Fabrication de microbatteries Li-ion à base de nanotubes de TiO2

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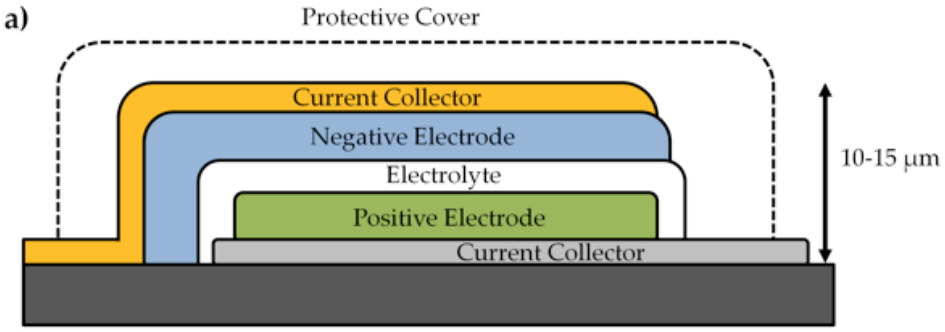
INSPIRING INNOVATION INNOVANTE PAR TRADITION

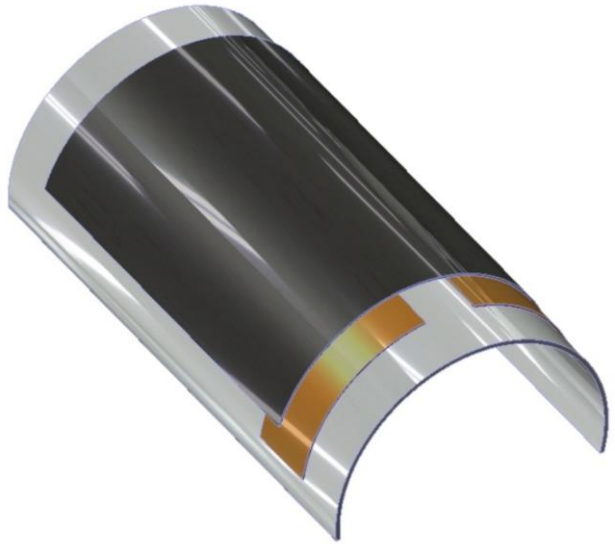
All-solid-state microbatteries

Motivation : shrink the size of power sources (volume and weight)

Alternative : All-solid-state microbatteries fabricated by thin film technologies



Schematic representation of a planar microbattery



Thin film microbattery on flexible substrate

Applications for low power microsystems

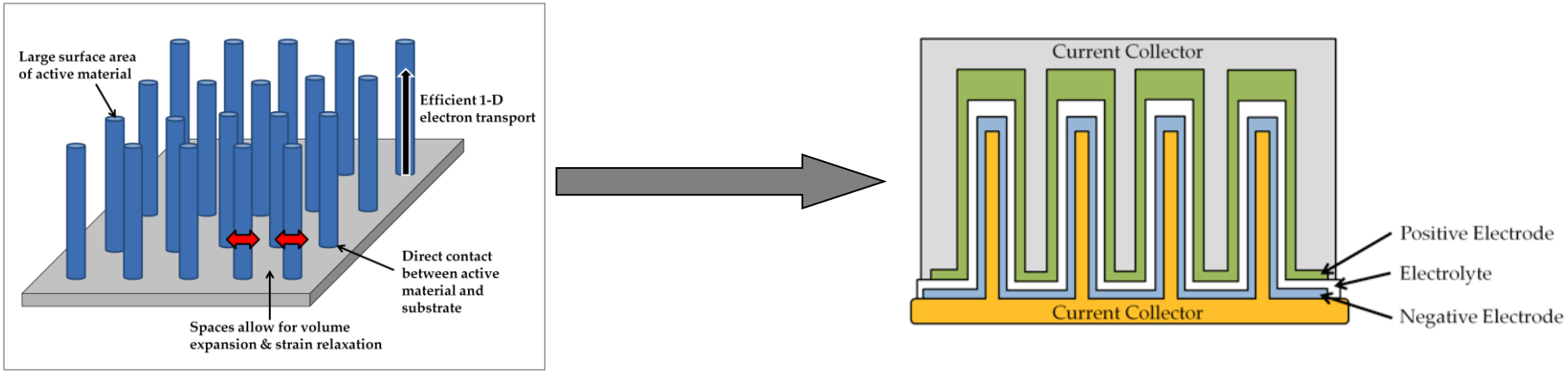
Smart cards, Sensors, RFID tags, Medical implants...

Challenges

Improve the performance while decreasing the size...

1. Investigate the synthesis of new electrode and electrolyte materials

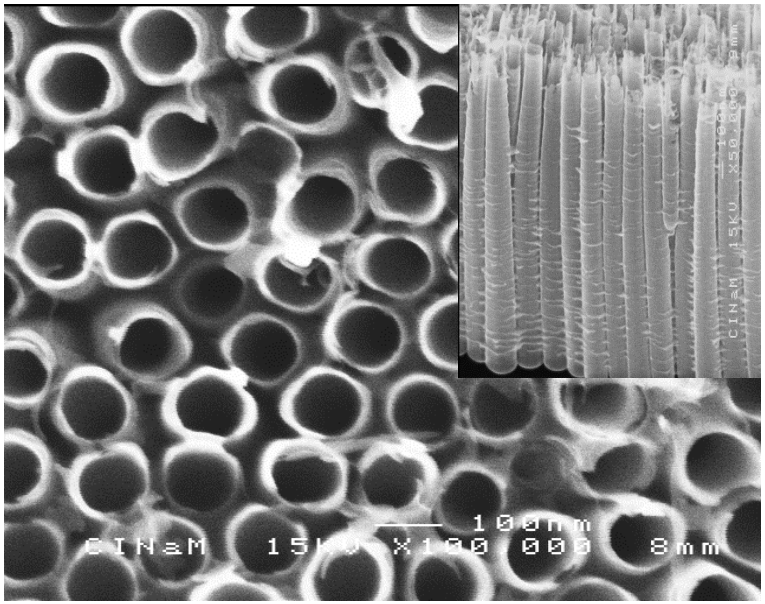
2. Nano-architectured electrodes (e.g. nanotubes, nanowires, etc…)

