Brussels, November 10th 2010

Development of an Internal Reforming Alcohol High Temperature PEM Fuel Cell Stack

IRAFC, JTI-FCH-JU-2008-1

A project supported by the Fuel Cells and Hydrogen Joint Undertaking

Project acronym: **IRAFC**
Grant agreement No.: **245202**
Duration : Jan 2010- Dec 2012

Project Overview – Participants

- **Advanced Energy Technologies** (Coordinator), Patras, *Greece*
- **University of Maria Curie- Sklodowska**, *Poland*
- **Nedstack Fuel Cell Technology BV**, *The Netherlands*
- **Centre National de la Recherche Scientifique**, CNRS, Strasbourg, *France*
- **Foundation for Research and Technology, Hellas- Institute of Chemical Engineering & High Temperature Chemical**, Patras, *Greece*
- **Institut für Mikrotechnik Mainz GmbH**, Mainz, *Germany*

Work Packages

•**WP1**: **Project Management**

•**WP2: Synthesis and characterization of novel high temperature polymer electrolyte membranes**

•**WP3: Reforming catalysts: synthesis and screening**

•**WP4**: Catalytic formulations into functional structures

•**WP5**: Electrochemical characterization of materials

•**WP6**: Single cell, stack design and testing

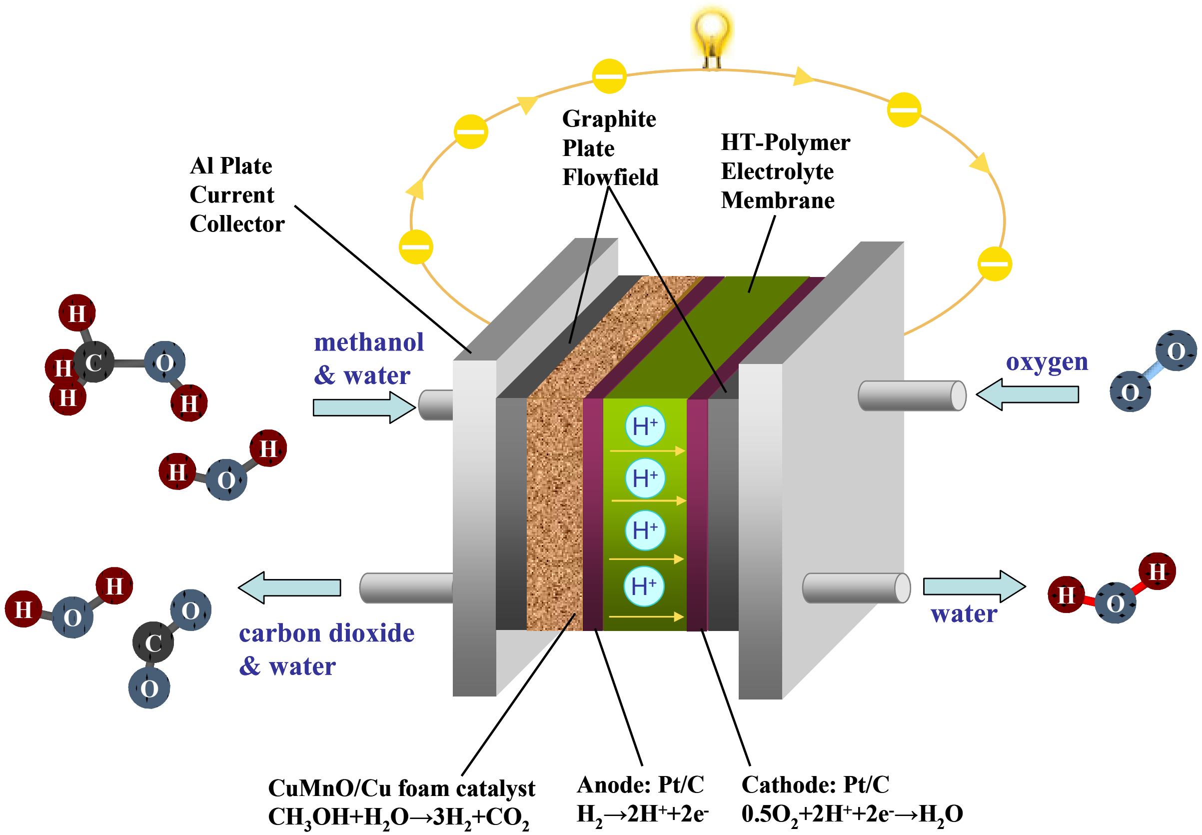
•**WP7**: Construction, long term testing of short stacks and integration of a 100W stack to a complete system

•**WP8**: Dissemination and public awareness

Main Idea

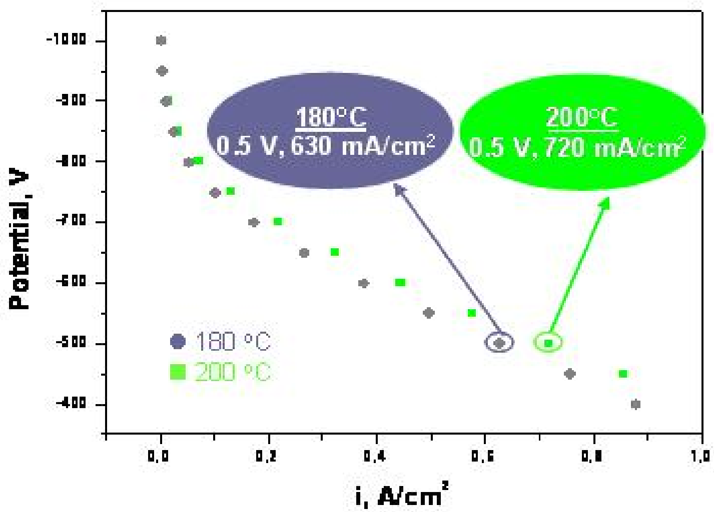
The increase of the operation temperature opens
new ways of direct combination of
the Fuel Cell with the Reformer

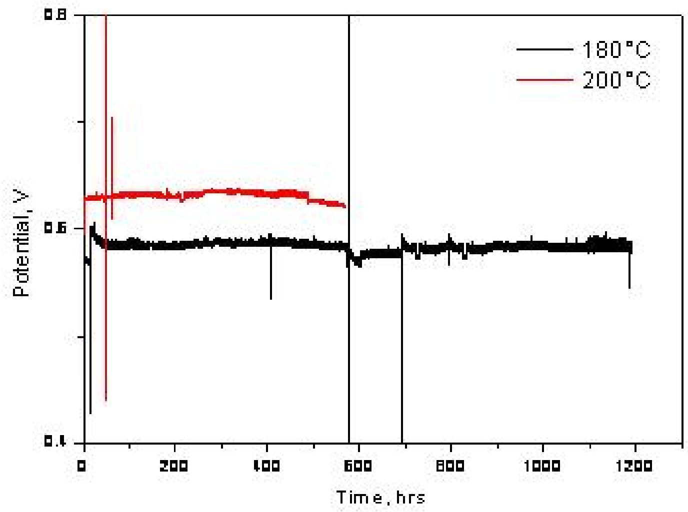
Internal Reforming Methanol Fuel Cell



Integrated reformed alcohol (methanol) HT-PEMFC configuration. The fuel cell is composed of a membrane electrode assembly (MEA) comprising a high-temperature protonconducting electrolyte membrane sandwiched between the anodic (methanol reforming catalyst for the production of CO-free hydrogen + anode electrocatalyst) and cathodic gas diffusion electrodes.

