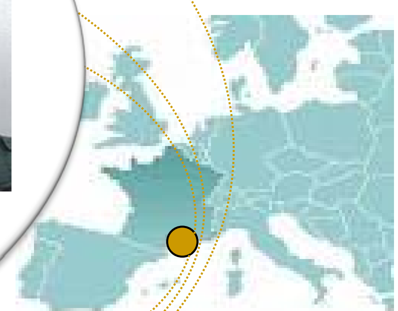
Carisma 2012 – 3, 4 and 5 september 2012

PhD February 2011 – January 2014

Innovative plasma polymerized membranes based on phosphonic acid groups for fuel cell

Joëlle BASSIL   Stéphanie ROUALDES



Institut Européen des Membranes – CC 047, Université Montpellier 2 – Place Eugène Bataillon – 34095 Montpellier – France
www.iemm.univ-montp2.fr

Outline of the presentation

- **Plasma polymerization process PECVD**
- **Phosphonic membranes**
- **Preparation of plasma membranes:**
  - Description of the device
  - Plasma parameters for the deposition of plasma polymerized films
- **Characterization of plasma membranes:**
  - **Micro structural characterizations**
    - Morphology by Scanning Electron Microscopy (SEM)
    - Chemical structure by Fourier Transform Infrared (FTIR) Spectroscopy
    - Chemical composition by Electron Spectroscopy for Chemical Analysis (ESCA)
  - **Physico-chemical characterization**
    - Thermal stability by Thermogravimetric Analysis (TGA)
  - **Proton conductivity characterization**
- **Prospects**

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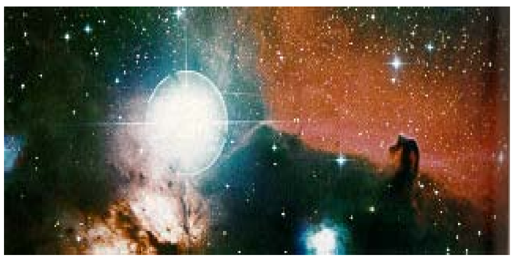
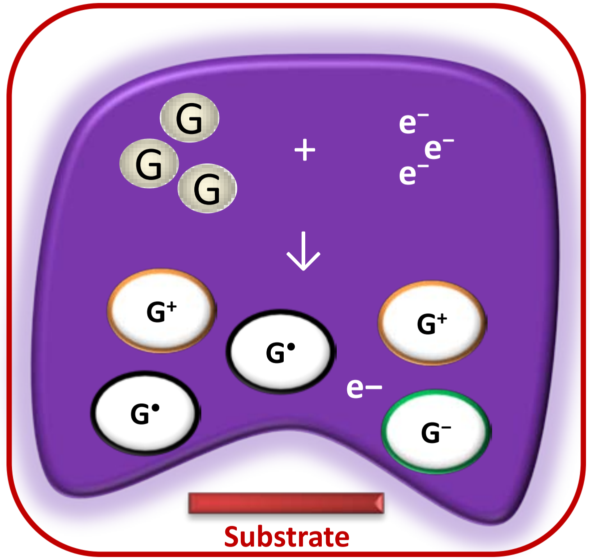
Procédé plasma PECVD

Plasma?

