Atelier #5 : Nanomaterials for Energy Storage Microdevices

Animators

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Contributors/Participants

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N A M e

GDR Nanomaterials for Energy Applications

Atelier #5 : Nanomaterials for Energy Storage Microdevices

Contours de l'atelier

Nanomaterials for energy storage microdevices: microbatteries, microsupercapacitors and related devices (hybrid, asymmetric, …)

and more specifically…

Atelier #5 : Nanomaterials for Energy Storage Microdevices

5. Nanomaterials for Energy Storage Microdevices
5.1. Introduction
Relation with RS2E (nanomaterials for energy storage) and GDR-NAME (nanomaterials for energy storage micro-devices)
5.2. Definition of electrochemical energy storage microsystemes
5.2.1. Capacitive-pseudocapacitive-Faradaic storage
5.2.2. Phenomena to model: ion-electron coupling, time scale
5.2.3. Nanomaterials elaboration (Atelier #1)
5.2.4. Area enlargement factor AEF (ratio surface/volume)
5.2.5. Criteria for the figure of merit: coulombic efficiency and energy yield, time constant, selfdischarge, cycling ability, ...)
5.2.6. Characterisation Techniques: Electrochemical techniques, Coupling with large/big instruments (in-situ/operando measurements), interfaces in microdevices, issues related to thin layers
5.2.7. Definition of electrochemical energy microdevice (Wh/kg vs mWh/cm^2), coupling with other energy harvesting devices (piezoelectrics, electrochromism, sensors…)
5.2.8. Applications: wearable, flexible, Internet des Objets (IoT),
5.2.9. Commercial products
5.3. Micro-batteries (Li, Li-ion, Zn-ion, others)
5.3.1. 3D Electrodes and flexibles designs
5.3.2. Electrolytes: liquid cristals, Self-assembled, biredox (ionogels), temperature impact
5.3.3. Design/components
5.4. Micro-supercapacitors
5.4.1. Electrodes
5.4.2. Electrolytes (ionogel) (PVA gel) (liquid) (solid), temperature impact, liquid crystal electrolytes
5.4.3. Design/composants
5.4.4. Dielectric Microcapacitors, Hybrid systems, …
5.5. Coupling
5.5.1. Systems autonomy coupling (energy harvester, energy conversion,…)
5.5.2. Device fonctionning coupling (sensors, electrochrome systems, etc…)
5.5.3. Interconnection problematic, compatibility (interaction with Atelier #6)

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Atelier #5 : introduction

I. Introduction

1. This workshop is dedicated to the use of nanomaterials in micro-devices dedicated to electrochemical energy storage = decision/choice of GDR NAME
2. Nanomaterials for energy storage macrodevices are already investigated and discussed in other networks : RS2E, GFECI, … A one-day seminar will be dedicated to this topic during Fall 2021 : « Nanomaterials for bulk energy storage devices : supercapacitors, Li-ion batteries, M-ion batteries, etc…” with a lecture from Professor Jean-Marie Tarascon on the role of physics in energy storage devices
3. A lot of topics and axis, some of them well defined, some others requiring inputs…

Metrics: 100-1000000 charge/discharge cycles / 1 µWh to 10 mWh/cm^2 / 1 to 1000 mW/cm^2

NAME
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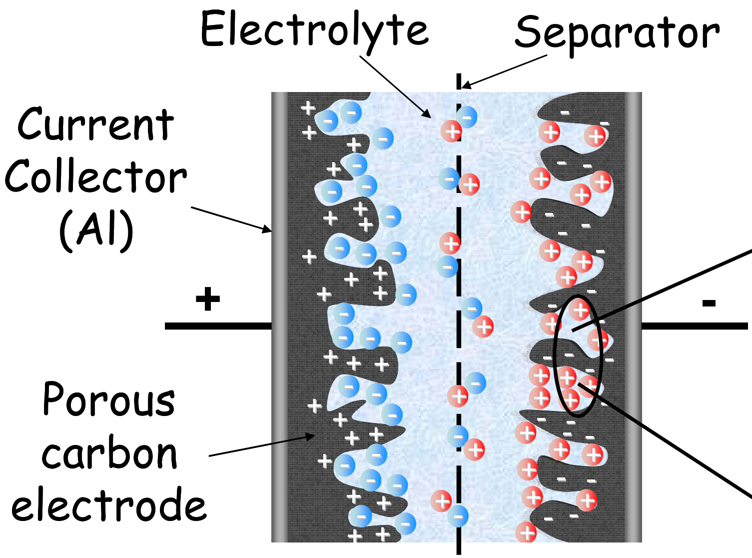
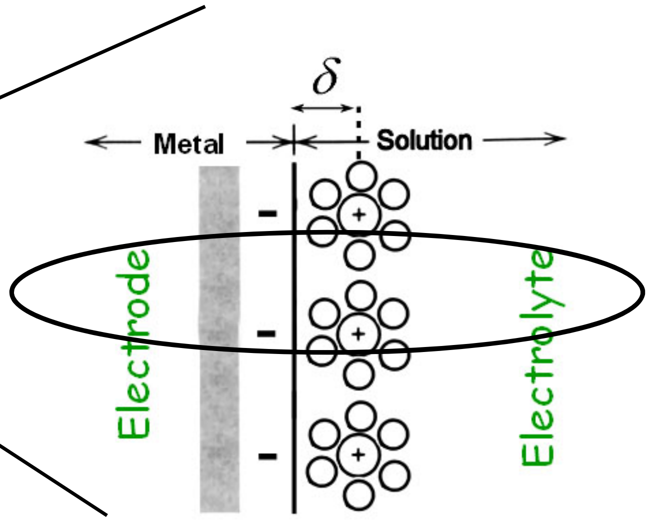
II. Electrochemical Energy Storage Microdevices

1. Charge Storage Mechanisms
   i. Capacitive storage
   ii. Pseudocapacitive storage
   iii. Faradaic storage

Capacitive charge storage

Adsorption of ions at electrode/electrolyte interface





Double layer capacitance

$$C \alpha \frac{S}{\delta}$$

Specific surface area

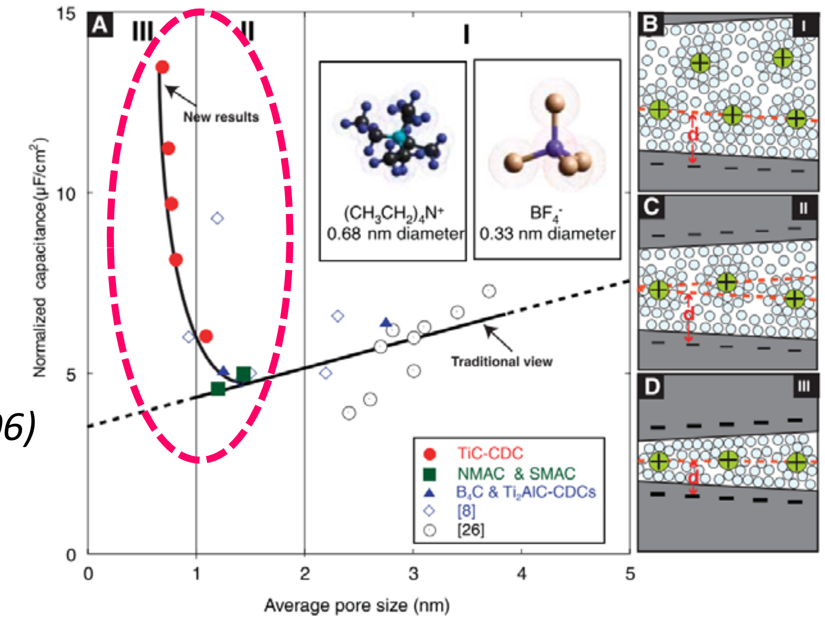
Thickness of the electrical double layer

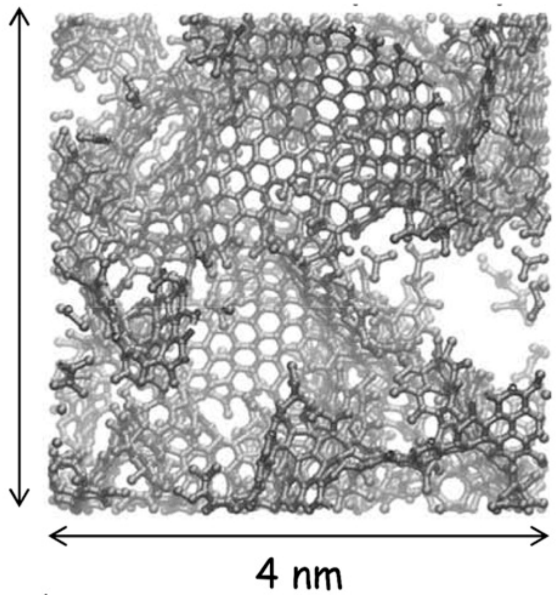
Materials to be used?

↘ δ ou ↗ S

Capacitive charge storage

Simon & Gogotsi, Science (2006)





But Activated Carbon

- limited control over pore size
- scattered data in literature → difficult to compare

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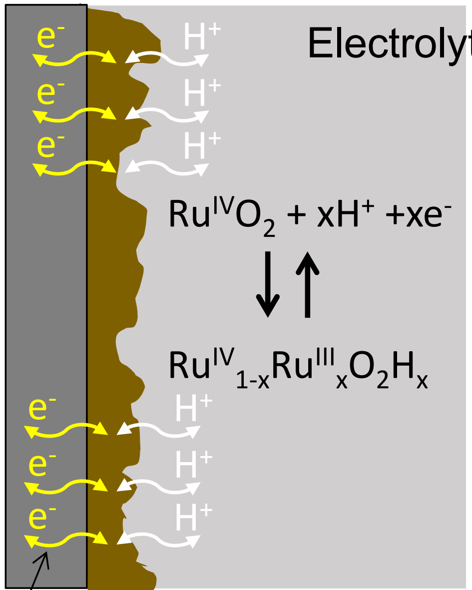
Pseudocapacitive charge storage

✓ Pseudocapacitive charge storage = redox-based reactions but « looks like » capacitive (meaning of the prefix « pseudo »)



Current collector

RuO_2 (pseudocapacitive material)

✓Surface adsorption of electrolyte cations

&

✓Fast reversible redox reactions at the surface of active materials

Adapted from: *J. W. Long, D. Bélanger, T. Brousse, W. Sugimoto, M. B. Sassin, O. Crosnier, MRS Bulletin 36, 513-522 (2011).*

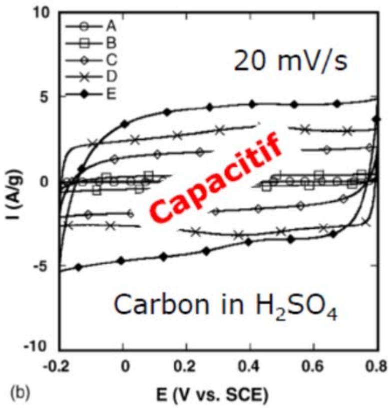
Journal of The Electrochemical Society, 162 (5) A5185-A5189 (2015)

JES FOCUS ISSUE ON ELECTROCHEMICAL CAPACITORS: FUNDAMENTALS TO APPLICATIONS

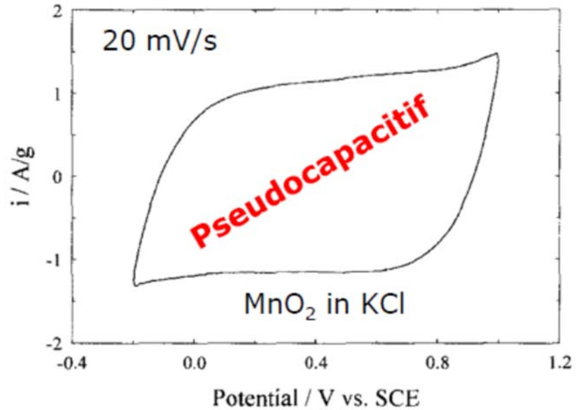
To Be or Not To Be Pseudocapacitive?

Thierry Brousse,[a,b,*,z] Daniel Bélanger,[c,*] and Jeffrey W. Long[d,*]

$Q = C \times \Delta U$ C is a constant all over ΔU



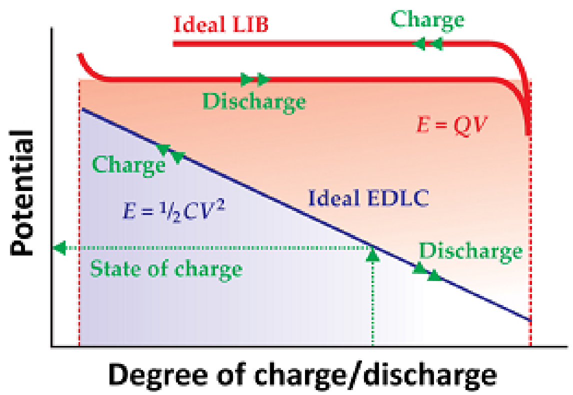
Mathieu Toupin et al, Journal of Power Sources 140 (2005) 203–210

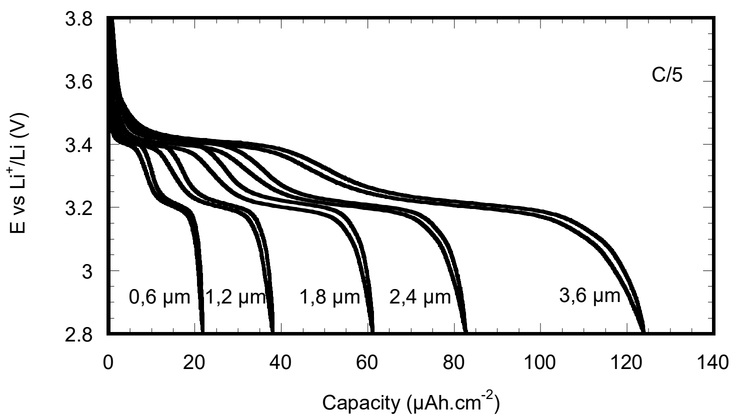


H.Y. Lee, J.B. Goodenough, J. Solid State Chem., ***144,*** *220 (1999).*

Faradaic charge storage

- ✓ Faradaic charge storage = process of charge storage based on redox reactions involving all the active mass of reactants (bulk process) : Ox + n ē ⇔ Red;
- ✓ Electrochemical intercalation reaction: MOy + x ē + x Li^+ ⇔ Li_xMOy
- ✓ Performance of a cell (or battery) will be determined by i) the kinetics of charge-transfer process and solid-state diffusion at each electrode ii) the nature and magnitude of structural changes
- ✓ Q= specific capacity = Delivered charge for a given mass of reactant (m) = (nF. m)/(3600.Molar mass) Ah.kg^{-1} or mAh g^{-1}. (Q = i t) , For thin films materials: areal capacity: µAh cm^{-2}; µAh cm^{-2} $µm^{-1}$; Specific energy = Q . V = Wh kg^{-1}





Courbes de décharge-charge de films de V_2O_5 orientés «*h00*» déposés sur titane par sputtering. Epaisseur: 0,3 µm à 6 µm; Electrolyte PC-$LiClO_4$.
C. Navone, R. Baddour-Hadjean, J. P. Pereira-Ramos, R. Salot, J. Electrochem. Soc., 153 (2006) A2287

II. Electrochemical Energy Storage Microdevices

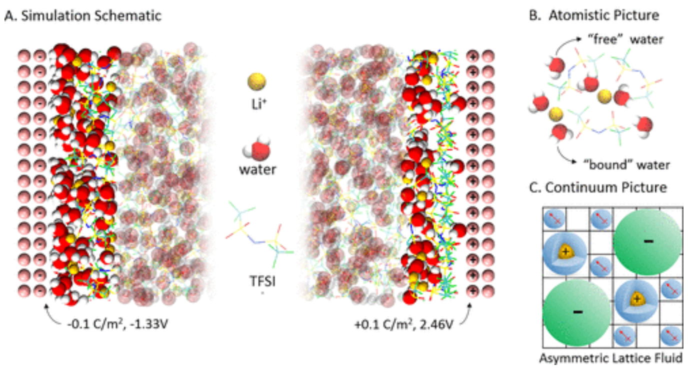
2. Simulations : coupling between ions, electrons, time scale

Benjamin Rotenberg, simulations

II. Definition of microdevices for electrochemical energy storage

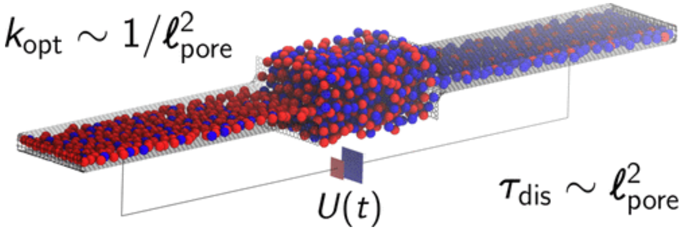
2. Modelling the relevant phenomena on the relevant length and time scales

Nanomaterials : realistic vs model structure, insulating vs metallic, rigid vs flexible…
Processes : ion transport, solvation, electron transfer… from Å&ps to µm&µs and beyond
Models : ab initio and classical molecular simulation, mescoscopic models, continuum theory
Questions : how to optimize energy/power density ? new concepts ?



