

Electrospinning

Technologie et application

Edith Laux, Laure Jeandupeux, Alexandra Kaempfer-Homsey,
Stefan Ramsayr, and Herbert Keppner

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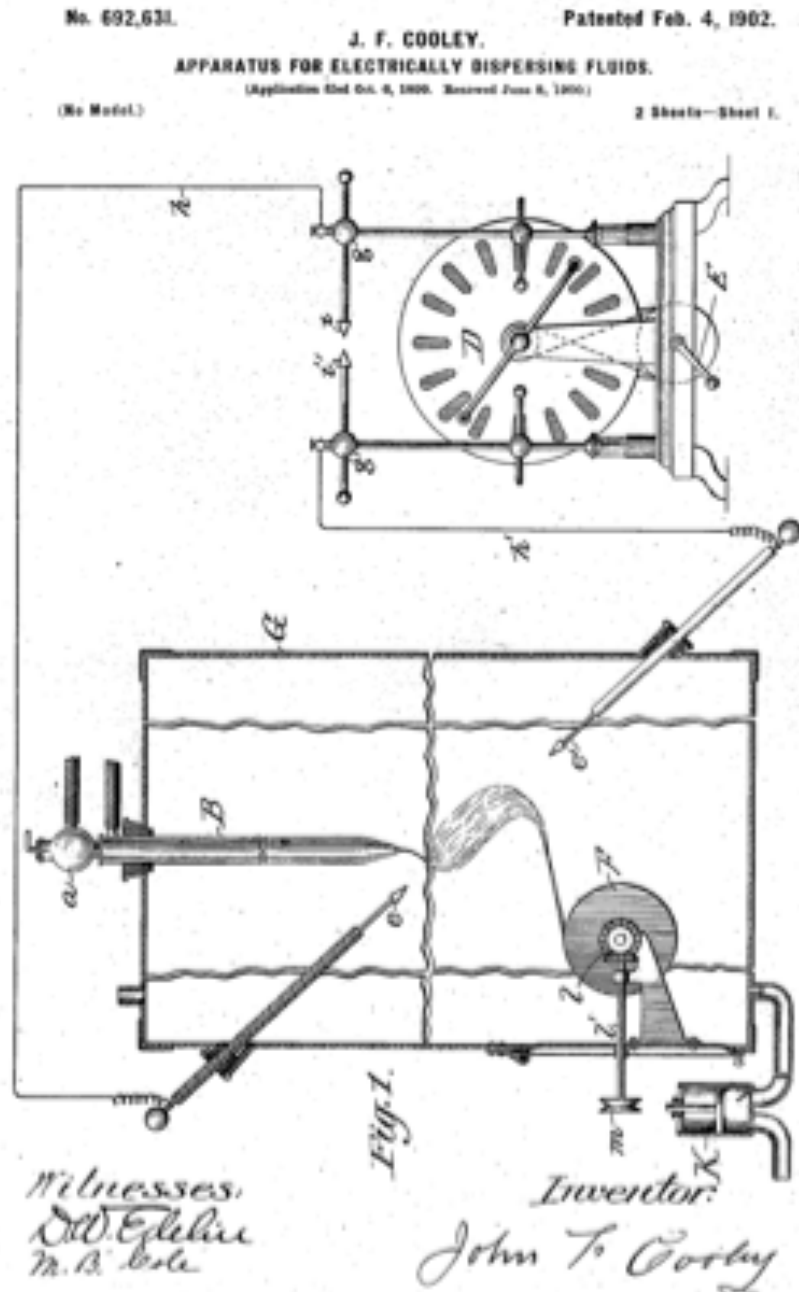
- Historique
- Principe de base
- Théorie, compréhension et maîtrise
 - Vitesse et diamètre du jet
 - Influence de la concentration
- Résultats
- Applications

Historique

- 16^e siècle:** **William Gilbert** observe l'émission de gouttelettes d'eau à proximité d'une pièce d'ambre électriquement chargée.
- 1887:** **C.V. Boys:** « *the old, but little known experiment of electrical spinning* » extraction de fibres de cire, Shellac, cire d'abeilles, gutta-percha (1,4 trans isoprène).
- Mai 1900:** **J.F. Cooley:** brevet: « *The process of electrospinning* ».
- 1934:** **A. Formhals et al.** "Process and apparatus for preparing artificial threads » U.S. Patent 1,975,504 ; Octobre 2, 1934.
- 1938:** Nathalie D et I. V. **Petryanov-Sokolov:** fibres par electrospinning de acetate de cellulose, pour faire des filtres dans les masques à gaz anti-fumées. En 1960 la production de 20 millions m² / année ont été revendiquées.
- 1964:** Geoffry Ingram **Taylor** présente la théorie pour l'electrospinning; « *Disintegration of water drops in an electric field*; Proc. Roy. Soc. A 280 (1382): 383 » la déformation caractéristique de la goutte s'appelle le cône de Tailor.

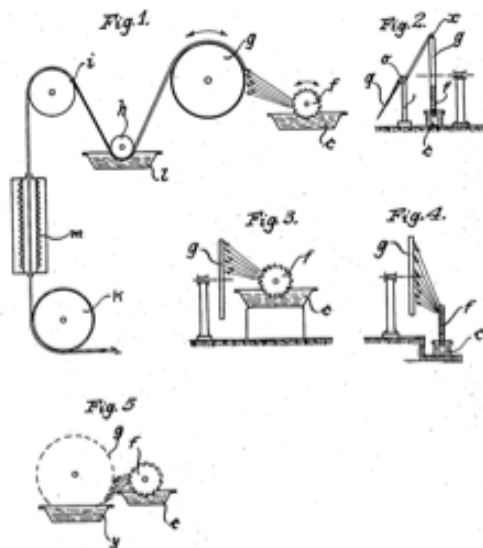
Cooley, J.F. Patent GB 06385

“Improved methods of and apparatus for electrically separating the relatively volatile liquid component from the component of relatively fixed substances of composite fluids” 19th May 1900



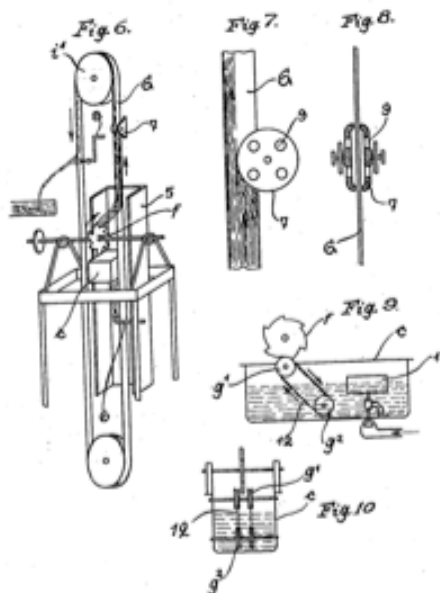
A. Formhals *et al.* "Process and apparatus for preparing artificial threads »
U.S. Patent 1,975,504 ; Octobre 2, 1934

Oct. 2, 1934. A. FORMHALS 1,975,504
PROCESS AND APPARATUS FOR PREPARING ARTIFICIAL THREADS
Original Filed Dec. 5, 1930 3 Sheets-Sheet 1



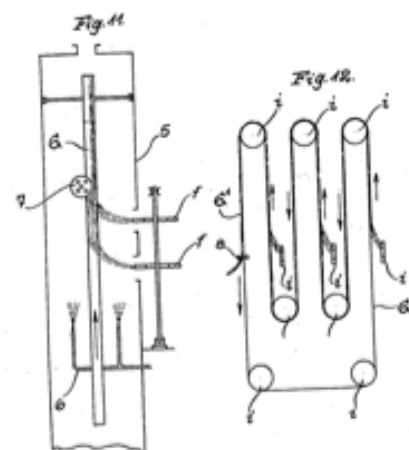
Inventor
Anton Formhals
by
Dean Fairbank Hirsch & Tuck
his Attys

Oct. 2, 1934. A. FORMHALS 1,975,504
PROCESS AND APPARATUS FOR PREPARING ARTIFICIAL THREADS
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Inventor
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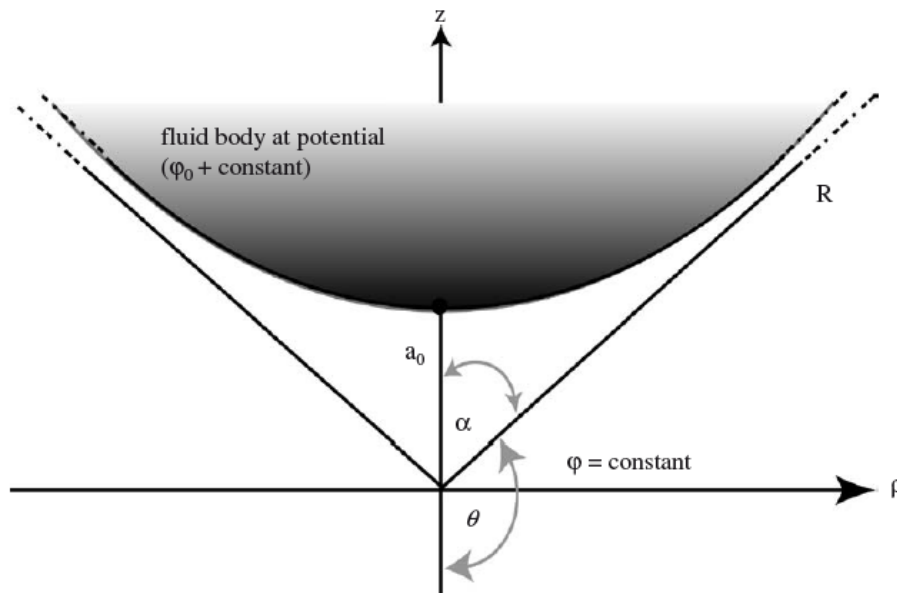
Oct. 2, 1934. A. FORMHALS 1,975,504
PROCESS AND APPARATUS FOR PREPARING ARTIFICIAL THREADS
Original Filed Dec. 5, 1930 3 Sheets-Sheet 3



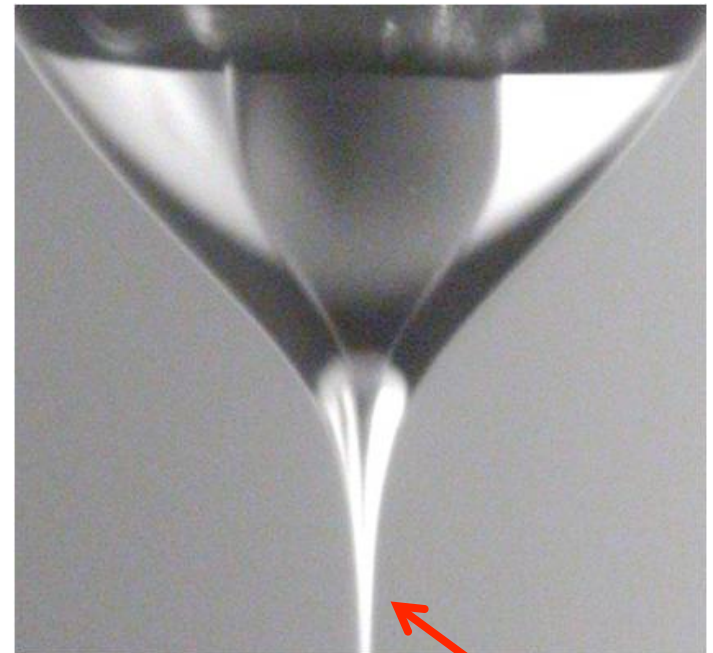
Inventor
Anton Formhals
by
Dean Fairbank Hirsch & Tuck
his Attys