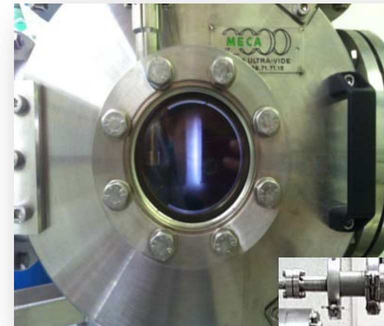
Hot plasma

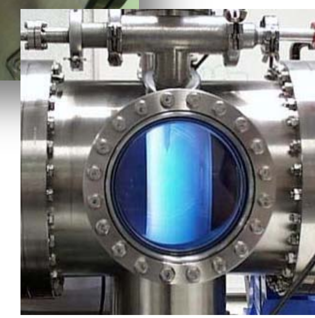




Basic mechanism

Cold plasma





At low pressure

Electrical power

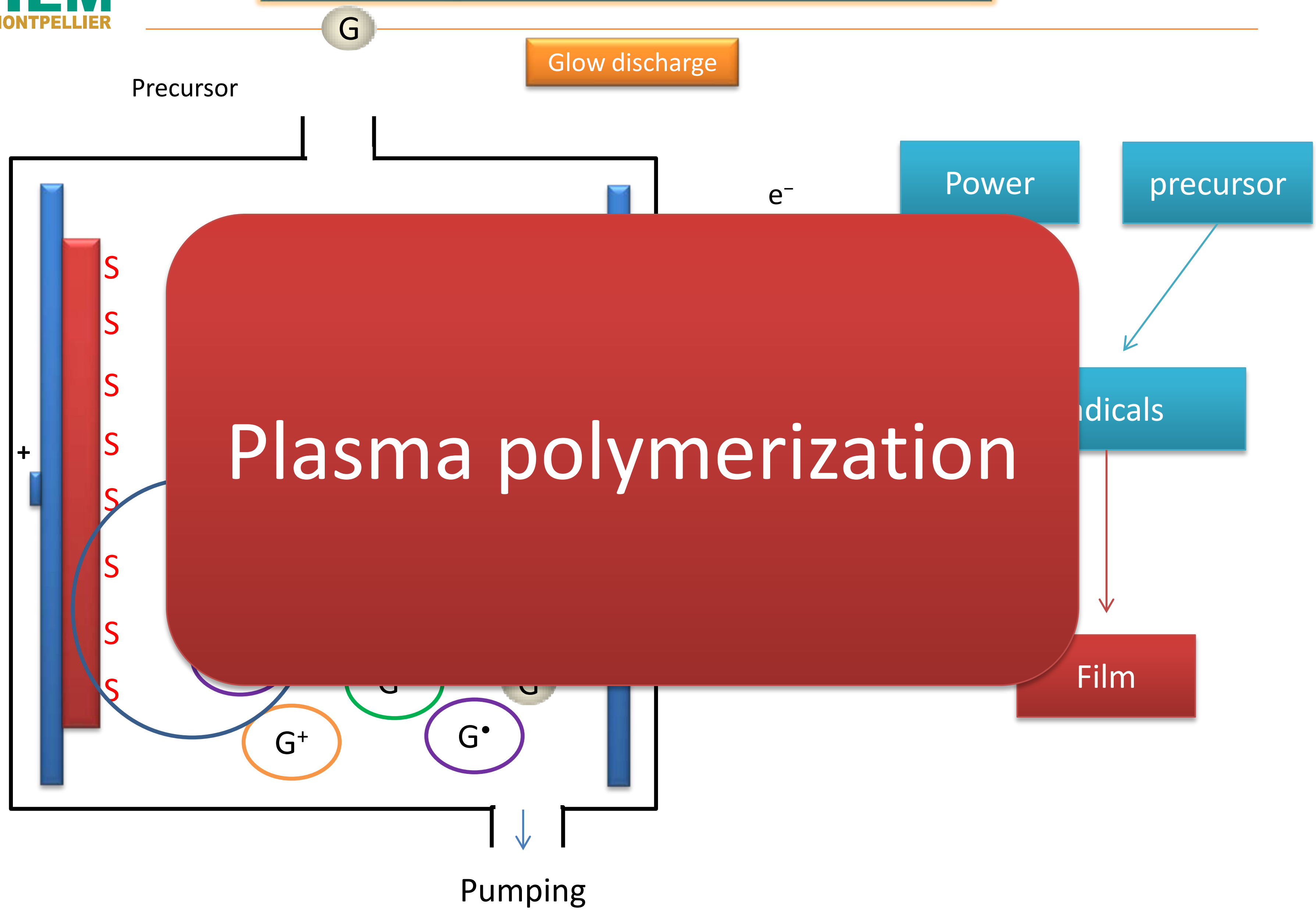
+

Gaseous precursor

Glow discharge → Plasma

IEM MONTPELLIER

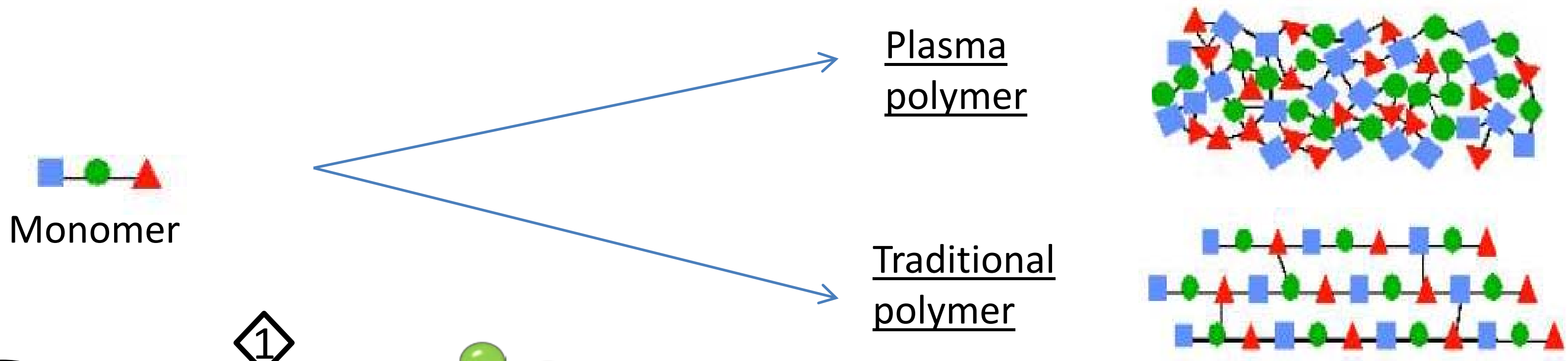
Plasma polymerization process PECVD

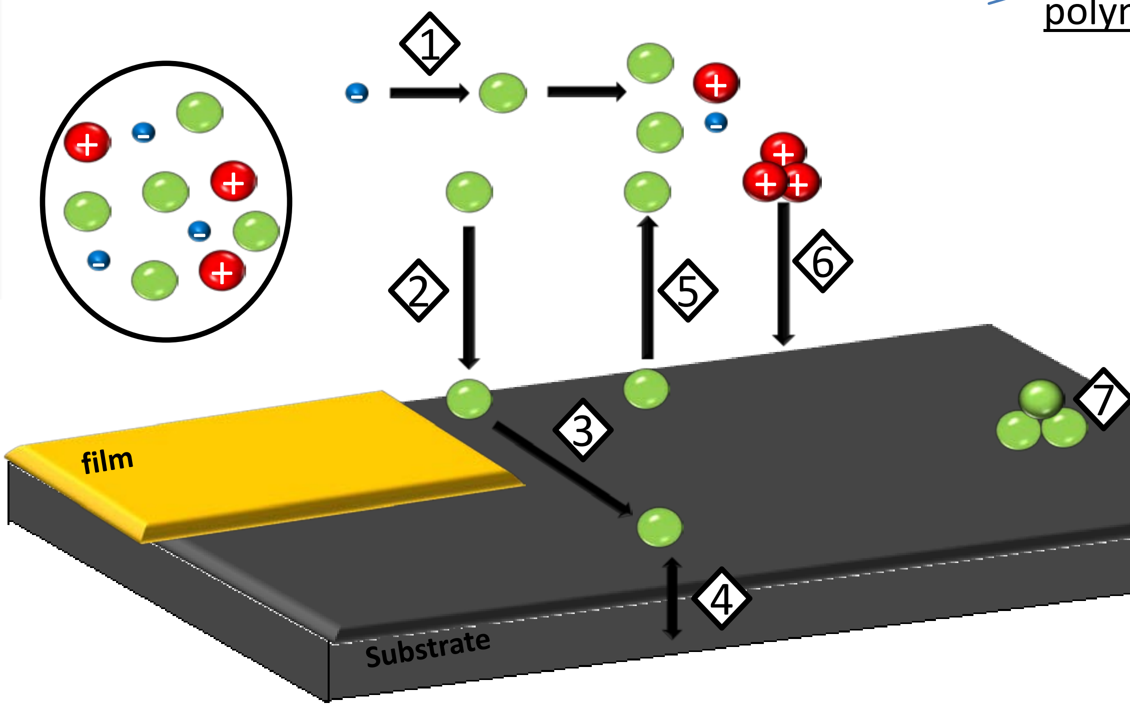


Plasma polymerization process PECVD

Plasma polymerization

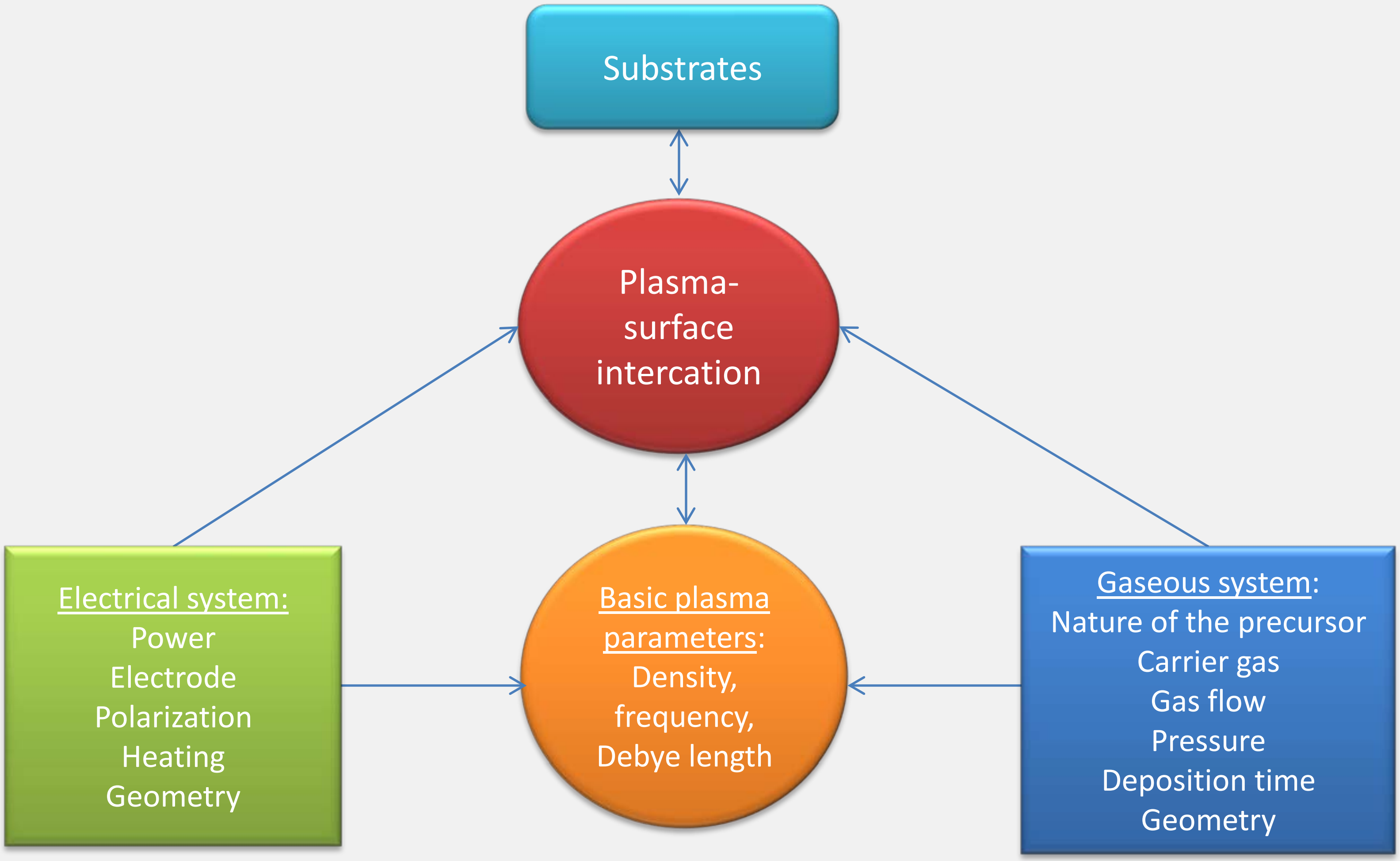
(Plasma enhanced chemical vapor deposition)





