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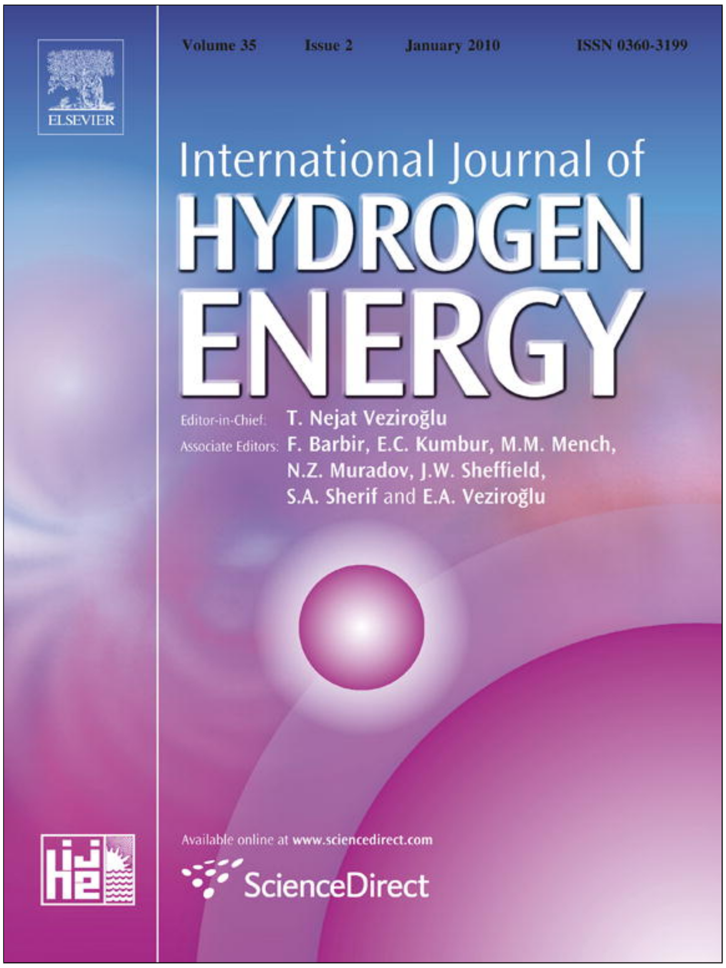
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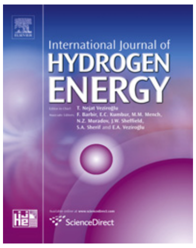

Technical communication

Electrolysis of LiOH for hydrogen supply

Thomas Laude [a,*], *Takehisa Kobayashi* [a], *Yuzuru Sato* [b]

[a] *Air Liquide Laboratories, 28 Wadai, Tsukuba, Ibaraki 300-4247, Japan*
[b] *Tohoku University, Graduate School of Engineering, Department of Metallurgy, Sendai 980-8579, Japan*

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ABSTRACT

The hydrolysis of lithium hydride (LiH) is a promising technique for the supply of hydrogen. LiH can be stored in sealed tanks or cartridges of ~6% mass effective hydrogen capacity. However, the lack of an efficient recycling method for the byproduct lithium hydroxide (LiOH) has been a limitation to its use. Here, we propose and demonstrate a recycling process based on the hot melt electrolysis of a LiOH–LiCl eutectic mixture at 380 °C. The electrolysis activation potential was measured at 3.08 V. Lithium production was observed around the cathode using differential scanning calorimetry (DSC) and cyclic voltametry. Current efficiency was estimated 37.9%, and the absence of LiCl decomposition was confirmed.

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1. Introduction

In recent years, interest has been growing for chemicals that reduce water and thus produce hydrogen by the simple addition of water. This concept is being considered as a hydrogen source for hydrogen-powered vehicles (ideally, with water recycled from the fuel cell) [1], and as a hydrogen source for industry (ideally, with water from a pipe). Although an added cost for the chemical processing (production or recycling) is involved, the high density of the chemicals enables savings on storage and distribution, compared with high pressure (HP) solutions. Therefore, a chemical supply is appealing to isolated regions or to situations involving space constraints.

