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High pressure PEM electrolysers: efficiency, life-time and safety issues

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First International Workshop
Durability and Degradation Issues in PEM Electrolysis Cells and its Components
March 12th-13th, 2013
Fraunhofer ISE | Freiburg | Germany

WATER

Electrolysis, thermocycles

Electric and heat energy

Natural and synthetic fuel

Conversion

Heat energy

H_2

Biomass, bioethanol

Conversion

Heat energy

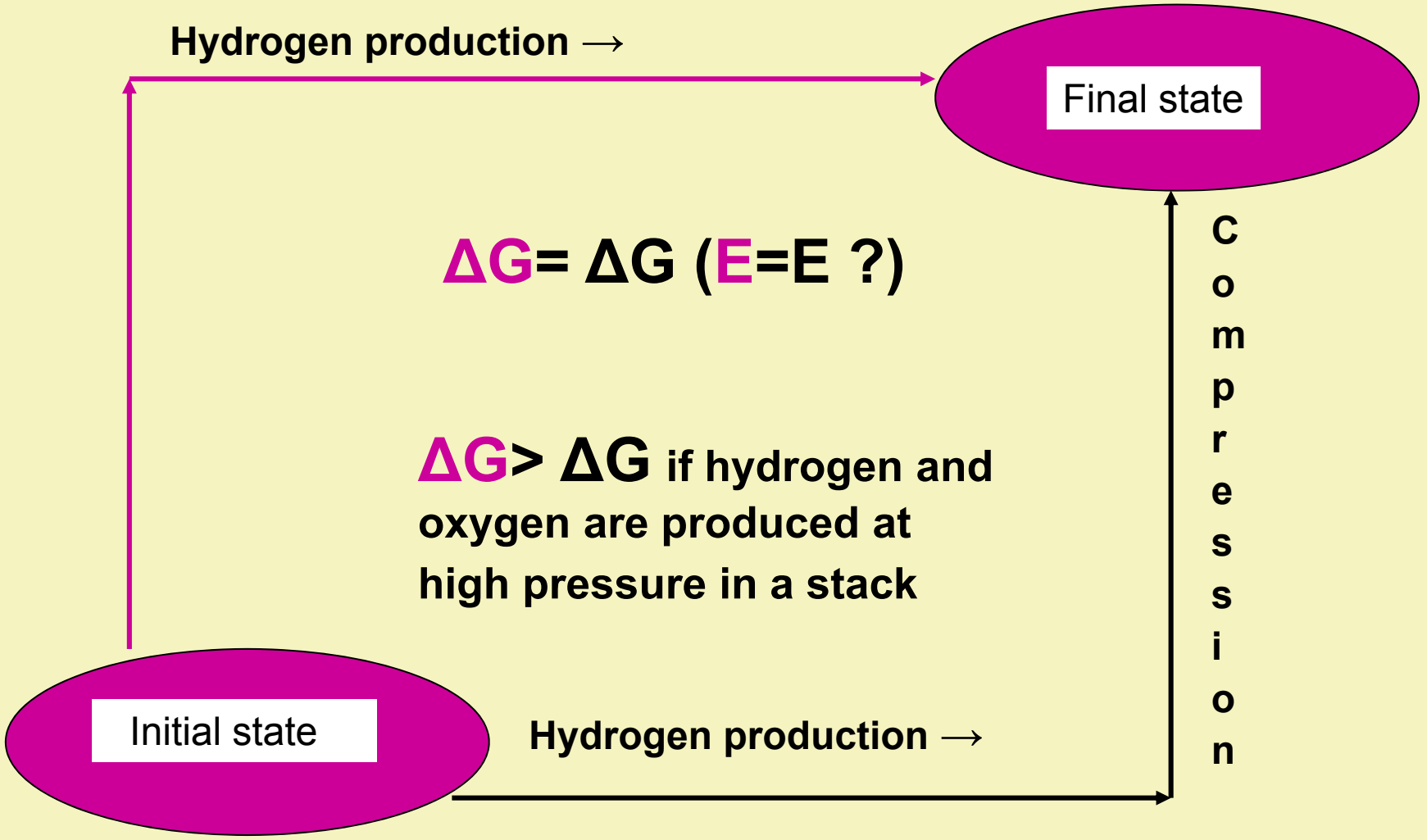
He reactor

HYDROGEN PRODUCTION

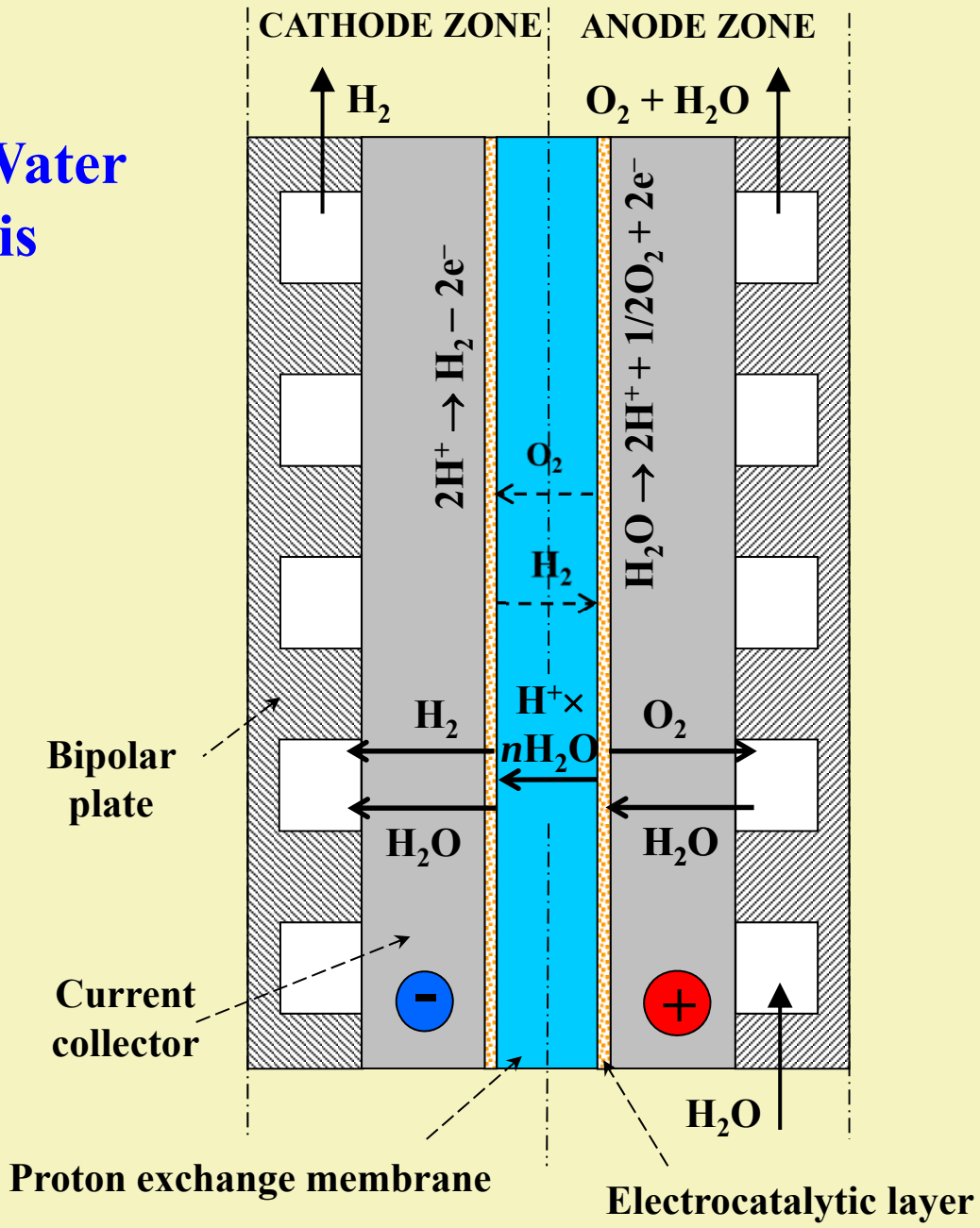
WHY DO WE NEED HYDOGEN UNDER HIGH PRESSURE AND HOW IT IS BETTER TO ORGANIZE HIGH PRESSURE HYDROGEN PRODUCTION BY ELECTROLYSIS?

