



Development of PEM Electrolysis at Elevated Temperatures

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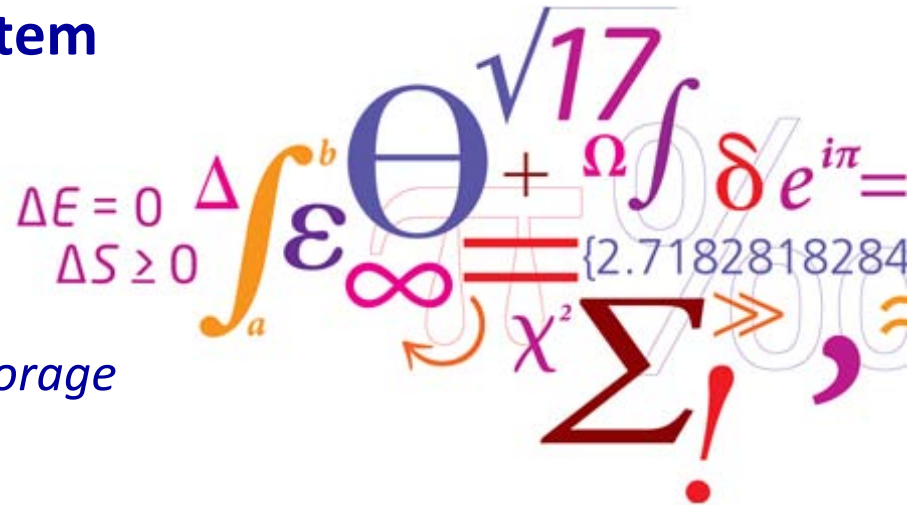
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Development of PEM Electrolysis at Elevated Temperatures

**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: "Danish-Chinese Centre for Intermediate Temperature Proton conducting Systems",
Danish National Research Foundation (DNRF)

Concept of Research

Elevated temperature ($\geq 120^\circ\text{C}$)

- 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

MEAs → Electrolyser

To replace/modify:

Nafion

Titanium

Titanium

IrO_2 , RuO_2 , Pt: Are they stable?

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 EC Funding: 2.4 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 $\geq 120^{\circ}\text{C}$
Anion conducting (Alkaline) membranes should be surveyed as well.

(2) Electrocatalysts:

Stability of IrO_2 based anodes and Pt cathodes at temp. $\geq 120^{\circ}\text{C}$ 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 electrolysers

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 $T > 100^{\circ}\text{C}$ then three ways to go:
 - a) Modify Nafion/Aquivion by adding hygroscopic fillers (steam or liquid water)
 - b) Doping with H_3PO_4 ! (only steam feeding)
 - c) Pressurising the cell and working with liquid water

3) Anion conducting membranes (alkaline "PEM" electrolysis)

