Electrowinning of Lithium from LiOH in Molten Chloride

Osamu Takeda, Mingming Li, Takahiro Toma, Keita Sugiyama, Masayoshi Hoshi, and Yuzuru Sato

Tohoku University, Aoba-ku, Sendai 980-8579, Japan

An investigation was carried out to determine the viability of electrowinning lithium from LiOH in molten chloride, with a view to developing a system for the storage and transportation of hydrogen using LiH as the storage medium. It was predicted from the chemical potential diagram for the Li–O–H system that Li metal cannot be electrowon from a LiOH-containing salt, as any Li generated by electrowinning readily reacts with LiOH to form Li2O. Electrolysis in molten LiCl–KCl at 744 K is much higher than that of NaOH (596 K). Furthermore, the thermal decomposition of LiOH to Li2O, which has melting point of 1843 K, means that it needs to be mixed with LiCl to decrease the liquidus temperature of the electrolytic bath at 541 K at the eutectic composition of LiOH–4 mol% LiCl.

Hydrogen storage and transportation using LiH.— The basic chemical reactions involved in the proposed system for the storage and transportation of hydrogen are as follows:

\[
\text{Synthesis of LiH (hydrogenation): } \text{Li}(l) + \frac{1}{2}\text{H}_2(g) = \text{LiH}(s) \quad [1]
\]

\[
\text{Production of H}_2 \text{ (hydrolysis): } \text{LiH}(s) + \text{H}_2\text{O}(l) = \text{H}_2(g) + \text{LiOH}(s) \quad [2]
\]

\[
\text{Regeneration of Li (electrolysis): } \text{LiOH}(l) = \text{Li}(l) + \frac{1}{2}\text{H}_2\text{O}(g) + \frac{1}{4}\text{O}_2(g) \quad [3]
\]

The hydrogenation is historically known as the production of LiH. The standard Gibbs free energy change of formation of LiH, \( \Delta G^\circ_\text{f} \), is \(-12 \text{ kJ mol}^{-1} \) at 1000 K, which means that there is sufficient driving force for hydrogenation (Eq. 1). Moreover, the fact that LiH has a large hydrogen-storage capacity and is chemically stable at ambient temperature and pressure means that efficient storage and transportation can be achieved simply by using a sealed container. Once transported from a supplier to the user, LiH can be reacted with water vapor to generate \( \text{H}_2 \) through the well-known hydrolysis reaction shown in Eq. 2. By using hot water vapor a high yield of \( \text{H}_2 \) can be achieved, resulting in a generated mass of \( \text{H}_2 \) of as much as 25% of the original mass of LiH. The LiOH by-product formed by \( \text{H}_2 \)-generation can then be returned to the supplier, where the Li is regenerated using molten salt electrolysis (Eq. 3).

Production of lithium metal.— Although the Li metal is typically produced industrially through the electrolysis of molten LiCl–KCl, it can also be produced from LiOH if it is first converted to LiCl using hydrochloric acid. While the additional step is considered undesirable from a financial point of view, with other methods of Li production also proving to be inadequate. Since the regeneration of Li metal from LiOH clearly represents a significant hurdle to the practical implementation of LiH-based hydrogen transport, a fundamental investigation into this issue was carried out as part of this study.

Thermodynamic Expectation

The electrolytic production of Na metal from pure molten NaOH, known as the Castner process, has been generally regarded as being representative of industrial hydroxide electrolysis. This, however, is not applicable to the electrolysis of pure LiOH, as the melting point of LiOH (744 K) is much higher than that of NaOH (596 K). Furthermore, the thermal decomposition of LiOH to Li2O, which has melting point of 1843 K, means that it needs to be mixed with LiCl to decrease the liquidus temperature of the electrolytic bath (541 K at the eutectic composition of LiOH–4 mol% LiCl).

From the standard decomposition potentials given in Fig. 1, it is apparent that the decomposition potential of LiOH is smaller than that of LiCl. This means that any chloride present in the electrolytic bath is not consumed, but rather it is only LiOH continuously fed into the cell that is electrolyzed. However, Li metal is not obtained by electrolyzing the LiOH–LiCl melt mixture, a subject which is described in greater detail later.

