Trans-Atlantic Workshop on Storage Technologies for Power Grids
Washington, October 19th-20th 2010

"Electrochemical Capacitors for Power Grid Storage technology:
State of the art and next challenges"

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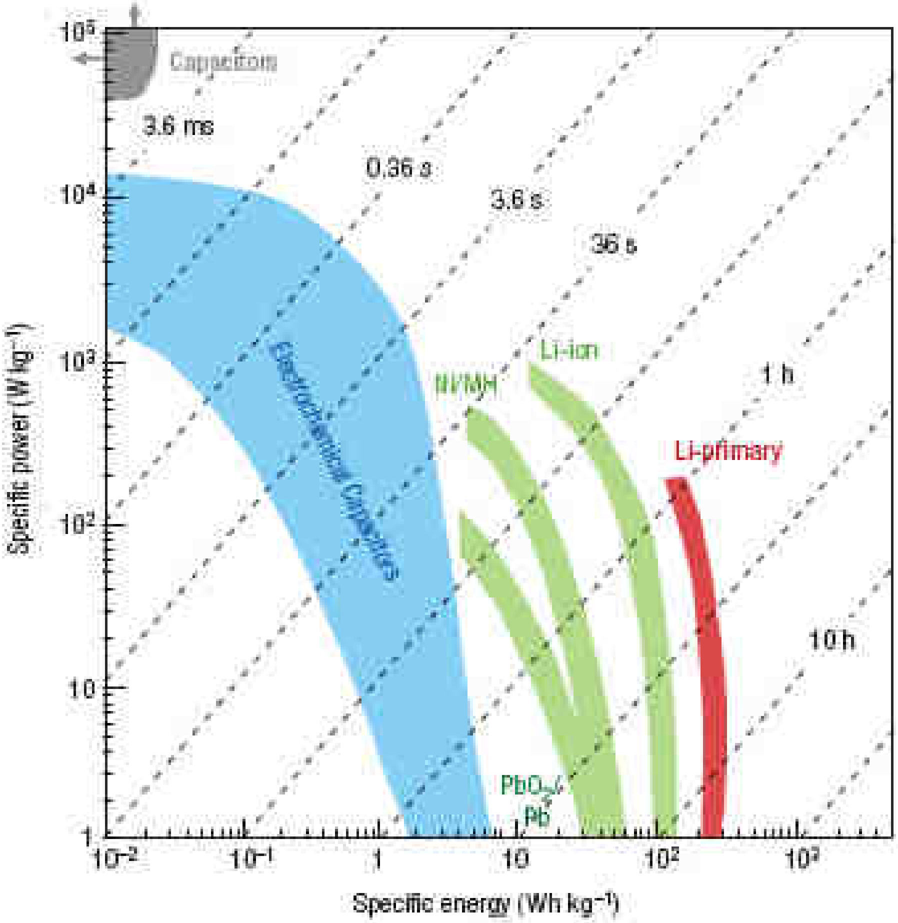
Electrochemical Capacitors

Electrochemical Capacitors:
- high power (10-20 kW/kg)
- medium energy density (5 Wh/kg)
- time constant about 1 – 5 s

→ **performance between capacitors and batteries**



ECs:
- Carbon-based (EDLCs)
- Oxide-based (pseudocapacitors)

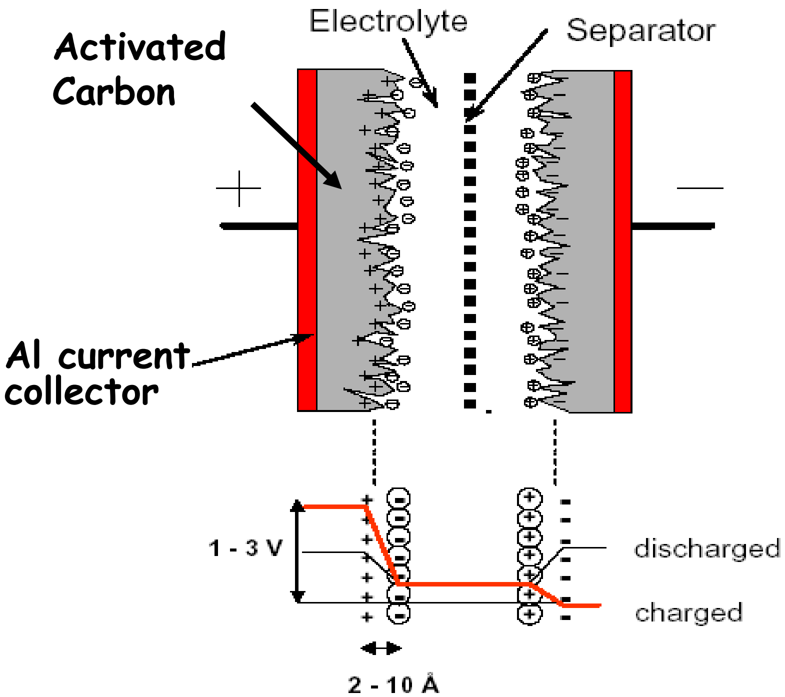
Electrochemical Double Layer Capacitors (EDLCs)