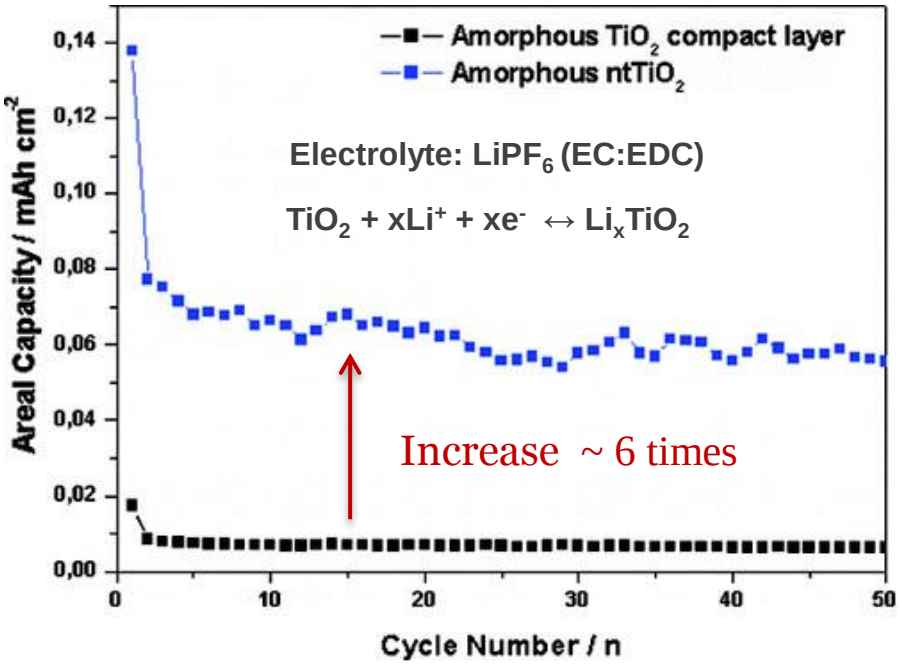


Advantages of nano-architectured electrodes:

- Larger specific area for Li^+ accommodation
- Support the volume changes during cycling
- Short diffusion length

Self-organized titania nanotubes as negative electrode for Li-ion microbatteries





No use of binder and additive

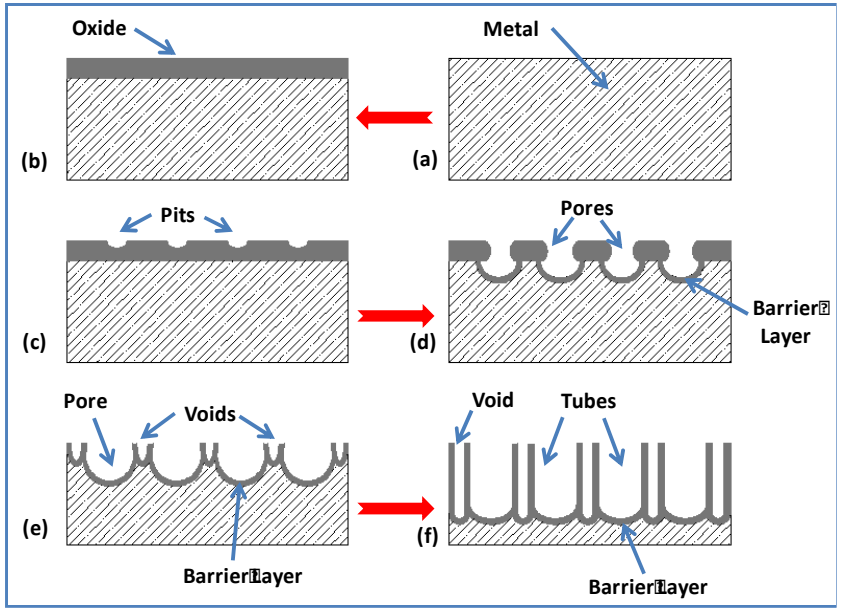
Ortiz et al, **Chem. Mater.**, 21, 63, 2009
Ortiz et al, **Electrochim. Acta**, 554, 4262, 2009
Ortiz et al, **Chem. Mater.**, 22, 1926, 2010
Djenizian et al, **J. Mat. Chem.**, 21, 9925, 2011

Fabrication of self-organized titania nanotubes

- Anodization in HF-containing electrolyte
- The formation mechanism of TiO_2nts is based on the competition between two reactions:

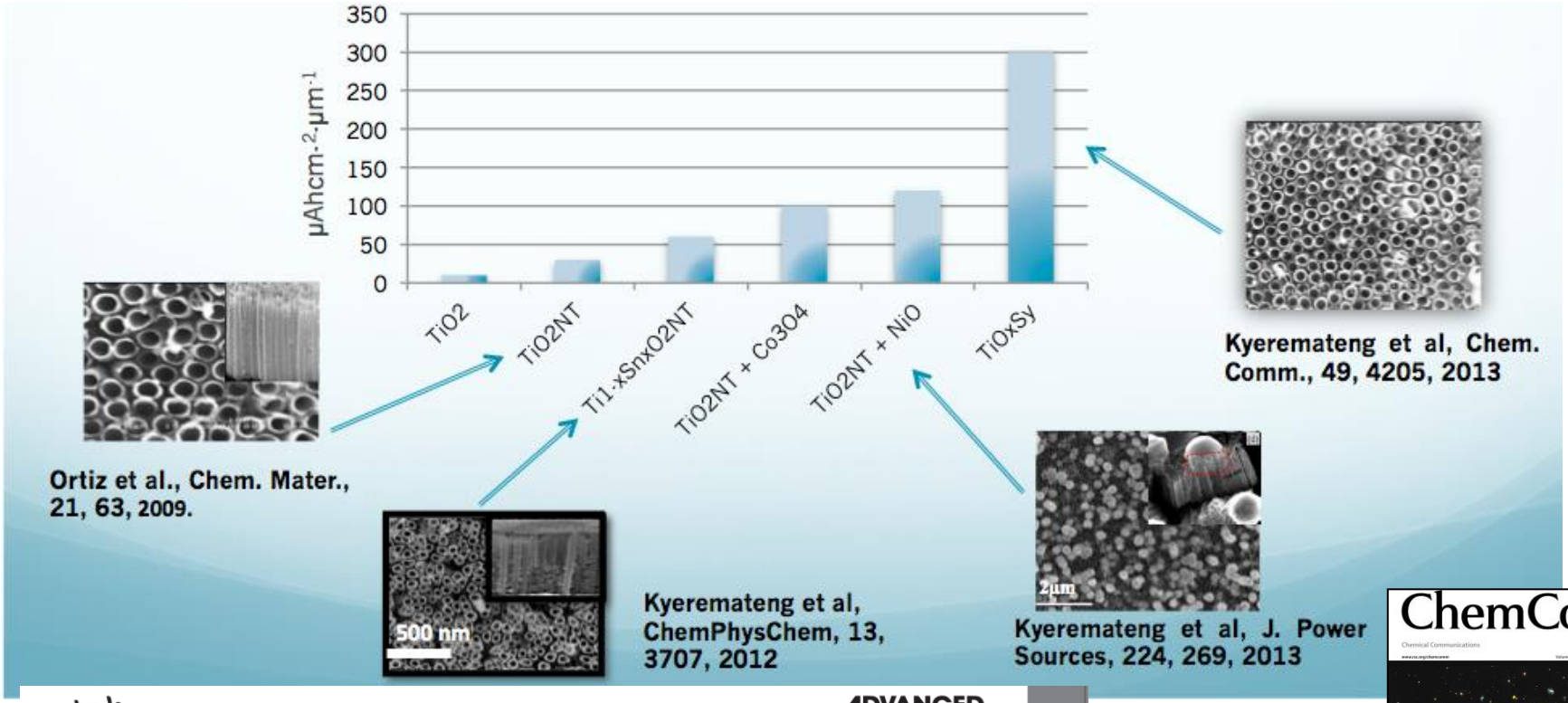
$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O$$



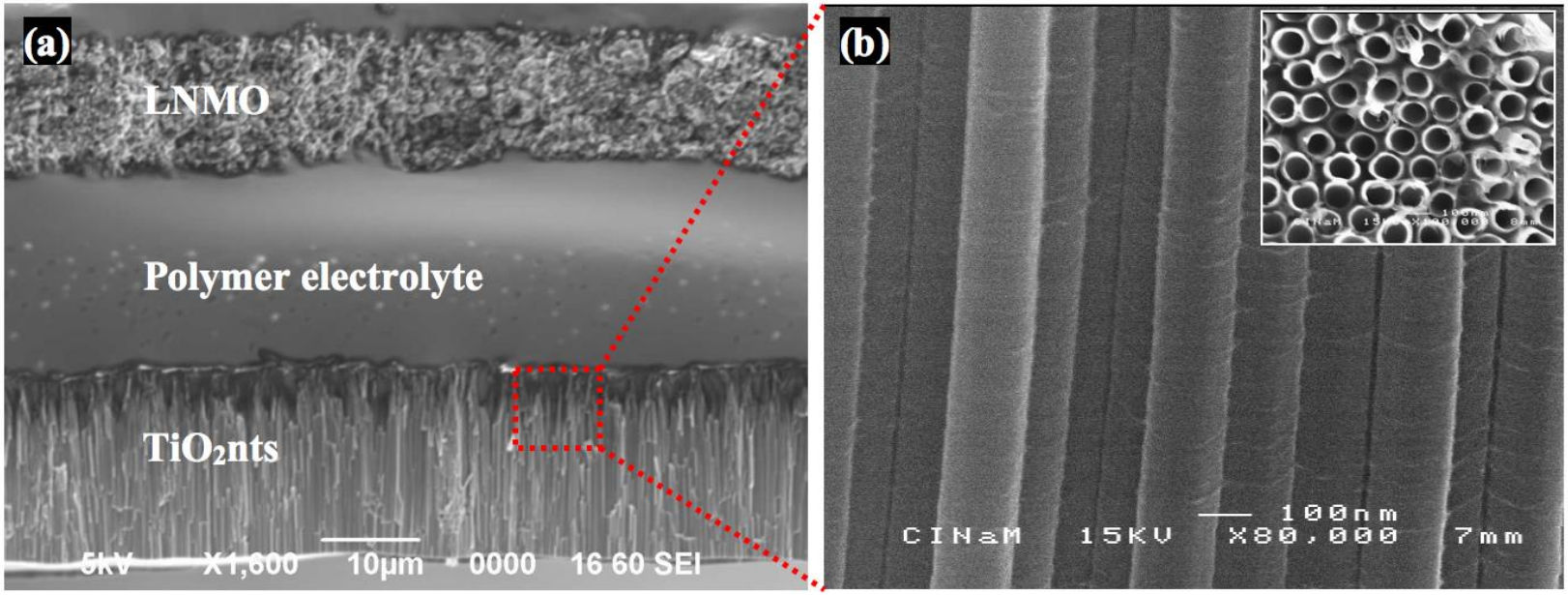
(a) starting metal, (b) initial oxide layer, (c) pits formed on the oxide layer, (d) pits grown into convex–shaped pores, (e) voids develop via field assisted dissolution, and (f) fully developed nanotube array.

