ELECTROWINNING OF METALLIC LITHIUM
FROM MOLTEN SALTS

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ABSTRACT

The cathodic behavior during electrolysis in LiCl-KCl eutectic melt has been studied under various currents and temperatures as part of developing a new process to produce lithium using Li$_2$CO$_3$ as a source of lithium. Electrolysis was carried out easily and the change of electrolyte near the cathode and anode was observed visually. The current efficiency of lithium deposition decreased at both lower and higher current under the condition of constant total electricity, and also decreased monotonously with increasing temperature at constant current. Furthermore, the use of a porous diaphragm between the cathode and anode increased current efficiency dramatically. It is considered based on the results that the decrease of current efficiency is mainly due to the reaction between lithium deposited and chlorine evolved at anode the and dissolved into the electrolyte. Furthermore, the content of potassium and sodium as the impurities in lithium metal were 0.18at% and 0.16at%, respectively.

INTRODUCTION

Lithium metal is widely used as an anode material for lithium primary batteries. However it is expensive and improvements to the production process are required to reduce the cost. In current process, metallic lithium is produced electrolytically by using molten eutectic LiCl-KCl electrolyte. This process has some problems. The source of lithium ion for the cathodic reaction is the electrolyte itself. This means that LiCl in the electrolyte is consumed during electrolysis and that LiCl must be fed into the electrolyte continuously to maintain the eutectic composition. Secondly, the working temperature for the electrolysis is considerably higher than the melting point of lithium. Furthermore, LiCl is expensive and is not easily handled due to its hygroscopicity.

To reduce the cost for producing lithium, a new process using a material other than LiCl for the source of lithium is required. A possible alternative material is Li$_2$CO$_3$ which is less expensive and is stable in the atmosphere due to its non-hygroscopic property. The reason why Li$_2$CO$_3$ less expensive is as follows: most lithium sources are aqueous solution sand Li$_2$CO$_3$ can be precipitated by adding carbonates. As a result, the primary lithium compounds is Li$_2$CO$_3$. This makes Li$_2$CO$_3$ cheap and pure, compared to other lithium salts such as LiCl.
Authors (1,2) have successfully used Li$_2$CO$_3$ as a lithium source for producing Al-Li alloys at 973K and have obtained high quality alloys at high current efficiency about 95%. For obtaining lithium metal, it is desired that the working temperature be reduced by finding alternative electrolyte to LiCl-KCl eutectic. Fray (3) has tried to produce lithium by using a chloride-carbonate melt. However, the working temperature is still high, about 800K.

In this work, the cathodic behavior in LiCl-KCl eutectic was studied as part of a project to produce lithium metal by using Li$_2$CO$_3$ as a source of lithium based on the electrochemical measurements and the current efficiency of the electrolysis.

**EXPERIMENTAL**

The apparatus used is shown in Figure 1. A melt container made of Pyrex glass, which contains LiCl-KCl eutectic electrolyte, is placed in a quartz outer tube with a water-cooled glass cap as an electrode holder. The cathode was assembled from three tungsten wires of 0.5mm diameter. Tungsten was chosen due to its chemical stability. A platinum screen was used as a cathode however, it became brittle and breakable, likely due to alloying by lithium. Furthermore, the cathodic potential was unstable. The anode was a high purity graphite rod 5mm in diameter. The reference electrode consisted of a silver wire and a small amount of melt sealed into a mullite tube. The melt mixture contained 5mol% AgCl dissolved into LiCl-KCl eutectic into which the silver wire was immersed. These electrodes and a thermocouple sheath were immersed into the electrolyte after melting. A transparent glass furnace was used so that the electrodes could be monitored visually. Prior to the experiment, the whole apparatus was evacuated and the atmosphere was replaced with argon, which was also introduced from an inlet during the experiment to remove the chlorine evolved at the anode.

The experimental method was controlled current electrolysis under various conditions. The current efficiency of lithium deposition was determined by measuring the volume of the hydrogen evolved as the product of the reaction between the lithium obtained and water. Cathodic and anodic potentials were measured simultaneously by using the current interruption method to determine the decomposition potential of LiCl. The interruption time was relatively long, typically 5s because the potential, especially at the cathode, changed slowly after interrupting the current. This was likely due to the concentration overpotential due to the consumption of LiCl in the melt near the cathode. After electrolysis the content of potassium and sodium as impurities in the metal were determined by using atomic emission spectroscopy.

The LiCl and KCl used were reagent grade chemicals and were purified by injecting dry HCl into individual melts (4). A eutectic mixture was prepared by mixing and melting the purified salts sealed in a glass tube under vacuum.
RESULTS AND DISCUSSION

Experiments were performed in the temperature range between 648K and 753K and in the current range from 100mA to 800mA. Only current is described in this paper because the current density was not well defined at the cathode where the initial tungsten wire cathode was thin and the surface area of lithium metal increased during electrolysis. The cathodic and anodic reactions and their potentials are as follows,

$$\text{Li}^+ + e^- = \text{Li}$$ \hspace{1cm} [1]

$$\text{Cl}^- = (1/2) \text{Cl}_2 + e^-$$ \hspace{1cm} [2]

where $a_{\text{Li}^+}$, $a_{\text{Cl}^-}$ and $P_{\text{Cl}_2}$ should be unity, and $a_{\text{Li}^{*+}}$ is a variable and dependent on the experimental conditions. $a_{\text{Li}^{*+}}$ should be about 0.6 by assuming Temkin's model in the bulk of LiCl-KCl eutectic melt. The result of a typical electrode potential measurement is shown in Figure 2. The anodic potential shifted in the negative direction quickly after the current interruption. However, the cathodic potential shifted in the positive direction in relatively slow manner. This phenomenon is considered to be due to the concentration overpotential as mentioned above. Namely, Li$^+$ cation is consumed during the deposition of lithium and the concentration of LiCl around the cathode decreases. This makes the cathodic potential negative and a relatively long time was required to compensate by diffusion. The decomposition potential was determined by taking the cathodic and anodic potentials 5s after the current interruption. As a result, 3.65V at 673K, which agreed well with 3.64V thermodynamically calculated for $a_{\text{Li}^{*+}} = 0.6$ in liquid state using Barin's compilation (5), was obtained. This means that the electrolysis could be essentially described thermodynamically and that no other electrode reaction such as alloying with cathode was observed.

