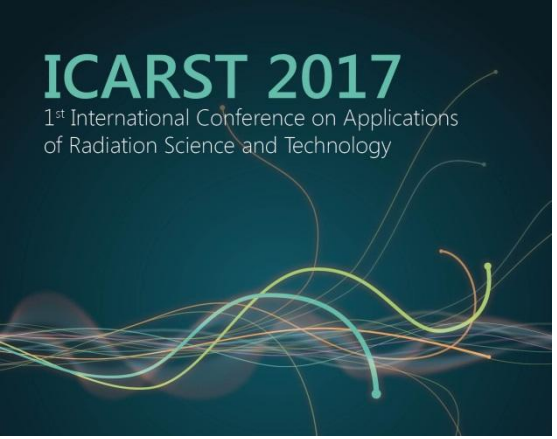


Advances in etched ion-track polymer membranes for environmental and microelectronic applications

Marie-Claude DUBOIS-CLOCHARD

Laboratoire des Solides Irradiés

CEA2/CNRS/Ecole Polytechnique

FRANCE

The site: the « Ecole Polytechnique » Engineer School

Plateau de Saclay (5km from CEA-Saclay site)

Laboratoire des solides Irradiés

EB facility
2,5MeV

Grand Accélérateur National d'Ions Lourds

Laboratoire commun CEA / DSM - CNRS / IN²P³

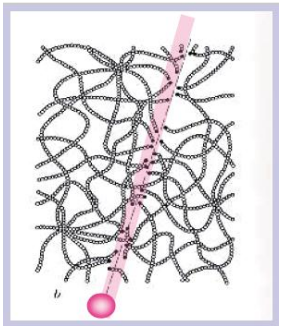
Mixt laboratory : CEA - Ecole Polytechnique – CNRS, UMR 7642
Management: Kees Van Der Beek
90 staff members – 6 teams among them XPnano : 8 permanent researchers

Irradiated polymers

Ionizing radiations

Swift Heavy Ions — GANIL

Electrons — LSI



gamma — CEA LIDyL

X, UV — USTL

plasmas — Faculté de Pharmacie

Solid Polymers: films, fibers, nanoparticles…

PVDF + copo, ETFE, PTFE + terpo — PUR — PP, PE — PET — PC

Irradiation Effects

Unsaturated bonds, radicals, oxidation
Crosslinking and scission, radiolysis gases

Radiografting

Film structure, physico-chemical properties

Materials

sterilization
ageing
radiolysis

← stability

new →

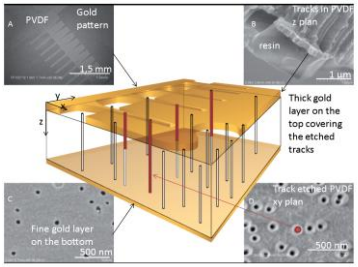
Functionnalization
nanostructuration

Track etching

Research Fields

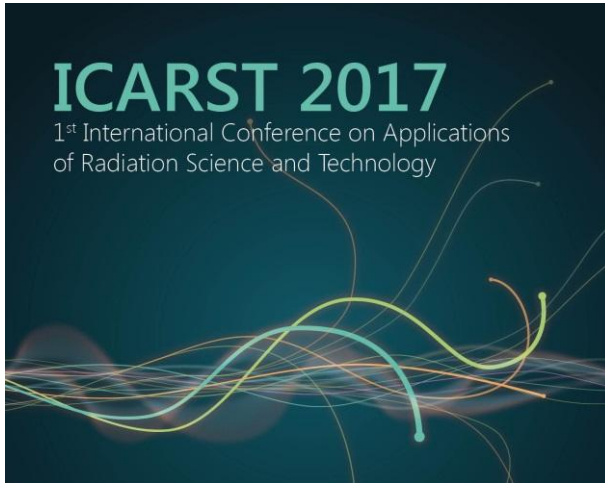
Energy

Nanoelectronic



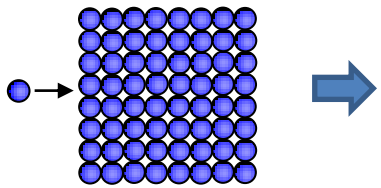
Environment/Health

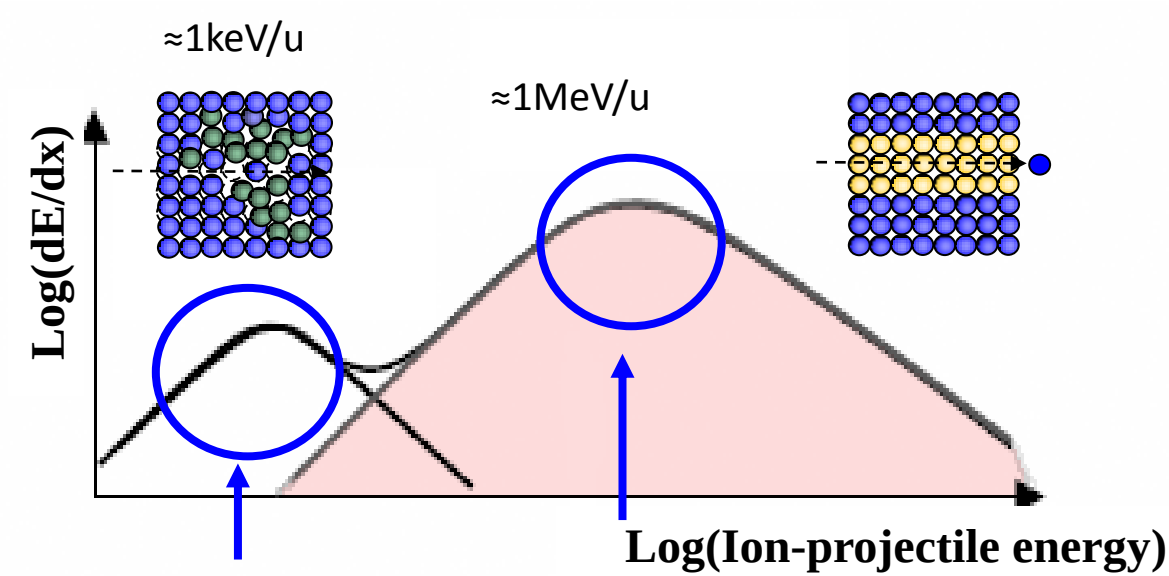
Tracks formation



Ion-matter interaction : Energy loss

Ion-matter interaction

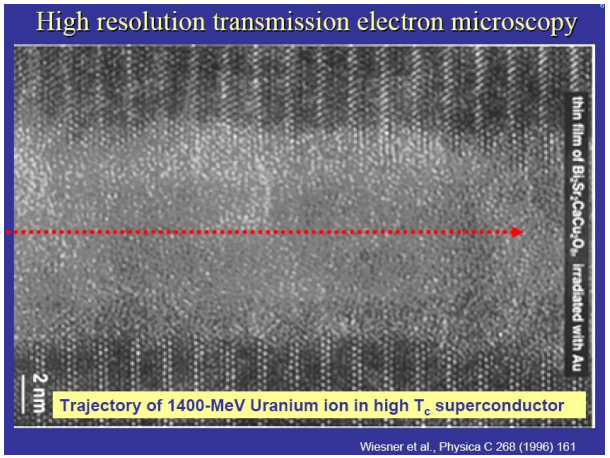




Nuclear collisions
$(dE/dx)_{nuclear}$

Electronic interactions
$(dE/dx)_{electronic}$

Tracks

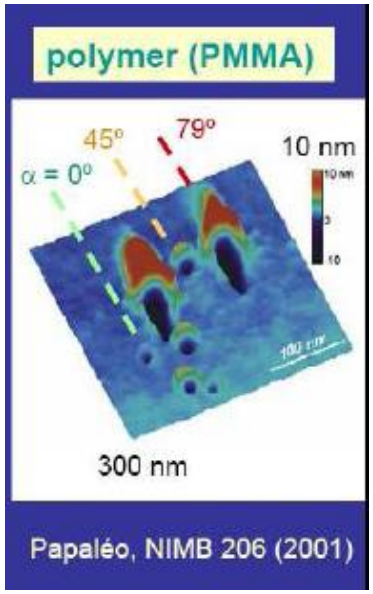


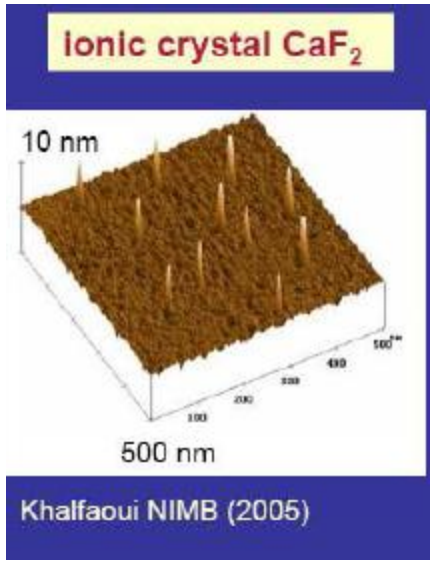
Deposited Energy per charged particle and per length unit

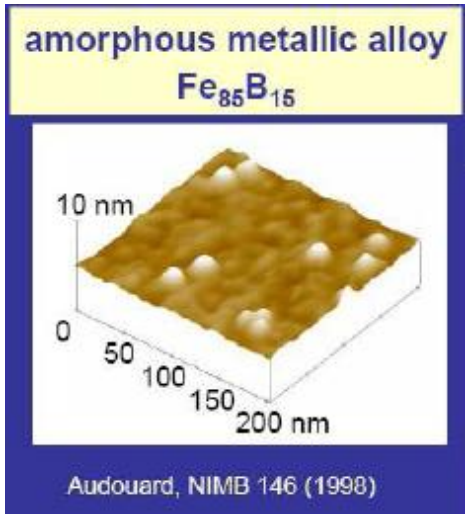
$$\left(\frac{dE}{dx}\right) \propto \frac{keV}{nm}$$

$$(dE/dx)_{Total}=(dE/dx)_{nuclear}+(dE/dx)_{electronic}$$

Tracks at the surface of some solids





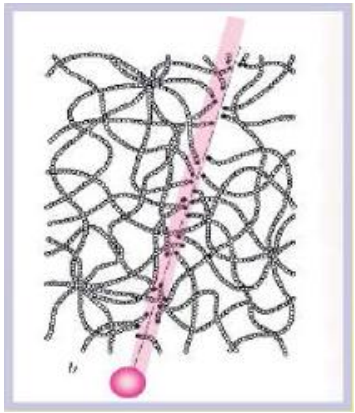


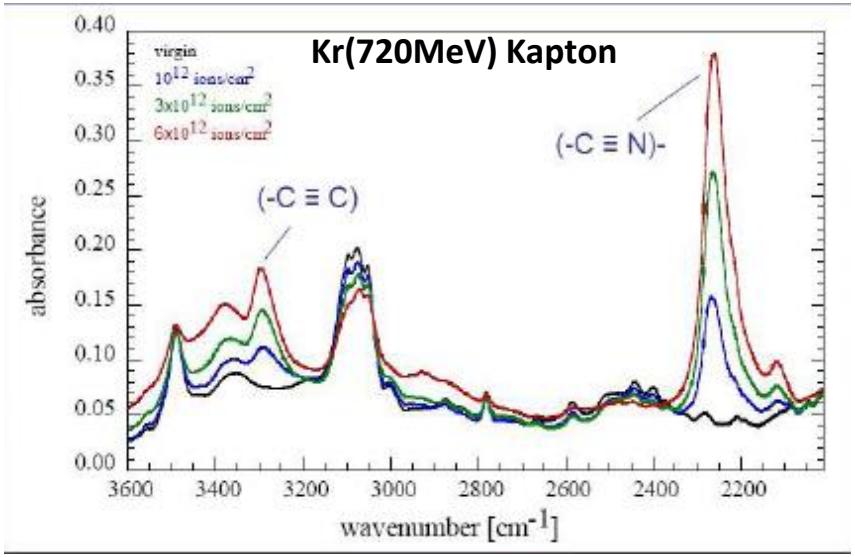
High sensitivity | Weak sensitivity

dE/dx threshold	~1 keV/uma	~20 keV/uma	~50 keV/uma
	Insulators	**Semi-conductors**	**Metals**
	Polymers	**Amorphous Si**	**Amorphous alloys**
	Oxydes	**GeS, InP, $Si_{1-x}Ge_x$**	**Fe, Bi, Ti, Co, Zr**
	Spinels	**Si, Ge**	**Au, Cu, Ag …**

