Development of PEM Electrolysis at Elevated Temperatures

Christensen, Erik

Publication date:
2013

Citation (APA):
Development of PEM Electrolysis at Elevated Temperatures

International Symposium: Water Electrolysis and Hydrogen as part of the future Renewable Energy System
10-11 May 2012, Copenhagen

Presented by: Erik Christensen
Department of Energy Conversion and Storage
Technical University of Denmark
**Projects completed 2011**

**WELTEMP:** “Water Electrolysis at Elevated Temperatures”,
European Commission, FP7

**HyCycle:** “Center for Renewable Hydrogen Cycling”,
Danish Council for Strategic Research (DSF)

**Projects ongoing 2012**

**MEDLYS**

**MEDLYS:** “Medium temperature Water Electrolysers”,
Danish Council for Strategic Research (DSF)

**PROCON**

**PROCON:** “Danish-Chinese Centre for Intermediate Temperature Proton conducting Systems”,
Danish National Research Foundation (DNRF)
Concept of Research

Elevated temperature ($\geq 120^\circ$C)
- To obtain higher efficiency (Kinetics and thermodynamics!)
(steam or liquid?)

Requires New Materials Development due to strongly increased demands to materials:

**Component:**
- Membrane
- Current collectors
- Bipolar plates
- Catalysts

**To replace/modify:**
- Nafion
- Titanium
- Titanium
- $\text{IrO}_2$, $\text{RuO}_2$, Pt: Are they stable?

MEAs $\rightarrow$ Electrolyser
The WELTEMP Project and the Partners
www.weltemp.eu

FP7, Collaborative Project, small or medium-scale focused research project
Duration: January 1st, 2008 - April 30th, 2011
Total costs: 3.2 million Euro

The Partners
Technical University of Denmark (Coordinator) - Denmark
Institute of Chemical Technology Prague - Czech Republic
Institute of Macromolecular Chemistry ASCR - Czech Republic
The Norwegian University of Science and Technology - Norway
IHT Industrie Haute Technologie SA - Switzerland
Acta S.p.A. - Italy
Tantalum Technologies A/S - Denmark
Danish Power Systems ApS - Denmark
The partners of HyCycle (Electrolysis and Photocatalysis, www.hycycle.dk)

Technical University of Denmark, DTU Energy Conversion (coordinator)

Center for Individual Nanoparticle Functionality (CINF), Department of Physics, Technical University of Denmark

Center for Atomic-scale Materials Design (CAMD)
Department of Physics, Technical University of Denmark

Department of Physics and Chemistry, University of Southern Denmark

Institute of Chemical Engineering, biotechnology and Environmental Technology
University of Southern Denmark

IRD Fuel Cells A/S, Denmark

Danish Power Systems ApS, Denmark

Tantaline A/S, Denmark
Objectives

(1) **Membranes:**
Temperature-resistant polymer membranes, *operational temperatures ≥ 120°C*
Anion conducting (Alkaline) membranes should be surveyed as well.

(2) **Electrocatalysts:**
Stability of IrO$_2$ based anodes and Pt cathodes at temp. ≥ 120°C should be demonstrated.
Low loadings!
New non-noble metal catalysts for use under alkaline conditions.

(3) **“Construction materials”:**
Development of current collectors and bipolar plates made in steel coated with tantalum, and having excellent corrosion-, contact resistance-, and conductive properties.

(4) **Membrane Electrode Assemblies (MEAs):**
Methods for preparation of membrane-electrode assemblies (MEAs) with targets of fabrication of MEAs single cell performance approaching 1.55 V at 1.0 A/cm$^2$ at a temperature above 120°C

(5). **Test Electrolysers:**
Design, construction and testing of a prototype electrolyzers
Concepts of Polymer Membrane Materials

1) PBI (polybenzimidazol)
   - Phosphoric acid doped (apparently not stable!)

2) PFSA (Perfluorosulfonic acid, Nafion, Aquivion)
   - Water is required to be present inside the structure - otherwise no proton conductivity
   - Water evaporates from the membrane at T > 100°C
     then three ways to go:
     a) Modify Nafion/Aquivion by adding hygroscopic fillers (steam or liquid water)
     b) Doping with H₃PO₄! (only steam feeding)
     c) Pressurising the cell and working with liquid water

3) Anion conducting membranes (alkaline “PEM” electrolysis)
Steam- or Pressurized Water Electrolysis?

STEAM electrolysis:
PFSA Membrane (Aquivion) doped with H₃PO₄

Anode: 0.98 mg/cm² IrO₂, Cathode 0.34 g/cm² Pt, GDL 0.5mm Ta coated steel felt, Aquivion membrane, 63µm thick, Temperature 130°C, Atmospheric Pressure

Pressurised LIQUID water electrolysis
PFSA Membrane (Aquivion)

Anode: 1.72mg/cm² IrO₂, Cathode 0.80 g/cm² Pt, GDL 0.5mm Ta coated steel felt, Aquivion membrane, 60 µm thick, Temperature 120°C, Pressure 3 bar
Ionic conductivities of membranes

Membrane materials:
(Mechanical) Reinforcement is important to conductivity

150°C, 6 bar, 100 % RH
Construction materials:
Tantalum coated steel to replace titanium