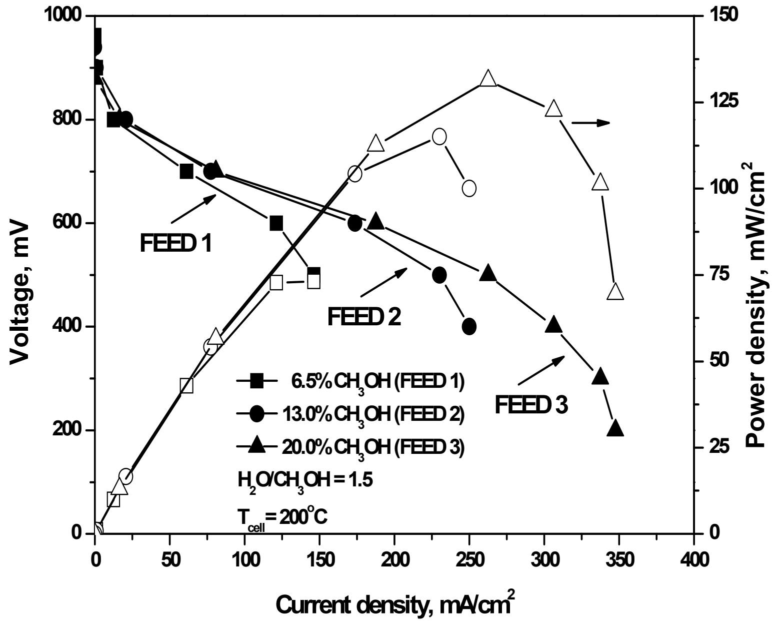
Proof of concept

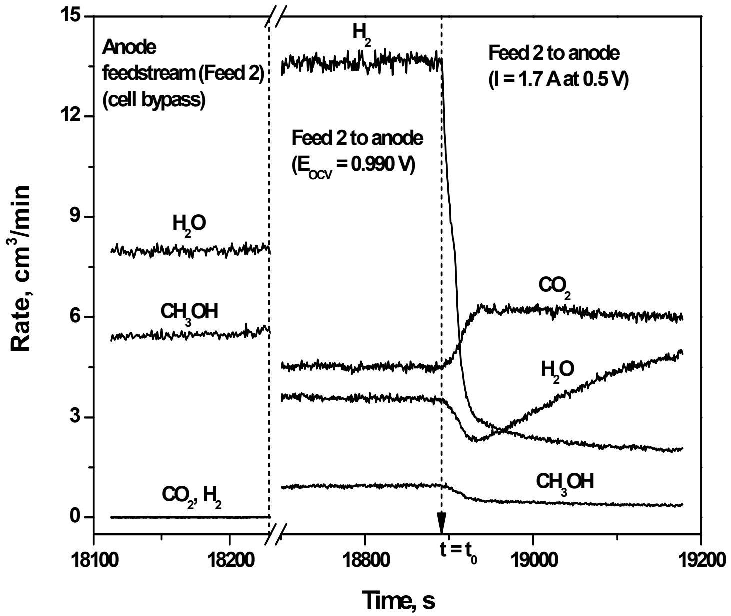




I-V and long term stability measurements of the TPS® type MEA

Proof of concept





Performance of IRAFC.
G. Avgouropoulos, J. Papavasiliou, M. K. Daletou, J. K. Kallitsis, T. Ioannides, S. Neophytides
Applied Catalysis B: Environmental 90 (2009) 628–632

Project goals

The ultimate goal of the project is to deliver:

-***An Internal-Alcohol-Reforming High-Temperature PEM fuel cell***

(IRAFC) **with the following characteristics**:

(i) 0.15 W/cm^2 at 0.7V, operating at 220°C
(ii) Specific (W/kg) and volumetric (W/m^3) power density similar to current, state-of-the-art high-temperature PEM fuel cells operating on hydrogen.

Critical components of the IRAFC

(i) New polymer ***membranes*** with improved thermal and chemical stability ***able to operate at 220°C***

(ii) New ***alcohol reforming catalysts*** with improved activity and stability able to provide ***stable hydrogen production*** in the anode environment

(iii) ***Bipolar plates specifically designed*** under the requirements of IRAFC operation.

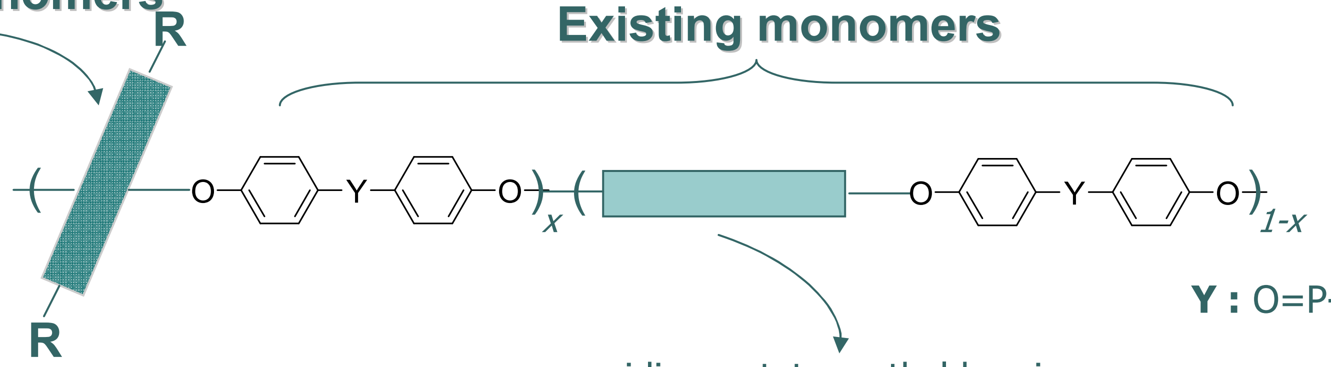
WP 2 : Synthesis And Characterization Of Novel High Temperature Polymer Electrolyte Membranes

Synthesis of linear aromatic polyethers containing side pyridine, terpyridine or carboxyl ester units

Copolymers with expected increased acid doping ability & potential crosslinking sites.