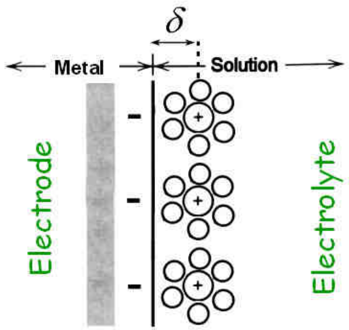
95% of the commercialized cells

→ high surface area carbons as active materials

Electrochemical Double Layer Capacitor basics

ECDL capacitor





Charge of the double layer C

$$C = (\varepsilon_0 \varepsilon S) / d$$

(about 10-20 μF.cm^{-2})

Ion adsorption onto Activated carbon

- high surface area (1500 m^2.g^{-1})

→ about 100 F. g^{-1} of carbon

- electrolyte: AN or PC-based electrolytes (cell voltage = 2.7V)

Supercapacitors:

- no redox reaction → ***high power***
- very high cyclability ***(> 10^6 cycles)***
- ***fast-rate discharge AND charge***
- ***low temperature*** operation (-40 °C)

Applications:

- high power for < 10s

→ complement to Li-ion batteries

1.2 EDLC Applications

Capacitive storage for Power Grids:

Power Quality:

→ grid stabilization: suppress voltage sags and swells due to high peak power demands (peak-shaving)

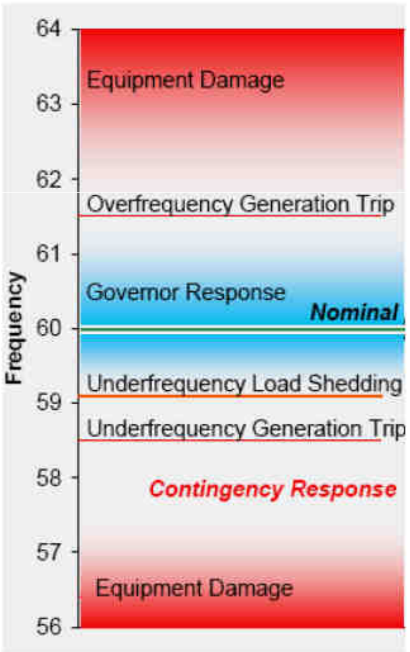


Fig. 4. The ac frequency range of a typical electric power system, showing operator-controlled and automatic control responses.[6]

Table 3. Top-level energy storage requirements for grid applications[9]

	Customer (load) applications		Power system operator applications		
Storage technology parameter	**Power quality**	**Backup power for outages**	**Regulation**	**Reserve power for grid stability and reliability**	**Load shifting and load leveling**
Capital cost (1) ($/kW)	400		700	300–1000	300 (load leveling) 400–1000 (peak shaving and load shifting) 650 (renewables)
Total U.S. market potential (GW)			30–40	70–100	80 (cost sensitive)
Storage system power level	Up to 100 kW	1 to 50 MW	Up to 200 MW	10 MW to 1	1 MW to 1 GW
Discharge time at rated power	0 to 5 s	Minutes to days	Seconds	0.2 to 2 h	1– 8 hours
Capacity (storage time)	Up to 1 min	Months to years	Seconds	~ 2 weeks	Hours to days
Lifetime (years)	5	20	20	40	7–10
Other			Long cycle length		

Basic Research Needs for Electrical Energy Storage, DOE Worshop, Washington, April 2-4, 2007

1. EDLC (Challenges)

Next Challenges for Supercapacitors

Increase the energy density to >10 Wh/kg
($E=1/2\ C.V^2$)

1. EDLCs: Carbons with controlled Pore Size to increase C
Control the carbon pore size to maximize Capacitance
→ designing carbons with tailored pore size

2. Multifunctionnal charge storage concept to increase C
Combining EDLC and pseudo-capacitive charge storage (DOE report 2007)
→ "pseudo-intercalation" reaction

3. Increasing the cell voltage
→ developing new electrolytes and architectures

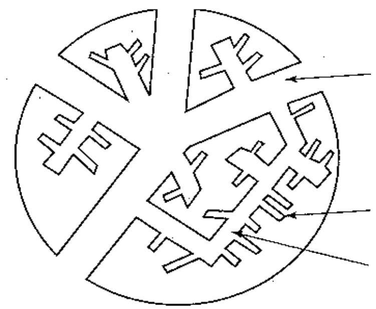
Active materials for EDLCs → Activated Carbon