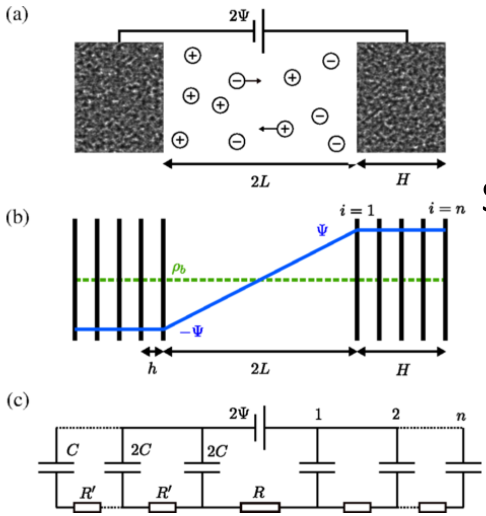
Theory of the Double Layer in Water-in-Salt Electrolytes

J. Phys. Chem. Lett. 2018



Charge Me Slowly, I Am in a Hurry: Optimizing Charge–Discharge Cycles in Nanoporous Supercapacitors

ACS Nano 2018



Blessing and Curse: How a Supercapacitor's Large Capacitance Causes its Slow Charging

PRL 2020

@International : Kornyshev (UK), Bazant (USA), Holm (DE), van Roij (NL)…

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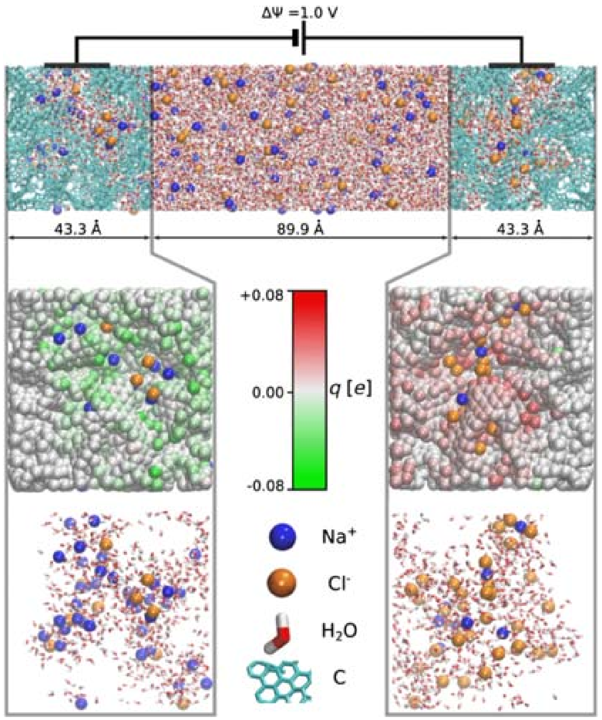
II. Definition of microdevices for electrochemical energy storage

2. Modelling the relevant phenomena on the relevant length and time scales



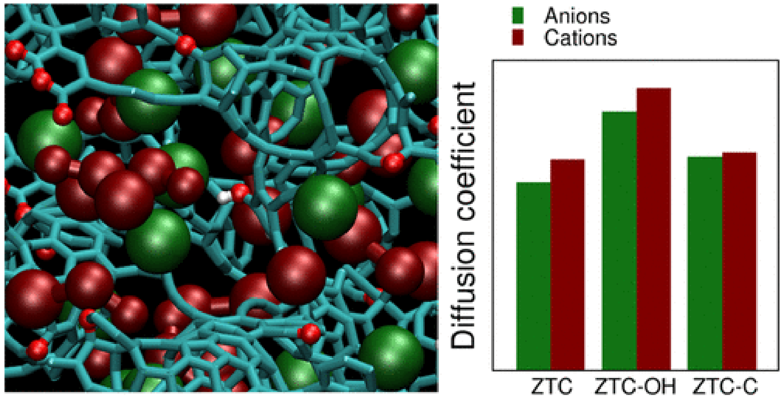
Blue Energy and Desalination with Nanoporous Carbon Electrodes: Capacitance from Molecular Simulations to Continuous Models

Michele Simoncelli,[1,†] Nidhal Ganfoud,[2] Assane Sene,[3,4] Matthieu Haefele,[1] Barbara Daffos,[3,4] Pierre-Louis Taberna,[3,4] Mathieu Salanne,[1,2,4] Patrice Simon,[3,4] and Benjamin Rotenberg[2,4,*]

Phys. Rev. X 2018

MetalWalls: A classical molecular dynamics software dedicated to the simulation of electrochemical systems

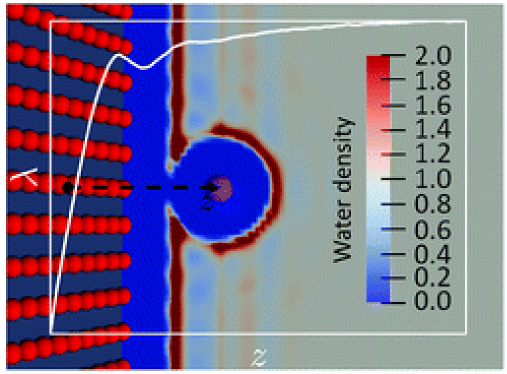
JOSS The Journal of Open Source Software https://gitlab.com/ampere2/metalwalls



Simulations of Ionic Liquids Confined in Surface-Functionalized Nanoporous Carbons: Implications for Energy Storage

El Hassane Lahrar, Irena Deroche, Camélia Matei Ghimbeu, Patrice Simon, and Céline Merlet*

ACS Appl. Nano Mater. 2021



A molecular density functional theory approach to electron transfer reactions

Guillaume Jeanmairet, *ab Benjamin Rotenberg, ab Maximilien Levesque, c Daniel Borgis cd and Mathieu Salanne abd

Chem. Sci. 2019

Lattice Boltzmann electrokinetics simulation of nanocapacitors

Adelchi J. Asta, Ivan Palaia, Emmanuel Trizac, Maximilien Levesque, and Benjamin Rotenberg

J. Chem. Phys. 2019

@NAME : PHENIX, CIRIMAT, PASTEUR…

ENERGIE RS2E

N A M e

GDR Nanomaterials for Energy Applications

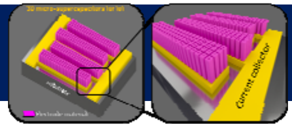
II. Electrochemical Energy Storage Microdevices

3. Link with Workshop 1: synthesis of nanomaterials

II. <u>Electrochemical Energy Storage Microdevices</u>

4. Surface/Volume ratio

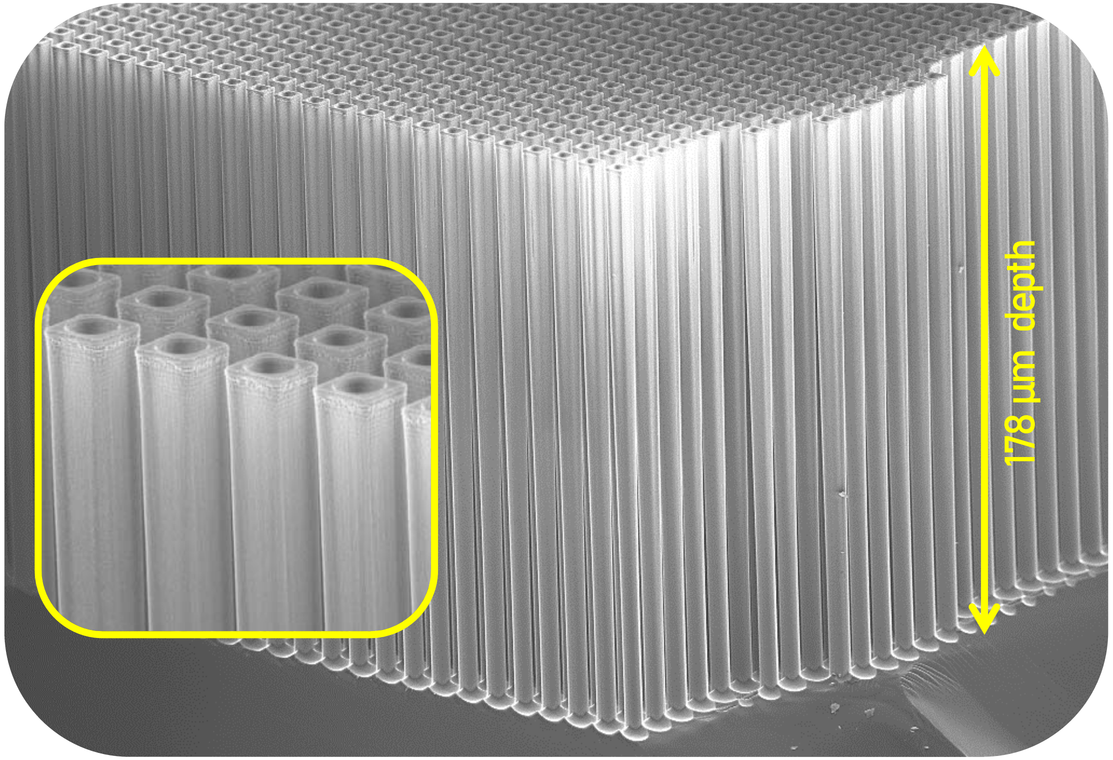
Surface/Volume ratio



Fabrication of 178 µm-depth Si micro-tubes in 2019

$$\mathbf{AEF} = \frac{\mathbf{S_{3D}}}{\mathbf{S_{2D}}}$$

AEF: Area Enlargment Factor (cm^2 developped by the 3D structure *vs* cm^2 of footprint area)

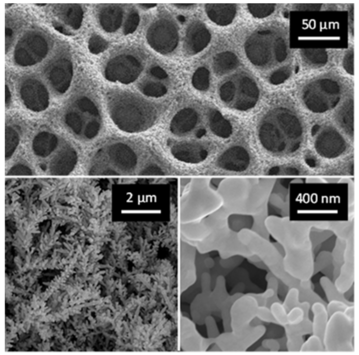


AEF ~ 70 (cm^2/cm^2 footprint area)

C. Lethien, J. Le Bideau, T. Brousse, *Energy Environ. Sci.*, 2019, 12, 96-115

Surface/Volume ratio

- **Benefits of porous electrodes for microbatteries and microsupercapacitors** (D. Pech)



Porous current collectors using the *dynamic H_2 bubble templating* (Cu, Pt, Au, Ti, Ru…)

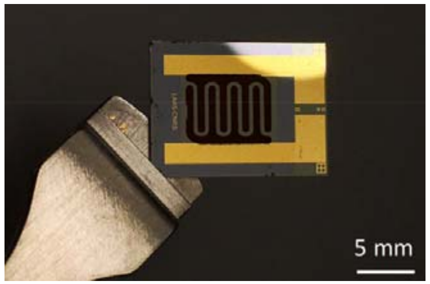
→ AEF up to 10 000 cm²/cm²

Active material electrodeposition

Energy (3D) = AEF x Energy (2D)

	Electrode	Areal performance	Lifetime	Ref.
microbattery	Porous SnAu anode	7.3 mAh/cm² (at C/10)	up to 6000 cycles (at 3C)	Sci. Rep. 10, 1045 (2020)
microbattery	Porous Prussian blue cathode	~ 650 µAh/cm² (at C/5)	up to 2000 cycles	Small (2021)
	Porous pseudocapacitive material (RuO_x-based)	14.3 F/cm²	> 5000 cycles	ACS Energy Lett. 6, 131 (2021)

- Low T process (IC-compatible)
- High areal capacity / capacitance
- High cyclability



Interdigitated all-solid-state micro-supercapacitor before electrolyte deposition and encapsulation.

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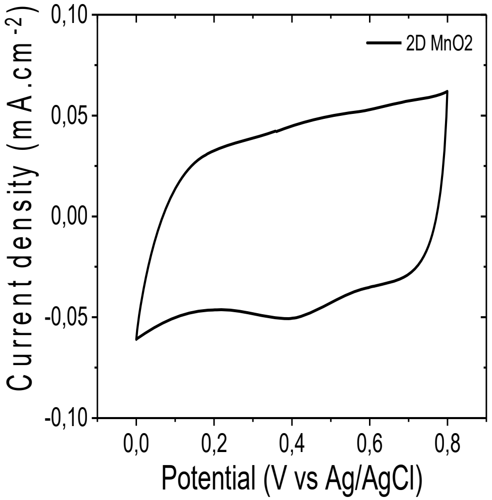
Surface/Volume ratio

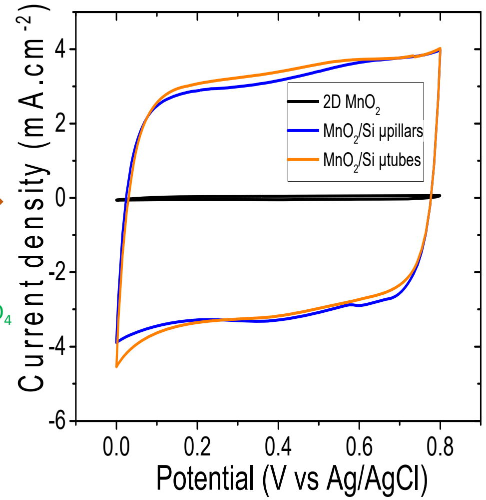
E. Eustache, et al. *Adv. Energy Mater.* Sept **2015**, Vol.5(18).

MnO$_2$ 2D deposition

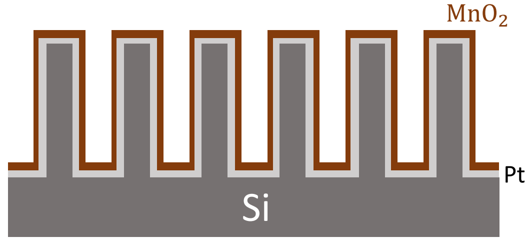


2D vs 3D

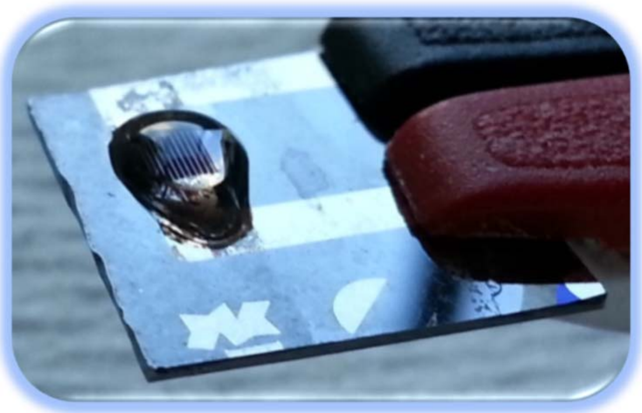
Scan rate : 5 mV/s
CV (3rd cycle) in Na$_2$SO$_4$ (0.5 M)



MnO$_2$ 3D deposition



Electrochemical analysis in 0.5M Na$_2$SO$_4$



Merit Criteria

II. Electrochemical Energy Storage Microdevices

5. Merit Criteria : energy efficiency, time response,self-discharge,…, durability (charge/discharge cycle number)

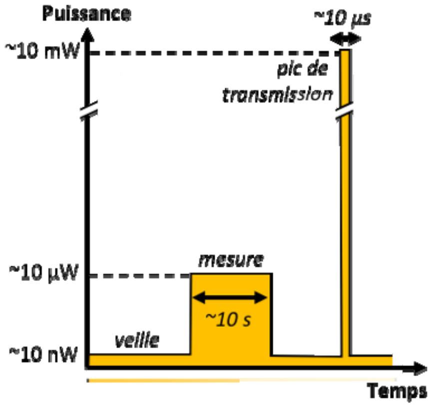
David Pech (LAAS): Merit Criteria for energy storage microdevices

For WSN and IoT applications

(microbatteries and/or micro-supercapacitors)

→ **High areal energy** (per footprint area)

→ **High areal power**
(short pulses required
for RF data transmission)



Typical energy consumption profile of a connected object.

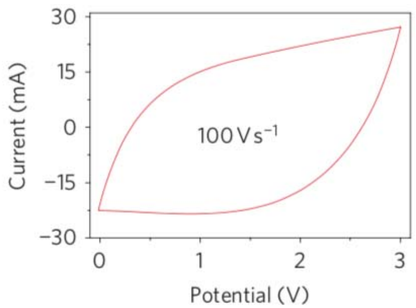
→ **High Cyclability** (maintenance-free for "Fit and Forget" applications)

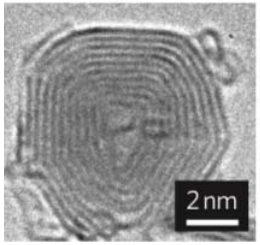
For ac line-filtering applications

(mostly micro-supercapacitors for replacement of traditional electrolytic capacitors)

→ **Ultrahigh-Power**

- RC time constants < 1 ms
- Capacitive behaviour at high frequencies (impedance phase angle close to -90° at 120 Hz ac)
- Ultrahigh scan rate ability (> 100 V/s)





Ex. *Onion-Like-C based micro-supercapacitors*

(D. Pech et al., Nat. Nanotechnol. 5, p. 651, 2010)

→ **Reliability** (have to sustain <u>millions of cycles of charge/discharge</u> without any failure)

Other performance charateristics: size, cell voltage, cyclability, ability to sustain low/high T, specific power, self-discharge, all-solid-state, specific energy, specific power, cost…

II. Electrochemical Energy Storage Microdevices

6. Characterization techniques

Pascal Roussel (UCCS) : Characterization techniques

"Usual" characterization techniques for nanomaterials with the same "problems" of limited amount of material, contrast between thin films and substrate, or XRD peak broadening due to the small size of coherent domains…

✓ To overcome these problems, strong interest in coupling two or more techniques (complementarity) (e.g. SEM + TEM + TomoX), XPS + TOF-SIMS, XAS + EELS, XRD + RAMAN

✓ Strong propensity for *in situ* and/or *operando* studies (strong need for large instruments facilities especially synchrotron and also design of adapted cells)