1. Electron collisions
2. Transport and adsorption
3. Surface diffusion
4. Diffusion in the substrate
5. Desorption
6. Ion bombardment
7. Deposit growth

Plasma polymerization process PECVD



Polymer-like → Ceramic (amorphous)

Plasma energy ↗

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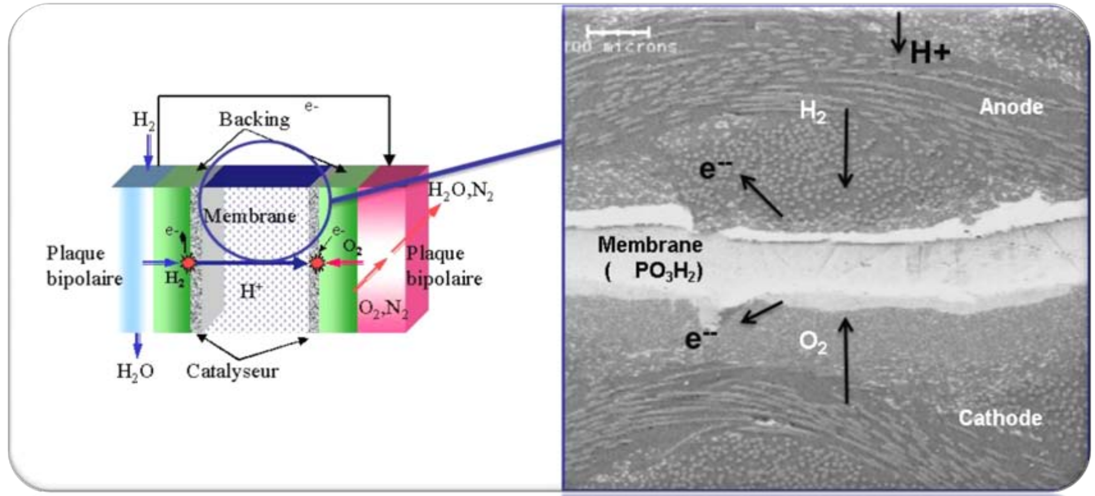
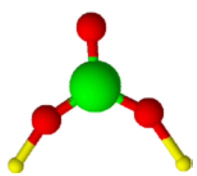
Phosphonic membranes

Objective:

- Elaboration by PECVD (from the precursor dimethyl allyl phosphonate) of hydrocarbon-based films containing phosphonic acid groups with a few microns thickness operating in fuel cells at temperature higher than 80°C (up to 150°C)