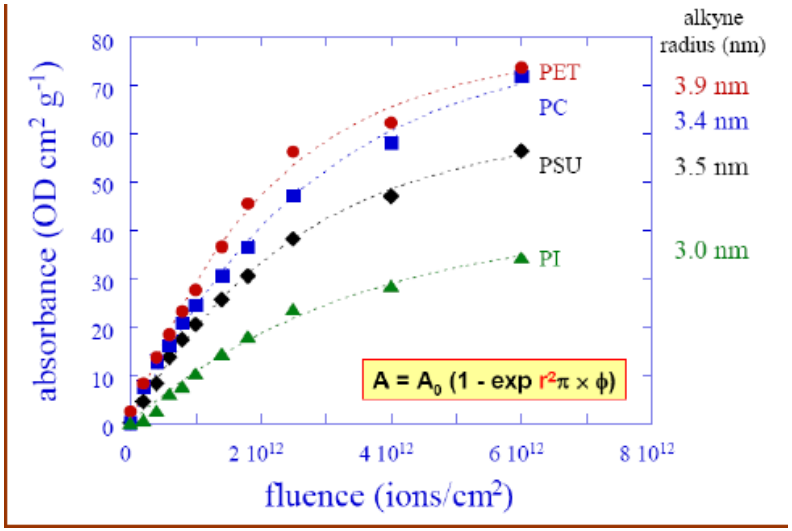
Defaults in a latent track in a polymer film

- Chain scission
- Amorphization
- Gaz formation (CO_n, C_nH_n,…)
- Radical formation
- Cross-linking
- Multiple bonds (ex. C=C, C≡C)





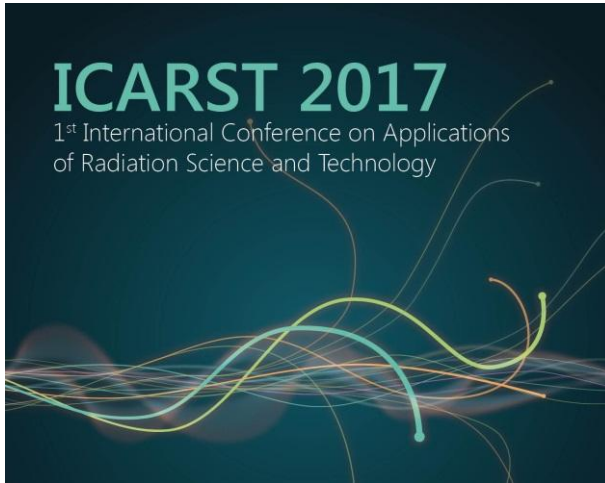
Steckenreiter et al, J. Polym. Sci. A37 (1999) 4318



C≡C *versus fluence*

Radio-grafting in latent tracks

Natacha BETZ « Ion-Track Grafting » NIM B 105 (1995) 55-62



Application to Polymer Electrolyte Membrane for fuel cell

Journal of Power Sources 195 (2010) 223–231

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Ion track grafting: A way of producing low-cost and highly proton conductive membranes for fuel cell applications

M.-C. Clochard[a,*], T. Berthelot[a], C. Baudin[a], N. Betz[a,1], E. Balanzat[b], G. Gébel[c], A. Morin[d]

[a] Laboratoire des Solide Irradiés, CEA - DSM/IRAMIS – CNRS UMR 7642 - Ecole Polytechnique, F-91128 Palaiseau, France
[b] CIMAP, CEA – CNRS – ENSICAEN BP 5133 F-14040 Caen, France
[c] CEA - DSM/INAC/SPrAM CEA-Grenoble 17 rue des Martyrs, F-38054 GRENOBLE Cedex 9, France
[d] CEA - DRT/LITEN/DTH/LCPEM CEA-Grenoble 17 rue des Martyrs, F-38054 GRENOBLE Cedex 9, France

5 patents

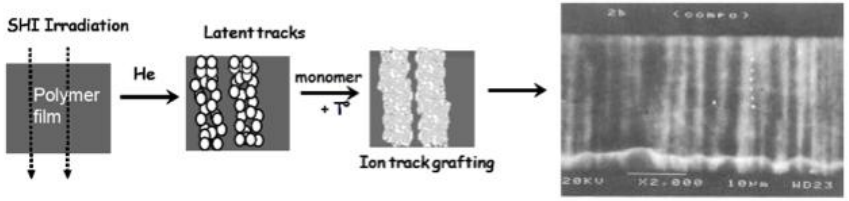
M-C. Clochard, T. Berthelot, C. Baudin, « Procédé d'élaboration de Membranes Conductrices de Protons de Pile à Combustible par Radiogreffage » CEA French patent (BD 1727) FR 0757875 ext PCT WO/2008/062726 **(2007)**

T. Berthelot, M-C Clochard, « Membranes Conductrices de Protons pour Pile à Combustibles présentant un gradient de protons et Procédés de Préparation desdites Membranes» CEA French patent (BD 10047) FR 0757873 ext PCT WO/2009/103925 **(2007)**

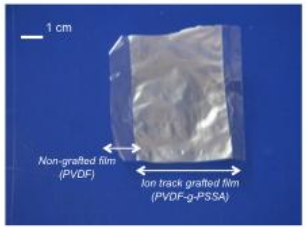
T. Berthelot, M-C Clochard, « Membranes Conductrices de Protons pour Pile à Combustible et Procédés de Préparation desdites Membranes» BD11266 French patent FR0955854 ext PCT WO/2010/062512 **(2009)**

E. Gallino, M-C Clochard, A. Morin, G. Gebel, "Suspension aqueuse comprenant des particules de catalyseur métallique et des particules de polymère spécifique utilisable pour la fabrication de couche active d'électrode" CEA-X-CNRS FR1252533 (**2012)**

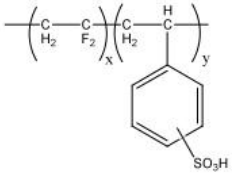
Ion-track membranes for fuel cell: creation of proton conductive channels



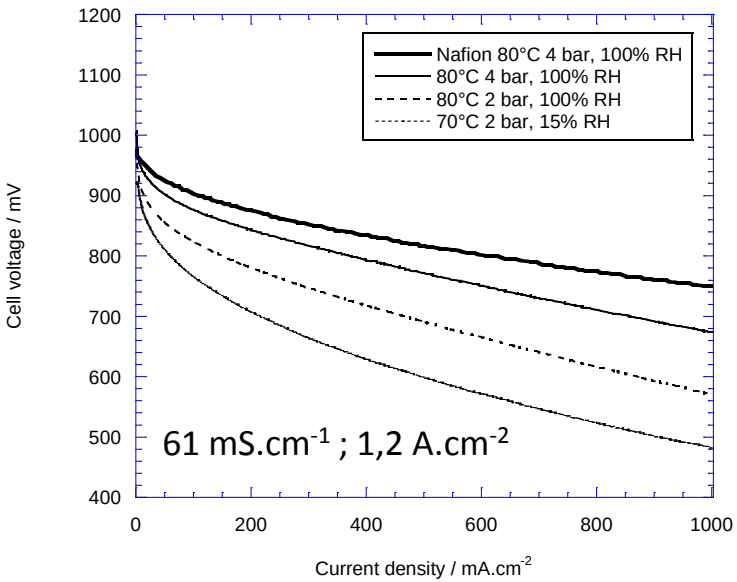
PVDF-g-PS dopé au Césium
5.10^7ions/cm²Y=1.7wt%



PVDF-g-PSSA
10^{10}ions/cm²Y=140wt%



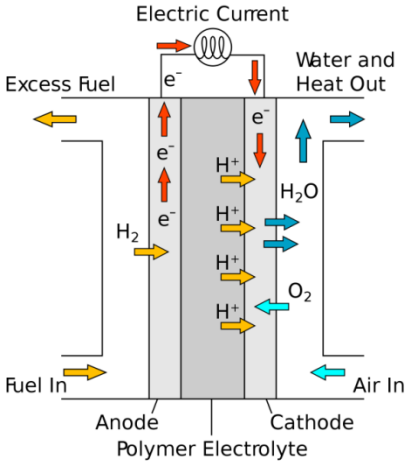
Substitution électrophile



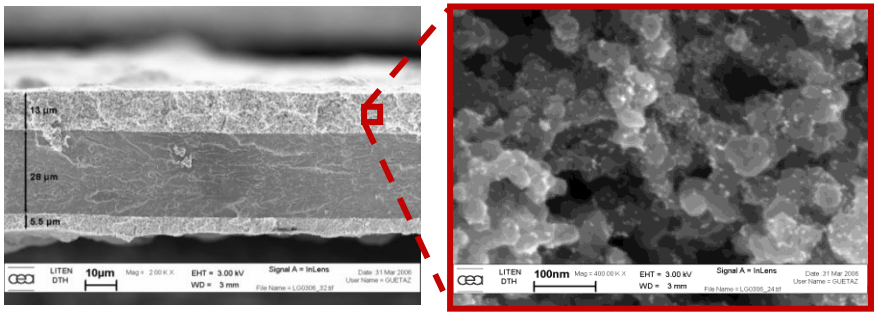
Identical efficiency as Nafion

(A) PEMFC for automotive (ex: GENEPAC PSA-CEA), (B) Stack and (C) single cell.

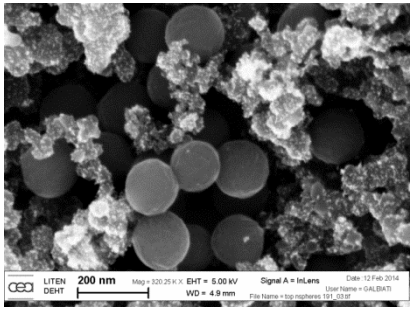
Perspectives: how improving the membrane-electrode interface ?