Théorie, compréhension, maîtrise

État initial
 $V = 0$ kV



État initial
 $V > 20$ kV

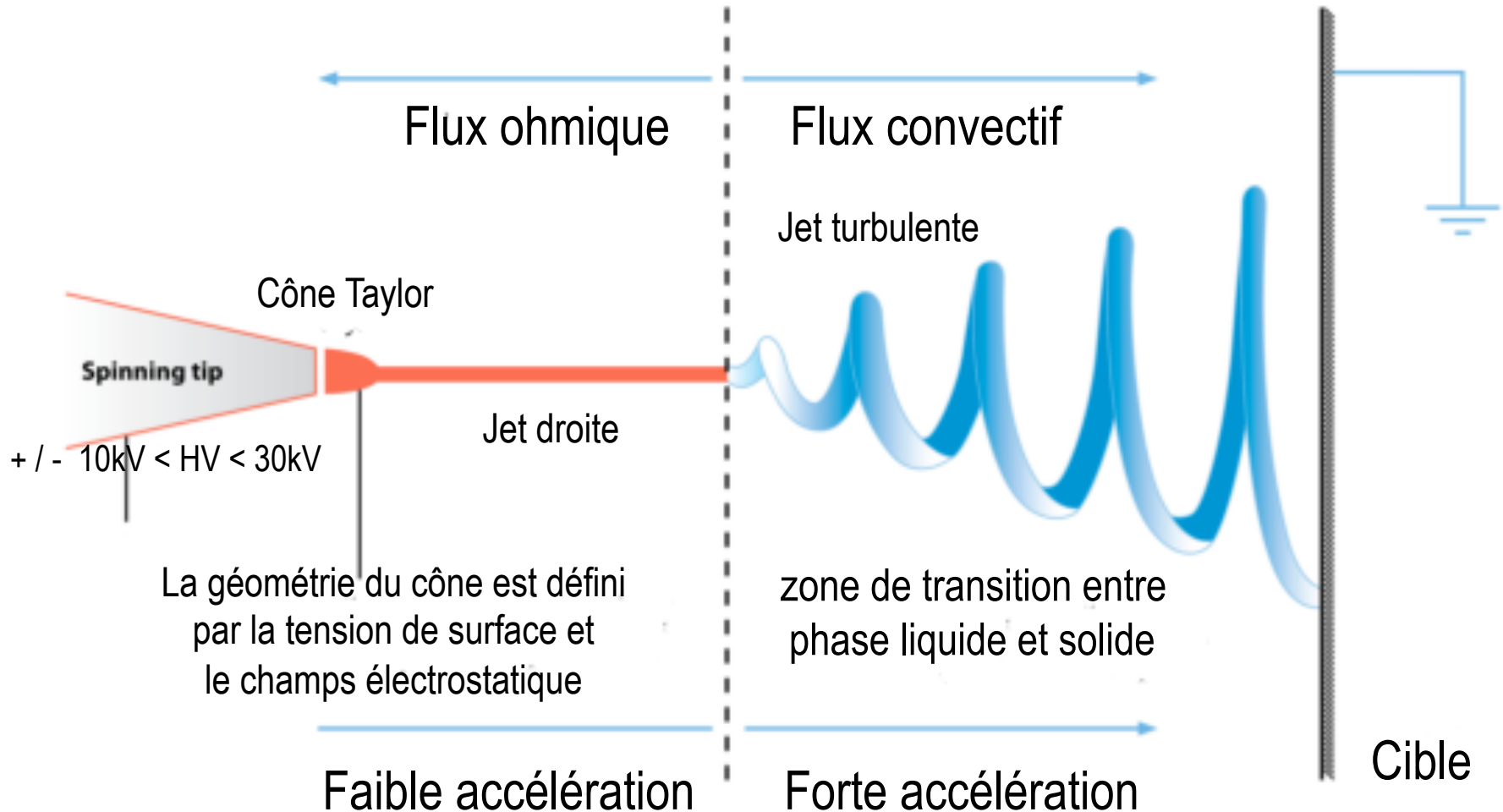


jet

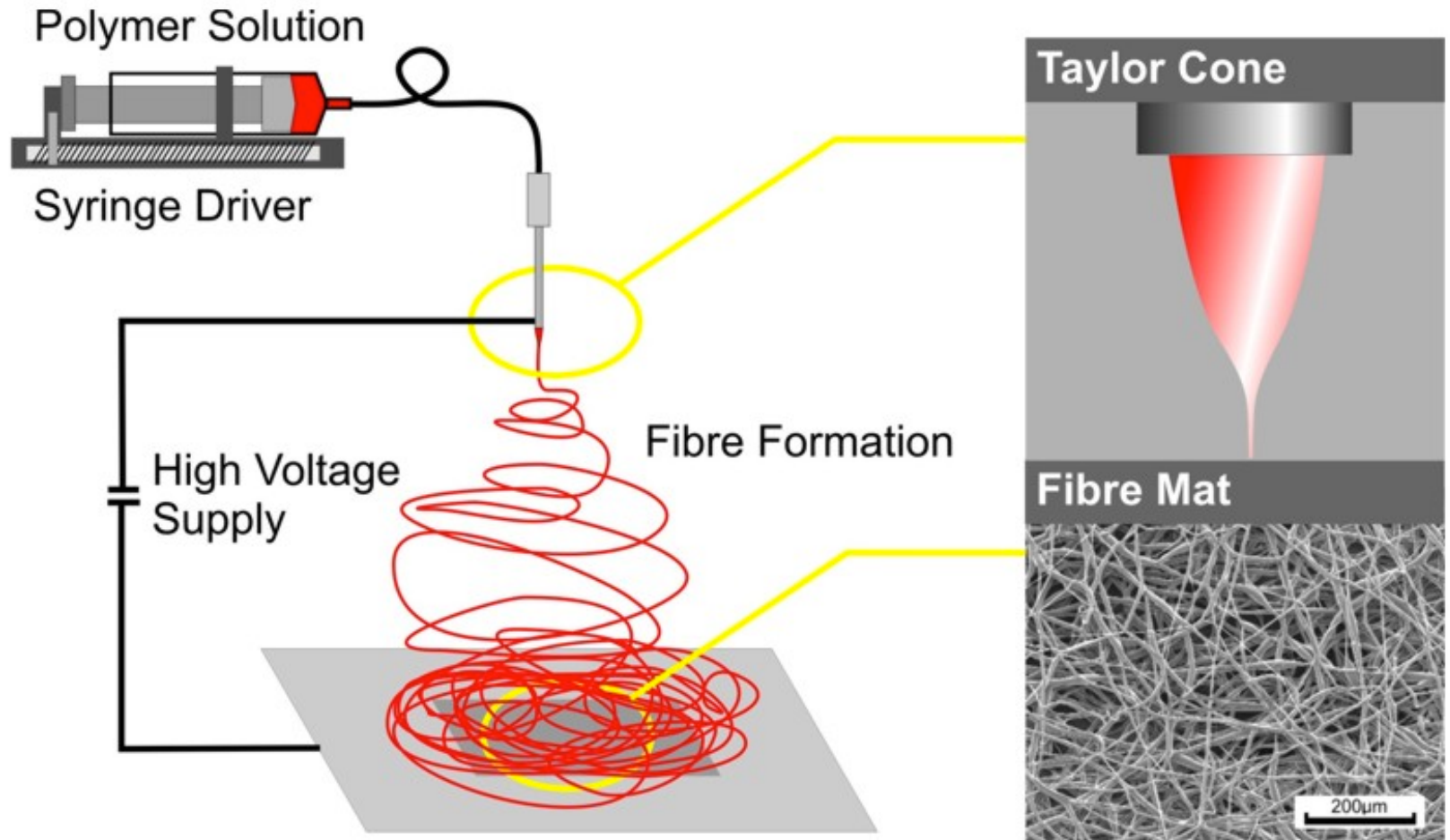
D.H. RENEKER et al. Electrospinning of Nanofibers
from Polymer Solutions and Melts
ADVANCES IN APPLIED MECHANICS, VOL. 41 43
ISSN 0065-2156 DOI: 10.1016/S0065-2156(06)41002-4

[http://
nanotechnologysolutions.files.wor
dpress.com/2013/07/imagen31.jpg](http://nanotechnologysolutions.files.wordpress.com/2013/07/imagen31.jpg)

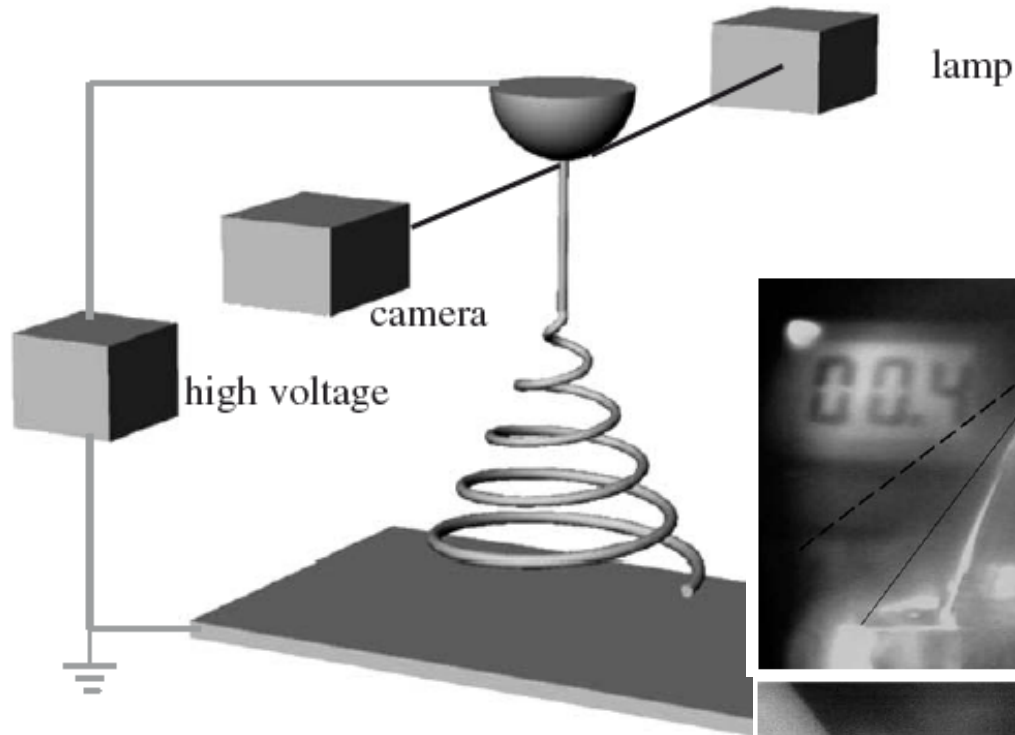
Principe de base, observation



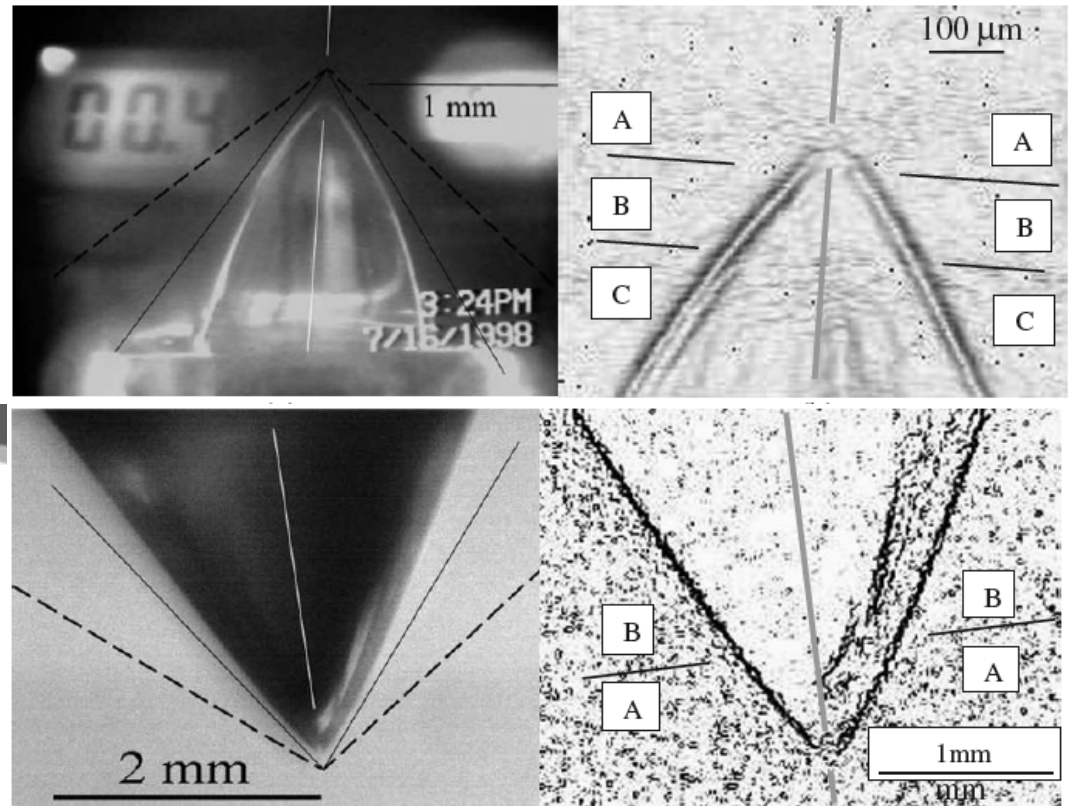
Principe de base



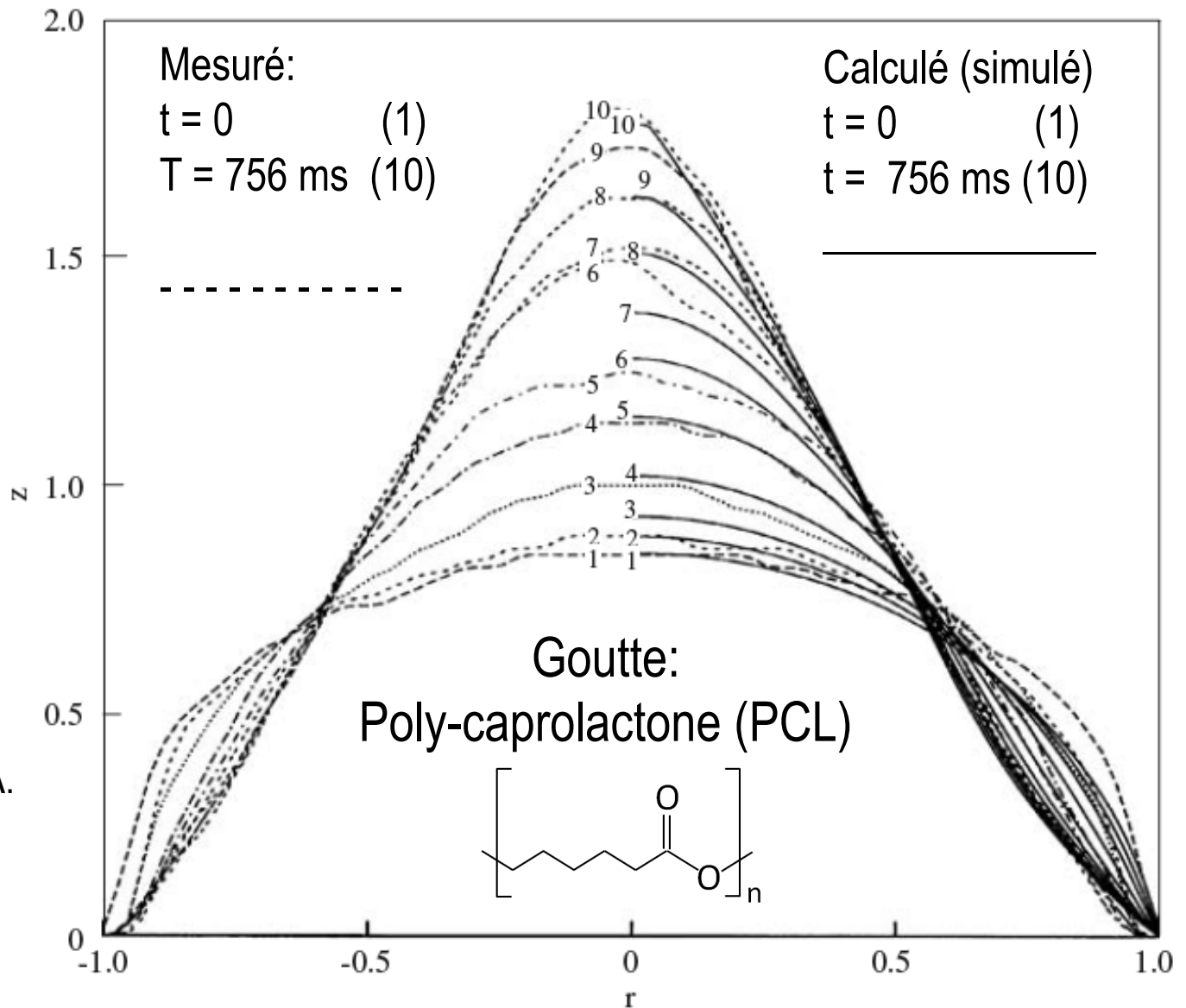
Théorie, compréhension, maîtrise



Yarin, A. L., Koombhongse, S., and Reneker, D. H. (2001b). Taylor cone and jetting from liquid droplets in electrospinning of nanofibers. *J. Appl. Phys.* 90, 4836–4846.