Phosphonic groups $P(O)(OH)_2$

Amphoteric character

Degree of self-dissociation

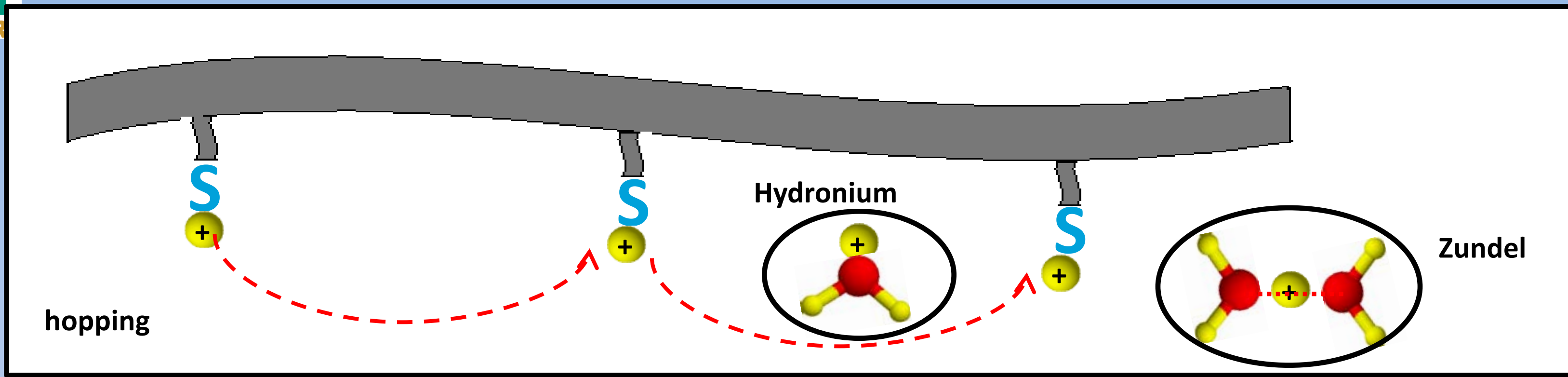
Good proton conductivity

Mobility of protons

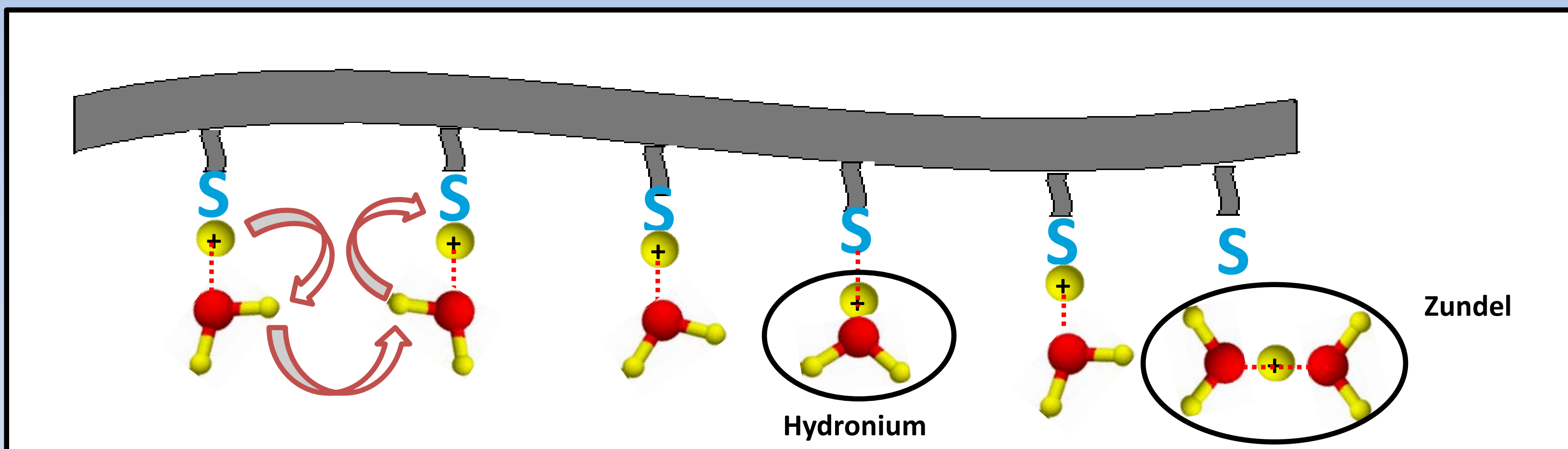
M. Schuster, T. Rager, A. Noda, K.D. Kreuer, J. Maier, J. Fuel Cells 5 (2005) 355

Phosphonic membranes

A

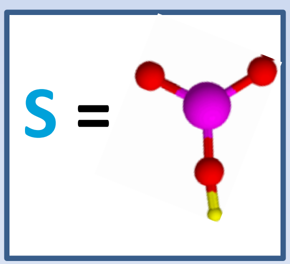


B



A

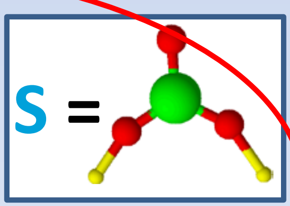
<u>Sulfonic acid functions</u>



- Weakly amphoteric
- Water-dependent

B

<u>Phosphonic acid functions</u>



- Amphoteric character leading to a significant degree of self-dissociation and promoting the formation of hydrogen bonds

Preparation of electrolyte membranes for fuel cells by plasma process

Researchers	Types of membranes prepared	Major result obtained
Inagaki et al 1991	SO_2 + pentafluorobenzène or tétrafluorobenzène or perfluorobenzène	σ (SO_2 + tétrafluorobenzène) = 4.10^{-2} $mS.cm^{-1}$ (room temperature)
Ogumi et al 1990	CF_3SO_3H + CF_3CH_2Cl	σ = 0,025 – 0,05 $mS.cm^{-1}$ (room temperature)
Uchimoto et al 2000	Plasma polymerization of 1,3-butadiène + méthyl benzène sulfonate	σ = 0,18 mS/cm (room temperature)
Brumlik et al 1994	Polymerization of trifluoroéthylène + CF_3SO_3H	σ = 0,58 mS/cm (room temperature)
Brault et al 2006	CF_3SO_3H / 1,3- butadiène CF_3SO_3H / styrène	σ = 9,8. 10^{-2} mS/cm (room temperature)
Prakash et al 2008	Silicate glass doped with phosphorus	σ = 0,254 mS/cm (T 100°C)
Mex et al 2001	Tétrafluoroéthylène / vinyl phosphonic acid	σ = 560 mS/cm (T 30 °C)

Modification par plasma des surfaces des membranes commerciales PFSA

Researchers	Types of modification	Major result obtained
Cho et al 2010	Plasma O_2/Ar for etching of Nafion®212	Improving the performance in fuel cell of 19%
Yasuda et al 1992	Plasma O_2 for surface treatment of Nafion®212	Decreasing the resistance, resitance = 2 $\Omega.cm^{-1}$
Choi et al 2001	Plasma Ar + bombardment of platinum	Decreasing the methanol crossover about 15%
Yoon et al 2002	Plasma Ar + pulverisation of platinum	Decreasing the methanol crossover about 44%
Walker et al 1999	Plasma hydrogen/hexane to elaborate a plasma thin film type polyethylene	Decreasing the methanol crossover about 15%
Feichtinger et al 2001	Plasma tétrafluoroéthane to elaborate a plasma thin film type poly fluoroethylene	Decreasing the methanol crossover about 15%
Kim et al 2004	Plasma tétraéthoxysilane to elaborate a plasma thin film type polysiloxane	Decreasing the methanol crossover from 40 - 70%
Finsterwalder et al 2001	Deposit of polyfluoroéthylène sulfoné on Nafion®	Decreasing the methanol crossover from 5 – 10 % , but the conductivity decreased.
Zylka et al 1991	Plasma O_2/Ar on Nafion®	Increasing the hydrophilicity and increasing the rugosity
Park et al 2003	Plasma O_2/Ar + H_2 on Nafion®	
Vargo et al 1995	Plasma H_2 / methanol	Increasing the hydrophilicity
Kuhn et al 2001	Plasma O_2 , plasma acide acrylique, plasma acrylonitrile, plasma allylamine	Increasing the adherence polymer/metal