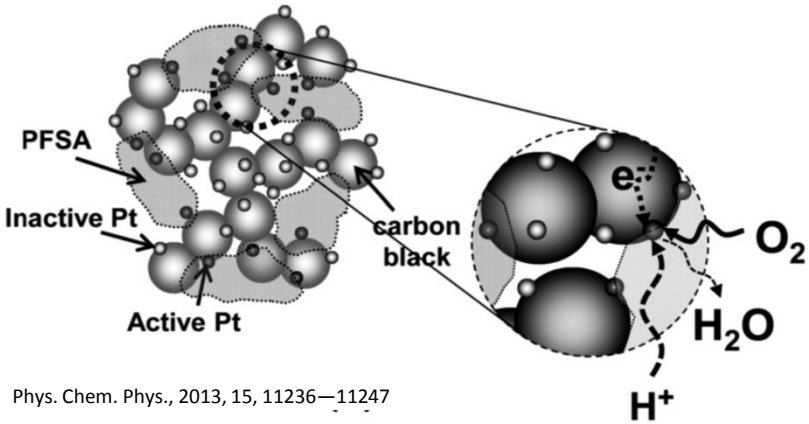
Commercial ink



Ink containing radiografted PVDF NPs



- On-going research
  - Understanding exchanges in active phases in the MEAs
  - Electrochemical cell adapted for TEM *in situ* (Nan'eau PROJECT)



Phys. Chem. Phys., 2013, 15, 11236—11247

Journal of Power Sources 296 (2015) 117–121

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

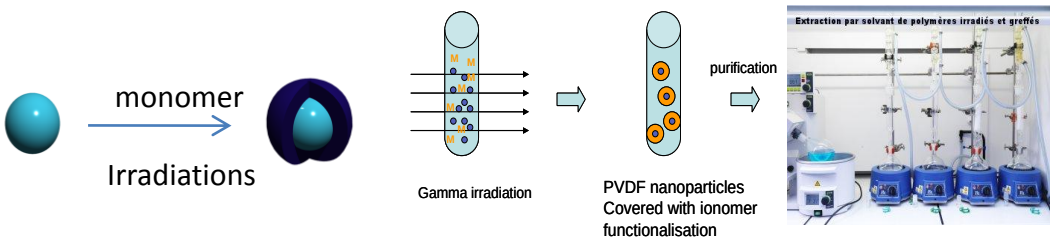
Short communication

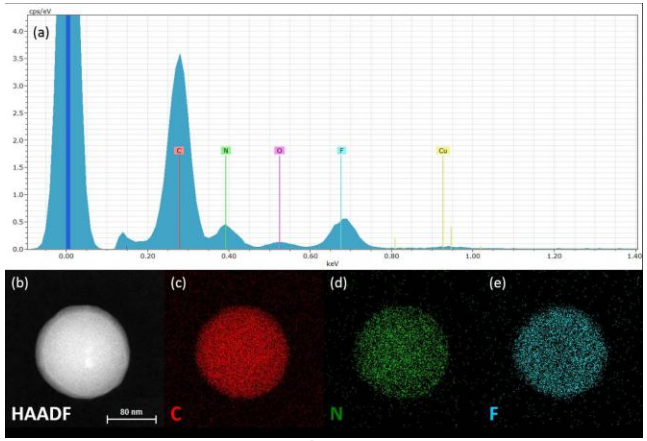
Poly(vinylimidazole) radiografted PVDF nanospheres as alternative binder for high temperature PEMFC electrodes

Samuele Galbiati [a, c], Pierre-Eugène Coulon [a], Giancarlo Rizza [a], Marie-Claude Clochard [a, *], Micaela Castellino [b], Marco Sangermano [b], Christine Nayoze [c], Arnaud Morin [c, **]

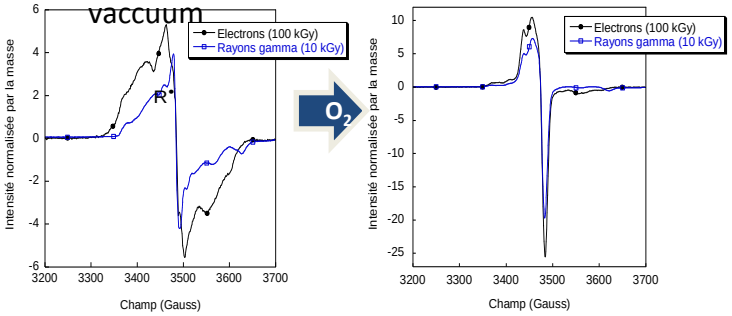
[a] Laboratoire des Solides Irradiés, CEA DSM/IRAMIS, CNRS UMR 7642, Ecole Polytechnique, Université Paris-Saclay, F-91128 Palaiseau, France
[b] Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[c] CEA-Grenoble DRT/LITEN/DHT/LCPEM, 17 rue des Martyrs, F-38054 Grenoble Cedex 9, France

In-situ radiografting

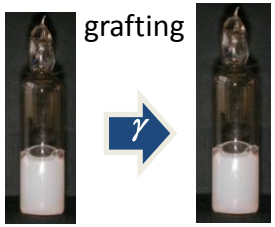




Alkyl radicals under vaccuum

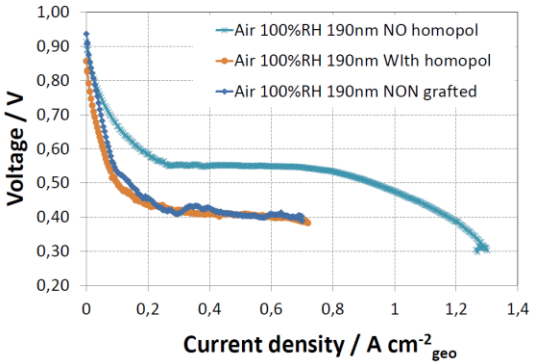


Irradiations + grafting



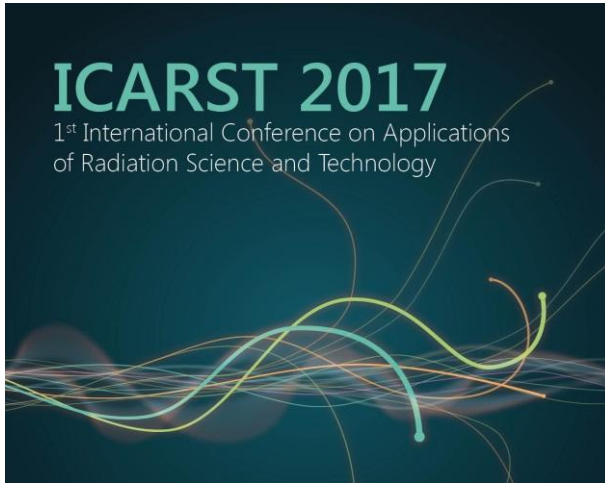
PVDF + monomer

Nsf 190 nm

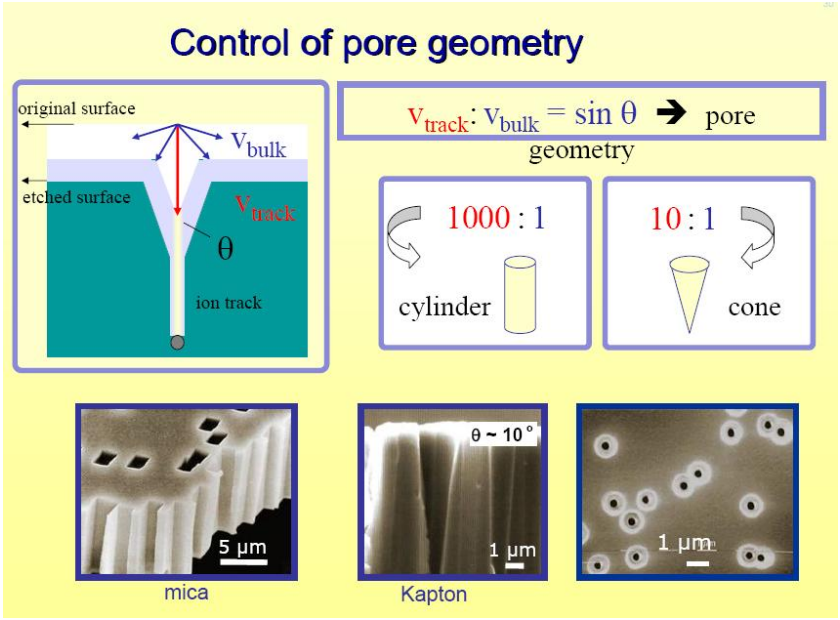


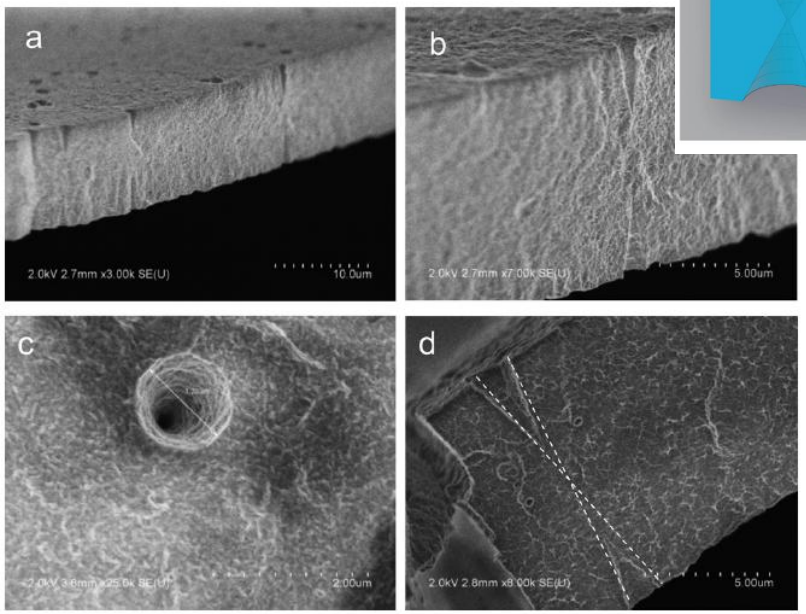
Other monomers of interest: vinyl imidazole doped phosphoric acid for high T°C fuel cell applications

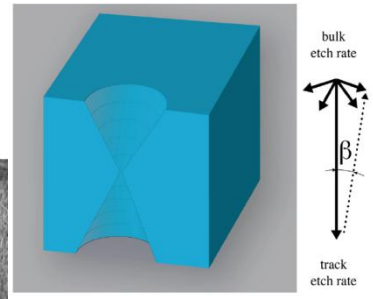
Track revealing : track-etching



Track etching

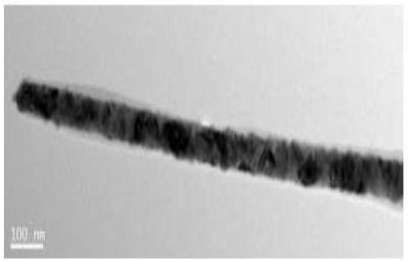


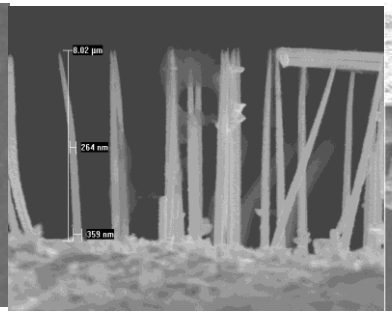




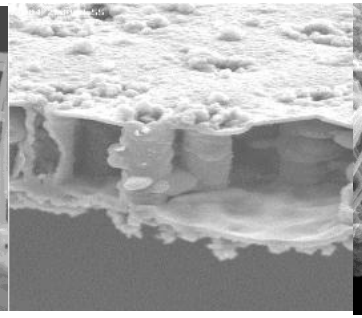
Template synthesis

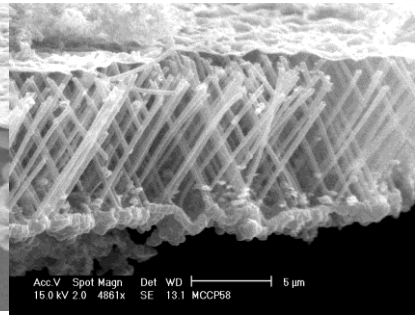
Cylindrical and conical metallic nanowires



