# Ultra high power carbon-based micro-supercapacitors

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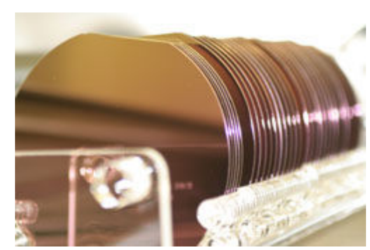

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# Outline

- Context:
  - Supercapacitors: principles and applications
  - Practical application: Autonomous Wireless Sensors Networks
  - Why micro-scale energy storage ?
  - State of the Art in micro-supercapacitors

- Ultra-high power carbon based micro-supercapacitors:
  - Technology + materials
  - Performance
  - Comparison with 3D capacitors

- Conclusions and perspectives

# Supercapacitors

•Electrochemical Double Layer Capacitors

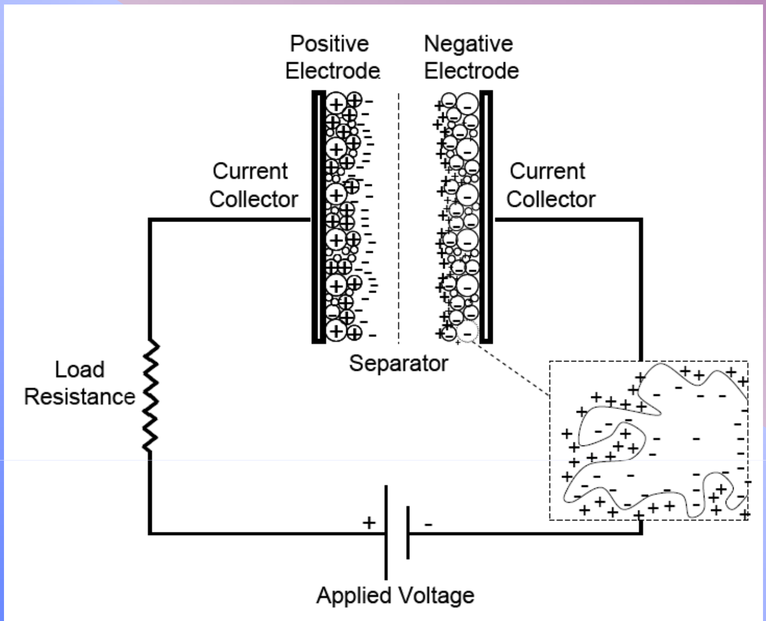
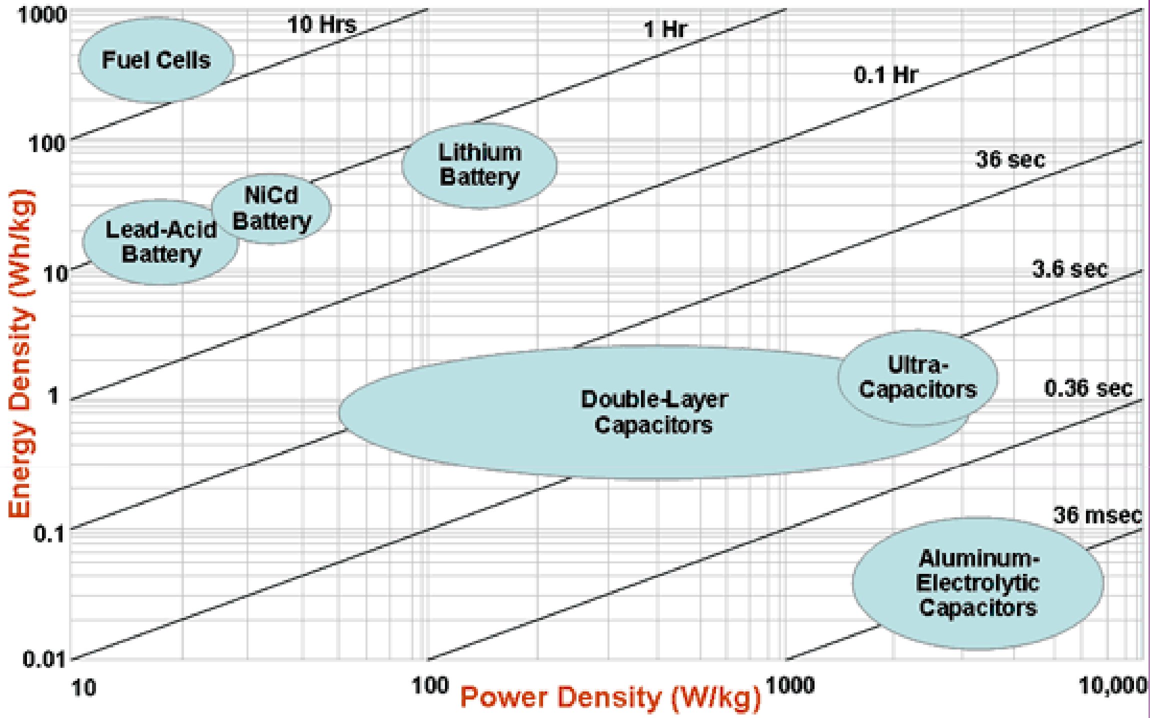



Figure 2

Schematic of an electrochemical double-layer capacitor.




Source US Defence Logistics Agency

| | | Material | | | Cell |
|---|---|---|---|---|---|
| Active material | Electrolyte | Density ($g/cm^3$) | C (F/g) | C ($F/cm^3$) | C ($F/cm^3$) |
| Activated Carbon | Organic (2.5 V) | 0,7 | 100 - 200 | 70 - 140 | 17.5 – 35 |
| Hydreous $RuO_2$ | Sulfuric acid (1V) | 2 | 650 | 1300 | 325 |

• Pseudo-capacitors:
  - Metal oxides: $RuO_2$, $MnO_2$
  - Conducting polymers: PPy

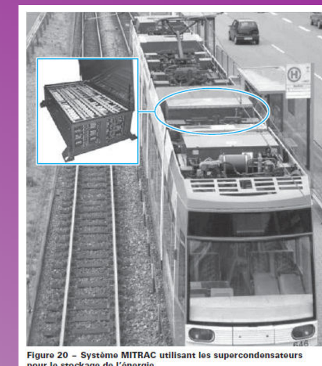
# Typical applications

Loading /unloading container ships:

Captures and stores regenerative energy during load; fuel saving of 40%


Transport:

- buses, tramways
- Hybrid cars




MWatt

KWatt

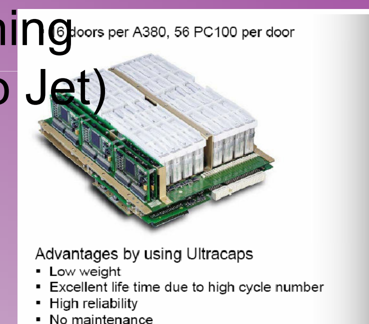
Power

Watt

mWatt

Tools: cutters, screw drivers…

Emergency door opening (AIRBUS A380 Jumbo Jet)




Portable electronics:

Memory maintenance

Battery auxiliary for power boosts

Self-powered applications…

J.R. Miller and A.F. Burke*, Electrochemical capacitors: challenges and opportunities for real-world applications*, Interface 2008, p. 53

# Self Powered Applications

**Increasing needs for self-powered applications**
(*nomad electronics, wireless sensors network, active RFID, biosensors, implanted microsystems…*)

## Embedded systems with a complete autonomy of energy

**Energy scavenging and harvesting** → **Energy storage and management** → **Applications**

*photovoltaïc, thermoelectric, piézoélectric, electromagnetic*

## Technological problems

**Microbatteries**

- ***Limited lifetime***
  (→ restriction on the autonomy of the whole system)
- ***Low power density***

***+ Temperature range, Integration, Pollution…***

→ **Energy storage in supercapacitors**

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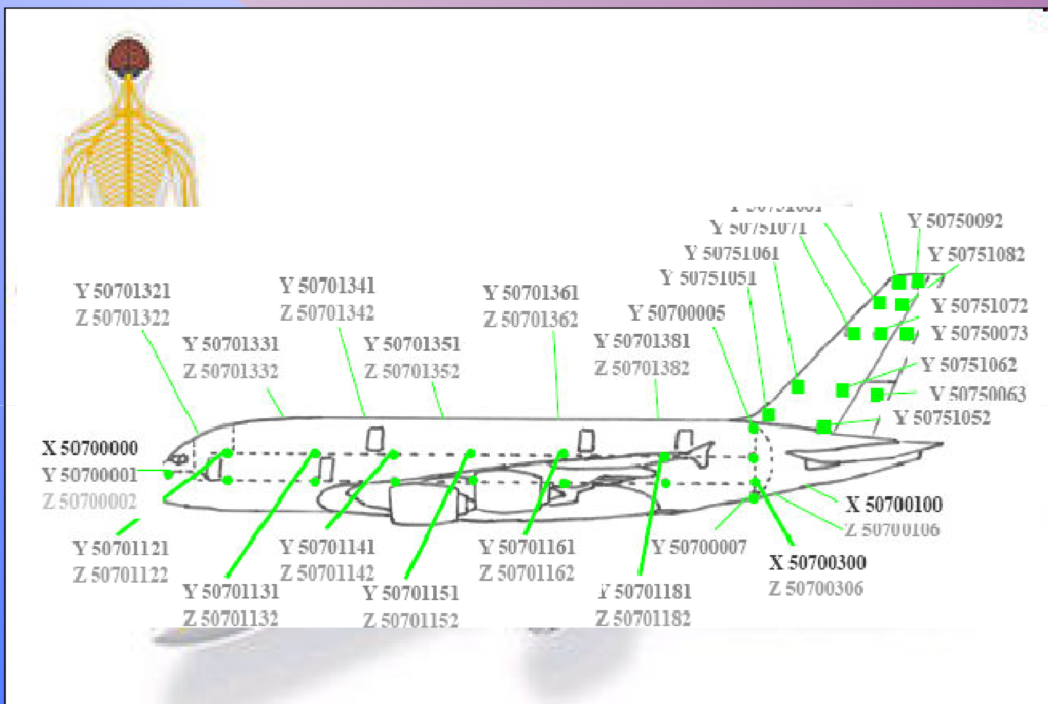
# Practical example: AutoSENS project