Otimization of the electrochemical performances



Challenge : achieve the fabrication of all-solid-state systems

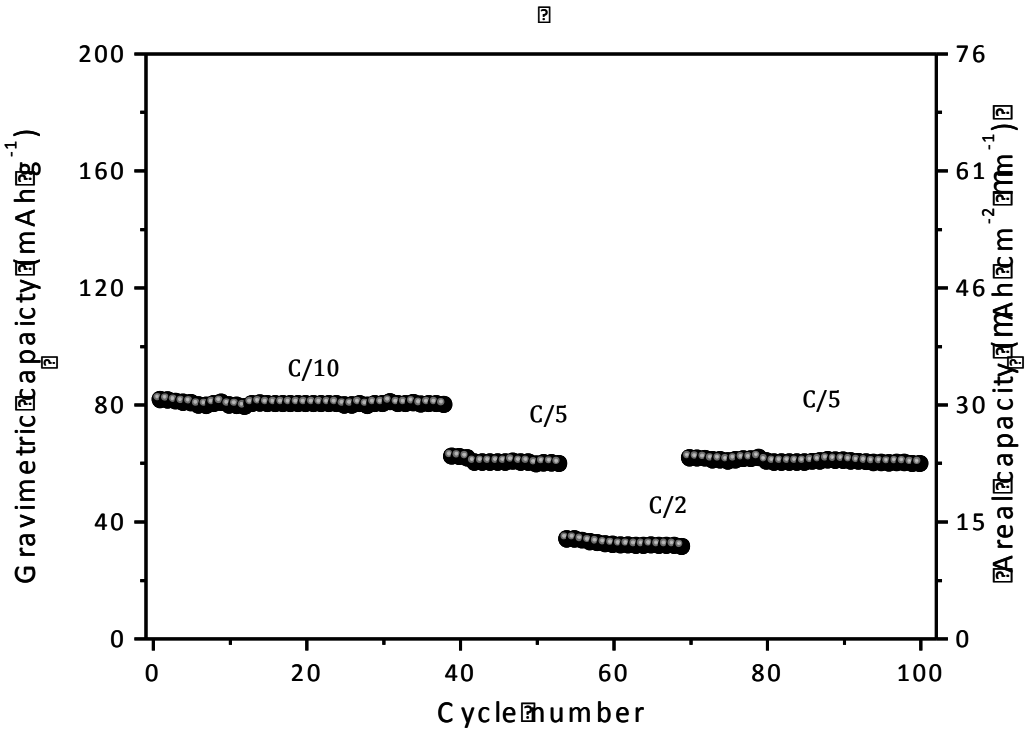
Fabrication of a solid-state Li-ion microbattery



SEM images of cross section of the all-solid-state battery composed of TiO_2nts/MA-PEG300/LNMO (a). Enlarged view of the self-organized TiO_2nt (b).

