Ultra high power carbon-based micro-supercapacitors

Magali Brunet, David Pech, Hugo Durou, Peihua Huang

Laboratoire d’Analyse et d’Architecture des Systèmes, CNRS, Université de Toulouse

Pierre-Louis Taberna, Patrice Simon
CIRIMAT, CNRS, Université de Toulouse

Yury Gogotsi, Vadym Mochalin, Min Heon
A.J. Drexel Nanotechnology Institute, Drexel University, Philadelphia
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

- Metal oxides: RuO$_2$, MnO$_2$
- Conducting polymers: PPy

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrolyte</th>
<th>Density (g/cm$^3$)</th>
<th>C (F/g)</th>
<th>C (F/cm$^3$)</th>
<th>C (F/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon</td>
<td>Organic (2.5 V)</td>
<td>0.7</td>
<td>100-200</td>
<td>70-140</td>
<td>17.5-35</td>
</tr>
<tr>
<td>Hydrous RuO$_2$</td>
<td>Sulfuric acid (1V)</td>
<td>2</td>
<td>650</td>
<td>1300</td>
<td>325</td>
</tr>
</tbody>
</table>
Typical applications

**Loading /unloading container ships:**
Captures and stores regenerative energy during load;
fuel saving of 40%

**Tools:** cutters, screw drivers…

**Transport:**
- buses, tramways
- Hybrid cars

**Emergency door opening**
(AIRBUS A380 Jumbo Jet)

**Portable electronics:**
- Memory maintenance
- Battery auxiliary for power boosts

**Self-powered applications…**

**Power**
- MWatt
- KWatt
- Watt
- mWatt

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
photovoltaïc, thermoelectric, piézoélectric, electromagnetic

Energy storage and management

Applications

Technological problems

Microbatteries

• Limited lifetime
  (→ restriction on the autonomy of the whole system)

• Low power density

+ Temperature range, Integration, Pollution...

Energy storage in supercapacitors
Practical example: AutoSENS project

Autonomous Wireless Sensors Network (WSN) for aircraft structural monitoring

Structural Health Monitoring (SHM)

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

→ Reduce inspection costs
→ Increase safety

Specifications for in flight measurement:
• 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**

Conversion: AC-DC ; DC-DC

Storage: **supercapacitors** (90 mF/cm²)

Carbon (life time)

Organic electrolyte (temperature range)

Take off => 1m.s⁻²@ 50 Hz
Cruise => 0.1m.s⁻²@ 50 Hz

===> **Piezoelectric generator**
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**

- **Maxwell PC5**
  - 14 mm x 23.6 mm x 4.8 mm
  - C = 4 F – 2.5 V

- **Cellergy CLX04P007L12**
  - 12 mm x 12.5 mm x 2 mm
  - C = 7 mF – 4.2 V

- **Selko Instruments GmbH**
  - 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


**Conducting polymers (Polypyrrole)**

- **Interdigital – 50 µm**

- **Flexible μ-supercapacitors**

- **AAO template**
State of the art

Carbon based μ-SC

- Dispenser Printing on PCB (Berkeley Univ., US)
  - 5 mm x 5 mm x 100 µm
  - $C = 0.1 \text{ mF/cm}^2$
  - 2 V
  - C.C. Ho et al., PowerMEMS 2006.

- Probe tip deposition + Origami™ process (MIT, US)
  - 350 µm x 350 µm x 40 µm
  - $C = 0.4 \text{ mF/cm}^2$
  - 0.6 V

- Printable Micro-Supercapacitor using SWCNT (Stanford Univ., US)
  - Solid Electrolyte: PVA / $\text{H}_3\text{PO}_4$ (water-based)
  - ~10 µm thick
  - $C = 1.2 \text{ mF/cm}^2$
  - 1 V
State of the art

- Inkjet printing (LAAS-CNRS, France)

**Active material**

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

Pros:
- High resolution

Cons:
- Limited thickness
- Emulsion stability difficult

400 µm x 600 µm x 2 µm

\[ C = 2.1 \text{ mF/cm}^2 \]
\[ E = 6.6 \text{ mJ/cm}^2 \]
\[ P = 44.9 \text{ mW/cm}^2 \]

