Water Electrolysis using Polymeric Electrolyte Membranes at Elevated Temperatures

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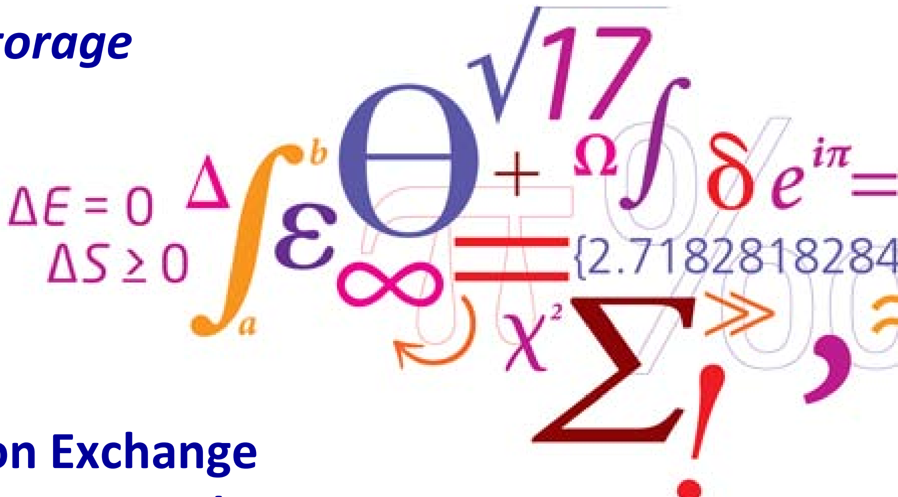


3rd CARISMA International Conference on Medium and High Temperature Proton Exchange Membrane Fuel Cells, 3-5 September 2012, Copenhagen

Fuel cells:

Where does *the fuel* come from?!

PEM electrolysis:

A *parallel world* of membranes, catalysts, stacks etc.

– More agressive conditions!

Concept of Research

Elevated temperature (≥120°C)
- To obtain higher efficiency (Kinetics and thermodynamics!)
(steam or liquid?)

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

Component:	*To replace/modify:*
Membrane	Nafion
Current collectors	Titanium
Bipolar plates	Titanium
Catalysts	IrO_2, RuO_2, Pt: Are they stable?

MEAs → Electrolyser

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)

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/cm² at a temperature above120°C

(5). Test Electrolysers:
Design, construction and testing of a prototype electrolysers

Concepts of Polymer Membrane Materials

1) PBI (polybenzimidazol)

- Phosphoric acid doped, steam (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 H_3PO_4! (only steam feeding)
c) Pressurising the cell and working with liquid water