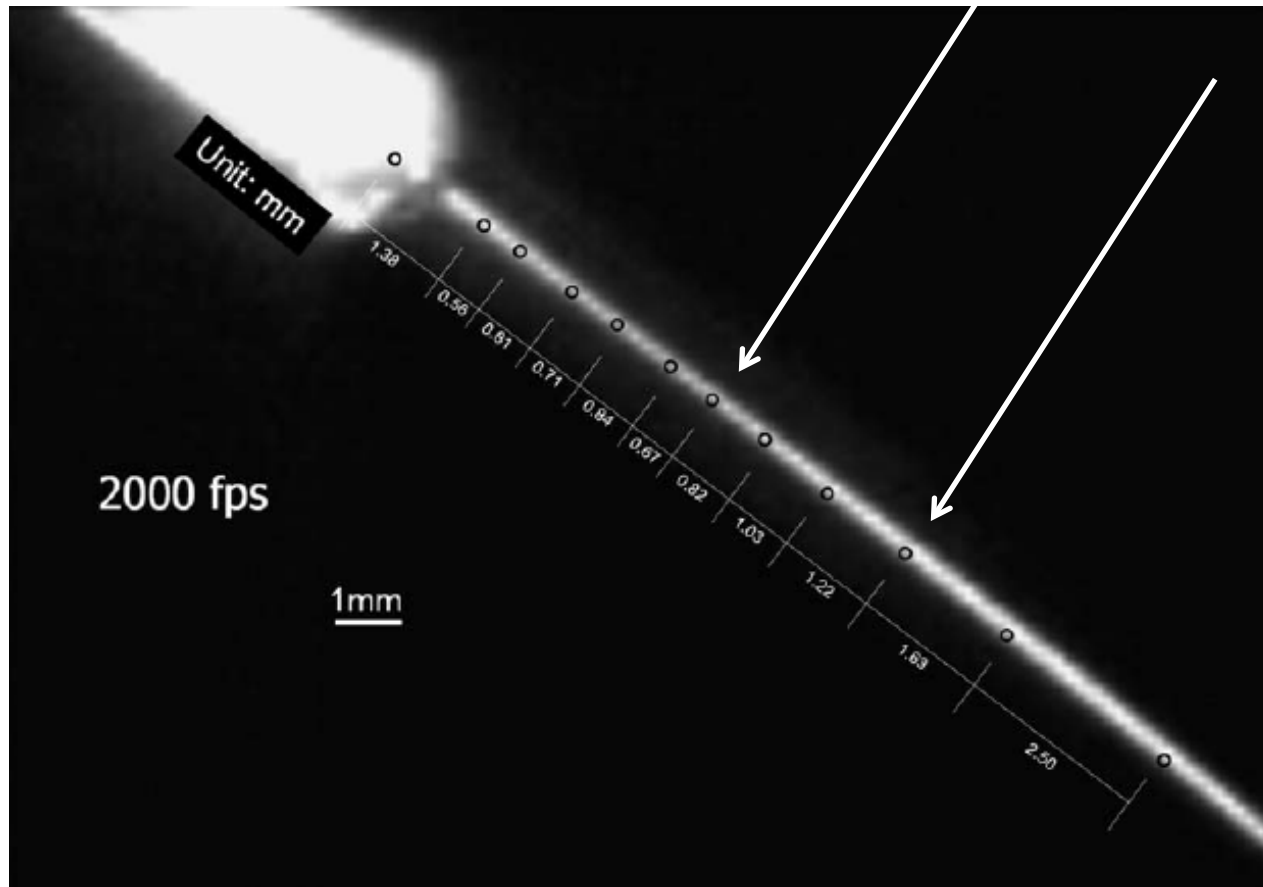
Développement de la déformation d'une goutte PCL par un champ électrique



Reznik, S. N., Yarin, A. L., Theron, A., and Zussman, E. (2004). J. Fluid Mech. 516, 349–377.

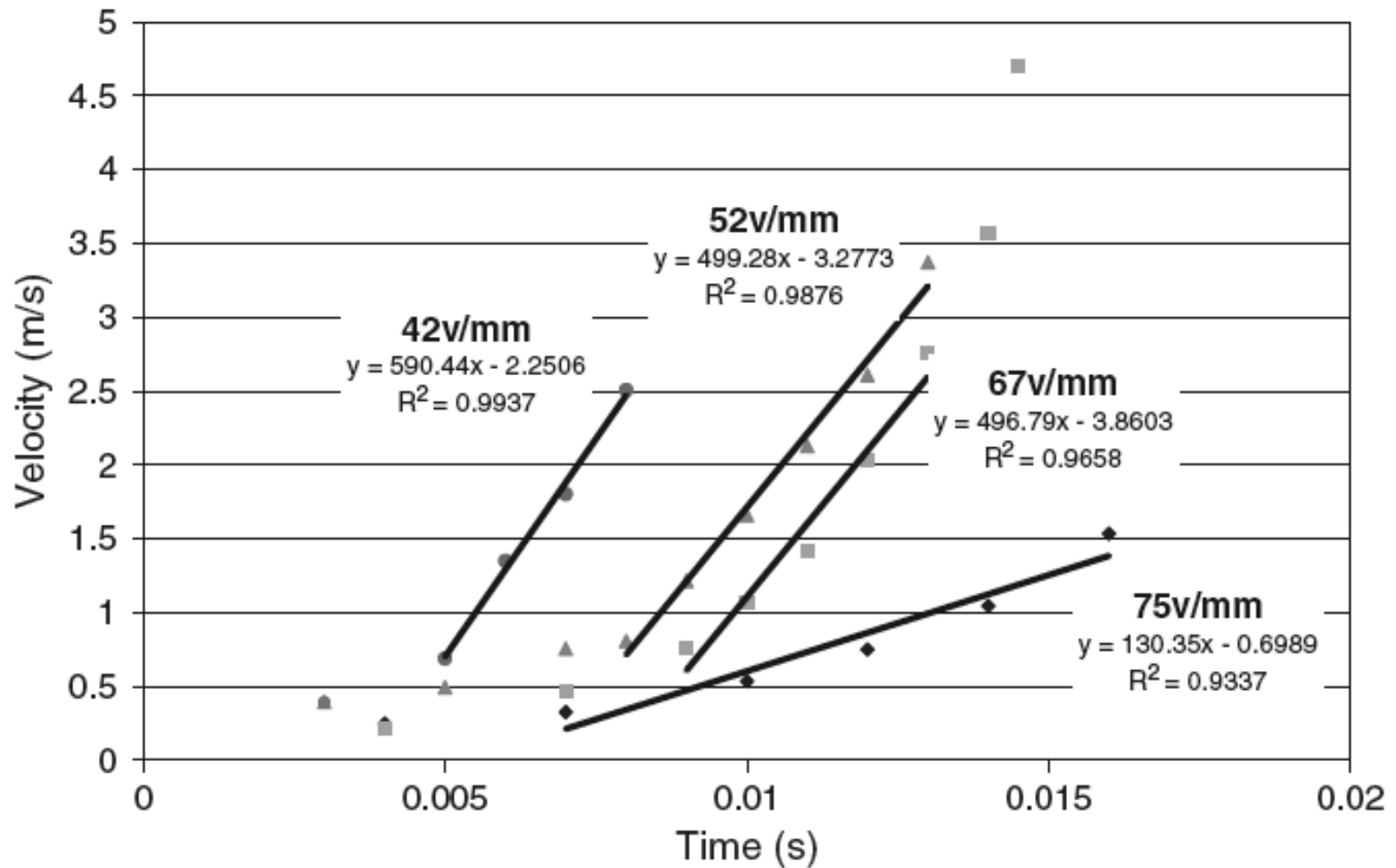
Vitesse et diamètre du jet, exemple PEO (polyéthylène oxyde)

Billes en verre transporté par le jet pour mesurer la vitesse

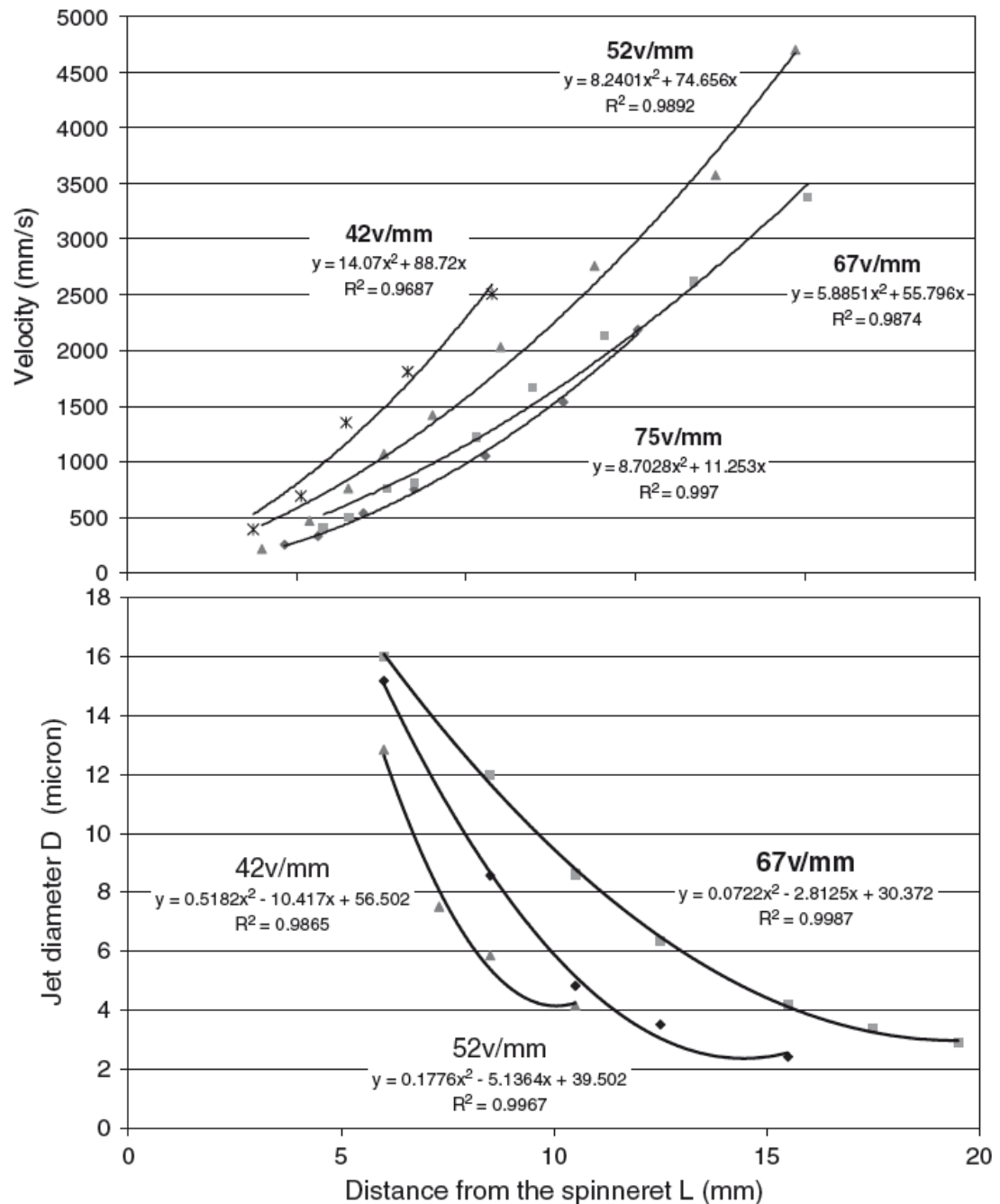


Xu, H., Yarin, A. L., and Reneker, D. H. (2003). Characterization of fluid flow in jets during electrospinning. Polym. Preprints 44, 51–52.

Vitesse et diamètre du jet, exemple PEO, jet droit



Vitesse et diamètre du jet exemple PEO jet droit

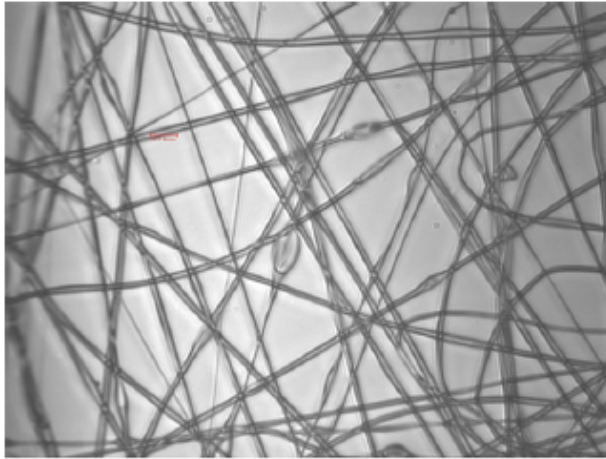


Xu, H., Yarin, A. L., and Reneker, D. H. (2003). Characterization of fluid flow in jets during electrospinning. Polym. Preprints 44, 51–52.

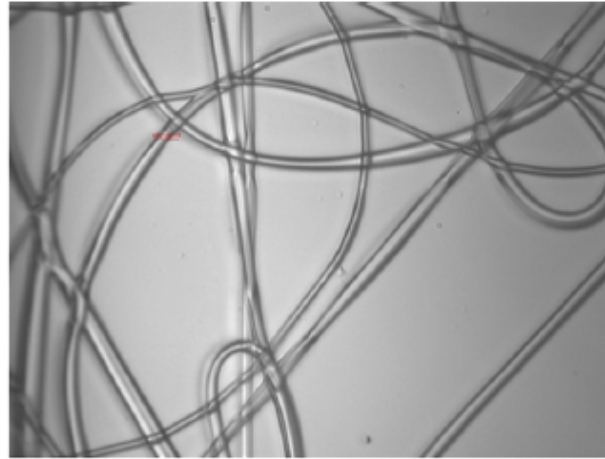
Influence de la concentration

Polyethylene co-vinyl alcohol dans 70:30 2-propanol

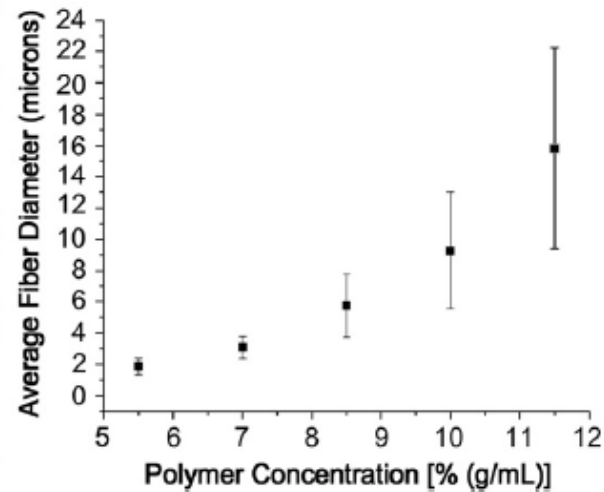
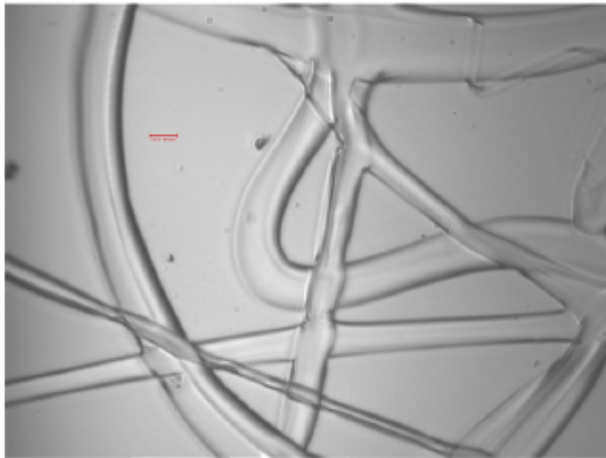
5.5 g /ml