A potential diagram for the Li–O–H system at 673 K constructed from thermodynamic data is shown in Fig. 2, in which the abscissa and ordinate axes show the hydrogen and oxygen potential, respectively. This was used to analyze the compatibility of the various elements, revealing that the stable region of Li is far from that of LiOH. This means that Li does not equilibrate with LiOH; or in other words, Li is not compatible with LiOH. The side reaction shown in Eq. 4 may occur at the cathode during the electrolysis of LiOH, and thus LiOH should be removed from the vicinity of the cathode to prevent the oxidation of Li metal.

\[
\text{Li}(l) + \text{LiOH}(l) = \text{Li}_2\text{O}(s) + \frac{1}{2}\text{H}_2(g); \quad \Delta G^\circ = -96.9 \text{ kJ mol}^{-1} \quad [4]
\]

Given these theoretical considerations, the experimental electrolysis of LiOH in this study was carried out in molten LiCl–KCl by only feeding it into an anode compartment that was separated by a diaphragm to prevent LiOH transport to Li deposited at the cathode. Electrolysis at lower temperatures was also explored using molten LiCl–KCl–CsCl.

Experimental

Sample preparation.— Pressed pellets of LiOH·H2O (>95%, Kanto Chemical Co. Inc.) measuring 5 mm in diameter and 8 mm

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in height were heated to 343 K in air and held until fully dehydrated, which was confirmed using gravimetry and powder X-ray diffraction analysis (XRD). 99% of crystal water in mass was removed (the mass of sample became 58% of that of feed material), and the peaks of LiOH·H₂O disappeared and the peaks of LiOH appeared in XRD pattern. Anhydrous LiCl (>99%, Kanto Chemical Co. Inc.) and anhydrous KCl (>99%, Kanto Chemical Co. Inc.) were mixed to give a eutectic composition of LiCl–41 mol% KCl, heated and held at 623 K under an argon flow for 12 hours, and then melted under HCl gas flow in a quartz container. Any moisture or oxygen in the molten salt was removed by the HCl gas, with excess HCl dissolved in the molten salt being subsequently removed by introducing argon prior to solidifying under vacuum. A similar method was also used to purify and prepare a LiCl–17 mol% KCl–26 mol% CsCl eutectic salt.

**Experimental apparatus and procedure.**—The electrolysis of LiOH in molten LiCl–KCl or LiCl–KCl–CsCl eutectic salts was carried out using the experimental apparatus shown in Fig. 3. In this, a nickel rod (3 mm diameter) or tungsten wire (1 mm diameter) was used as the working electrode (the cathode in electrolysis), with Ag/AgCl and a graphite rod (6 mm) used as the reference and counter electrode, respectively. A pre-prepared salt was placed in a 99.5% alumina crucible, and the tip of the anode was shrouded with a porous magnesia diaphragm (apparent porosity: 20%, thickness of wall: 5 mm) to provide an anode compartment. A port set on top of tube covering the anode was used to introduce LiOH pellets (ca. 0.02 mol (0.46 g)) after melting the electrolytic bath. Cyclic voltammetry (CV) and galvanostatic electrolysis (0.05 ∼ 0.5 A · cm⁻²) were subsequently carried out at 548–673 K using a potentio/galvanostat (HZ-3000, Hokuto Denko Co.). The precise electrolytic conditions used are summarized in Table I and Table II.

Given the use of a porous diaphragm, there was the expectation that OH⁻ ions would be limited to the anode compartment (at least under the electric field during electrolysis), and that the only anions near the cathode would be Cl⁻. The material deposited on the cathode by electrolysis was mechanically recovered in a glove box (<1 ppm H₂O), and the products were put into a glass holder to be covered with a polyimide film in order to avoid the reaction with air. Phases in the products were analyzed through the film using XRD. The current efficiency of Li deposition was evaluated from the amount of H₂ generated through its reaction with water (Eq. 5). After the measurement of hydrogen volume by displacement of water, the mole number of

**Figure 1.** Standard decomposition potentials of related chemicals.

**Figure 2.** Potential diagram for the Li−H−O system at 673 K.

**Figure 3.** Experimental apparatus used to investigate the electrochemical behavior of molten LiOH−LiCl and its electrolysis.

| Exp. No. | Electrolytic bath | Temperature, T / K | Amount of LiOH added, n / mol | Current density in cathode, i / A · cm⁻² | Electricity passed, Q / C | Current efficiency of cathode, εC (%) |
|---------|-------------------|--------------------|-------------------------------|------------------------------------------|--------------------------|-------------------------------------|
| A       | LiCl–KCl          | 673                | 0.0194                        | 0.3                                      | 1871                     | 84.5                                |
| B       | LiCl–KCl          | 673                | 0.0297                        | 0.3                                      | 2866                     | 84.2                                |
| C       | LiCl–KCl–CsCl     | 573                | 0.0196                        | 0.3                                      | 1893                     | 83.8                                |
| D       | LiCl–KCl–CsCl     | 573                | 0.0301                        | 0.3                                      | 2904                     | 85.5                                |
hydrogen was determined through the gas state equation.

\[
\text{Li}(s) + \frac{1}{2} \text{H}_2\text{O}(l) = \text{LiOH} \text{ (in water)} + \frac{1}{2} \text{H}_2(g) \quad [5]
\]