New diol monomers

Existing monomers



Y : O=P-Ph, SO_2

pyridine or tetramethyl bearing monomers

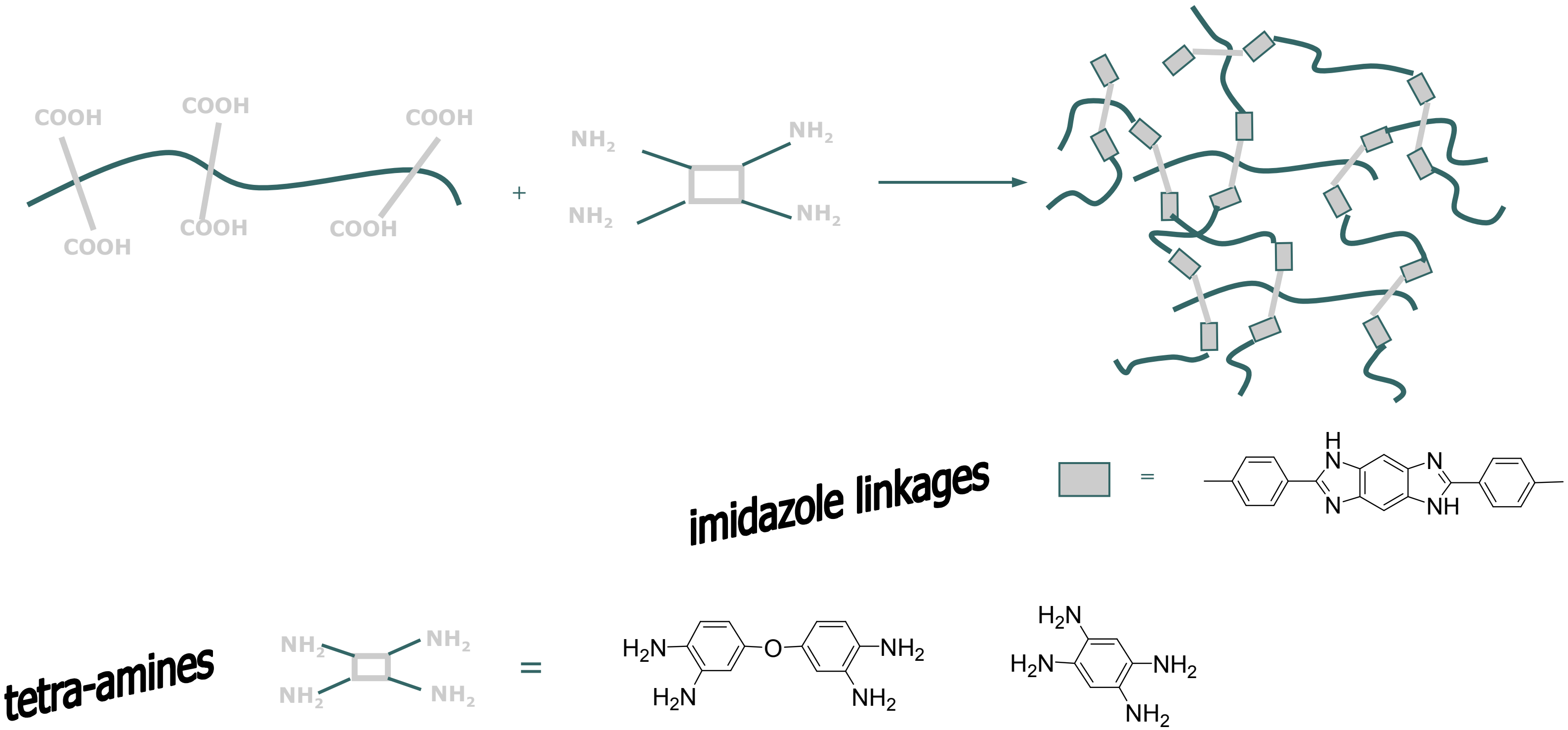
R = Crosslinking Sites

pyridine, terpyridine or carboxyl ester units

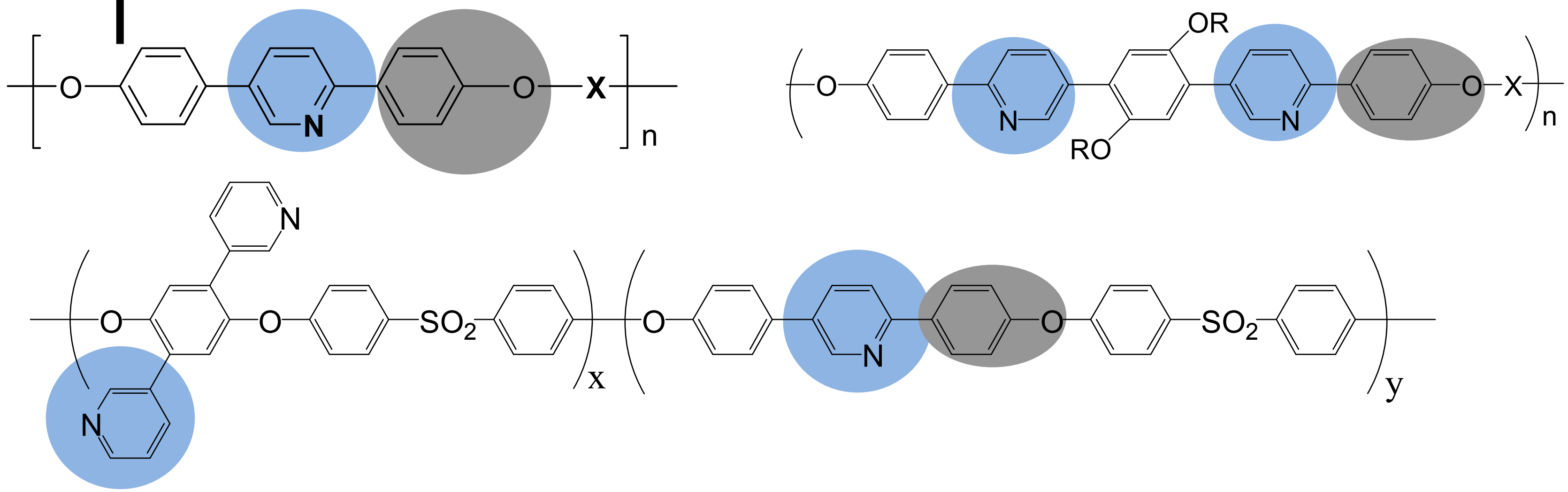
Characterization of the resulting copolymers by thermal, mechanical analyses and evaluation of their phosphoric acid uptake.

WP 2 : Synthesis And Characterization Of Novel High Temperature Polymer Electrolyte Membranes

Attempts of crosslinking through Imidazole Formation



Route to Design and Synthesis of Novel Polymers (Aromatic Polyethers bearing Polar Groups)



Structural Characteristics

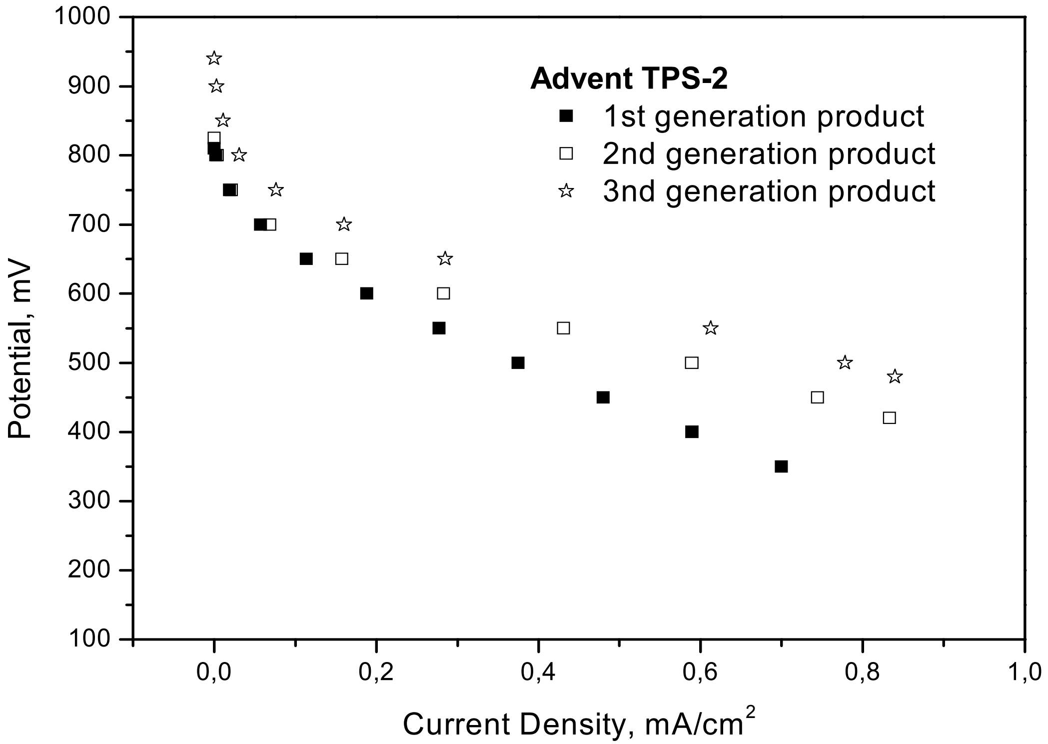
- **Aromatic Polyether**
  - High Thermal Stability
  - High Chemical Stability
- **Pyridine Polar Group**
  - H^+ Acceptor site
  - Hydrogen Bond site

- Monomer Preparation
- Polymerization via polycondensation
- Characterization via H-NMR, GPC, DMA, TGA, FT-iR, Tensile testing
- Selection of the best membranes for MEA construction and testing

N.Gourdoupi, A.K. Andreopoulou, V. Deimede, J.K. Kallitsis *Chem.Mater.*, *15,* 5044, **2003**

E.K. Pefkianakis, V. Deimede, M.K. Daletou, N. Gourdoupi, J.K. Kallitsis *Macromol. Rapid Commun.*, *26*, 1724, **2005**

Membrane and MEA interface optimization-Advent TPS-2

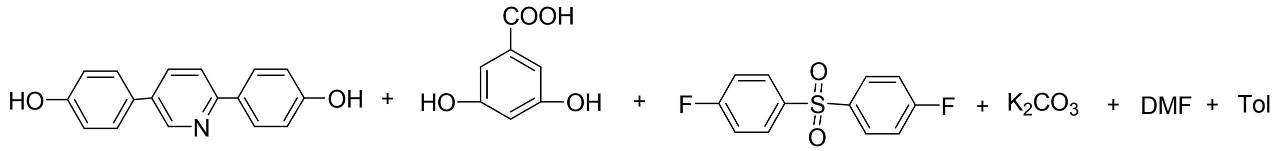


Temperature: **180 ºC**
Ambient pressure
Feed : H_2/air
Anode: 1.2
Cathode: 2.0

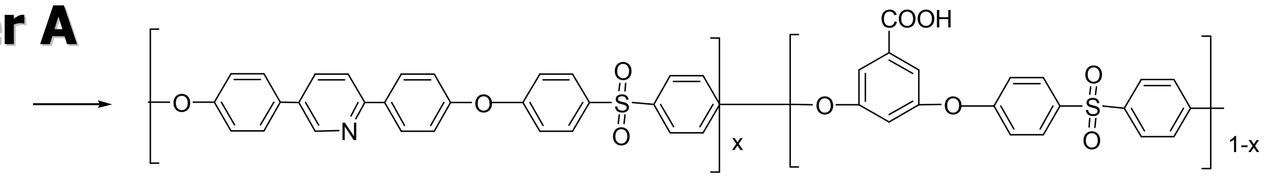
Advent TPS-2	Performance		Increase in performance
	I (mA/cm²) at 0.5V	V (mV) at 0.2 A/cm²	
1st generation	375	594	-
2nd generation	590	631	55%
3rd generation	780	683	110%