$NaBH_4$ has been widely studied [2], but has limitations because of the high cost of chemical processing and complex heterogeneous catalysis of the hydrolysis. Aluminum metal [3] is cost competitive but the hydrolysis is slow, even when activated. On the other hand, some alkali chemicals (Na, NaH, Li and LiH) are strongly reductant, and therefore no hydrolysis activation is required. LiH is particularly attractive due to its low mass and mild pyrophoric character. LiH has been considered as a solution for hydrogen supply [4], but an efficient LiOH recycling scheme was yet to be developed. Recycling lithium is necessary in view of its cost [5] and limited availability.

In this study, we demonstrate a recycling approach based on direct LiOH electrolysis, which offers the prospect of a cost-effective solution. While the current efficiency is only ~38% at this stage, this technique can be expected to become cost competitive thanks to the low activation energy of LiOH electrolysis, and the straightforward process. Alternatively, thermal decomposition of LiOH to Li_2O, followed by electrolysis of molten Li_2O (reported with carbonate-fluoride eutectic mixture at 750–900 °C [6]) could be considered, but this is more

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[*] *Corresponding author*

E-mail addresses: thomaslaude@uminokai.net, thomas.laude@airliquide.com (T. Laude).

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temperature demanding. Also, LiOH could be converted to LiCl (additional step), and then electrolyzed in molten LiCl–KCl (traditional method of processing lithium ore or brine [7]), but LiCl electrolysis requires higher activation energy and higher temperature. Other original techniques such as aqueous LiOH electrolysis with mercury amalgam [8], or LiOH carbo-reduction [4] have also been considered.

2. Using the LiH–LiOH cycle as a hydrogen source

For safe distribution and storage, LiH powder can be packaged in sealed tanks or cartridges, protected from fire. Fine powdered LiH supplied with liquid water under air can release hydrogen with spontaneous ignition. In a dry environment, LiH combustion is possible, with the release of caustic fumes, although this requires a continual ignition source [9]. Lithium compounds constitute a minor environmental issue, as they progressively degrade to lithium carbonate on CO_2 absorption (carbonate can be recycled). Packaging in an oil slurry has also been proposed [4], but this hinders both hydrolysis and recycling, besides reducing storage capacity.

The LiH–LiOH cycle proposed here comprises three primary reactions:

Hydrolysis, $LiH + H_2O \rightarrow LiOH + H_2$ (1)

Molten salt electrolysis,
$LiOH \rightarrow Li + [(1/2)\text{-}x]H_2 + 1/2(1\text{-}x)O_2 + xH_2O$ (2)

Hydrogenation, $Li + 1/2H_2 \rightarrow LiH$ (3)

For hydrogen supply, the hydrolysis reaction (1) is well known [10], and has been shown to proceed at high yield (90%, Li metal basis) on hot vapor input [11], leaving a waste of LiOH and water. The high affinity of LiOH for water (formation of a mono-hydrate decomposed over 150 °C [12]) increases the waste mass but ensures that the vapor fixes on active LiH grains rather than on the tank walls. It also ensures dry hydrogen on output. As the LiH hydrolysis is very active, the hydrolyzer needs no catalyst and it is suitable for high hydrogen flow. The heat released by the active powder ($\Delta G = -172.5$ kJ/mol at 25 °C) is expected to raise the tank temperature locally; however, this is not detrimental to the process, as long as the heat is properly dissipated. The hydrolysis rate is known to decrease with temperature and pressure [13], and this is favorable for heat management. Several simple hydrolyzer designs have been considered [11]. Fig. 1 presents an original LiH hydrolyzer, in which hydrogen is re-circulated to carry the water vapor to the reactor.