The accompanying reactions at the graphite anode were estimated to be as follows:

\[
\text{Cl}^- = \frac{1}{2}\text{Cl}_2(g) + e^-; \quad E^0 = 3.63 \text{ V vs. Li}^+/\text{Li} \text{ at 623 K} \quad [6]
\]

\[
\text{OH}^- = \frac{1}{2}\text{H}_2\text{O}(g) + \frac{1}{4}\text{O}_2(g) + e^-;
\]

\[
E^0 = 2.87 \text{ V vs. Li}^+/\text{Li} \text{ at 623 K} \quad [7]
\]

\[
\text{OH}^- + \frac{1}{4}\text{C} \quad (s) = \frac{1}{2}\text{H}_2\text{O}(g) + \frac{1}{4}\text{CO}_2(g) + e^-;
\]

\[
E^0 = 1.84 \text{ V vs. Li}^+/\text{Li} \text{ at 623 K} \quad [8]
\]

The evolution of water and oxygen was expected to occur prior to the evolution of chlorine, as the electrode potential of Eq. 6 is higher than that of Eq. 7 and 8. On the other hand, it is known that \text{OH}^- \text{ ion could decompose to } \text{O}_2^- \text{ ion according to Eq. 9.}^{18}

\[
\text{OH}^- = \frac{1}{2}\text{O}_2^- + \frac{1}{2}\text{H}_2\text{O}(g) \quad [9]
\]

In the case, the following anodic reaction could occur.\(^{19}\)

\[
\frac{1}{2}\text{O}_2^- = \frac{1}{4}\text{O}_2(g) + e^- \quad [10]
\]

Therefore, a portion of \text{OH}^- \text{ may be electrolyzed by the two step reaction although it is difficult to distinguish the reaction mechanisms. Anyway, } \text{O}_2 \text{ and } \text{H}_2\text{O could be generated by the electrolysis. Water contained in the exhaust argon flow was absorbed by anhydrous } \text{CaCl}_2, \text{ allowing the presence of} \text{Cl}_2 \text{ gas at the anode to be evaluated by then passing the gas into } \text{KI solution and titrating it with } \text{Na}_2\text{S}_2\text{O}_3 \text{ solution. Similarly, } \text{CO}_2 \text{ gas at the anode was evaluated by introducing the exhaust into a } \text{Ba(OH)}_2 \text{ solution and measuring the mass of } \text{BaCO}_3 \text{ precipitation. The emission of } \text{CO}_2 \text{ was also confirmed and measured by gas chromatography.}

**Results and Discussion**

In the cyclic voltammogram of LiCl–41 mol% KCl in the cathode compartment at 673 K given in Fig. 4, the reduction and oxidation current of Li metal can be seen to be almost the same.

Given that electrolysis commenced with an electrolytic bath devoid of LiOH, the gradual decrease in the anode potential observed after feeding LiOH into the anode compartment implies a change in the anode reaction from \text{Cl}_2 \text{ generation to a reaction involving } \text{OH}^- \text{ ions. This was confirmed by the fact that } \text{Cl}_2 \text{ was not detected in the exhaust gas after LiOH addition, which means that the chloride in the electrolytic bath was not consumed. The overall drop in the anode potential (ca. 0.2 V) was, however, much smaller than was expected based on calculations. Moreover, the cathode potential remained almost constant throughout electrolysis.}

For the electrolysis with an electrolytic bath in which LiOH preliminary was added, Cl\(_2\) was not detected from the beginning of the electrolysis. The electrodes were removed from the molten salt and a photograph of the cathode is provided in Fig. 5a. This shows how the tip of the alumina tube covering the cathode rod was broken to allow the metal deposited on an interspace tungsten spiral cathode to be recovered for analysis.

![Figure 4. Cyclic voltammogram of LiCl–41 mol% KCl in the cathode compartment at 673 K. Scan rate: 100 mV·s\(^{-1}\).](image)

The XRD pattern of the metallic product recovered from the cathode (Fig. 5b) confirms that Li metal was successfully obtained; the

![Figure 5. (a) Photograph showing the cathode after galvanostatic electrolysis in molten LiCl–KCl, which was achieved by feeding LiOH into an anode compartment shrouded with a porous magnesia diaphragm (Exp. B). (b) XRD pattern of the product recovered from the cathode.](image)
large peaks evident in the low-angle region being attributable to the polyimide film covering the samples. In some experiments, the current efficiency of the cathode was as high as 84% (Table I), and the water absorbed by the CaCl₂ reached 93–95% of the stoichiometric amount described by Eq. 7 and/or 8. The generation of CO₂ was, however, only about 44.5% of the stoichiometric amount defined by Eq. 8 (Table II).