- **Hydrogen transportation and storage is a critical issue and a majority of hydrogen storage and transportation systems require hydrogen under an increased pressure**
- **Hydrogen under an increased pressure could be produced by electrolysis due to "electrochemical" compression just inside the stack or pressurized at the outlet**
- **"Electrochemical" compression could be efficient mainly at solid or solid polymer electrolyte electrolysis**
- **Among solid and solid polymer electrolyte systems PEM electrolyzers with Nafion type membrane are mostly developed – the question is: Does advantage of high pressure hydrogen production inside the electrolysis stack compensate all other disadvantages of high pressure electrolysis operation?**

Pressurized hydrogen production with "electrochemical compression" and with mechanical compression



PEM (SPE) Water Electrolysis



Overall reaction: $H_2O \rightarrow 1/2O_2 + H_2$

ADVANTAGES AND DISADVANTAGES OF ELECTROCHEMICAL COMPRESSION

Advantages	Disadvantages
Reduction of energy consumption for compression	Reduction of current efficiency
Absence of hydrogen compressor	Electrolyzer safety problems
Reduction of overvoltage	Increase of equilibrium potential difference
	Reduction of stack component life time
Electrolyzer price decrease?	**Electrolyzer price increase?**

PLATINUM METALS IN PEM ELECTROLYZER. Pressure influence?

Catalysts for electrolyser anode:

Ru>**Ir (IrO_2)** **>Pt**>Rh~*Pd*

Mixed oxides Ir-Ru-Sn, Ir-Ru-Ti and so on

Platinum metals on oxide carrier?

2,0 mg/cm^2 of Ir were used in most part of experiments

Catalysts for electrolyzer cathode: **Pt**>Pd>Ir

Pt/C

Alloys Pt-Pd, Pt-Ni, Pt-Co and so on

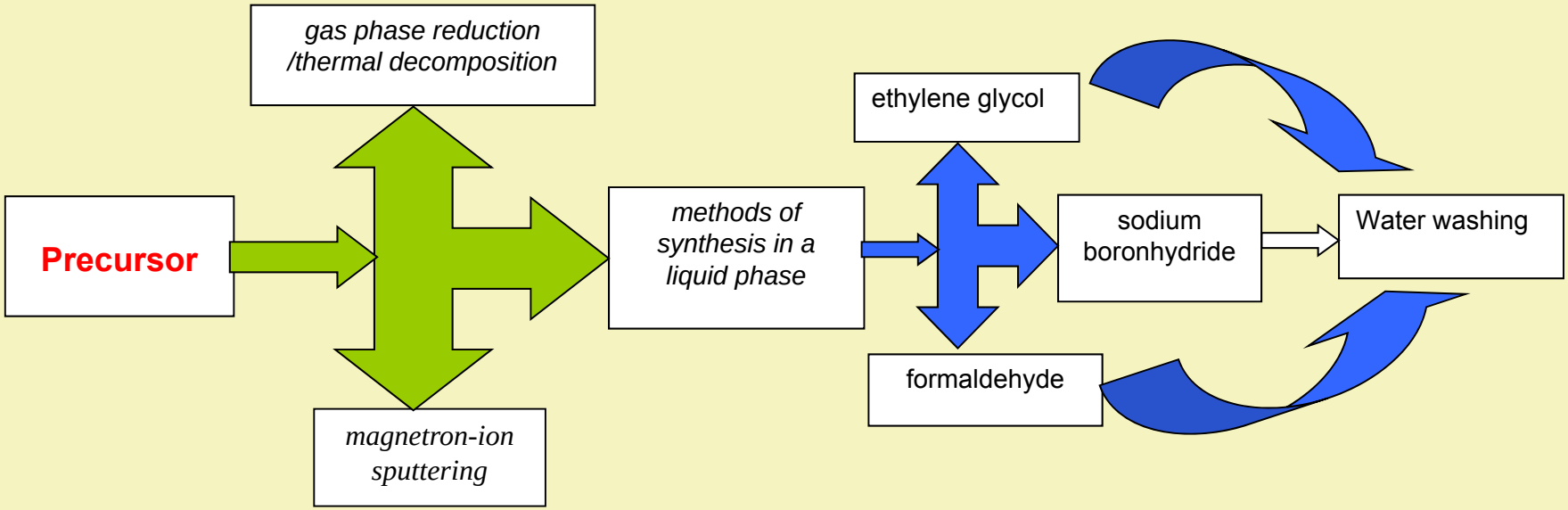
0,5 mg/cm^2 of Pt were used in most part of experiments

Current collector and bipolar plates surface protection – titanium protected by Pt.

0,5 mg/cm^2 of Pt were used in most part of experiments

Electrocatalysts synthesis for PEM systems

Well-known chemical methods for catalysts synthesis for the PEM electrochemical devices can be divided into high-temperature (thermal decomposition, the reduction in a reducing atmosphere (hydrogen); liquid phase and physical (eg, magnetron-ion sputtering, ion implantation, vapor deposition) ones. Each of these methods has its advantages and disadvantages.



methods of catalysts synthesis

CATHODE Pt/C CATALYST SYNTHESIS

Typical process using “liquid” chemical method

CARBON CARRIER

⇓

WASHING IN THE ORGANIC SOLVENT
(to clean from oils and fats)

⇓

WATER WASHING

⇓

THE TREATMENT WITH LIQUID PHASED OXIDANT
($H_2SO_4 + H_2O_2$)
(to purify from inorganic impurities)

⇓

WATER WASHING

⇓

DRYING (70^0C, air)

⇓

TERMAL TREATMENT (400^0C)
(functionalization)

⇓

POWDERING, FRACTIONATION
(up to 20 μm)

⇓

SUSPENDING
(the solvent is water or other)

⇓

HEATING with STIRRING

⇓

Pt PRECURSOR SOLUTION INJECTION

⇓

pH CORRECTION

⇓

REDUCING AGENT INJECTION

⇓

TEMPERATURE EXPOSURE

⇓

SEDIMENTATION

⇓

CONTROL OF COMPLETE RERDUCTION

⇓

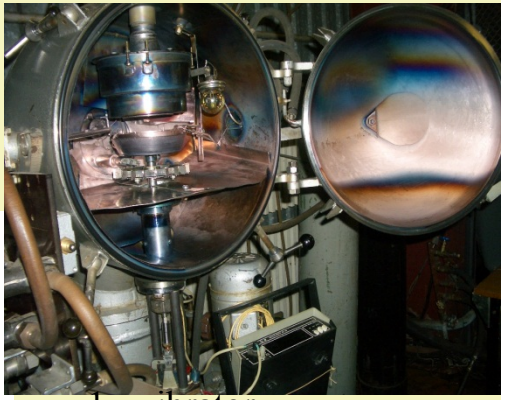
WATER WASHING (centrifugation)

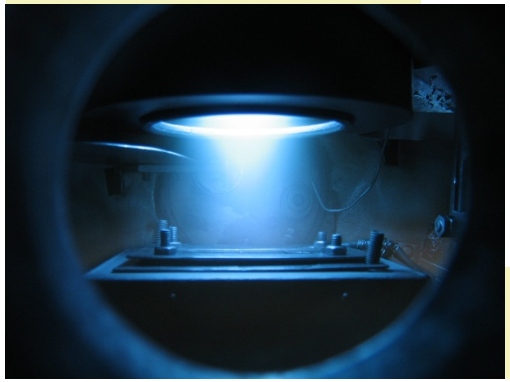
⇓

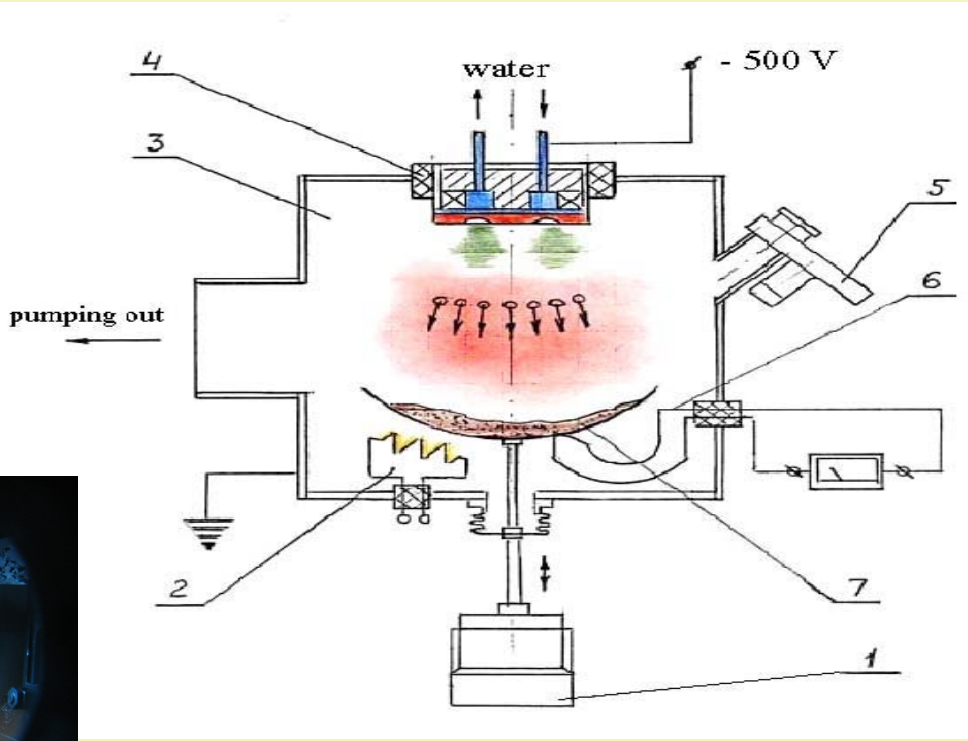
POWDERING

CATHODE Pt/C CATALYST SYNTHESIS
Physical methods of catalysts synthesis

Physical methods extremely attractive, because they allow deposition of metals at low temperatures and do not require cleaning (washing) catalysts from precursor components. It is practically 1 stage technology. Pt particle size about 5-8 nm was obtained.







