

LIOH ELECTROLYSIS, AN INTRODUCTION

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Validated by

Project Manager (if applicable)	Group Manager(s)	Program Director(s)	Scientific Direction or Team Expert
T. Laude (12/2007)	T. Laude (12/2007)		B. Jurcik (12/2007)

Approved for Distribution by Benjamin Jurcik (24/04/2008)

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Function / Entity	Names	Function / Entity	Names
R&D Group Manager(s):	Thomas Laude, Christophe Claeys	AXANE	Eric Claude, Patrick Sanglan, Frederic Touvard
R&D Program Director(s):	Francoise Barbier	AL Ingeniere	Aurelien Leon
R&D Management team:	(Abstract)Martha Heitzmann, Philippe Queille, Jean Yves Thonnellier, Marc Till	ALJ JAG	Francois Jackow, Yasuo Sato, Jean-Francois Lecouffe, Ikuo Hirase, Shinji Miyoshi, (Full)Megumi Eto
R&D Scientific Direction:	Benjamin Jurcik	Head office	Frederic Barth, Gregory Olocco, Laurent Ferenczi
R&D Project Team:	Aude Cuni	DTA	Thomas Charbonneau, Gerard Marot, Alain Ravex
Sponsor(s):			
Owner(s):			
SIS representative(s):			
DPI representative(s):	(Abstract) De Cuenca		
ALL	Circulation		
Real database	CTI		
DRTC	(Abstract) Rob Benesch, Philippe Coignet, Robert Gagliano, Pavol Pranda, Diana Stefanescu, Pascal Tessier, Tony Thampan, Tracey Jacksier, Pascal Tromeur		
CRCD	(Abstract)Raphaelle Imbault, Simon Jallais, Mathieu Lefebvre, Frederick Lockwood, Serge Moreau, Philippe Renault		

Abstract

Hydrogen can be supplied by lithium hydride hydrolysis: $\text{LiH} + \text{H}_2\text{O} \Rightarrow \text{LiOH} + \text{H}_2$. This is a hydrogen supply solution that could be applied for existing Industrial Merchant customers as well as for fuel-cell customers. LiH powder enables high storage density, low cost distribution, low cost storage, and high-power supply.

For cost competitiveness and to conserve Li metal, recycling LiOH to LiH is necessary. We proposed that this could be done in two steps, electrolysis to metal Li, and then hydrogenation. However LiOH electrolysis was not reported in previous art. This was identified as a key technical hurdle to be overcome for the viability of this process.

On the other hand, the electrolysis of NaOH to Na is known as the “Castner-Tiegel” process, and is a similar process. This process was the industrial production method for sodium metal until 1930.

We have demonstrated that a Castner-Tiegel type process can be applied for LiOH electrolysis (experimental campaign by T. Kobayashi at Tohoku university). The melting temperature of LiOH being notably higher than that of NaOH, it is preferable to use an eutectic melt such as LiOH-LiCl. Here, we discuss important parameters of the LiOH electrolyser, such as cell design and material selection.

Key words: hydrogen, chemical storage, LiH, LiOH, electrolyzer

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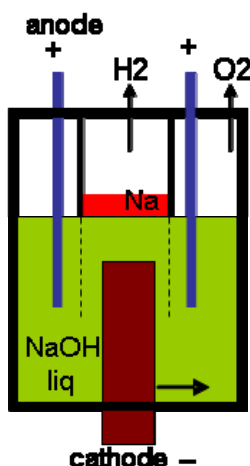
SCOPE

This report describes the main technical aspects of LiOH electrolysis, which is a key step for hydrogen supply by the LiH-LiOH cycle.

It was written in the framework of the hydrogen chemical storage project, mostly as an introduction to an experimental campaign led by T. Kobayashi at Tohoku university (see corresponding report).

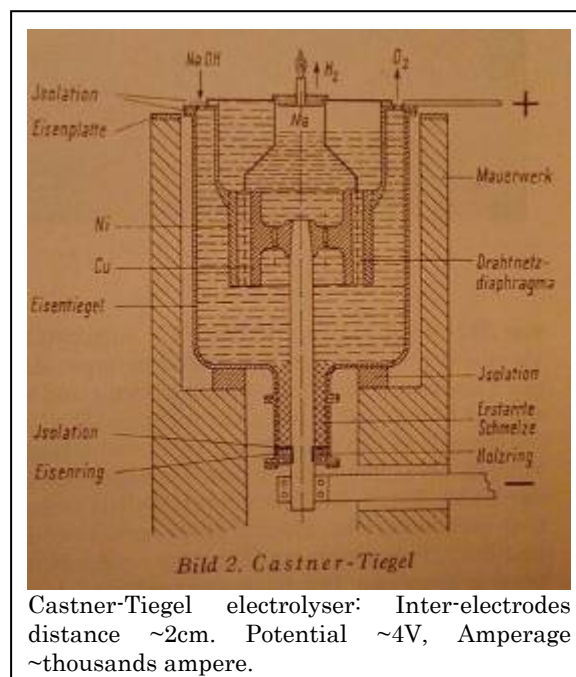
1. CASTNER TYPE NAOH ELECTROLYSIS

The electrolysis of LiOH is not reported experimentally. However, the electrolysis of sodium hydroxide NaOH by “Castner-Tiegel” process is known. It was the industrial production method for sodium metal until 1930.