Linear aromatic polyethers containing side crosslinkable units

Copolymers with free carboxylic side groups

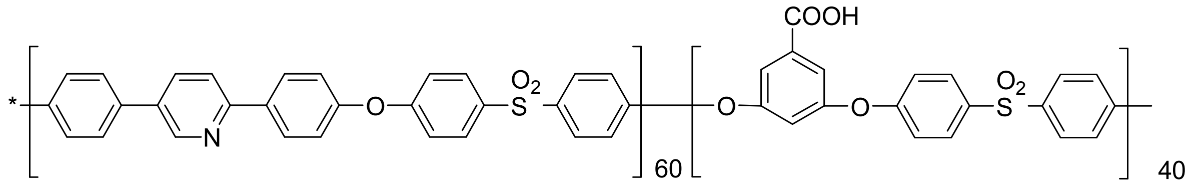


Copolymer A

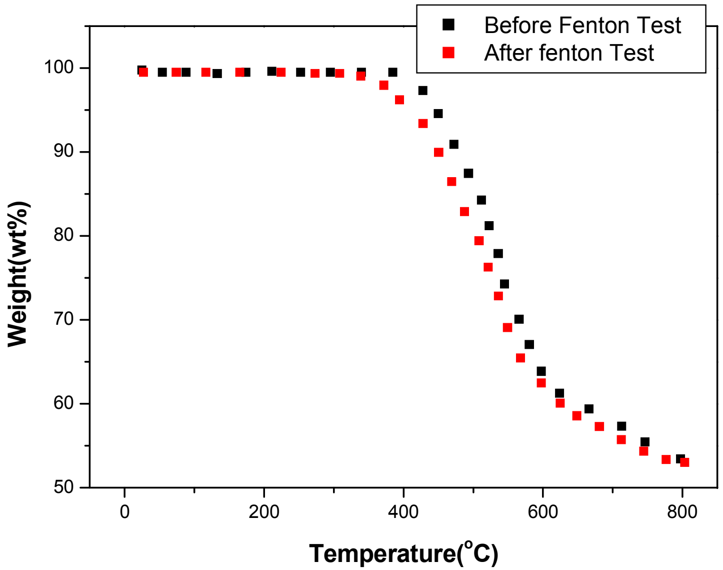


	Copolymer	x - y	H-NMR	Film Integrity
1	**MX145**	60-40	**60-40**	✓ ✓ ✓
2	**MX149**	65-35	**55-45**	✓ ✓ ✓
3	**MX150**	75-25	**46-54**	✓
4	**MX151**	80-20	**70-30**	×
5	**MX152**	60-40	**53-47**	✓ ✓
6	**MX153**	75-25	**71-29**	✓ ✓ ✓
7	**MX154**	85-15	**59-41**	×
8	**MX157**	60-40	**54-46**	✓ ✓ ✓
9	**MX159**	80-20	**71-29**	×
10	**MX160**	85-15	**70-30**	×

Thermal Properties of the Copolymers with free carboxylic side groups

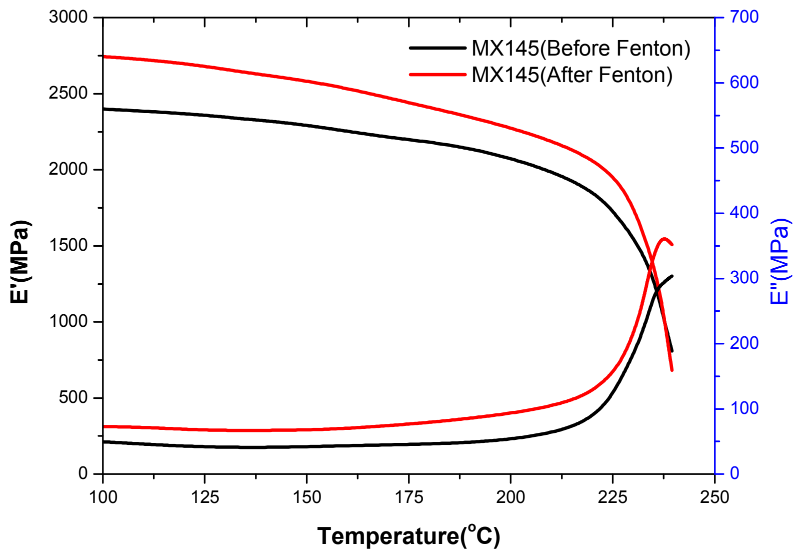


TGA



TGA *thermographs in nitrogen atmosphere of the copolymers* ***MX145(60-40)***
before *(----) and* ***after*** *Fenton Test(----)*

DMA

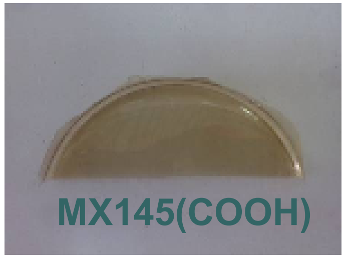


Temperature dependence of the ***storage (E')*** *and* ***loss (E'')*** *modulus for the copolymers* ***MX145(60-40) before*** *(----) and* ***after*** *Fenton Test(----)*

Crosslinking of Carboxyl bearing polymers

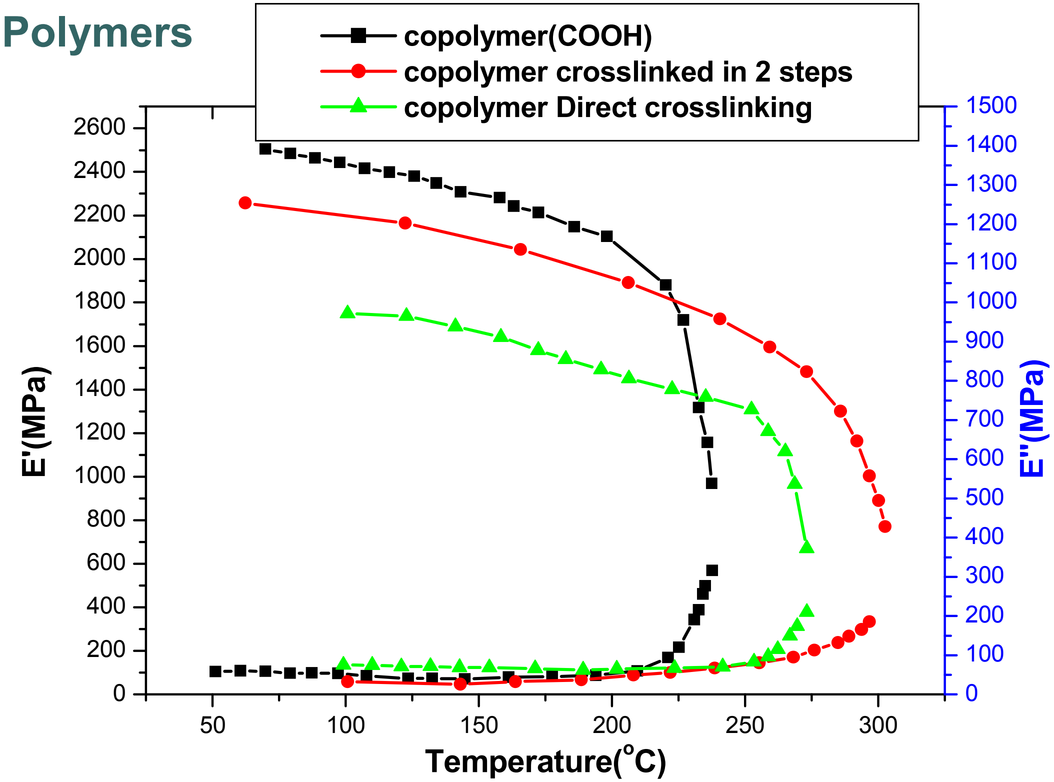
Soluble fraction

Time (h)	MX145 (COOH)	MX196 cross	MX197 cross
1	100%	0%	0%
5	100%	0%	0%
24	100%	3,5%	3%



Properties of the Crosslinked Polymers

DMA



Linear aromatic polyethers containing side crosslinkable units

CODE	x/y[a]	x/y[b]	Mn[c]	Mw	I	FILM	Tg
B1	80/20	79.5	10000	28000	2.8	-	-
B2	60/40	70	14400	33800	2.3	+	215
B3	60/40	66.6	22000	46110	2.0	+	198
B4	70/30	77	22000	44400	1.9	+	204
B5	80/20	82.5	20300	55670	2.7	-	-
B6	60/40	68	16780	34550	2	+	198
B7	80/20	88.7	25400	78800	3.1	--	-
B8	70/30	83.4	23900	64150	2.6	+	225
B9	60/40	73	33800	92100	2.7	+	228
B10	**80/20**	**80**	**65000**	**156000**	2.4	+	230
B11	50/50	67	48950	142500	2.9	+	226

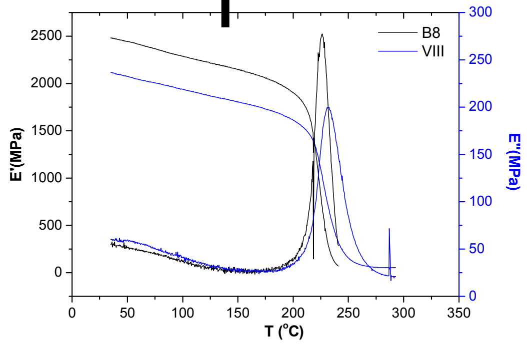
[a] Compositions as determined by the monomers' feed ratio
[b] Compositions as determined by the ^{1}H NMR
[c] GPC in $CHCl_3$