Autonomous Wireless Sensors Network (WSN) for aircraft structural monitoring

## Structural Health Monitoring (SHM)



Autonomous communicating sensors network


*(Partnership with Airbus)*

On board sensors to detect cracks, corrosion, delamination, and other damages

→ Reduce inspection costs

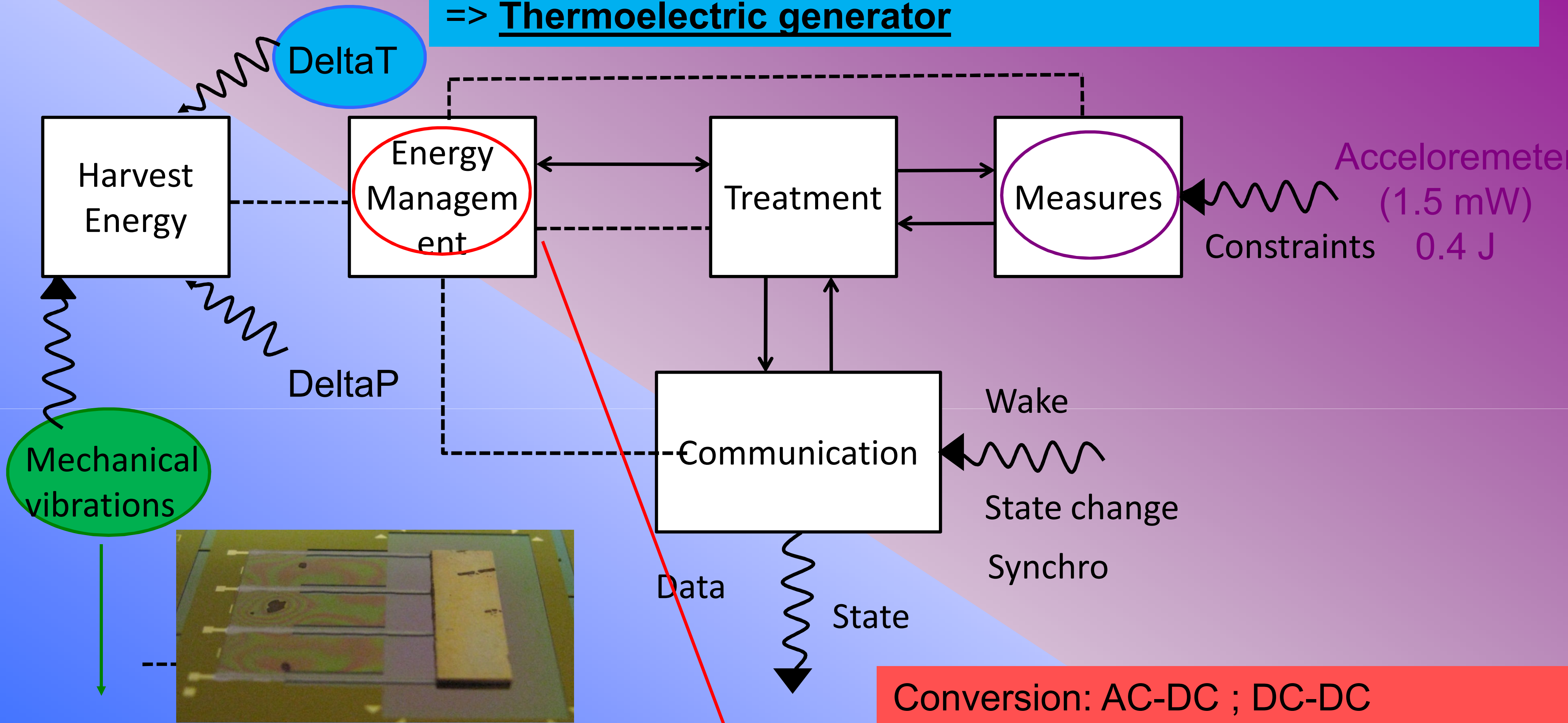
→ Increase safety

<u>Specifications for in flight measurement :</u>

- Temperature : -50°C / +85°C
- Lifetime : 40 years ; 5000h/year
- High power uptake / delivery required
- Node thickness < 5mm

# Practical example: AutoSENS project

Take off: Ground = +40°C to -20°C => 12000 m = -60°C
=> **Thermoelectric generator**




Take off => 1m.s$^{-2}$@ 50 Hz
Cruise => 0.1m.s$^{-2}$@ 50 Hz
=> **Piezoelectric generator**

Conversion: AC-DC ; DC-DC

Storage: **supercapacitors** (90 mF/cm$^2$ )

- **Carbon (life time)**
- **Organic electrolyte (temperature range)**

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# Why micro-scale ?

## *Short term :*

- **Monolithic integration**

- **Local storage for MEMS type devices (energy harvesting, sensors)**
**= minimisation of connections**

## *Long term :*

- **Large scale fabrication = low cost, reliability**

- **Enhancement of performance: energy and power densities**

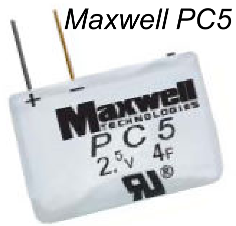
→ *Better accessibility to ionic species*

→ *Optimal use of active material : Surface / Volume* ↗

# State of the art

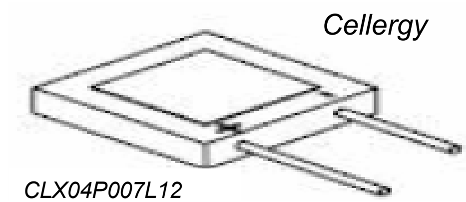
## Micro-supercapacitors

- Commercial devices



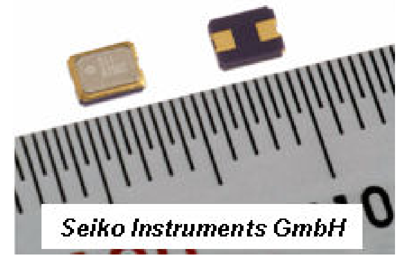

14 mm x 23.6 mm x 4.8 mm

C = 4 F – 2.5 V




12 mm x 12.5 mm x 2 mm

C = 7 mF – 4.2 V



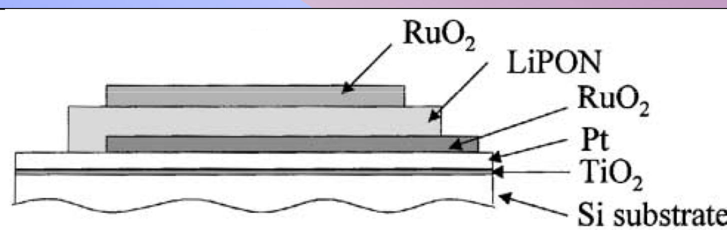

3.2 mm x 2.5 mm x 0.9 mm

C = 14 mF – 2.6 V

- Metals oxides

All solid-state

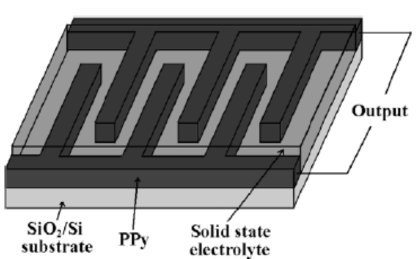
$RuO_2$ + LiPON




Y.S. Yoon *et al.*, J. Power Sources 101 (2001) 12 & J. Electroceram. 17 (2006) 639.

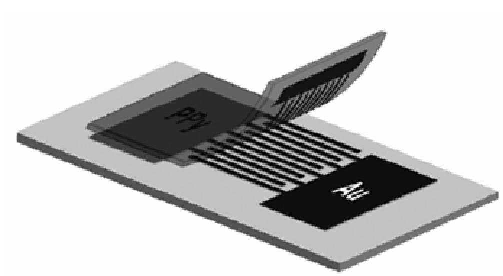
- Conducting polymers (Polypyrrole)

Interdigital – 50 µm



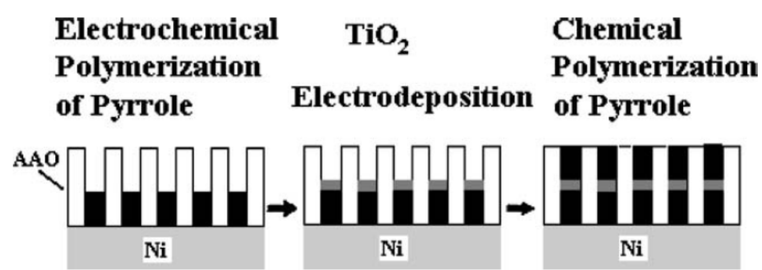

W. Sun & X. Chen, Microelectron. Eng. 86 (2009) 1307.

Flexible µ-supercapacitors




J.H. Sung *et al.*, J. Power Sources 162 (2006) 1467.

