Novel Developments in Alkaline Water Electrolysis

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Renewable energy sources: solar, hydro, wind power etc.

Hydrogen cycle

Splitting of water

Transport, storage

Elect. Energy → Fuel cell

Catalytic Combustion → Heat, Safety

Combustion → Automotive

A. Züttel, A. Borgschulte, L. Schlapbach, *Hydrogen as a future energy carrier*, 2008
History of Water Electrolysis: known for over 200 years

- ~1800: Electrolytic Water splitting (Ritter, Nicholson, Carlisle)
- 1834: First use of the term «electrolysis» by Faraday
- 1900: Oerlikon introduces first bipolar electrolyzer (2.5V, Zürich)
- 1939: First 10’000Nm³/h (900kg/h) electrolyzer
- 1948: Zdansky develops pressure electrolyzer for Lonza
- 1951: First commercial 30bar electrolyzer (Lurgi)
- 1967: Zero-Gap Design

- Water electrolysis accounts for > 5% of hydrogen production
- Most of hydrogen is used on side for the production of Ammonia (Haber Bosch Process)
  conversion of heavy petroleum sources by hydrocracking
  cooling of generators
  steel & glas manufacturing

Lurgi-Zdansky prototype alkaline electrolyser, 1949
Hydrogen Report Switzerland 2010/2011

IHT Industrial alkaline electrolyzer

Svein Sunde, NTNU, Trondheim, Halder Topse Catalysis Forum, 2006
**Alkaline Water Electrolysis:**

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \]

1) bipolar plates
2) electrode meshes
3) separator membrane
4), 5) H\textsubscript{2} and O\textsubscript{2} ducts
6) electrolyte ducts

Zero-gap geometry

Membrane to separate H\textsubscript{2} and O\textsubscript{2}, conduction of OH- via KOH in open pore network

**Production rate:** 760 m\textsuperscript{3}/h H\textsubscript{2}, equ. to 3.3 MW\textsubscript{el}

**Energy Consumption:** 4.3 - 4.6 kWh/m\textsuperscript{3} H\textsubscript{2}

H\textsubscript{2} purity: 99.8 - 99.9 vol\%, O\textsubscript{2} purity: 99.3 - 99.6 vol\%

556 cells, cell \( \phi \) 1.6 m, length: 12 m, weight: 90 t

- 100 installed units

**Source:** Svein Sunde, NTNU, Trondheim, Halder Topse Catalysis Forum, 2006

**Electrolyser at IHT, Giovanola SA, Monthey, CH**
Alkaline water electrolysis  Historical aspects

- Long established and well mature technology
- Reliable and safe
- Significantly efficient (~ 80%)
- The most extended technology at a commercial level

By 1902 over 400 industrial alkaline electrolysers world wide
- primarily for ammonia production (fertilizer industry)
- plants based on low cost hydroelectricity

Principle of a bipolar electrolyzer design

Aswan Dam - Egypt
Source:
http://sitemaker.umich.edu/sec004_gp5/the_aswan_high_dam_benefits

Aswan Electrolyser (KIMA)
165MW - 37000 m³H₂/h
Source: ELT
State of the Art – IHT technology

Peru (1965) 5,200 Nm3/h H₂
7 x 3.5 MW – 25MW

Zimbabwe (1975) 21,000 Nm3/h H₂
28 x 3.5 MW – 100MW
Electrolysis of Water: \( \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \)

Water electrolysis is an electrochemical process in which electricity is used to split water into Hydrogen and Oxygen.

Published items with «alkaline water electrolysis» in the title (web of knowledge):

- Total: 578
- 1931 Patent on alkaline water electrolyser

(For comparison: ~20,000 items for «solid oxide fuel cell».)

Published items with «alkaline water electrolys*» in the title, excluding patents:

- Total: 182

- 1973 Oil crisis, OPEC oil embargo
- 2010 EU National Renewable Energy Action Plan

Reason for actual interest:
- Era of cheap petroleum will end
- Alternative fuels are needed
Three main technologies of water electrolysis

**Alkaline Electrolysis**
- **Anode**
  - \( \text{O}_2 \) [\( \text{+} \)]
  - \( \text{H}_2 \) [\( \text{−} \)]
- **Cathode**
  - OH
- Separator: Asbestos (past)
  - Zirfon® (current)
- Liquid electrolyte of KOH
  - 50-120°C
  - 1 – 60 bar
- Commercial, MW scale

**PEM Electrolysis**
- **Anode**
  - \( \text{O}_2 \) [\( \text{+} \)]
- **Cathode**
  - \( \text{H}_2 \) [\( \text{−} \)]
- Solid polymer electrolyte membrane (Nafion®)
- 60-100°C
- Commercial, smaller scale