A: Steel felt (uncoated)
B and C: Tantalum coated steel felts
D: Labscale flowplates coated with tantalum

Flowplates and anodic current collectors ("GDL"): Titanium not stable – replaced by tantalum coated steel

CVD: Chemical Vapor Deposition
\[ 2\text{TaCl}_5 (g) + 5\text{H}_2(g) \rightarrow 2\text{Ta} + 10\text{HCl}(g) \uparrow \quad (800^\circ \text{C}) \]
Desired corrosion rate in 85 % H$_3$PO$_4$: ≤ 0.1mm/year

Corrosion rate of **TITANIUM** vs. temperature and the extent of polarization

<table>
<thead>
<tr>
<th>$v_k$ [mm/a]</th>
<th>80 °C</th>
<th>120 °C</th>
<th>150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>-500 mV</td>
<td>43</td>
<td>498</td>
<td>2283</td>
</tr>
<tr>
<td>$E_{kor}$</td>
<td>31</td>
<td>451</td>
<td>2142</td>
</tr>
<tr>
<td>750 mV</td>
<td>0.2</td>
<td>437</td>
<td>2815</td>
</tr>
<tr>
<td>2000 mV</td>
<td>0.4</td>
<td>485</td>
<td>2632</td>
</tr>
<tr>
<td>2500 mV</td>
<td>0.2</td>
<td>-</td>
<td>41</td>
</tr>
</tbody>
</table>

Corrosion rate of **TANTALUM** vs. temperature and the extent of polarization.

<table>
<thead>
<tr>
<th>$v_k$ [mm/a]</th>
<th>80 °C</th>
<th>120 °C</th>
<th>150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>-500 mV</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.3</td>
</tr>
<tr>
<td>$E_{kor}$</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>500 mV</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>2000 mV</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>2500 mV</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>
Catalyst Materials/Catalyst Support Materials:

**Cathode: Pt/C**

**Anode: IrO$_2$** with or without *support*

**Supports:**
- SnO$_2$
- SnO$_2$–Sb$_2$O$_3$ (electronic conduct.)
- SnO$_2$–Sb$_2$O$_3$–“SnHPO$_4$” (elect. + proton!)
- TiO$_2$ (non-conductive supports: SnO$_2$–Sb$_2$O$_3$–“SnHPO$_4$”)
- SiC - can also provide an improved performance!

PEM steam electrolysis at 130 °C and atmosphere pressure. The anode loadings were 0.7 mg cm$^{-2}$ IrO$_2$, 1.4 mg cm$^{-2}$ IrO$_2$/SnO$_2$, 1.4 mg cm$^{-2}$ IrO$_2$/ATO, and 1.4 mg cm$^{-2}$ IrO$_2$/SnP-ATO, respectively. The cathode was made of 40 % Pt/C at a loading of 0.7 mg Pt cm$^{-2}$. Membranes used were PA doped Aquivion (0.05 mm).
Alternative concept: Alkaline MEAs

Durability issue?

Life test obtained with the ACTA alkaline MEA 475 mA/cm²), $T_{\text{cell}} = 40$ °C.
Now more than 6000 h!

Performance problem: Main issue is ionomer for catalyst layer preparation (Teflon was used).
Active non-noble metal catalysts were developed for both anode and cathode!
Medium temperature/Intermediate temperature cell

Temperatures: 200-400°C

MEDLYS and PROCON projects:

Inorganic proton conducting membranes:

CsH$_2$PO$_4$
Nb-P
Bi-P
Nd-P
etc.

Various alternative (non-noble element) catalysts will be tested.
Achievements/Breakthroughs

• PEM Steam electrolysis can be carried out

• PFSA membranes can be made conductive at high temperatures by phosphoric acid doping.

• Reinforced membranes provide higher conductivity

• Pressurised cells reached higher performances than steam electrolysers at 130°C (until now...)

• Tantalum coated steel felt as anode GDL

• MEAs based on anion conductive/alkaline membranes can be prepared, high durability at temp. up to 60°C have been observed.
• Alkaline MEAs, working without noble metals.
Application perspectives

The research represents a survey of various types of electrolyser technologies: 

*Acidic PEM, Alkaline PEM, Liquid water feeding, steam electrolysis (÷SOEC)*

**PEM: decentralized units**       **Alkaline: Centralized units**

For large scale use in the nearer future according to governmental plans, alkaline technologies will be important!

*(Denmark: 50 % of total electricity consumption from sustainable sources in 2020=> Large electricity storage capacity will be needed very soon!)*
Acknowledgements

David Aili
Aleksey Nikiforov
Martin Kalmar Hansen
Jerry Xu
Carsten Prag
Annemette Hindhede Jensen

Martin Paidar, ICTP
Milan Kouril, ICTP
Li Qingfeng
Irina Petrushina
Jens H. von Barner
Chao Pan

Niels J. Bjerrum

Partners:

DTU Physics
SDU
TUM
IRD Fuel Cells

ICTP, Czech Republic
IMC, Czech Republic
NTNU, Norway
IHT, Switzerland
Acta Nanotech, Italy
Tantaline A/S, Denmark
Danish Power Systems, Denmark
Thank You for your attention!