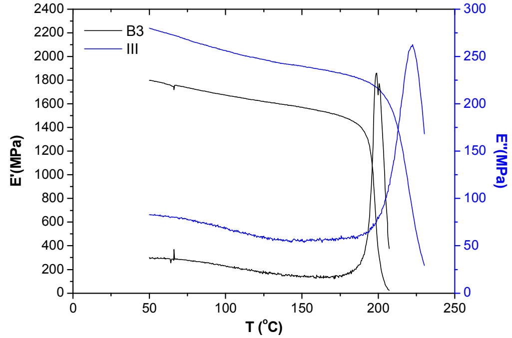
Crosslinking of side double bonds

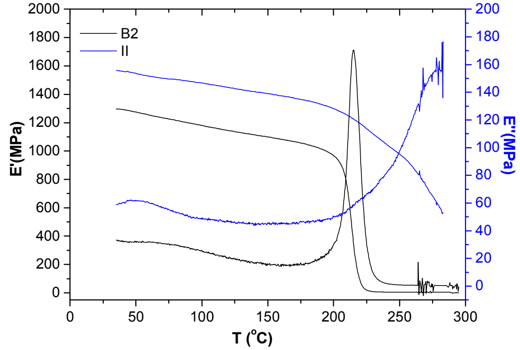
Copolymer	CODE OF CROSSLINKED POLYMER	eqdb/ eqCrosslinker	Tg	Solubility in DMA[c]
B1	I	0.93	-	-9,7
B2	**II**	**0.3**	**280**	**-2,7**
B3	III	0.93	222	-18
B4	IV	0.93	214	-14,5
B4	IVa	0.3	250	-9
B8	VIII	0.3	232	-8
B9	**IX**	**0.5**	**290**	**-1.7**
B9	IXa	0.3	290	-5
B10	**X**	**0.5**	**232**	**-1.5**