The scheme of installation for ionic magnetron evaporation with vibrator

1 - vibrator
2 - heater
3 - technological chamber
4 - magnetron
5 - stroboscopic window
6 - thermocouple
7 - powder

Parameters of electrocatalysts samples synthesized by magnetron-ion sputtering

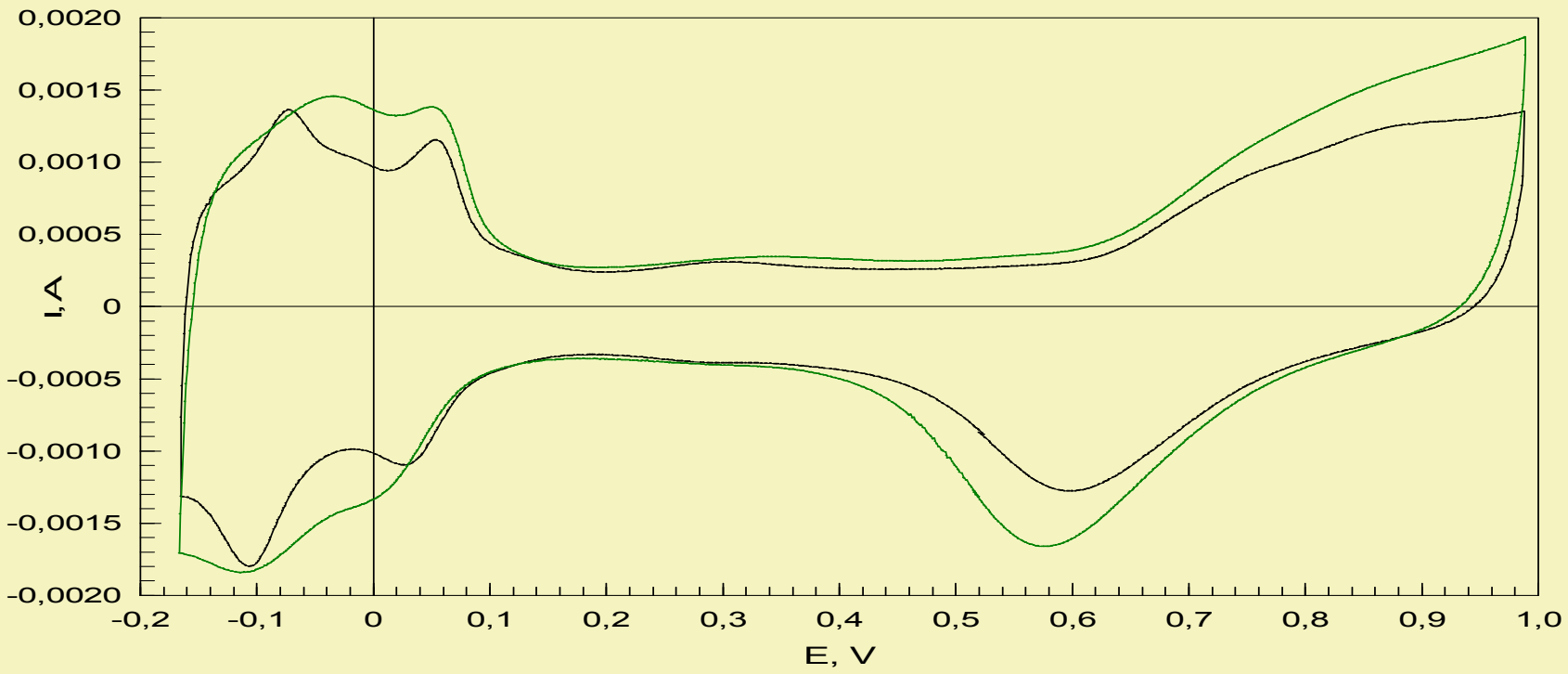
№	Vulcan XC-72 (hydro-philic)	Vulcan XC-72 +10%F4 (hydro-phobic)	Specific surface, m2/g	Pt content, wt %	Relative discharge current	Bias voltage, V	Time of deposition , min.
1	+		68	58	1	- 60	90
2	+		41	53	2	- 55	45
3	+		49	37	2	- 70	45
4		+	32	16	4	- 60	21
5		+	48	32	1,5	- 60	60

Comparison of Catalysts Synthesized by Liquid Phase Reduction and Magnetron Sputtering Methods

№	Electrocatalysts	Specific surface, m^2/g	Particle size, nm	Specific activity (relative units)
1	10% Pt on Vulcan XC-72R with 10% PTFE	92	2,8 – 3,9	1,00
2	10% Pt on carbon nanotubes	100	2,8 – 3,7	1,10
3	10% Pt on carbon nanotubes	56	5,3-8.4	1,15
4	10% Pt on Vulcan XC-72R with 10% PTFE	38	5,5-8,5	1,03

Blue –magnetron synthesis

Pink – liquid phase synthesis



Black – Pt10/Vulcan XC-72 (Magnetron)
Green – Pt10/Vulcan XC-72 (Additional Ar-ions implantation)