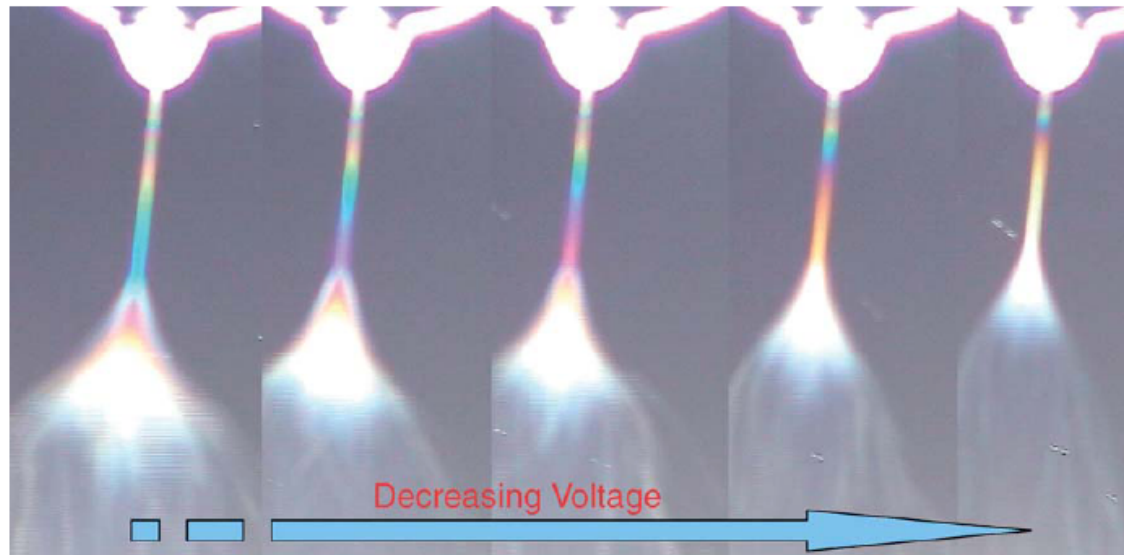
8.5 g /ml



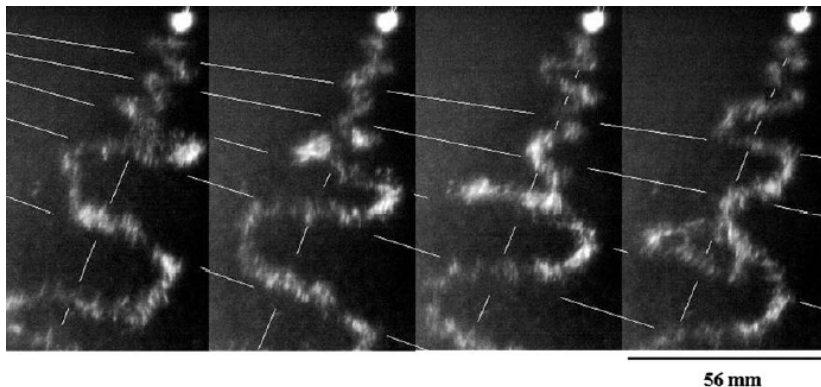
11.5 g /ml



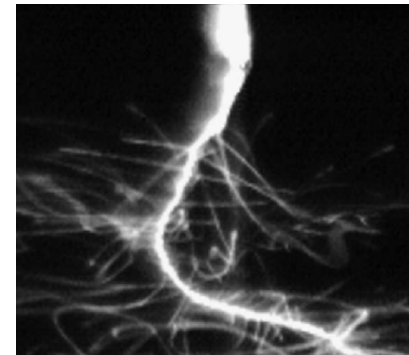
Flux convectif: bifurcation des jets



Xu, H., Yarin, A. L., and Reneker, D. H. (2003). Characterization of fluid flow in jets during electrospinning. *Polym. Preprints* 44, 51–52.



Guirlande de 15% PCL solution 7.5 kV, 140mm gap
(Reneker, et al. *Polymer* 43, 6785–6794.)



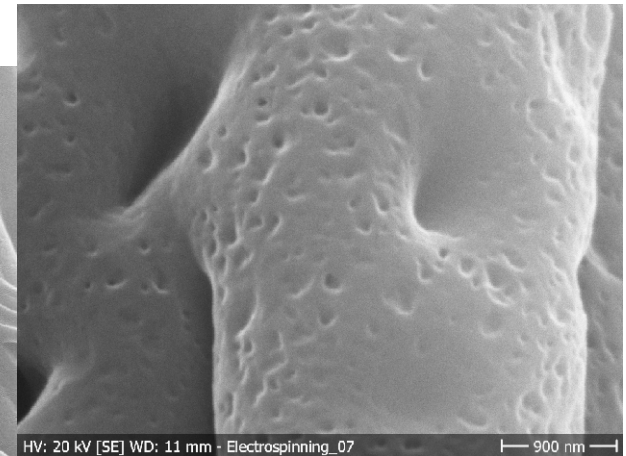
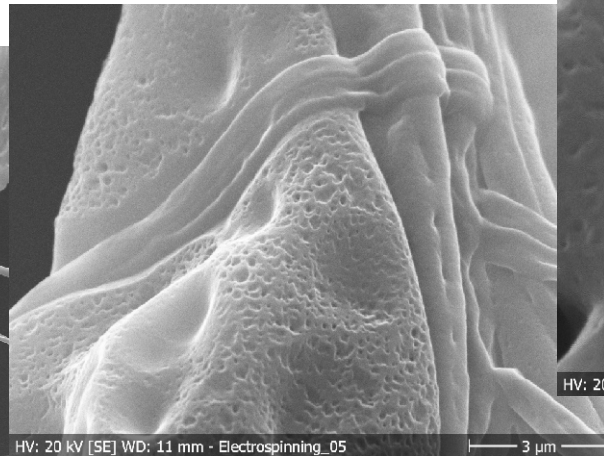
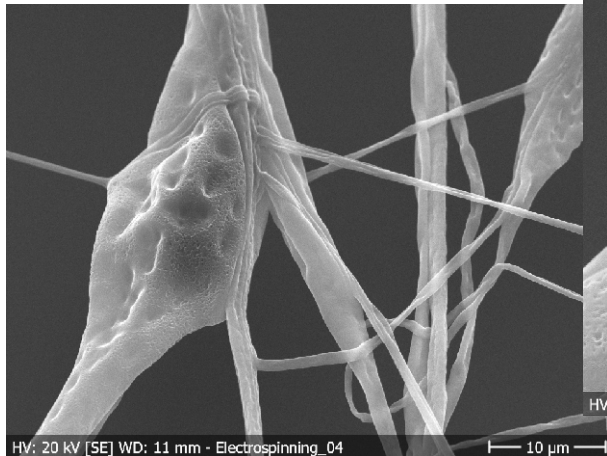
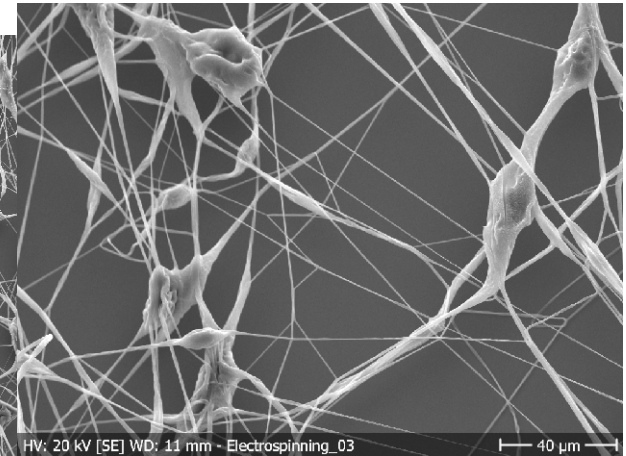
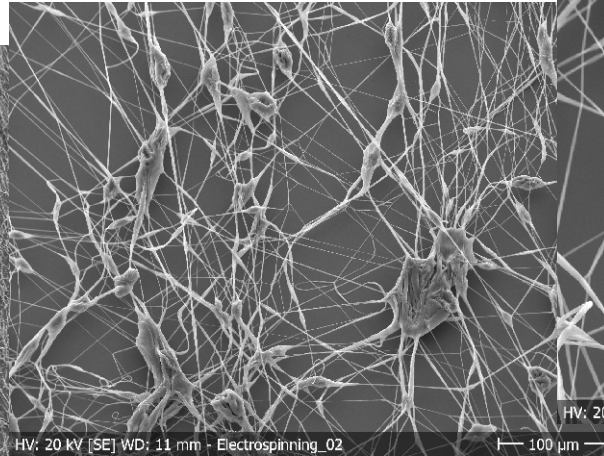
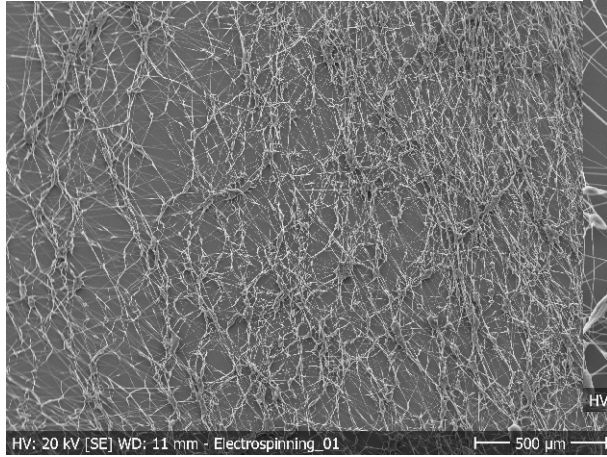
Bifurcation 15% PCL solution 10 kV
(Yarin et al., *J. Appl. Phys.* 98, 064501.)

Conclusion intermédiaire

- Il est possible d'effectuer de l'électrospinning avec tous les matériaux condensables, notamment des polymères en solution, des sol-gels et des matériaux fondus.
- Le diamètre des fibres et l'arrangement est une fonction de la tension appliquée (typiquement entre 10kV et 30 kV), de la distance entre l'éjecteur et l'écran, du type de matière, des additifs.
- La viscosité du liquide « spinnable » contenant des solvants + précurseurs est typiquement entre 0.8 Pa·s et 4 Pa·s (800 centipoise et 4000 centipoise).

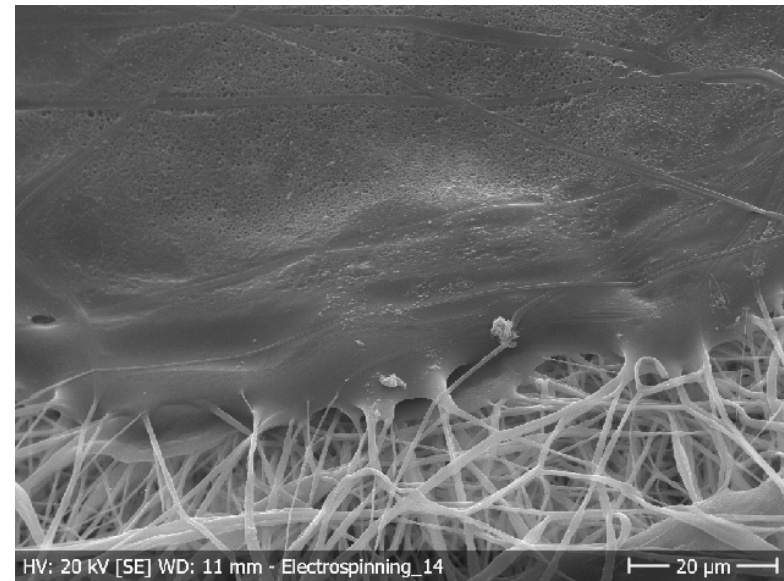
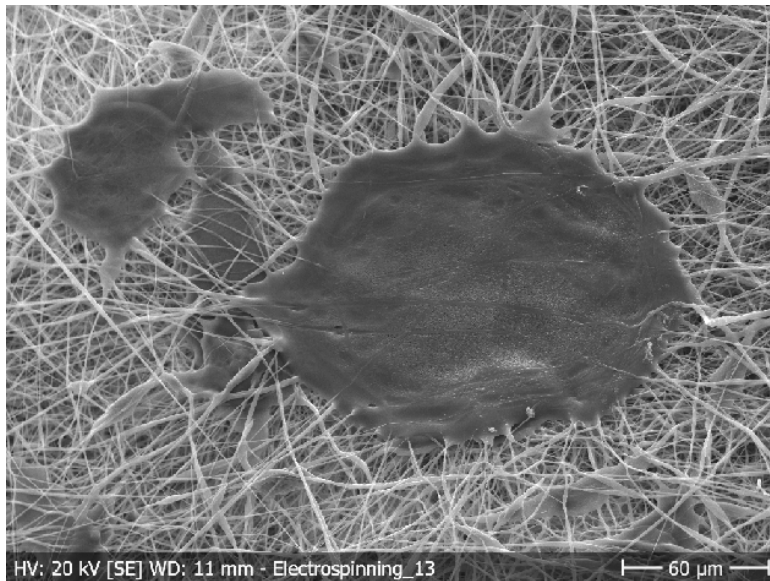
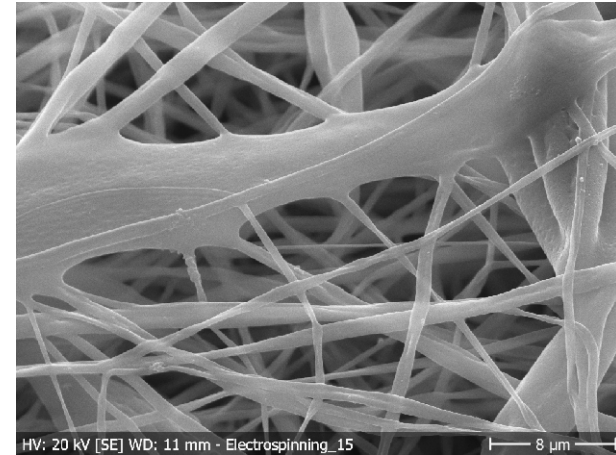
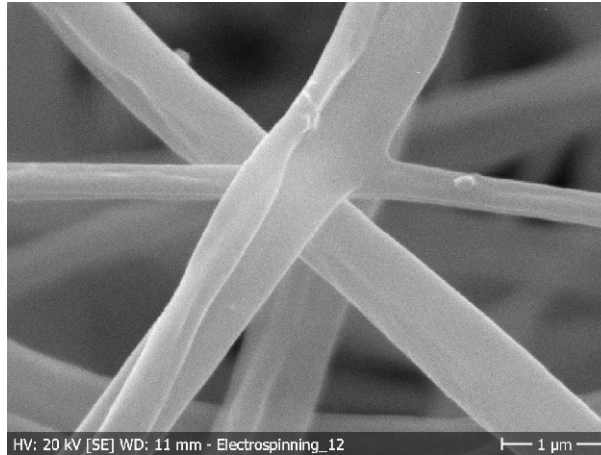
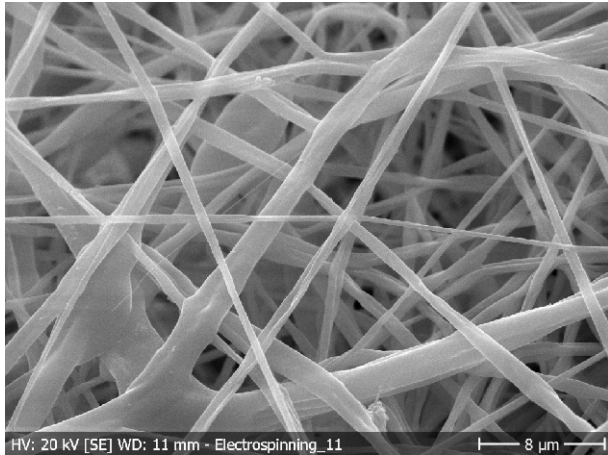
Résultats