With Castner-Tiegel method, electrolysis is performed (0 to 20C) above the NaOH melting temperature (318C). Molten salt enables high ionic conduction.

Metal sodium migrates to the top of the melt, and is separated from anode O₂. Cathode is kept under sodium metal level to avoid short-circuits. Electrodes are separated by a dense iron net. Na is extracted from top, using a spoon with holes (continuous extraction through an hollow cathode is also possible). Production is continuous (continuous NaOH feeding). Away from electrodes, NaOH is kept unmelted, for sealing and thermal insulation.



Castner-Tiegel electrolyser: Inter-electrodes distance ~2cm. Potential ~4V, Amperage ~thousands ampere.

The primary reactions are expected as (double ionic migration):

- Anode: $\text{NaOH} \rightarrow \text{Na}^+ + e + 1/2 \text{H}_2\text{O}_{\text{gas}} + 1/4\text{O}_2$
- Cathode: $\text{NaOH} + e \rightarrow \text{OH}^- + \text{Na}$

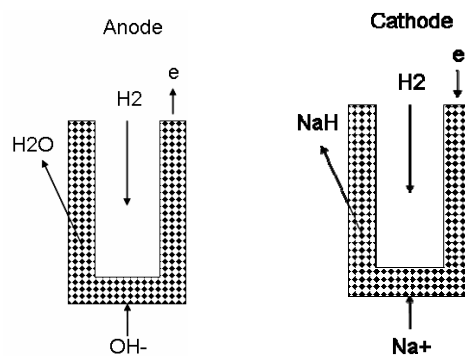
Hence global: $\text{NaOH} \rightarrow \text{Na} + 1/2 \text{H}_2\text{O}_{\text{gas}} + 1/4\text{O}_2$

However practically, global reaction is reported as $\text{NaOH} \rightarrow \text{Na} + 1/2 \text{H}_2 + 1/4\text{O}_2$

This is usually explained by the migration of H_2O to cathode and additional reaction at cathode: $\text{H}_2\text{O} + \text{Na} \rightarrow \text{NaOH} + 1/2\text{H}_2$

However it is surprising that no H_2O is reported at the anode, considering the high temperature. We believe the reaction could also be explained differently, for instance by the formation and migration of Na_2O (Na_2O is soluble in NaOH):

- Anode: $2\text{NaOH} \rightarrow 2e + \text{Na}_2\text{O} + 1/2\text{O}_2 + 2\text{H}^+$
- Cathode: $\text{Na}_2\text{O} + \text{H}^+ + e \rightarrow \text{Na} + \text{NaOH}$, and $\text{H}^+ + e \rightarrow 1/2\text{H}_2$