Some surface increase and amorphization after ion implantation take place

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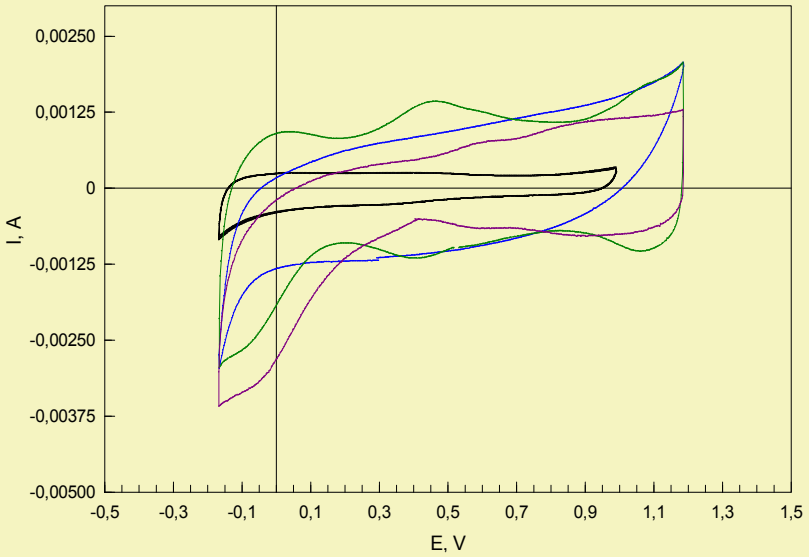
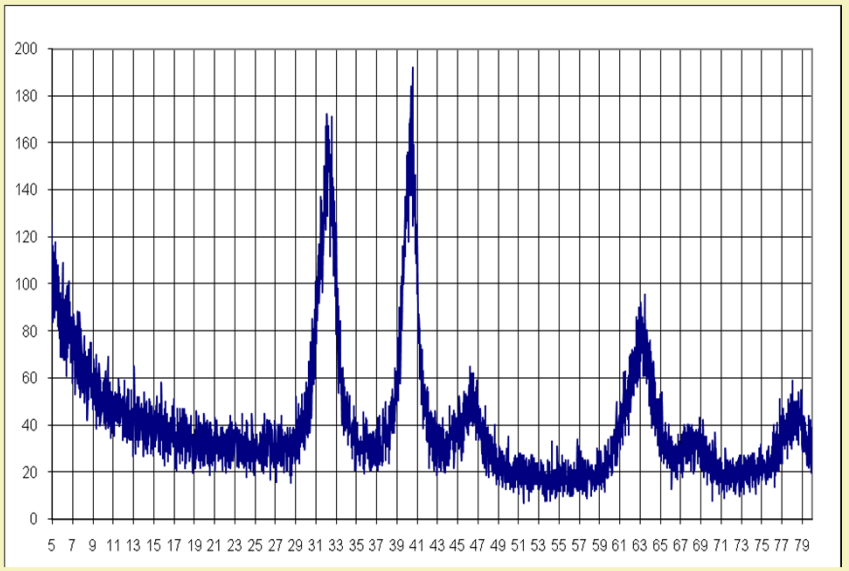
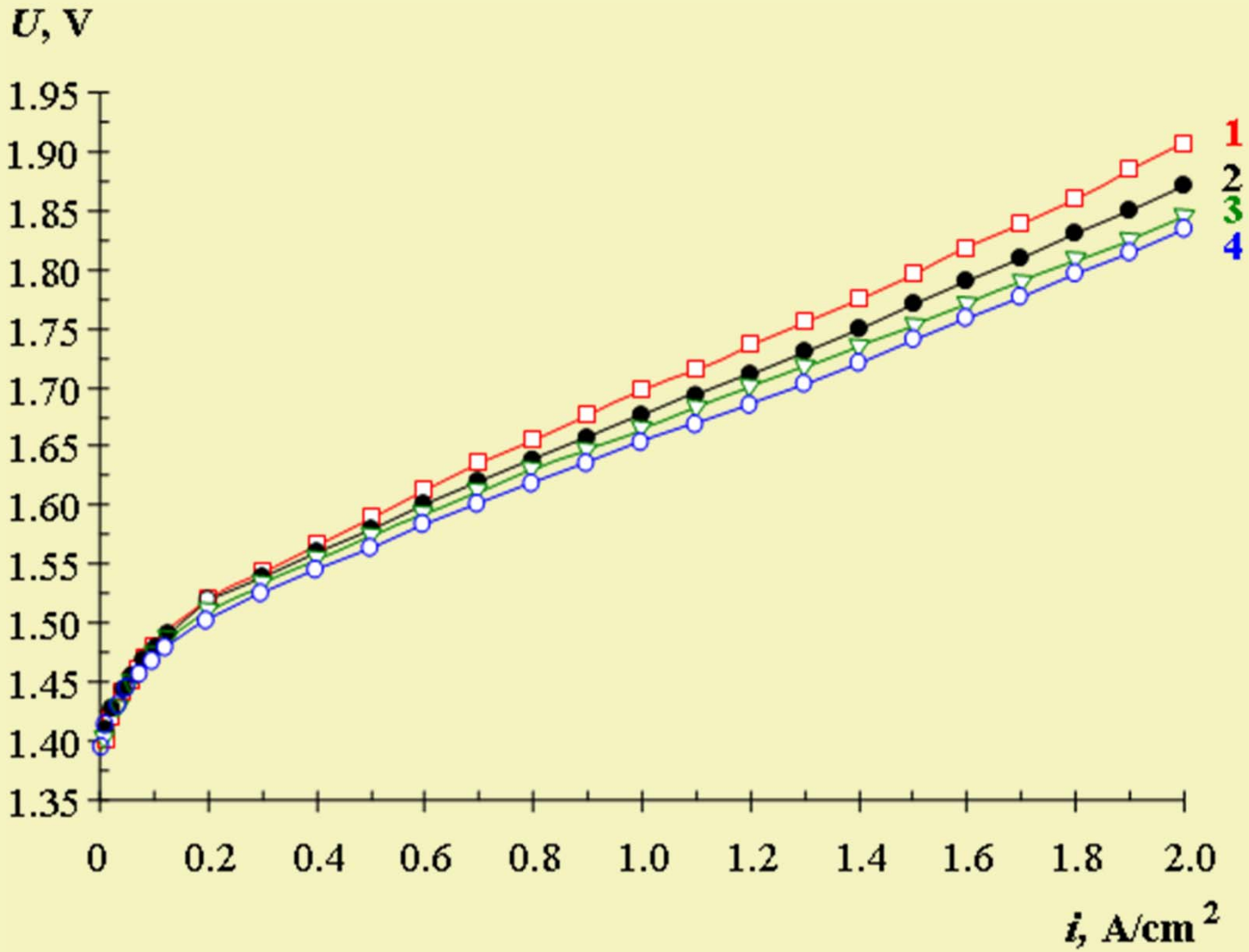


Green - RuO2; Violet- IrO2;
Blue- IrO_2:RuO_2:Sn_2 (30:30:40 % mol.);
Black- SnO2



XRD-pattern for a IrO_2:RuO_2:Sn_2 (30:30:40 % mol.); catalyst

The electrocatalysts based on IrO_2 and RuO_2 synthesized by thermal decomposition have particle size less than 50 nm. The resulting single-phase catalyst composition IrO_2:RuO_2:SnO_2 (30:30:40% mol.) had activity similar to the pure iridium but the total content of platinum metals was about 30% less.

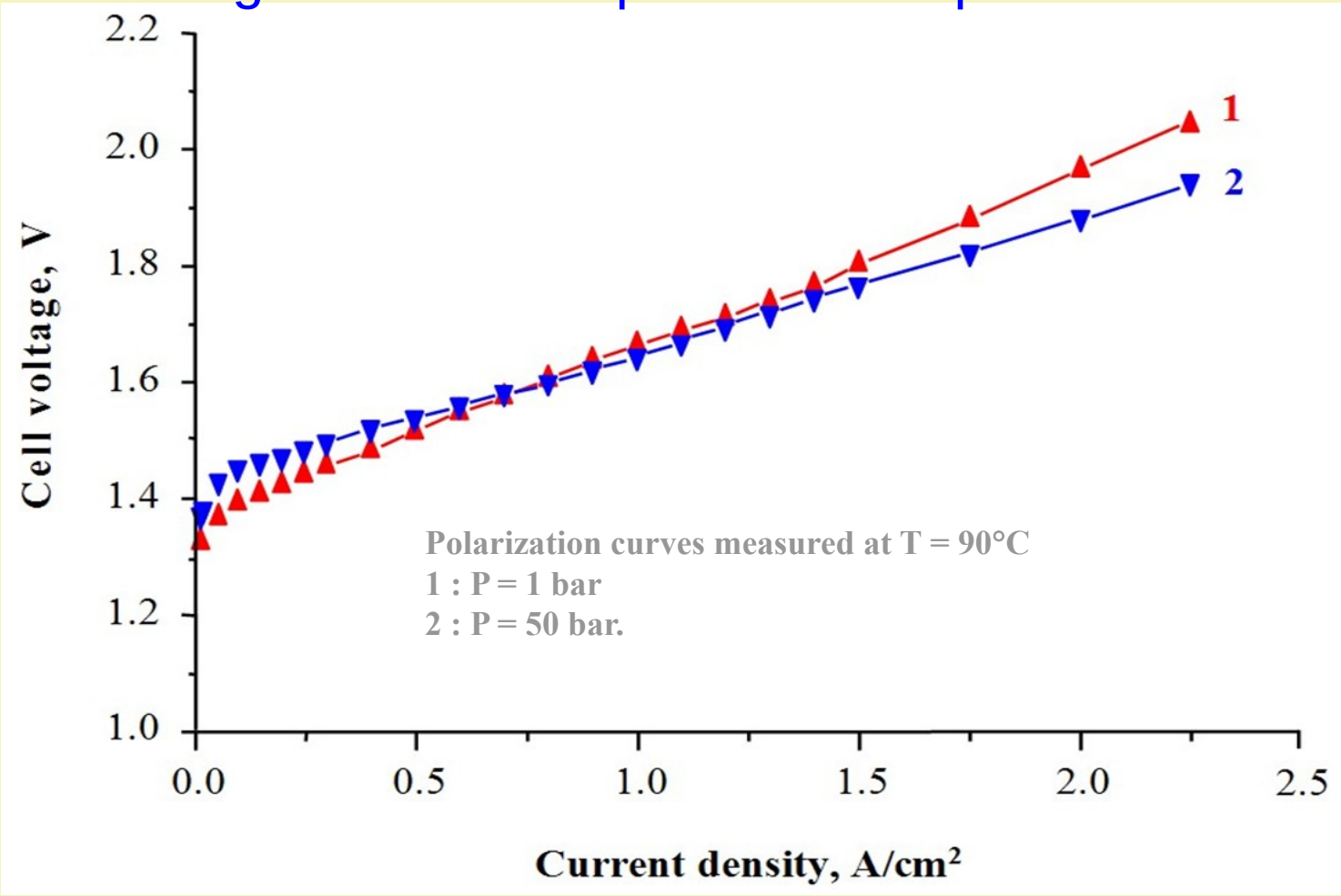


Current-voltage performances of single PEM electrolysis cell (operating area of 7 cm^2, Nafion®-115 membrane, anodic water supply) at 90°C and atmospheric pressure with different catalysts:
1 – Pd40/Vulcan XC-72 (0.7 mg/cm^2 of Pd) on the cathode, Ir (2.4 mg/cm^2) on the anode;
2 – Pt40/Vulcan XC-72 (0.7 mg/cm^2 of Pt) on the cathode, Ir (2.4 mg/cm^2) on the anode;
3 – Pt40/Vulcan XC-72 (0.7 mg/cm^2 of Pt) on the cathode, $Ru_{0.3}Ir_{0.3}Sn_{0.4}O_2$ (2.4 mg/cm^2) on the anode;
4 – Pt40/(CNTs+CNFs) (0.7 mg/cm^2 of Pt) on the cathode, $Ru_{0.3}Ir_{0.3}Sn_{0.4}O_2$ (2.4 mg/cm^2) on the anode.