HE-ARC travaux pratiques, THV 20 (Dyneon) / Acétone

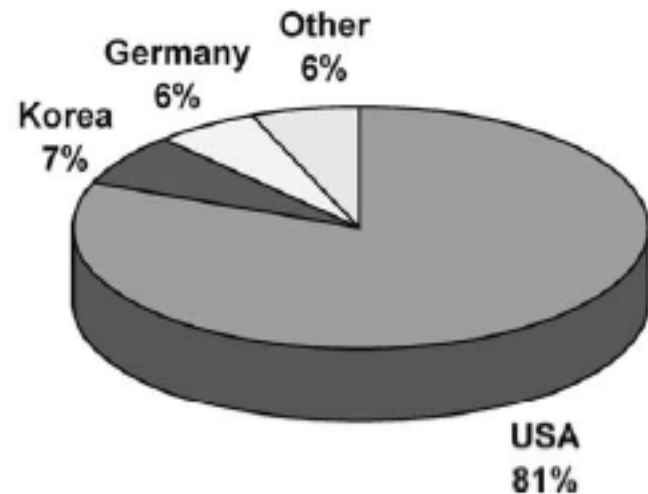
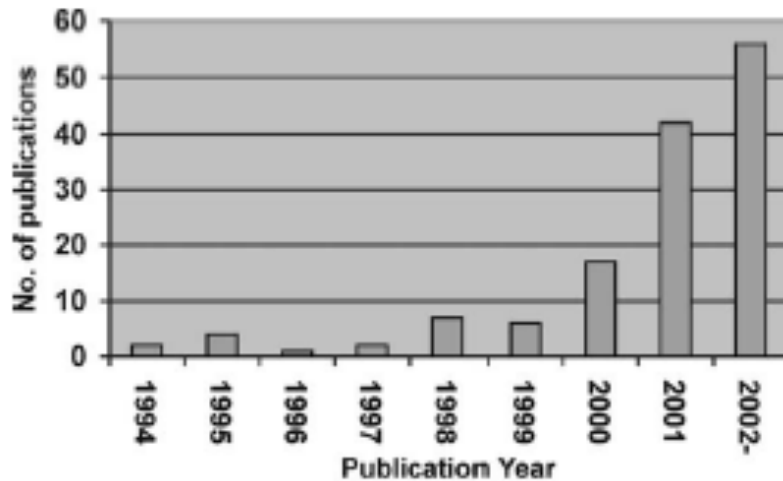
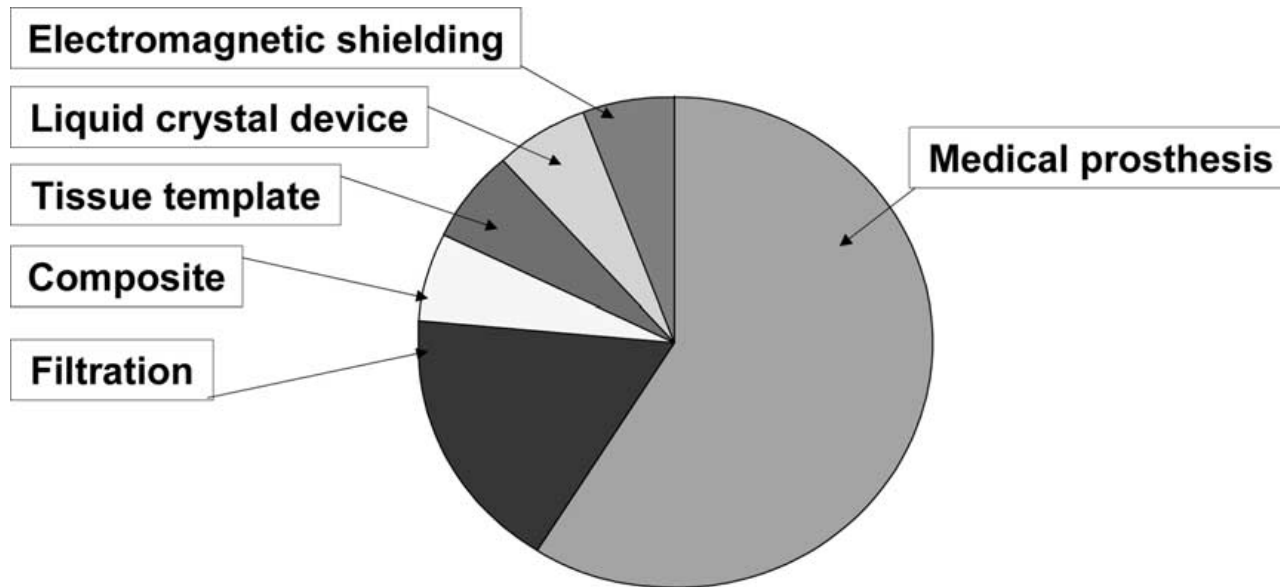


E. Laux, S. Ramseyer

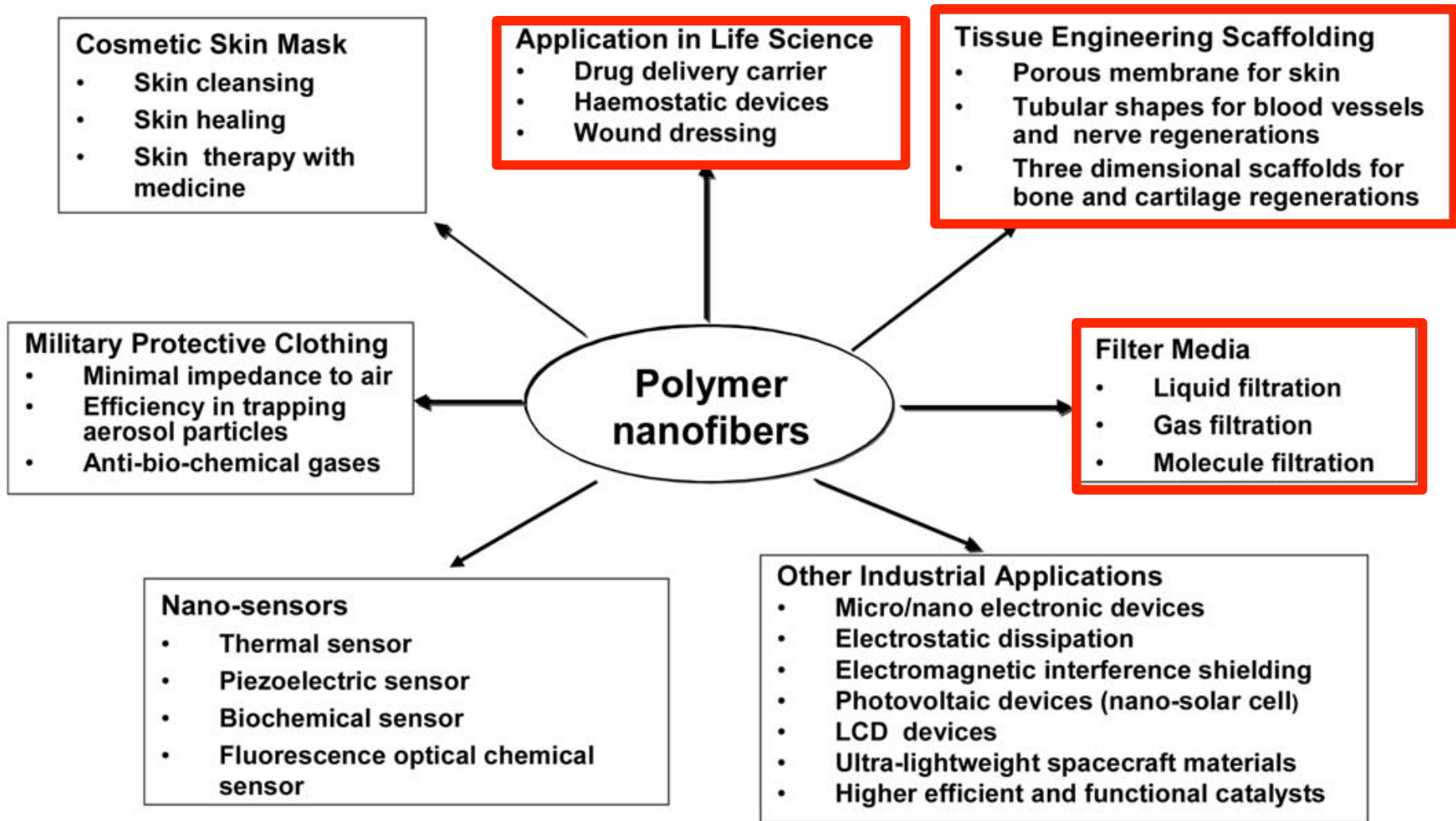
Observations



Applications



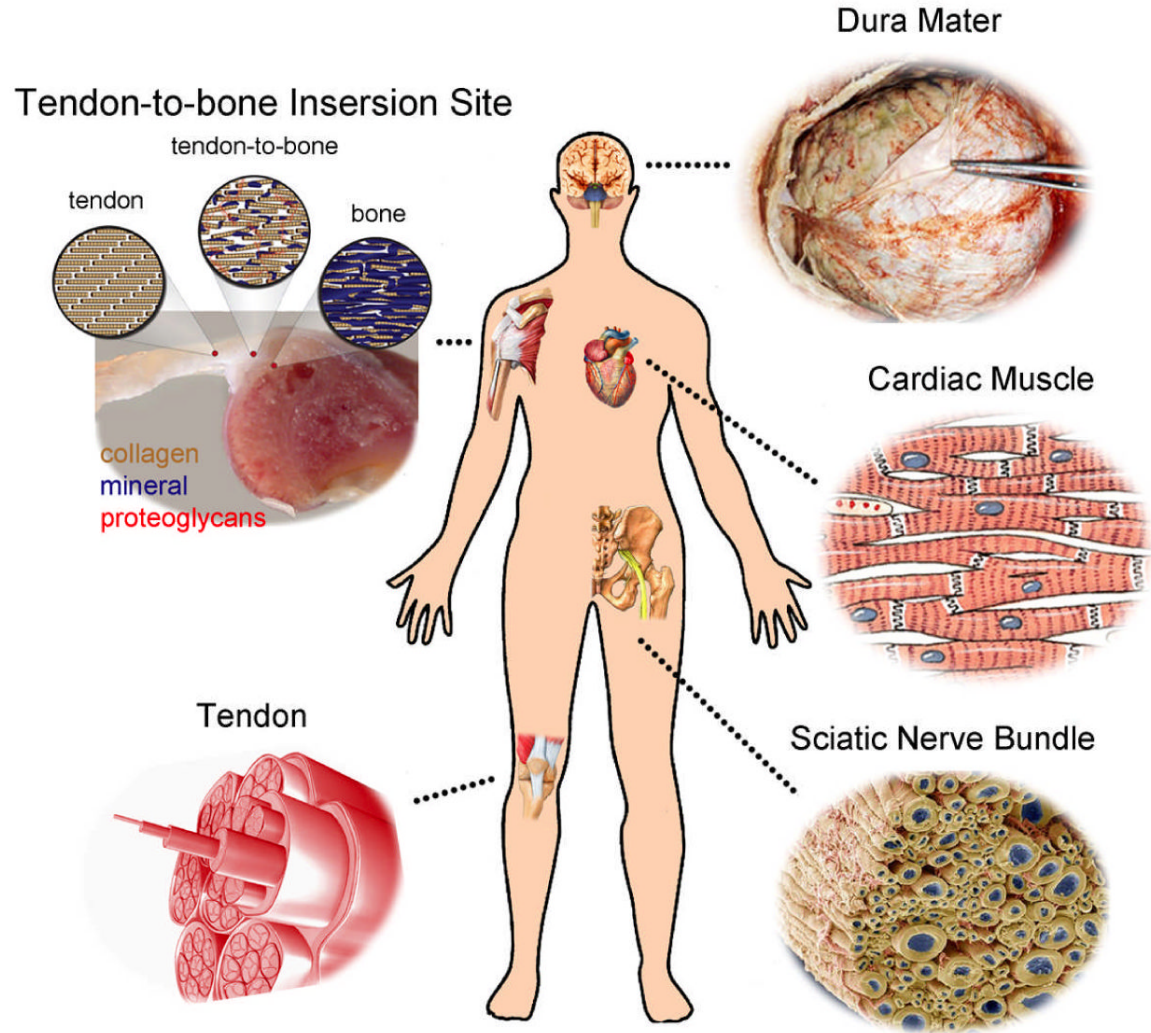
Applications pour l'électrospinning



Applications dans la médecine régénérative

Des différents organes montrent des structures cellulaires caractéristiques.