**Solid Oxide Electrolysis**
- **Anode**
  - \( \text{O}_2 \) [\( \text{+} \)]
- **Cathode**
  - \( \text{H}_2 \) in steam
- Gas tight solid oxide electrolyte, most common:
  - \((\text{Zr,Y})\text{O}_{2-δ}\)
  - 700-1000°C
- Research/Demonstration
Alkaline Water Electrolysis

Advantages:

- Well developed technology
- Use of non-noble catalysts
- Long-term stability
- Units up to 750 Nm³/h (3.4 MW)

Challenges:

- Increase the current density
- Extend partial load capability
- Dynamics of the overall system
- Long term stable diaphragm

Thermodynamic properties as a function of temperature for the decomposition of liquid and gaseous water

\[ \Delta G = \Delta H - T \Delta S \]

- the total energy demand \( \Delta H \) for water splitting is lower in the vapour phase than in the liquid phase
  - the energy for vaporization can be provided thermally instead electrically
- the minimum demand for electrical energy \( \Delta G \) decreases with increasing temperature
  - thus the total efficiency can be improved by providing part of the splitting energy thermally instead electrically
- the thermal energy \( T \Delta S \) for the endothermic reaction increases with increasing temperature
  - replacement of electrical by thermal energy
- the improved reaction kinetics at elevated temperatures are lowering overvoltage

\[ \Delta H_{298K} = 286 \text{kJ/mol} \]
\[ \Delta S_{298K} = 163 \text{J/mol} \cdot K \]
\[ \Delta G_{298K} = 237 \text{kJ/mol} \]

\( \Delta H \): stand. Enthalpy
\( \Delta G \): stand. Gibbs free Energy
\( T \): Temperature K
\( \Delta S \): Entropy
### Chemistry of Alkaline Water Electrolysis

A schematic illustration of a basic water electrolysis system.

- Electrons are consumed by hydrogen ions (protons) to form hydrogen on the **Cathode**
- Hydroxy ions (anions) transfer through electrolyte solution to **Anode**
- OH⁻ ions give away electrons → electron flow

#### Electrolyte:
Potassium hydroxide not as corrosive as acids

#### Electrodes:
Nickel (high activity, low cost)

#### Diaphragm:
Asbestos (past), zirfon (new) prevents intermixing of H₂ and O₂ permeable to OH⁻ ions

<table>
<thead>
<tr>
<th>Cathode (HER)</th>
<th>Anode (OER)</th>
</tr>
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<tbody>
<tr>
<td>(2H_2O + 2e^- \rightarrow H_2 + 2OH^-)</td>
<td>(2OH^- \rightarrow \frac{1}{2} O_2 + H_2O + 2e^-)</td>
</tr>
</tbody>
</table>

cell voltage versus current density at a high and low operation temperature

\[ \Delta G = \Delta H - T \Delta S \]

Typical I–U curves for an electrolyzer cell at high and low temperatures

The difference between the two I–U curves is mainly due to the temperature dependence of the overvoltages

\[ U_{\text{thermoneutral}} = 1.48 \text{V} \]
\[ U_{\text{reversible}} = 1.23 \text{V} \]

\[ U_{\text{in}} = \frac{\Delta H}{zF} \]
\[ U_{\text{rev}} = \frac{\Delta G}{zF} \]

Energy efficiency

\[ \eta_e = \frac{U_{\text{in}}}{U} \]

\[ \Delta H: \text{ stand. Enthalpy H}_2\text{O splitting} \]
\[ \Delta G: \text{ stand. Gibbs free Energy} \]
\[ T: \text{ Temperature K} \]
\[ \Delta S: \text{ Entropy} \]

Specific conductivity vs. molarity of KOH at 30, 60 and 100°C comparing reported data to proposed equation.

Typical Tafel plots for both hydrogen and oxygen evolution


Generation of heat mainly due to electrical inefficiencies

Electrical barriers include electrical resistance of:
- the circuit ($R_1, R_2$)
- activation energies of the electrochemical reactions on the surfaces of the electrodes
- availability of electrode surfaces due to partial coverage by gas bubbles formed
- Membrane resistance
- resistances to the ionic transfer within the electrolyte solution

**Electrolyzer cell potential:**

$$E_{cell} = E_0 + \eta_a + |\eta_c| + I * R$$

$E_0$: equilibrium cell potential

$\eta_{a,c}$: anodic, cathodic over potential

$I$: Applied current

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8th International Symposium Hydrogen & Energy, 16.-21. February 2014, Zhaoqing, China
Electrical resistance and bubble phenomena in alkaline water electrolysis

Illustration of the contributions of anode and cathode polarisation to the cell voltage of an alkaline water electrolysis cell.