OPERATION PRESSURE INFLUENCE ON CATALYST AND CATALYST LAYER LIFE-TIME WAS NOT OBSERVED!

Exception is a reduction of Pt/C activity (for about 10-20% at 50 bar) at frequent turn on - turn off cycles at high pressure: possibly hydrogen peroxide production at cathode is the reason of the life-time decrease due to polymer membrane and carbon carrier degradation

ENERGY CONSUMPTION
at High and Low pressure operation



No significant impact of pressure on current-voltage performances.

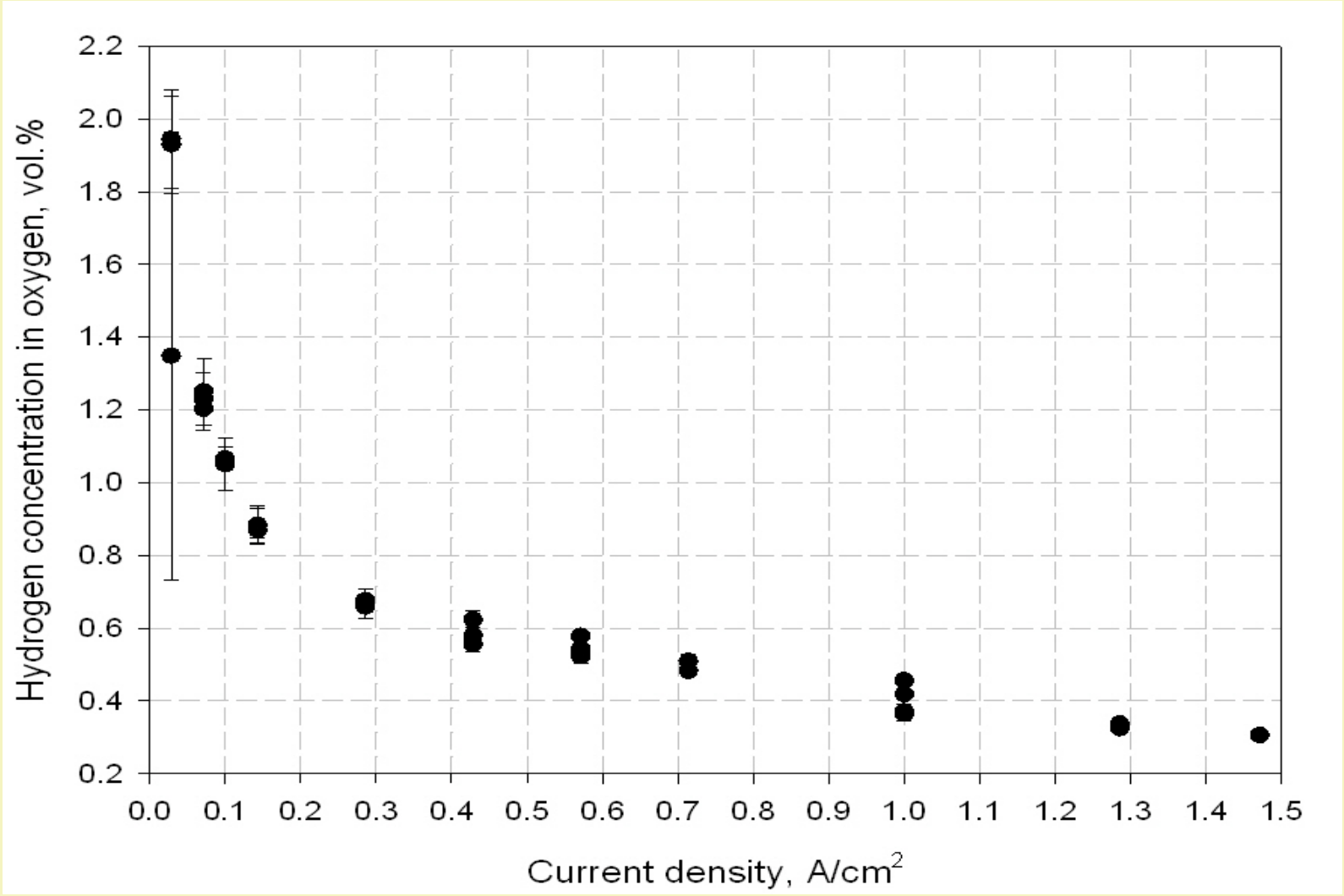
At low current density - thermodinamic influence, at high current density – kinetic (mass transport) influence

Gas Purity, Current Efficiency, Safety

T / °C	10	20	40	60	85
P^m_{O2}/cm^2.Pa^{-1}.s^{-1}	2.1x10^{-12}	2.3x10^{-12}	3.7x10^{-12}	5.3x10^{-12}	8.4x10^{-12}
D_{O2} / cm^2.s^{-1}	2.1x10^{-7}	2.5x10^{-7}	4.2x10^{-7}	6.5x10^{-7}	1.1x10^{-6}
P^m_{H2}/cm^2.Pa^{-1}.s^{-1}	3.8x10^{-12}	4.6x10^{-12}	7.6x10^{-12}	1.2x10^{-11}	2.0x10^{-11}
D_{H2} / cm^2.s^{-1}	3.9x10^{-7}	4.9x10^{-7}	8.7x10^{-7}	1.5x10^{-6}	2.6x10^{-6}
D_{H2}/D_{O2}	1.9	2.0	2.1	2.3	2.4

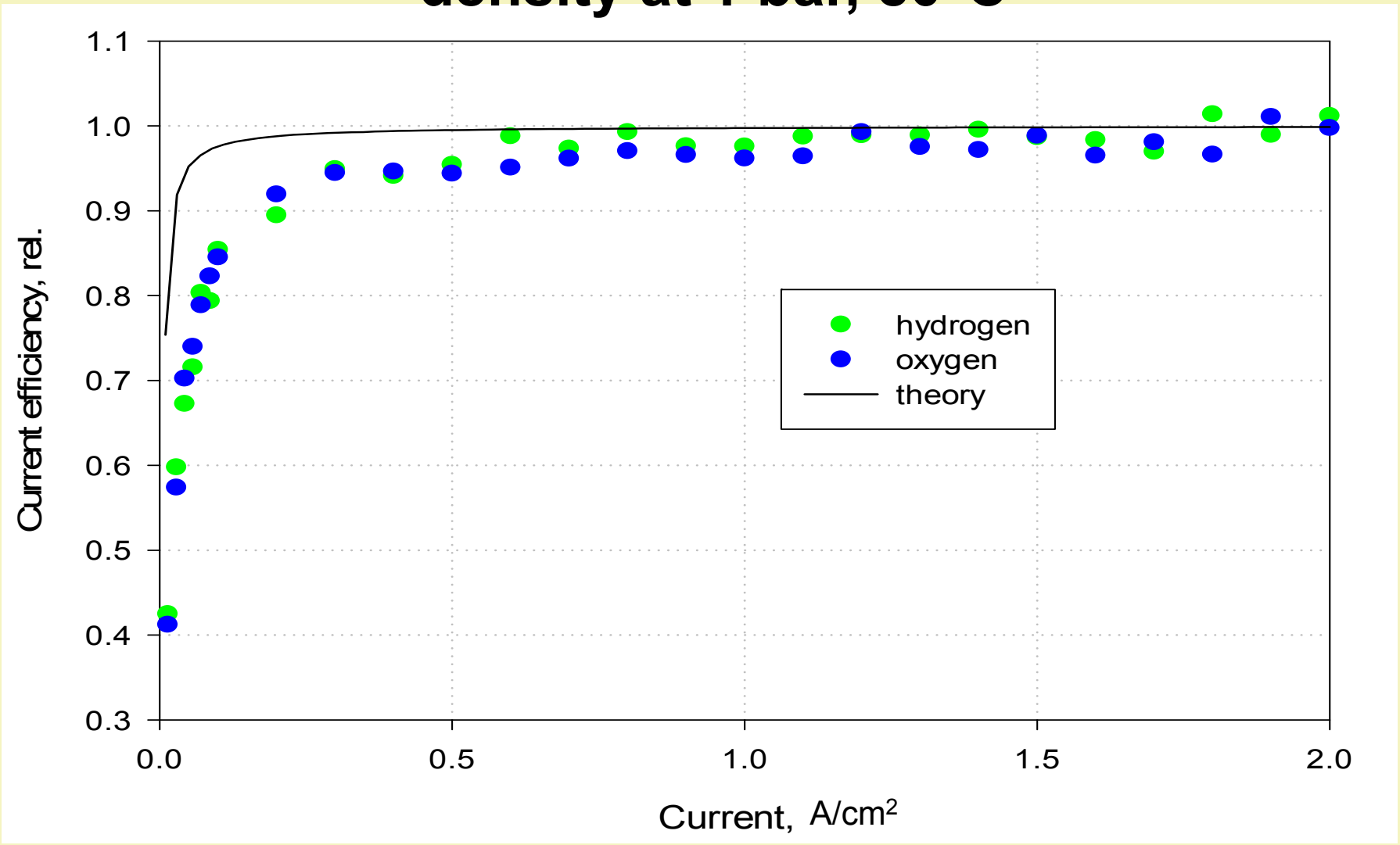
H_2 and O_2 permeability and diffusion coefficient in fully hydrated Nafion 117 at different temperatures.