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

Nafion®

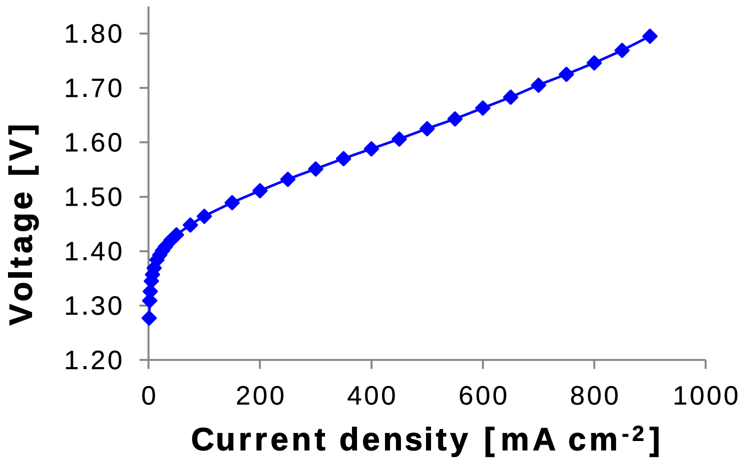
PBI

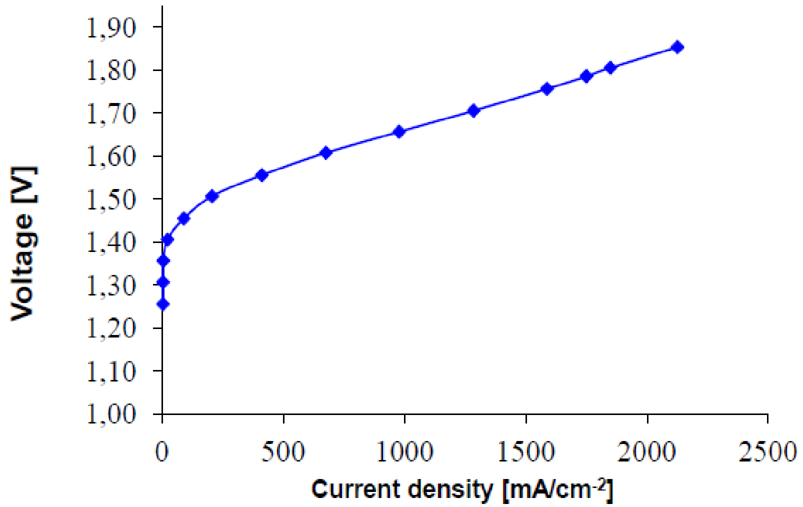
Aquivion™
“Short side chain”-PFSA

Steam- or Pressurized Water Electrolysis?

STEAM electrolysis:
PFSA Membrane (Aquivion)
doped with H_3PO_4

Pressurised LIQUID water electrolysis
PFSA Membrane (Aquivion)



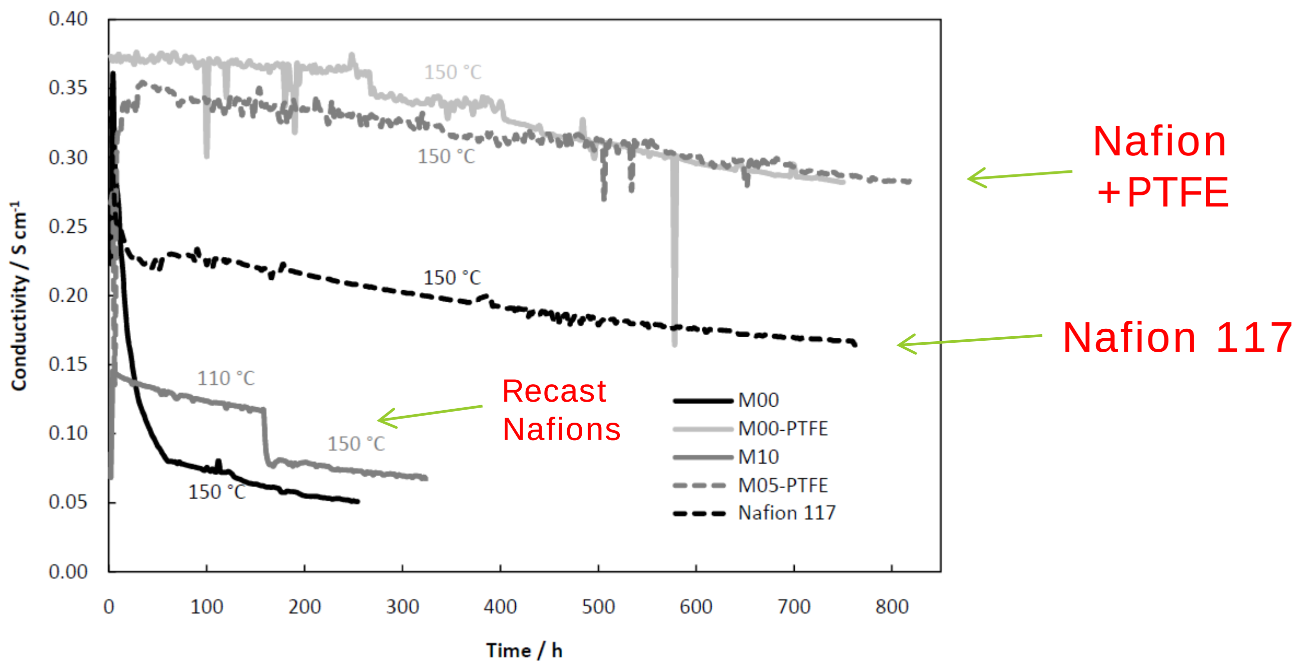


Anode: 0.98 mg/cm2 IrO_2, Cathode 0.34 g/cm2 Pt, GDL 0.5mm Ta coated steel felt, Aquivion membrane, 63µm thick, Temperature 130°C, Atmospheric Pressure