N. Plylahan, M. Letiche, M. Barr, T. Djenizian, **Electrochem. Commun.**,43, 121, 2014

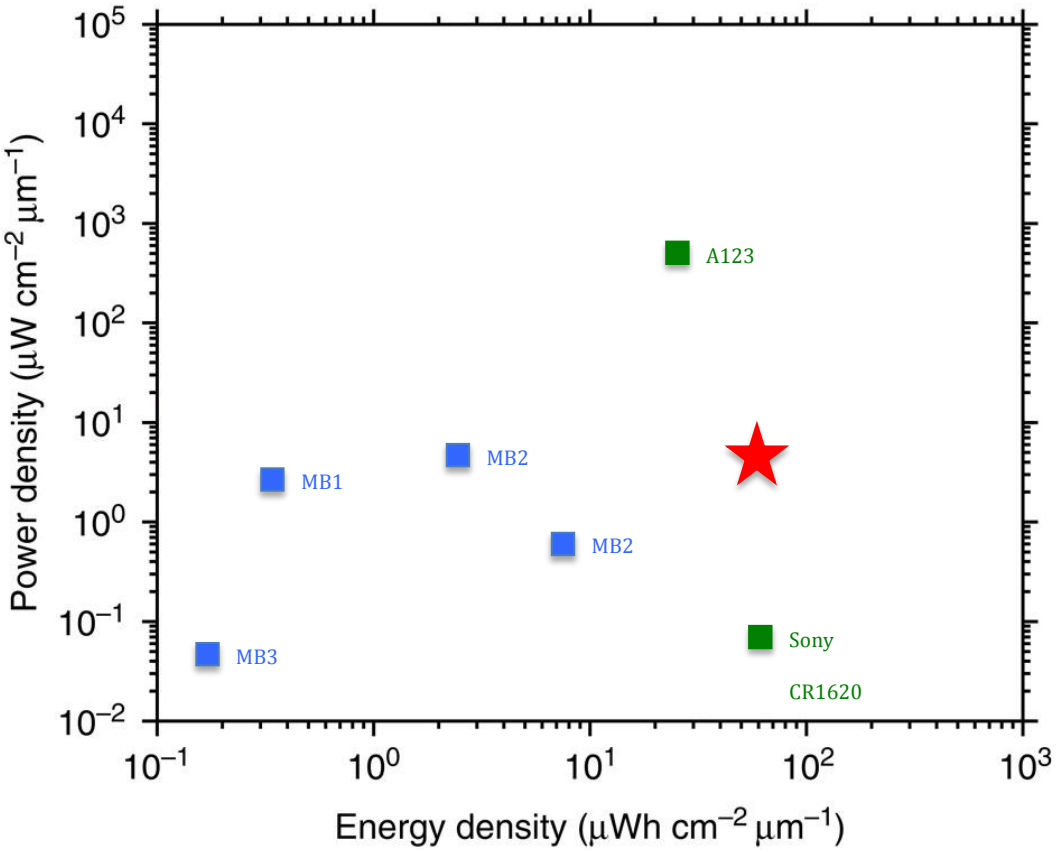
Electrochemical characterization



Discharge capacity versus anode at multi C-rate

N. Plylahan, M. Letiche, M. Barr, T. Djenizian, **Electrochem. Commun.**,43, 121, 2014

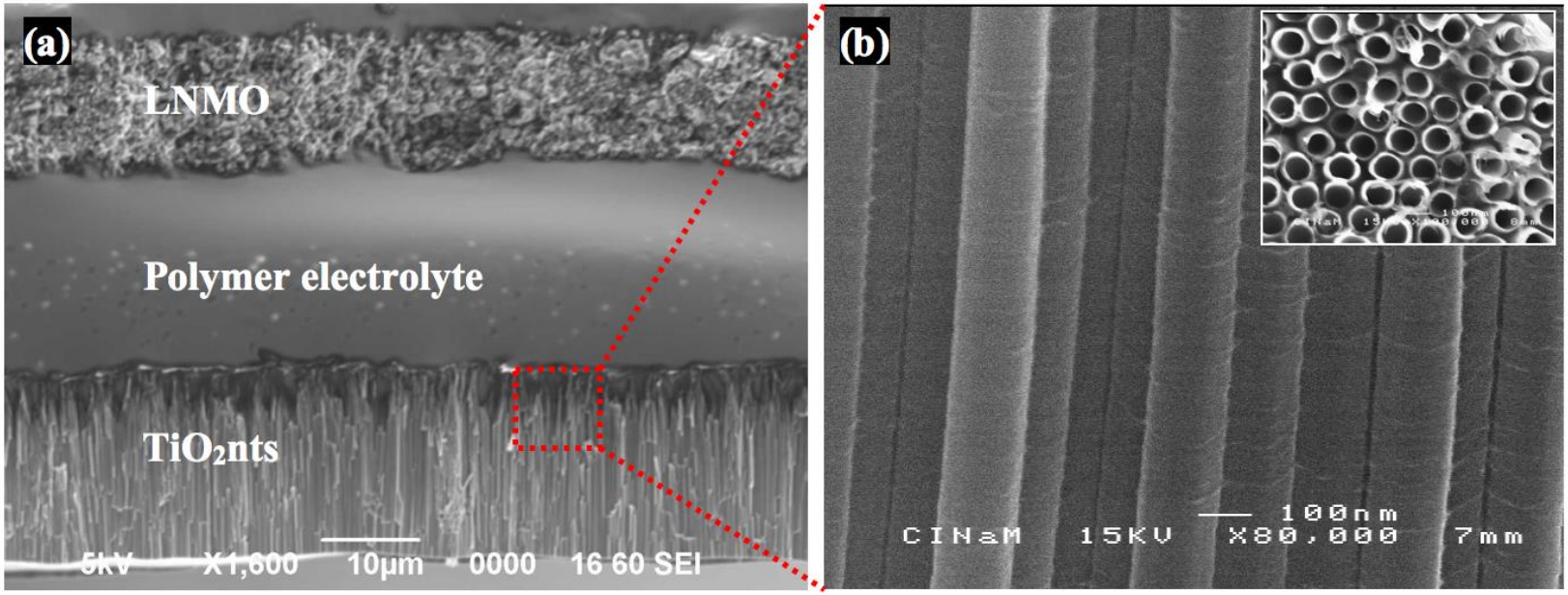
Electrochemical performance



Ragone plot of our all-solid-state cell at C/10 compared to microbatteries having 3D electrodes (MB1 through MB3) and commercial batteries that deliver high power (A123) and high energy (Sony). Adapted from J.H. Pikul, et al, Nat Commun 4 (2013) 1732.

N. Plylahan, M. Letiche, M. Barr, T. Djenizian, Electrochem. Commun.,43, 121, 2014

Fabrication of a solid-state Li-ion microbattery



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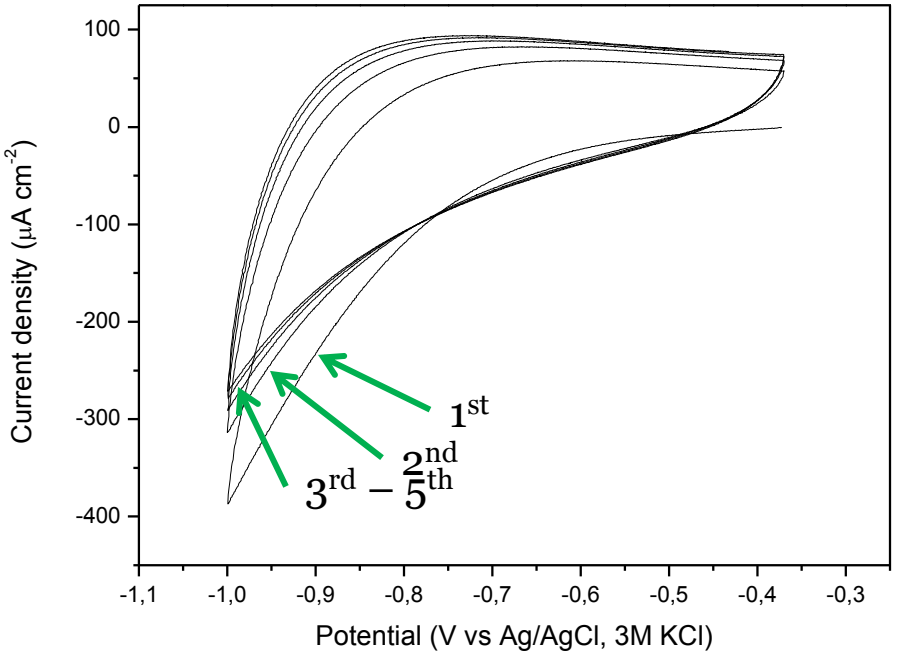
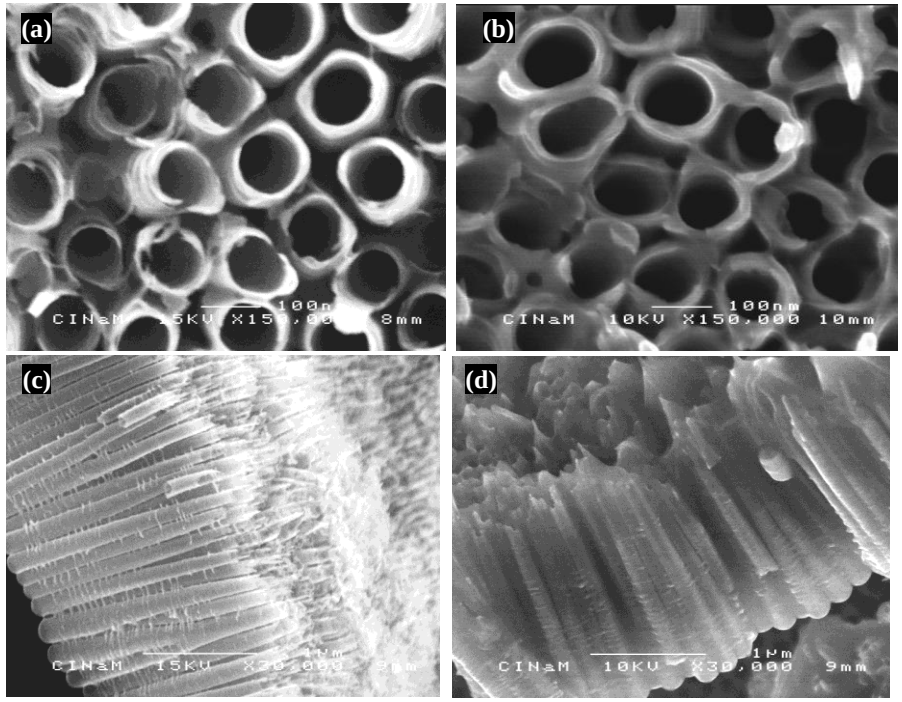
Conformal electrodeposition of polymer electrolyte