La grande variation des structures réalisés par electrospinning permettent d'adapter les structures pour favoriser la croissance (prolifération et différenciation) des cellules spécifiques (structures scaffold)

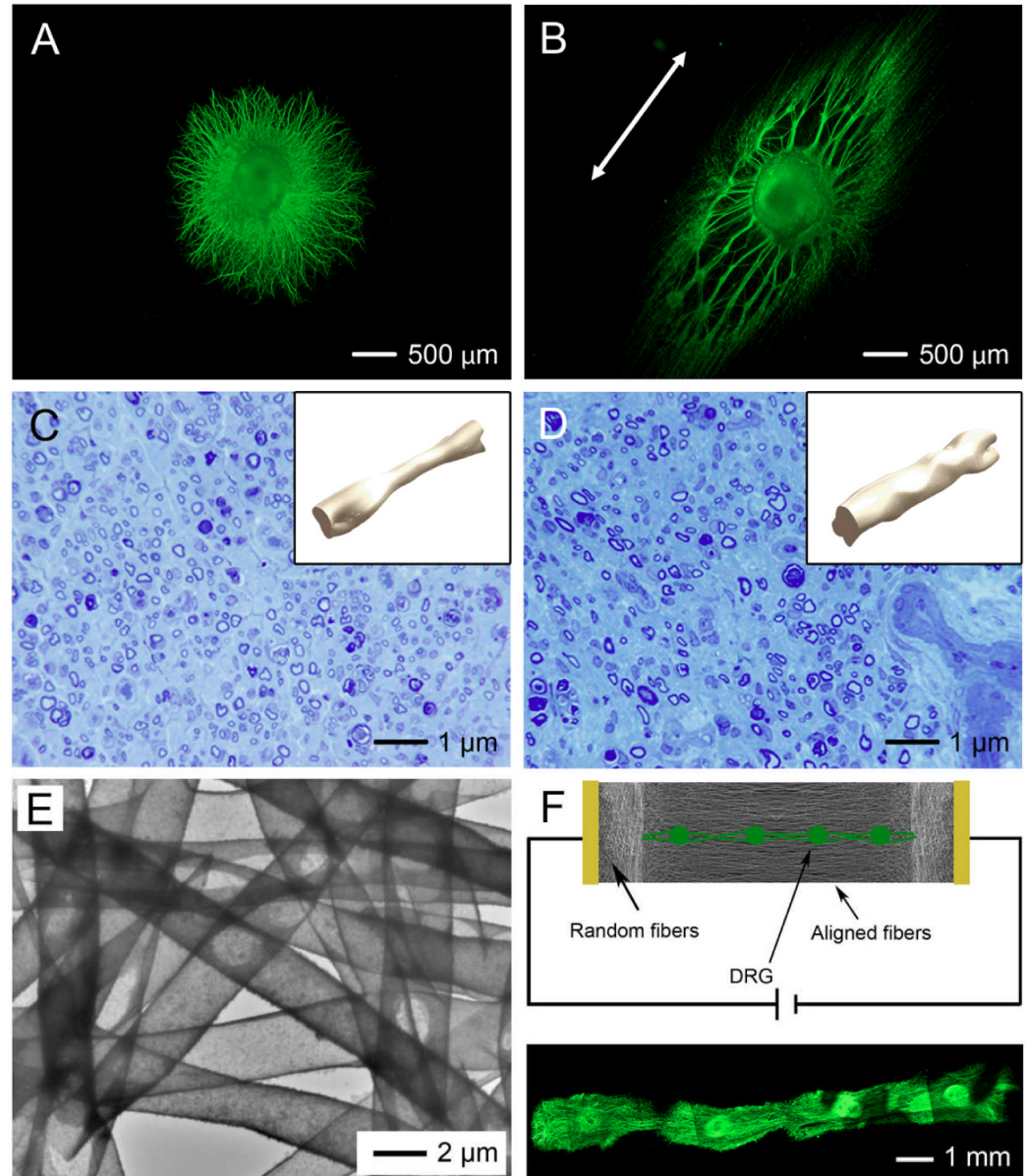


exemples

Ganglion spinaux
de poulet (DRG); croissance dans
un scaffold aléatoire (A)
Un scaffold orienté par
electrospinning

Section à travers des cellules DRG
dans une structure de scaffold
aléatoire (C) et des cellules conduit
conduit par un scaffold de poly(3-
caprolactone) nanofibers fait par
electrospinning (D)

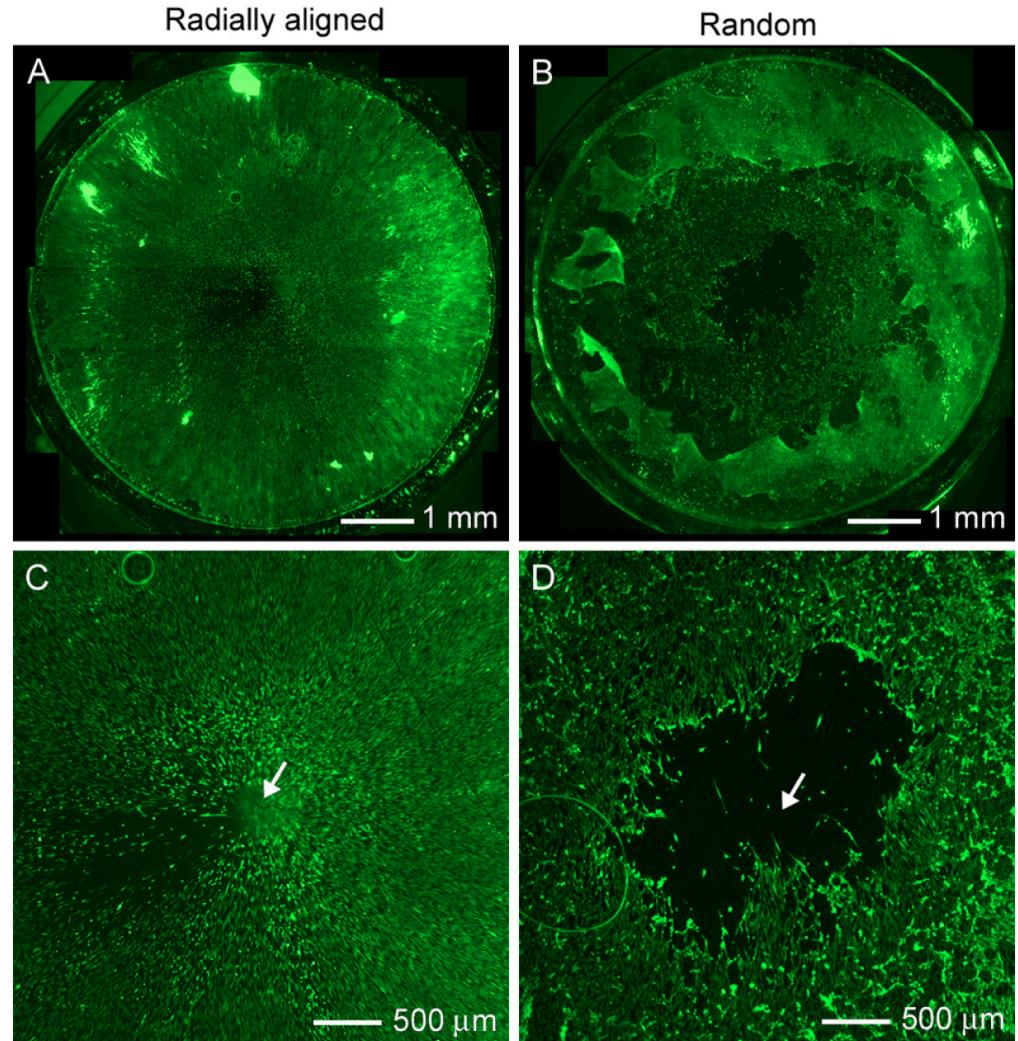
Stimulation électrique de DRG
culturs sur des PPY nanofibres
alignés mène à une meilleure
connection intraneural (E, F)



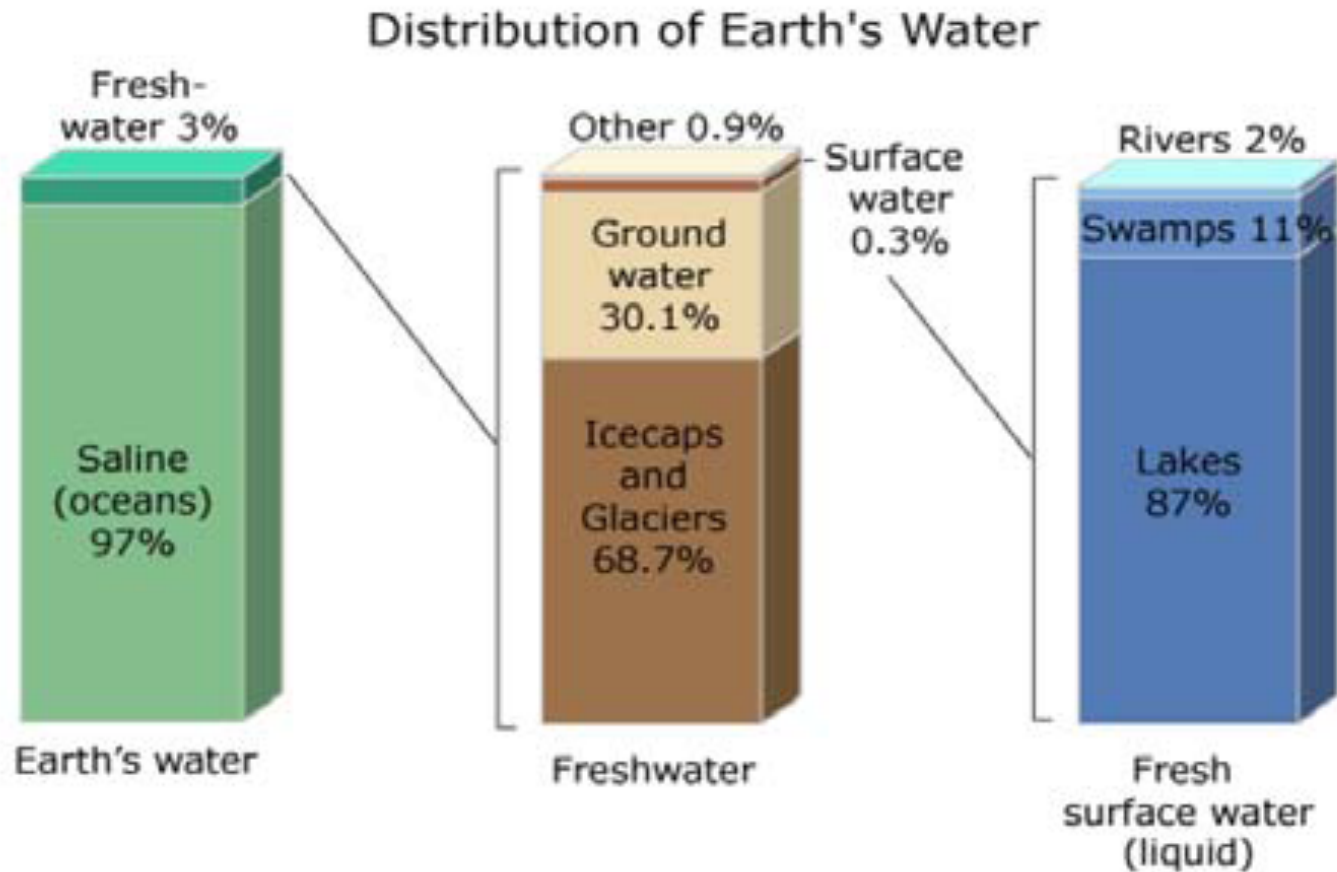
Plus d'exemples

Micrographe de fluorescence observant la réparation de dura mater: A: sur des structures radialement alignés, B des structures non-alignées.

Xie J, MacEwan MR, Li X, Sakiyama-Elbert SE, Xia Y. ACS Nano. 2009; 3:1151. [PubMed: 19397333]