After starting the electrolysis, the deposition and growth of lithium metal on the tungsten cathode were observed through the furnace wall. Initially, the lithium metal appears as a thin film on the surface of the tungsten wire. The lithium soon forms a spherical droplet and moves up the tungsten wire due to the very small density of lithium. Finally, the droplet was positioned at the surface of the electrolyte along the tungsten wire. The droplet was initially silver colored and the electrolyte near the droplet was transparent and colorless. However, the color of the electrolyte near the droplet became darker as the electrolysis proceeded. This is likely a metal fog of dissolved lithium in the electrolyte even though the solubility of lithium in the chloride is less than that of other alkaline metals in their molten chlorides (6). The metal fog seems to be sensitive to temperature because the dark color became deeper as the temperature increased. On the graphite anode, active evolution of chlorine bubbles and slightly yellow color to the electrolyte around the anode due to chlorine dissolution were observed.

The main cause for low current efficiency for lithium deposition is the reaction of lithium with chlorine, residual water or oxygen in the electrolyte or atmosphere. Two pathways are assumed for the reaction based on the above observation around the electrodes. One is through the metal fog. In this case, only dissolved lithium in the electrolyte as metal fog reacts while the bulk of lithium in droplet form hardly reacts with the above oxidative agents. Another is through the dissolved chlorine which reacts not only
with the metal fog but also the lithium droplet. It is important to know which pathway is responsible for decreasing the current efficiency. Figure 3 shows the current efficiency obtained for various currents at 673K when the total electricity passed was fixed at 250C. A maximum efficiency was observed at 400mA of current and the current efficiency decreased for both lower and higher currents. At high currents, much more chlorine is evolved in a given time, but metal fog was not increased compared with lower currents. This suggests that the latter pathway plays more important role than the former. It should be noted for lower current that a long time is required for completing the electrolysis due to the constant charge passed. This means time for diffusion of dissolved chlorine or metal fog in the electrolyte so the current efficiency decreases at lower current. The effect of temperature on the current efficiency at a constant current of 200mA is shown in Fig.4. It is clear that increasing temperature decreases the current efficiency monotonously. This result is reasonable because both metal fog and chlorine dissolved in the electrolyte may increase and they react easily with each other at higher temperature. As these results may still be ambiguous, an alternative experiment was performed. A porous crucible was used as a diaphragm between the cathode and anode. The crucible was made of 99.5% alumina with micro pores as a result of sintering at a temperature of about 1500K. This was immersed in the electrolyte bath shown in Figure 1, and the graphite rod anode was placed into it. This diaphragm should prevent the reaction of dissolved chlorine and lithium fog during electrolysis. The result is shown in Figure 5 on which the results of Figures 3-4 are superimposed for comparison. The current efficiency using the diaphragm was excellent, 97.4%. This suggests that the main pathway for decreasing current efficiency is the reaction of dissolved chlorine with lithium, both metal fog and bulk droplet, because the condition of metal fog should be independent of the presence of the diaphragm. If the metal fog is the main pathway, the current efficiency should not increase to such a high value because most of the metal fog does not return to form bulk lithium but is lost by reaction with any oxidative agents.

It is important to analyze the purity of the lithium obtained to assess its quality. After the experiment, the metal was separated carefully from solidified electrolyte in a glove box and was dissolved in distilled water to analyze potassium and sodium by using atomic emission spectroscopy. The composition was 0.18at% (1.03wt%) potassium and 0.16at% (0.55wt%) sodium, respectively. The origin of sodium is not clear, but is probably from a very small amount of NaCl contained in reagent grade LiCl and KCl. Sodium is easily deposited even if the concentration of NaCl is very low because the decomposition potential is on the order of KCl, LiCl and NaCl at these temperature ranges. Potassium is hardly deposited, but the concentration of KCl in the electrolyte near the cathode could be considerably higher during electrolysis because of decreasing amounts of LiCl. This promotes potassium deposition. It is likely that lowering the current will effectively reduce both the potassium and sodium contents.

CONCLUSIONS

As this work is a first step for developing a new process to produce lithium metal by means of Li₂CO₃ as a source of lithium, the factors affecting the current efficiency of the cathode was studied. Electrolysis was carried out under various conditions of temperature and current during visual observation of the electrodes. Metal fog of lithium
and chlorine dissolution into eutectic LiCl-KCl electrolyte were observed during the electrolysis. The current efficiency of lithium deposition shows a maximum at 200mA for the variation of current, and decreases monotonously with increasing temperature. Furthermore, the highest value was obtained by using a porous diaphragm between the cathode and anode. It is concluded that the main reason for decreasing the current efficiency is due to dissolved chlorine from the anode. The impurities of potassium and sodium in the lithium were found to be 0.18at% and 0.16at%, respectively.

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Figure 1. Schematic diagram of the apparatus for electrolysis.

Figure 2. Typical potential change for current interruption during the electrolysis.
**Figure 3.** Current efficiency for lithium deposition at 673K.

**Figure 4.** Temperature dependence of current efficiency for lithium deposition at constant current of 200mA.
Figure 5. Current efficiency for lithium deposition under various conditions.