Electrolysis in molten LiCl–KCl–CsCl eutectic salt was also carried out, as this allowed the temperature to be lowered to 573 K. This was also successful in producing Li metal through the same electrolysis process, with the current efficiency of the cathodes being in the order of 83.8–85.5% (Table I). There is therefore no significant difference in the current efficiency between using either a LiCl–KCl or LiCl–KCl–CsCl eutectic. The water absorption in CaCl₂ reached a similar level of 94–95% of the stoichiometric amount in Eq. 7 and/or 8, yet CO₂ generation was reduced to just 21% of the stoichiometric amount in Eq. 8 (Table II). The CO₂ generation decreased even further to only 0.2% when the temperature was lowered to 548 K; and although an oxygen analysis was not conducted, it can be inferred from this that the rate of reaction between the graphite anode and OH⁻ is reduced at lower temperatures. The generation of CO₂ was also found to decrease with decreasing anode current density, although the reasons for this are not clear.

Conclusions

The electrowinning of Li metal from LiOH in a molten LiCl–KCl or LiCl–KCl–CsCl eutectic salt has been successfully demonstrated by feeding LiOH into an anode compartment separated from the cathode by a porous magnesia diaphragm. This prevents the side reactions between Li metal and LiOH that makes the direct electrowinning of Li from LiOH unviable, as was confirmed through theoretical calculation. More importantly, this new method of electrowinning is capable of cathode current efficiencies of 84–86%, values which are not significantly affected by the temperature of the molten salt. However, the generation of CO₂ at the graphite anode was found to greatly decrease when the temperature of electrolysis is lowered.

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References

1. Y. Sato and O. Takeda, Molten Salts Chemistry: From Lab to Applications, edited by Frederic Lantelme and Henri Groult, 451 (Elsevier Inc., Burlington, MA, USA, 2013).
2. M. Li, O. Takeda, M. Hoshi, and Y. Sato, Abstracts of the 60th Annual Meeting of the Int. Soc. Electrochem. (CD-ROM Proc.) (2009).
3. O. Takeda, M. Li, M. Hoshi, and Y. Sato, Abstracts of 41th Symp. Molten Salt Chem., Japan, 41 (2009).
4. T. Laude, T. Kobayashi, and Y. Sato, Int. J. Hydrogen Energy, 35, 585 (2010).
5. P. E. Landolt, J. Electrochem. Soc., 102, 285C (1955).
6. I. Barin, Thermochemical Data of Pure Substances, (VCH Verlagsgesellschaft mbH, Weinheim, Germany 1989).
7. C. Haertling, R. F. Hanzahan Jr., and R. Smith, J. Nuclear Mater., 349, 195 (2006).
8. V. C. Y. Kong, F. R. Foulkes, D. W. Kirk, and J. T. Hinatsu, Int. J. Hydrogen Energy, 24, 665 (1999).
9. G. J. Kipouros and D. R. Sadoway, JOM, 5 (May), 24 (1998).
10. A. W. McClaine, R. W. Breault, C. Larsen, R. Konduri, J. Rolfe, F. Becker, and G. Miskolczy, Proceedings of the 2000 U. S. DOE Hydrogen Program Review, NREL/CPS-570-28890 (2000).
11. A. A. J. Smeets and D. J. Fray, Trans. Inst. Min. Metall., 100, C42 (1991).
12. J. F. Cooper, B. B. Ebbinghaus, K. Peterman, and S. Weinland, Fundamentals of Electrochemical Process Design: A Tutorial and Anodic Process: Fundamental and Applied Aspects, 495–11, ed. J. B. Talbot, et al. (Pennington, NJ: Electrochemical Society, 1995).
13. T. Wallace, Chem. Industry, 22, 876 (1953).
14. N. A. Reshetnikov and G. M. Unzhakov, Zhur. Neorg. Khim., 3, 1435 (1958).
15. E. Elchardus and P. Laffitte, Bull. Soc. Chim. Fr., No. 51, 1572 (1932).
16. A. W. McClaine, H. K. Breault, and A. D. Pelton, Special Report to the Phase Equilibria Program, Part D: The 60 ternary common-ion systems involving (Li, Na, K, Rb, Cs) and (F, Cl, Br, I), 2 (American Ceramic Society; Westerville, Ohio, 1987).
17. T. A. Czuppon, S. G. Knez, and D. G. Newsome, Encyclopedia of chemical technology, 4th edition, Vol. 13 (John Wiley & Sons, New York, 1995).
18. G. Delarue, J. Electroanal. Chem., 1, 13 (1959).
19. Y. Kado, T. Goto, and R. Hagiwara, J. Electrochem. Soc., 160, E90 (2013).