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  – Technology + materials
  – Performance
  – Comparison with 3D capacitors

• Conclusions and perspectives
**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)
Results with activated carbon
YP-50F (1700 m²/g)

Tests in 1M Et₄NBF₄/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

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>Potential window</th>
<th>Electrode Capacitance</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 mm²</td>
<td>2 V</td>
<td>0.5 mF/cm²</td>
<td>Berkeley</td>
</tr>
<tr>
<td>0.12 mm²</td>
<td>0.6 V</td>
<td>1.6 mF/cm²</td>
<td>MIT</td>
</tr>
<tr>
<td>-</td>
<td>1 V</td>
<td>4.8 mF/cm²</td>
<td>Stanford</td>
</tr>
<tr>
<td>25 mm²</td>
<td>2.5 V</td>
<td>18 mF/cm²</td>
<td>LAAS</td>
</tr>
</tbody>
</table>
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


Thickness = 7 µm

\[
C = 0.258 \text{ mF} = 1.7 \text{ mF/cm}^2
\]

\[
E = 4.6 \text{ mJ/cm}^2
\]

\[
P = 592 \text{ mW/cm}^2
\]

μ-supercapacitors - EPD

Active material comparison:

Stack capacitance (F cm⁻³)

Volumetric energy (Wh cm⁻³)

 Highlight on micro-scale effect:

<table>
<thead>
<tr>
<th>Number of interdigital electrodes</th>
<th>4</th>
<th>8</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width, $w$ (µm)</td>
<td>1175.0</td>
<td>537.5</td>
<td>218.8</td>
</tr>
<tr>
<td>Length, $l$ (mm)</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Interspace, $i$ (µm)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Surface of the conducting electrodes (mm$^2$)</td>
<td>21.15</td>
<td>19.35</td>
<td>15.75</td>
</tr>
<tr>
<td>Mean path (µm)</td>
<td>176.1</td>
<td>86.3</td>
<td>46.1</td>
</tr>
<tr>
<td>Surface of the cell (mm$^2$)</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>
### μ-supercapacitors versus SoA

- Comparison with SoA μsupercapacitors:

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

\[
P_{\text{max}} = \frac{U_0^2}{4R_s}
\]

<table>
<thead>
<tr>
<th>Institution</th>
<th>Type</th>
<th>Component Dimensions</th>
<th>Maxim voltage</th>
<th>Maximum Scan rate</th>
<th>Component capacitance</th>
<th>Specific capacitance</th>
<th>ESR</th>
<th>Energy</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berkeley 2006</td>
<td>Dispenser</td>
<td>0.25</td>
<td>2</td>
<td>0.005</td>
<td>0.1</td>
<td>0.1</td>
<td>--</td>
<td>0.2</td>
<td>--</td>
</tr>
<tr>
<td>MIT 2006</td>
<td>Origami</td>
<td>0.0012</td>
<td>0.6</td>
<td>0.05</td>
<td>0.001</td>
<td>0.4</td>
<td>--</td>
<td>0.072</td>
<td>--</td>
</tr>
<tr>
<td>Berkeley 2009</td>
<td>CNT forest</td>
<td>0.35</td>
<td>0.6</td>
<td>0.05</td>
<td>0.149</td>
<td>0.43</td>
<td>--</td>
<td>0.077</td>
<td>0.28</td>
</tr>
<tr>
<td>LAAS 2009</td>
<td>Inkjet</td>
<td>0.023</td>
<td>2.5</td>
<td>1</td>
<td>0.046</td>
<td>2</td>
<td>6</td>
<td>44.9</td>
<td></td>
</tr>
<tr>
<td>LAAS 2010</td>
<td>EPD - AC</td>
<td>0.25</td>
<td>3</td>
<td>1</td>
<td>1.33</td>
<td>5.7</td>
<td>4.4</td>
<td>23.9</td>
<td>506</td>
</tr>
<tr>
<td>LAAS 2010</td>
<td>EPD - OLC</td>
<td>0.25</td>
<td>3</td>
<td>200</td>
<td>0.258</td>
<td>1</td>
<td>3.8</td>
<td>4.64</td>
<td>592</td>
</tr>
</tbody>
</table>

- Energy: up to 2 orders of magnitude higher than SoA
- Power: 3 orders of magnitude higher than SoA
### μ-supercapacitors versus 3D capacitors

• Can μ-supercap compete with 3D capacitors?