A qualitative comparison of the energy losses caused by reaction resistances: ohmic resistance, ionic resistance and bubble resistance.

Effect of current density on \( \text{O}_2 \) bubble growth. Effect of current density on \( \text{H}_2 \) bubble growth.

Square of radius \([R]\), vs time \([t]\), for Oxygen and Hydrogen bubbles, growing on a nickel expanded metal gauze at natural convection at room temperature and atmospheric pressure during electrolysis in a 30 wt% KOH solution.
Design / gas bubble covering of electrodes

Catalysts

design / chemistry / temperature / gas bubbles

laws of nature, temperature

Electrical resistance leads to heat generation wastage of electrical energy as heat

ELYGRID Project aims at contributing to the **reduction of the total cost** of hydrogen produced via electrolysis coupled to renewable energy sources (mainly wind turbines), and focusing on **mega watt size electrolyzers** (from 0.5 MW and up).

**Main coals:**
- Big size alkaline electrolyzers
- Reduction of Total Cost of Ownership (TCO)
- Prototyping and testing with intermittent feeding
- Industrialization and market oriented approach
WP2: Development of separator membranes

Alkaline Electrolysis

- High OH⁻ conductivity via KOH in open pore network during gas production
- Chemical and mechanical stability
  - separator thickness ↓
  - operating temperature ↑, pressure ↑, c(KOH) ↑
  - Efficiency ↑

Only one separator commercially available: Zirfon®Perl (Agfa), 0.5 mm thickness

- Membran to separate H₂ and O₂
- Conduction of OH⁻ via KOH in open pores
- Zero-gap geometry

56% porosity of Asbestos membrane
Mg₃Si₂O₅(OH)₄

10 µm
Alternative filler material

Mineral base fillers

- $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ Chrysotile Asbestos
- $\text{CaSiO}_3$ Wollastonite
- $(\text{Mg,Fe})_2\text{SiO}_4$ Olivine
- $\text{BaSO}_4$ barite 99% purity

Synthetic based fillers

- $\text{BaTiO}_3$ 98% purity, perovskite str., electroceramics
- $\text{ZrO}_2$ 3YSZ (TOSOH), technical ceramics, SOFC

Chemical corrosion experiment

- $T = 85^\circ\text{C} - 120^\circ\text{C}$
- KOH (25wt% - 35wt%)
- filler : KOH = 20 mM : 200 mM
- $t(h) = 50, 150, 255, 500; 1000; 2000; 4000; 8000$

Method:
ICP-MS (Inductively coupled plasma mass spectroscopy)
NOVAL MEMBRANE DEVELOPMENT

Inorganic powder

Organic solvent

Organic binder

NMP

PSF

Milling media: 2-3mm YZO spheres
Velocity: ca. 0.67 m/s
Time: 24 hours
tape casting and phase phase inversion process

Reinforcement: PPS net (Polyphenylensulfid)

coated PPS substrate thickness of coating: 0.2 – 1.5 mm
Pore size distribution determined by Bubble Point Measurement (BPM)

**POROLUX™ 1000**

**Measuring principle**
- Pressure Step

| Max pressure | 35 bar |
| Min pore (1) | 18 nm |
| Max pore (2) | 500 µm |
| Max flow    | 200 l/min |
| Sample holders | 13-25-47 mm |
| Pressure sensors | 2-50 bar |
| Flow sensors | 10-200 l/min |
| FBP regulator | 5-30 ml/min |
Laboratory Electrolyser, ambient conditions vs Pilot Electrolyser (IHT) 80°C, 30 bar, 12 cells

- Analysis of current—voltage curves at increased **temperature and pressure**

![Graph](image)

- Asbestos 2.5 mm
- Barite 0.5 mm
Nitidor Pilot Electrolyser, 0.2 Nm$_3$/h, 5 cells

significant influence of temperature to cell voltage
Alkaline Electrolysis: Summary and Outlook

- Alkaline Electrolysis is still a promising and robust process for large scale hydrogen production

**Challenges:**

- Increase of power density
- Reduction of anode and cathode overpotential
- Improving the electrocatalytic properties of the electrodes
- New gas separator diaphragms for better system efficiency

Correlate **microstructure/ porosity**
(total porosity, pore size distribution, tortuosity, …) with

**material properties** (wettability, physisorption, chemisorption …) and

**cell performance** at working conditions (> 85°C, > 30 bar)
Thank you for your attention

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