P.Millet et al.
Report on FP6 project

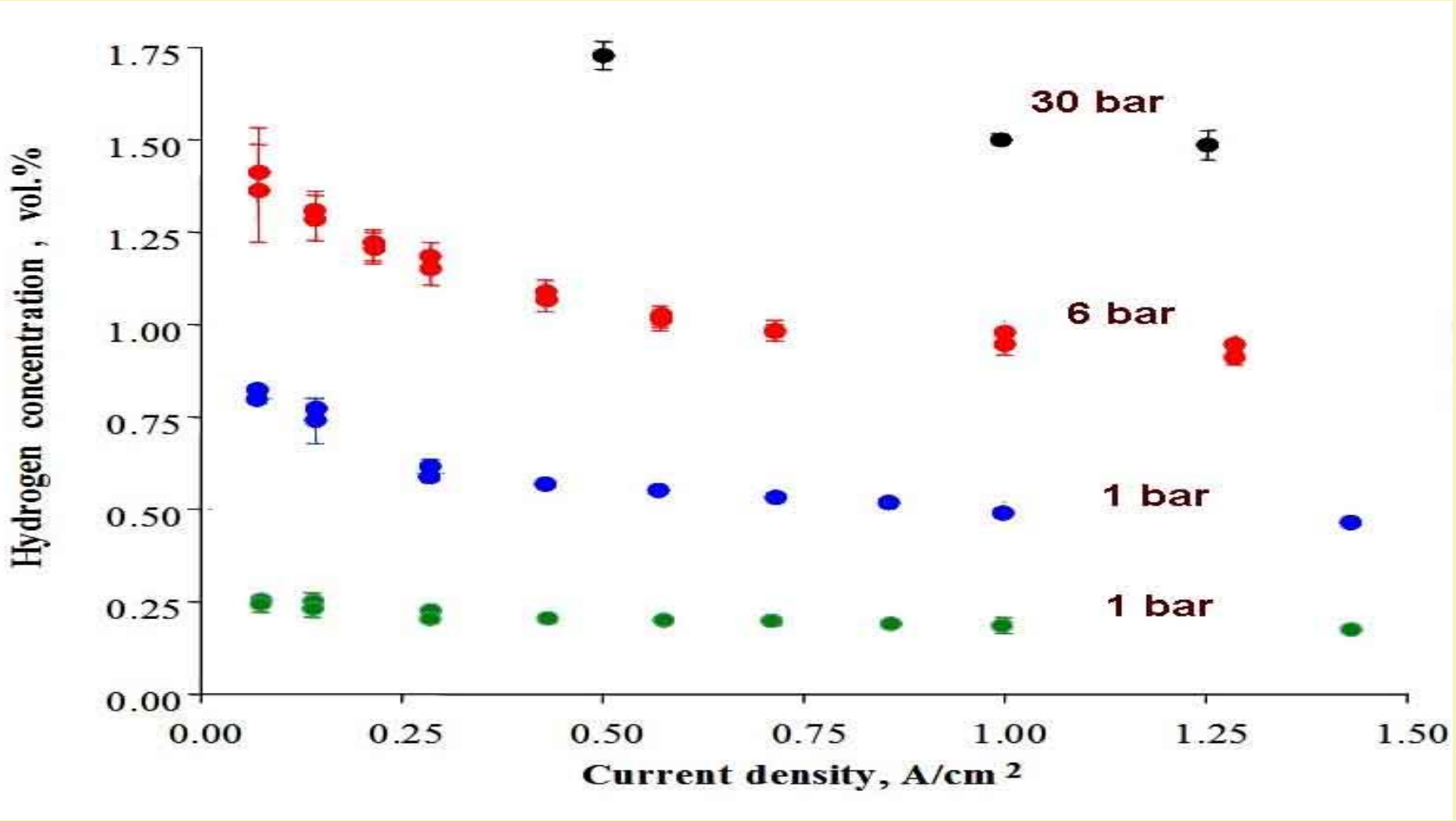


- **HYDROGEN CONCENTRATION IN ELECTROLYTIC OXYGEN**
- Cathode – Pt on carbon (40% mass.) – 1,6 mg/cm^2 , Anode – Ir – 2,0 mg/cm^2. 70 C

Dependence of current efficiency upon current density at 1 bar, 80°C



For numerical estimations diffusion and dissolved hydrogen transport with hydrated protons were taken into account

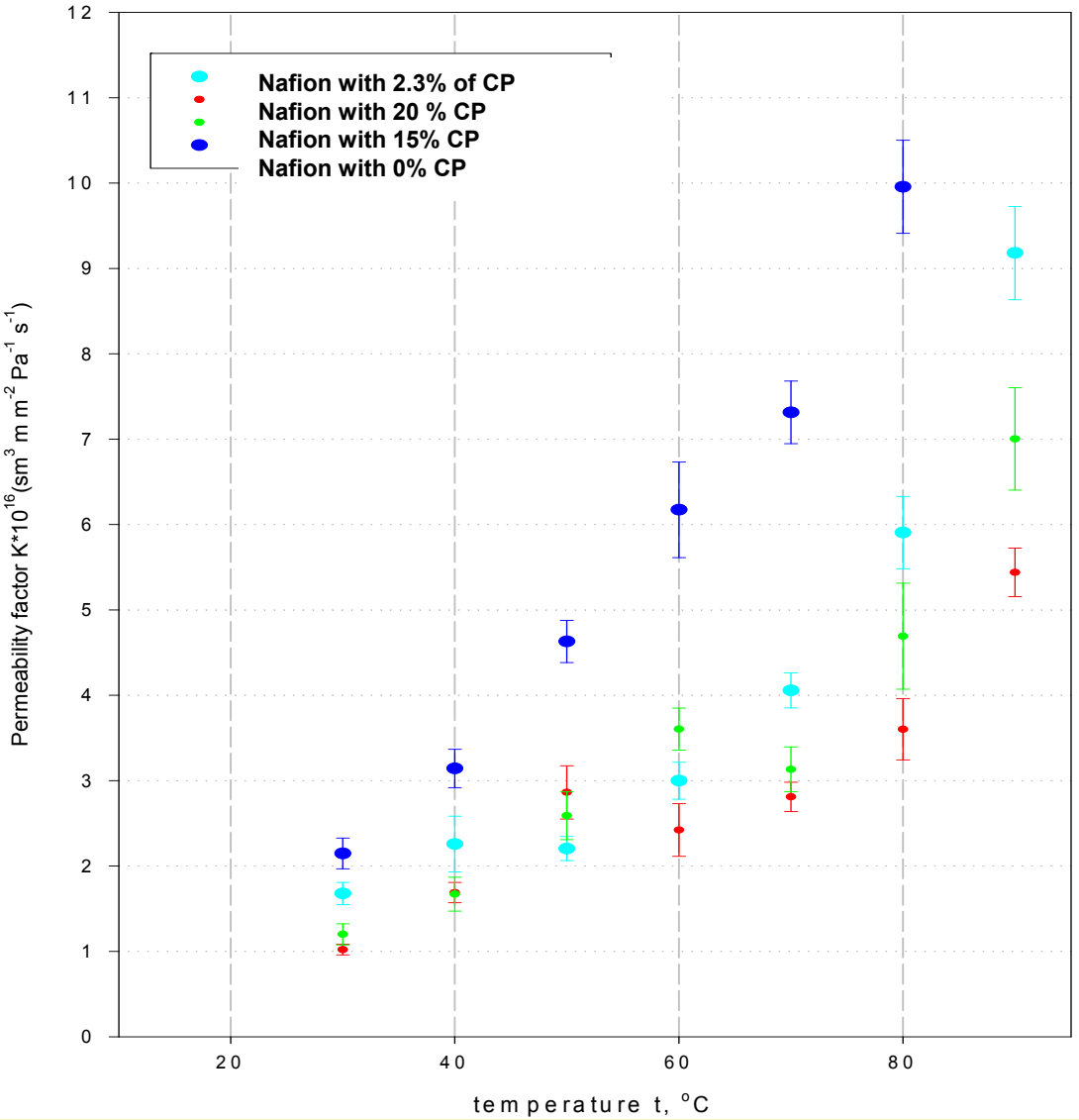


Hydrogen concentrtion in oxygen upon current density (statistics for 10 MEAs)

Membrane thickness – 50 mcm

At 1 bar - green – with hydrogen oxidation catalyst on current collector.