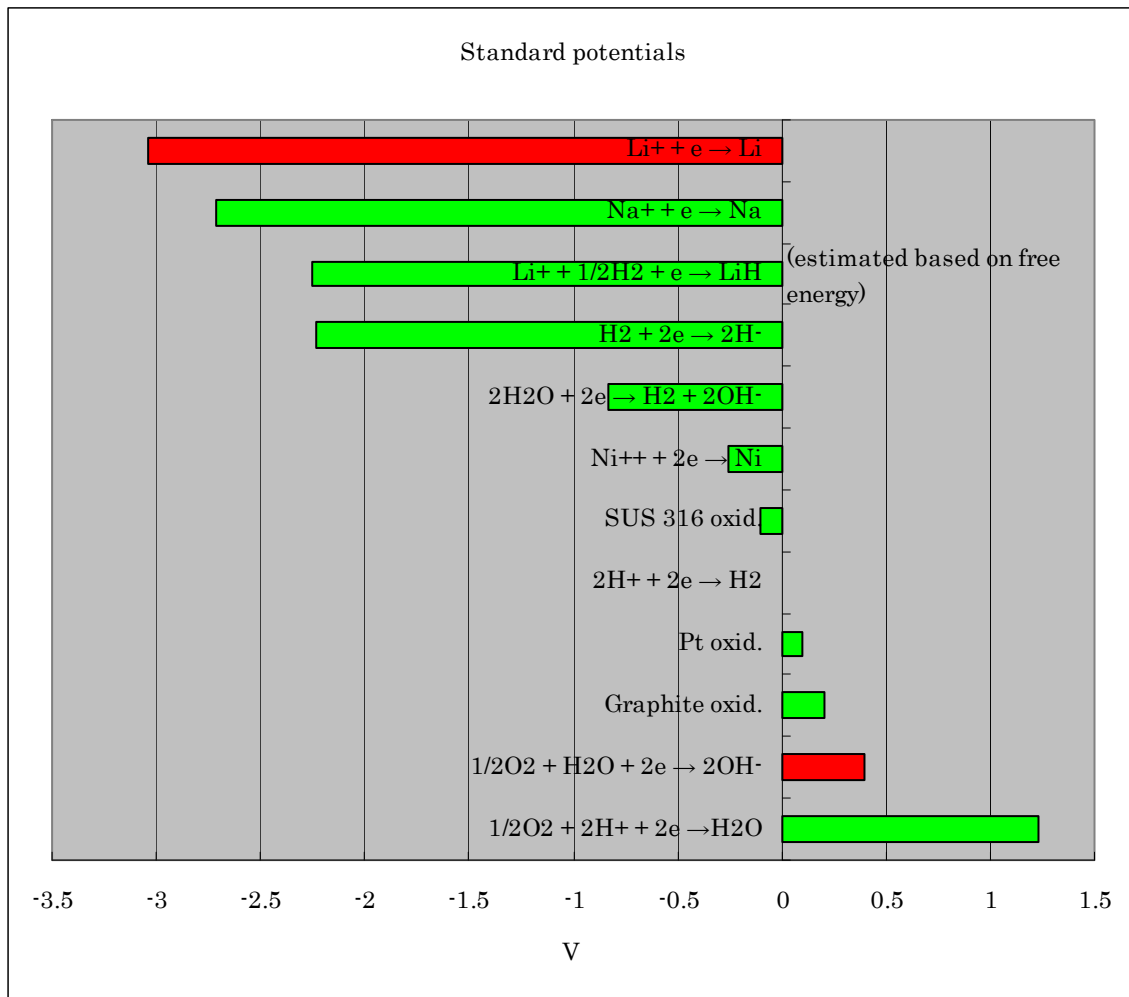
It is also possible to input H_2 at anode and change reaction to (Millenium-Air Products patent [3.1.5]):

Anode: $\text{NaOH} + \text{H}_2 \rightarrow \text{Na}^+ + e + \text{H}_2\text{O}_{\text{gas}}$

This is beneficial because part of the electrical input is replaced by H_2 input and it reduces anode electrochemical corrosion.

However, we believe this is not practical because gas input on electrolyser is traditionally not efficient (3 phase reaction) (H_2 price competitiveness to electricity must also be considered).

3. LiOH ELECTROLYSIS



Standard potential for reduction (mainly from [2.1]). In red: main potentials for LiOH electrolysis, which difference is 3.44V. (For real activation potential, temperature should be considered and potential for LiOH ionic separation should be added.)

LiOH is very similar to NaOH, and hence can follow a Castner-Tiegel type process. Lithium reactions involved are expected to be similar to those of sodium. The electrolyser activation potential is slightly higher for lithium (over 3.4V).

LiOH melting point is notably higher than that of NaOH (450C compared to 318C). This is an engineering difficulty, especially with the consideration that molten LiOH is highly corrosive.

For this reason, it is preferable to electrolyse LiOH at a lower temperature using an eutectic mix, such as:

- LiI(55%)-LiOH(45%) -> melts at 180C

- LiCl(37%)-LiOH(63%) -> melts at 262C

cathode	Li+ + e -> Li			(second step) Li + 1/2H2-> LiH				
	molecule	Li+	Li	molecule	Li	H2	LiH	
	coef	1.0	1.0		coef	1.0	0.5	1.0
	mg/min	4.32	4.32		mg/min	4.32	0.63	4.95
	ml/min				ml/min		7.00	
anode	OH- -> 1/2H2Ogas + 1/4O2 + e				(optional) OH- + 1/2H2 -> H2Ogas + e			
	molecule	OH-	H2O	O2	molecule	OH-	H2	H2O
	coef	1.0	0.5	0.25	coef	1.0	0.5	1.0
	mg/min	10.59	5.61	4.98	mg/min	10.59	0.63	11.21
	ml/min		7.00	3.50	ml/min		7.00	14.00

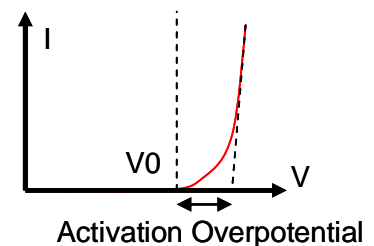
Ideal reaction rates per 1 Ampere.