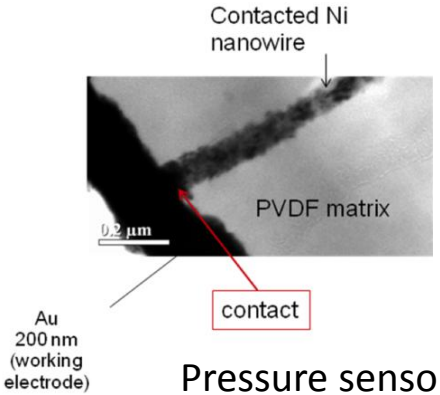


PPy nanotubes

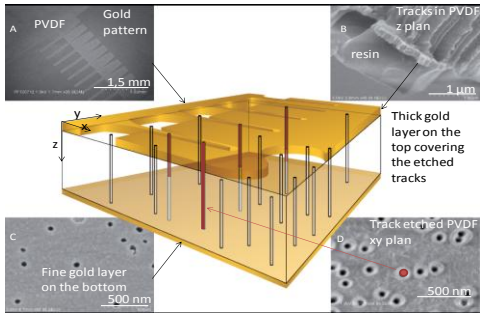


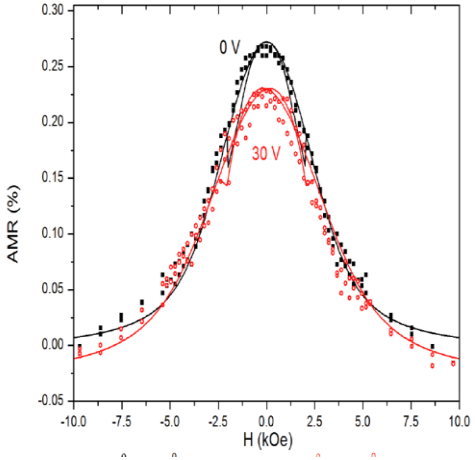


Template synthesis: Nanoelectronics - spintronics



Pressure sensor (G. Melilli)



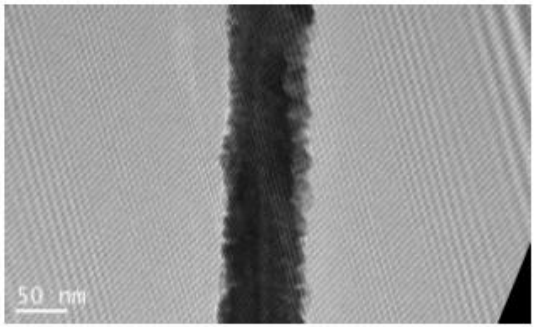


P.Do Chung et al., MRX (2014)

Challenge for **MRAM**

Controlling magnetic domain wall playing on the nanowire geometry

For the first time, we have imaged 2 head-to-head magnetic wall domains on single nanowire. This result have been confirmed par calculation.



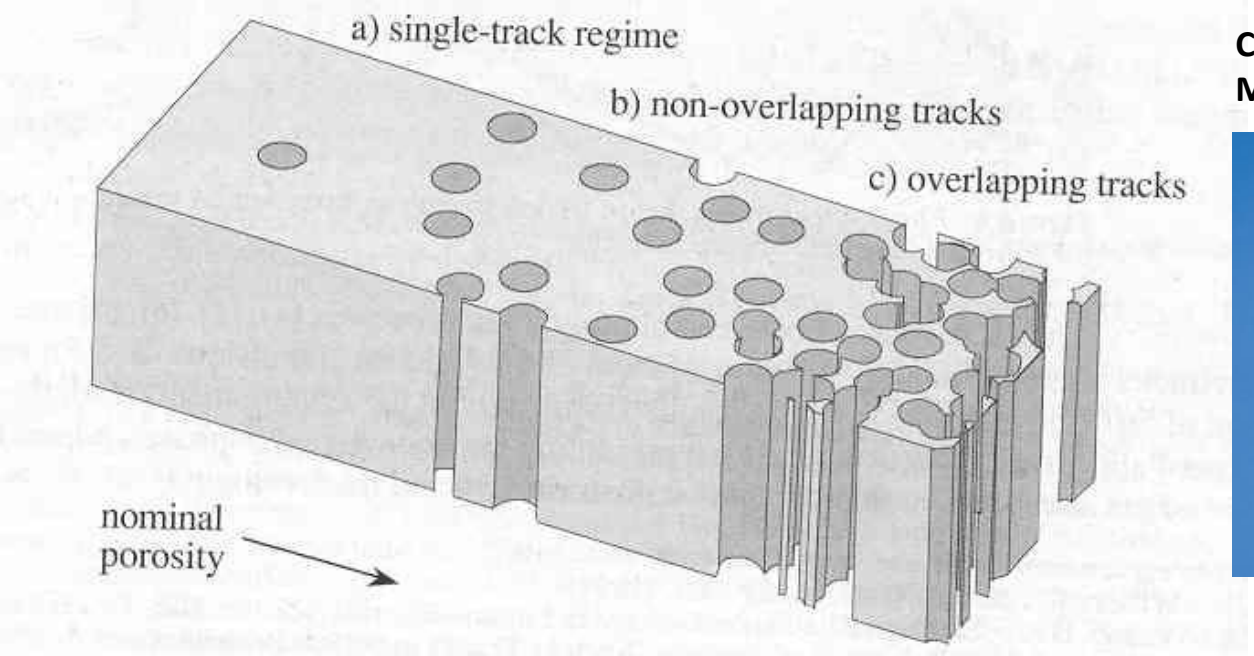
Hologram Image 1

TEM magnetic holography

NANO LETTERS Letter pubs.acs.org/NanoLett

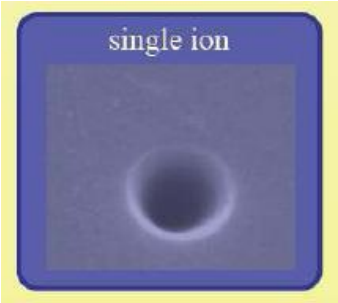
Biziere, Nicolas; Gatel, Christophe; Lassalle-Balier, Rémy; Clochard, Marie-Claude; Wegrowe, Jean-Eric; Snoeck, Etienne "Imaging the fine structure of a magnetic domain wall in a Ni nano-cylinder » Nanoletters (2013)

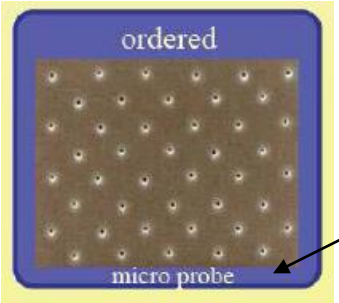
1srt application: membranes for filtration



Commercial products (Nuclepore, Poretics) Millipore®, Whatman®…

Ions species: C… Xe… U Fluence: 1…10^{13}ions/cm^2





Developed at GSI (Germany)

Membrane recent developments:
fabrication on hybrid membranes based on nanoporous graphene

Materials Letters 184 (2016) 47–51

Contents lists available at ScienceDirect

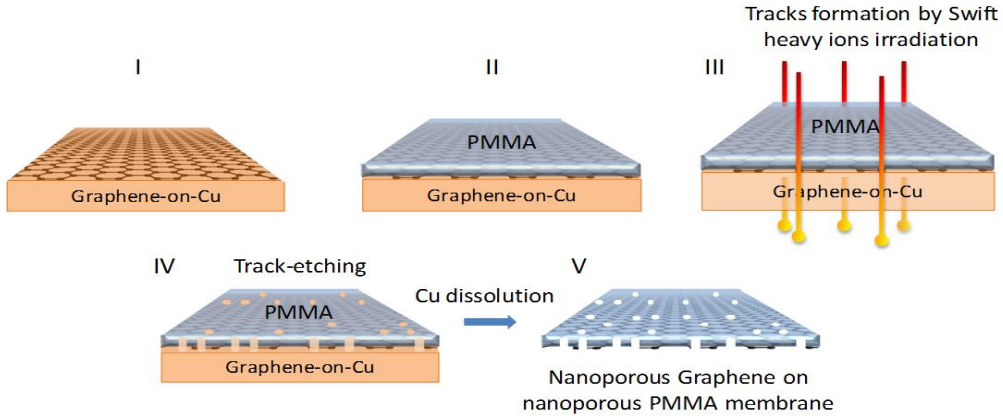
Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Large area fabrication of self-standing nanoporous graphene-on-PMMA substrate

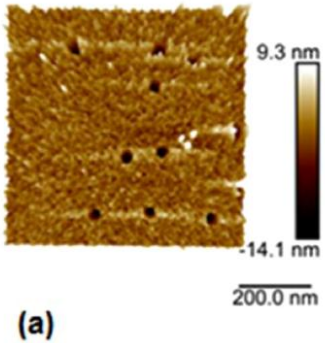
M.-C. Clochard [a], G. Melilli [a], G. Rizza [a], B. Madon [a], M. Alves [a], J.-E. Wegrowe [a], M.-E. Toimil-Molares [b], M. Christian [c,d], L. Ortolani [c], R. Rizzoli [c], V. Morandi [c], V. Palermo [d], S. Bianco [e], F. Pirri [e], M. Sangermano [e,*]

[a] Laboratoire des Solides Irradiés, CNRS, CEA-DRF-IRAMIS, Ecole Polytechnique, Université Paris-Saclay, PAlaiseau Cedex, 91128 France
[b] Materials Research Department, GSI Helmholtz Centre for Heavy Ion Research, Planckstr. 1, Darmstadt, 64291 Germany
[c] CNR-IMM Sezione di Bologna, via Gobetti 101, Bologna, 40129 Italy
[d] CNR-ISOF, via Gobetti 101, Bologna, 40129 Italy
[e] Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia, Corso Duca degli Abruzzi 24, Torino, 10129 Italy

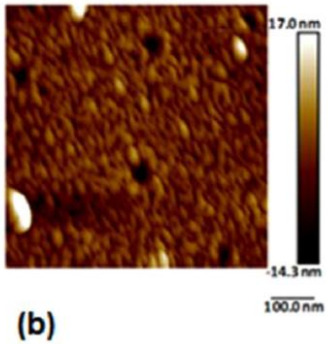


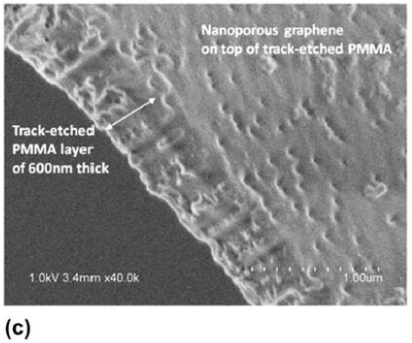
Characterization of nanoporous graphene-on-PMMA substrate