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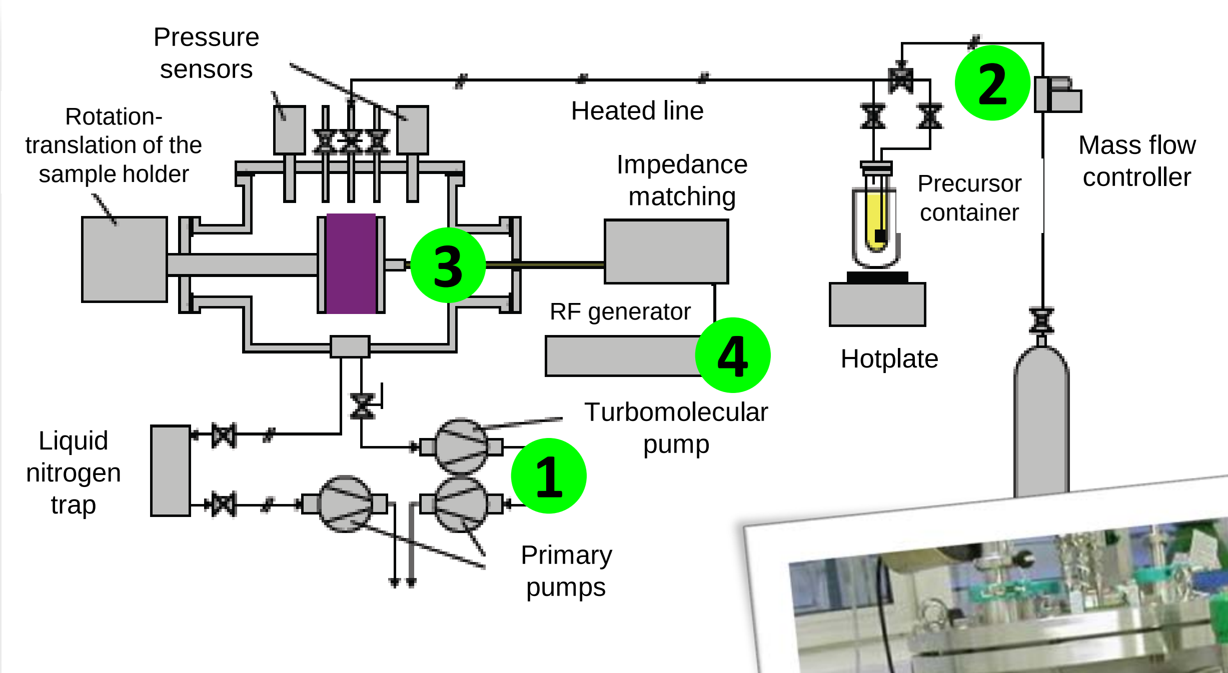
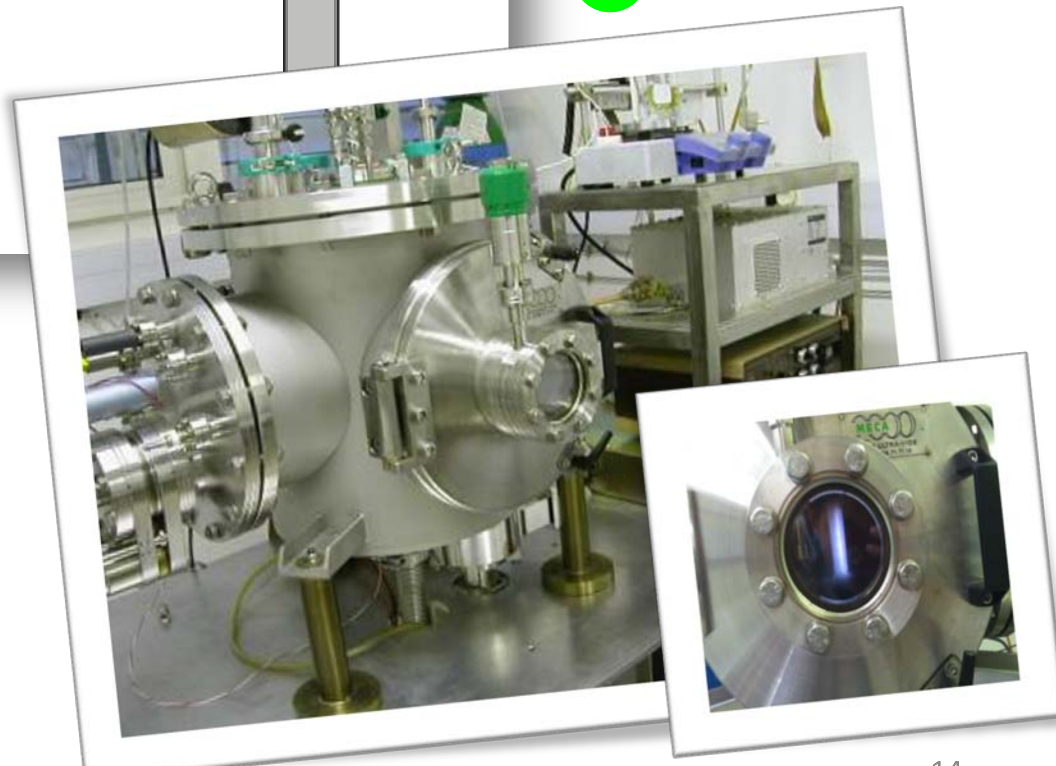
Description of the device



1. **Vacuum system with primary pump and turbo molecular pump**
2. **Introduction system of the precursor**
3. **PECVD chamber**
4. **RF power supply**

Feasibility of preparation of phosphonic membranes by plasma enhanced chemical vapor deposition PECVD using allyl dimethyl phosphonate as a precursor.



Plasma parameters for the deposition of plasma polymerized films

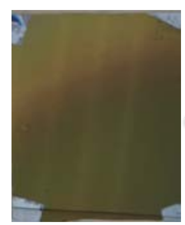
Fixed parameters

- Nature of the precursor (Allyl dimethyl phosphonate)
- Geometry of the reactor
- Nature of the carrier gas (argon)
- Temperature of the precursor (70°C)
- Rotation degree of the electrode (7 rad.s^{-1})
- Electrodes gap (2 cm)
- Flow of the carrier gas (3 sccm)
- Reactor heating (60°C)

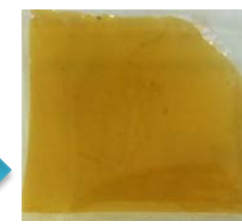
Experimental parameters

- Power: 40 – 200 W
- Gas flow: 1,8 – 6 sccm
- Deposition time: 10 – 180 minutes
- Gas pressure: 0,1 – 0,4 mbar
- Choice of the substrates (silicon wafer, Nafion® 212, PTFE…)
- Pre-treatments applied to the substrates
- Post-treatments applied to the membranes prepared
- Heating of the electrode substrate holder
- Polarization of the electrode substrate holder

$CH_2{=}CH{-}CH_2{-}PO(OCH_3)_2$



Substrates:
Silicon wafer
Nafion® 212



Optimization of experimental plasma parameters for development of new plasma membranes and the correlation of these parameters with the structural and functional properties of manufactured membranes

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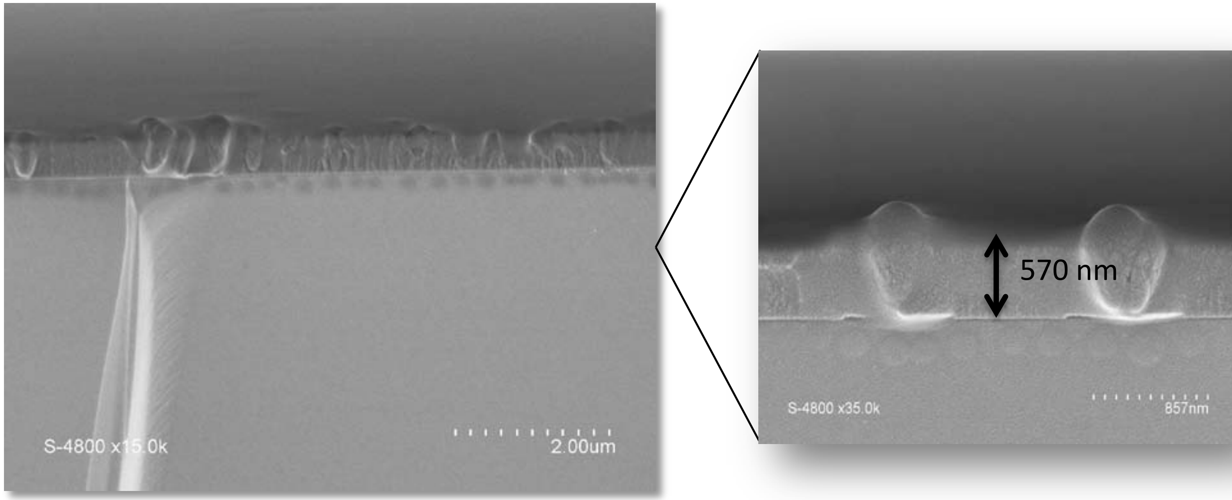
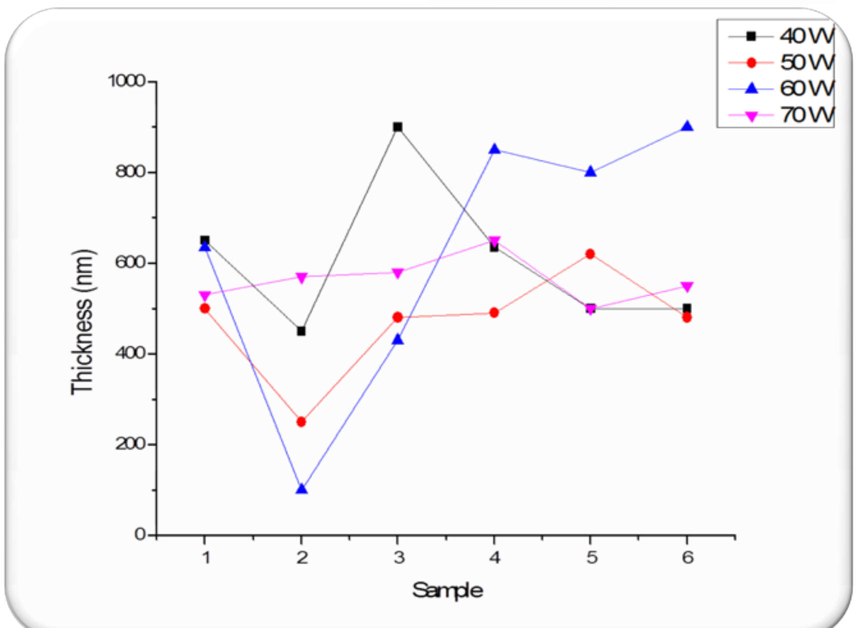
Morphology by scanning electron microscopy (SEM)