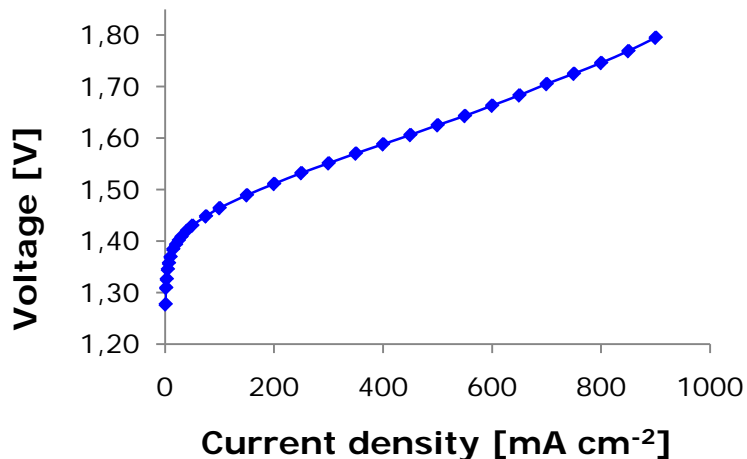
Nafion®

PBI

Aquivion™
“Short side chain”-
PFSA

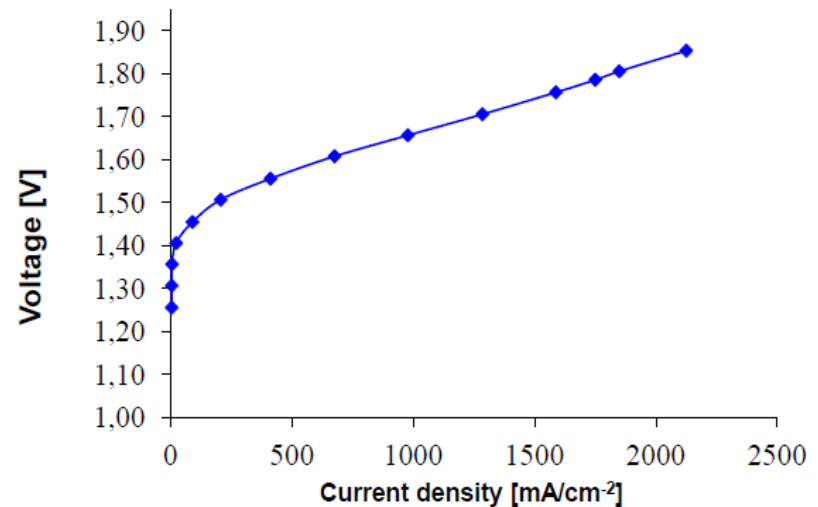
Steam- or Pressurized Water Electrolysis?

STEAM electrolysis:
 PFSA Membrane (Aquivion)
 doped with H_3PO_4



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

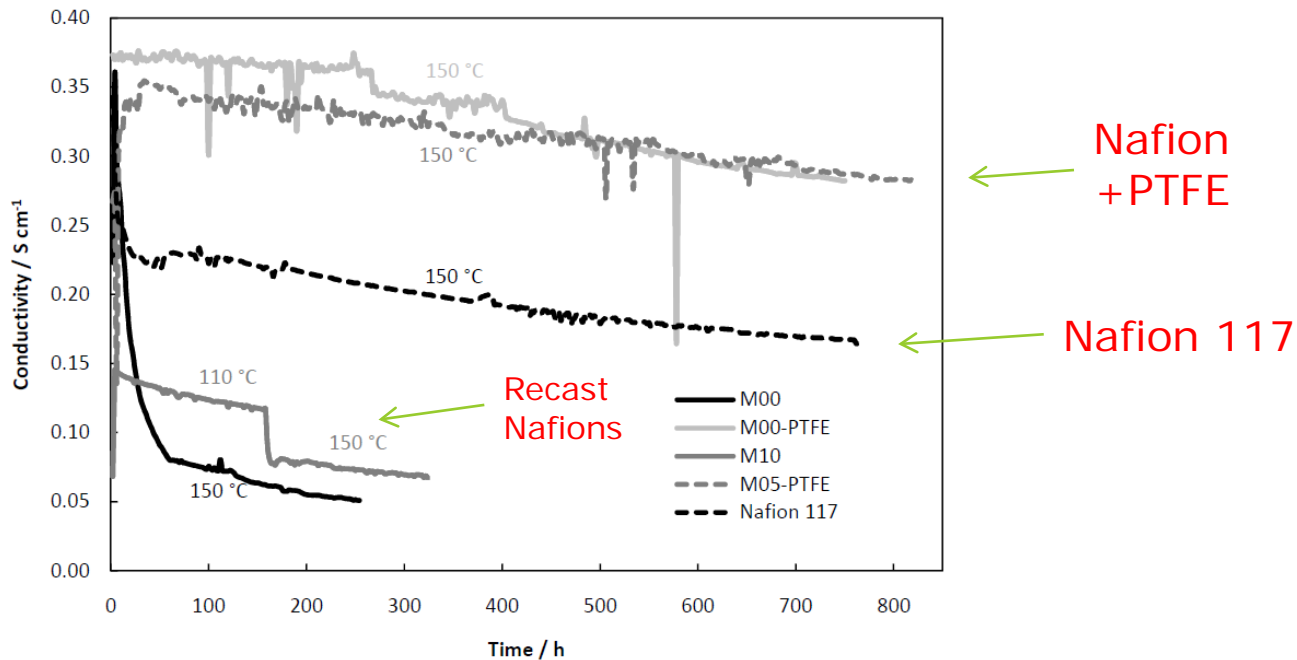
Pressurised LIQUID water electrolysis
 PFSA Membrane (Aquivion)