Activated carbons:

Physical or Chemical activation → Porous network → *High SSA* ~1500 m²/g

A. G. Pandolfo and A.F. Hollenkamp, J. Power Sources 157 (2006) 11-27

BUT poor control on pore size …

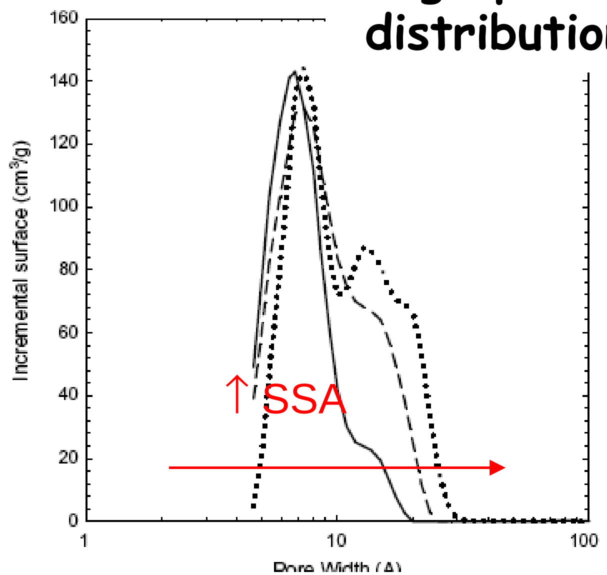


Macropores : > 50 nm

Micropores : < 2 nm

Mesopores : 2 nm - 50 nm

Large pore size distribution



O. Barbieri et al. / Carbon 43 (2005) 1303–1310

1. Anomalous capacitance increase in carbon nanopores

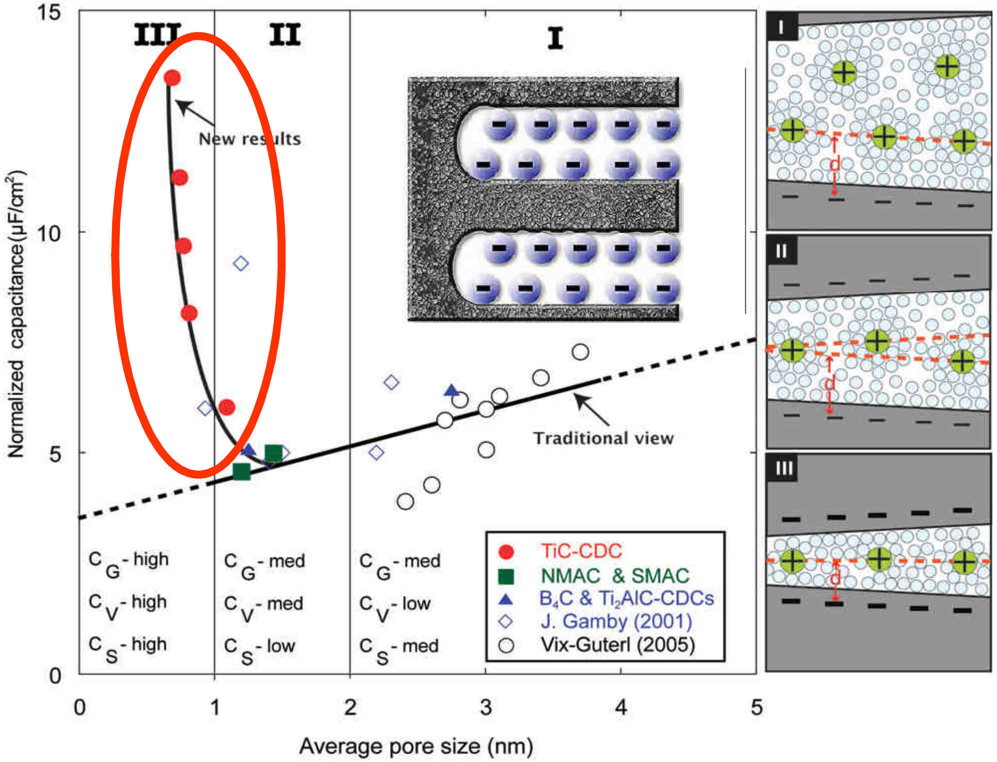
Selective etching of metal from carbide (TiC, SiC, ZrC…)

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

Why CDCs? → Very fine pore size control (unimodal)