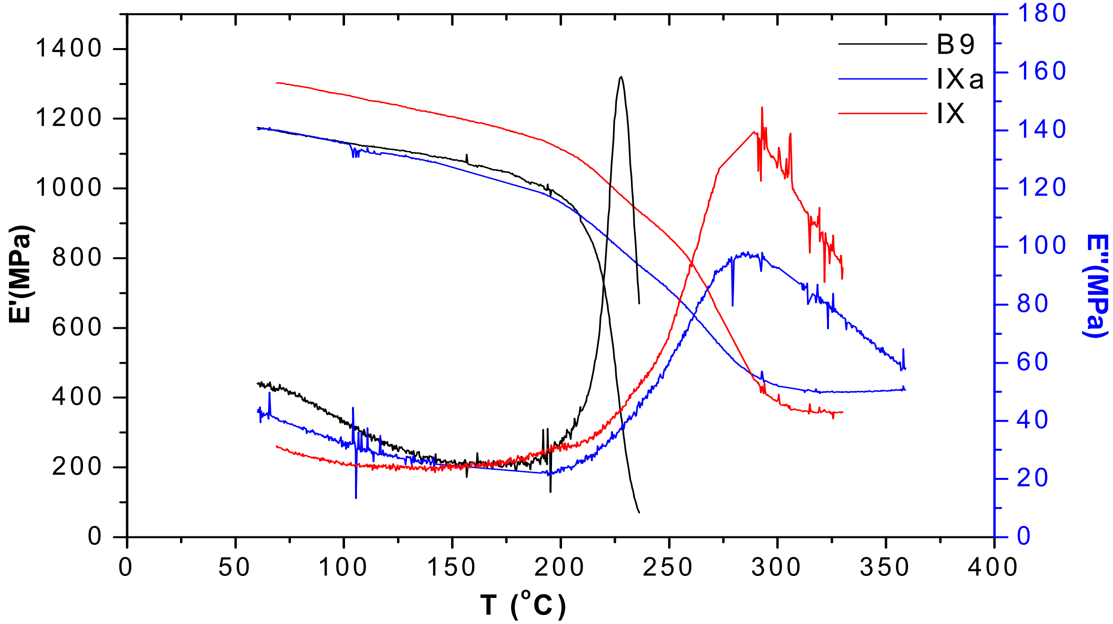
[C] For 5 hours at 55 ^{o}C

Crosslinking of side double bonds

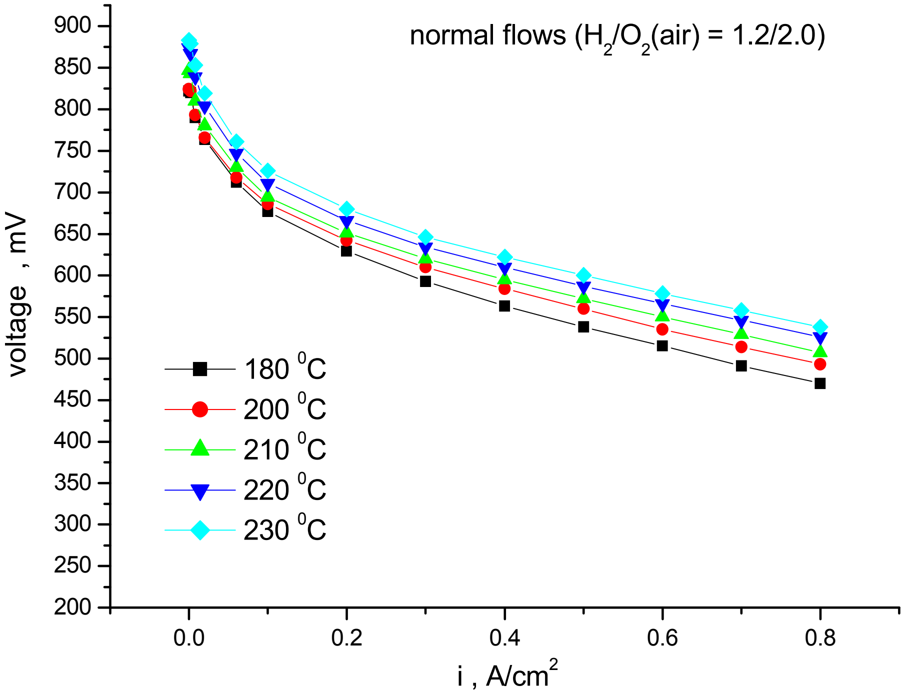


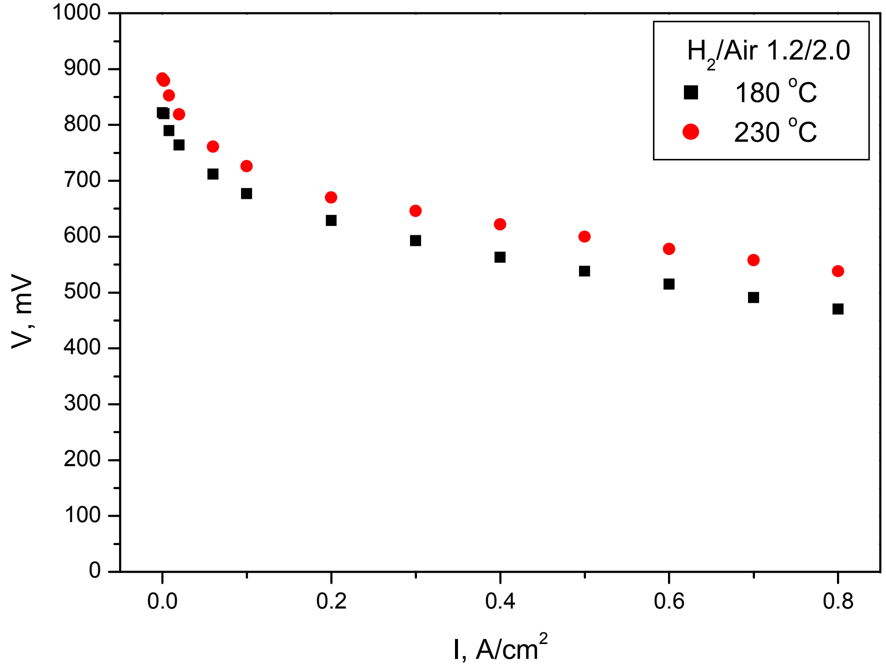






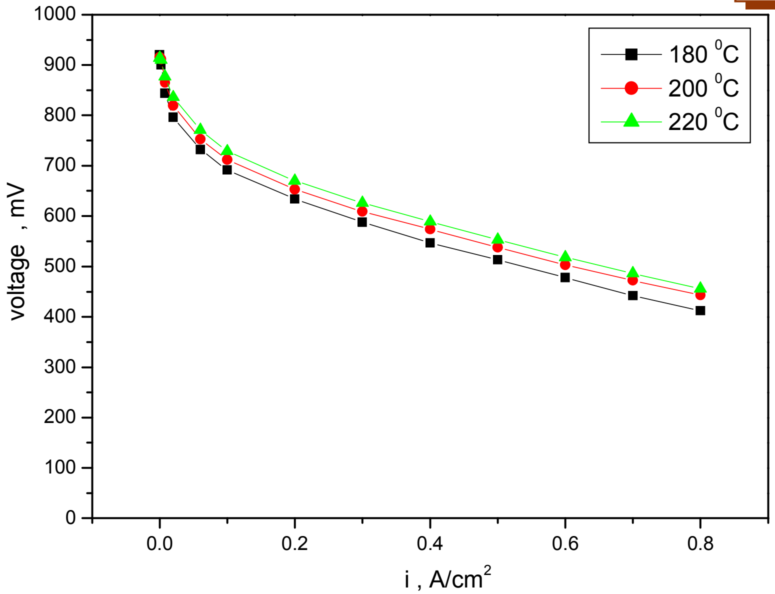
Increase of the Operation Temperature

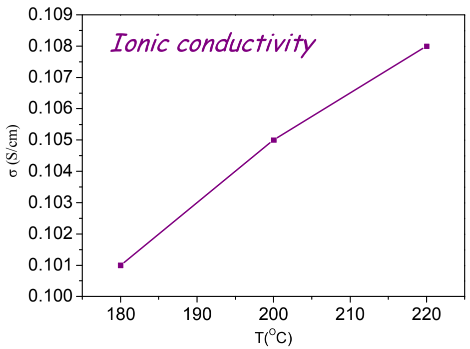




Increase of the Operation Temperature of the MEAs based on Crosslinked Copolymers B

I-V Curves of MEA 1



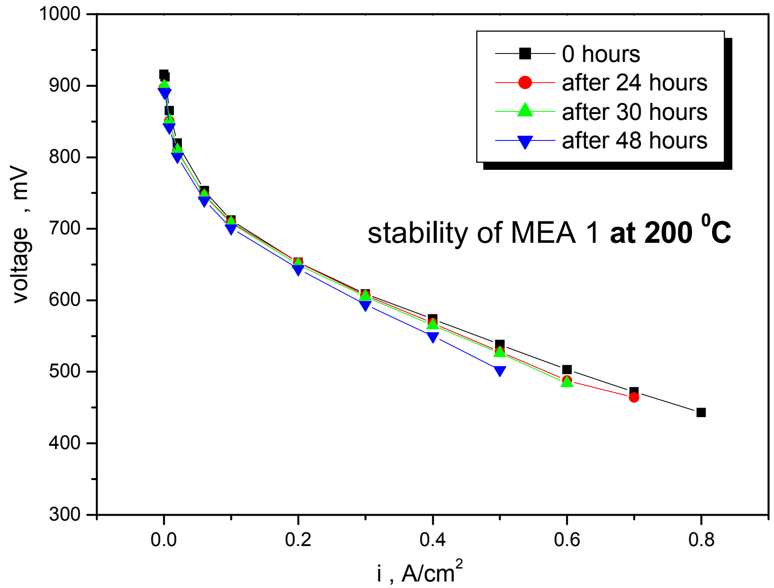


Hydrogen / Air

DL of MEA 1 = 250%

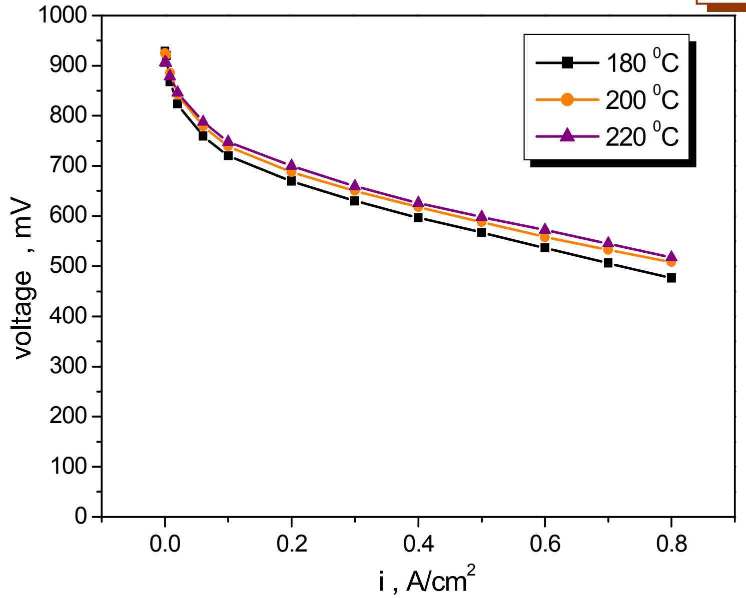
Temperature (°C)	**180**	**200**	**220**
Voltage (mV) at $0.2 A/cm^2$	634	653	670
Current at 500 mV	0.53	0.6	0.67
Conductivity (S/cm)	0.101	0.105	0.108

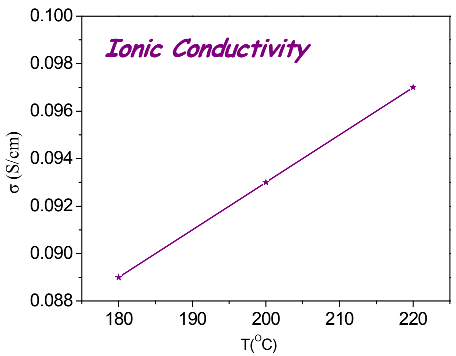
STABILITY of MEA 1 at 200°C



Increase of the Operation Temperature of the MEAs based on Crosslinked Copolymers B