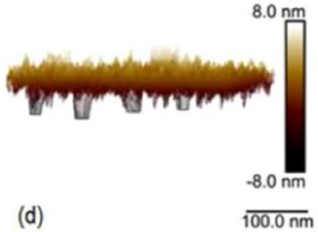
PMMA side



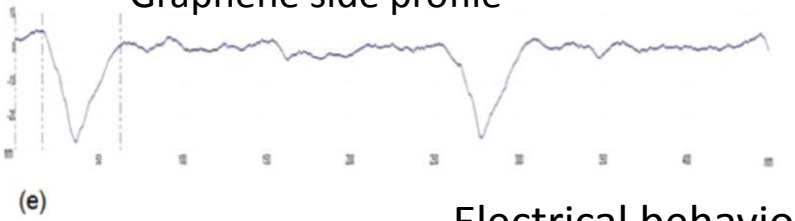
Graphene side

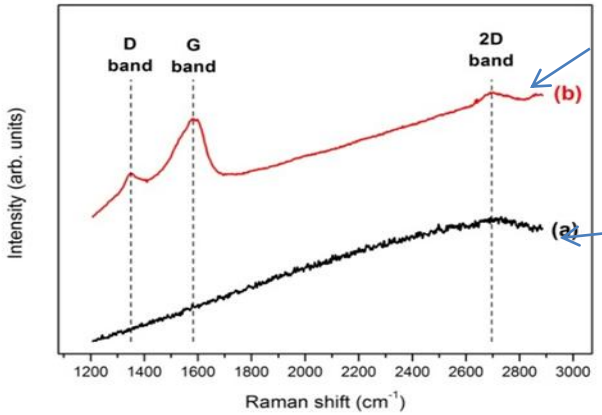






Graphene side profile

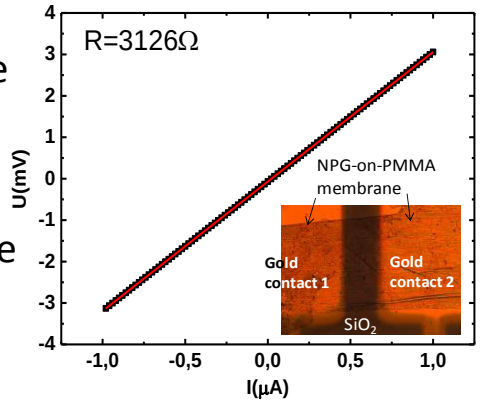


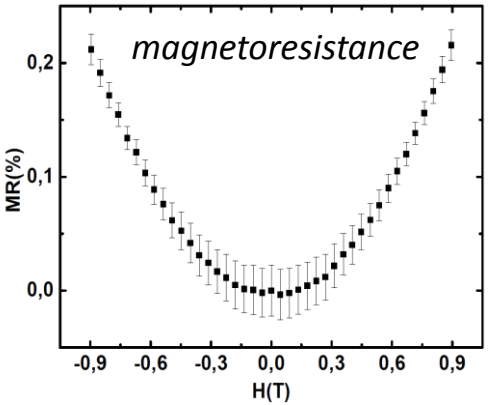


Graphene side

PMMA side

Electrical behaviour

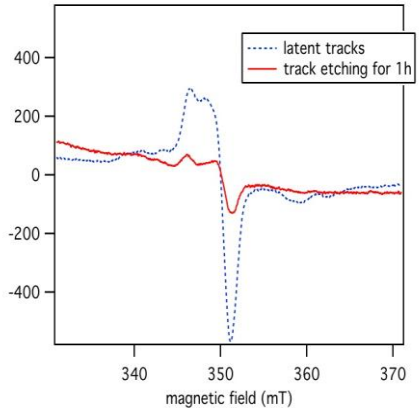


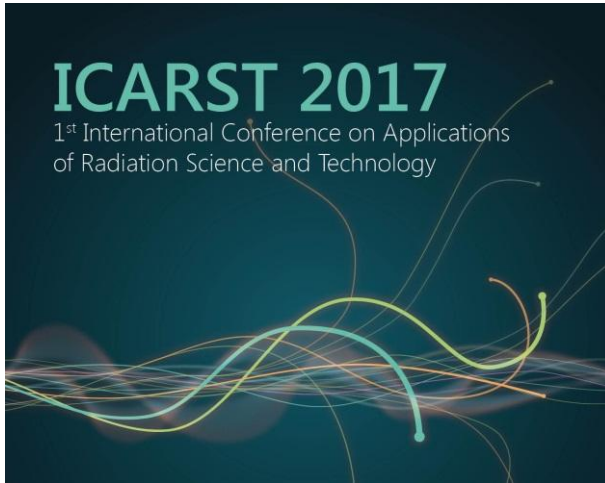


Perspectives: excellent candidates for water desalination and/or field emission transitors…

How to chemically modify pore interior?

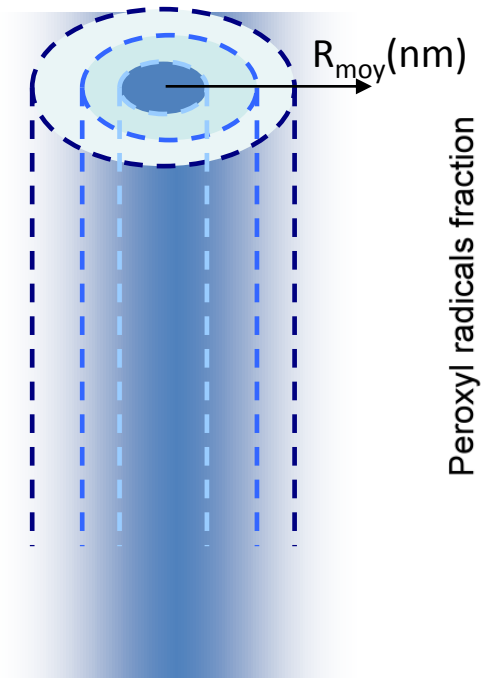
Remanence of radicals after etching

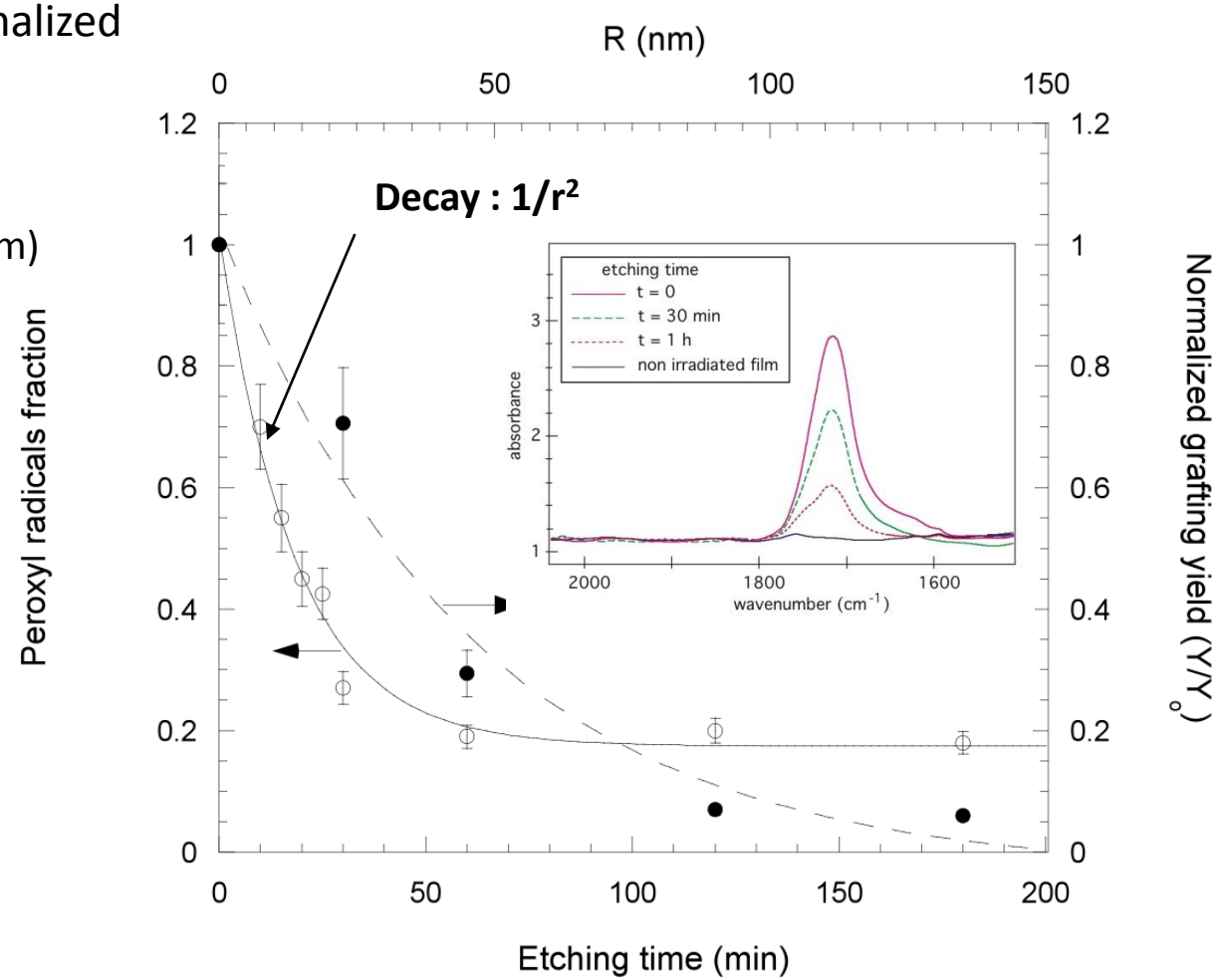




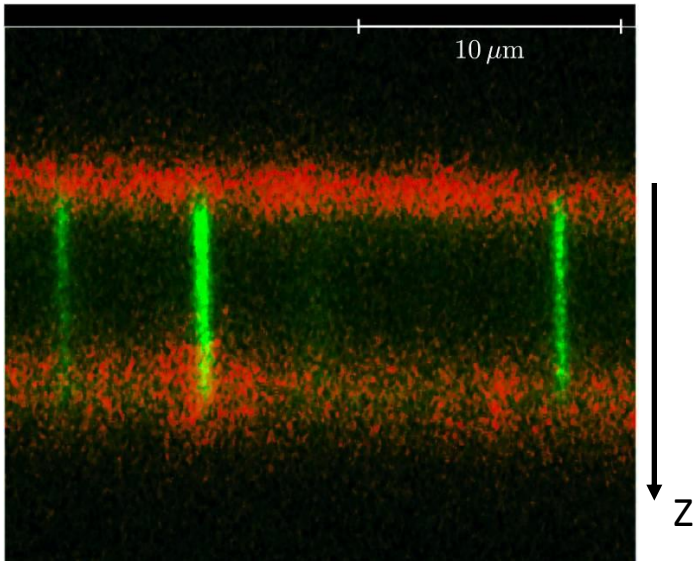
Remaining radical fraction profile per track

f averaged and normalized to a single track





Radiografting localization: Double labelling



Images CLSM of PVDF-g-PAA membranes modified with ethylenediamine prior to radiografting.
Images are xz-plan (cross-section) re-building of xy-plan series.

Red: Fluorescein isothiocyanate reacts with amine functions, i.e. oxydation

green: Alexa Fluor R hydrazide reacts with carboxylic acids, i.e. poly(acrylic acid).

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Nuclear Instruments and Methods in Physics Research B 265 (2007) 309–313

NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Nanoporous β-PVDF membranes with selectively functionalized pores ☆

O. Cuscito [a], M.-C. Clochard [a,*], S. Esnouf [a], N. Betz [a], D. Lairez [b]

[a] *LSI, Ecole Polytechnique, CEA-DSM, CNRS, 91128, Palaiseau Cedex, France*
[b] *Laboratoire Léon Brillouin, CEA-Saclay, 91191 Gif-sur-Yvette Cedex, France*

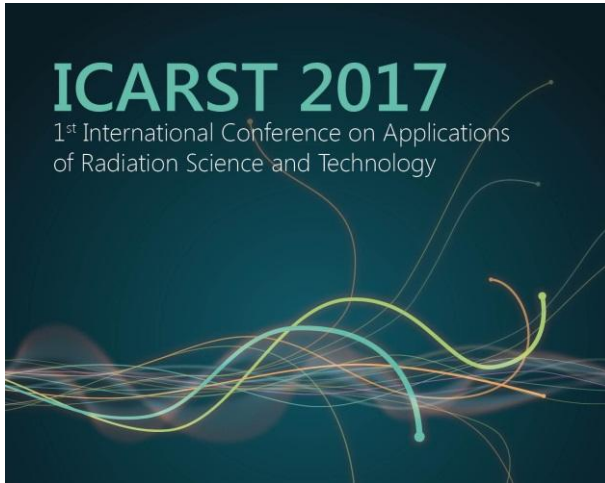
Available online 15 September 2007

Applied Research: Early warning sensors for monitoring toxic metal ions

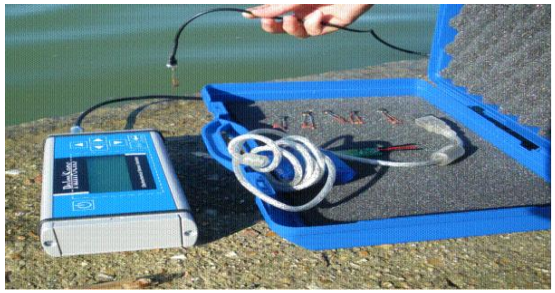
CAPTOT Technology

POLLUTEC 2012

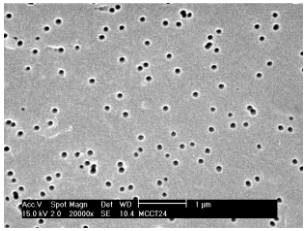
Travis Wade receiving the award of « Salon Pollutec » ex-project ECOSISTEM