Pores smaller than the solvated ion size are accessible to the ions

High capacitance in micropores



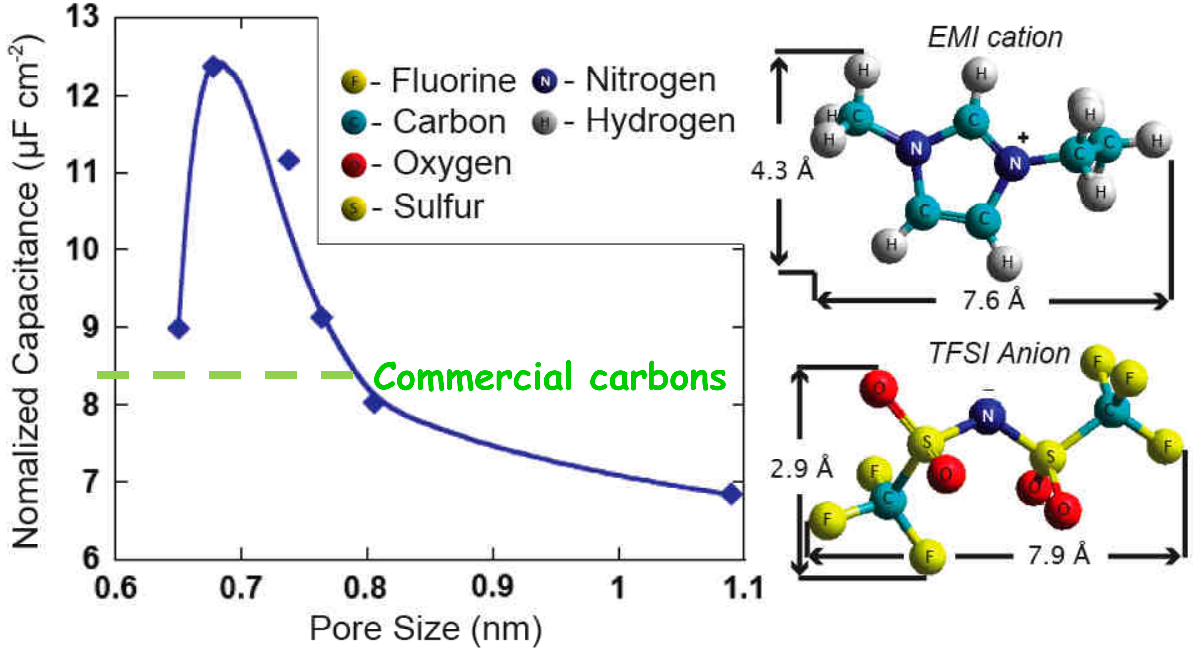
Hypothesis:

→ Micropores accessible thanks to the distortion of the ion solvation shell

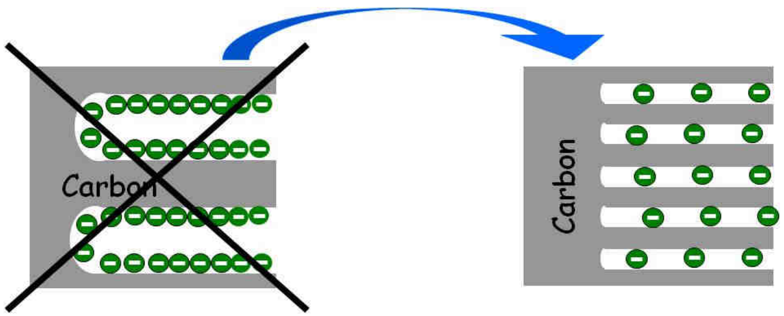
J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P.L. Taberna and P. Simon, *Science* 313, 1760-1763 (2006)

1. Anomalous capacitance increase in carbon nanopores

Capacitance change vs carbon pore size in solvent-free electrolyte



1. From +50% to 100% increase capacitance vs commercial AC
2. Maximum at approx. 0.7 nm → when ion size ~ pore size!!!



Maximum Capacitance when pore size ~ ion size!!

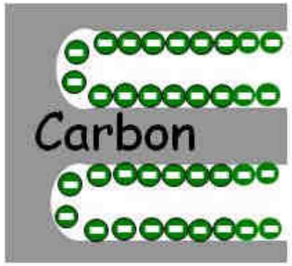
Why ? → *still unclear!*

1. Carbons: summary and perspectives

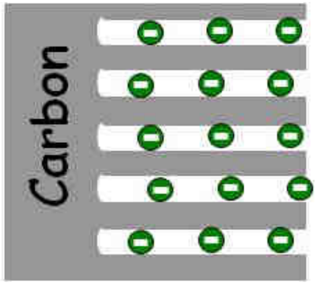
Summary for carbon materials:

1. Anomalous capacitance increase in micropores thanks to ion partial desolvation → high-energy EDLCs (+100% Cvol.)
2. Recast the double layer theory in sub-nanopores

from



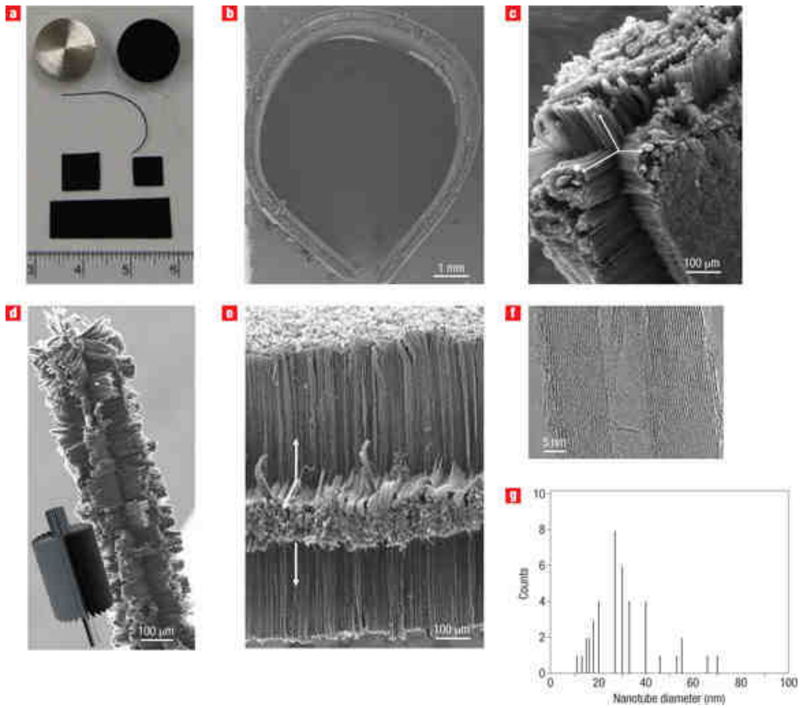
to



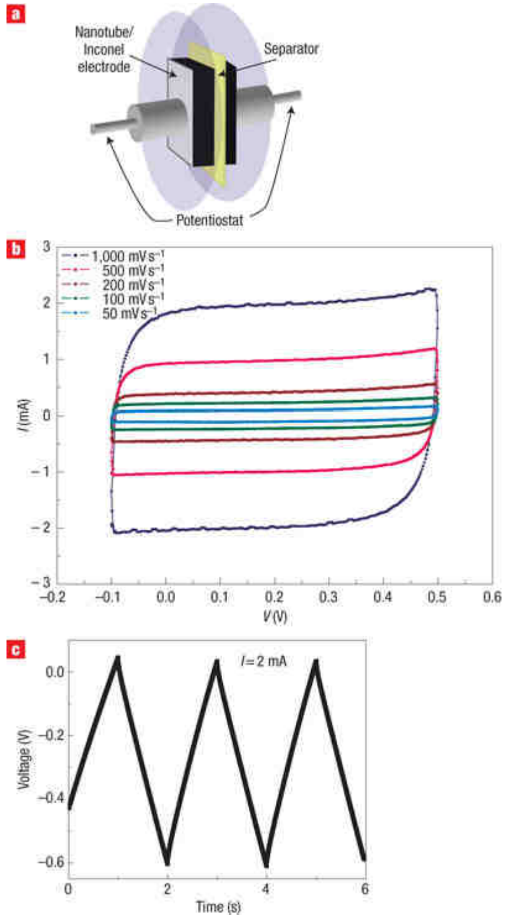
Challenges:

1. designing carbons with controled pore size
   → new (cheap) synthesis routes (from biomass or others)
2. understanding the « anomalous capacitance » effect to fully exploit this effect:
   → in-situ experiments needed (NMR, XRD) coupled with modeling

What about nanostructured carbons (CNTs, nanofibers…)?



Talapatra et al., Nature Nanotechnology 1 (2) 112-116 Nov. 2006



High P with low E density (capacitance is at least twice less than activated carbons)

→ Applications for AC line filtering (grid/storage system interface)

1. Carbons: perspectives

→ AC line filtering (grid/storage system interface)

Graphene-based Double-Layer Capacitor (Science, September 2010)