Fading in the cathodic current upon cycling suggests the successive deposition of the polymer layer



SEM confirms the deposition of the polymer

N. Plylahan, S. Maria, T. N. T. Phan, M. Letiche, H. Martinez, C. Courreges, P. Knauth, and T. Djenizian, **Nanoscale Res. Lett.**, 9, 544 (2014)

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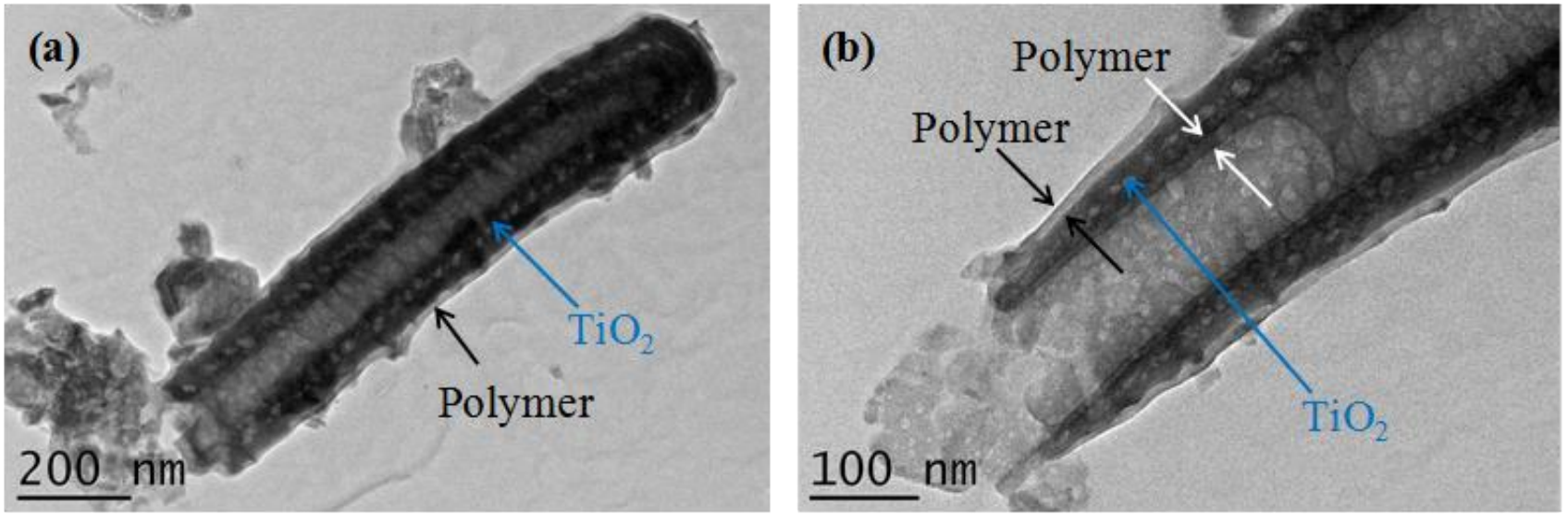
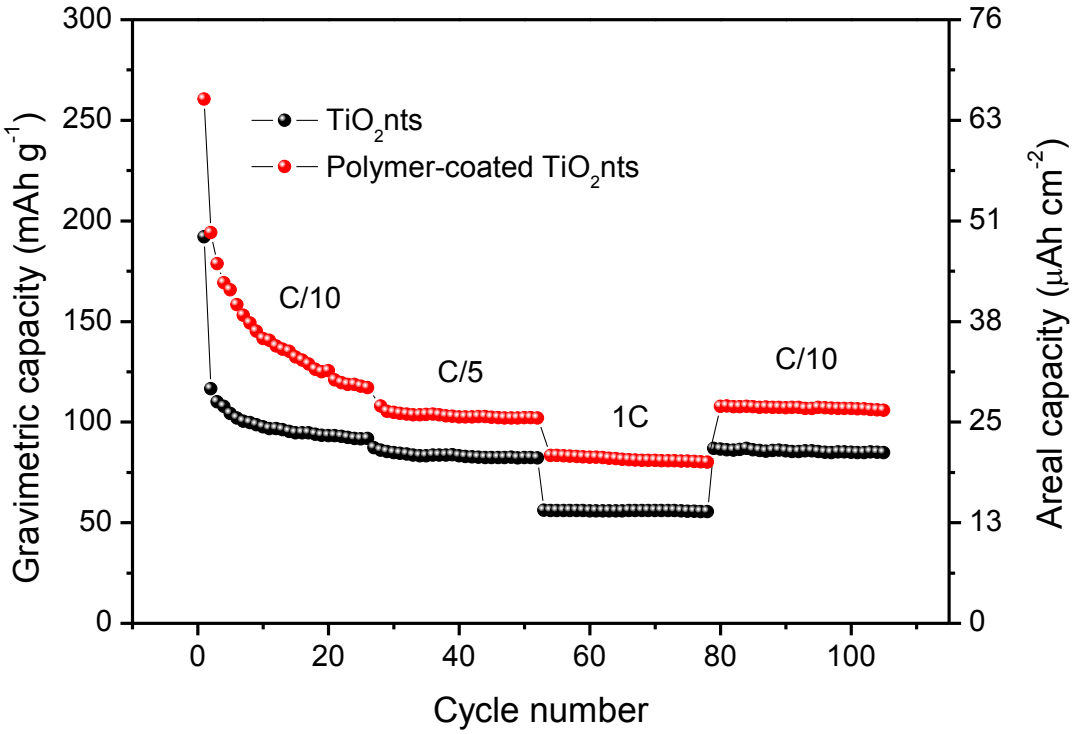