Theoretically the hydrogen storage capacity of LiH is as high as 25.36% mass (H_2 molar mass/LiH molar mass). However, the practical capacity for transport (assuming an empty-to-full exchange supply) is deduced from waste (LiOH and water) mass. The quantity of water trapped is not precisely known, but 90% yield hydrolysis with half the LiOH hydrated, corresponds to 6.1% mass hydrogen capacity (H_2 mass/waste mass, chemical only), whereas 90% yield hydrolysis without water trapping corresponds to 8.4% mass (waste can be dried before return). For comparison, modern compressed storages (trailers, bundles etc.) allow 0.5–0.8% mass.

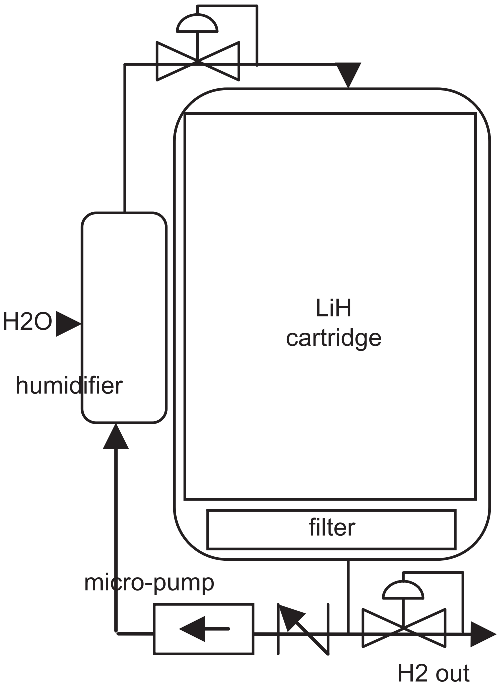

Fig. 1 – Example of a LiH hydrolyzer design. Hydrogen is re-circulated to carry the water vapor from the humidifier (a hydrophobic membrane for instance). Internal hydrogen pressure is limited by the pre-reactor regulator.

Molten salt LiOH electrolysis (2) is reported here for the first time. We use an eutectic mixture LiOH–LiCl (70%–30% mol ± 1%) that melts at 325 °C [14], and permits no Cl_2 evolution thanks to the high activation potential of LiCl electrolysis. Lower melting temperature (LiOH melting point is 450 °C) simplifies reactor design and reduces alkaline corrosion. Besides, it is believed that solid Li_2O forms near the LiOH melting point [15]. The technology to further hydrogenate Li to LiH (3), and thus complete the recycle process, is available [16], and could be continuously performed on the electrolyzer output.

The quantity of water exhausted during the electrolysis (x) is unknown, but is expected to be near 0 with the present setup. For comparison, the electrolysis of melted NaOH (Castner cell) is well known (main industrial sodium production route until 1930 [17]). Its electrode reactions are $NaOH + e \rightarrow OH^- + Na$ (cathode) and $NaOH \rightarrow Na^+ + e + 1/2H_2O + 1/4O_2$ (anode). However, water is not reported at the anode, and instead hydrogen is produced at the cathode. Also, the current efficiency (molar ratio of Na produced to electron flow) is reportedly below 50%. This is usually explained by the migration of the anodic H_2O to the cathode and the subsequent hydrolysis of half the Na metal produced [17]. One improvement of the Castner design is to stop the non-ionic exchanges with an ionic membrane placed between the electrodes. This was reported for (H_2 assisted) NaOH electrolysis [18] with 80% current efficiency. However, at present no equivalent membrane is available for lithium-ions.