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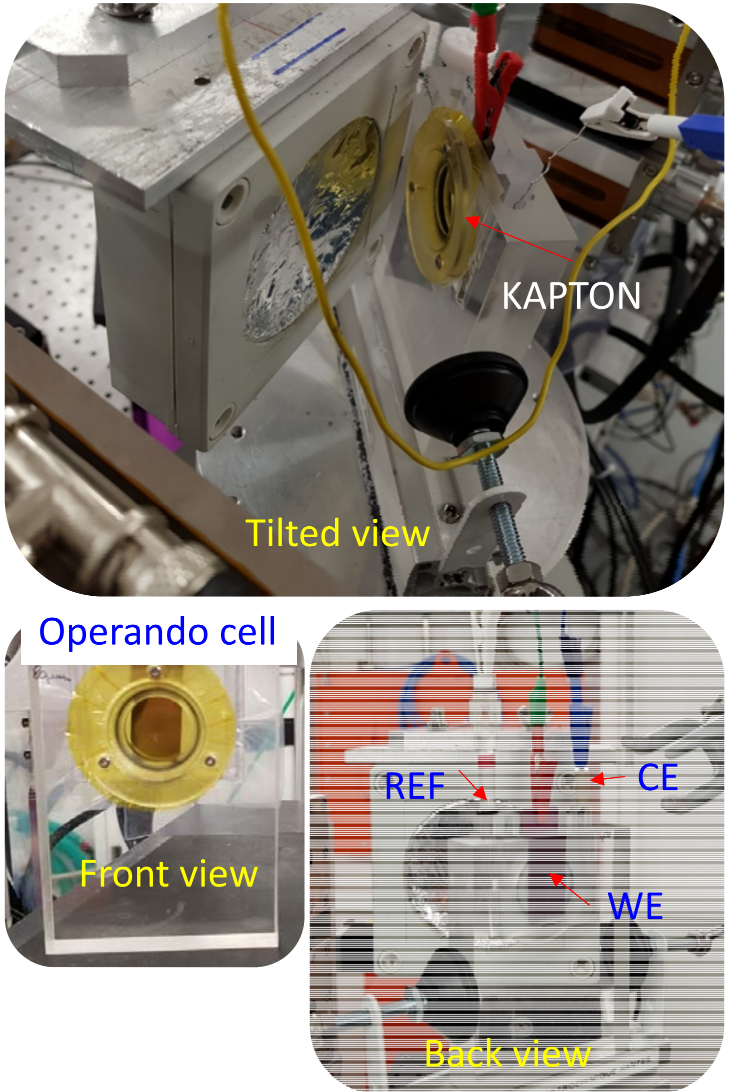
Cell Design for in-operando (Oxidation states evolution by quick EXAFS)



❖ <u>3 electrodes cell:</u> designed to investigate thin films at the V-K edge (IMN), RE = Hg/HgO and CE = Pt wire, WE = VN film on Silicon wafer

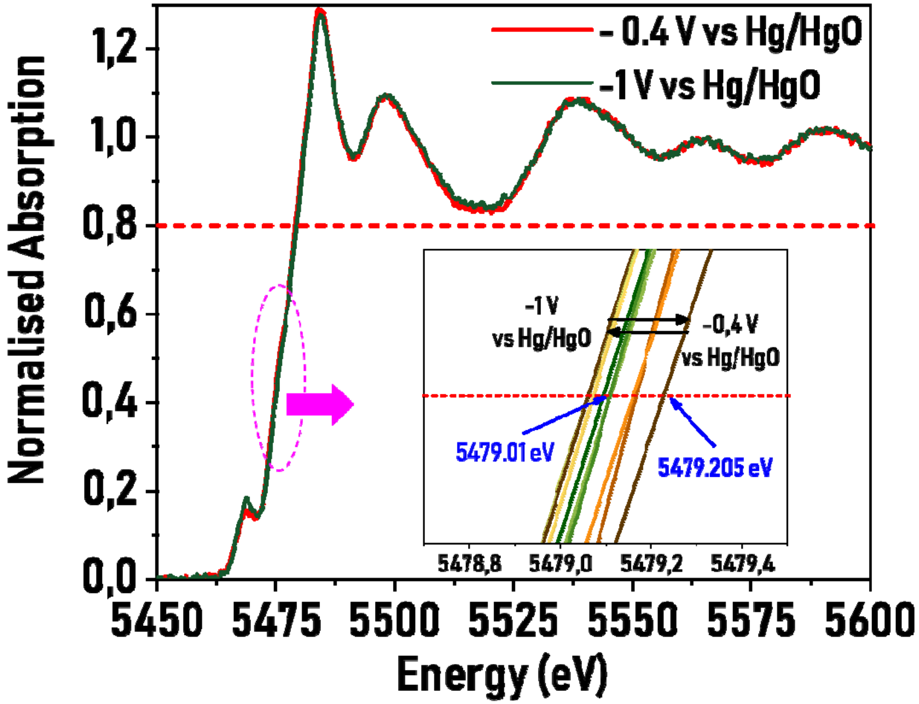
❖ Transmission means. not possible owing to the Si wafer ⇨ <u>Fluorescence measurement (reflexion)</u>

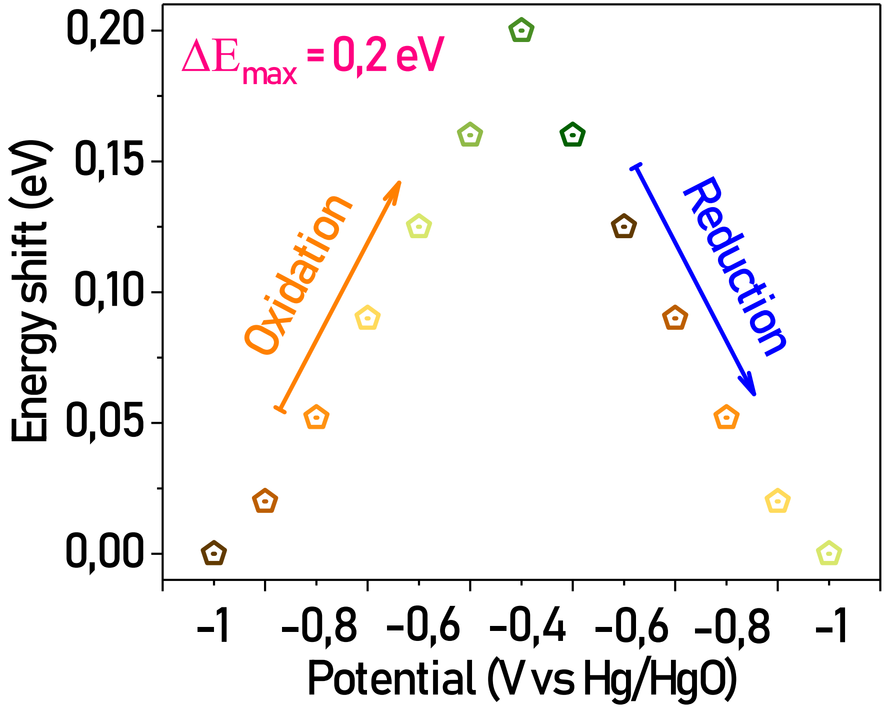
❖ <u>Issue:</u> find the best signal to noise ratio ⇨ maximizing the VN mass loading while limiting the electrolyte thickness

Energy Environ. Sci., 2020,**13**, 949-957

Cell Design for in-operando (Oxidation states evolution by quick EXAFS)

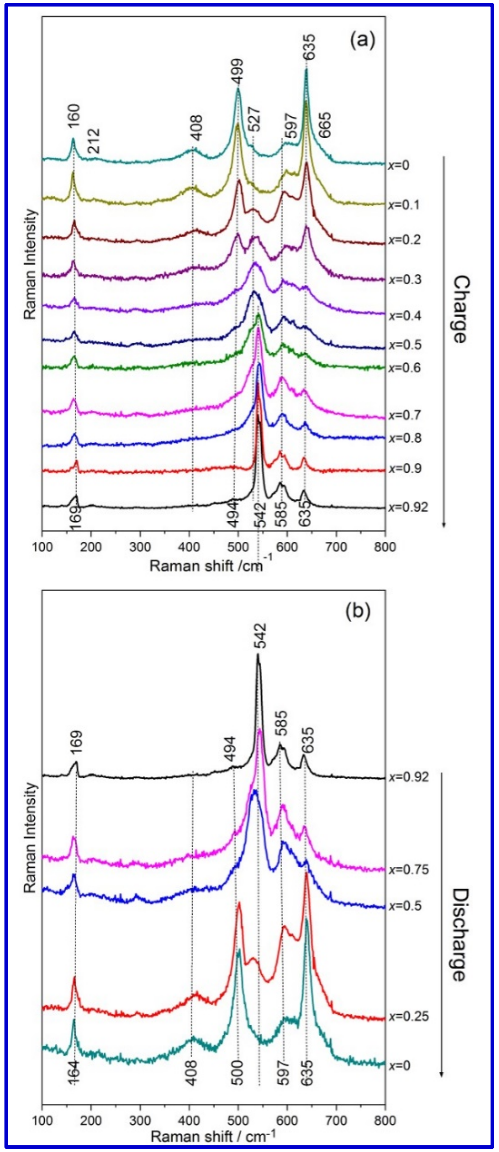
Analyses performed on 1 µm-thick VN thin film in KOH 0.5 M



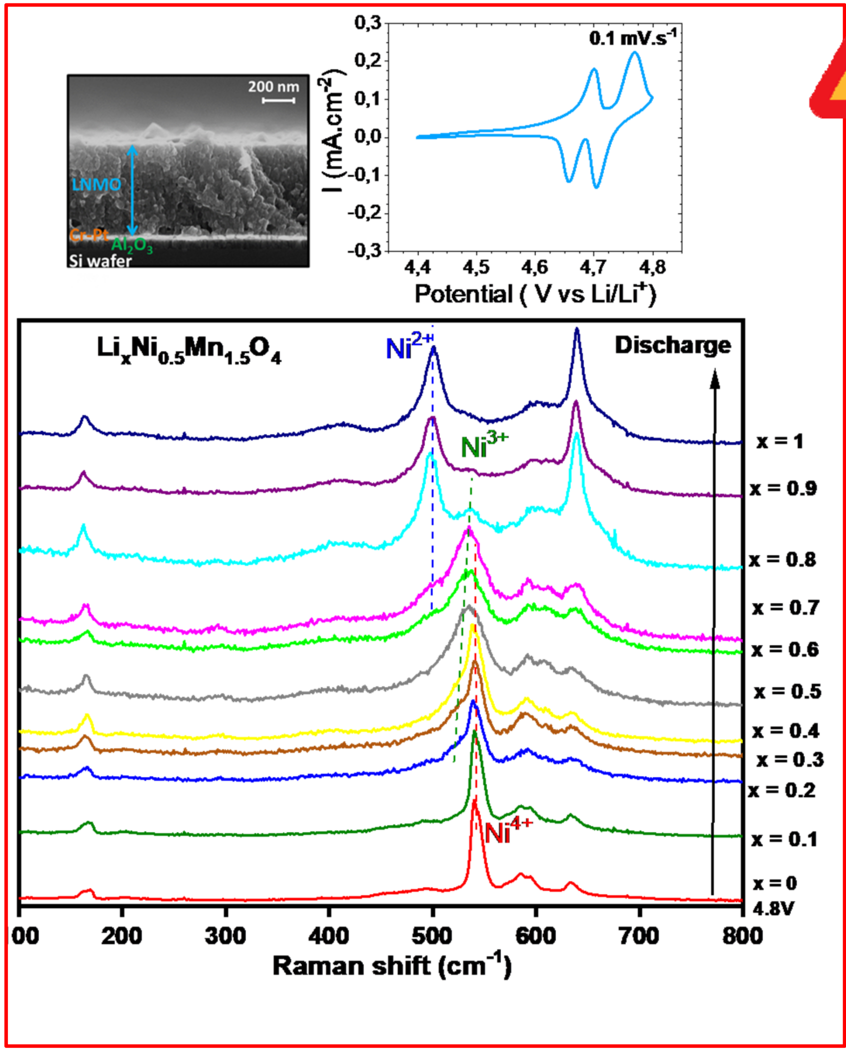


- ❖ Shift of the absorption edge upon charge/discharge cycles
- ❖ Combined TOF-SIMS / XPS analyses to check the presence of oxides vs nitrides

Ex-situ Raman study of the Li extraction/insertion mechanism in thin films electrodes : the LNMO case



Composite electrode versus thin film



It is sometimes better to make good *ex-situ* rather than poor operando

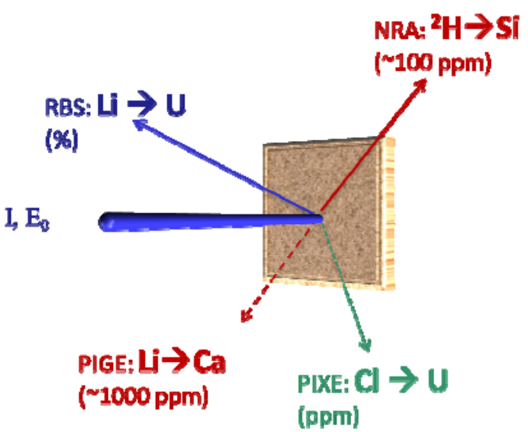
- Modification of the Ni-O bond strength directly related to the change in the Ni valence state.
- Quantitative estimation from Raman spectra of the Ni^{2+}, Ni^{3+} and Ni^{4+} relative amounts, very consistent with the electrode SOC.
- Raman spectroscopy is a fast, reliable and quantitative probe of SOC and self-discharge phenomenon in the LMNO cathode.

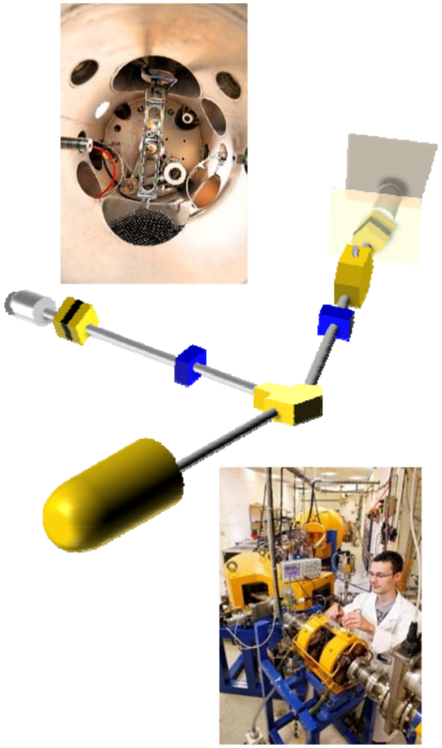
*- A. Bhatia, Y. Dridi, J. P. Pereira-Ramos, R. Baddour-Hadjean, J. Mater. Chem. A, (**2021**) just accepted.*

- A. Bhatia, , C. Leviel, M. Hallot, J. P. Pereira Ramos, Ch. Lethien, R. Baddour-Hadjean, P. Roussel, to be submitted

Ion beam Analysis applied to electrochemical devices
(NIMBE/LEEL) Hicham KHODJA, Mathieu PINAULT

Principle of Ion Beam Analysis

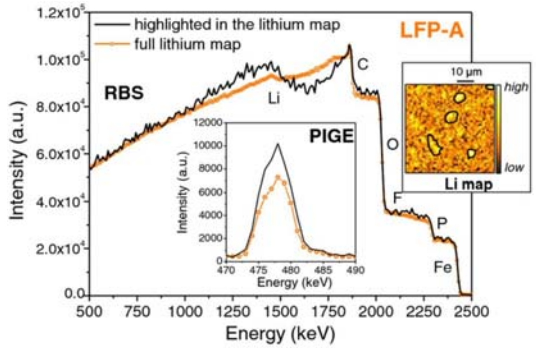


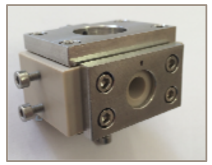


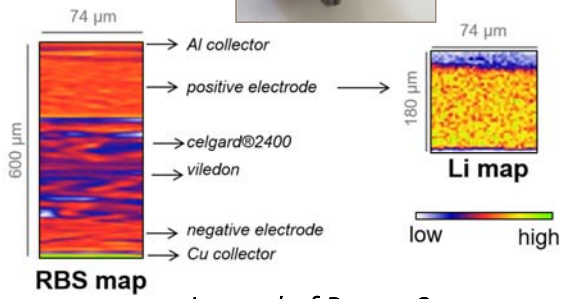
- ✓ Absolute quantification of all elements (H→U)
- ✓ Specific Sensitivity for light element
- ✓ Spatial Resolution ~ (µm x µm x 0,1 µm)

Application for Batteries

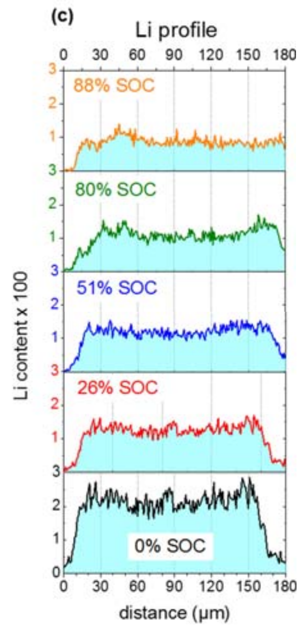
Journal of The Electrochemical Society, 164 (14) A3538-A3544 (2017)







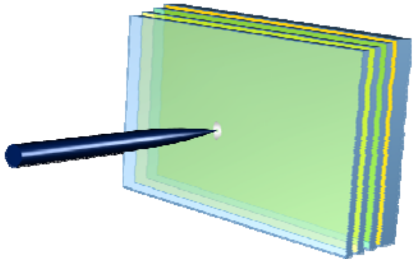
Journal of Power Sources 393 (2018) 37–42

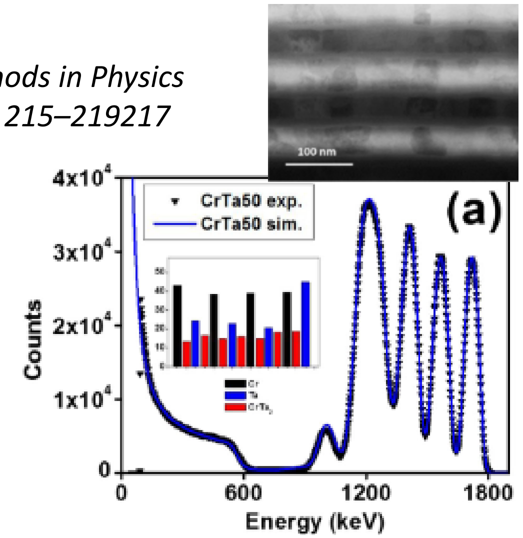


Ion beam Analysis applied to electrochemical devices
(NIMBE/LEEL) Hicham KHODJA, Mathieu PINAULT

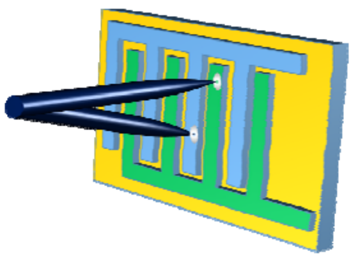
Possible Inputs for microbatteries-type devices