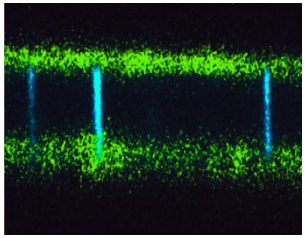


CAPTOT Technology



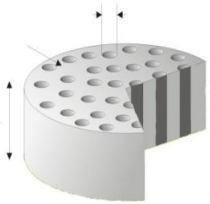
Sensor for toxic metal ions

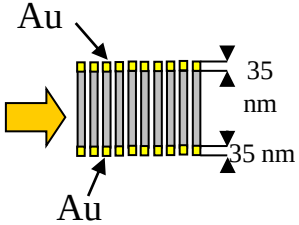


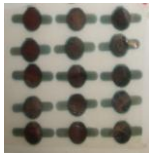


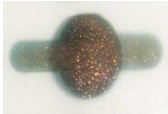
membrane

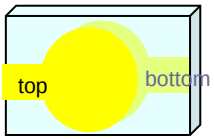
9 µm

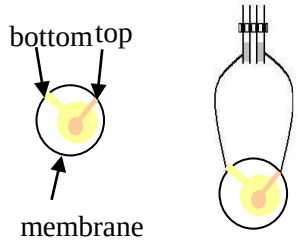


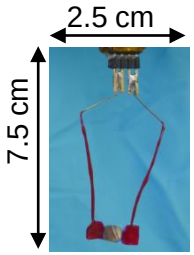




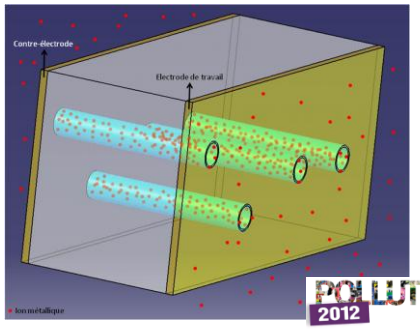


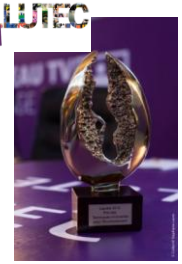




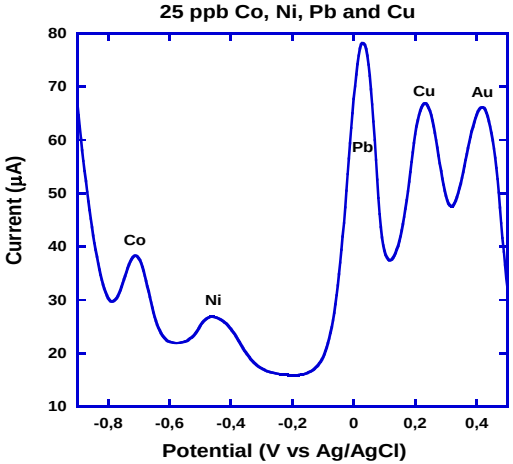


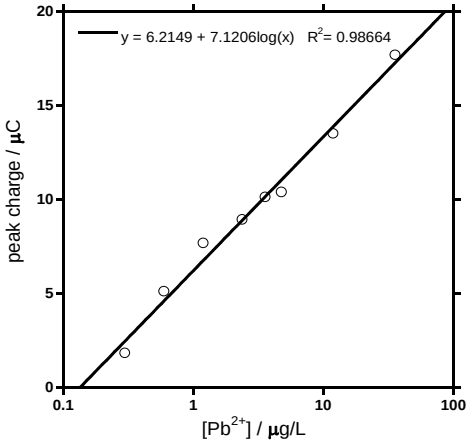
Labscale demonstrator



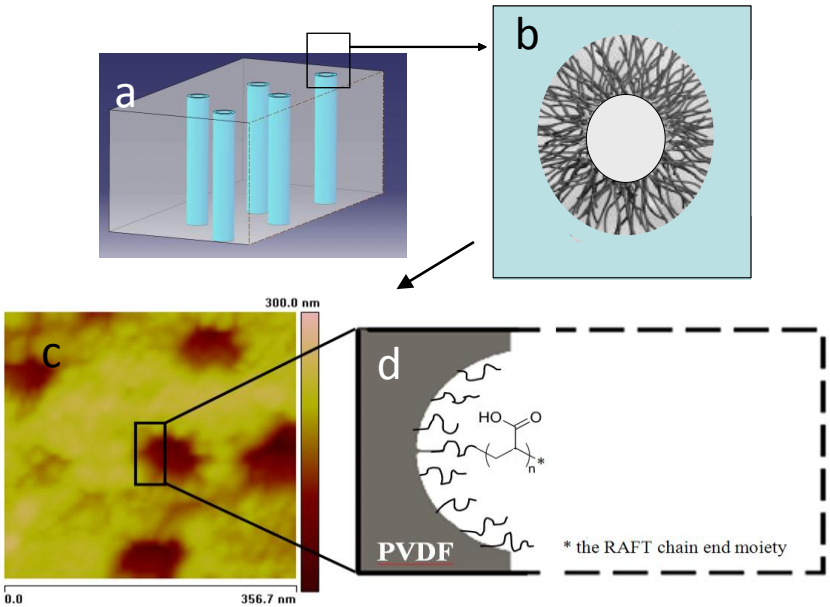


Prices OSEO et POLLUTEC en 2012





Controlled radical polymerization inside nanopores

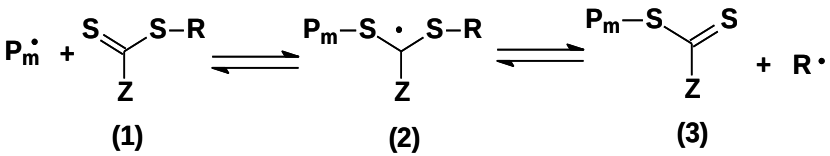


Radiation induced RAFT mechanism

(I) SHI irradiation $\longrightarrow$ I • Radicals trapped in the crystallites of PVDF

$$I\bullet \xrightarrow[k_i]{\text{Monomer}} P_1^{\bullet}$$

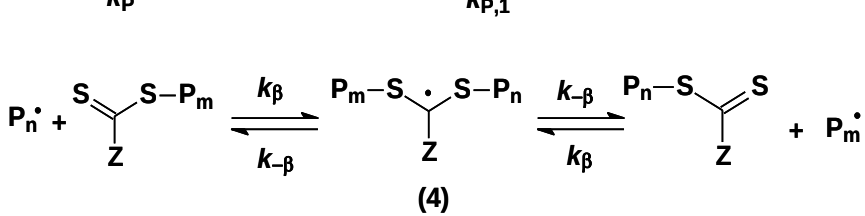
(II)



(III)

$$P_n^{\bullet} \xrightarrow[k_P]{\text{Monomer}} P_{n+1}^{\bullet} \qquad R\bullet \xrightarrow[k_{P,1}]{\text{Monomer}} P_1^{\bullet}$$

(IV)



(V)

$$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{\langle k_t \rangle} P_{n+m}$$

HACETTEPE ÜNİVERSİTESİ

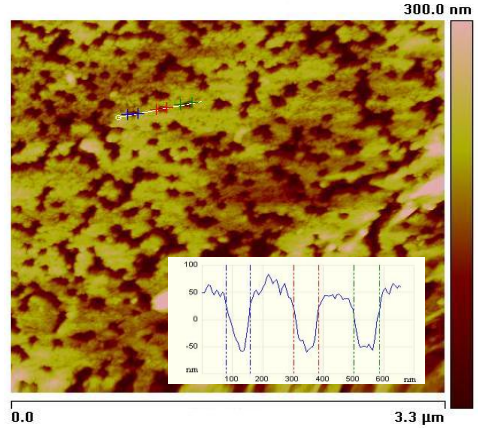
AFM : nanopore filling

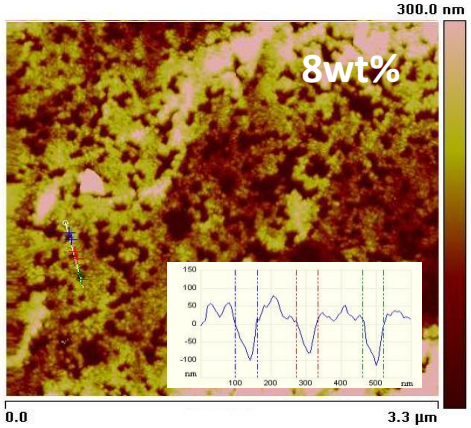
R=25nm

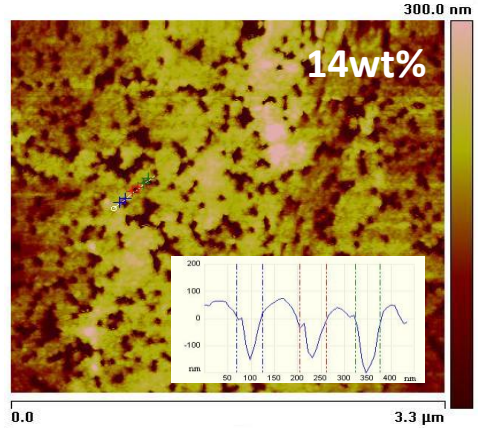
PVDF-g-PAA membrane

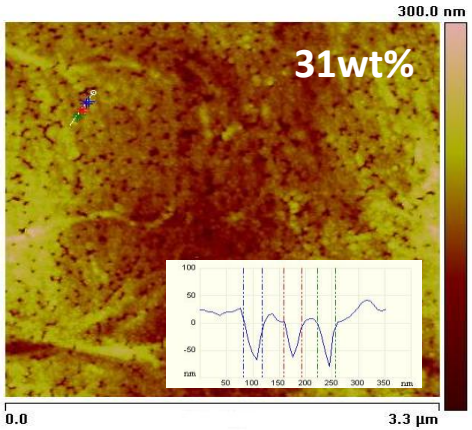
$^{78}Kr^{31+}$, fluence 10^{10} ions/cm^2

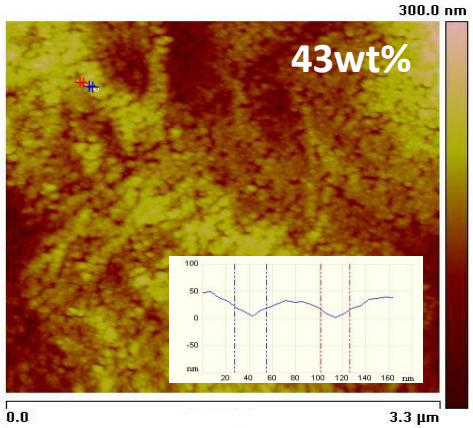
RAFT = 3-benzylsulfanylthiocarbonylsulfanyl propionic acid (BPATT)