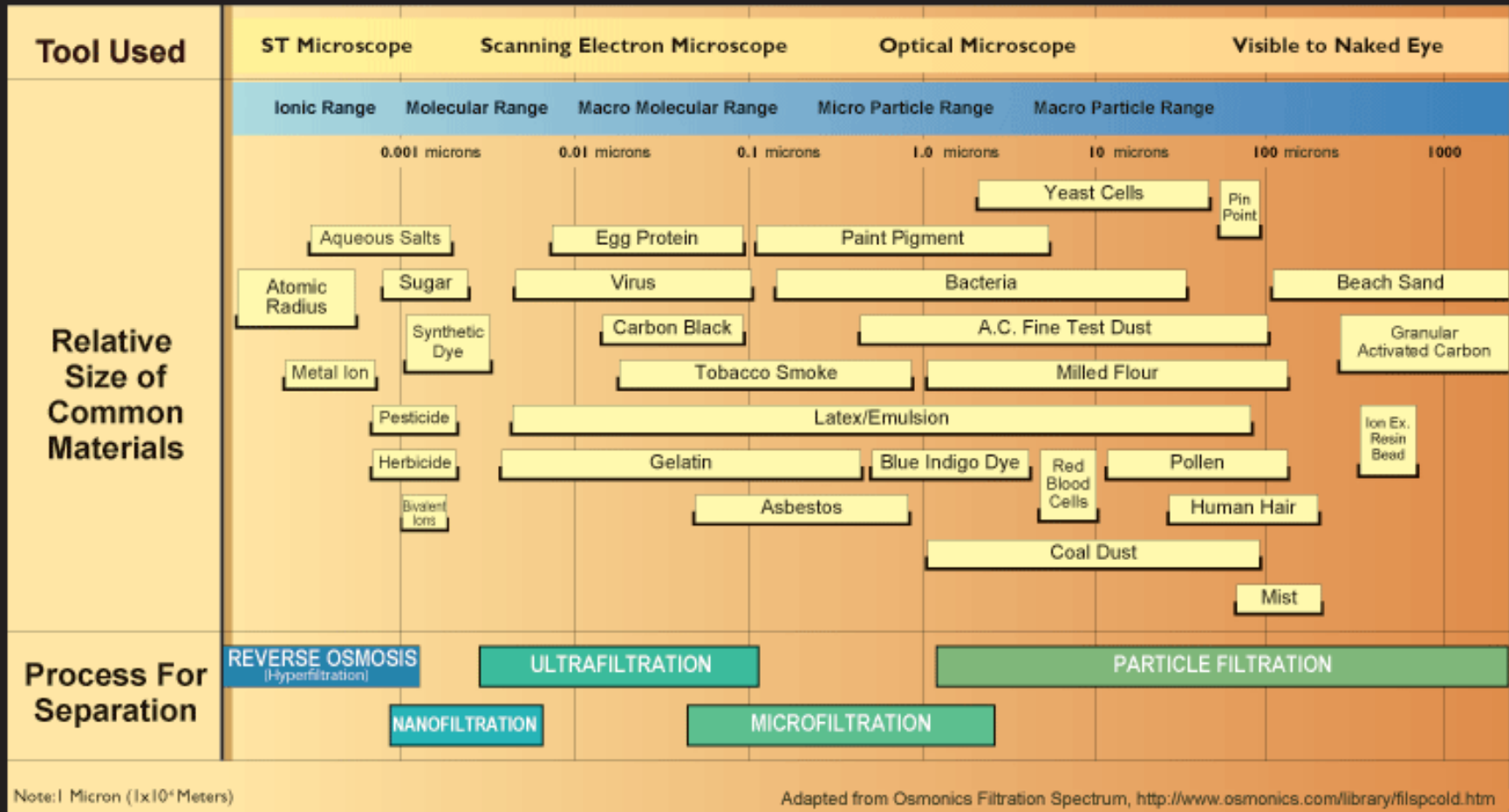


Nanofiltration d'eau



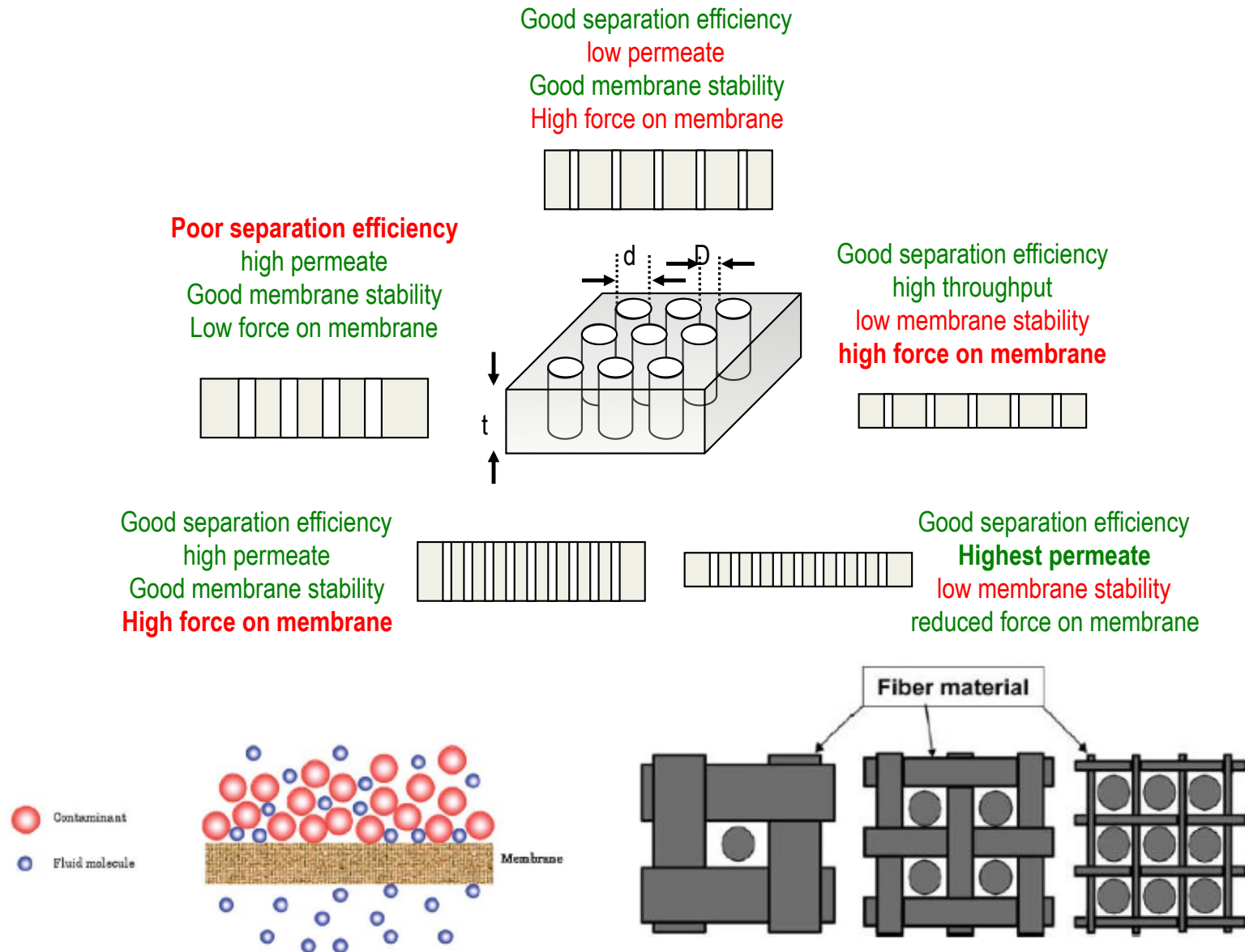
http://en.wikipedia.org/wiki/water_crisis

The Filtration Spectrum



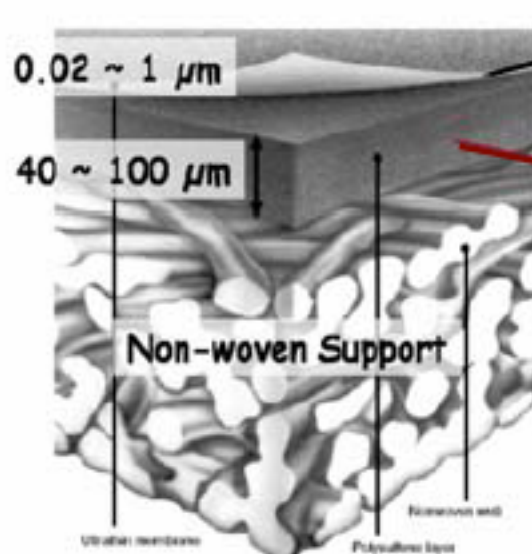
Source: Adapted from <http://http://www.sasconsulting.ca/Files/Spectrum.jpg>

Problème à résoudre



1. Composite membranes with conventional and E-spun support

Conventional composite membranes

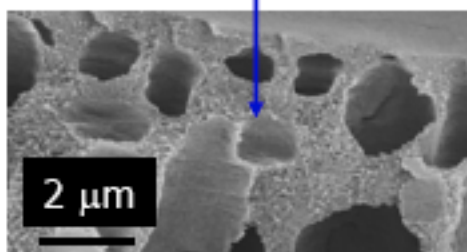


Top coating layer
(next slides)

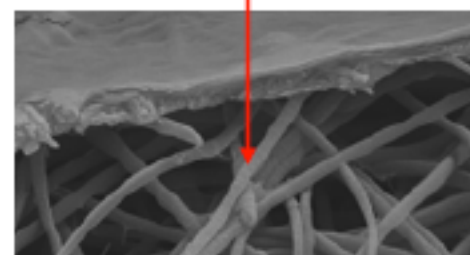
*Flow rate/area is increased
Due to higher
surface pore density*

1. Mid-layer Support

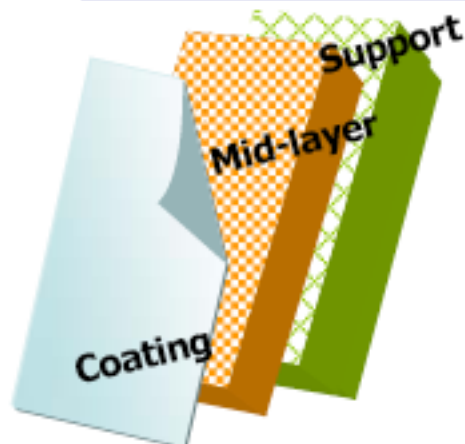
1. Conventional
mid-layer support



2. **Nano-fibrous**
mid-layer support

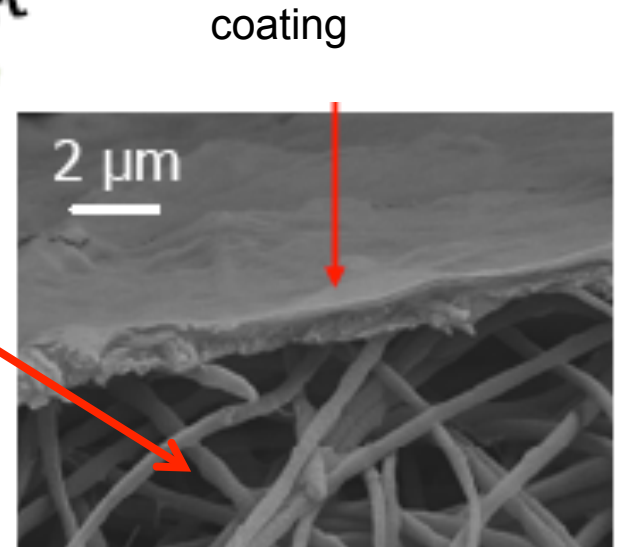
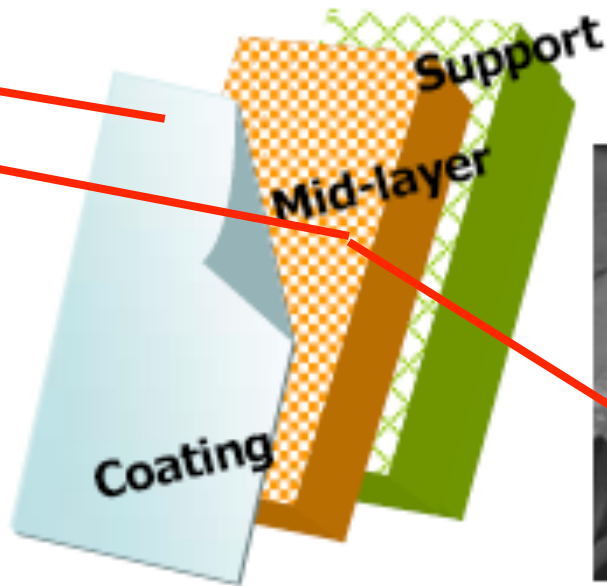
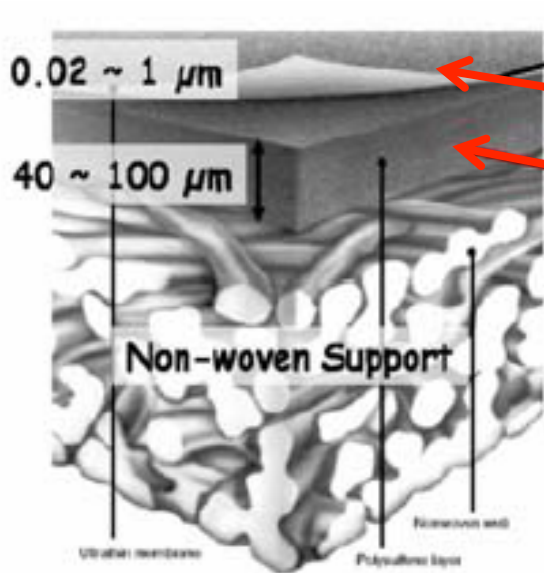


Three-Tier Approach

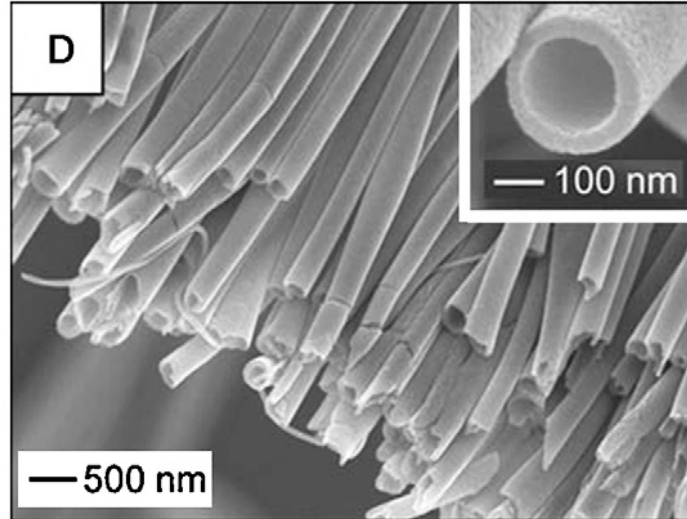
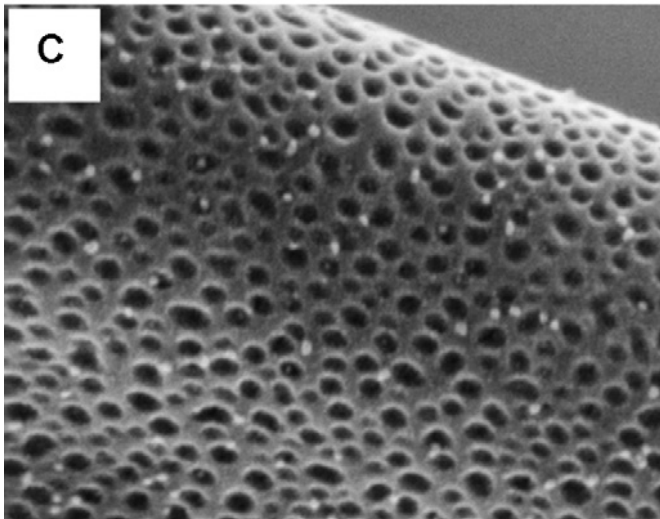
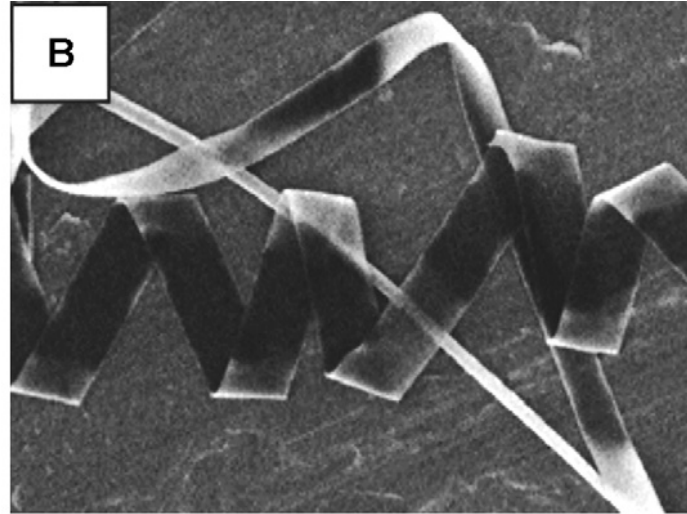
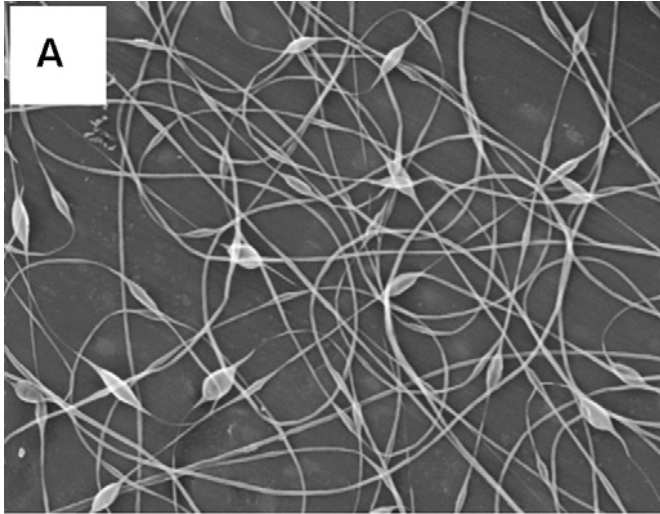