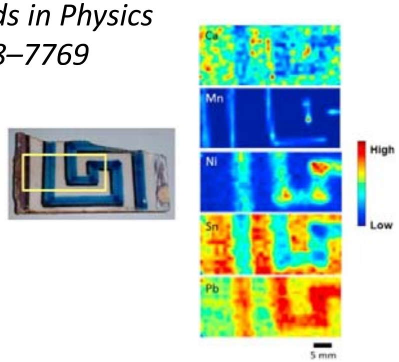
Nuclear Inst. and Methods in Physics Research B 450 (2019) 215–219217



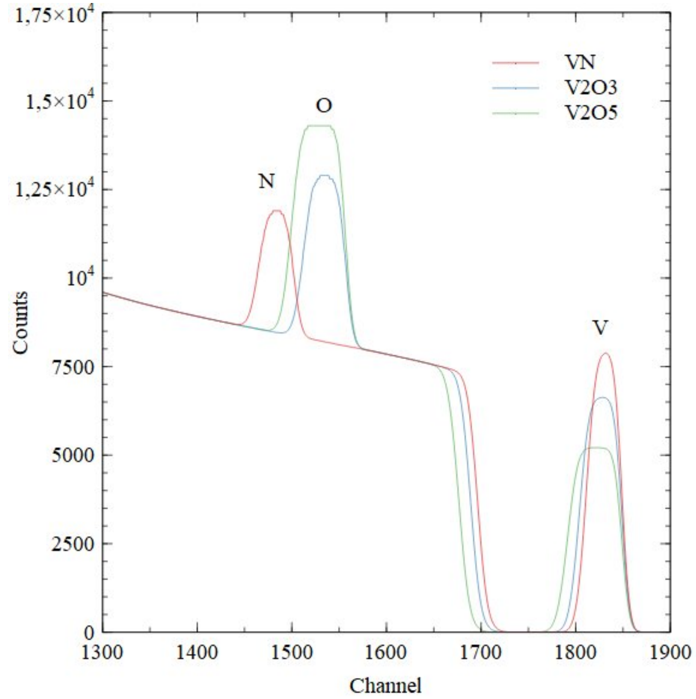


Nuclear Inst. and Methods in Physics Research B 422 (2018) 68–7769





VN (300 nm) → V_2O_3, V_2O_5



- ✓ Fast and easy determination of stoichiometry V, N, O.
- ✓ *Operando possible*

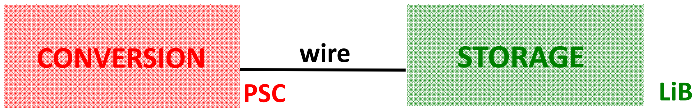
II. <u>Electrochemical Energy Storage Microdevices</u>

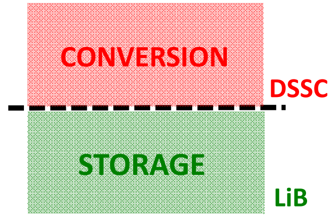
7. EESM and coupling with other micro/nanodevices

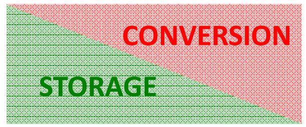
Christel LABERTY-ROBERT, Natacha KRINS and Jeremy SUM (LCMCP)

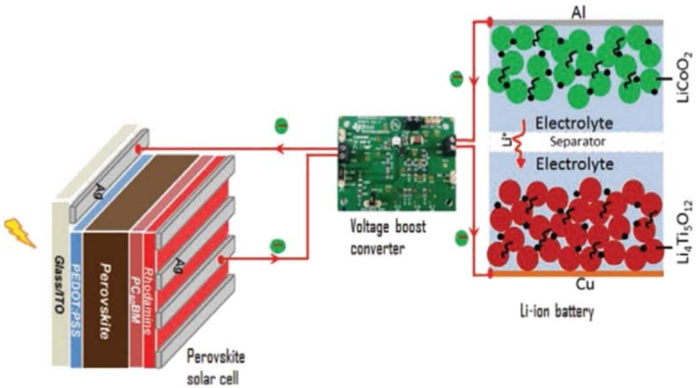
ii. Last trends in the domain : **Energy conversion & Li-ion battery storage**

Conventional coupling — *Advanced coupling*

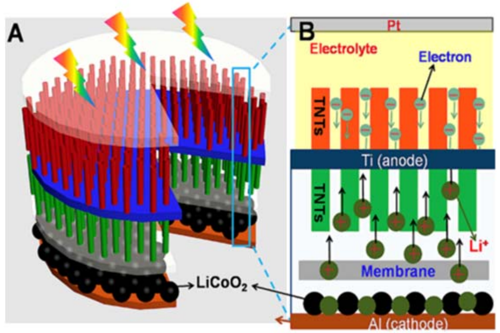




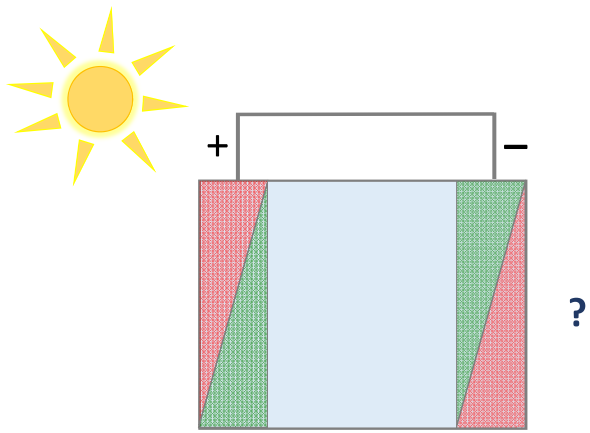




Gurung et al., Adv. Energy Mater. ***2017****, 7, 1602105*



Guo et al., Nano Lett. ***2012****, 12, 5, 2520*

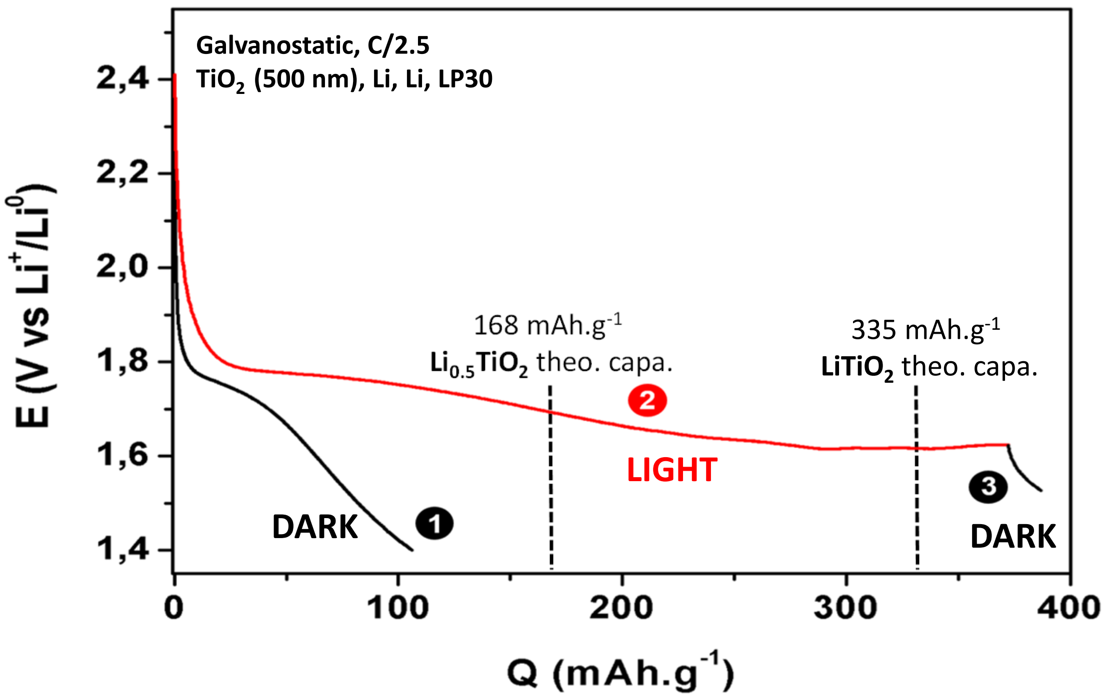


Bifunctional Li-ion battery electrodes

N A M e
GDR Nanomaterials for Energy Applications

Christel LABERTY-ROBERT , Natacha KRINS and Jeremy SUM (LCMCP)

iii. Where is the GDR NAME in this state of the art : Photo-sustained discharge



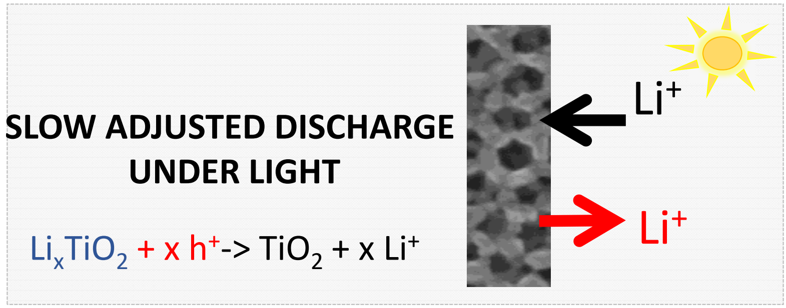


PHOTO-SUSTAINED DISCHARGE

Intensity of photo-charge : **8 µA**

=> Recharge: ~ **4h30** ($Li_{0,5}TiO_2 \rightarrow TiO_2$)

*Nguyen et al, **2017**, J. Mater. Chem. A, 5, 5927–5933*

iV. Position of nanomaterials (if applicable)

Control of the electrode architecture to harvest light and charges recombination/separation (crystallite size grain boundaries, interfaces,..)

II. Electrochemical Energy Storage Microdevices

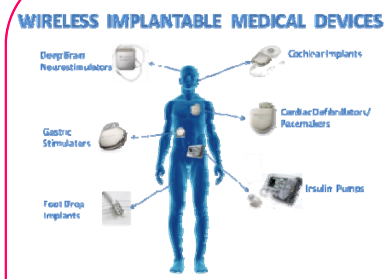
8. Ongoing applications and future uses

Christophe Lethien : Powering the Internet of Things (IoT) (IEMN)

IoT = world-wide network of interconnected objects

WSN: Wireless Sensors Network

➡ Monitor the environnement and transmit data

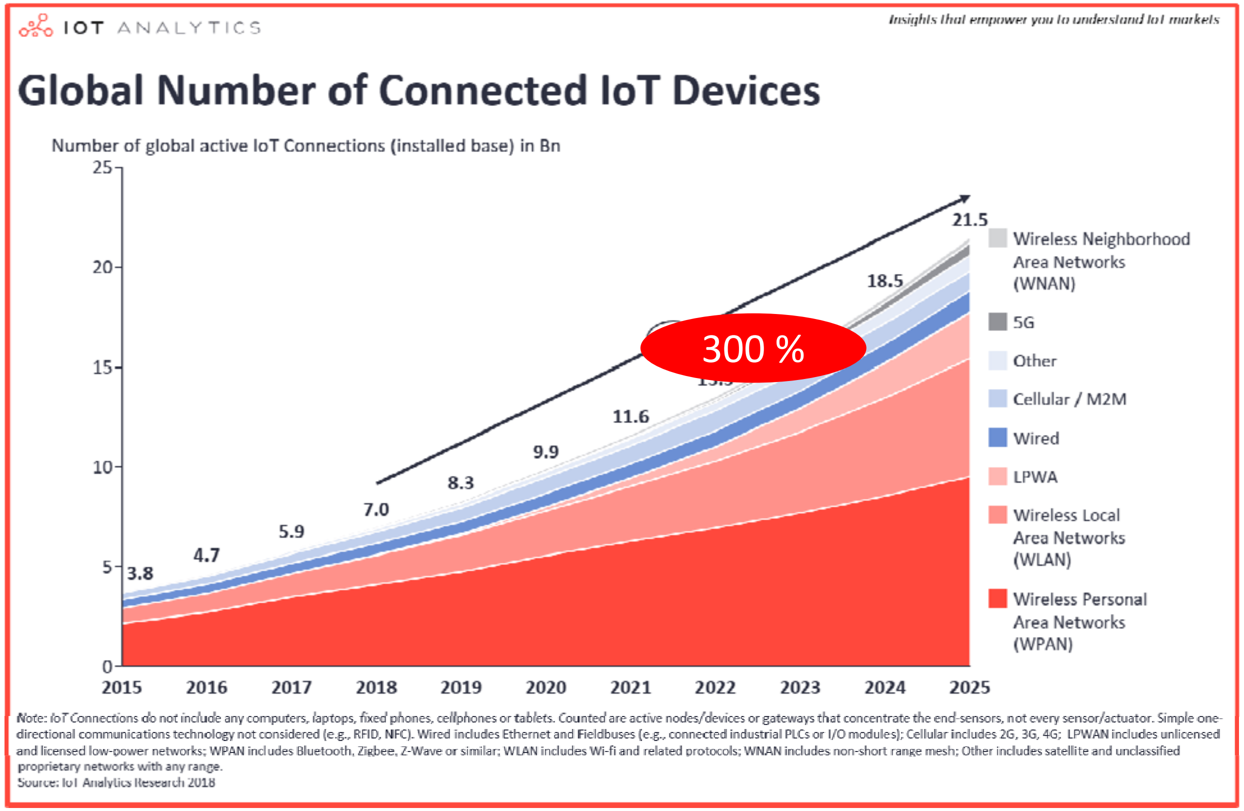


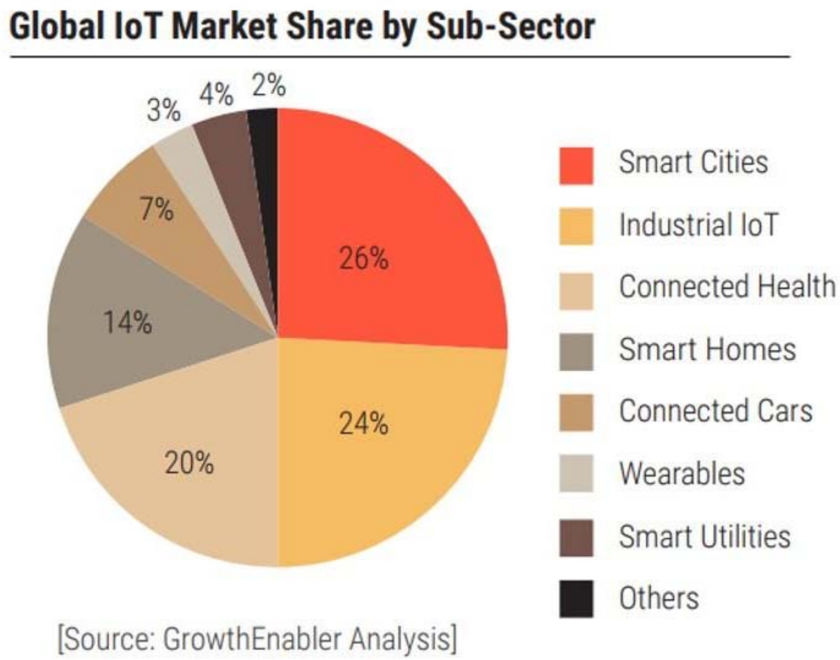
Healthcare IoT (drug delivery, health monitoring…)

Structural Health monitoring

Environmental monitoring (agriculture monitoring, food quality monitoring, animal tracking, …)

Market analysis and fields of use





- 2018 – 2025: ↗ 300 % of connected sensors
- 70 % of IoT applications in smart cities, Health and industrial fields

Power sources for Internet of Things (IoT)

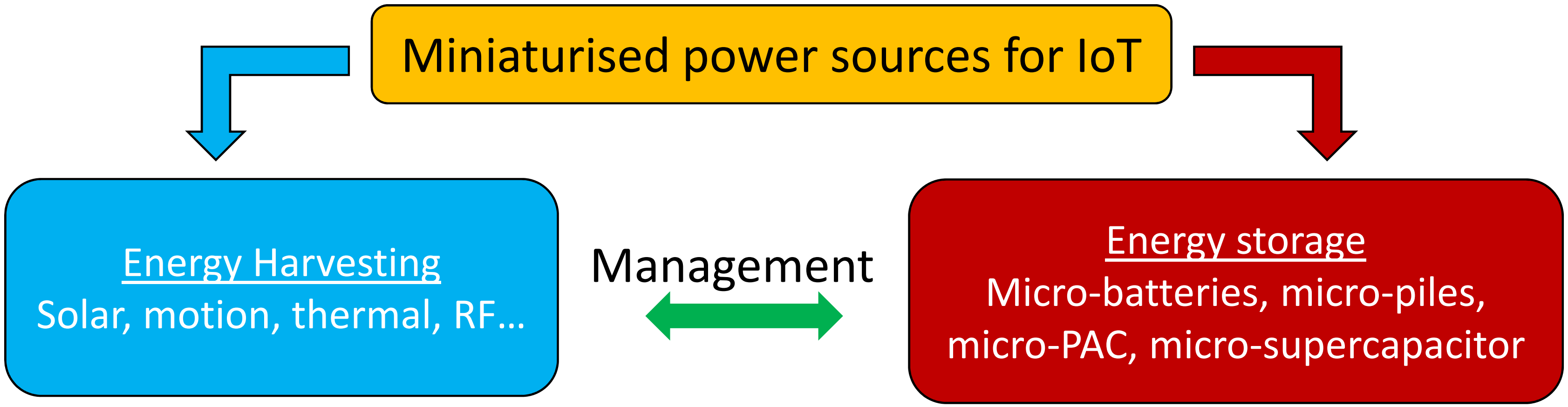
B3130 *Journal of The Electrochemical Society*, **165** (8) B3130-B3136 (2018)

JES Focus Issue on Ubiquitous Sensors and Systems for IoT

Review—Power Sources for the Internet of Things

Abhi Raj[1,2] and Dan Steingart[2,3,*,z]

[1]*Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544, USA*
[2]*Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey 08544, USA*
[3]*Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544, USA*



Combination between multi-energy harvesting sources

with multi-energy storage devices

Aline Rougier (ICMCB) : IoT

Example : Activation of an Electrochromic Display

Battery

Electrochromic Display

ENERGY

Ynvisible's displays have the lowest energy consumption on the market for most use-cases. For static usage (when the display maintains the same image) the display consumes a maximum of 0.28 µW per cm^2 segment area. For dynamic usage, the power consumption depends on the number of display updates per day according to the formula below.