3. LiOH electrolysis experiment

3.1. *Experimental details*

LiCl powder (Kanto Chemical 99%) was mixed with LiOH powder (Sigma Aldrich 98%) in the proportion of LiOH 75 g – LiCl 85 g (70%–30%mol ± 1%). The mix was placed in an alumina crucible, and air dried for 12 h at 180 °C. Temperature was reduced to 80 °C and the crucible was quickly transferred to a quartz reactor (70 × 700 mm) inserted in a vertical furnace (see Fig. 2). Three nickel electrodes (2 mm diameter) and a thermocouple, each enclosed in an alumina tube (with inner diameter 6 or 10 mm), were positioned in the reactor, hanging over the mix. The junction between each alumina tube and the enclosed electrode was sealed with epoxy or rubber. The junction between the quartz lid and each alumina tube was sealed with an O-ring. Reactor air was replaced with Argon, using a rotary pump. Argon flow was set at 100 ml/min throughout the experiment. Reactor temperature was raised to 380 °C, well over the melting point of the mixture (some remaining moisture was vaporized and condensed around the reactor lid). After melting, each electrode and the thermocouple were lowered 1 cm deep into the melt, measuring the electric resistance to detect the melt surface. Electrolysis was then started.

3.2. *Results and discussion*

We performed a constant current electrolysis at 1.5 A, with current density 1.5 A/cm^2 (estimated from a tainted area on the cathode after the experiment), close to the reported value of an industrial Castner electrolyzer (2 A/cm^2) [17]. During the first 30 min, we electrolyzed only the remaining moisture in LiOH–LiCl, as determined by a low inter-electrode potential (~1.6 V), close to the water electrolysis activation potential (1.23 V). Following this, the potential rose rapidly to the expected potential of LiOH electrolysis, between 3.75 and 3.95 V. Temperature was stabilized at 383 °C, current flowing.

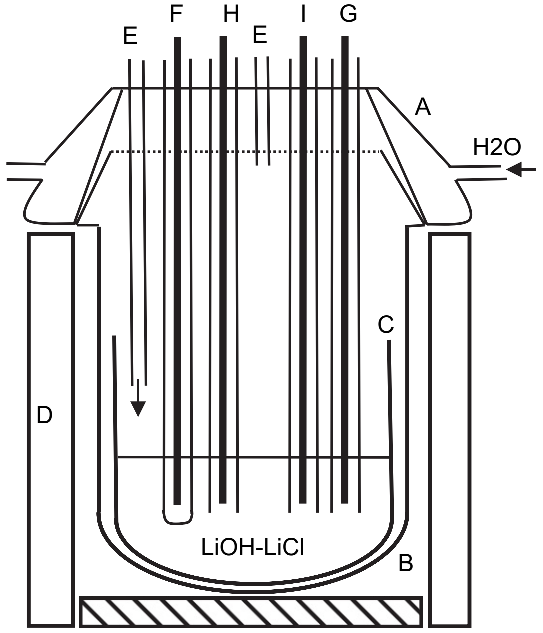

Fig. 2 – Experimental set-up (vertical dimension reduced). A: Quartz lid with water cooling, B: Quartz reactor, C: Alumina crucible, D: Electrical furnace, E: Argon in/out, F: Thermocouple in closed alumina tube, G: Nickel cathode in open alumina tube, H: Nickel anode in open alumina tube, I: Nickel quasi-reference electrode in open alumina tube.

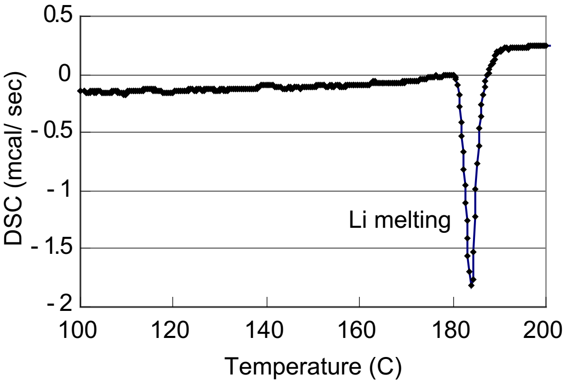

Fig. 3 – DSC measurement of the material surrounding cathode. Lithium metal is identified by its melting point signature at 184 ± 1 °C.