Anode: 1.72mg/cm2 IrO_2, 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

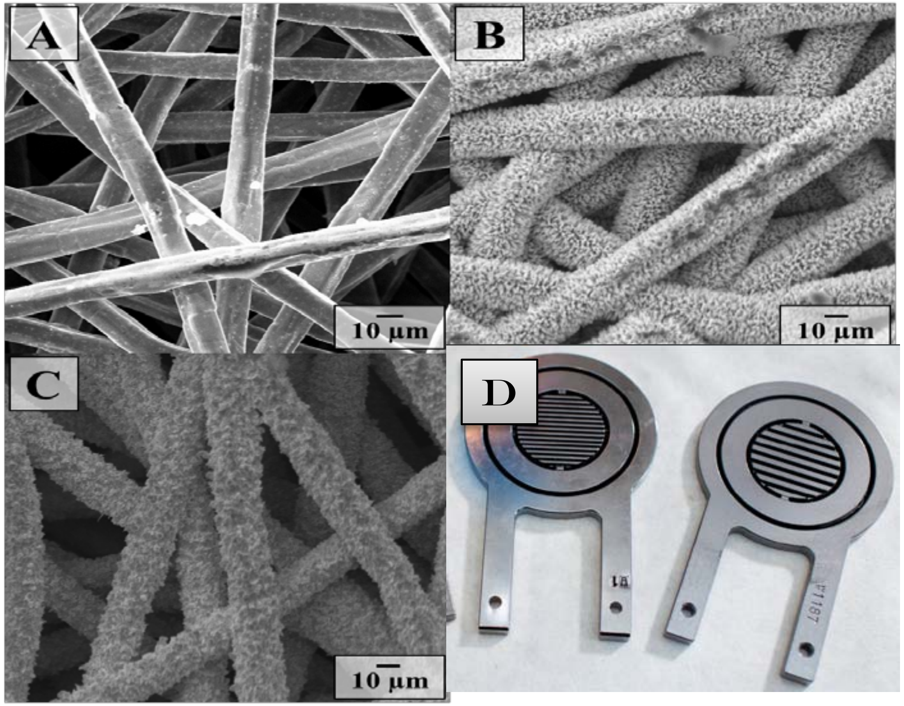
Membrane materials:
(Mechanical)Reinforcement
is important to conductivity



150ºC, 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"):
For H_3PO_4 doped membranes Titanium is not stable
– replaced by tantalum coated steel: improves corrosion stability and contact resistance

CVD: Chemical Vapor Deposition

$$2TaCl_5\,(g) + 5H_2(g) \rightarrow 2Ta + 10HCl(g)\uparrow \quad (800^{o}C)$$

Desired corrosion rate in 85 % H_3PO_4: ≤ 0.1mm/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*

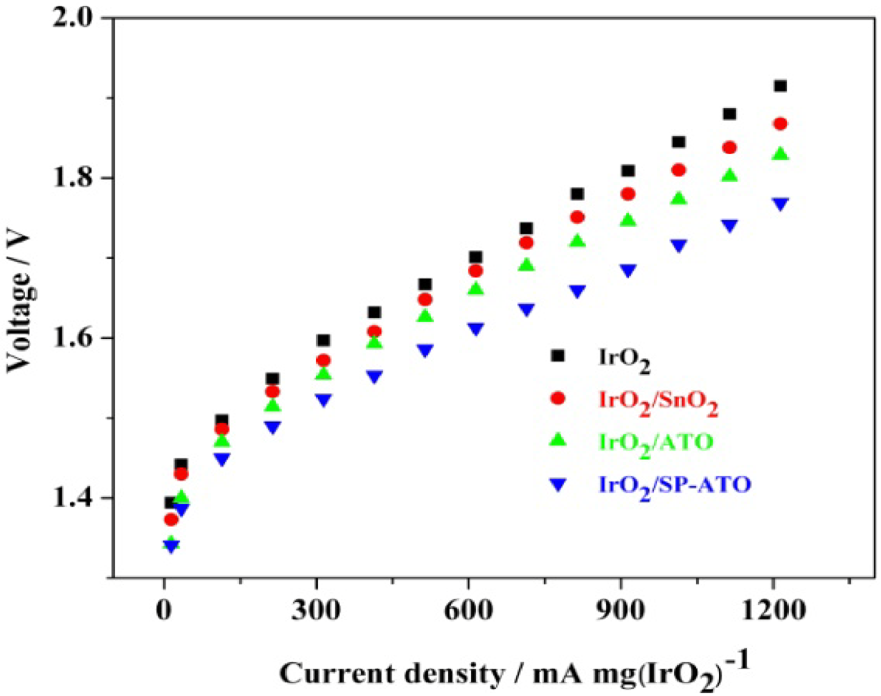
Catalyst Materials / Catalyst Support Materials:

Cathode: Pt / C

Anode: IrO_2 with
or without *support*

Supports:
SnO_2
$SnO_2–Sb_2O_3$ ("ATO",electronic onduct.)
$SnO_2–Sb_2O_3$-"$SnHPO_4$"(elect.+proton!)

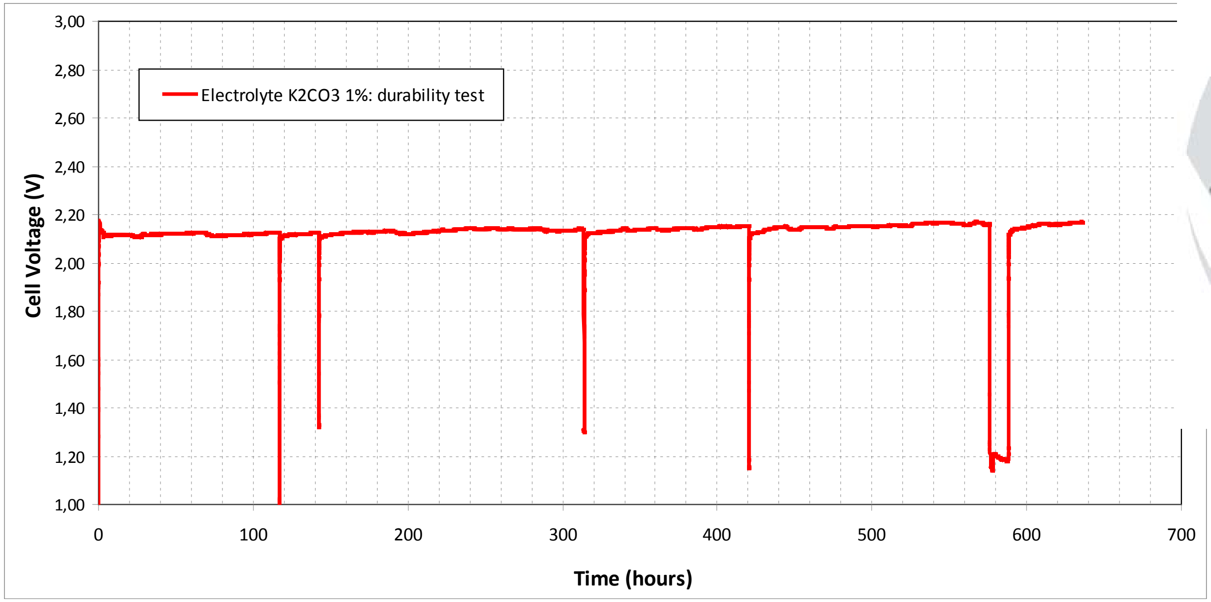
TiO_2 (non-conductive supports:
SiC - can also provide an improved performance !)



PEM steam electrolysis at 130 °C and atmosphere pressure.
The anode loadings were 0.7 mg cm^{-2} 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 ?



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_{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^{0}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 are 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^{o}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^{o}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!)

Future R&D materials development priorities

- Problem:Not yet a replacement for IrO_2 in PEM-WEs available
  - limits (*acidic*) PEM to smaller units.
- PEM R&D should probably aim for high temp. *and* high pressure
- For high pressure PEMEC: metal foam-like materials for flowpatterns (mechanical support for membranes)
- Design and manufacturing processes for bipolar plates
- Anion conductive membranes, and particularly *ionomers for MEA electrodes* (÷ IrO_2 and Pt!)
- Inorganic proton conducting materials and ”intermediate temperature” electrolysers (÷ IrO_2 and Pt?!)