Power calculation

$P = 0.28 + 0.01 \times n$ µW/cm^2

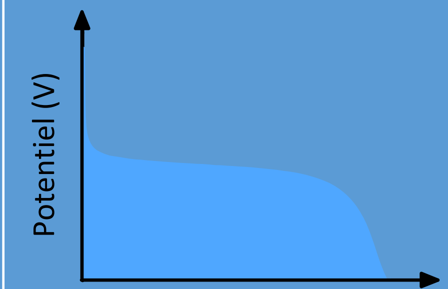
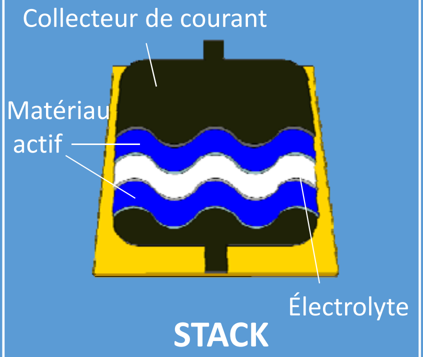
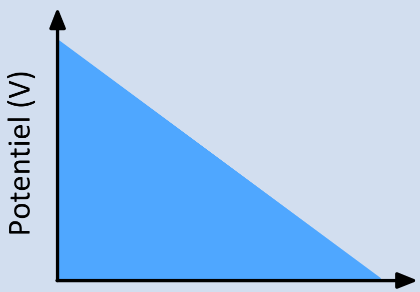
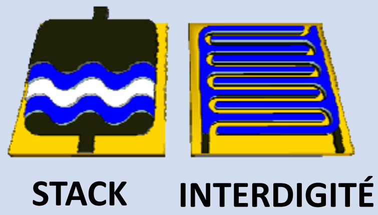
n is the number of full display updates per day

NAME
GDR Nanomaterials for Energy Applications

II. Electrochemical Energy Storage Microdevices

9. Comparison with existing commercial microdevices

Electrochemical Energy Storage Microdevices

Micro-batterie	**Profil de décharge** 	**Configuration** 	**Performances:** **100-10000 cycles de charge décharge** **1-10 mWh/cm²** **1-10 mW/cm²**
Micro-supercondensateur	Profil de décharge 		Performances: 10000-1000000 cycles de charge décharge 1-100 µWh/cm² 10-1000 mW/cm²

NAMe
GDR Nanomaterials for Energy Applications

III. Micro-batteries (Li, Li-ion, Zn-ion,other chemistries):

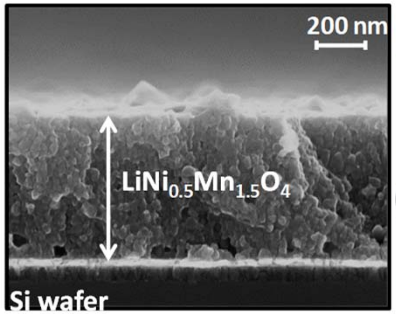
1. Electrodes
2. Electrolyte
3. Design/components

Baddour-Hadjean Rita, Pereira-Ramos Jean-Pierre (ICMPE)
Li, Li-ion, Zn-ion Microbatteries

Advantages of studying 2D electrodes thin films:

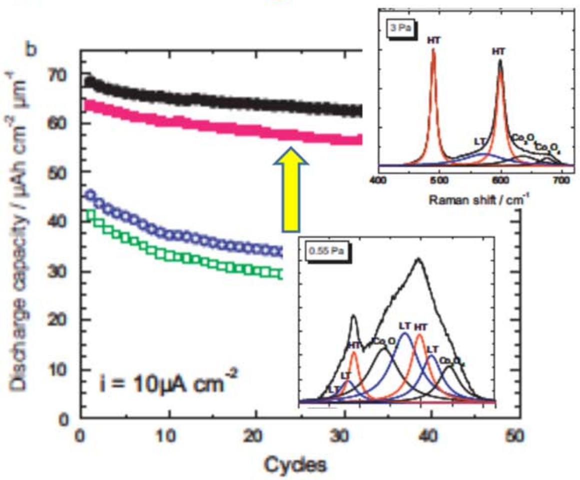
- Access to the intrinsic material properties (pure thin film ≠ composite)
- Nanosize effect, preferential orientation influence the electrochemical performance
- Raman spectroscopy is very sensitive to nanostructured materials (≠ DRX):

- In the starting material : defects, impurities, secondary inactive phases…
- In the operating electrode material : new electroformed phases, new Li-O bonds, change in M-O bond strength…



ICMPE · ANR Agence Nationale de la Recherche · iemn · UCCS

Efficient and quantitative probing of (active) and cubic (inactive) phases in $LiCoO_2$ thin films



Electrochimica Acta
Volume 60, 15 January 2012, Pages 121-129

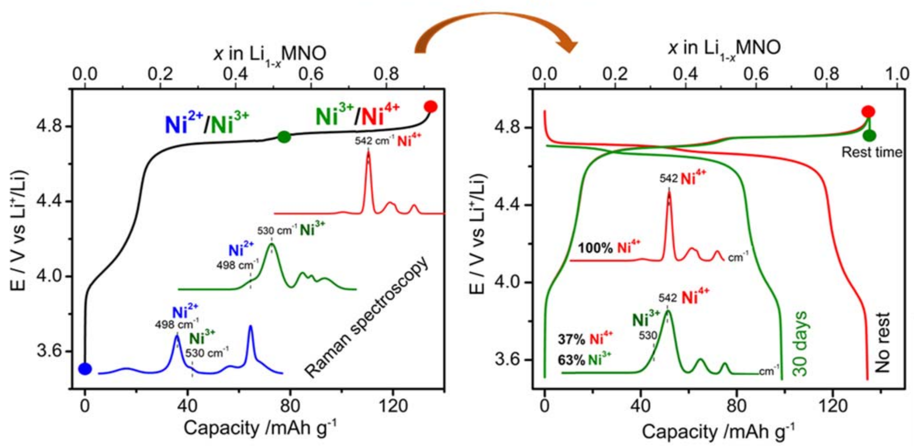
High performance sputtered $LiCoO_2$ thin films obtained at a moderate annealing treatment combined to a bias effect

Sophie Tintignac, Rita Baddour-Hadjean, Jean-Pierre Pereira-Ramos, Raphaël Salot

ICMPE · liten ceatech

Fast, reliable and quantitative probe of SOC and self-discharge in the LMNO thin film cathode

J. Mater. Chem. A HOT Papers, 2021, Doi: 10.1039/D1TA00




Baddour-Hadjean Rita, Pereira-Ramos Jean-Pierre (ICMPE)

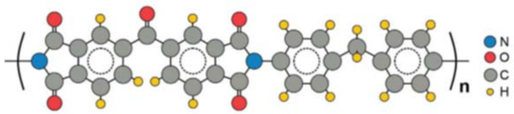
Li, Li-ion, Zn-ion Microbatteries

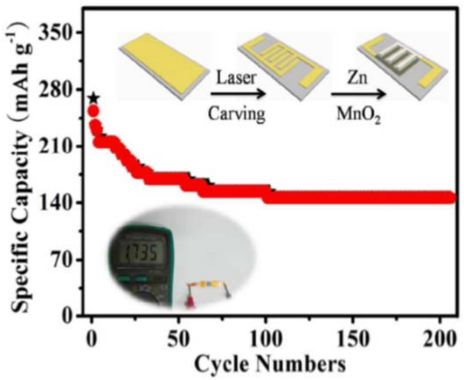
Microbatteries beyond Li-ion: last trends in the domain

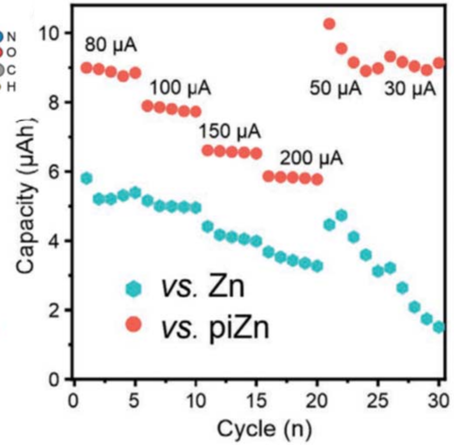
- Essentially microbatteries with Zn as negative
- Aqueous electrolyte ZnSO4 /Zn(CF3SO3)2 2M pH4
- Gel electrolyte (PVA, PAM...); good electrochemical stability 2.3V; good ionic conductivity (a few 10^{-2} S/cm)
- Positive electrode: MnO_2 (electrodeposited, hydrothermal), PANI, VO_2 (B), $Na_2V_6O_{16}$ nH_2O (hydrothermal)
- Negative electrode : electrodeposited Zn
- 30 µAh/cm^2 (PANI) to 300 µAh/cm^2 (VO_2); voltage 1.4–1V ; 0.7 V for VO_2(B)
- Interest to develop organic medium; optimistic results on Zn behavior!

Aqueous microbattery : Improvement of Zn cycling by protection with polyimide layer (300-500 nm spin coating+UV+220°C), pH4
Electrodeposited MnO_2 /$ZnSO_4$ 2M + Polyacrylamide (PAAm)//Zn electrodeposited ; capa 14 µAh 60% capacity retention over 1000 cycles; interdigited electrodes
M. Zhu et al, Adv. Mater. 33 (2021) 2007497

Aqueous microbattery: MnO_2-Zn
MnO_2/$ZnSO_4$ 2M+0.1M $MnSO_4$/Zn Electrodeposits (0.23mg/cm^2 on gold)
Substrates laser etching; 1.4V ; 58 µAh/cm^2(100 µA/cm^2); interdigited electrodes
280mAh/g BUT -50% fade after 50 cycles (MnO_2 dissolution)
compete with ARZIBs
A G. Sun et al 2013, J Mat Chem. 6 (2018) 10926



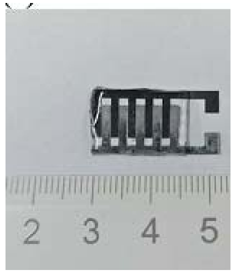


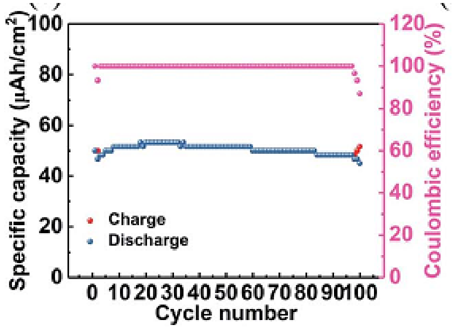


NAME
GDR Nanomaterials for Energy Applications

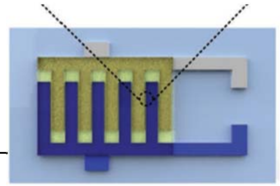
Baddour-Hadjean Rita, Pereira-Ramos Jean-Pierre
Li, Li-ion, Zn-ion Microbatteries

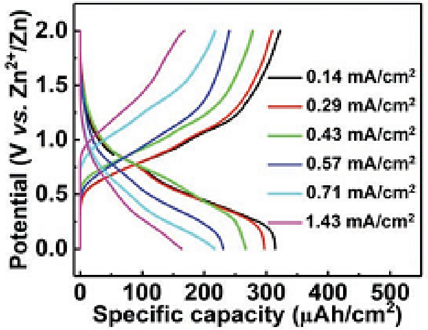
Microbatteries with gel electrolyte
MWCNT-MnO_2 hydrothermal/hydrogel $ZnSO_4$-PAM-$MnSO_4$/MWCNT-Zn
+ : deposited slurry **-** : electrodeposited Zn nanoflakes;interdigited electrodes; laser carving ;
Flexible PU substrate; E = 1.2V ; 116 µAh/cm^2 (at 100 µA/cm^2) ;
Power 0.1-0.3 mW/cm^2 ; Energy 58-12 µWh/cm^2
50 Cycles at 50 µAh/cm^2 (1 mA/cm^2 ; 1.9V-0.8V); 96 % retention after 100 cycles
X. Du et al Sustainable Energy Fuels 4 (2020) 4173-4721

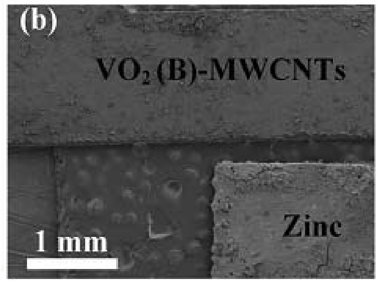




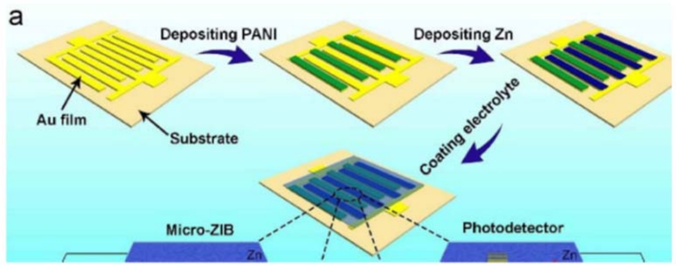
Microbatteries with gel electrolyte
VO_2 (B) MWCNT/hydrogel PVA-Zn(CF_3SO_3)$_2$/Zn electrodeposited nanoflakes -MWCNT
E = 0.7V; 314 µAh/cm^2; 188 µWh/cm^2; 0.6 mW/cm^2
Flexible PDMS (polydiméthylsiloxane) substrates
J. Shi et al Adv. Energy Mater. 9 (2019) 1901957

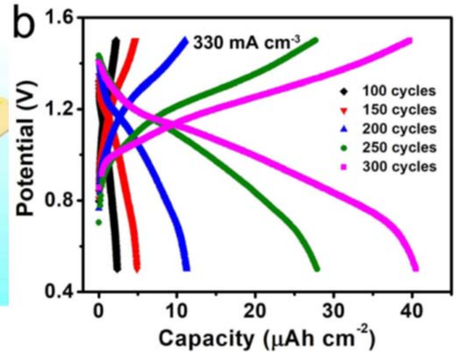

ZIMB





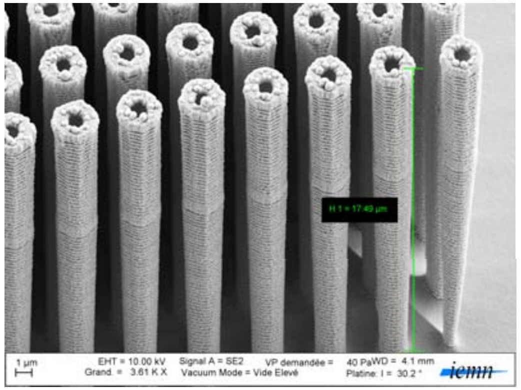
Microbatteries with gel electrolyte
PANI/PVA-Zn(CF_3SO_3)2/Zn ; electroplating of PANI and Zn on interdigited Au electrodes
Polymer gel electrolyte PVA-Zn(CF_3SO_3)$_2$; 10-30 µAh/cm^2; 1V;
High electrochemical stability of PVA-Zn(CF_3SO_3)$_2$: 2.3V ;
High ionic conductivity 3.67 10^{-2} S/cm
S. Bi et al ChemElectroChem 6 (2019) 3933-3939

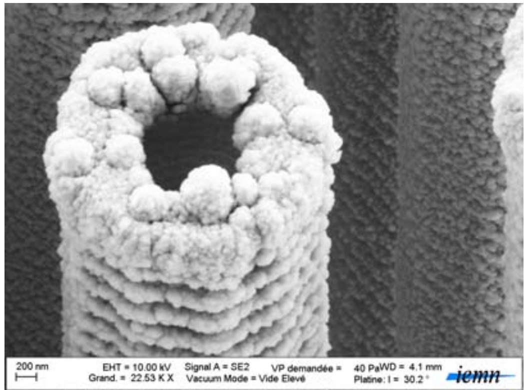




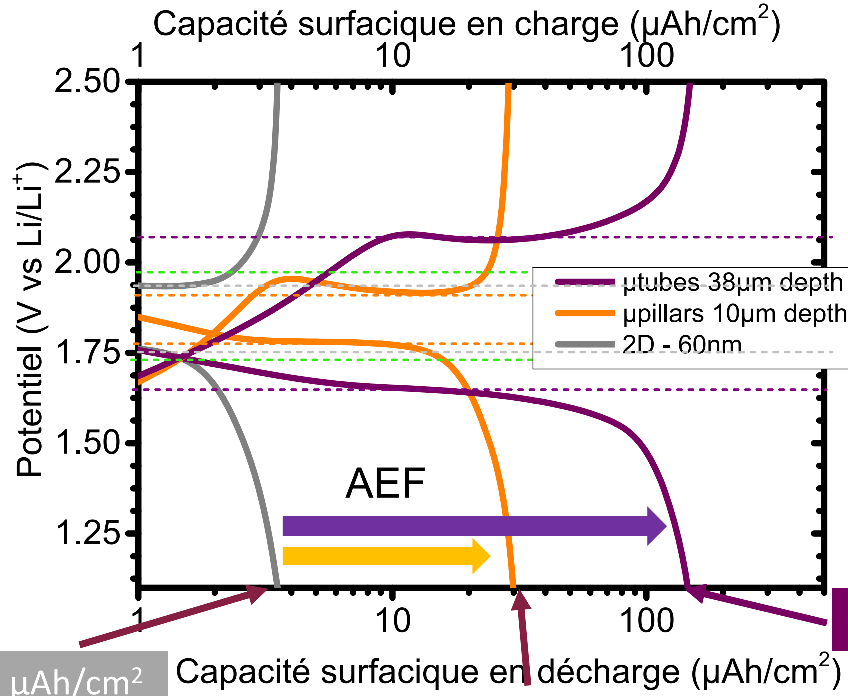
C. Lethien: high performance 3D on chip µ-batteries

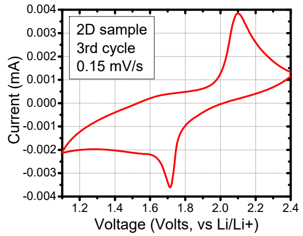
Continuous conformal deposition of materials on this 3D skeleton using only ALD