AAO template

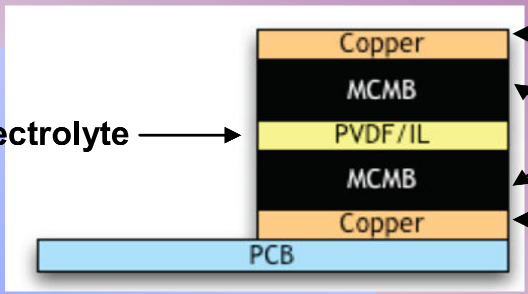


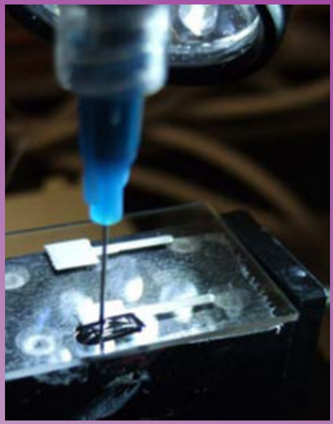

L. Liu *et al.*, J. Solid St. Electrochem. 11 (2006) 32.

# State of the art



- Dispenser Printing on PCB (Berkeley Univ., US)



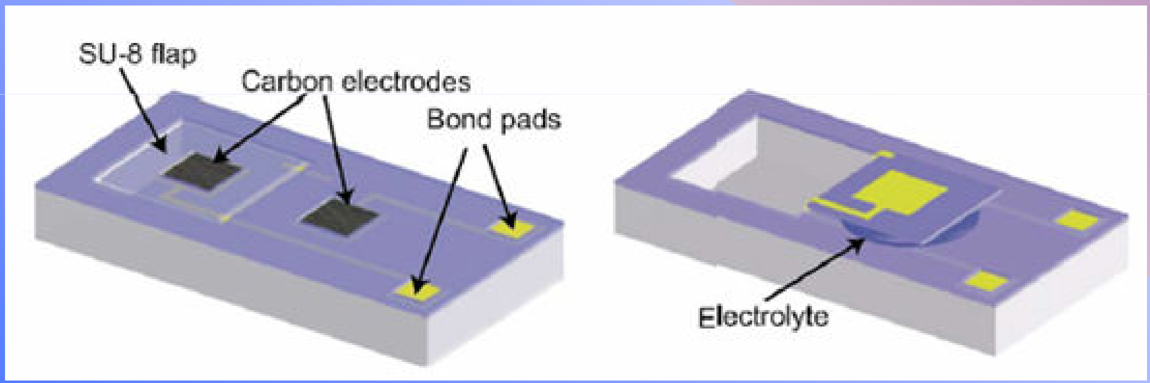
5 mm x 5 mm x 100 µm

C = 0.1 mF/cm$^2$

2 V

C.C. Ho *et al.*, PowerMEMS 2006.

- Probe tip deposition + Origami$^{TM}$ process (MIT, US)




350 µm x 350 µm x 40 µm

C = 0.4 mF/cm$^2$

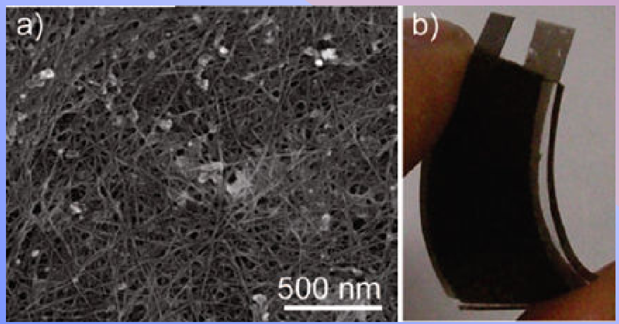
0.6 V

H.J. In *et al.*, Appl. Phys. Lett. 88 (2006) 083104.

- Printable Micro-Supercapacitor using SWCNT (Stanford Univ., US)

Solid Electrolyte : PVA / $H_3PO_4$ → (water-based)

M. Kaempgen *et al.*, Nano Letters 9 (2009) 1872.




~10 µm thick

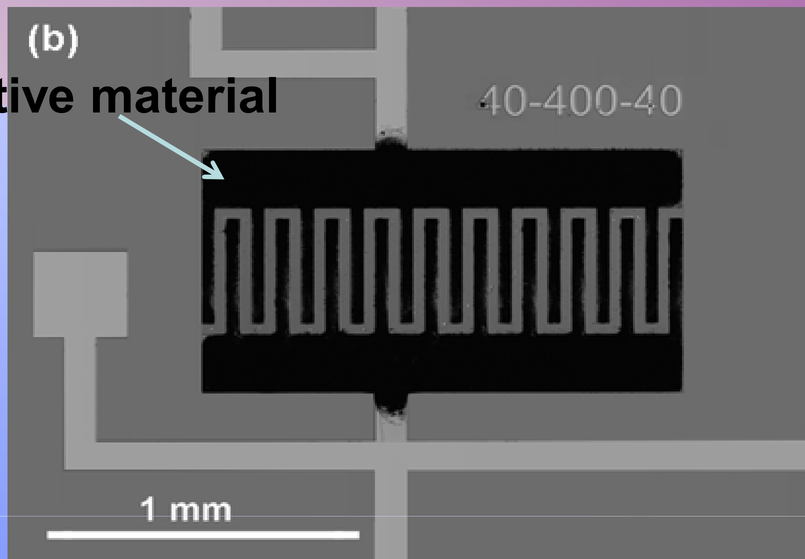
C = 1.2 mF/cm$^2$

1 V

# State of the art



- Inkjet printing (LAAS-CNRS, France)




**Width: 40 µm – Length : 400 µm – Interespace : 40 µm**
**Thickness: 1-2 µm (0.64 mm² / electrode)**

400 µm x 600 µm x 2 µm

C = 2.1 mF/cm²

2.5 V

*E = 6,6 mJ/cm²*

*P = 44,9 mW/cm²*

D. Pech, M. Brunet, P-L Taberna, P. Simon, N. Fabre, F. Mesnilgrente, V. Conédéra, H. Durou, *Journal of Power Sources 195 (2010) 1266.*

**Pros:**

→ High resolution

**Cons:**

⇒ Limited thickness

⇒ Emulsion stability difficult

# Outline

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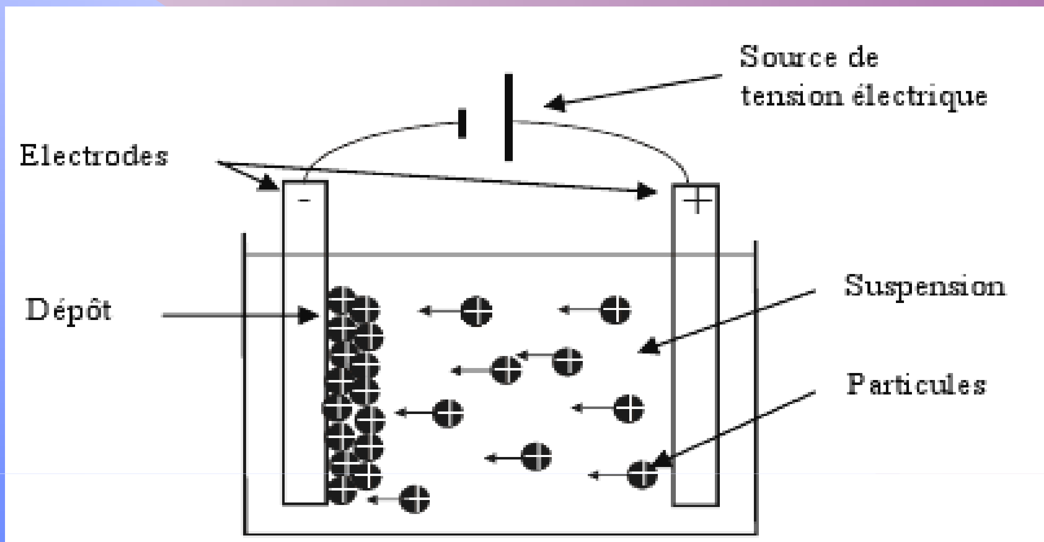
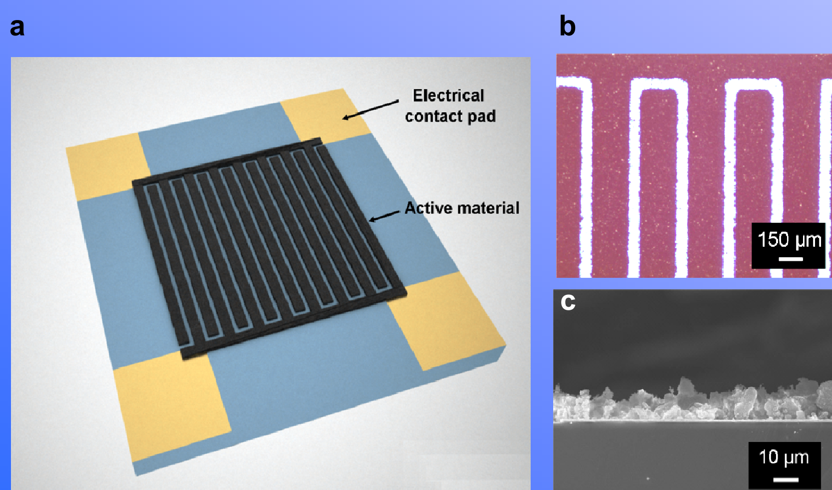
# μ-supercapacitors – EPD