Metal production rate was estimated by collecting the material around cathode within its surrounding alumina tube, dropping it in water and measuring the volume of (H_2) gas generated. This was done twice, at 30 min and at 46 min. The result showed 12.5% current efficiency (molar ratio of Li produced to electron flow) for the first 30 min (due to the remaining moisture in LiOH–LiCl), and 37.9% current efficiency in the following 16 min. Most of the current loss is assumed to be due to inter-electrode chemical crossing, possibly water crossing as in a Castner cell. In a separate experiment, the metallic cathode material was analyzed by

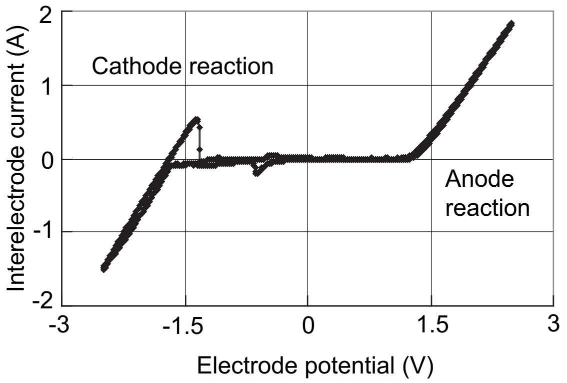

Fig. 4 – Cyclic voltametry measurement with potentiostat connected to the anode, cathode and quasi-reference electrode. The three electrodes were approximately equidistant. The potential was measured, first between the reference and the cathode, and then between the reference and the anode, in two successive runs. In both runs, the cathode-anode potential was risen until 2.5 V was reached between the reference and the measured electrode.

differential scanning calorimetry (Mac Science DSC 3300) and lithium metal was identified by its melting point signature at 184 ± 1 °C (Fig. 3).

The activation potential of LiOH electrolysis was deduced as 3.08 V, from potential versus current measurement. An estimation from the free energy of the reaction $LiOH(l) \rightarrow Li(l) + 1/4O_2 + 1/2H_2O(g)$ at 700 K [19] gives 2.80 V. The difference is expected to be equal to the LiOH ionic dissociation potential.

A cyclic voltametry measurement was done with a potentiostat measuring the potential between a quasi-reference electrode and successively the cathode and the anode (see Fig. 4). Anode behavior indicated a single reaction on the potential range (expected $LiOH \rightarrow Li^+ + e + 1/2H_2O + 1/4O_2$). We did not observe a peak corresponding to LiCl dissociation ($LiCl \rightarrow Li^+ + e + 1/2Cl_2$), nor a peak corresponding to anode corrosion (expected $Ni + 2LiOH \rightarrow 2Li^+ + 2e + Ni(OH)_2$). The cathode showed one main reaction (expected $LiOH + e \rightarrow OH^- + Li$), with reverse current at 1.7 V on potential decrease (cell working in generator mode). This indicates a (Li) metal deposition on the cathode during electrolysis. A small peak was observed near 0.5 V in the cathodic scan, possibly linked to the remaining water electrolysis. A minor peak was also noted near 1.2 V, possibly resulting from a metallic impurity.

We could confirm that Cl_2 was not produced on the anode (from LiCl) by KI (potassium iodine) test. Gas from the anode was passed through a KI solution, electrolysis being conducted at 4 V for 15 min. No color change was observed. For comparison, we allowed pure Cl_2 to flow through the same solution, at a rate consistent with a LiCl dissociation, and a strong color change was observed.

4. Conclusions

In this study, the direct electrolysis of LiOH with a current efficiency of 37.9% has been demonstrated. This offers prospect of LiOH recycling, and thus of utilizing the LiH–LiOH cycle as a hydrogen supply solution.

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