Negative TiO_2 electrode deposited by ALD





Electrolyte: 1M LiTFSI, EC/DEC 1:1

C rate ~ C/3

3D Tubes, 150 µAh/cm²

2D, 3.5 µAh/cm²

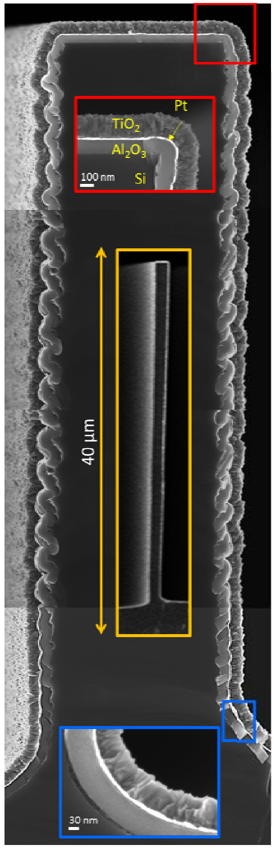
3D pillars, 30 µAh/cm²

max AEF # 30 (generation 1)

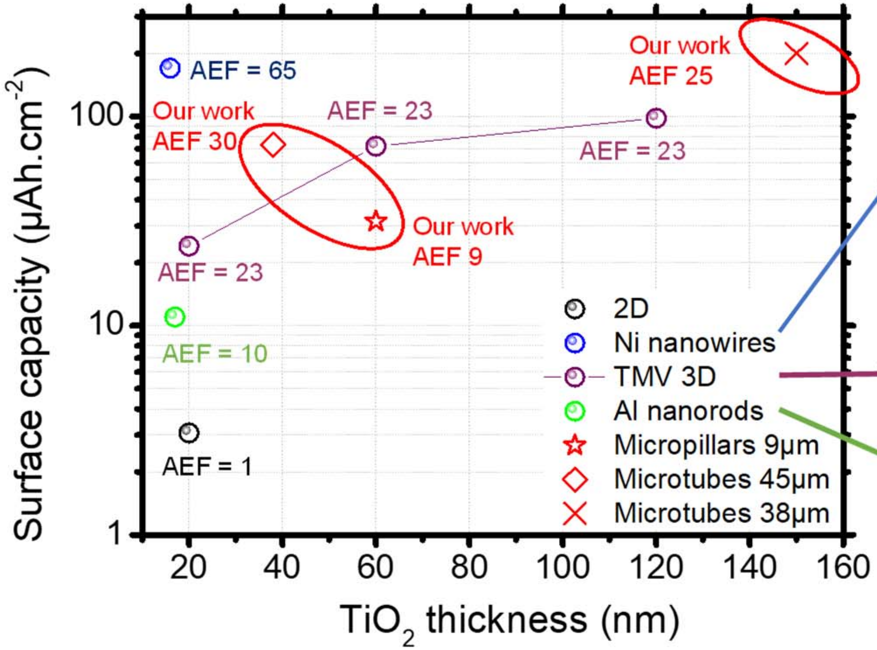
iemn

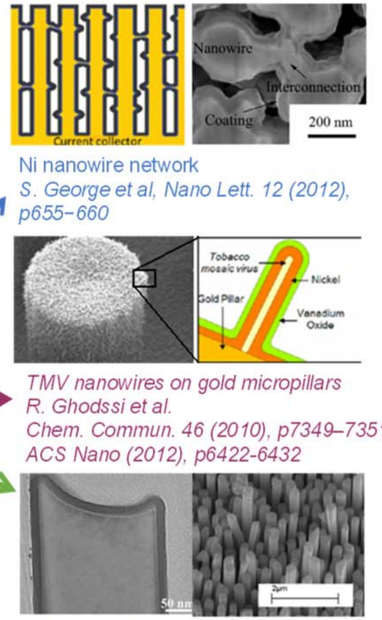
Eustache *et al*, Adv. Energy Mater. 4, 8 (2014) 1301612

Continuous conformal deposition of materials on this 3D skeleton using only ALD



Comparison with state-of-the-art





Ni nanowire network
S. George et al, Nano Lett. 12 (2012), p655–660

TMV nanowires on gold micropillars
R. Ghodssi et al.
Chem. Commun. 46 (2010), p7349–7351
ACS Nano (2012), p6422-6432

Al nanorods
P Simon et al, Uppsala University and CIRIMAT,, Nano Lett. 9 (2009), p3230–3233

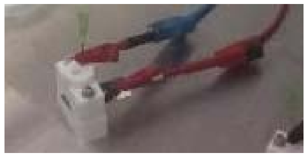
iemn

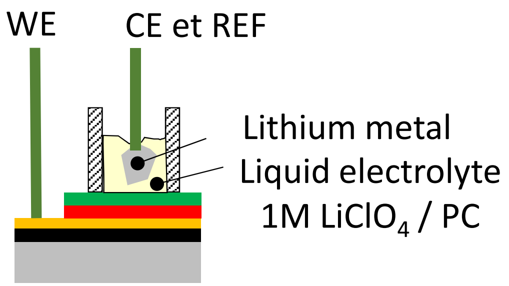
Eustache *et al*, Adv. Energy Mater. 4, 8 (2014) 1301612

C. Lethien: Solid Electrolyte

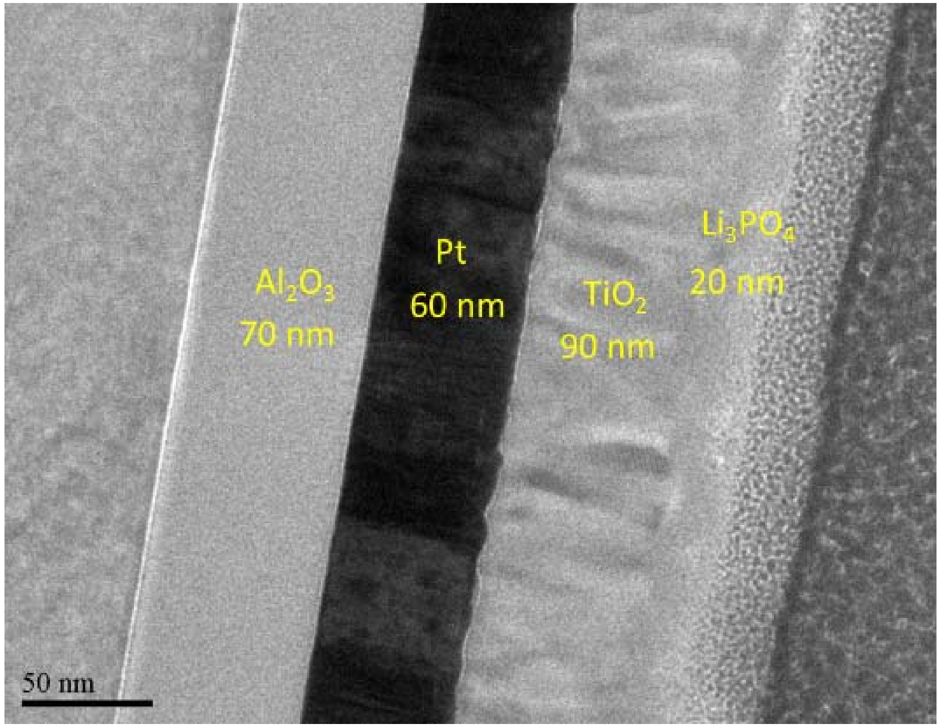
Li$_3$PO$_4$ solid electrolyte using ALD

❖ Electrochemical validation of Li$_3$PO$_4$ on flat substrate: bilayer study of TiO$_2$/Li$_3$PO$_4$ deposited by ALD





Investigated stacking: Si / Al$_2$O$_3$ (70 nm) / Pt (60 nm) / TiO$_2$ (90 nm) / Li$_3$PO$_4$ (20 nm)



Submitted to a communication in November 2015

Rannou Patrice, Maréchal Manuel, Sadki Saïd, FUNCTIONAL SOFT-MATTER FOR ENERGY GENERATION, HARVESTING & STORAGE (BATTERIES)

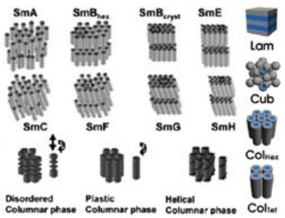


Topic : Micro-batteries - Solid electrolyte for microbatteries

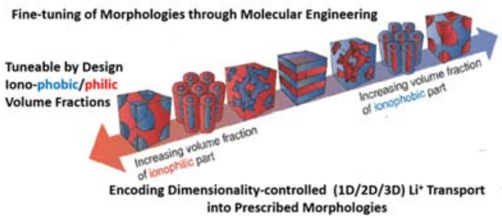
Cristal liquid electrolytes for self healing batteries

RESEARCH HIGHLIGHT: TILCs as *safer-by-design* high-performance electrolytes for PLSSBs

Thermotropic Liquid Crystals (TLC)
⇨Self-healing
⇨Self-Assembly



Thermotropic Ionic Liquid Crystals (TILCs) as electrolytes 2.0 encoding chemistry-neutral, *safer-by-design* and high performance (Li^+, Na^+, K^+ etc.) cation transport



BATTERY 2030+

Key Enabling Technologies toward (Gen. 4a/4b) high performance *safer-by-design* recyclable self-healing PLSSBs

SyMMES's Ref: *ChemSusChem* **14(2)**, 665-661 (2021) **DOI**: 10.1002/cssc.202001995
Adv. Funct. Mater. **29(49)**, 1905054 (2019). **DOI**: 10.1002/adfm.201905054
SyMMES's Patent: FR3041358, EP3353262, US20180261886, WO/2017/050769

Since 1997, JRU#5819 (CNRS/CEA/UGA): https://www.symmes.fr/en
125-130 staff
- **60** Tenured (CNRS+CEA+UGA) researcher including 16 Engineers/Tech. staff
- **45-50** B.Sc.+M.Sc. students, PhDs & PDFs

Two Research Topics
- **Energy Generation, Harvesting & Storage**
  CAMPE & STEP Teams
- **Life Sciences**
  CIBEST & CREAB teams

SyMMES
SYSTÈMES MOLÉCULAIRES ET NANOMATÉRIAUX POUR L'ÉNERGIE ET LA SANTÉ


N A M e
GDR NAnoMaterials for Energy applications

ON GOING+RECENT GRANTS
02/22⇨02/24:
H2020-MSCA-IF-2020-HOPES
09/20⇨09/23:
H2020-LC-BAT-14-2020-HIDDEN
10/19⇨03/24:
ANR-2019-CITADEL
10/19⇨03/23:
ANR-ASTRID-2019-ECOPE
•11/12⇨04/16:
EU-FP7-ENERGY-NEST
•10/13⇨09/16:
EU-FP7-ENERGY-BACCARA

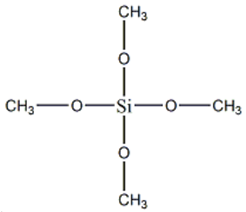
- acidic sol-gel route

Molar ratios :

$EMImTFSI/Si(OMe)_4 = 0.5$

$HCOOH/Si(OMe)_4 = 4$

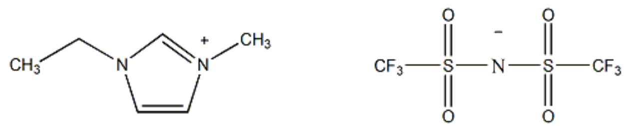
Alkoxysilane



Acid :

HCOOH

Solvent and ions : EMImTFSI

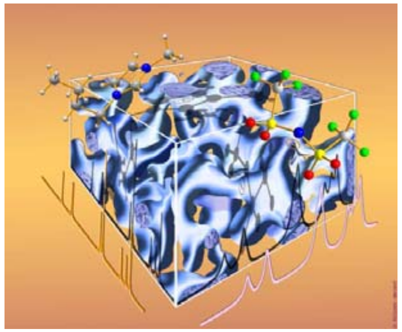


$Si(OMe)_4 + 4H_2O \xrightarrow[\text{Hydrolysis}]{HCOOH/EMImTFSI} Si(OH)_4 + 4MeOH\uparrow \xrightarrow[\text{Condensation}]{HCOOH/EMImTFSI} SiO_{(2-x)}(OH)_y + 2H_2O\uparrow$

SOL

GEL

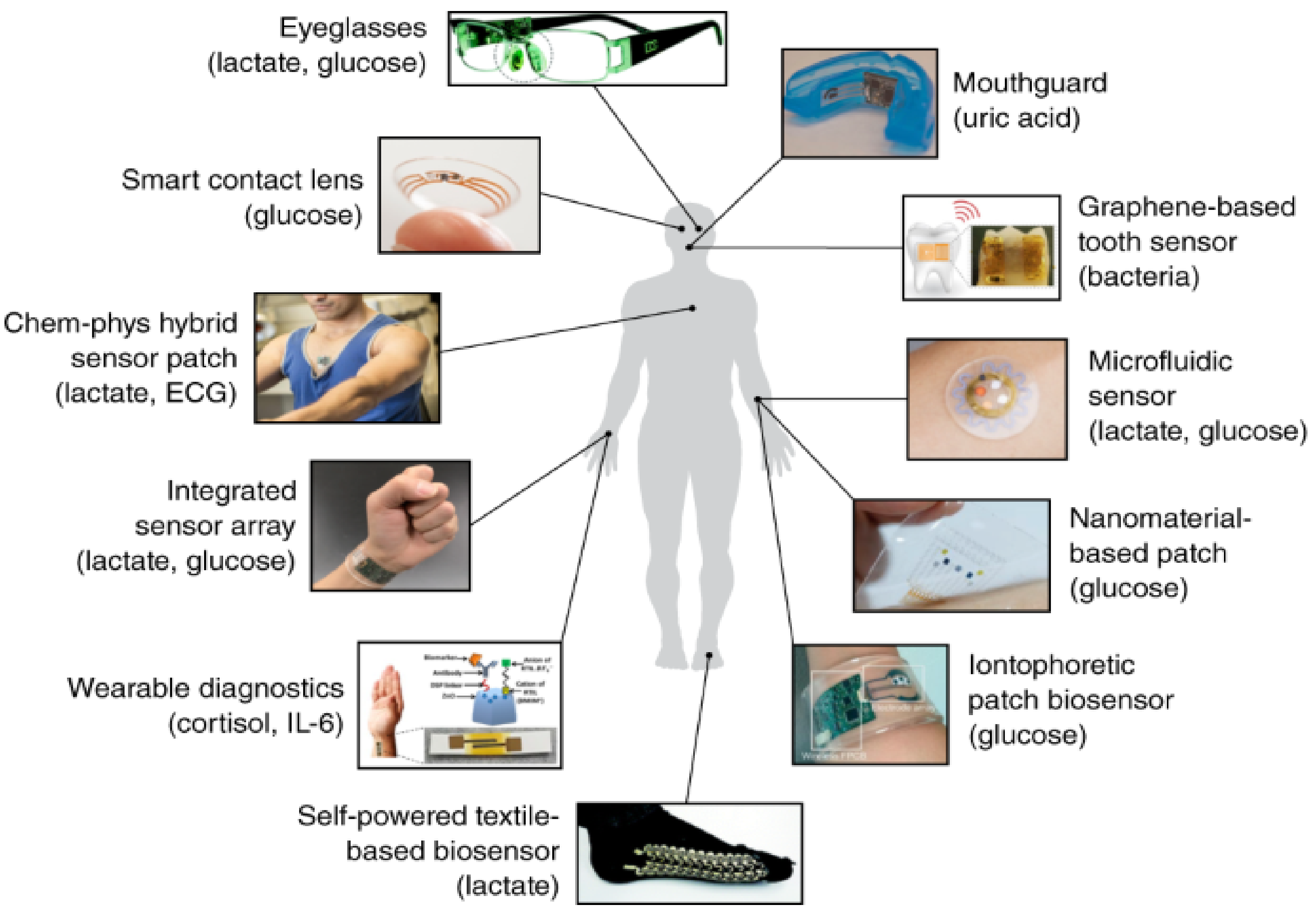
Interpenetrated mesoporous silica and ionic liquid networks w/ liquid like properties

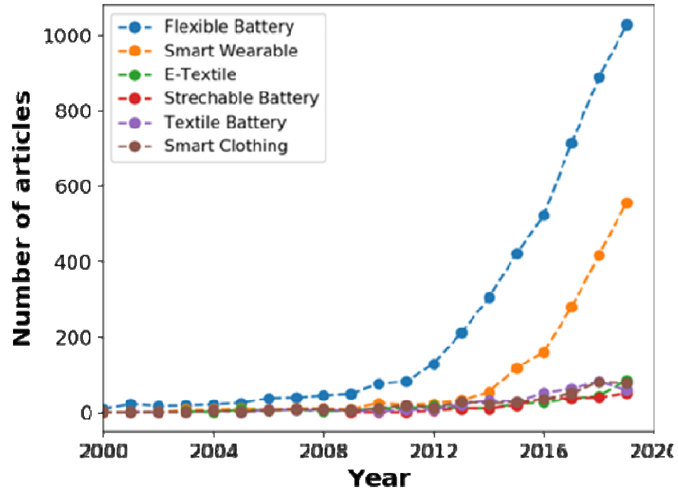


ENERGIE RS2E

ANR

Main applications of flexible electronics





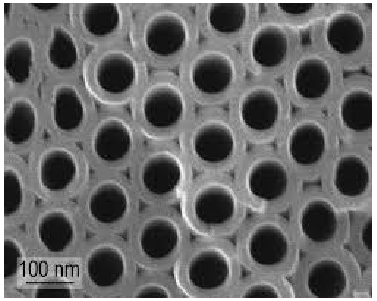
Number of scientific articles for flexible and stretchable batteries in the last 20 years.