***Principles : Charged particles in suspension migrating under potential***




**Experimental :**

- 95 vol.% ethanol – 5 vol.% water
- 0,3 wt.% of carbon
- $MgCl_2$ : 10 wt.% (charges + ligant)




***Pros :***

- Adhesive and dense films
- Collective deposition
- Thickness => 80 µm

***Cons :***

Limited resolution : 50 µm (can be improved)

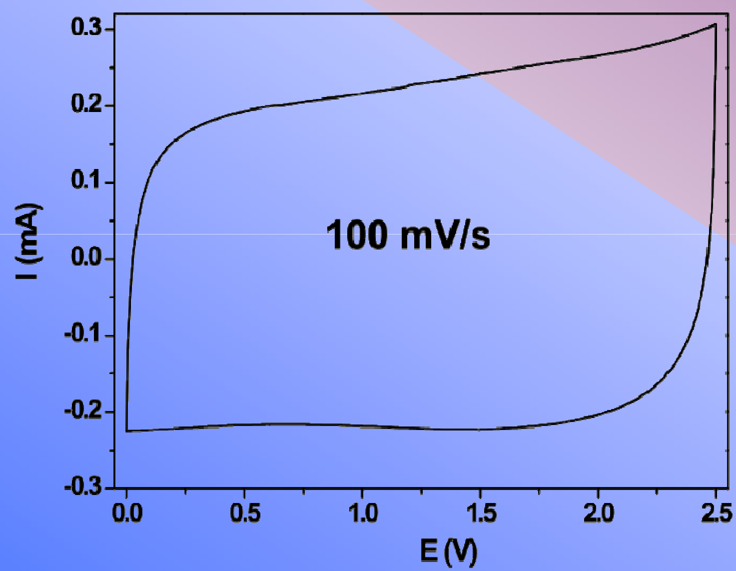
# µ-supercapacitors - EPD



**Results with activated carbon**

**YP-50F (1700 m²/g)**

Tests in 1M $Et_4NBF_4$/anhydrous propylene carbonate electrolyte in a glove box




Thickness = 5 µm

**C = 18 mF/cm²**

( 4.5 mF)

*E = 23,9 mJ/cm²*

*P = 506 mW/cm²*

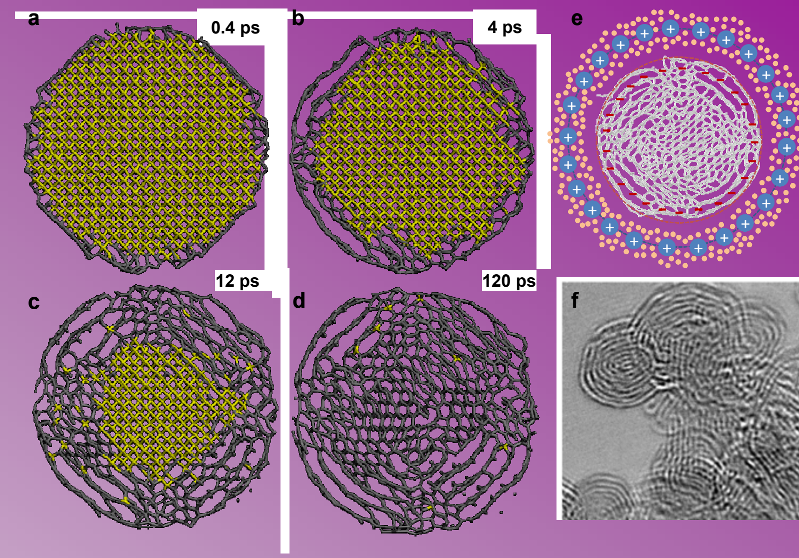
| **Dimensions** | **Potential window** | **Electrode Capacitance** | **Institution** |
|---|---|---|---|
| 25 mm² | 2 V | 0.5 mF/cm² | Berkeley |
| 0.12 mm² | 0.6 V | 1.6 mF/cm² | MIT |
| - | 1 V | 4.8 mF/cm² | Stanford |
| 25 mm² | **2.5 V** | **18 mF/cm²** | LAAS |

# μ-supercapacitors - EPD

## Results with OLC

OLC = Onion Like Carbon *(Drexel University)*

From annealing of nanodiamonds at 1800°C under vacuum
- 520 m²/g
- Pore size = 6 nm



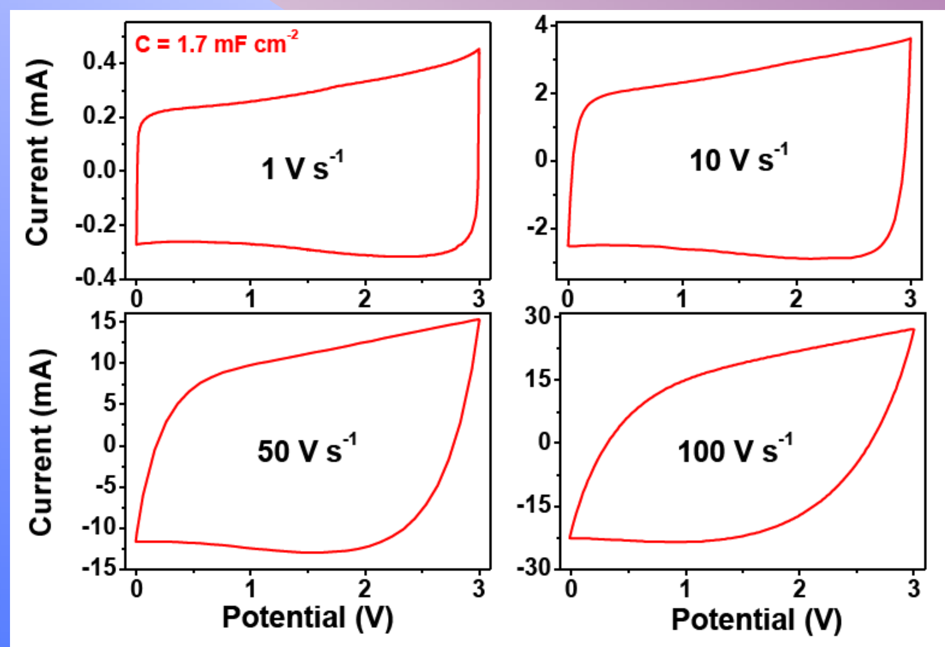

Osswald, S., Yushin, G., Mochalin, V., Kucheyev, S.O. & Gogotsi, Y. *J. Am. Chem. Soc.* **128**, 11635-11642 (2006).