At 130-300 bar hydrogen concentration may exceed explosion limit!!!



Regulation of proton exchange membrane gas permeability by inorganic nanostructured materials modification – one of solutions of gas purity and current efficiency problems.

PFM Electrolysis Parameters at Different Pressure

Pressure, bar	Hydrogen concentration,%	Current efficiency, %
1	> 99,99	>0,99
30	> 99	>0,96
130	> 98	>0,93
300	> 98	>0,90

1 A/cm^2,1.70-1.73 V, 80^{o}C, modified membrane (250 micrometers), hydrogen oxidation catalysts on current collector (Hydrogen purity with catalytic burner – 99,999%)

Main parameters of degradation after 1100 h (about 200 turn on – turn off cycles) at 50 bar and 80°C

- ***U = E + ηa + ηk + IR*** 50 bar, 80oC and 1 A/cm2 U=1,702 V (start), U=1,769 V (after 600h). ΔU=0,067 V, **ΔIR=0,054 V Catalyst degradation → 0,013 V**
- **At 1 bar** ΔU=0,023 V, **ΔIR=0,016 V**

- Increase of stack resistance up to 20%
- (mainly due to current collector and bipolar plate surface oxidation and hydrogen embrittlement)
- Decrease of catalyst active surface area and specific activity less than about 5%

(manly due to carbon carrier at cathode oxidation and mixed oxide agglomeration and dissolution)

Decrease of current efficiency about 2%

(mainly due to membrane destruction)

Important problem at turn on – turn off cycles:

Hydrogen peroxide production at cathode after turn off with following membrane and carbon carrier oxidation

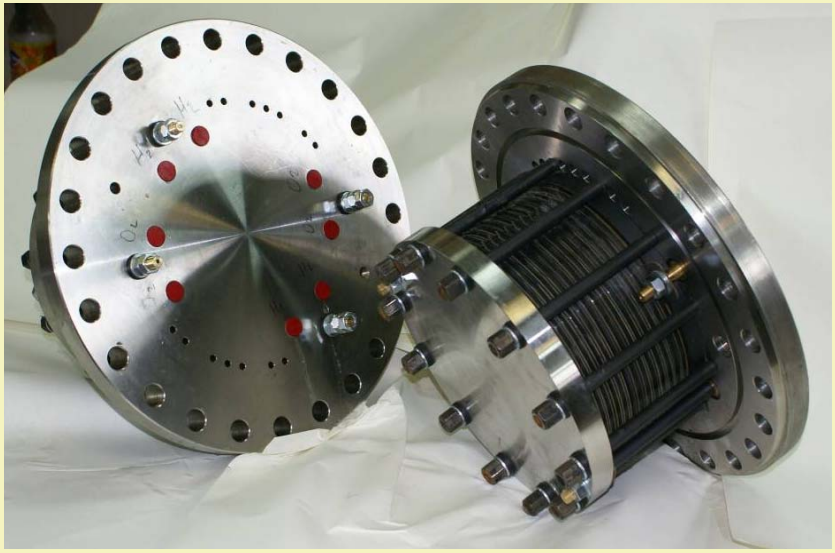
PRACTICAL REALIZATION OF HIGH PRESSURE ELECTROLYSIS

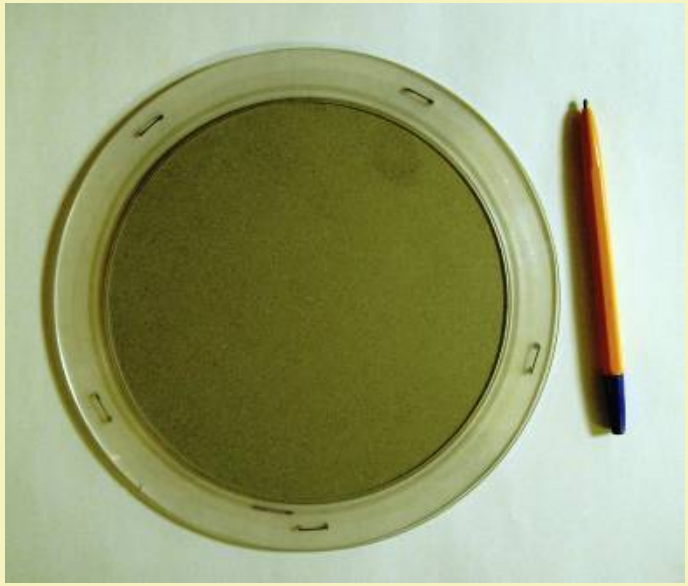
Performances of PEM water electrolysers

- Power consumption 4.0-4.2 kW*hour/m^3 of H_2
- Voltage on the cell 1.67-1.72 V at i=1 A/cm^2 and t=90°C
- Operating pressure up to 30 bars and more
- Hydrogen purity > 99.99%
- Noble metal content in catalytic layer:
  anode 1.0-2.0 mg/cm^2
  cathode 0.5-1.0 mg/cm^2
- Life time (average) > 20000 hours

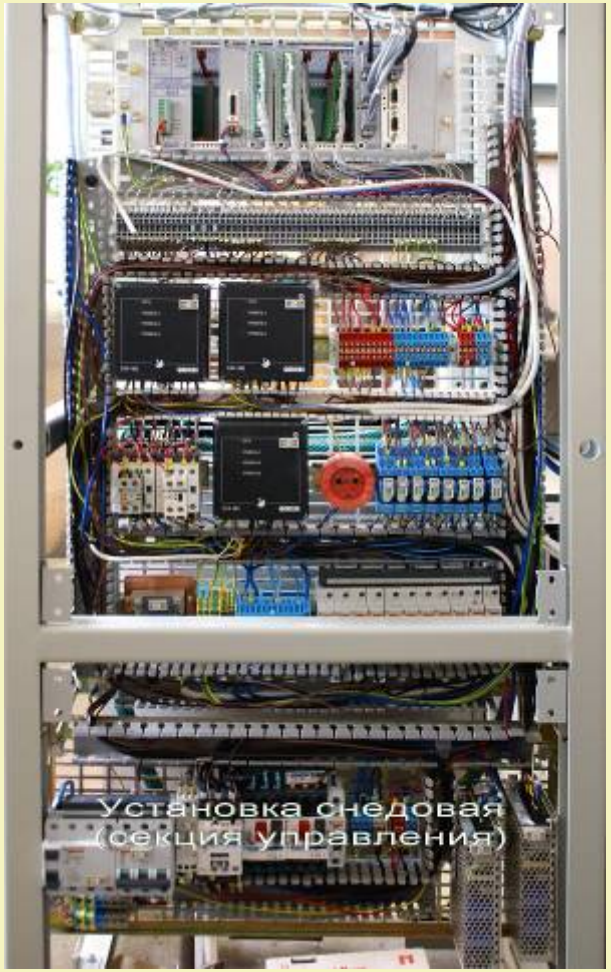
PEM electrolysers developed by NRC "Kurchatov Institute" with productivity up to 2 m^3/hour and operating pressure up to 30-50 bars. Last Federal Project – electrolyser for 10 m^3/hour and 130 bar.