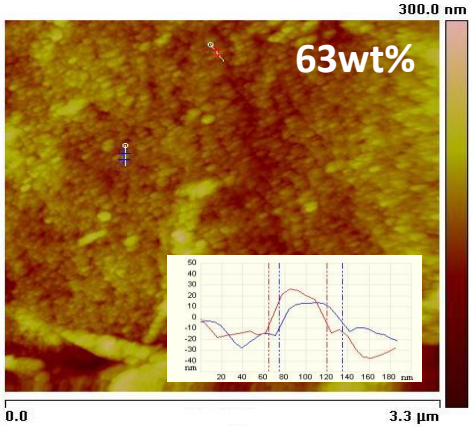






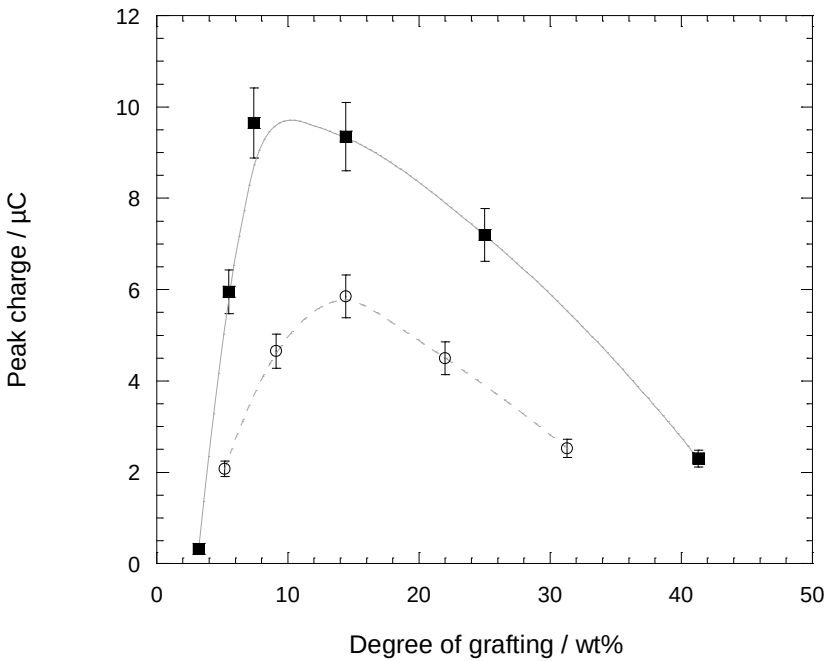


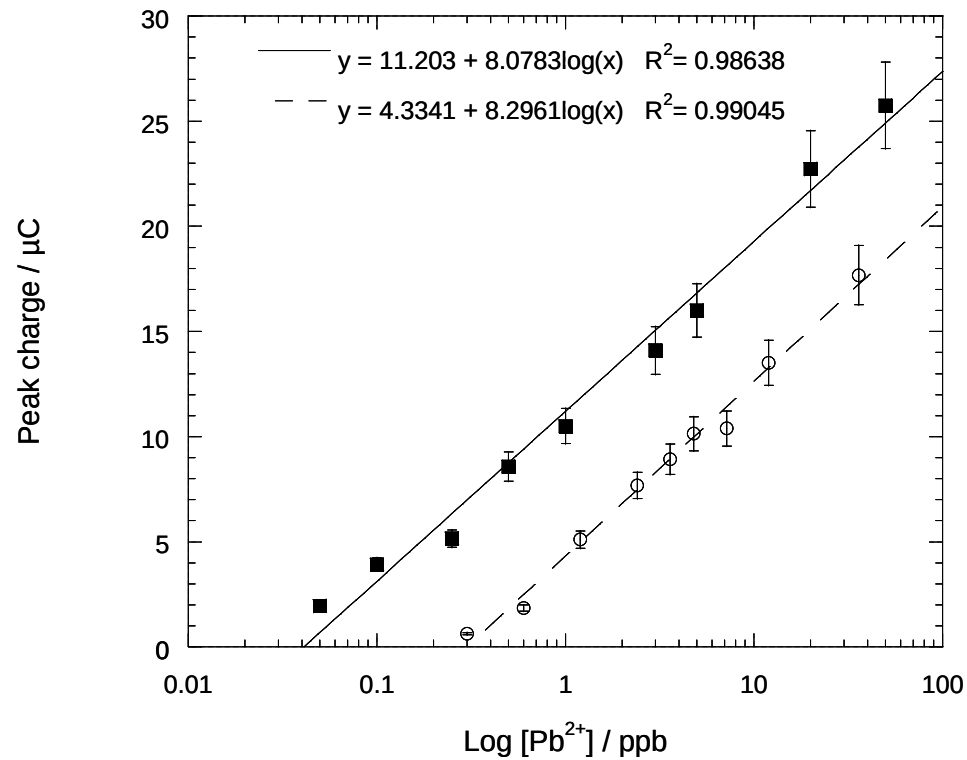




RAFT-mediated radical polymerization = improvement of sensors sensitivity

Enhancement of the efficiency of the sensors for water quality detection by a factor two





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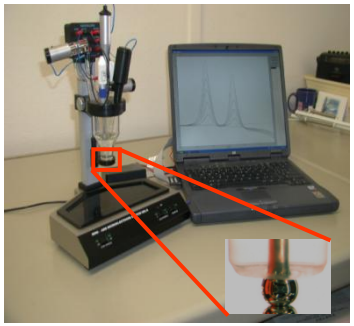
HACETTEPE ÜNİVERSİTESİ

Murat Barsbay, Olgun Güven, Haad Bessbousse, Travis L. Wade, François Beuneu, Marie-Claude Clochard « Nanopore size tuning of polymeric membranes using RAFT-mediated radical polymerization J. Memb. Sci. (2013)

Hg^{2+} detection

Existing portable technologies



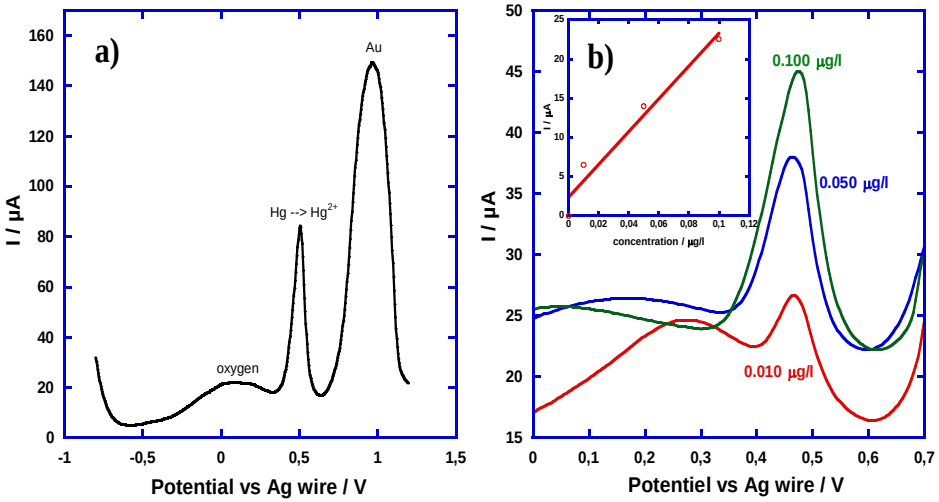
Mercury drop electrode

+ relatively expensive
+ somewhat portables
+ wide range of detectable ions
+ very sensitive
- Difficult to use
- Mercury

Ion Selective Electrodes

+ cheap
+ Portable
+ real-time analysis
+ easy to use
- Interferences
- Limited to some ions
- Lack of sensitivity

CAPTÔT performances



Limit of detection for Hg^{2+} 0.01 ppb

Radiation Physics and Chemistry 118 (2016) 48–54

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Poly(4-vinyl pyridine) radiografted PVDF track etched membranes as sensors for monitoring trace mercury in water

H. Bessbousse, N. Zran, J. Fauléau, B. Godin, V. Lemée, T. Wade *, M-C. Clochard *

Laboratoire des Solides Irradiés, UMR7642, Ecole Polytechnique, 91 128 Palaiseau, France

International market

Source: CEA BEM may 2012

Type of segment

Surveillance of potable water network

Surveillance of industrial wastewater

Surveillance of aquatic environments

Application segment

Fabrication processes

Consumers

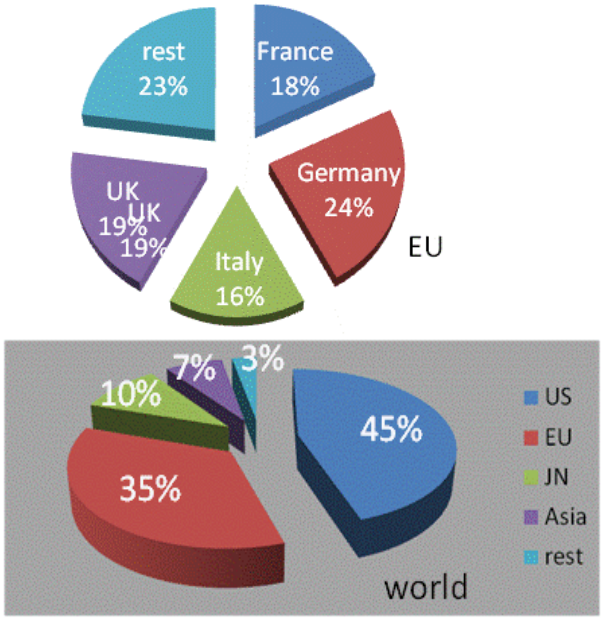
Ground

Biomedical

Fishing

Agriculture

Equipment sales distribution



❑ **Estimation of heavy-metal analysis market**

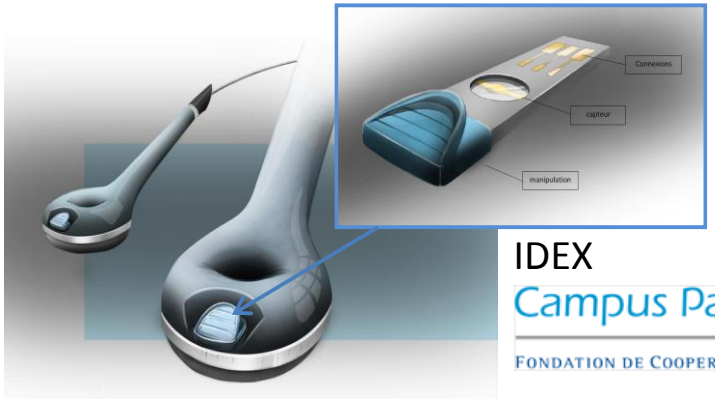
	World		France	
	Weak hypothesis	Strong hypothesis	Weak hypothesis	Strong hypothesis
Total accessible market	59.85 Millions $	190.72 Millions $	3.8 Millions $	12 Millions $

*1 time/month analyses for a theoretical level of pollution between 10 and 50 ton/year

** Daily analyses for a theoretical level of pollution >3000 tons/year

Valorization: toward a technological transfert

- Identified industrials



IDEX
Campus Paris Saclay
FONDATION DE COOPERATION SCIENTIFIQUE

VALOTEC

10 prototypes / year
+ strip-electrodes

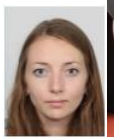
oxyphen A full Service Provider for customized Membrane Solutions

Licencing ? (5 patents)

- Potential targets:

Water actors: **BRGM**, KWR(NL), Cogent(UK), Suez Environnement, Veolia (SARP)…

Analyses companies: **SGS**, (CETIM)HYTEC, Methrom(US), Trace Detect (US), Sens Aqua (No), Liquum (Fin), Applitek (Be), Elta (Fr), Trace2O (UK), Palmsens (NL), Mesureo(Fr), thermofisher(Fr), Modern Water (UK), Private medical analyses laboratories …