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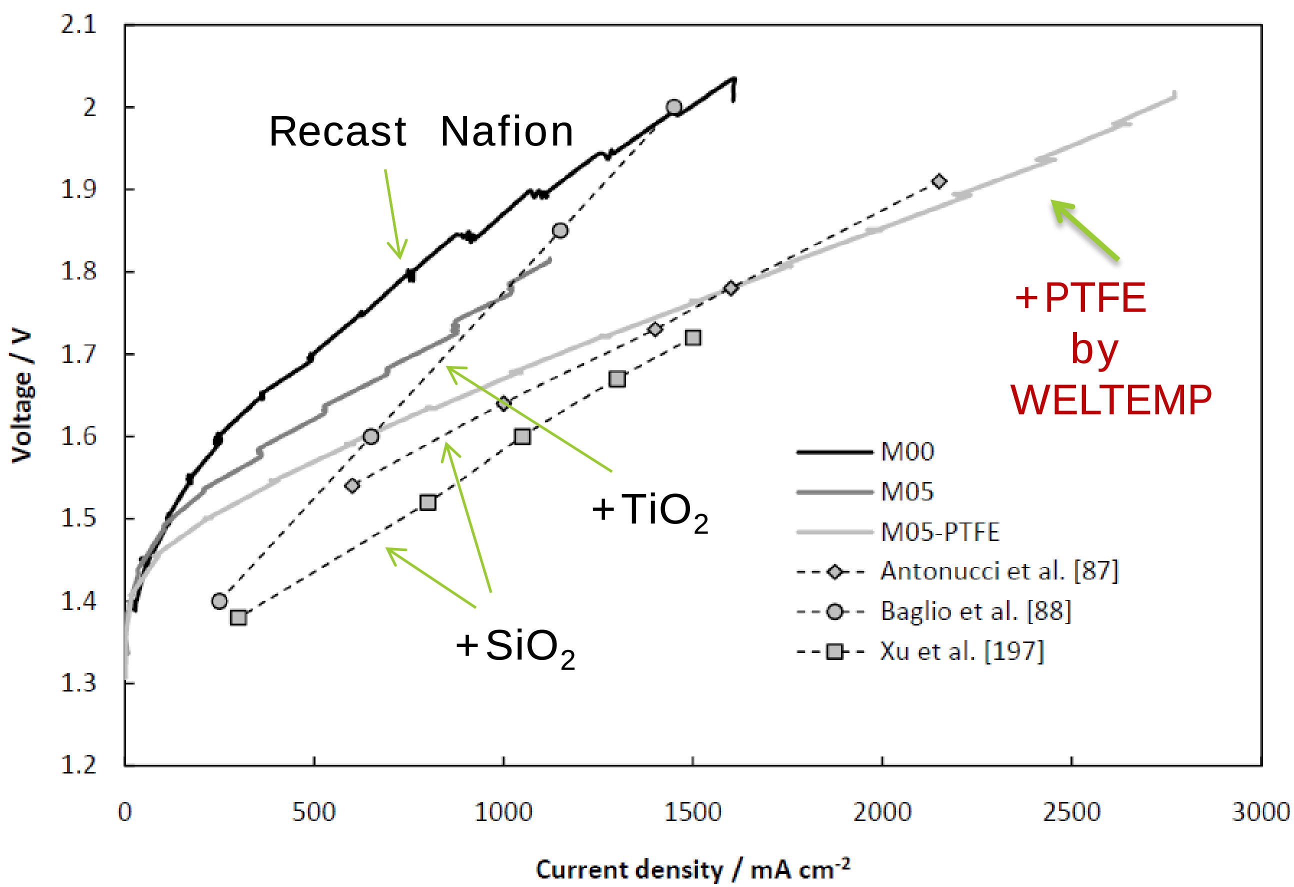
Thank You for your attention!

Supplementary Information

Comparison of performances of modified Nafion MEAs,120ºC and 2-3 bar



High performances are obtained, but best labscale PEM at 80ºC are comparable

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

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Danish Power Systems ApS	Denmark

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