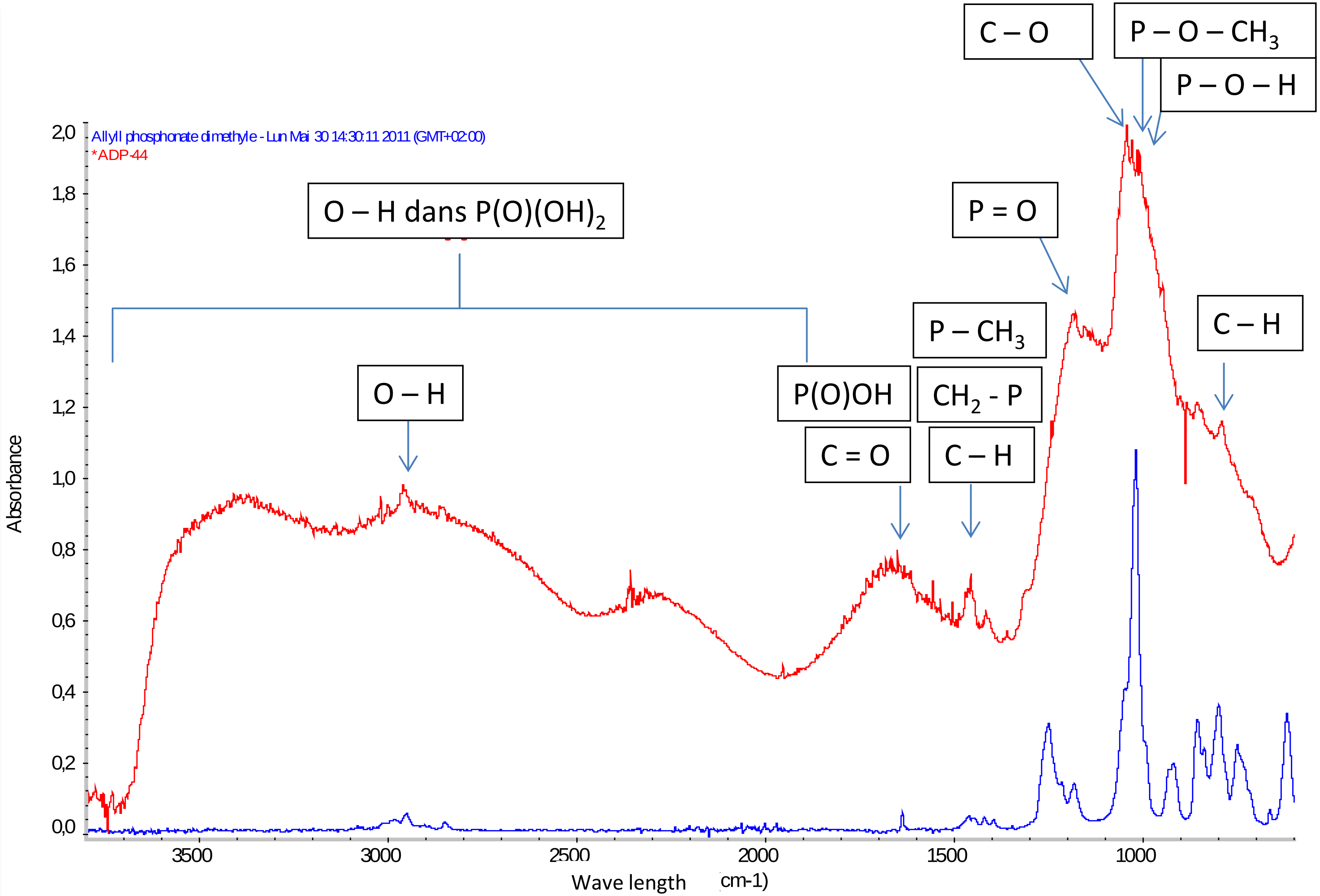


- Dense
- Uniform
- Pinhole-free
- Adherent on the substrate
- Similar morphology for all membranes



- <u>Thickness</u>:
  500 – 1000 nm

Chemical structure by fourier transform infrared (FTIR) spectroscopy



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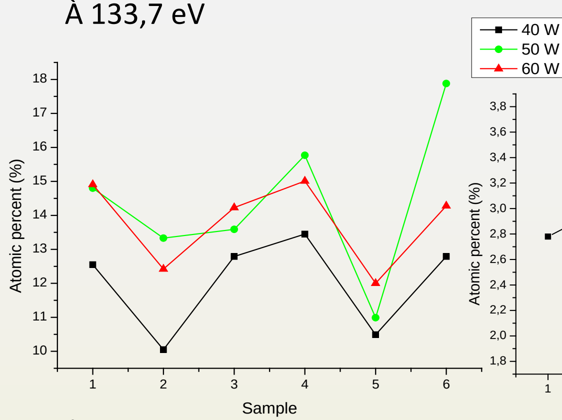
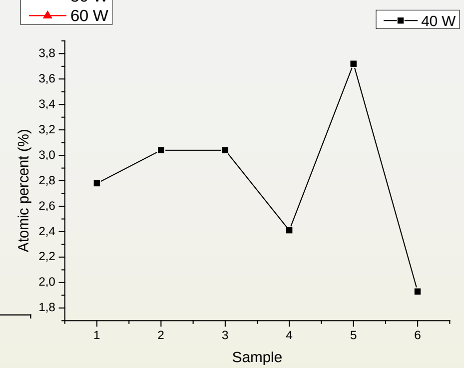
Chemical composition by electron spectroscopy for chemical analysis (ESCA)