#### 3D capacitors

<table>
<thead>
<tr>
<th>Institution</th>
<th>Dimensions</th>
<th>Vmax</th>
<th>Capacitance</th>
<th>ESR</th>
<th>Energy</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAAS 2006</td>
<td>4.90E-03</td>
<td>12</td>
<td>0.006</td>
<td>0.83</td>
<td>0.44</td>
<td>43200</td>
</tr>
<tr>
<td>LAAS 2009</td>
<td>6.25E-04</td>
<td>8</td>
<td>0.065</td>
<td>6.88</td>
<td>2.10</td>
<td>2330</td>
</tr>
<tr>
<td>NXP 2001</td>
<td>1.00E-01</td>
<td>30</td>
<td>0.003</td>
<td>14.5</td>
<td>1.35</td>
<td>15500</td>
</tr>
<tr>
<td>NXP 2008</td>
<td>1.00E-04</td>
<td>6</td>
<td>0.044</td>
<td>1.0</td>
<td>0.79</td>
<td>9000</td>
</tr>
<tr>
<td>Univ. Maryl</td>
<td>1.27E-04</td>
<td>4</td>
<td>0.1</td>
<td>1.27</td>
<td>0.80</td>
<td>3160</td>
</tr>
</tbody>
</table>

#### μ-supercapacitors

<table>
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<td>1</td>
<td>3.8</td>
<td>4.64</td>
</tr>
</tbody>
</table>

### Advantages of 3D capacitors:

- Vmax
- ESR

Power!
μ-supercapacitors versus 3D capacitors

• Can μ-supercap compete with 3D capacitors?

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

LAAS-CNRS

Electrochemical etching, AR = 128, w = 0.7 µm

Brunet et al., MME 2009

NXP

DRIE, AR = 20, TiN/Al₂O₃, 3 layers

Klootwijk, Roozeboom et al., EDL 2008

University of Maryland

Banerjee et al., Nature Nano 2009
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
**Acknowledgment**

**Technical:**

- Clean room facilities at LAAS-CNRS

**Funding:**

- Project AUTOSENS (Fondation de la Recherche Aéronautique et Espace)

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

Thank you for your attention.
Nyquist plots

a) Activated Carbon

b) Onion Like Carbon
Conclusion:

High power densities reached thanks to enhanced nanostructured carbon + microstructured electrodes + no organic ligand
<table>
<thead>
<tr>
<th>Component</th>
<th>Leakage current</th>
<th>Charging time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell BCap 5F</td>
<td>3 μA/F</td>
<td>72 h @ 25 °C</td>
</tr>
<tr>
<td>Kanthal LK 1F</td>
<td>3,3 μA/F</td>
<td>70 h @ 25 °C</td>
</tr>
<tr>
<td>Panasonic Goldcap 1F</td>
<td>0,7 μA/F</td>
<td>150 h @ 25 °C</td>
</tr>
<tr>
<td>CapXX HW207 0,4F</td>
<td>5 μA/F</td>
<td>70 h @ 25 °C</td>
</tr>
</tbody>
</table>
μEDLC – Thin films

CDC (Carbide Derived Carbon)

\[ \text{TiC}_\text{(s)} + 2 \text{Cl}_\text{(g)} \rightarrow \text{TiCl}_4\text{(g)} + \text{C}_\text{(s)} \]

→ Technology adapted to micro-fabrication

→ High density material: 180 F/cm\(^3\) (Activated carbon = 50 F/cm\(^3\))