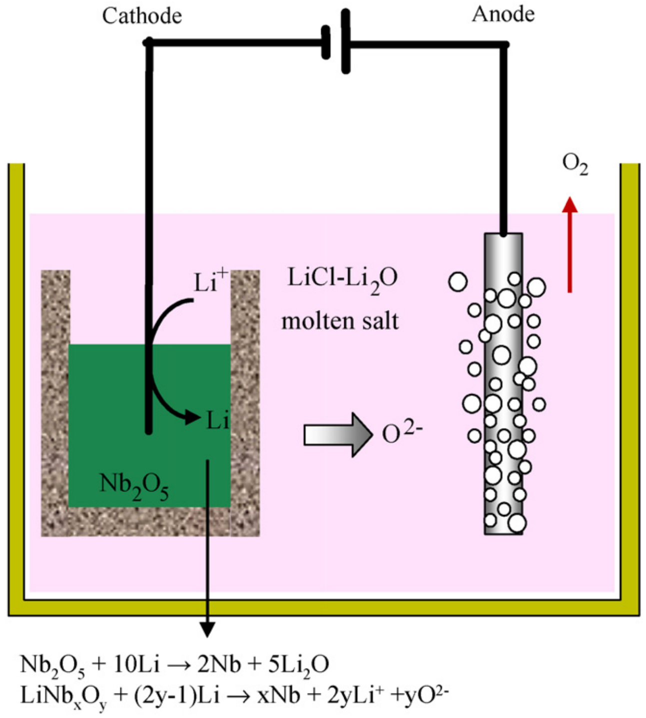

Fig. 4. Process concept of the electrolytic reduction of Nb_2O_5 in a LiCl-3 wt% Li_2O molten salt at 650 °C.

The EC mechanism, where the Li metal takes part in the reduction of niobium oxide, may be evidenced by the behavior of Li_2O during the reduction of Nb_2O_5. The Li_2O concentration in the molten salt was measured during the electrolytic production of metallic niobium. Fig. 5 shows the variation of the Li_2O concentration in the electrolyte bulk during the electrolytic runs with 0.8 and 2.0 A. As can be seen, the amount of Li_2O in the molten salt decreases according to Faraday's law of an electrolysis regardless of the applied current, indicating that the electrochemical reduction of Nb_2O_5 proceeds via an electrolysis of Li_2O. On the other hand, the concentration of the O^{2-} ion gradually increases in the cathode according to reactions (2)–(4). As a result, the O^{2-} ion moves to the electrolyte bulk by diffusion due to a difference in the Li_2O concentration between the inside and the outside of the magnesia basket. That is why the Li_2O concentration of the electrolyte bulk is higher than the theoretical value at the latter part of the run in Fig. 5. Such a diffusion of the O^{2-} ion from the cathode to the electrolyte bulk helps to prevent a depletion of the Li_2O in the electrolyte bulk during the reduction of metal oxides. This concept allows for a decrease in the reactor volume and in the operating cost as well as a stable operation in a large-scale reactor [9].

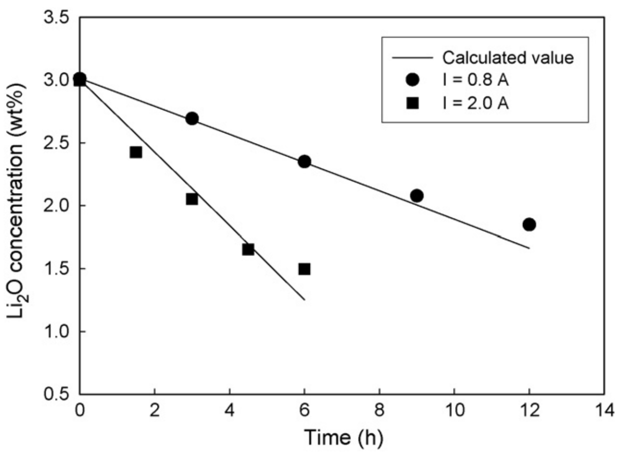

Fig. 5. Variation of the Li_2O concentration in the electrolyte as a function of the reaction time.

Fig. 6. Photograph of the reduced sample after the electrolytic run.