M Nasreldin, et al, Adv. Mater. Technol., 2020, 2000412

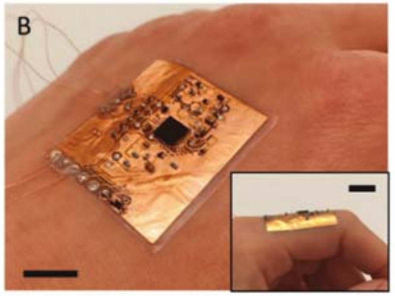
Microbatteries/nanostructured electrodes for flexible systems

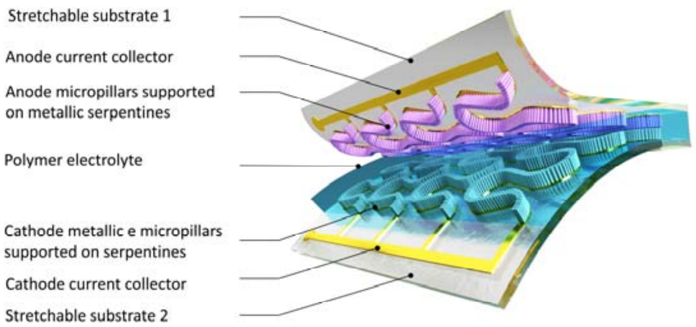
Advantages of nano-architectured electrodes: nanowires, nanotubes, core-shell nanoparticles,…

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

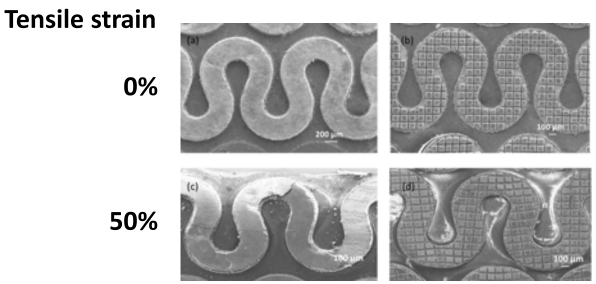


e.g. Fabrication of TiO_2 nanotubes (negative electrode for Li-ion microbatteries) by anodization





M. Nasreldin, et al, Energy Storage Mater. 2020, 33, 108



Higher capacities and better mechanical properties due to the presence of micro-nanostructures

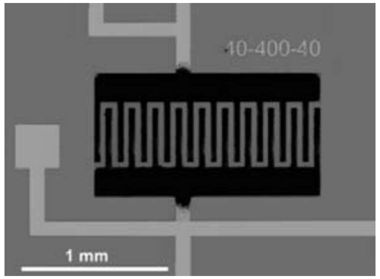
IV. Micro-supercapacitors

1. Electrodes
2. Electrolyte
3. Design/components
4. Towards dielectrics microcapacitors , hybrides systems , …

David Pech (LAAS), C-based and 3D Electrodes

1) C-based materials

Activated C, Onion-Like Carbon,
Carbon Nanowalls,
Carbide Derived Carbon

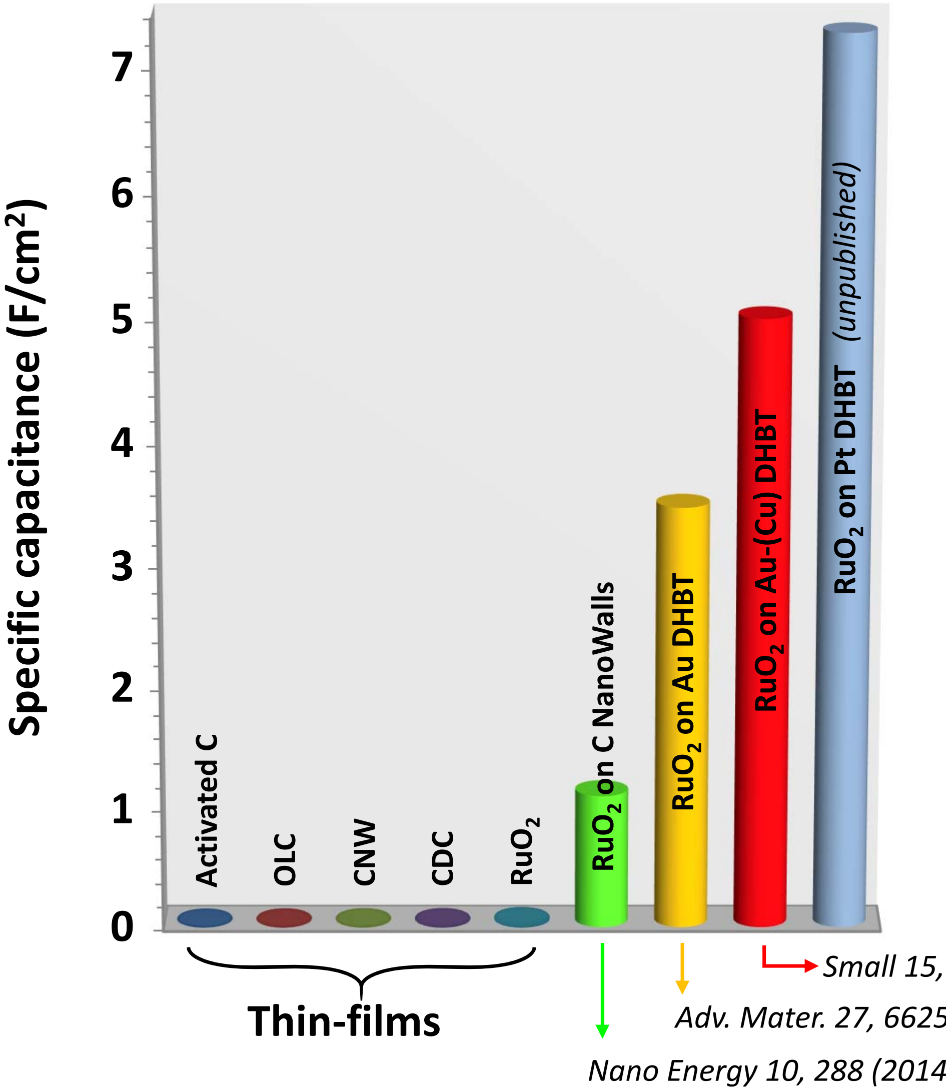


2) 3D Pseudocapacitive Materials

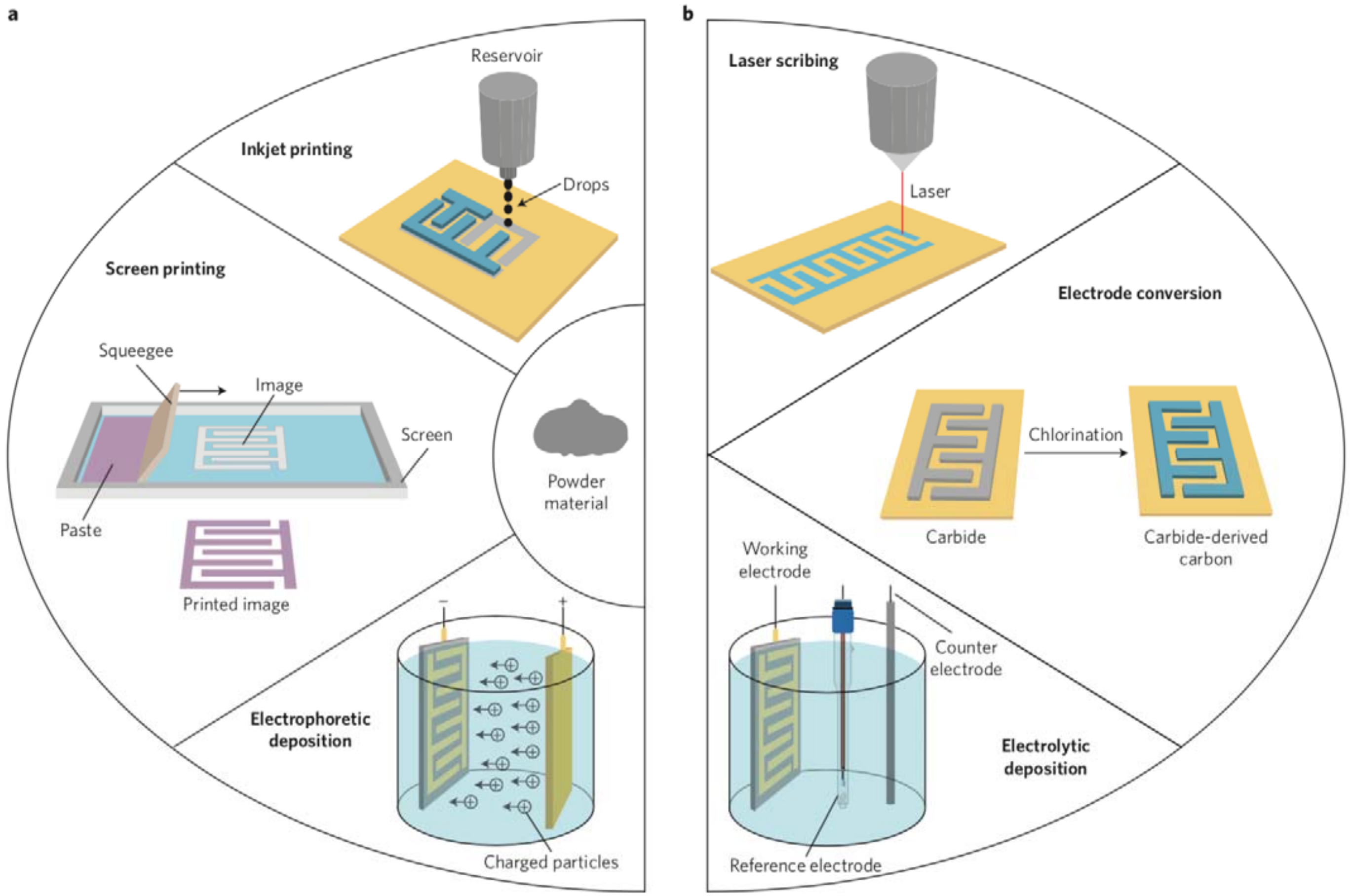
RuO_2, MnO_2…

↓ *3D Support*

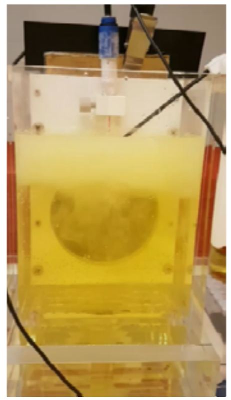
3D Electrodes



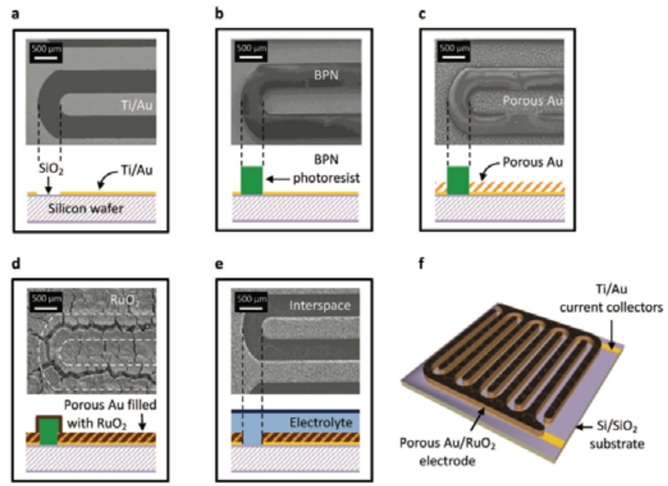
David Pech, Technological processes (electrodes materials → devices)



Collective fabrication at the wafer-level
(ex. electrodeposition)



WE: wafer 4'
CE: Pt grid
REF: Ag/AgCl

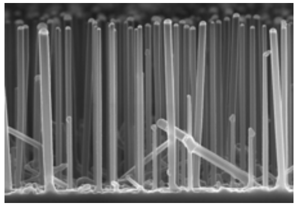


A. Kyeremateng, T. Brousse, D. Pech, **Nat. Nanotechnol.** vol. 12 p. 7 (2017).

Gentile Pascal, Sadki Saïd, Bottom-Up conjugated/conducting polymers-coated Silicon Nanostructures for Integrated On-chip EDLCs Silicon

Si nanostructure by CVD

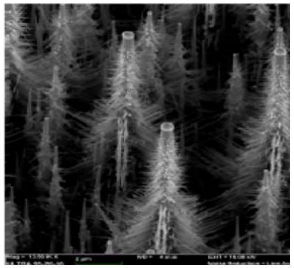
- Nanowires:



F. Oehler et al., Nanotech., 20, **2009**, 245602.

❶ **Super-nanostructuration**

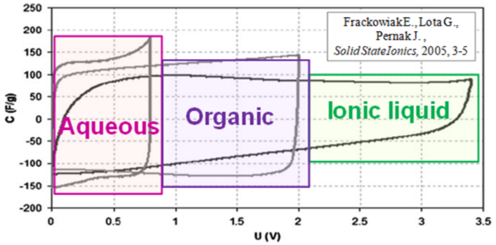
- Dense & highly doped NWs
- From SiNWs to SiNTrs



Si-NTrs

- Electrolyte:

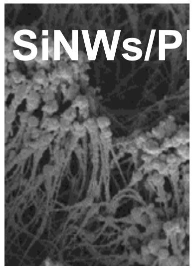
❷ **From PC to ILs**

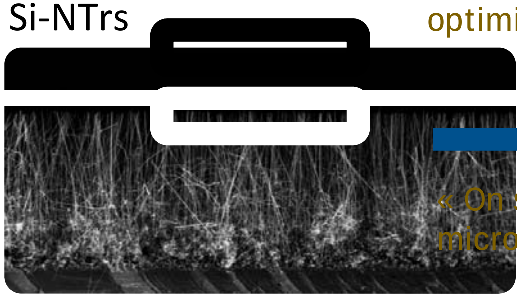


- ***Pseudo*capacitors:**

❸ **coating**

- ALD coating
- Electrodeposition of conjugated polymers, or oxide coating





Nanostructure optimization

- Capacitance increases.
- Structuration process depending on the application.

« On ship » microintegration

- Industry compatible processes.
- « All silicon » microdevices.
- Microstructuration for on ship applications.

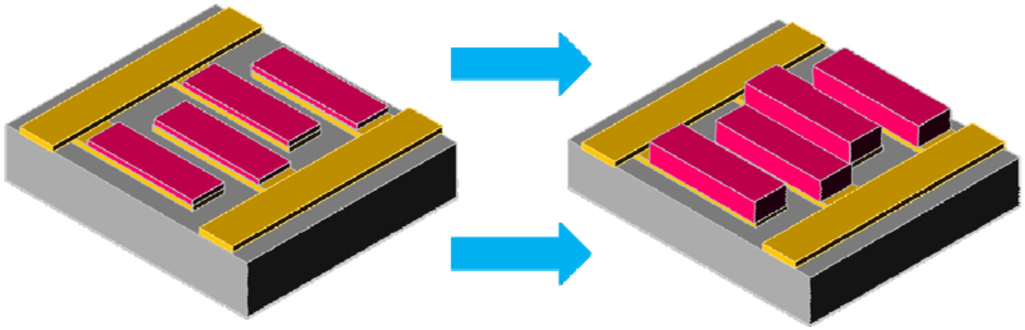
Surface functionalization

- Conformal passivation layer
  - **Increase of Umax and stability**
- Pseudo-capacitive materials
  - **Significant increase of the capacitance**

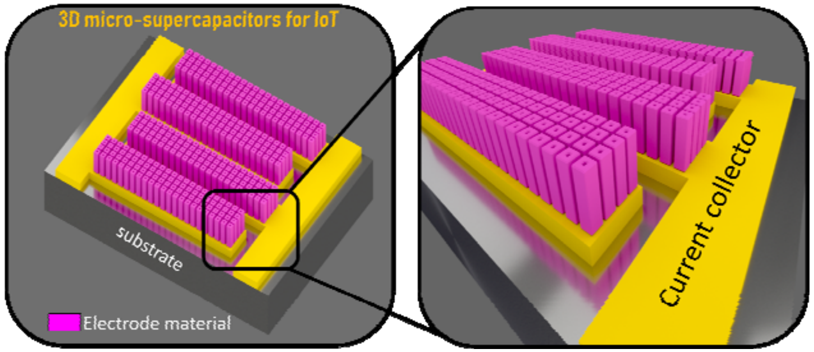
T. Brousse (IMN) et C. Lethien (IEMN): high performance 3D on chip MSC

On chip Micro-supercapacitors based on pseudocapacitive materials for miniaturized IoT devices