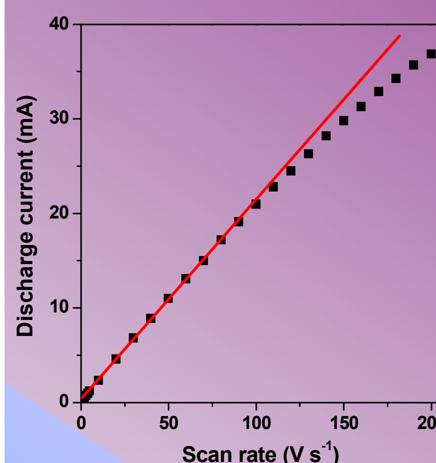
Thickness = 7 μm

**C =** 0,258 mF
= 1.7 mF/cm²

*E =4.6 mJ/cm²*

*P = 592 mW/cm²*

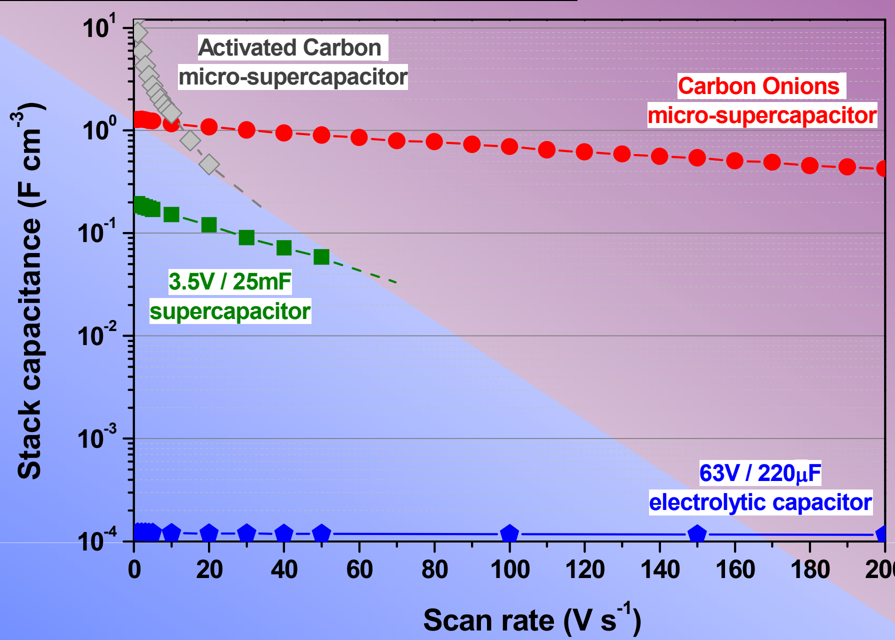


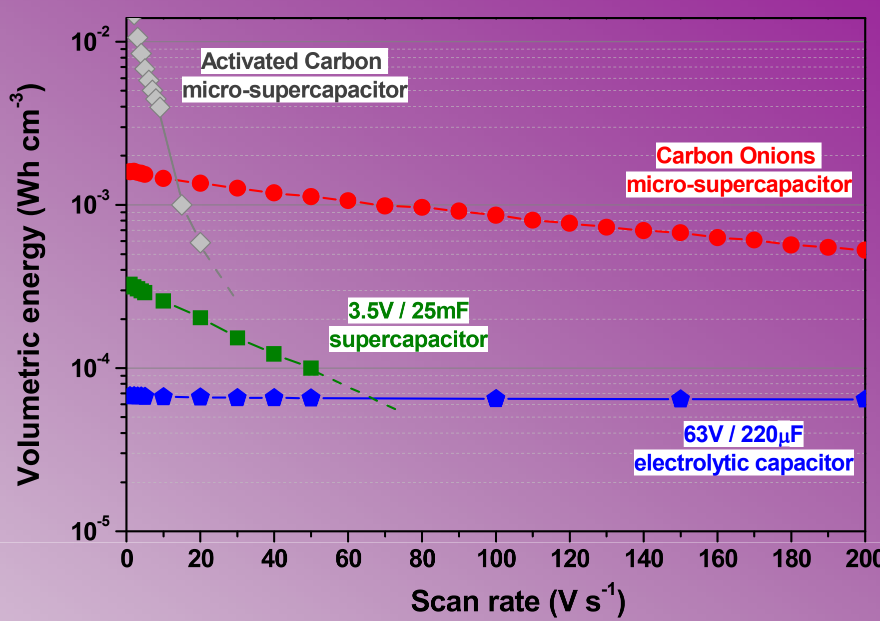



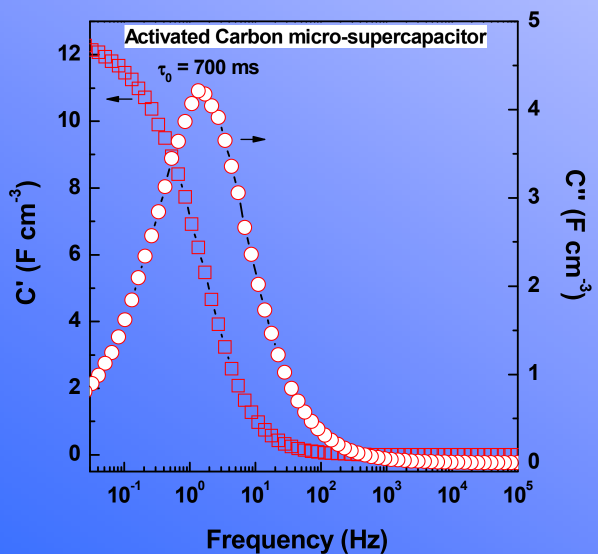

D. Pech, M. Brunet, et al., **Nature Nanotechnology** 9 (2010) 651

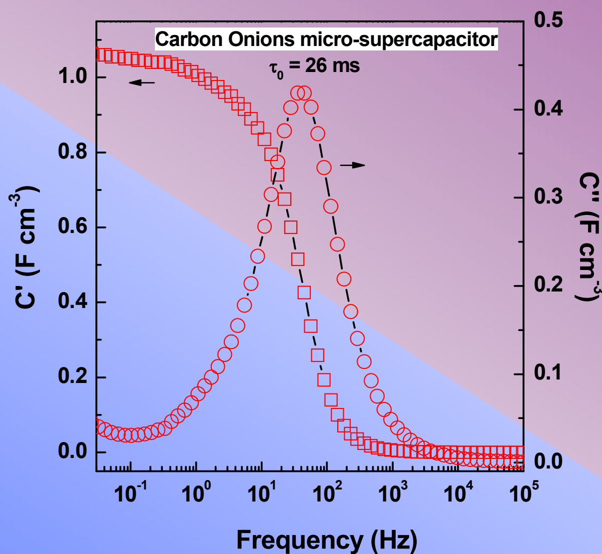
# µ-supercapacitors - EPD

## Active material comparison:



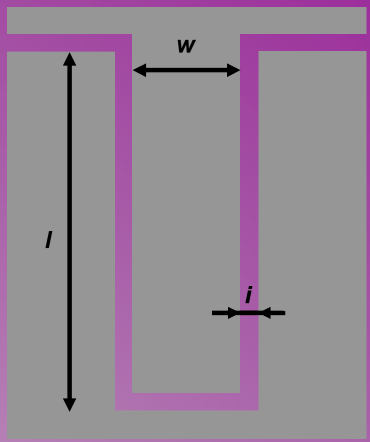



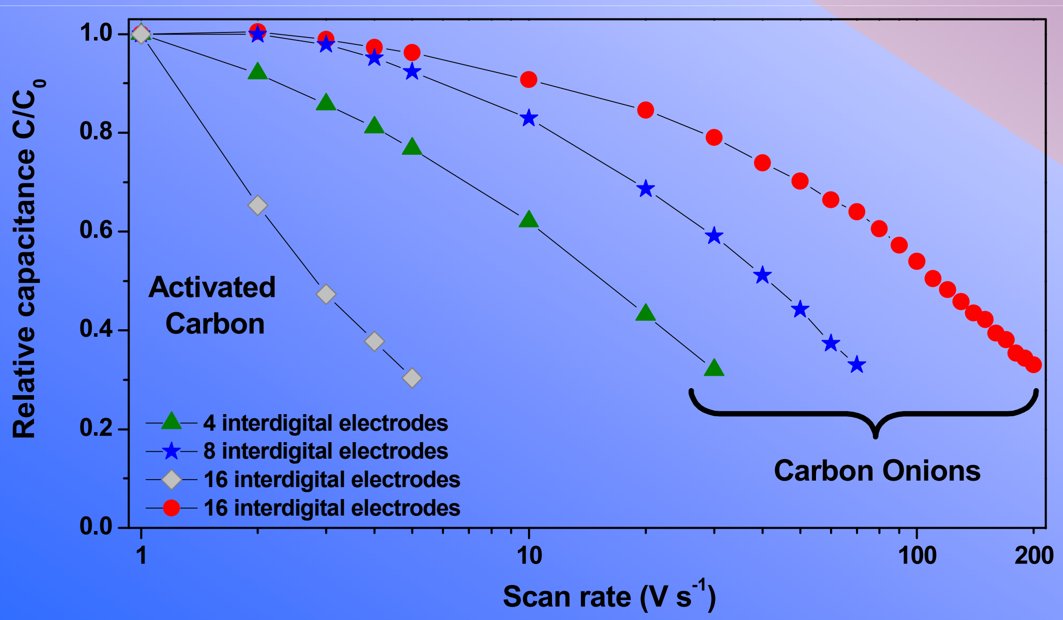

D. Pech, M. Brunet, et al., **Nature Nanotechnology** 9 (2010) 651

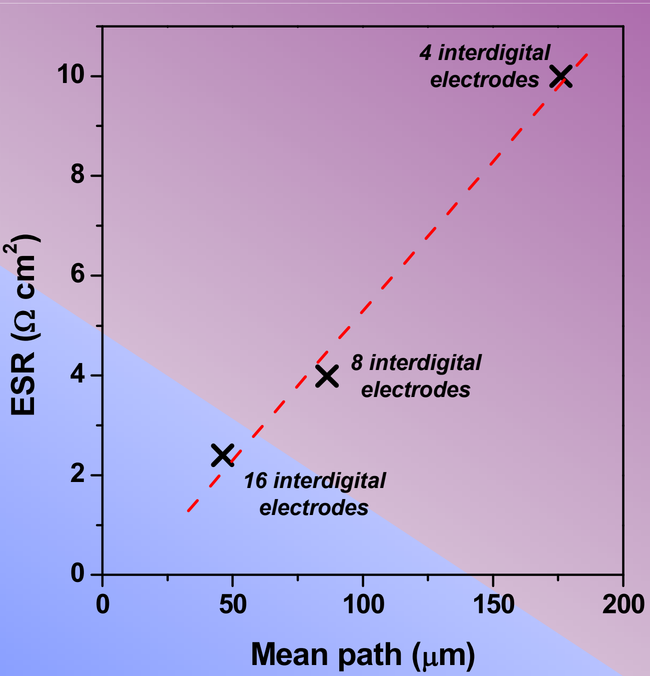
# µ-supercapacitors - EPD

## Highlight on micro-scale effect:

| Number of interdigital electrodes | 4 | 8 | 16 |
|---|---|---|---|
| Width, *w* (µm) | 1175.0 | 537.5 | 218.8 |
| Length, *l* (mm) | 4.5 | 4.5 | 4.5 |
| Interspace, *i* (µm) | 100 | 100 | 100 |
| Surface of the conducting electrodes ($mm^2$) | 21.15 | 19.35 | 15.75 |
| Mean path (µm) | 176.1 | 86.3 | 46.1 |
| Surface of the cell ($mm^2$) | 25 | 25 | 25 |