After the completion of the electrolytic run, the magnesia basket is removed from the cathode assembly to collect the metal powder. Fig. 6 shows the cathode assembly from which the magnesia basket is removed after the electrolytic run. The metallic niobium containing the molten salt sticks to the cathode conductor even after the removal of the magnesia basket. Pure metallic powder was collected after washing and drying of this mixture.

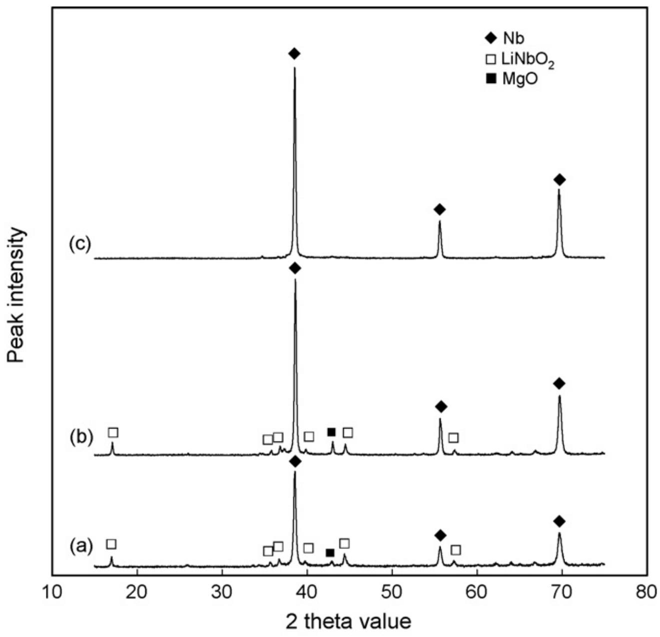

Fig. 7. X-ray diffraction patterns of the reduced sample with a variation of the supplied charges; (a) 100%, (b) 120% and (c) 150% charges of the theoretical charges necessary for the complete reduction of Nb_2O_5.

The crystalline structure of the reduced samples after the electrolytic reduction for various periods of times has been determined by the XRD method. In this work, we supplied 100 (5 h at 1.2 A), 120 (6 h at 1.2 A) and 150% (7.5 h at 1.2 A) of the theoretical charges necessary for a complete reduction of Nb_2O_5, respectively. As can be seen in Fig. 7(a and b), the characteristic peaks of $LiNbO_2$ were observed as a minor product besides the main peaks at $2\theta = 38.5$, 55.6 and 69.5 assigned to the metallic niobium. This result indicates that the mixed oxides such as $LiNbO_3$ or $LiNb_3O_8$, which are formed in the cathode during the electrolytic run, may be reduced to the metallic niobium via a lower oxidation state such as $LiNbO_2$. These $LiNbO_2$ peaks disappear due to conversion to the metallic niobium by supplying 1.5-fold charges to the theoretical value as can be seen in Fig. 7(c). The characteristic peak intensity of metallic niobium increases with the electrolysis duration which is associated with the amount of supplied charges. By an elemental analysis, the oxygen content was found to be 0.38 wt% in the sample treated during 7.5 h at 1.2 A.

4. Conclusions

The characteristics of an indirect electrochemical reduction of Nb_2O_5 have been investigated for a preparation of metallic niobium. $LiNbO_3$ and $LiNb_3O_8$ as intermediates during the electrolytic production of metallic niobium are formed by a reaction between Nb_2O_5 and Li_2O in the molten salt phase. The produced lithium niobates as well as Nb_2O_5 are successfully reduced to metallic niobium according to the following reactions;

$$Li^+ + e^- \rightarrow Li$$

$$Nb_2O_5 + 10Li \rightarrow 2Nb + 10Li^+ + 5O^{2-}$$

$$LiNb_xO_y + (2y-1)Li \rightarrow xNb + 2yLi^+ + yO^{2-}$$

Also, oxygen gas is produced by an electrolysis of Li_2O and an ionization of the lattice oxygen of Nb_2O_5 at the anode. The Li_2O concentration in the molten salt decreases according to Faraday's law of an electrolysis up to the reaction time regardless of the applied current, indicating that the electrochemical reduction of Nb_2O_5 proceeds via an electrolysis of Li_2O. This work suggests that the indirect electrolytic reduction technology by using a LiCl-Li_2O molten salt is an efficient tool for preparing metallic niobium from Nb_2O_5.

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