I-V Curves of MEA 2



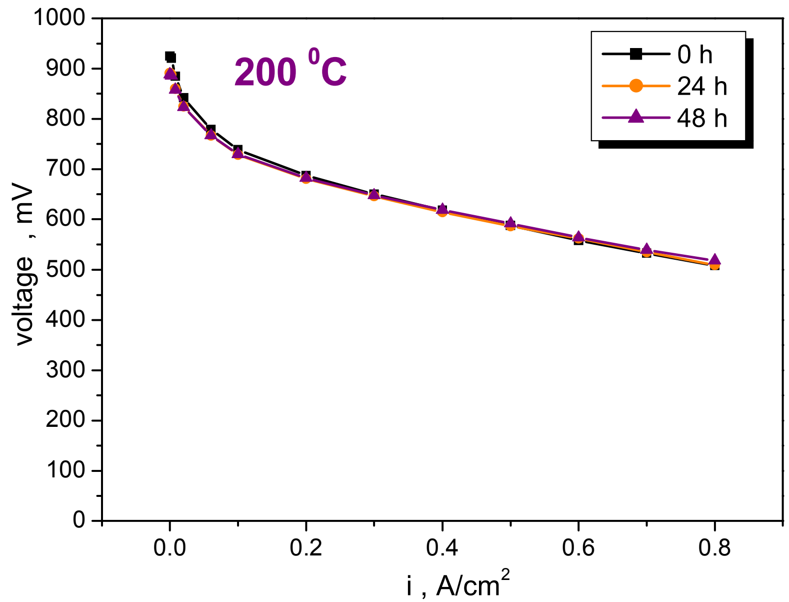


Hydrogen / Air

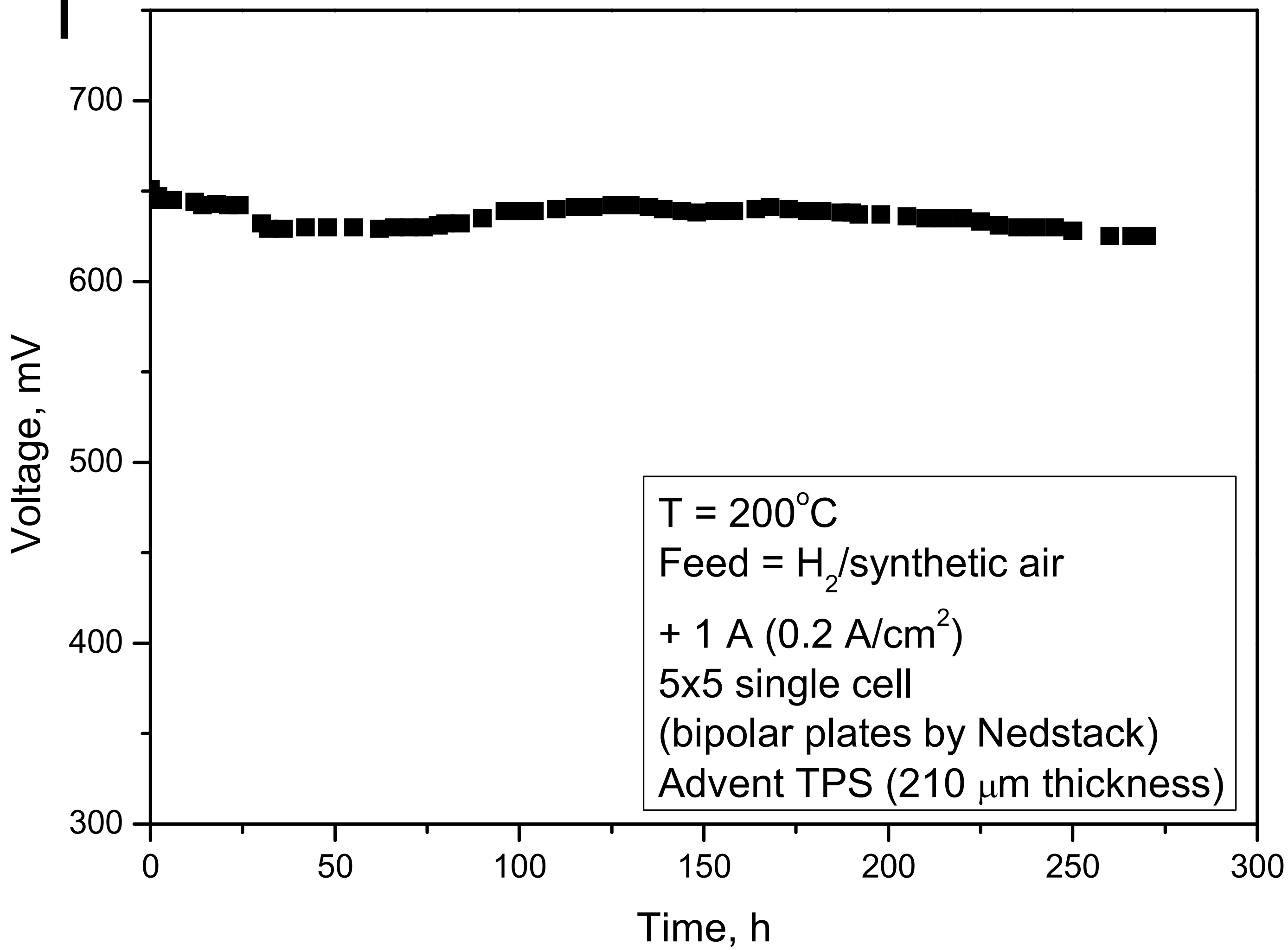
DL of MEA 2 = 195%

Temperature (°C)	**180**	**200**	**220**
Voltage (mV) at 0.2A/cm²	670	687	700
Current at 500 mV	0.7	0.8	>0.8
Conductivity (S/cm)	0.089	0.093	0.097