- A thin layer of polymer is clearly observed on the outer wall, from the top to the bottom of the tube.
- The thickness of the conformal polymer layer is around 10 nm.

N. Plylahan, S. Maria, T. N. T. Phan, M. Letiche, H. Martinez, C. Courreges, P. Knauth, and T. Djenizian, **Nanoscale Res. Lett.**, 9, 544 (2014)

Improvement of the electrochemical performance

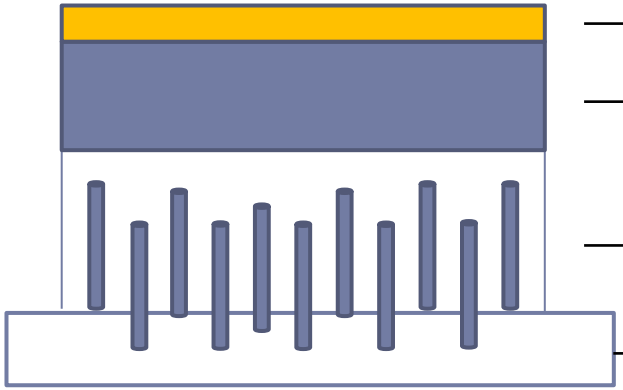


The Electropolymerised cell gives a capacity of about **112 mAh/g** as compared to **80mAh/g** for the non-electropolymerized sample.

N. Plylahan, M. Letiche, M. Barr, B. Ellis, S. Maria, T. N. T. Phan, E. Bloch, P. Knauth, and T. Djenizian, **J. Power Sources**, 273, 1182 (2015).

N. Plylahan, A. Demoulin, C. Lebouin, P. Knauth, T. Djenizian, **RSC Adv.**, 5, 28474 (2015).

All-solid-state microbattery fabricated by depositing $LiMn_2O_4$ using PVD

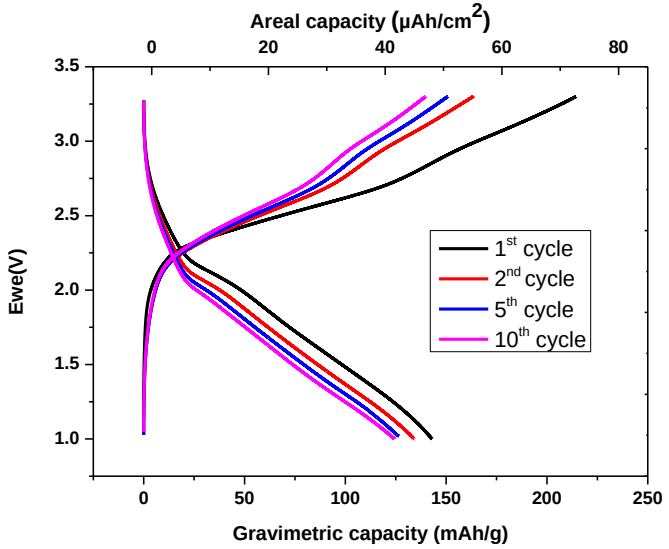


Al. current collector (≈ 500nm)

Amorphous LMO (≈ 1.25µm)

Electropolymerised titania

Ti current collector



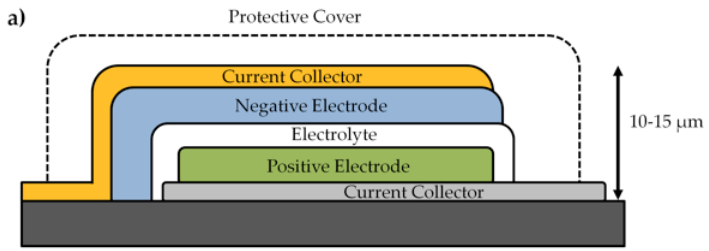
Galvanostatic cycling of the microbattery at C/10 rate