PEM Electrolysis Stack for 130 bar





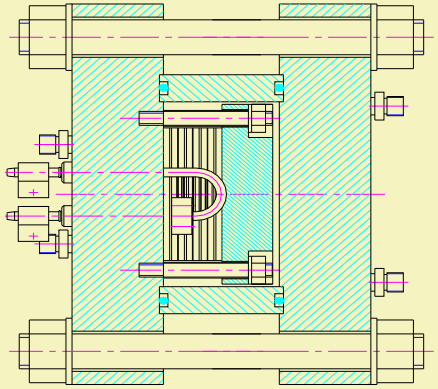
PEM ELECTROLYZER for 130 bar



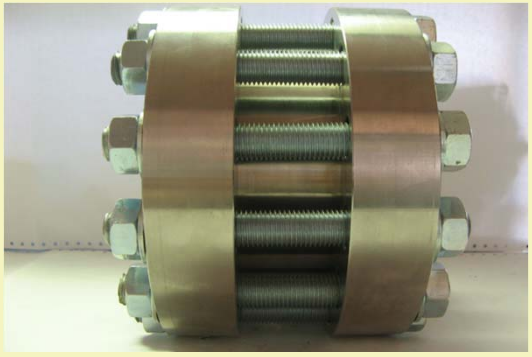
Control system

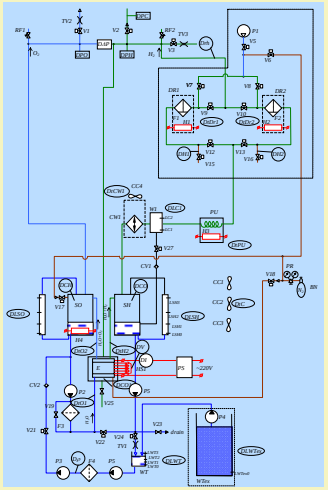
130 bar PEM electrolyzer test station

DEVELOPMENT OF HIGH PRESSURE PEM ELECTROLYZERS

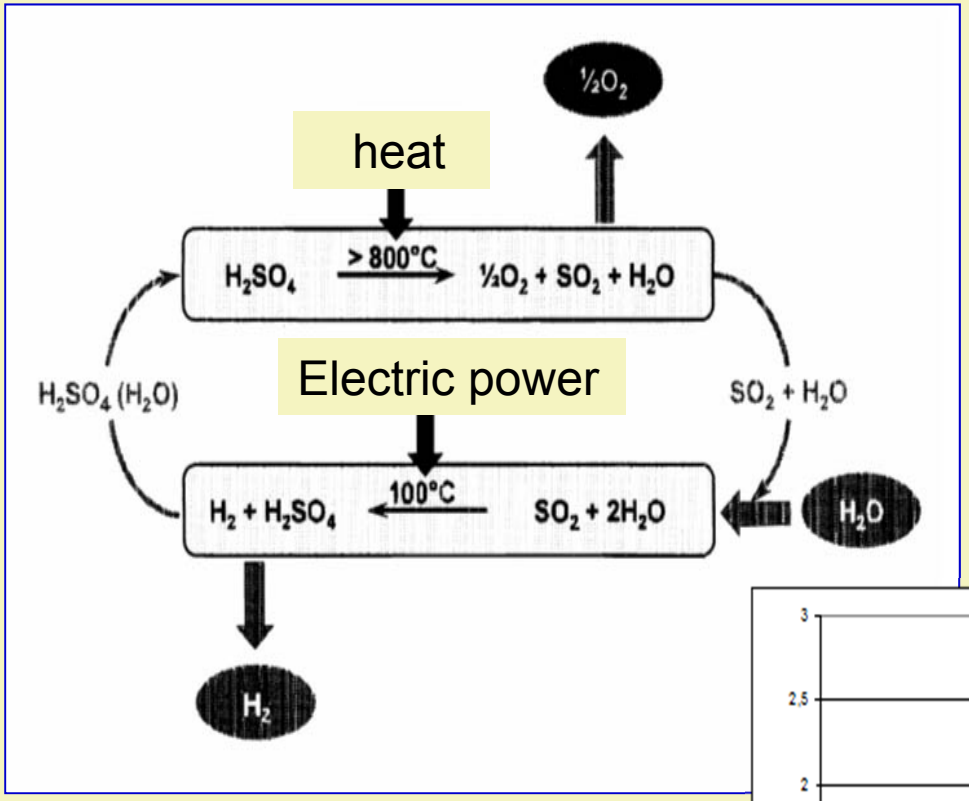


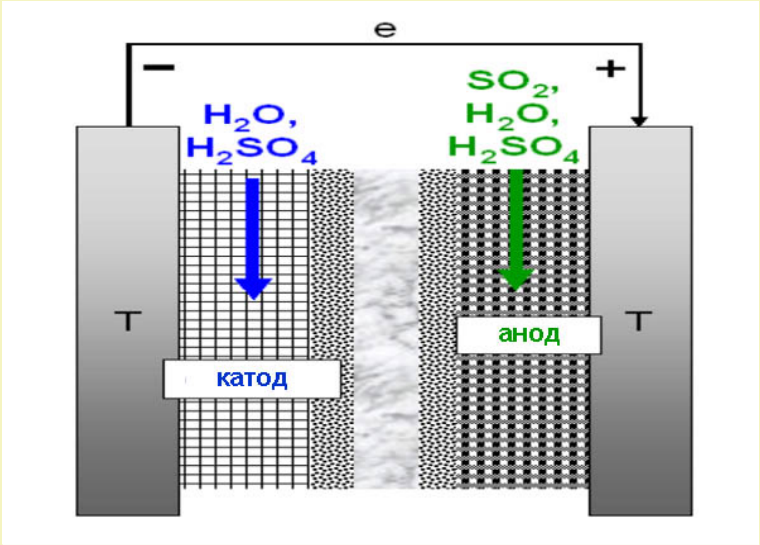
- pressure, MPa, up to - 30
- productivity (hydrogen), l/h - 100
- hydrogen purity, %o vol - 99,993
- current density, A/cm^2, up to - 1,0
- power consumption, kW·h/m^3(normal), up to - 4,2
- **Joint project with Hydrogen Works (Spain)**

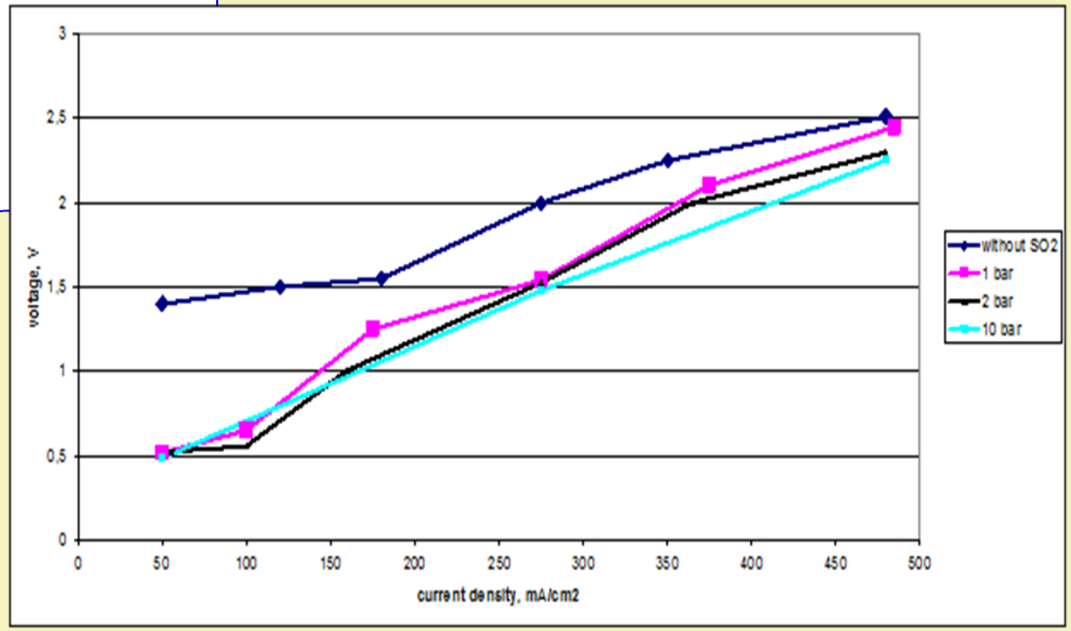




PEM Electrolysis for Thermoelectrochemical Cycle – high pressure is a good approach to a problem solution







1.SO2 + 2H2O → H2SO4 + H2
(electrolysis, 30-80°C)
2. H2SO4 → H2O + SO2 + 1/2O2
(thermolysis, 700-900°C)

Decrease of electric power consumption for 20-30%

CONCLUSIONS

- Price for electrolyzer with “electrochemical” and mechanical compression seems to be similar at large scale production
- Price advantage for “electrochemical” compression may be obtained at decentralized energy supply for < 1 MW
- High pressure hydrogen electrolysis at present time may be efficient or reasonable from economic point of view up to operating pressure 200-300 bar

  (absence of hydrogen compressor, standard hydrogen tanks use for storage)
- “Electrochemical” compression of hydrogen creates problems with gas purity, current efficiency, platinum metals loading and life-time (mainly at often turn off – turn on cycles)
- Modified (new?) membranes and new materials or efficient technologies for current collector and bipolar plates surface protection are required

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THANK YOU FOR YOU ATTENTION