P2p

À 133,7 eV

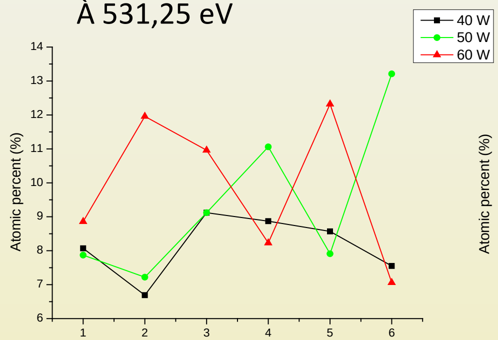


À 133 eV

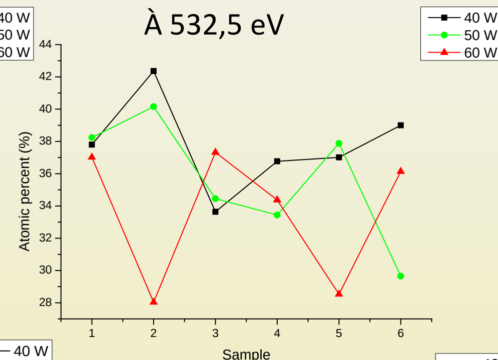


O1s

À 531,25 eV

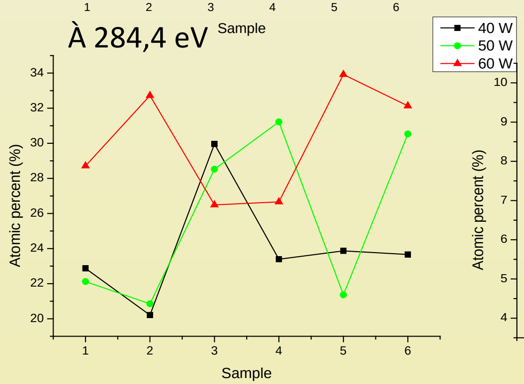


À 532,5 eV

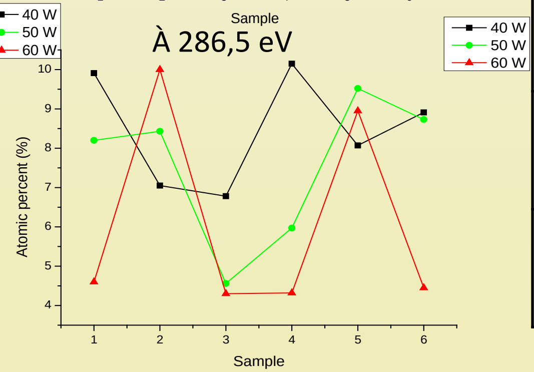


C1s

À 284,4 eV

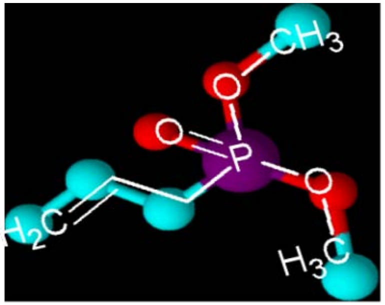


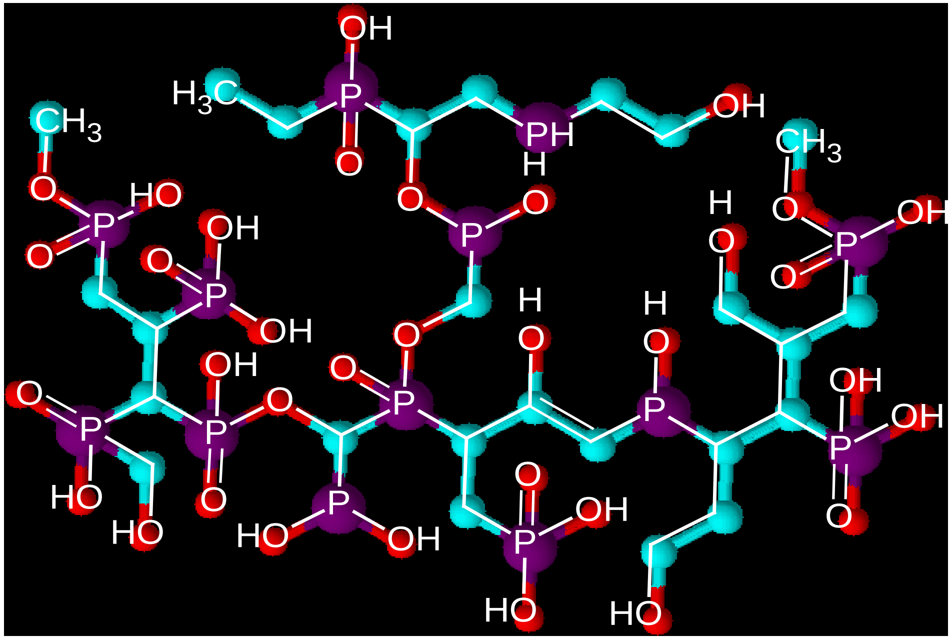
À 286,5 eV



Peak position (eV)	Assignment
284,4	**C** – H
286,5	**C** – O, **C** – P
284,29	**C** = O
531,25	**O** = P, **O** = C
532,5	P – **O** – C, P – **O** – H, P – **O** – CH_3
133,7	**P** – O – C, **P** – O – H, **P** – H, **P** – C
133	**P** in phosphate

IRTF + XPS → Presence of bonds P = O and $P(O)(OH)_2$ in our membranes





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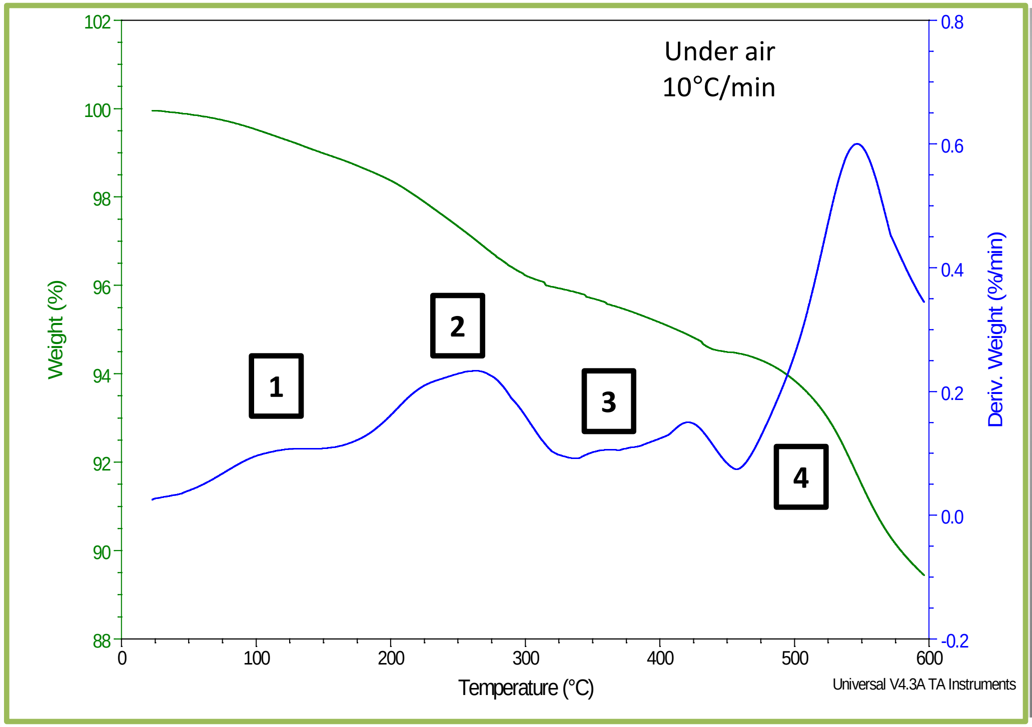
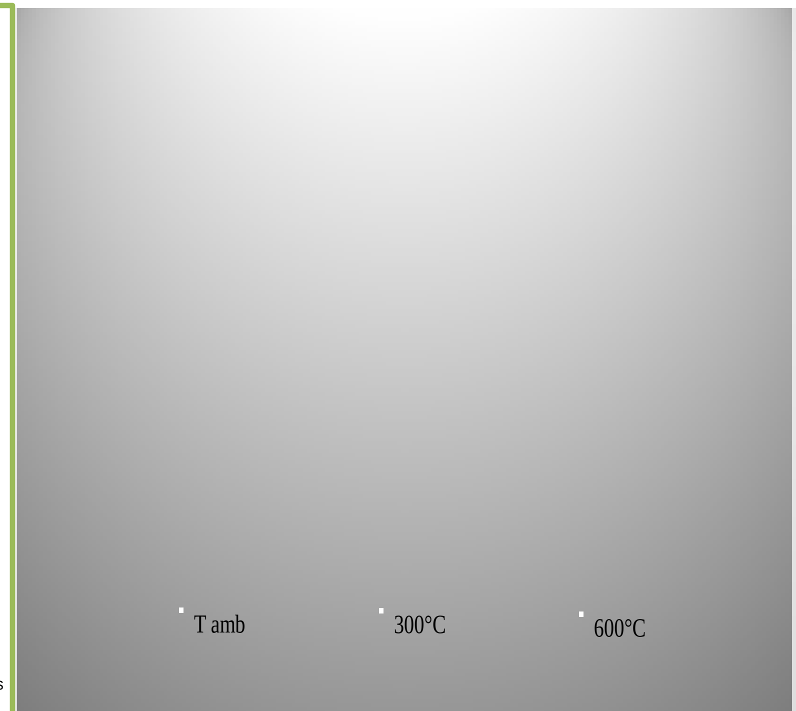
Thermal stability by thermogravimetric analysis (TGA)