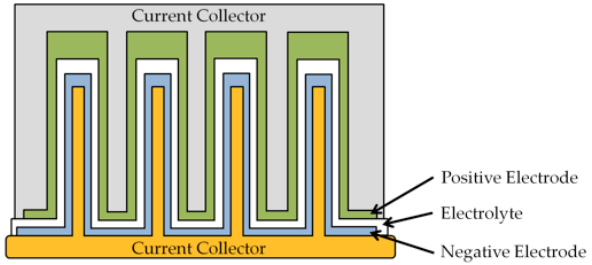
Potential range = 1-3.3V

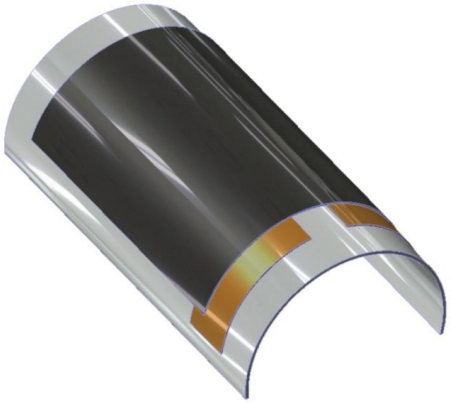
G. Salian, A. Demoulin, C. Lebouin, F. Vacandio, P. Knauth, and T. Djenizian, submitted

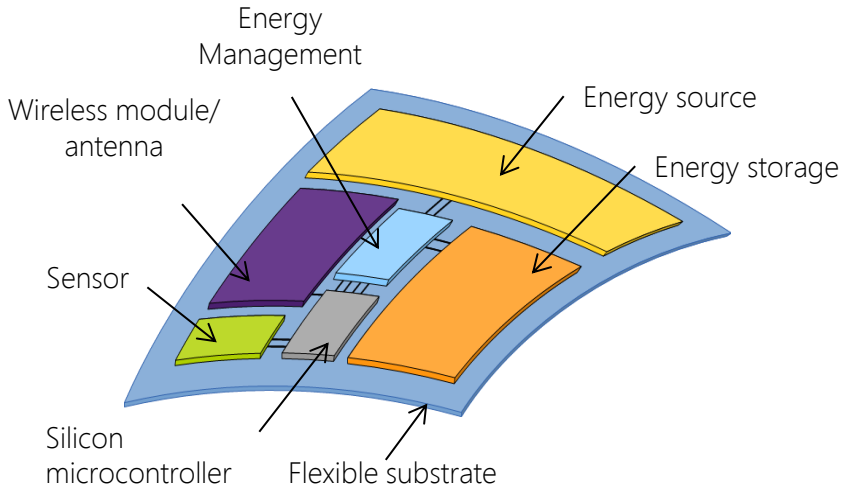
Projets de recherche

Microbatteries Li-ion sur substrats souples



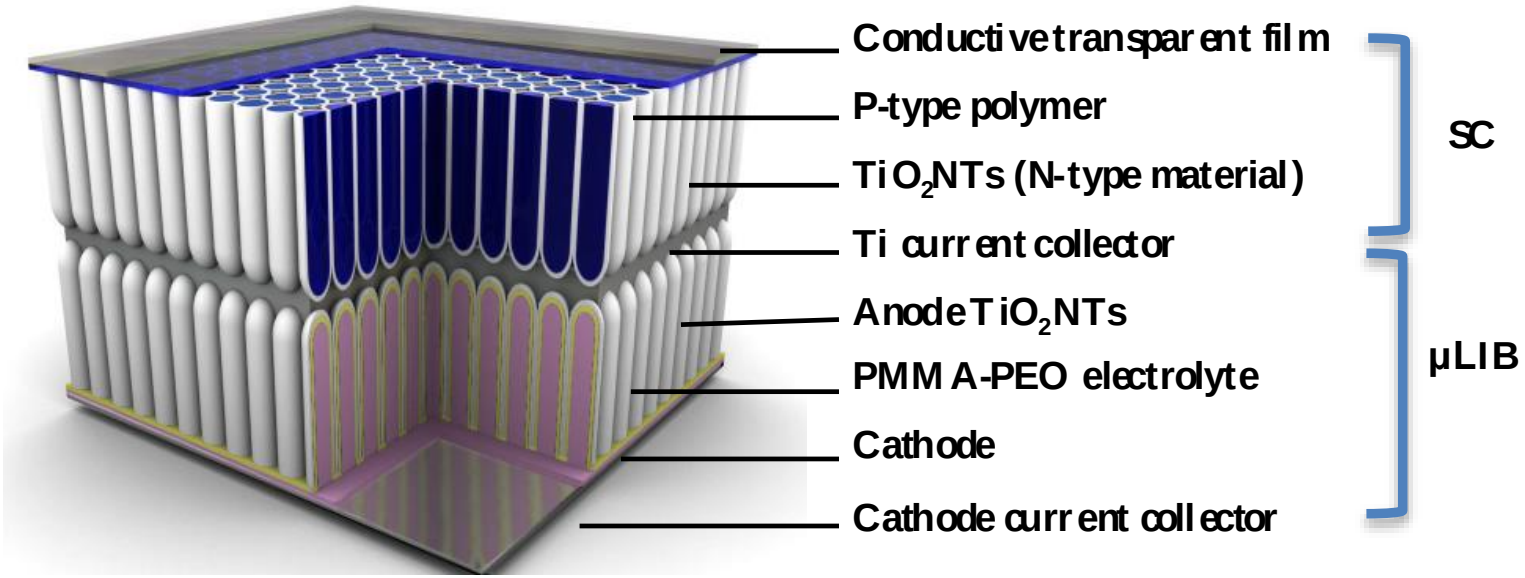






Projets de recherche

Microbatterie solaire réalisée à partir d'une bicouche de nanotubes de TiO2



Conclusions

TiO_2nts/PEG/ LNMO microbattery has been fabricated

The conformally coated TiO_2nts with PMMA-PEG carrying LiTFSI as polymer electrolyte has been achieved by electropolymerization process

The performance of the cell is improved when TiO_2nts are conformally coated with the polymer electrolyte

Outlook :

- microbatteries on flexible and stretchable substrates
- Self-charging system and coupling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Thank you for you attention