# µ-supercapacitors versus SoA

- Comparison with SoA µsupercapacitors:

$$E = \frac{1}{2} C(U_0^2 - U_f^2)$$

$$P_{max} = \frac{U_0^2}{4R_s}$$

| Institution | Type | Component Dimensions | Maxim voltage | Maximum Scan rate | Component capacitance | Specific capacitance | ESR | Energy | Power |
|---|---|---|---|---|---|---|---|---|---|
| | | cm² | V | V/sec | mF | mF/cm² | Ω.cm² | mJ/cm² | mW/cm² |
| Berkeley 2006 | Dispenser | 0,25 | 2 | 0,005 | 0,1 | 0,1 | -- | 0,2 | -- |
| MIT 2006 | Origami | 0,0012 | 0,6 | 0,05 | 0,001 | 0,4 | -- | 0,072 | -- |
| Berkeley2009 | CNT forest | 0,35 | 0,6 | 0,05 | 0,149 | 0,43 | -- | 0,077 | 0,28 |
| LAAS 2009 | Inkjet | 0,023 | 2,5 | 1 | 0,046 | 2 | | 6 | 44,9 |
| LAAS 2010 | EPD - AC | 0,25 | 3 | 1 | 1,33 | 5.7 | 4,4 | 23,9 | 506 |
| LAAS 2010 | EPD - OLC | 0,25 | 3 | 200 | 0,258 | 1 | 3,8 | 4,64 | 592 |

- Energy : up to 2 orders of magnitude higher than SoA
- Power: 3 orders of magnitude higher than SoA

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# μ-supercapacitors versus 3D capacitors

- Can μ-supercap compete with 3D capacitors?

### *3D capacitors*

| Institution | Dimensions | Vmax | Capacitan | ESR | Energy | Power |
|---|---|---|---|---|---|---|
| | cm² | | mF/cm² | Ohm.cm² | mJ/cm² | W/cm² |
| LAAS 2006 | 4,90E-03 | 12 | 0,006 | 0,83m | 0,44 | 43200 |
| LAAS 2009 | 6,25E-04 | 8 | 0,065 | 6,88m | 2,10 | 2330 |
| NXP 2001 | 1,00E-01 | 30 | 0,003 | 14,5m | 1,35 | 15500 |
| NXP 2008 | 1,00E-04 | 6 | 0,044 | 1m | 0,79 | 9000 |
| Univ. Maryl | 1,27E-04 | 4 | 0,1 | 1,27m | 0,80 | 3160 |

### *μ-supercapacitors*

| | | | | | | |
|---|---|---|---|---|---|---|
| LAAS 2010 | 0,25 | 3 | 5.7 | 4,4 | 23,9 | 0,506 |
| LAAS 2010 | 0,25 | 3 | 1 | 3,8 | 4,64 | 0,592 |

- Advantages of 3D capacitors:
  - Vmax
  - ESR

  } Power !

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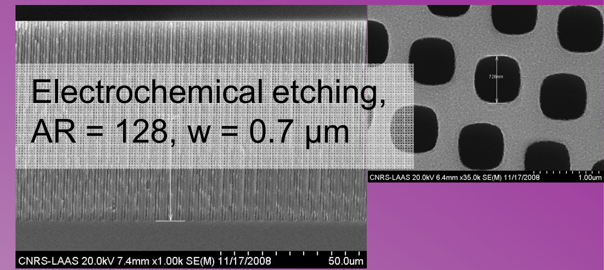
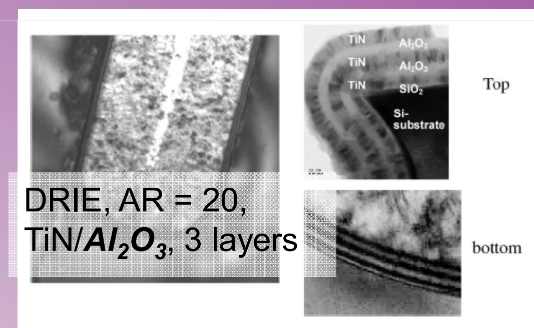


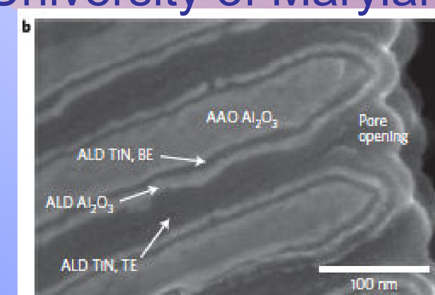

Brunet et al., MME 2009

NXP




Klootwijk, Roozeboom et al., EDL 2008

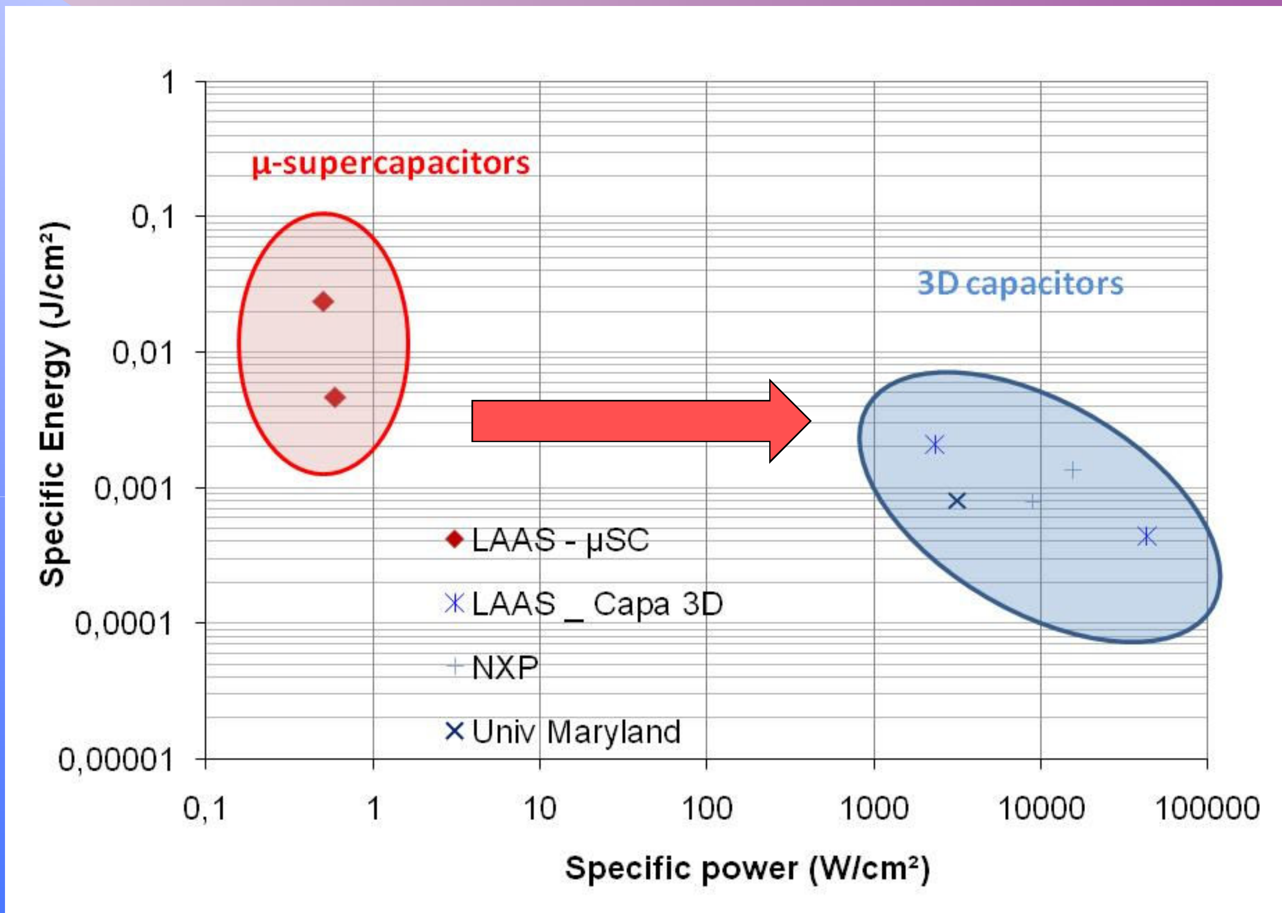
University of Maryland




Banerjee et al., Nature Nano 2009

# µ-supercapacitors versus 3D capacitors

- Can µ-supercap compete with 3D capacitors?

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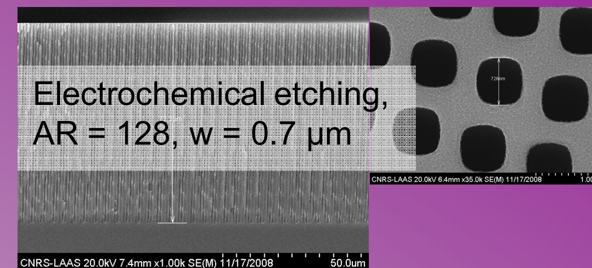
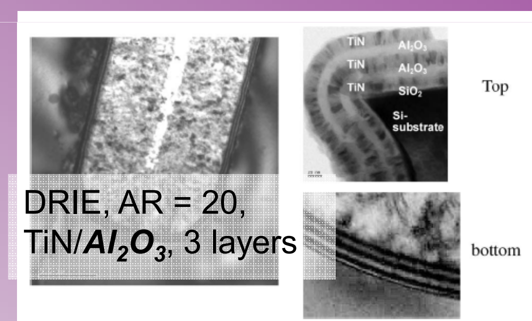


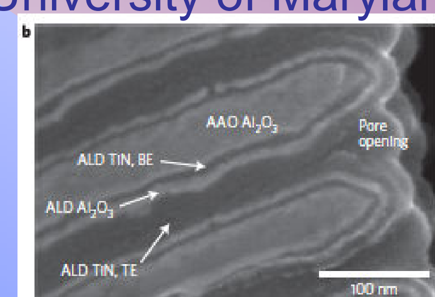

Brunet et al., MME 2009

NXP




Klootwijk, Roozeboom et al., EDL 2008

University of Maryland




Banerjee et al., Nature Nano 2009

- Improve µ-supercap power:
  - Reduce ESR through improved design / electrolyte / material
  - Increase voltage window : hybrid configuration ?

