

Electrowinning of Metallic Lithium from Molten Salts

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Introduction

As lithium metal is expensive and is widely used as a anode material of lithium primary battery, reducing the cost of production is required by improving the process. In current method, metallic lithium is produced by using molten eutectic LiCl-KCl electrolyte. This process has some problems. At first, the source of lithium ion for cathodic reaction is the electrolyte itself. This means that LiCl in the electrolyte is consumed in the progress of electrolysis and that LiCl must be fed into the electrolyte continuously to keep the composition. At second, the working temperature of 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, new process using other materials for the source of lithium is required. An alternative material is assumed to be Li_2CO_3 that is less expensive and is stable in the atmosphere. Another electrolyte other than LiCl-KCl eutectic should be searched to decrease the working temperature. Authors^{1,2)} successfully used Li_2CO_3 as a lithium source for producing Al-Li alloy at 973K and obtained high current efficiency of about 95%. Fray³⁾ also tried to produce lithium by using chloride-carbonate melt. However, the working temperature is still high, about 800K.

In this work, it was tried to deposit lithium in LiCl-KCl eutectic and the condition of deposition was studied based on the electrochemical measurements and the current efficiency.

Experimental

Apparatus used is shown in Fig.1 It consists of a melt container, a graphite anode, a tungsten cathode, an Ag/AgCl reference electrode and a thermocouple. Electrolyte was LiCl-KCl eutectic mixture. Melt container made of Pyrex glass was contained in a quartz tube. Transparent glass furnace was employed to observe the phenomena on the electrodes visually.

Experiments were carried out under constant current at 673K and 713K and the quantity of electricity was recorded. Electrode potentials were measured by using current interruption method to determine the decomposition potential of LiCl. Current efficiency of lithium deposition was determined by using the reaction of lithium with water. Purity of lithium was analyzed by using ICP.

LiCl and KCl used were purified by passing though dry HCl into the melt⁴⁾. Eutectic mixture was prepared by mixing and melting the component salts in glass tube sealed under vacuum.

Results and Discussion

Decomposition potential obtained, 3.62-3.65V

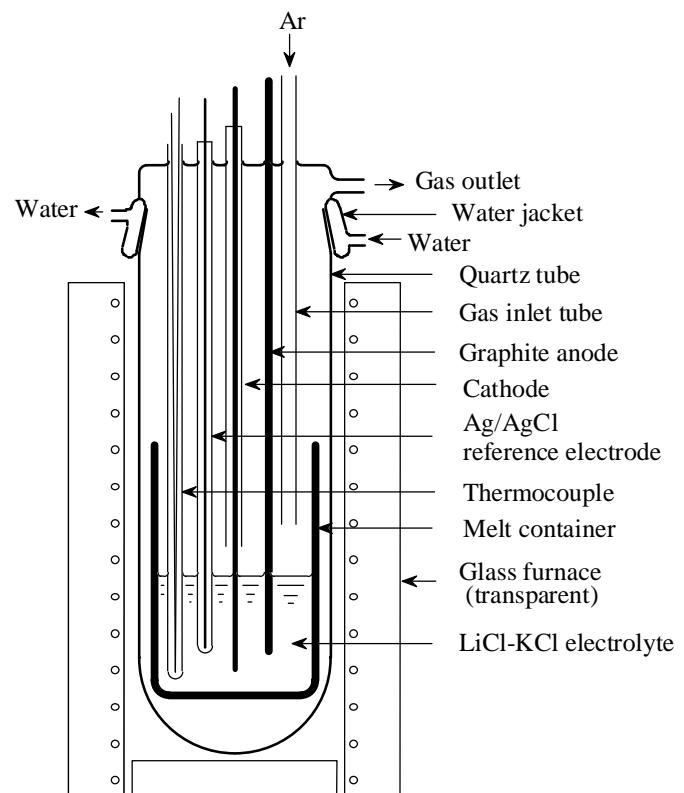


Fig.1 Apparatus for electrowining of lithium.

at 713K, agreed well to literature value. A phenomena like metal fog was observed visually near the cathode. Results of current efficiency of lithium deposition are shown in Table 1. Current efficiency increases with increasing current. It probably due to shorten the time of electrolysis and indicates the loss of lithium is due to the reaction with chlorine evolved at anode.

Table 1 Current efficiency of the deposition of metallic Li (same quantity of electricity).

Current/mA Temp./K	100	200	400
673	87.4%	88.1%	91.1%
713		83.6%	

Conclusion

Experiment for obtaining lithium was carried out from LiCl-KCl eutectic melt to study the optimum condition of cathode reaction. Current efficiency decreased with increasing the time of electrolysis and increasing temperature. Detailed results will be presented at 13th international symposium on molten salts.

References

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