STABILITY of MEA 2 at 200°C

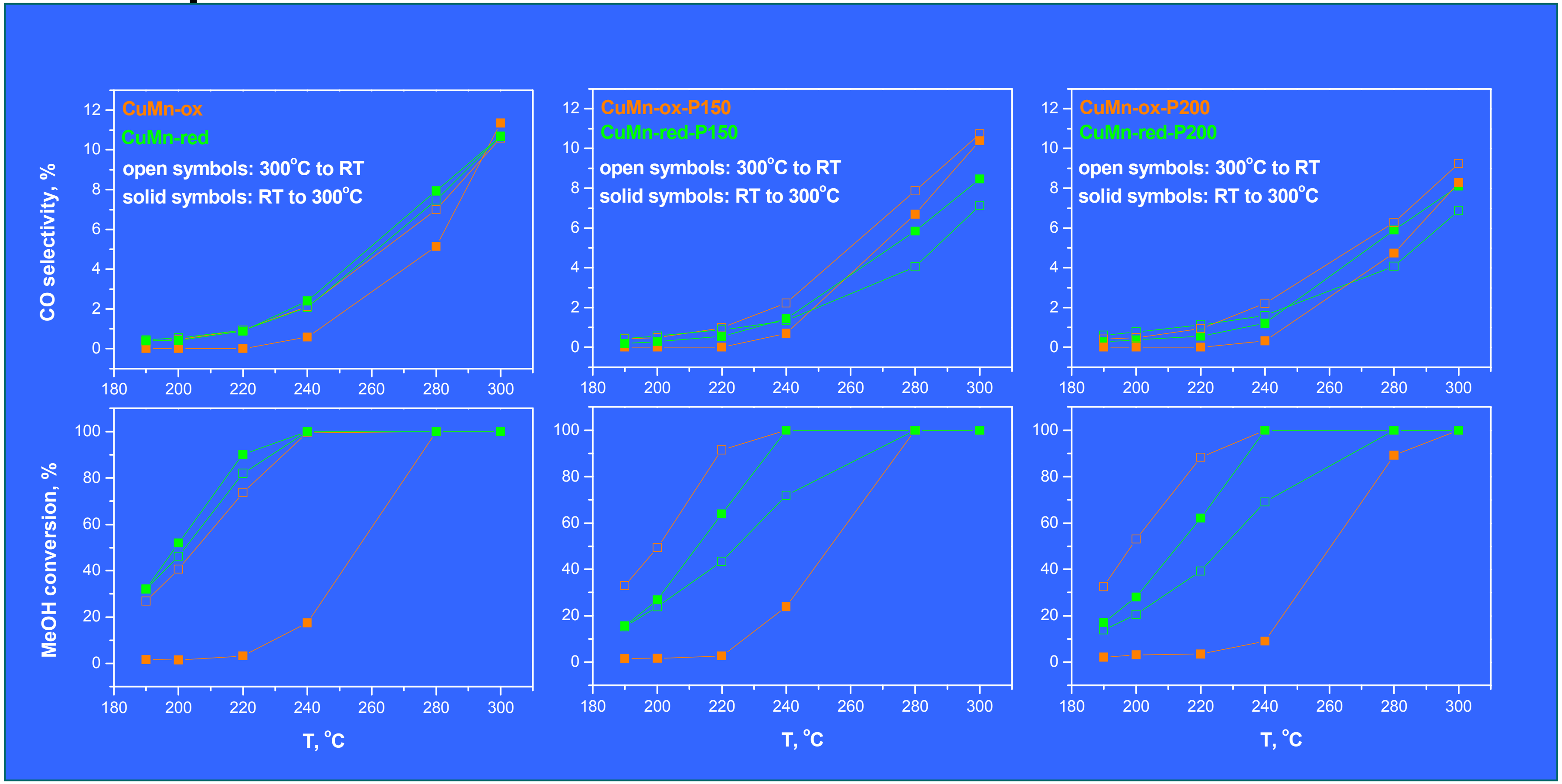


Increase of the Operation Temperature



WP3: Reforming catalysts: synthesis and screening

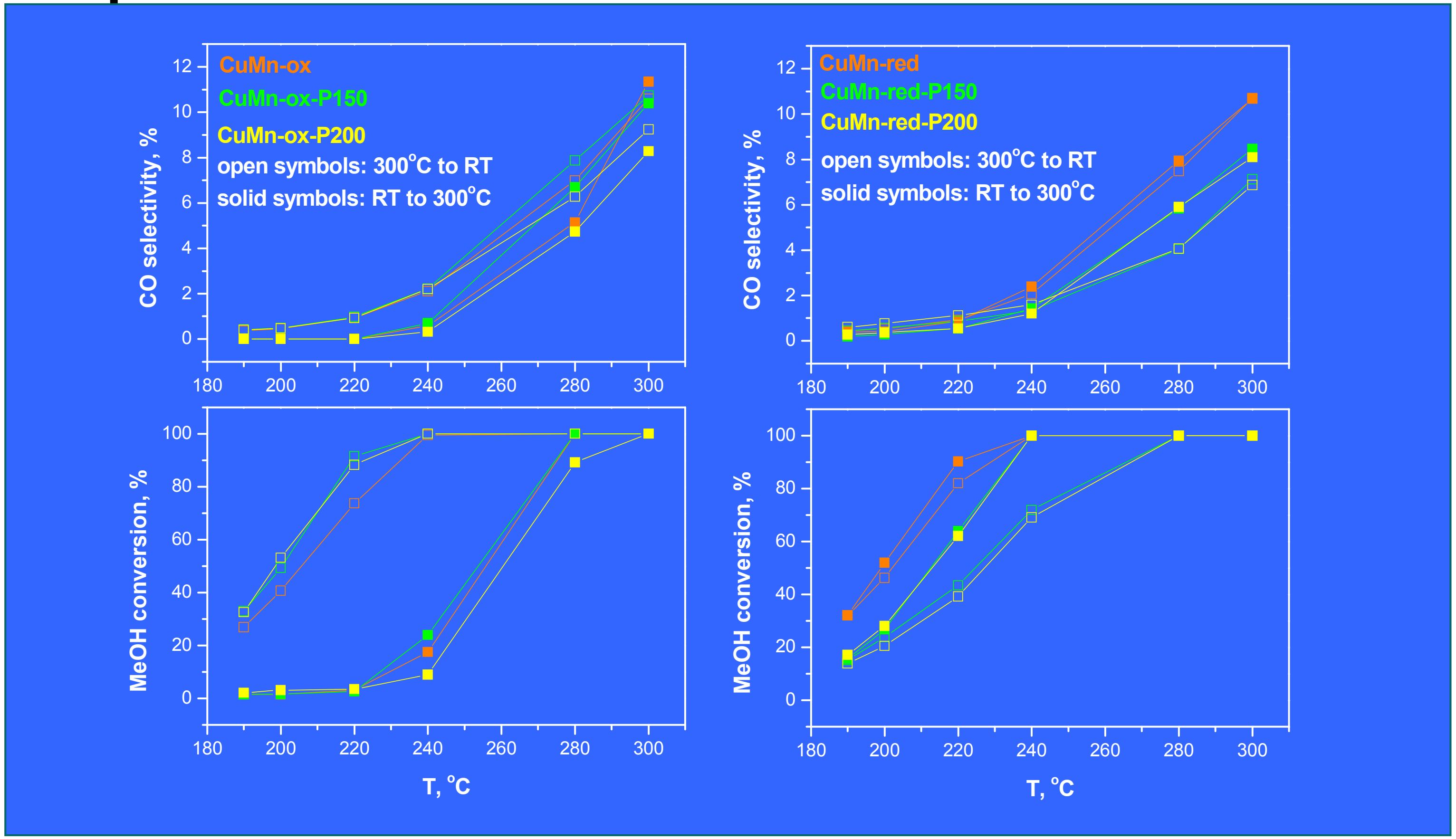
First results on CuMnOx catalysts



✓The catalytic activity of oxidized samples is higher when the reaction T goes from higher to lower values

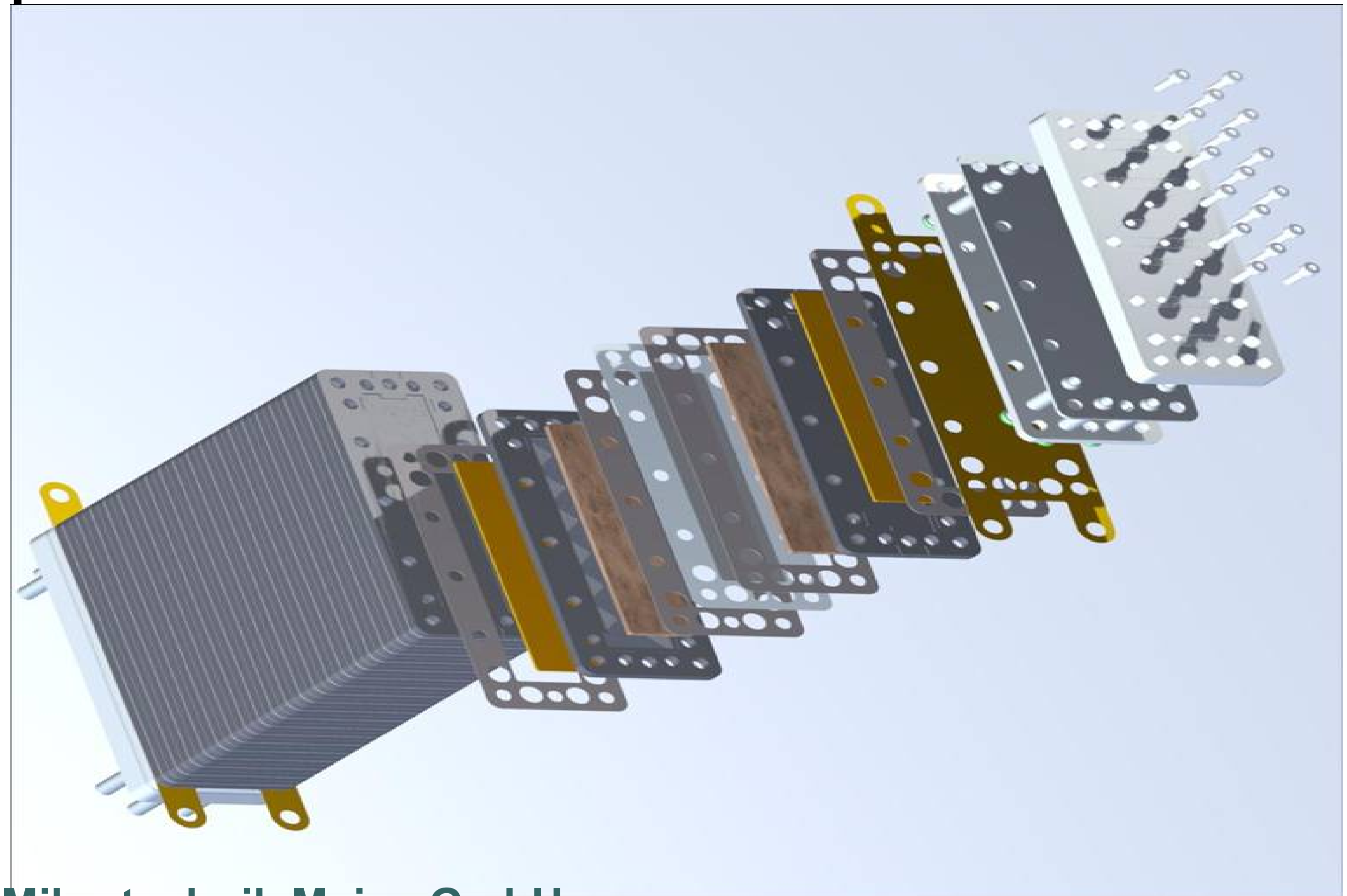
✓ The exposure T to H_3PO_4 doesn't affect significantly the samples activity

First results on CuMnOx catalysts



- ✓ In oxidized samples, the exposure to H_3PO_4 has no negative effect
- ✓ In reduced samples, H_3PO_4 causes deactivation

Schematic of the proposed fuel cell stack assembly



Institut für Mikrotechnik Mainz GmbH
Advanced Energy Technologies
Nedstack Fuel Cell Technology BV

Project deliverables

D1.1 Management. Procedures preparation, implementation and proposal improvement

D1.2 Financial, technical, progress, management, mid-term reports

D2.1 Synthesis of new generation membranes based on Advent polymer

D2.2 Characterization of new generation membranes

D3.1 Methanol/ Ethanol reforming catalysts

D3.2 Thorough characterization of structural, redox and adsorptive properties of the catalysts

D3.3 Report on 500 h long term catalyst testing

Project deliverables

D4.1 Preparation of reforming structured catalysts according to C1 configuration

D4.2 Preparation of an electrode with the reforming catalyst integrated in the hydrophobic layer (C2 configuration)

D4.3 Preparation of an electrode with fully mixed reforming catalyst/electrocatalyst (C3 configuration)

D5.1 Electrochemical testing of membranes

D5.2 Electrochemical testing of new electroreforming anode catalysts

D5.3 Understanding of electrochemical interface properties and electrocatalytic mechanism.

D6.1 Construction of bipolar plates which can operate at 190-200°C

D6.2 Single cell long term testing of most promising materials prepared in WP1, WP2 and WP3

D6.3 Post mortem characterization of electrocatalysts, catalysts, membranes and bipolar plates

Project deliverables

D7.1 Construction of 100W stack, BOP components and control system

D7.3 System integration and 500 hrs test

D7.4 Report on system control strategy

D8.1 Internal dissemination and knowledge management through a secure access site

D8.2 Web site dedicated to the scientific community

D8.3 Public Dissemination (papers in specialized and non specialized press, technology transfer brokerage events)

D8.4 Plan for the Use and Dissemination of the foreground

Advent Technologies SA

- ADVENT TECHNOLOGIES develops new materials and systems for renewable energy technologies, such as high temperature PEM fuel cells and hydrogen clean up.

- Advent is primarily focused on high temperature PEM fuel cell membranes and components.

- Advent also participates in projects for the development of flexible organic photovoltaics (OPV's)

- The Company is currently headquartered in Athens, Greece with research and pilot manufacturing facilities in Patras, Greece.

History

European and Greek Grants
JOULE III 1998-2001
APOLLON 2002-2005
PYTHAGORAS 2004-2006
PEMHYGEN 2003-2007
PROMETHEAS 2002-2006
APOLLON-B 2006-2009

UNIVERSITY OF PATRAS

FORTH ICE - HT

Polymer Chemistry Laboratory
University of Patras

Electrocatalysis Laboratory
FORTH-ICEHT

Development of revolutionary technology in the area of High Temperature MEAs

Funding from PRAXE and institutional and industrial investors from Greece and abroad (e.g. Piraeus Bank Capital Management VC, Sunlight Systems, Velti, Eltpa-Provoli, Dolphin Capital, ILPRA etc.)

Incorporation of
ADVENT TECHNOLOGIES SA (2005)
and establishment of the
ADVENT TECHNOLOGIES NORTH AMERICA INC (2006)

From basic research to a product