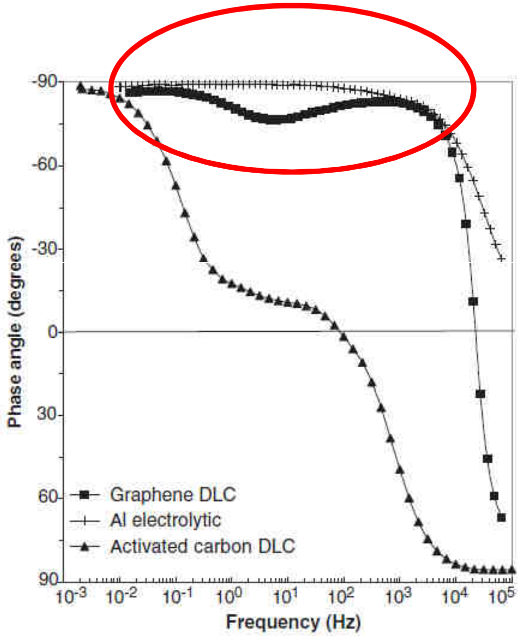
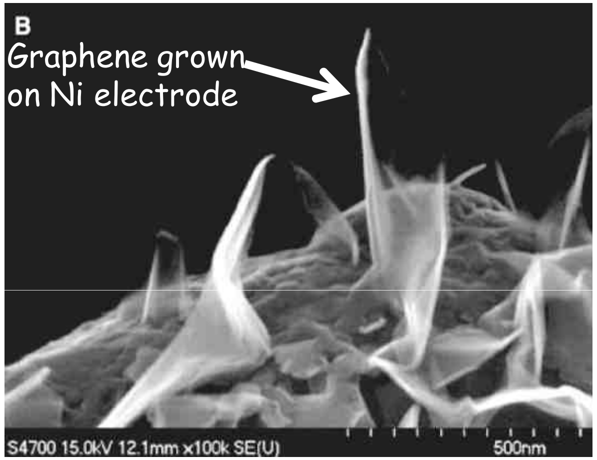


Fig. 2. Impedance phase angle versus frequency for the graphene nanosheet DLC. Measurements from a commercial DLC having an activated carbon electrode and an aluminum electrolytic capacitor are shown for comparison.



-90° phase angle at 120Hz

Store 50 times more charge than electrolytic capacitors

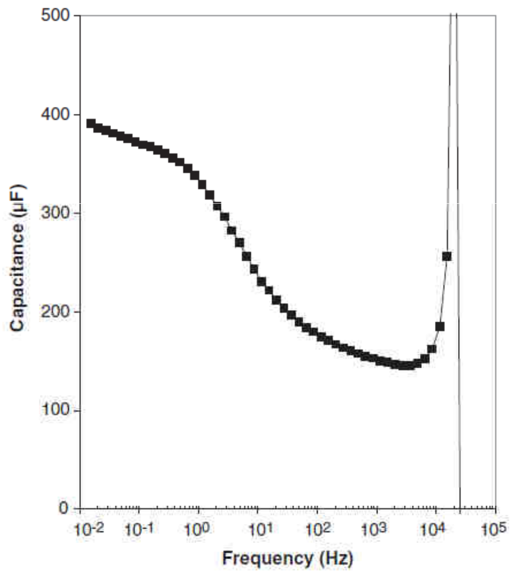
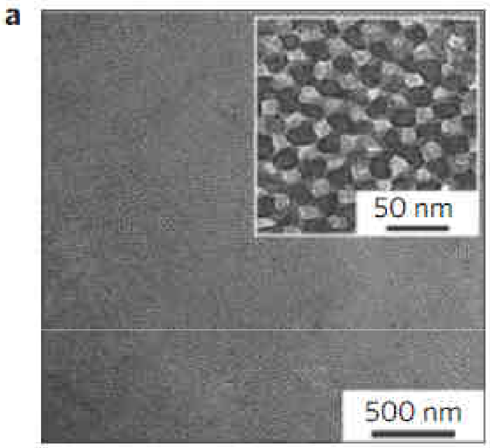


Fig. 4. Capacitance versus frequency of the graphene nanosheet DLC, assuming a series-RC circuit model. Capacitive behavior is shown up to ~10^4 Hz.

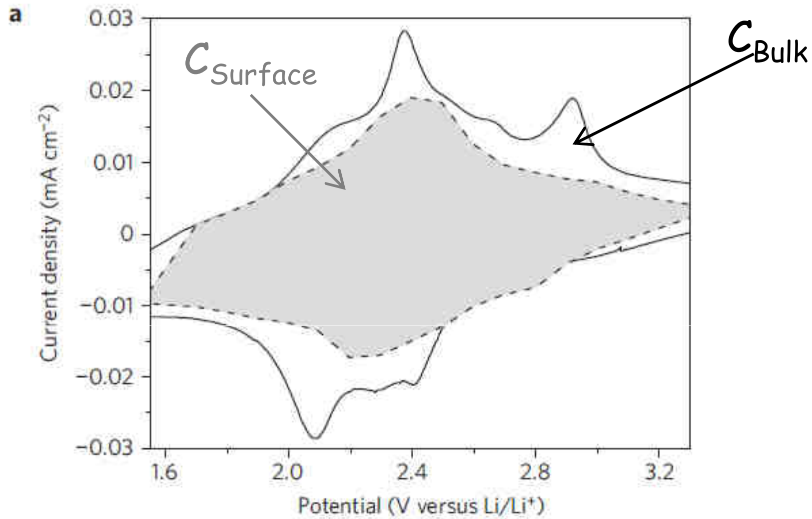
John R. Miller, R. A. Outlaw, B. C. Holloway in Science 327 (2010) 1637-1639

