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

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CEA2/CNRS/Ecole Polytechnique
FRANCE
The site: the « Ecole Polytechnique » Engineer School

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

Laboratoire des solides Irradiés

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, LSI)
- Electrons (GANIL, 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

Fuel cell
Tracks formation
Ion-matter interaction: Energy loss

Deposited Energy per charged particle and per length unit

\[
\left( \frac{dE}{dx} \right)_{\text{Total}} = \left( \frac{dE}{dx} \right)_{\text{nuclear}} + \left( \frac{dE}{dx} \right)_{\text{electronic}}
\]

Nuclear collisions
\[\left( \frac{dE}{dx} \right)_{\text{nuclear}} \approx 1\text{keV/u}\]

Electronic interactions
\[\left( \frac{dE}{dx} \right)_{\text{electronic}} \approx 1\text{MeV/u}\]
Tracks at the surface of some solids

<table>
<thead>
<tr>
<th>High sensitivity</th>
<th>Weak sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>dE/dx threshold</td>
<td>~1 keV/uma</td>
</tr>
<tr>
<td><strong>Insulators</strong></td>
<td><strong>Semi-conductors</strong></td>
</tr>
<tr>
<td>Polymers</td>
<td>Amorphous Si</td>
</tr>
<tr>
<td>Oxydes</td>
<td>GeS, InP, Si₁₋ₓGeₓ</td>
</tr>
<tr>
<td>Spinels</td>
<td>Si, Ge</td>
</tr>
</tbody>
</table>
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)


C≡C versus fluence
Radio-grafting in latent tracks

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

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d CEA – DIF/IIHEN/DIF/LCPMB CEA-Grenoble 17 rue des Martyrs, F-38054 GRENOBLE Cedex 9, France

5 patents


E. Gallino, M-C Clochard, A. Morin, G. Gébel, "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-PSA**: $10^{19}$ ions/cm² Y=140 wt.%

- **PVDF-g-PS** doped au Cesium $5 \times 10^7$ ions/cm² Y=1.7 wt.%

**Substitution électrophile**

**Identical efficiency as Nafion**

- **(A) PEMFC for automotive (ex: GENEPAC PSA-CEA)**
- **(B) Stack**
- **(C) single cell**
Perspectives: how improving the membrane-electrode interface?

• 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
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 a, 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
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In-situ radiografting

Irradiations → PVDF nanoparticles Covered with ionomer functionalisation

Gamma irradiation

Alkyl radicals under vaccum

\[ \text{ROO} \] \[ \text{O}_2 \]

Irradiations + grafting

PVDF + mono

Other monomers of interest: vinyl imidazole doped phosphoric acid for high T°C fuel cell applications
Track revealing : track-etching
Track etching

Control of pore geometry

- \( v_{\text{track}} : v_{\text{bulk}} = \sin \theta \rightarrow \text{pore geometry} \)
- 1000:1 cylinder
- 10:1 cone

Template synthesis

Cylindrical and conical metallic nanowires

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

Challenge for MRAM

Controlling magnetic domain wall playing on the nanowire geometry

TEM magnetic holography

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)
1st application: membranes for filtration

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

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

Developed at GSI (Germany)
Membrane recent developments: fabrication on hybrid membranes based on nanoporous graphene
Characterization of nanoporous graphene-on-PMMA substrate

Perspectives: excellent candidates for water desalination and/or field emission transitors...
How to chemically modify pore interior?

Remanence of radicals after etching

![Graph showing remanence of radicals after etching]
Remaining radical fraction profile per track

$f$ averaged and normalized to a single track

$R_{\text{moy}}$ (nm)

Decay: $1/r^2$
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. oxida
tion

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

Nanoporous β-PVDF membranes with selectively functionalized pores

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

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b Laboratoire Léon Brillouin, CEA-Saclay, 91191 Gif-sur-Yvette Cedex, France

Available online at www.sciencedirect.com

ScienceDirect


www.elsevier.com/locate/nimb

Available online 15 September 2007
Applied Research: Early warning sensors for monitoring toxic metal ions

CAPTOT Technology

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

Sensor for toxic metal ions

Prices OSEO et POLLUTEC en 2012

Labscale demonstrator
Controlled radical polymerization inside nanopores

Radiation induced RAFT mechanism

(I) \[ \text{SHI irradiation} \rightarrow \text{I} \cdot \quad \text{Radicals trapped in the crystallites of PVDF} \]

(II) \[ \text{I} \cdot + \text{Monomer} \xrightarrow{k_i} \text{P}_1^* \]

(III) \[ \text{P}_m^* + \text{S} \xrightarrow{k_p} \text{P}_{m+1}^* \quad \text{R} \cdot + \text{Monomer} \xrightarrow{k_{p,1}} \text{P}_1^* \]

(IV) \[ \text{P}_n^* + \text{S} \xrightarrow{k_{p,1}} \text{P}_{n+1}^* \quad \text{P}_m^* + \text{S} \xrightarrow{k_{p,1}} \text{P}_{n+1}^* \]

(V) \[ \text{P}_n^* + \text{P}_m^* \xrightarrow{<k_q>} \text{P}_{n+m}^* \]
AFM: nanopore filling

R = 25 nm

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

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

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
Estimation of heavy-metal analysis market

<table>
<thead>
<tr>
<th></th>
<th>World</th>
<th>France</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak hypothesis</td>
<td>Strong hypothesis</td>
</tr>
<tr>
<td>Total accessible market</td>
<td>59.85 Millions $</td>
<td>190.72 Millions $</td>
</tr>
</tbody>
</table>

*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

10 prototypes / year + strip-electrodes

- 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 ...

2016-2018
From a demonstrator to a prototype

Demonstrator 1st generation (2008)

Demonstrator 2nd generation

Artview of the final prototype

Prototype 1st generation (2017) a reality!

with integrated potenstiostat
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\[1\].

CAPTOT is planned to be used as a tool to dynamically test performances towards \( \text{UO}_2^{2+} \) uptake and release of the radiografted functionnalisations (prof. Al-Sheikhly team).

From:
Perspectives in nanofluidics
Coming back to fundamentals...

**Ionic conductivity experiment**

\[ V = V_0 \sin(\omega t) \]

**Results**

Size selection

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**The concept of entropic rectifier facing experiments**

D. Lairez\(^1\), M.-C. Clochard\(^2\) & J.-E. Wegrowe\(^2\)

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!
Thanks to