# µ-supercapacitors - Challenges

## Encapsulation of liquid organic electrolyte

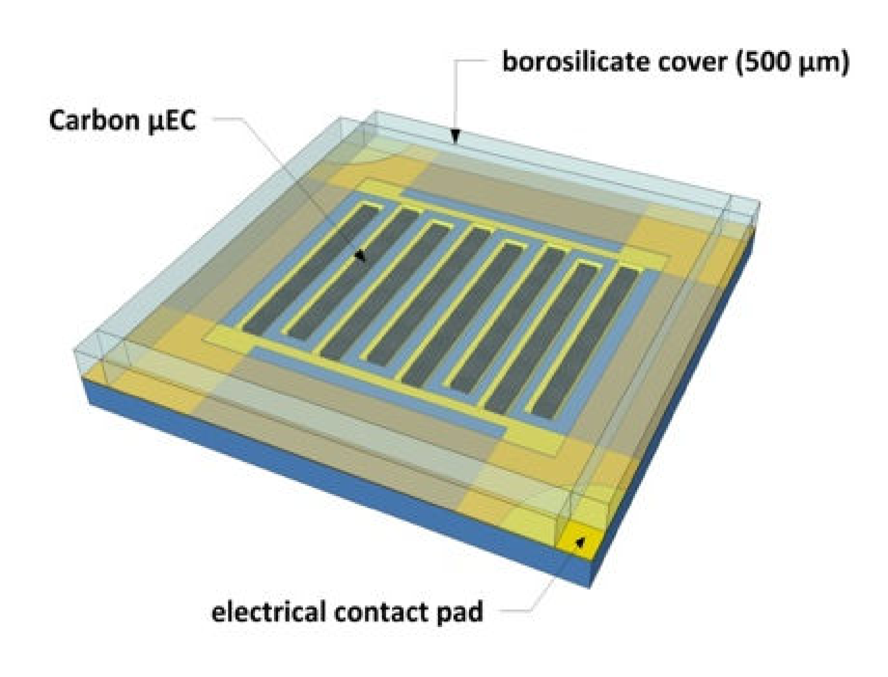
→ Wafer-level packaging

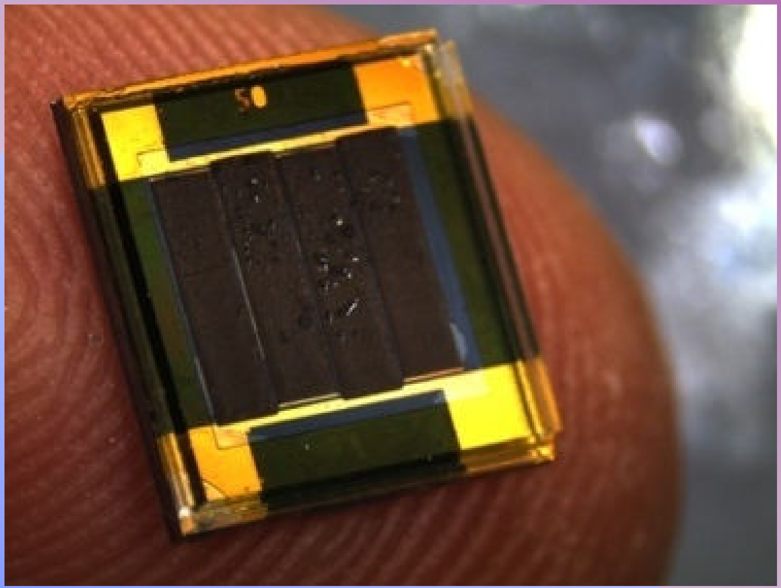
→ Low temperature process (< 150°C)

→ Water tightness: must be processed in glove box → 2.5V range with organic electrolytes

**Process:**

1. *Cover lid: photosensitive glue on glass*
2. *Electrolyte deposition*
3. *Bonding*
4. *Two pass dicing for uncovering electrical contacts*



# Conclusions and Perspectives

- *Conclusions :*
  - Enabled technologies for storage on-chip:
    - Electrophoretic deposition of active material
    - Liquid, water-tight, low temperature encapsulation
  - Benefits of micro-scale and enhanced materials demonstrated

    => Ultra-high power components

- *Perspectives:*
  - *More power:*
    - Improved design: e.g. interspace down to nanoscale
    - Improved materials: OLC, CNT…etc
    - Improved electrolyte
  - *More Energy:*
    - Thicker electrodes
  - Test in real environment with energy harvesting microsystem, electronics, sensor

LAAS-CNRS

# Acknowledgment

**Technical:**

- Clean room facilities at LAAS-CNRS

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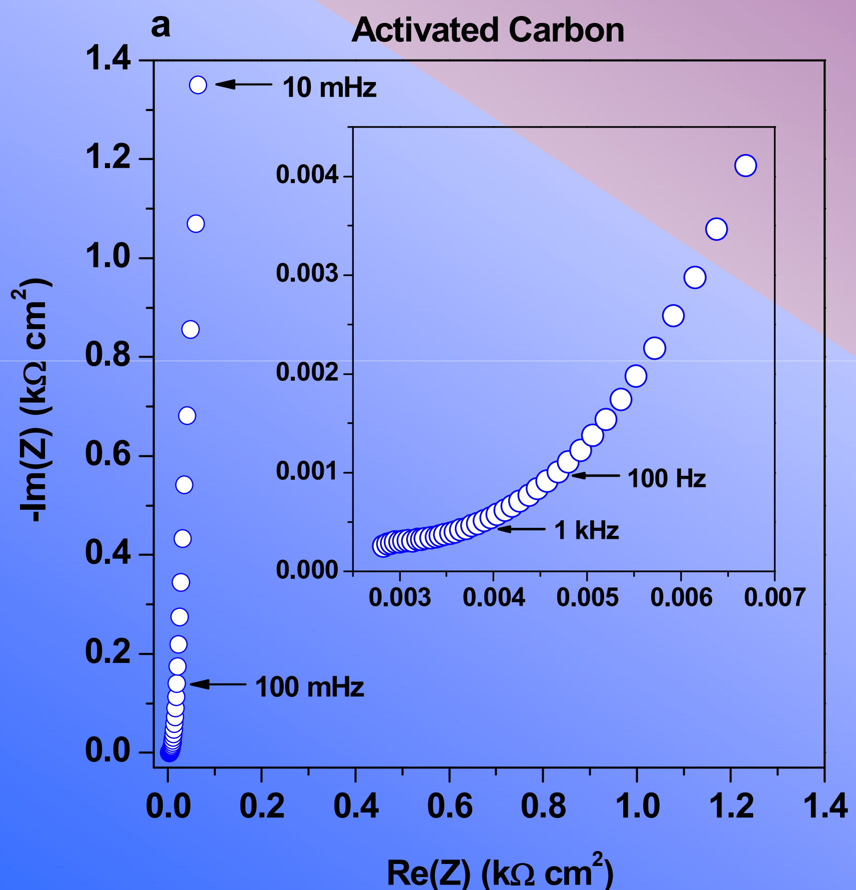
– Project **AUTOSENS** (Fondation de la Recherche Aéronautique et Espace)

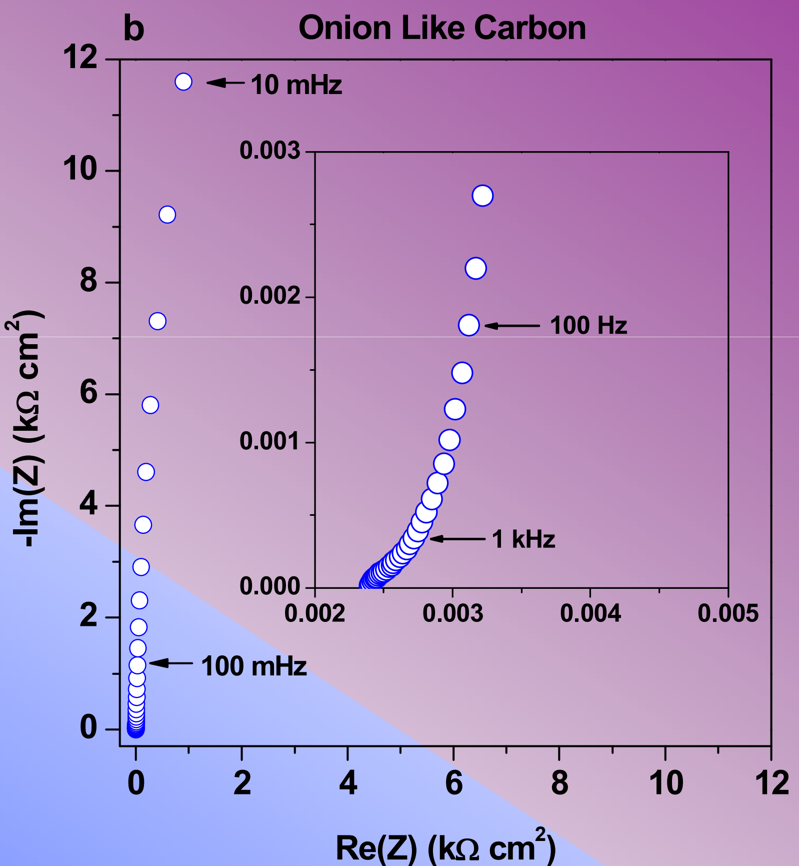
– Projet **µsupercapacitors** (PUF:Partner University Fund, France- US exchange)