2. Pseudo-capacitive Materials

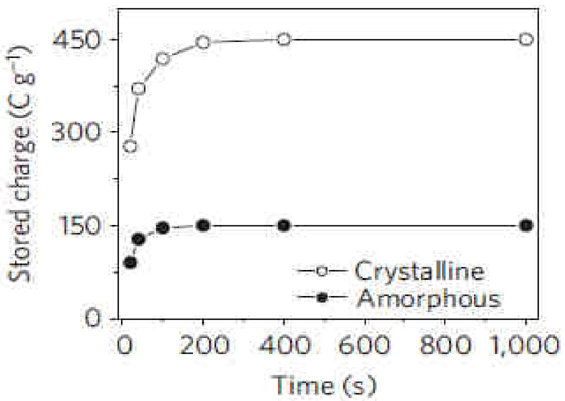
Pseudo-capacitance: fast, surface redox reaction known for RuO_2, MnO_2 (...)



Nanostructured crystalline
Mesoporous MoO_3



1) Fast redox reaction: $Li^+ + xe^- + MoO_3 \rightarrow Li_xMoO_3$
2) No diffusion limitation

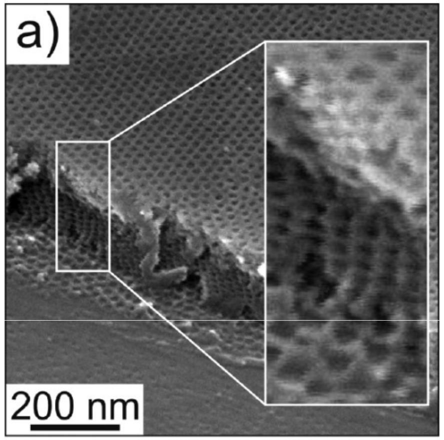


Surface capacitance is 3 times larger than the theoretical one

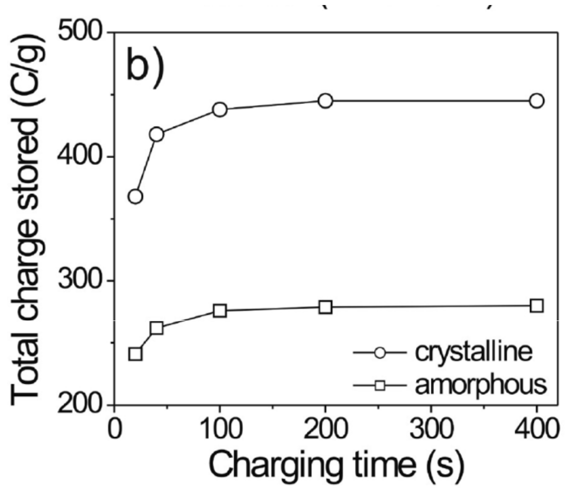
→ **New reaction mechanism concept: "Pseudo-intercalation" reaction**

T. Brezesinski, J. Wang, S. H. Tolbert, B. Dunn Nature Materials 9 (2010) 148-151

Nanostructuration of mesoporous cristalline oxides



Nanostructured crystalline Mesoporous Nb_2O_5



B. Dunn et al., JACS 132, (2010) 6982-6990

Capacitance x2

(same results with V_2O_5, Ta_2O_5, TiO_2)

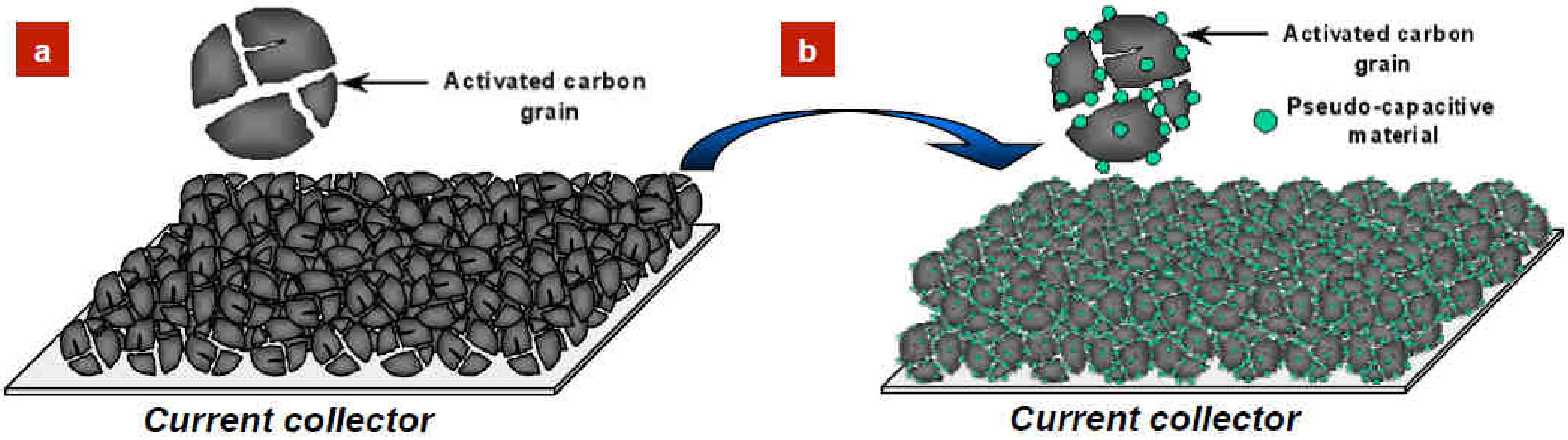
→ Taking advantage of this "new" reaction mechanism to prepare high pseudo-capacitive materials and explore various oxides, nitrides