4. ELECTROLYSER EFFICIENCY OPTIMISATION

Molten salt electrolysis is usually energy efficient because the reactions are endothermic in nature. However, there are various types of heat losses and consequently electrolysis efficiency typically ranges between 40% and 80%.

First, in a Castner type process, there may be heat loss through side-reactions (possibly $\text{Li} + \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{H}_2 + \text{LiOH}$ with water migration between electrodes, see part 1.). This would reduce efficiency by a factor two. To avoid this, we consider using an ionic membrane, and hence stop any non-ionic flow.

Another type of heat loss comes from reactants displacement for electrolysis, and result in overpotentials on top of activation/open circuit potential. For molten salt electrolysis of LiOH, the main overpotentials are expected as:



- overpotential for joule heating loss by current flow in the melt: $(d/\sigma) I$, where d is the inter-electrode distance and σ is ionic conductivity.
- overpotential for ionic barrier crossing on electrodes
- (if H2 input) overpotential for H2 adsorption on electrode (typically as high as 1V).

Activation potential does not depend on the electrolyser apparatus design or operation, but the overpotentials do. To optimize electrolysis efficiency, we can say that:

- There is a trade off between short Inter-Electrode distance (to reduce to current flow losses) and chemical separation between electrodes. A metal grid or an ionic membrane separation enables better trade off.
- There is a trade off for the operating current. High current improve reactor throughput and imply lower capital cost, but energy efficiency degrades as $1/V(I)$ [energy input is $I.V(I)$, but useful output is proportional to I]. Also, high current reduce air contamination on the cell, as it increases reaction rate at constant air leaking rate.
- Increasing the effective electrode surface is favorable (it reduces the ionic barriers on electrodes, helps ionic flow, and increase electrode durability).

In addition, if the internal heat production inside reactor cannot balance external heat loss (imperfect thermal insulation of the reactor) and heat absorbed by the reaction, it is necessary to heat the reactor. In that case, there is an additional heat loss due to this heating. However it is probable that external heating is unnecessary at very high currents (industrial case).

5. ELECTROLYSER ENGINEERING CONSIDERATIONS

Material for the tank

Molten LiOH causes severe alkali corrosion. Only some metals, especially Nickel, are suitable (Ni plating is not acceptable). Stainless steel may be acceptable too. (Ceramics are unfavorable for alkaline corrosion, and plastics have poor thermal resistance.).

Also, it is favorable to limit melting of LiOH to reaction zone, protecting the apparatus with a solid LiOH crust.

Material for electrodes

As can be seen from the electrochemical potential figure (p.6), the anode reaction: $\text{OH}^- \rightarrow \text{e} + 1/2 \text{H}_2\text{O}_{\text{gas}} + 1/4\text{O}_2$ has an oxidation potential higher than any metal (Ni, Pt or graphite,..). Hence the anode suffers electrochemical corrosion.

Possible solutions include:

- Using a sacrificial Ni like anode (Ni(OH)_2 will probably sink below the anode).
- Using a sacrificial graphite electrode (outgasing CO_2). However, the mechanical resistance of graphite in the melt is problematic
- Input H_2 on the anode. (discussed in part 1.)

Cathode material does not suffer electrochemical corrosion. A nickel or copper electrode is acceptable.

Reactor sealings

Sealing is needed because Li metal burns in air, and because melted LiOH readily absorbs CO_2 . However, this requirement is mild on industrial type apparatus as production rate may be far higher than leaking rate.

Sealing material may be:

- Solidified LiOH
- A metal such as Copper which offers good ductility, and enough thermal and corrosion resistance. However, this can not be used where electrical insulation is needed.
- Teflon, if used below 250C.
- Ceramic or glass, if limited sealing is acceptable

Other design considerations

- It is favorable to limit LiOH melting to a controlled reaction zone (better sealing, lower corrosion, better thermal insulation,...). This is possible on industrial Catsner-Tiegel apparatus thanks to high current heating the melt.
- In order to initiate the melting of LiOH at the beginning of electrolysis, it is possible to add water in the hydroxide. Water is electrolysed preferentially, releasing heat for LiOH melting.
- Some heat can be transferred between gas lines in and out (if there are), to reduce heat loss from gas flow.

6. STATE OF OUR RESEARCH

Today, LiOH electrolysis to Li metal has been proved feasible with LiOH-LiCl eutectic mix (see corresponding report).

Next step is to improve experimental knowledge. In particular, we need to:

- Analyze gas output on electrode in order to distinguish different reactions on electrodes.
- Check if an ionic membrane can suppress H₂ output on cathode (shift reaction) by stopping the non-ionic flow (and hence increase efficiency).
- Optimize energy efficiency

When this is done, it will be possible to design an industrial level prototype for continuous operations.

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