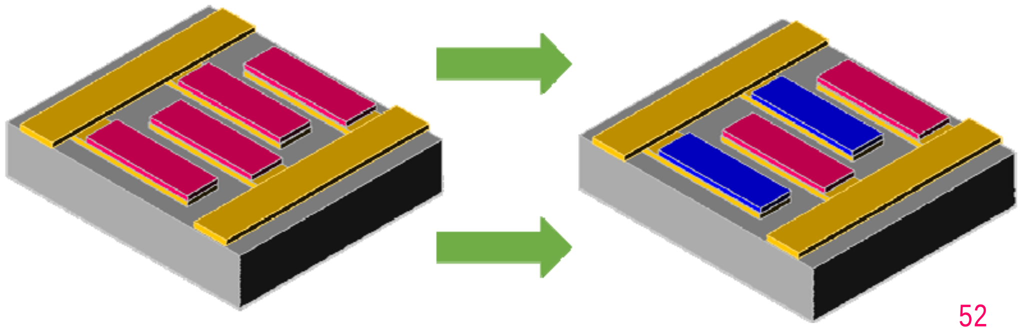
From thin to thick films



From planar to 3D films



From symmetric to asymmetric configuration

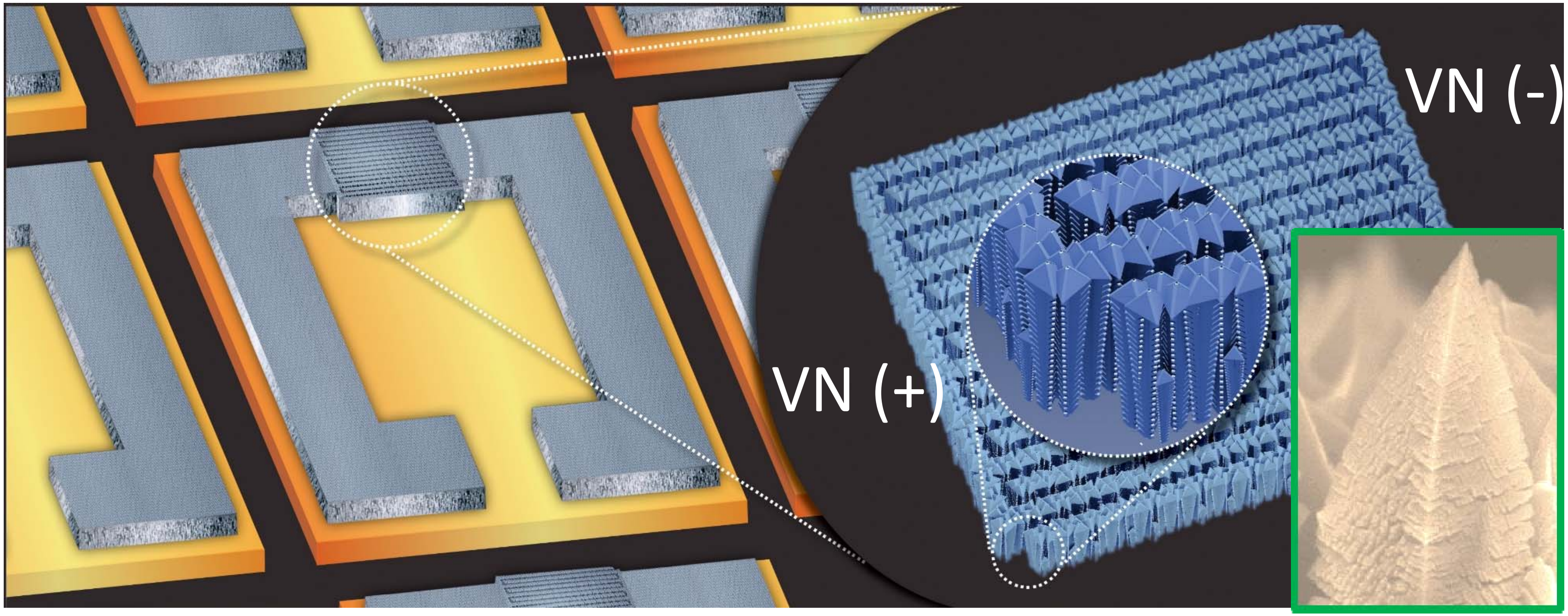


C. Lethien, J. Le Bideau, T. Brousse, *Energy Environ. Sci.*, 2019, 12, 96-115

Sputtered vanadium nitride films for on chip MSC

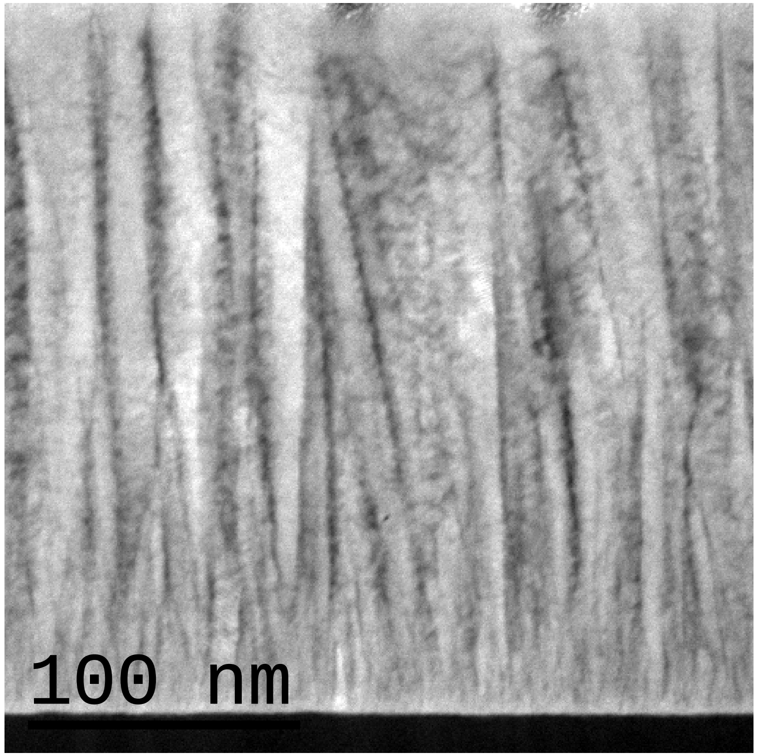
Fabrication process using CMOS compatible technique

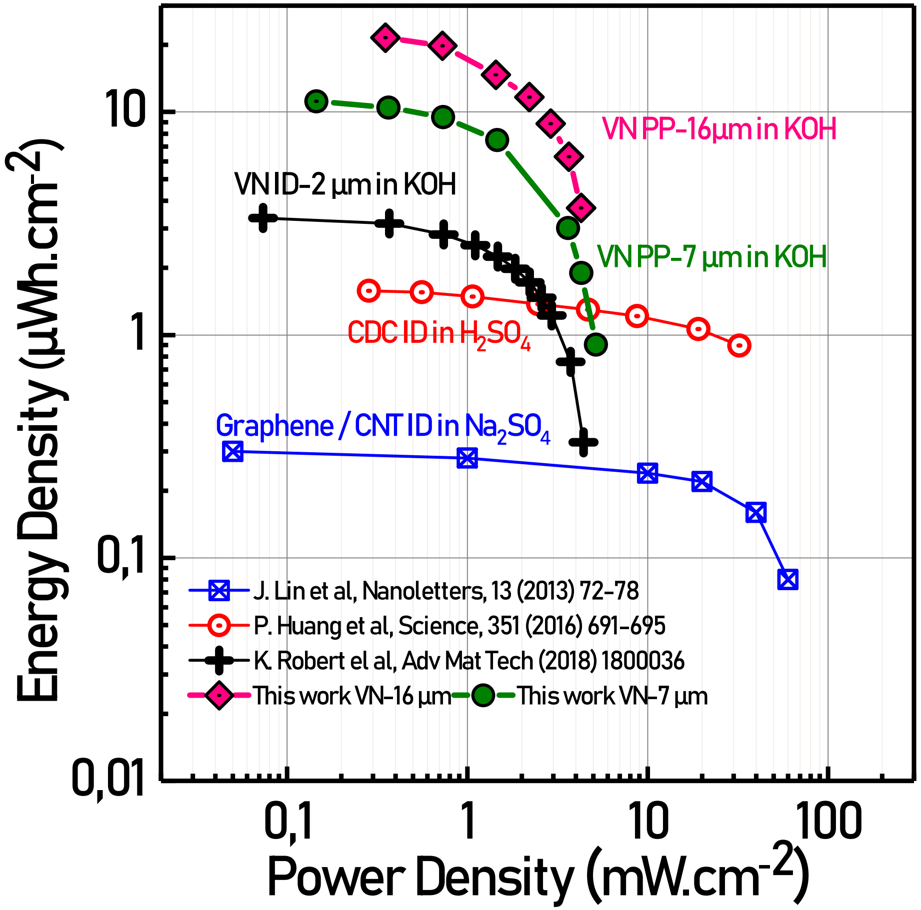
⇨ On chip VN / VN symetric interdigitated MSC at the wafer level



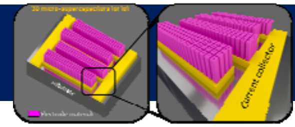
Sputtered vanadium nitride films for on chip MSC

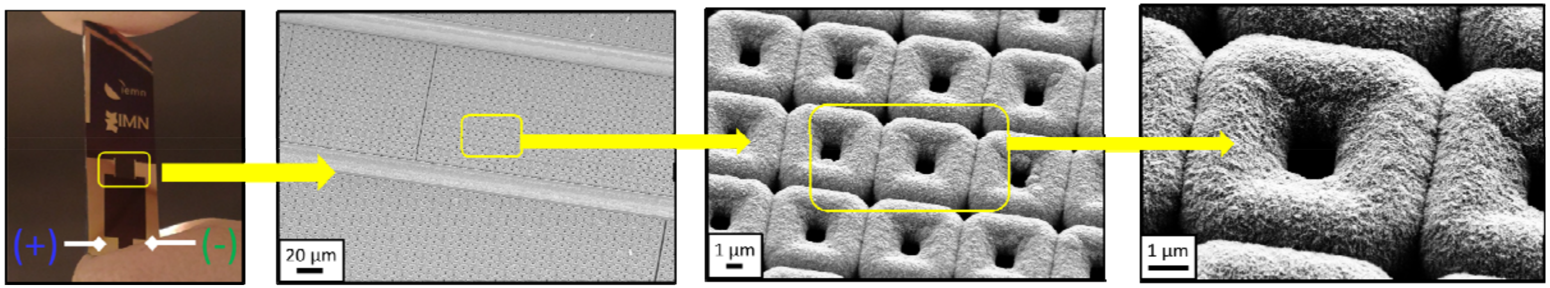
VN / VN micro-supercapacitors based on ID & parallel plate configurations



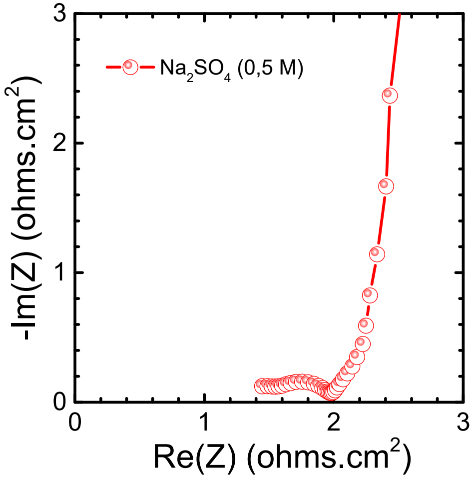


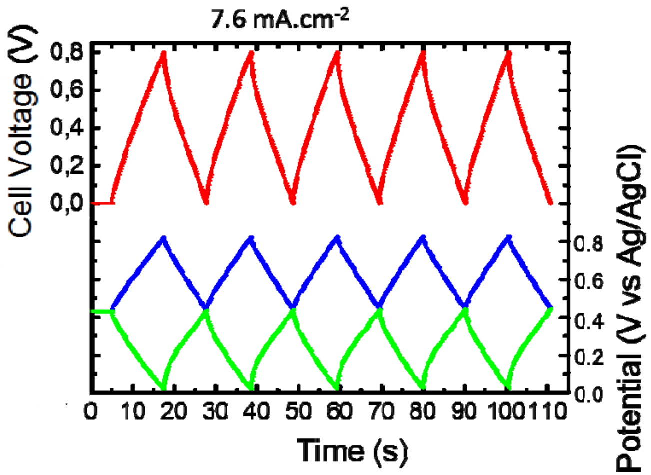
On chip MSC based on 3D pseudocapacitive electodes

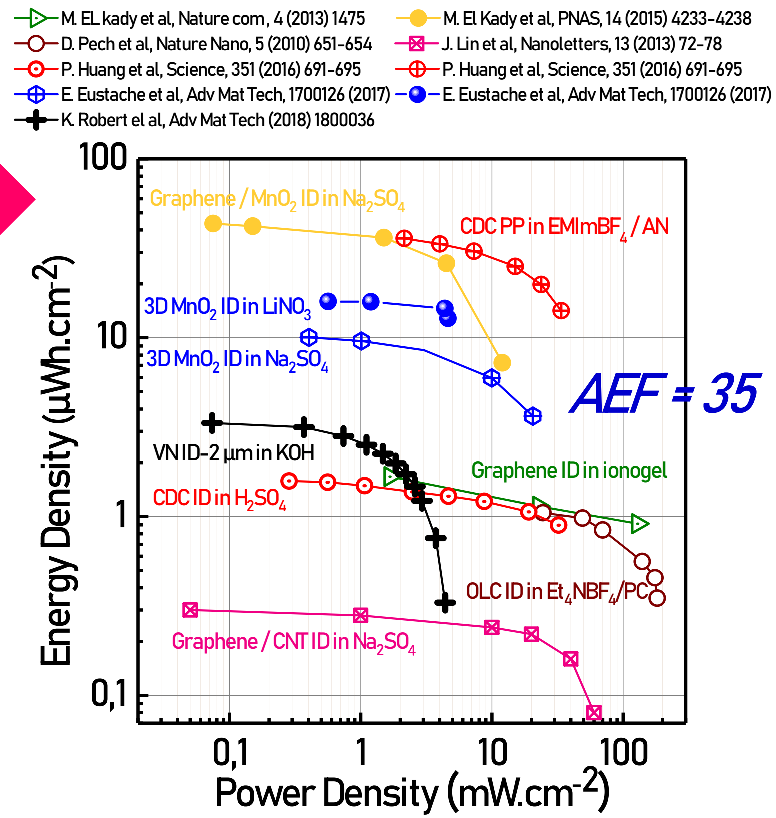




Electrochemical analysis in 0.5M Na_2SO_4

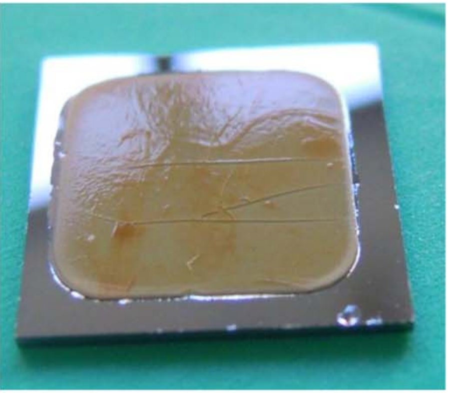


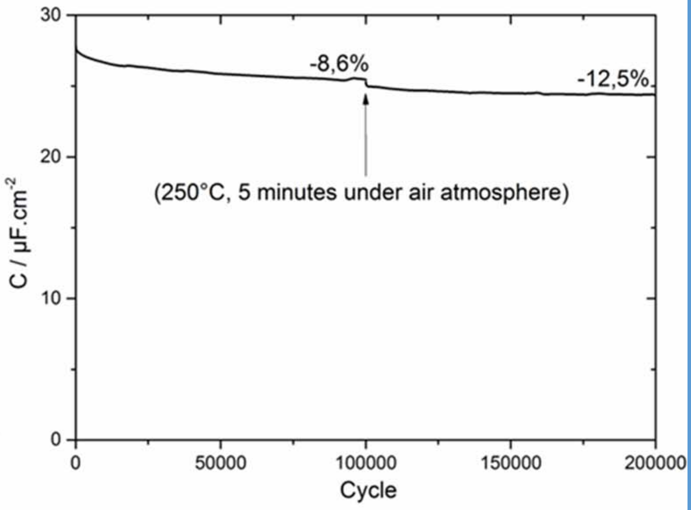


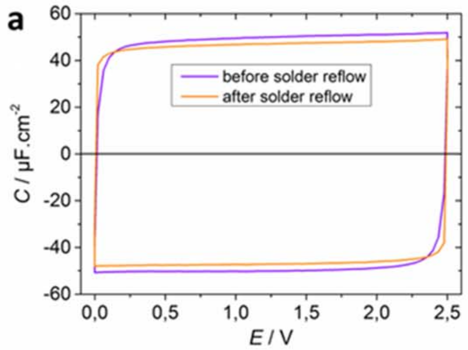


C. Lethien, T. Brousse *et al*, Adv. Energy Mater. 2015, 1500680
C. Lethien, T. Brousse *et al*, Adv. Mater. Technol. 2017, 1700126

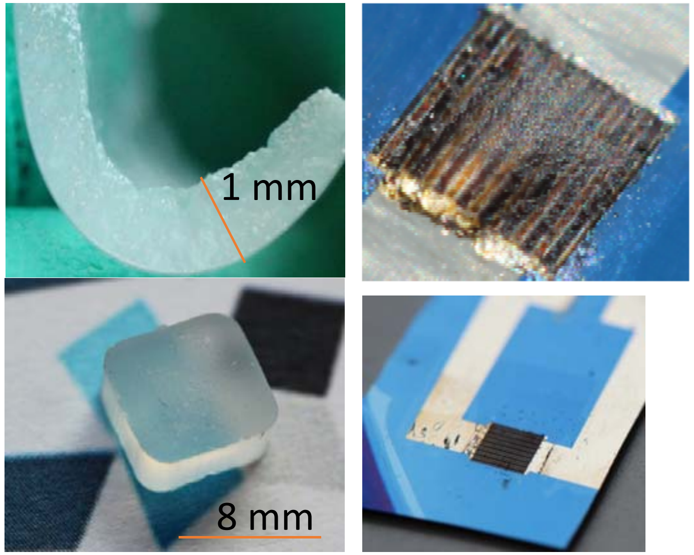
Jean Le Bideau (IMN) : ionogels as electrolytes

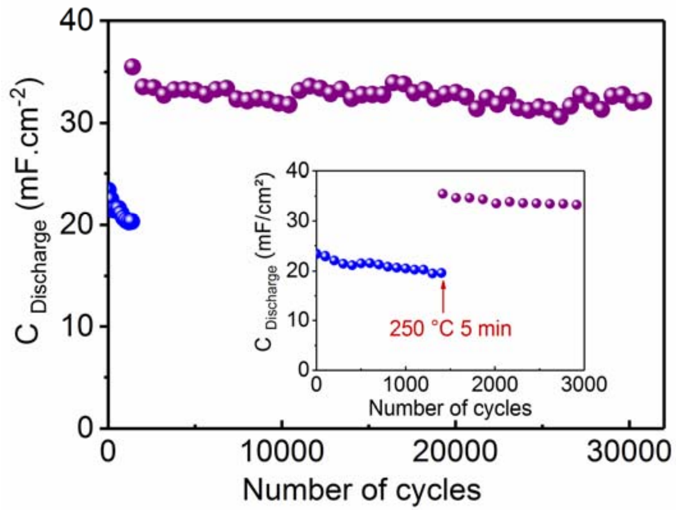






Ionogel can be used as solid-like electrolytes for SCs together with various electrode materials





IV. Coupling

1. Systems autonomy coupling (energy harvester, energy conversion,…)
2. Coupling for activation of devices (sensors, electrochromic systems, etc…)
3. Interconnection problematic, compatibility (interaction with Atelier #6)

Perspectives and thoughts

a. Complementary expertises in the GDR, what do we need to solve technical issues and scientific challenges? (metrology, …)?
b. Microdevices Coupling
c. Normalisation : how important is it?
d. From microsystems to macrosystems
e. We need translators !!

Thanks for your attention

Questions?