2. Pseudo-capacitive materials: perspective

1. Synthesis of mesoporous cristalline oxides and/or nitrides (...)

2. New synthesis routes (fine-tuning porosity, upscaling)

3. Decorating high specific surface area carbons with these mesoporous materials...



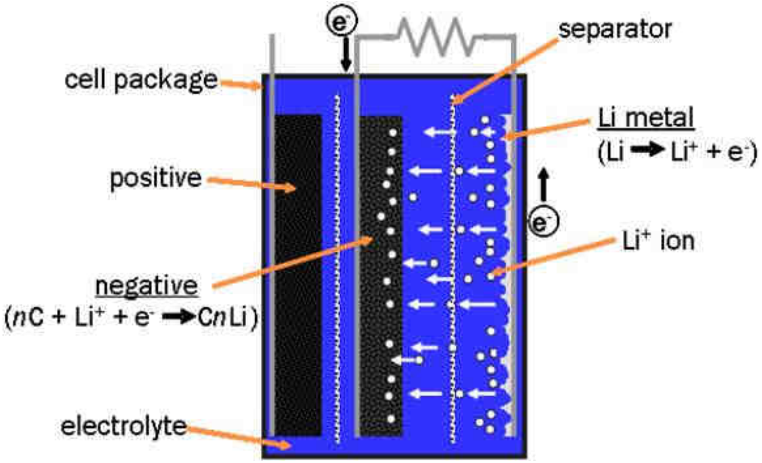
P. Simon and Y. Gogotsi, Nature Materials 7 (2008) 845-854

... to combine Double Layer capacitance and pseudo-intercalation capacitance

3. Increasing the cell voltage

1. Combining a battery-like electrode to a capacitive electrode

The Li-ion capacitor (JSR Corp.)



Negative electrode: Li^+ / Cgraphite
$6C + x\ e^- + x\ Li^+ \leftrightarrow LixC_6$
Pre-lithiated graphite

Positive electrode: Activated Carbon
$xC + xe^- + xY^+] \leftrightarrow [xC^-, xY^+]$

http://jmenergy.co.jp/en/index.html

Cell Voltage (V)	C (F) / Ah	Energy (Wh/kg)	R_{DC} (mΩ)	Power max. (kW/kg)
3.8 - 2.2	2200 / 1	14	2.3	8

*Self discharge after 3 months ** 100C at 100% DOD

BUT:
- high power uptake?
- low T behaviour?
- cyclability at high DOD?

Added value vs high power Li-ion cells questionable

3. Increasing the cell voltage

2. Designing new electrolytes

Today's best performance:

Acetonitrile-based electrolytes* (CH_3-CN) + 1M NEt_4BF_4 (60 mS/cm @25°C)

E_{cell}=2.7V, $T_{operation}$-40°C / +70°C

*Japan: carbonate-based electrolytes (PC) but lower conductivity (15 mS/cm @25°C) since AN forbiden (safety)

Research directed towards:
- replacement of acetonitrile
- implementing Ionic Liquids

Key (unsoved) issues:
- conductivity
- conductivity at T< roomT

Still no real breakthough

Future research directions for capacitive storage

1. Carbon

a) Synthesis of carbons with controlled pore size
→ new (cheap) synthesis routes (from biomass or others)
b) Basic work needed to understand the anomalous capacitance increase
→ coupling in-situ experiments to modeling
c) Nanostructured carbons (CNTs, graphene) for high power (filtering)

2. Pseudo-capacitive materials

a) Synthesis of mesoporous cristalline oxides and/or nitrides (...)
b) New synthesis routes (fine-tuning porosity, upscaling)
c) Decorating high specific surface area carbons with pseudo-capacitive materials

3. Electrolyte

a) Ionic Liquid mixture to decrease T operation (eutectic mixtures?)

Thanks for your attention