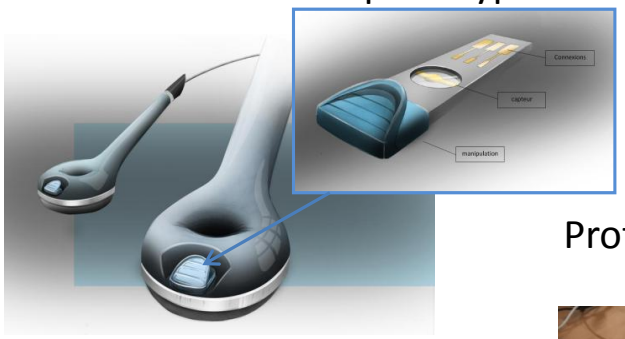


ANR 2016-2018

From a demonstrator to a prototype

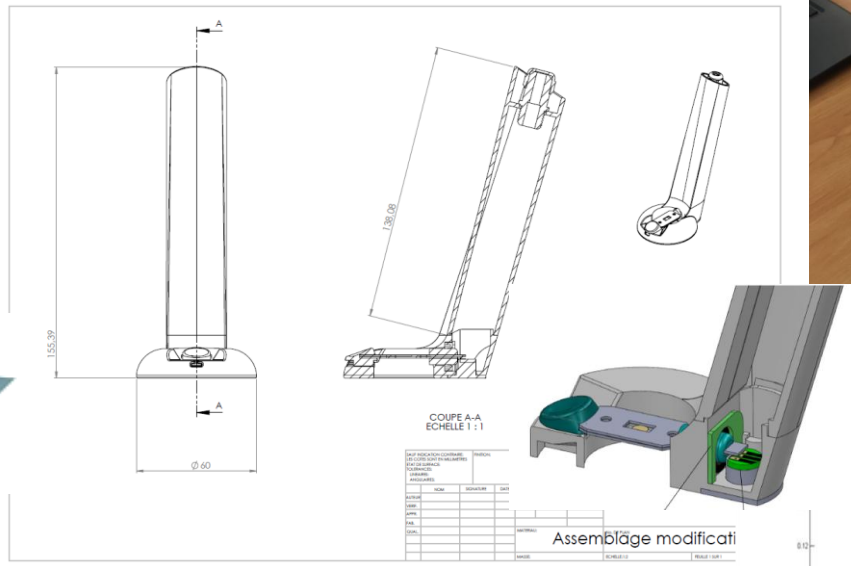
Demonstrator 1st generation (2008)

Artview of the final prototype

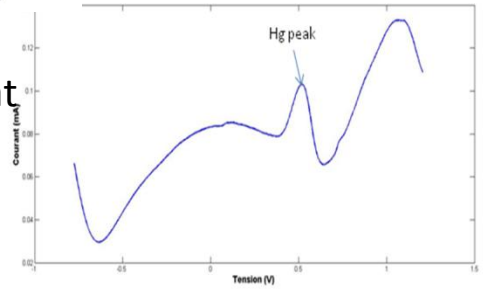


Prototype 1st generation (2017) a reality!

Demonstrator 2nd generation

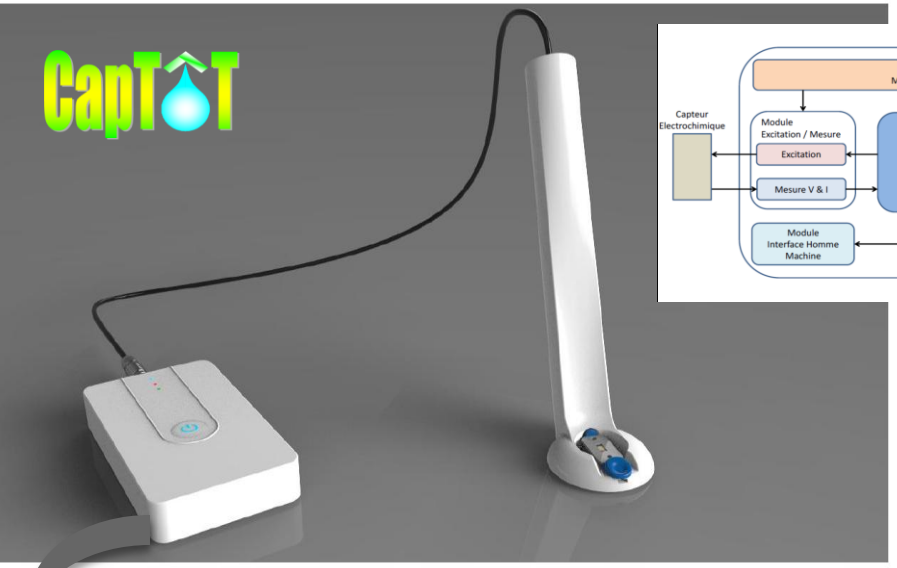


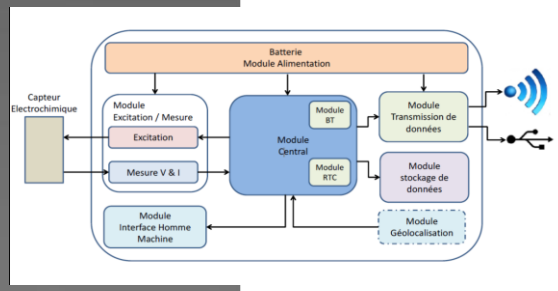
with integrated potenstiostat

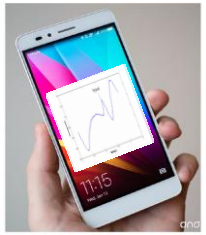


VALOTEC

Perspective: Uranium detection using CAPTOT







CAPTOT is based on polymer radiografting technique and ASV.

ASV is an established technique for the determination of Uranium trace levels (< 1ppb) in water[1] .

$UO_2 \leftarrow UO_2^{2+} + 2e^-$

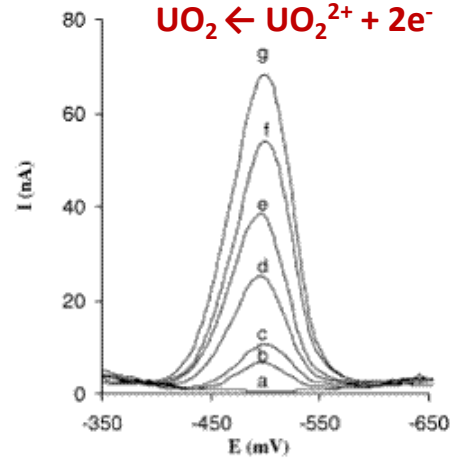


Fig. 7. Adsorptive stripping voltammograms for concentration of U(VI): curves 'a' = 0, 'b' = 1×10^{-8}, 'c' = 2×10^{-8}, 'd' = 5.3×10^{-8}, 'e' = 7.6×10^{-8}, 'f' = 1×10^{-7} and 'g' = 1.2×10^{-8} M, at optimal conditions of 0.05 M acetate buffers (pH = 6.7), [DPA] = 5×10^{-5}, accumulation potential = −0.20 V, accumulation time = 150 s, and scan rate = 30 mV s^{-1}.

From:
[1] M.B. Gholivand et al. "Cathodic adsorptive stripping voltammetric determination of uranium(VI) complexed with 2, 6-pyridine dicarboxylic acid" Talanta 65 (2005) 62–66.

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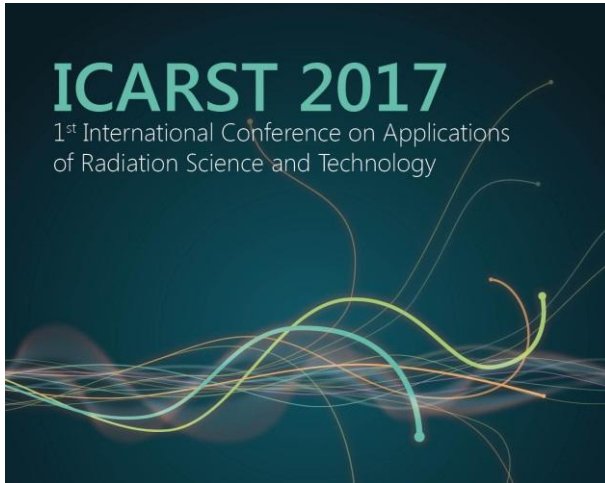
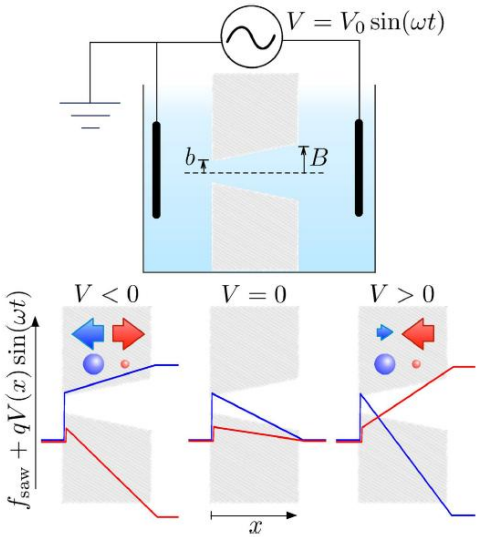
CAPTOT is planned to be used as **a tool to dynamically test performances towards UO_2^{2+} uptake and release** of the radiografted functionnalisations (prof. Al-Sheikhly team).

Perspectives in nanofluidics

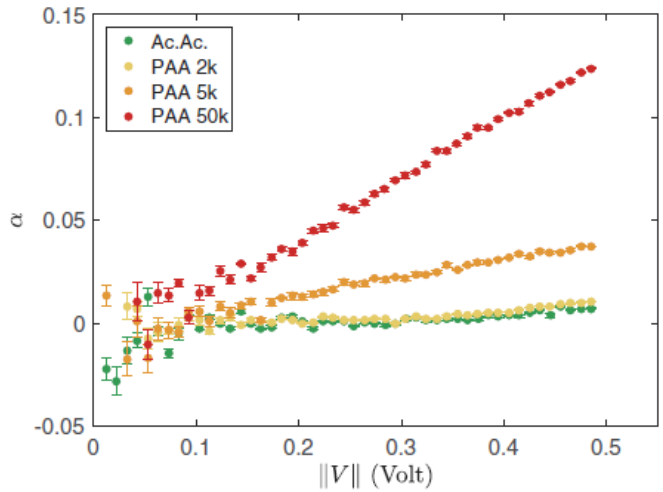


Coming back to fundamentals…

Ionic conductivity experiment



Results



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The concept of entropic rectifier facing experiments

D. Lairez[1], M.-C. Clochard[2] & J.-E. Wegrowe[2]

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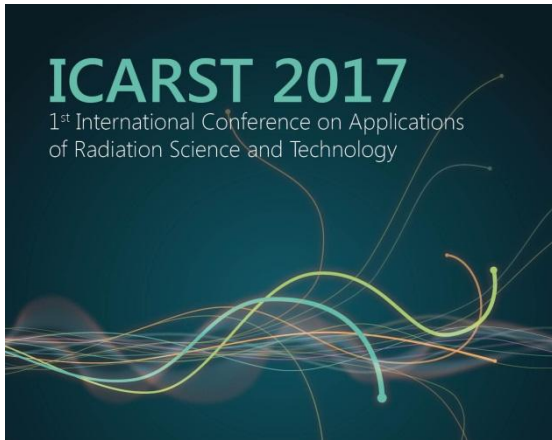
The transport of molecules in confined media is subject to entropic barriers. So theoretically, asymmetry of the confinement length may lead to molecular ratchets with entropy as the only driving force for the biased transport. We address experimentally this question by performing alternative ionic current measurements on electrolytes confined in neutral conical nanopores. In case anions and cations widely differ in size, we show that rectification of ionic current can be obtained that depends on ions size and cycle frequency, consistently with the entropic ratchet mechanism.

… a world to explore!

THANK YOU FOR YOUR ATTENTION!



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