Good thermal stability up to 150°C

⇕

1 Loss of free water molecules

2 Loss of bound water molecules

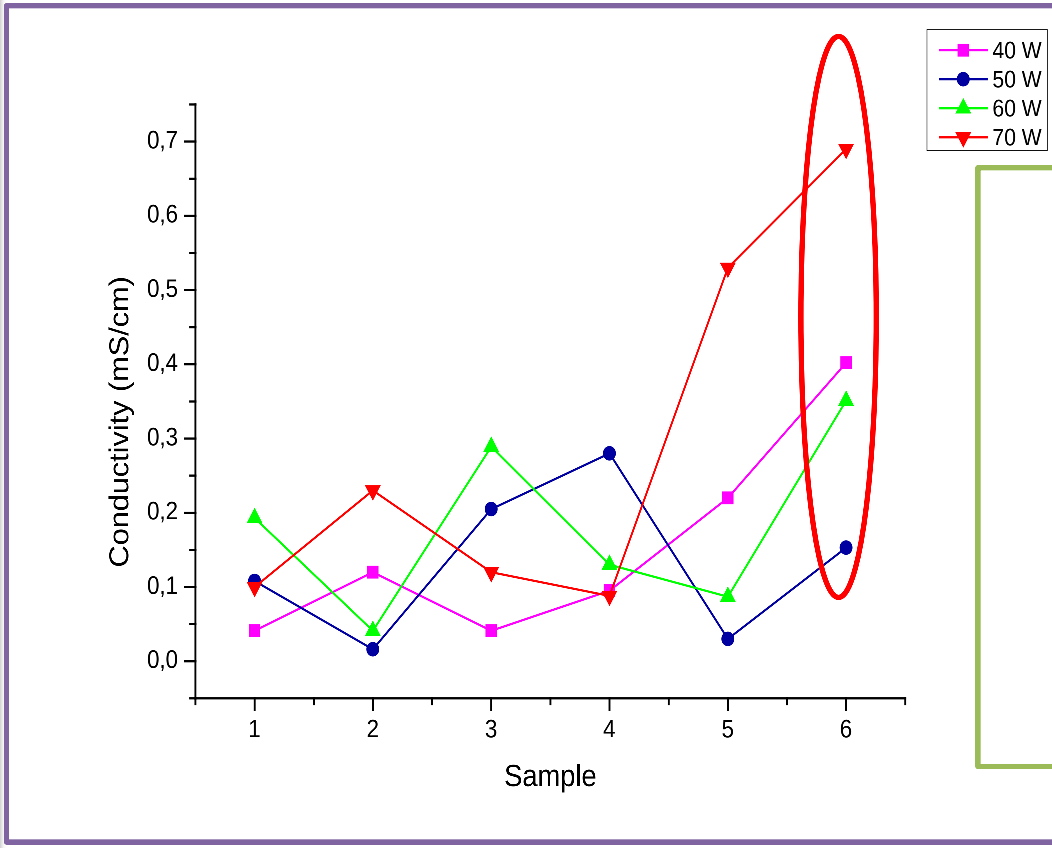
3 Cleavage of the bond C – P

4 Oxidation of phosphorus atoms in the remaining structure

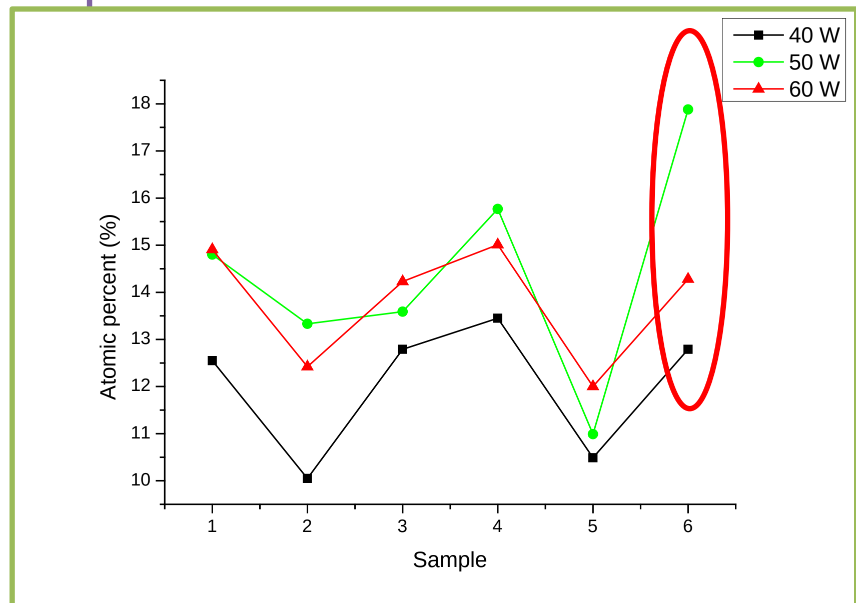
The phosphonic membranes can operate in fuel cells at temperatures in the range 80 – 150°C

Proton conductivity characterization

Proton conductivity



Chemical composition of the phosphorus P2p by ESCA



- σ = **0,016 - 0,69** mS/cm (at room temperature and 100 % RH) (σ_{Nafion} = 20 mS/cm)
- These values are in the same order as those of plasma phosphonic membranes present in the literature (Prakash et al: 0,254 mS/cm at 100°C)
- These values are lower than those of phosphonic membranes prepared by conventional method (Parvole et al: 22 mS/cm at 100°C and 50 % RH, Kato et al: 37 mS/cm at 130 °C and 100% RH)

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Prospects

- Optimization of PECVD parameters to obtain thin proton conducting membranes with microstructural and functional properties suitable for the fuel cell application

- Realization of proton conductivity tests under different conditions of temperature and relative humidity

- Testing the membranes in fuel cell

Thank you

Questions ?