**Thank you for your attention.**

# µEDLC - EPD

## Nyquist plots

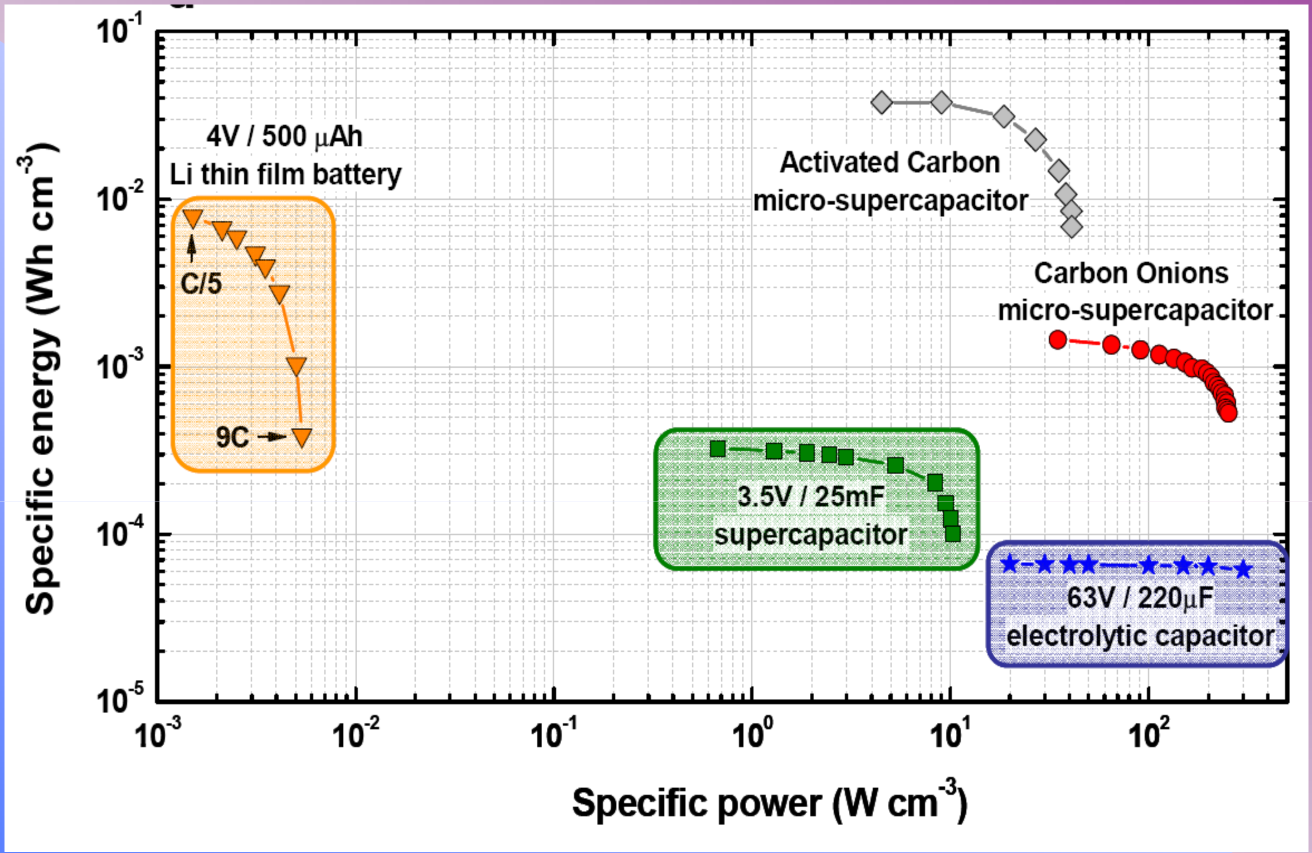


# μEDLC - EPD



## Comparison with macro-scale devices




Energy and Power by cm$^3$ of stack – Composants tested in dynamic conditions.

## Conclusion:

High power densities reached thanks to enhanced nanostructured carbon + microstructured electrodes + no organic ligant

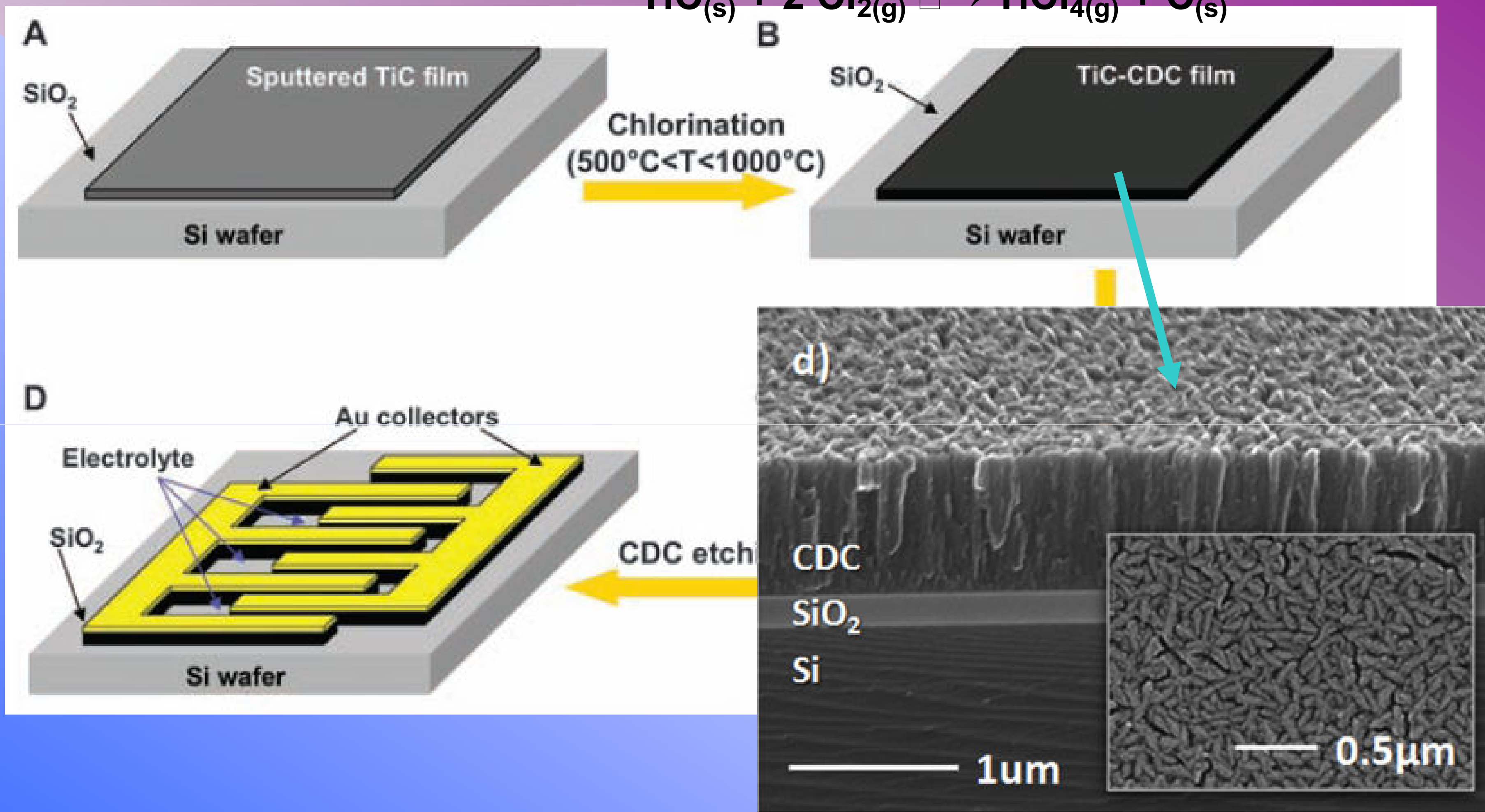
| Componant | Leakage current | Charging time |
|---|---|---|
| Maxwell BCap 5F | 3 µA/F | 72 h @ 25 °C |
| Kanthal LK 1F | 3,3 µA/F | 70 h @ 25 °C |
| Panasonic Goldcap 1F | 0,7 µA/F | 150 h @ 25°C |
| CapXX HW207 0,4F | 5 µA/F | 70 h @ 25 °C |

# µEDLC – Thin films

**CDC (Carbide Derived Carbon)**

(PhD. P. Huang)

$TiC_{(s)} + 2\,Cl_{2(g)} \rightarrow TiCl_{4(g)} + C_{(s)}$




→ ***Technology adapted to micro-fabrication***

→ ***High density material:*** ***180 F/cm³ (Activated carbon = 50 F/cm³)***

*J. Chmiola et al.*, Science *328* (2010) *480*.