- Higher pore volume
- Much higher surface pore density

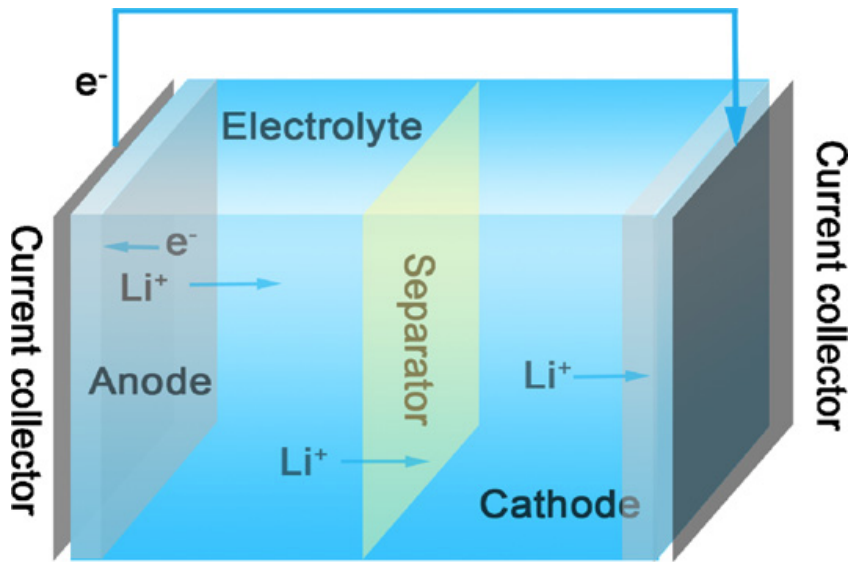
***Payoff: up to ~5 times
increase in filtration efficiency***



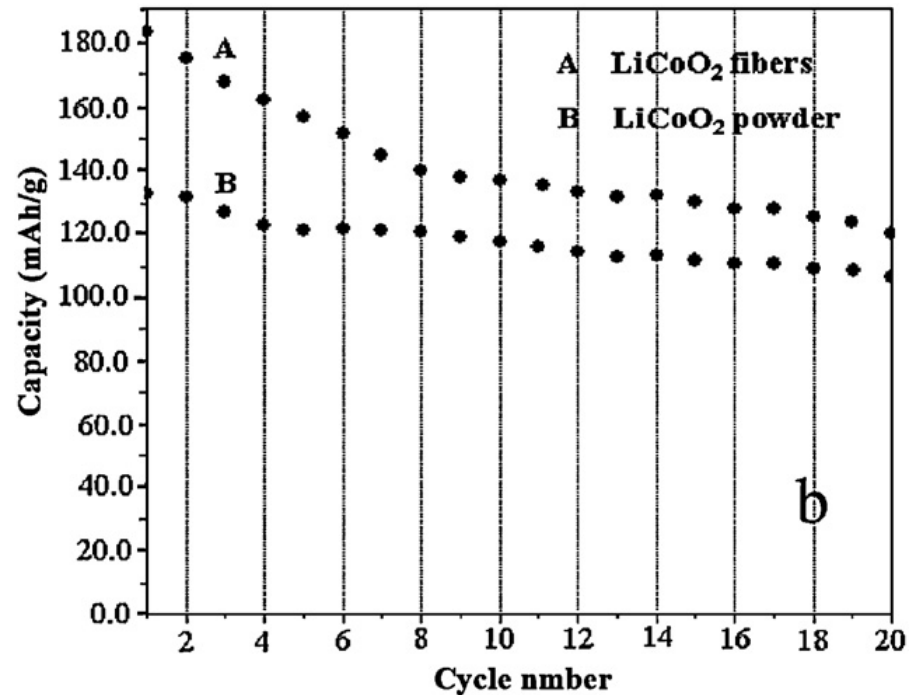
Application pour Li-Batteries



Piles à Lithium

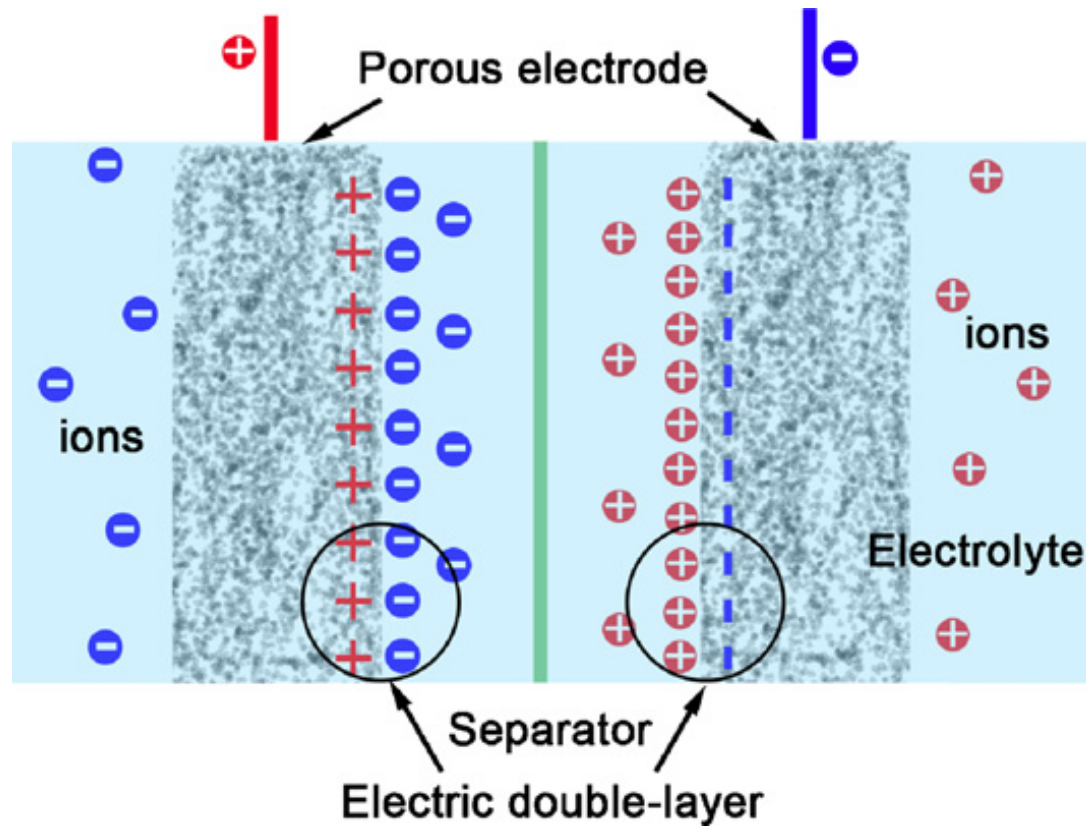


Comparaison de nombres de cycle charge-décharge d'une pile à Lithium avec des électrodes $LiCoO_2$ avec soit sous forme de poudre (B) ou des fibres par électrospinning / sol-gel.



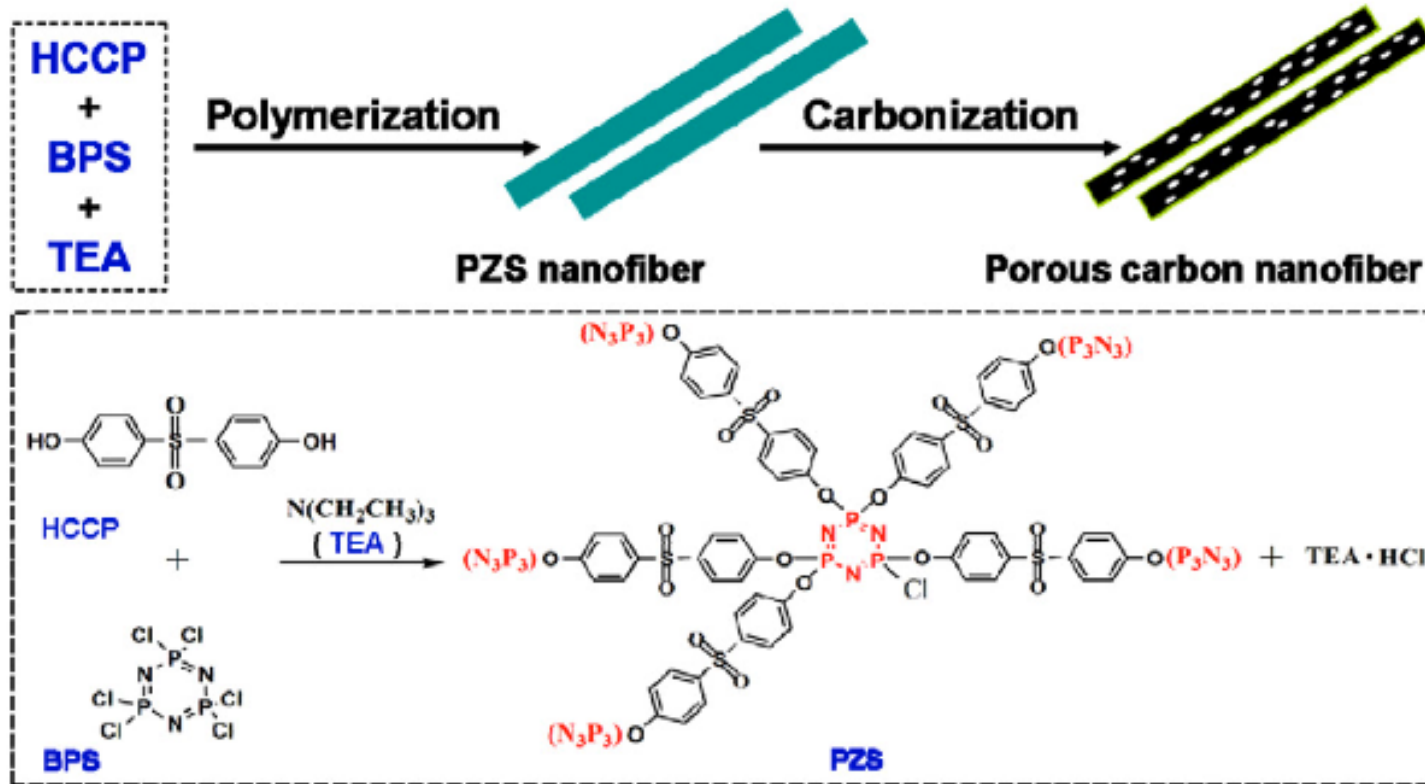
Y.X. Gu, D.R. Chen, M.L. Jiao, J. Phys. Chem. B 109 (2005) 17901–17906

Supercapacité



Potentiel: électrodes en carbone mais en très grande surface

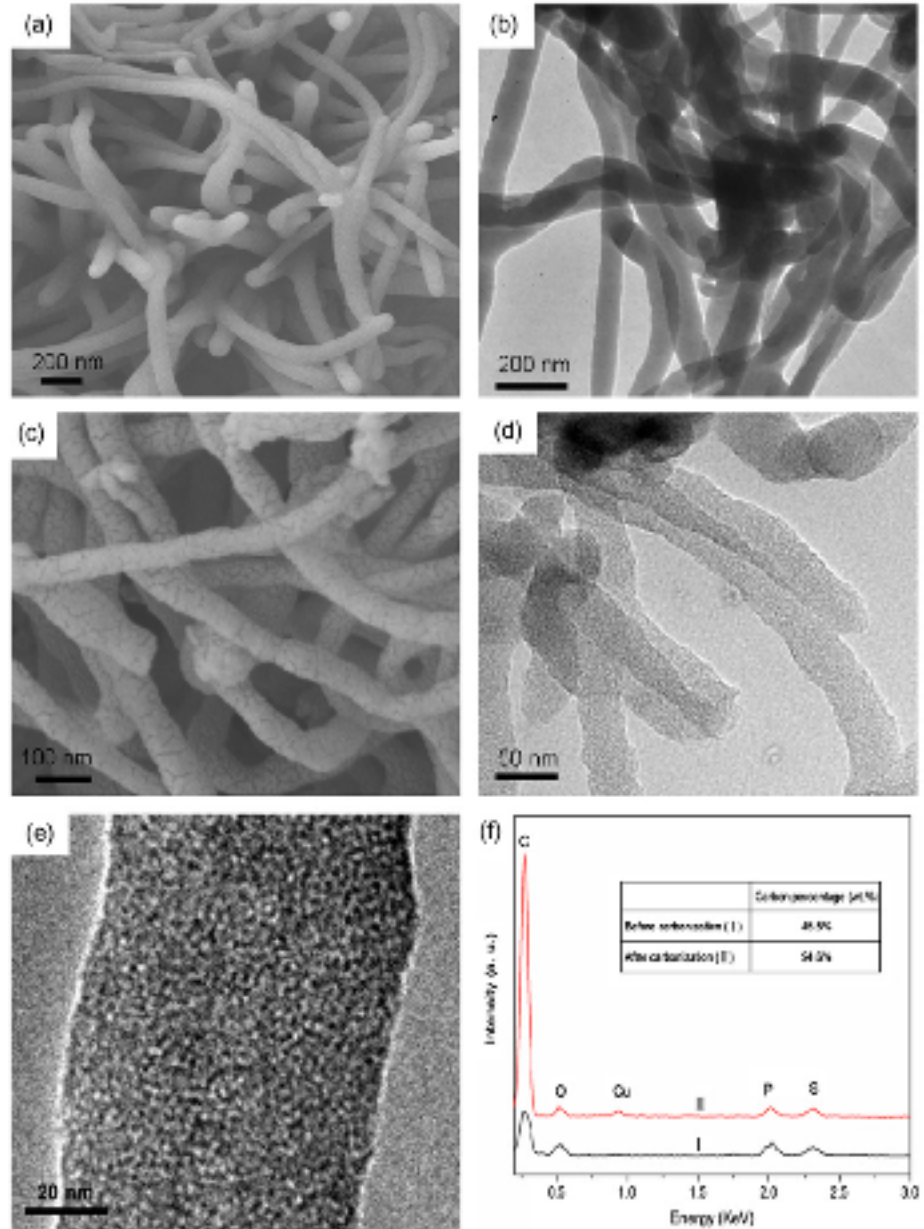
Carbonisation de fibres



Poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) (PZS)

Mise en forme des électrodes (a, b)
 poreuses et carbonisation à 900 °C en N₂
 (c, d)
 surface: 540m² g⁻¹
 0.37m³ g⁻¹,

Jianwei Fu et al. CARBON
 49 (2011) 1033 – 1051



conclusion

- La technique de l'électrospinning ouvre de multiples possibilités dans les domaines ou:
- Un grand rapport surface doit être généré
- Différent que les nano-poudres il y a un lien entre les nanostructures
- La grande surface peut être activé pendant le « spinning » ou par post-traitement.
- Les domaines en pleine développement sont:
 - La médecine régénérative
 - La nano filtration d'eau
 - Les systèmes de stockage d'énergie.