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

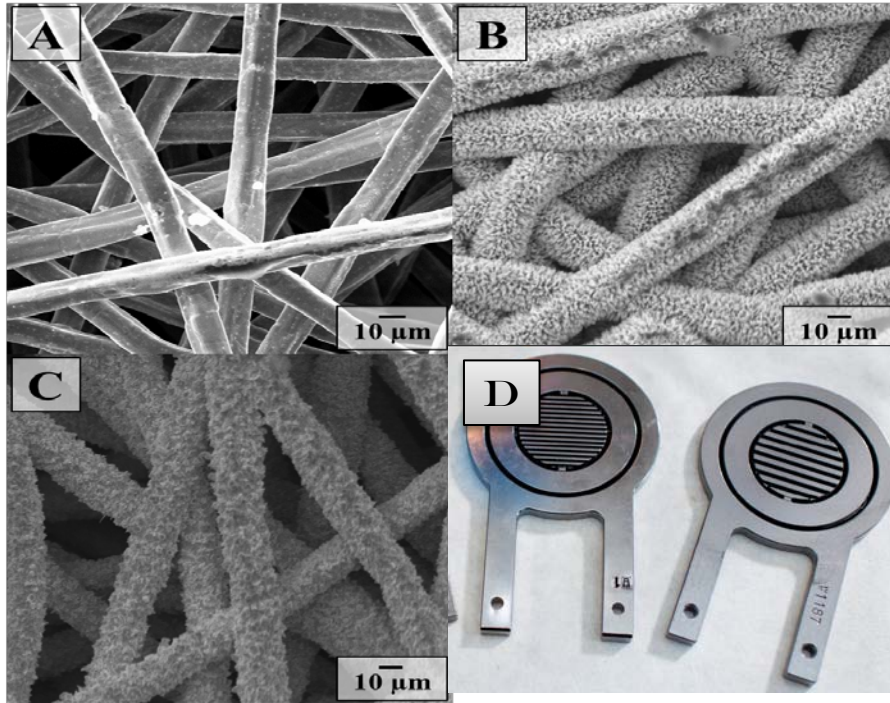
Membrane materials:
(Mechanical) Reinforcement is important to conductivity



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



**Desired corrosion rate in 85 % H_3PO_4 :
 $\leq 0.1\text{mm/year}$**

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

v_k [mm/a]	80 °C	120 °C	150 °C
-500 mV	43	498	2283
E_{kor}	31	451	2142
750 mV	0.2	437	2815
2000 mV	0.4	485	2632
2500 mV	0.2	-	41

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

v_k [mm/a]	80 °C	120 °C	150 °C
-500 mV	<0.01	<0.01	0.3
E_{kor}	<0.01	<0.01	<0.01
500 mV	<0.01	<0.01	<0.01
2000 mV	<0.01	<0.01	<0.01
2500 mV	<0.01	<0.01	<0.01

Catalyst Materials/Catalyst Support Materials:

Cathode: Pt/C

**Anode: IrO₂ with
or without support**

Supports:

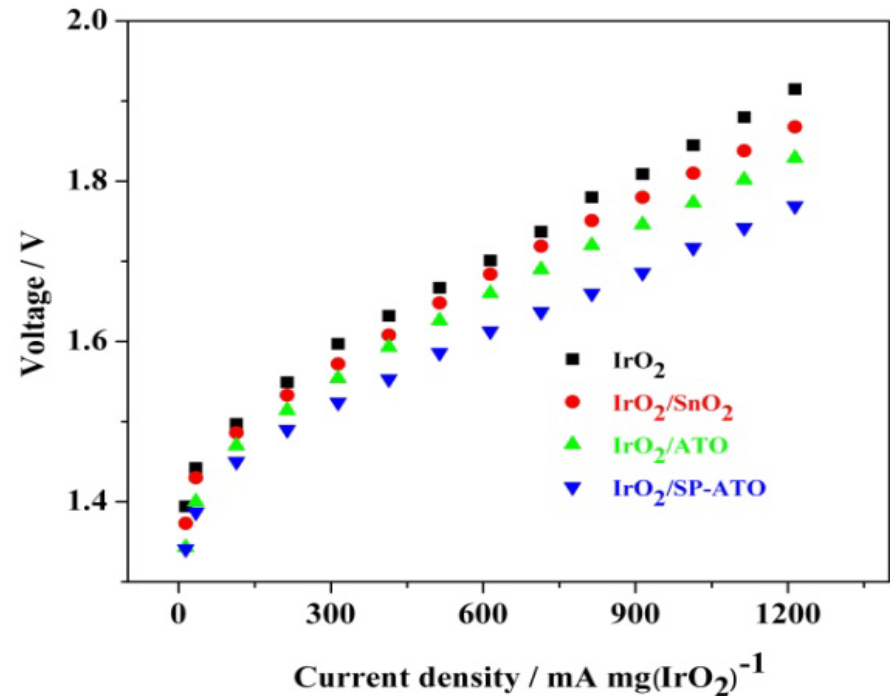
SnO₂

SnO₂-Sb₂O₃ (electronic onduct.)

SnO₂-Sb₂O₃-"SnHPO₄" (elect. + proton!)

TiO₂ (non-conductive supports:

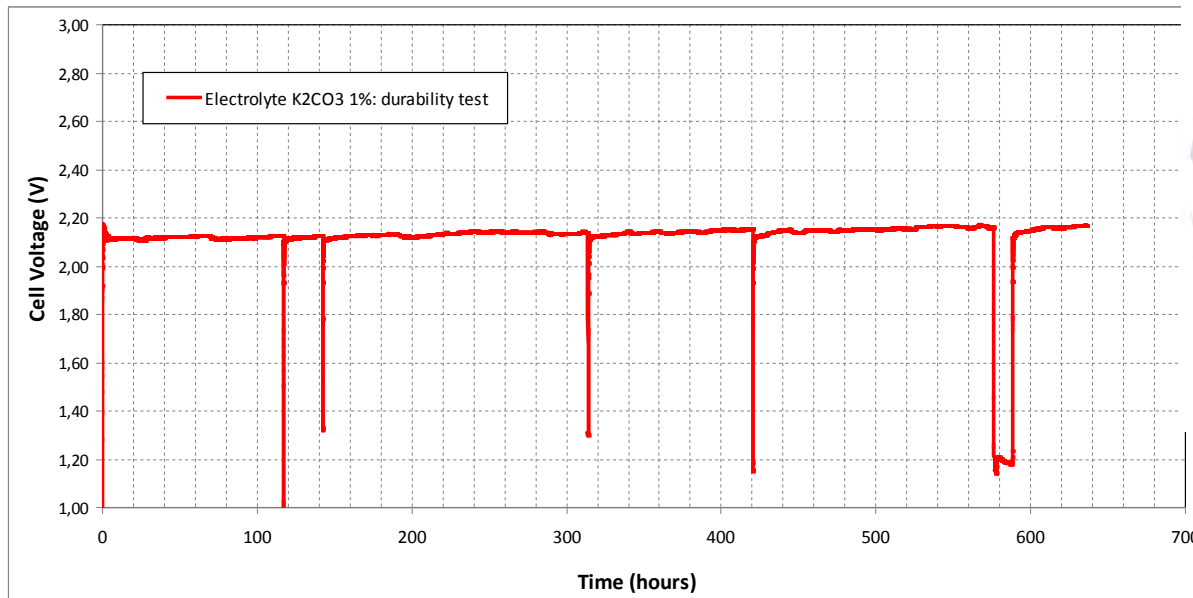
SiC - can also provide an improved performance !)



PEM steam electrolysis at 130 °C and atmosphere pressure. The anode loadings were 0.7 mg cm⁻² IrO₂, 1.4 mg cm⁻² IrO₂/SnO₂, 1.4 mg cm⁻² IrO₂/ATO, and 1.4 mg cm⁻² IrO₂/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 ?



AES100 – 300 Stacks
from Acta-nanotech
30 bars, no compressor
alkaline membranes

Life test obtained with the ACTA alkaline MEA (475 mA/cm^2), $T_{\text{cell}} = 40^\circ \text{ C}$.
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_2PO_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 electrolyzers 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!)

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Thank You for your
attention!