UNIVERSITE D'ORLEANS

Centre de Recherche sur la Matière Divisée

Stockage de l'énergie dans des supercondensateurs à base de matériaux carbonés

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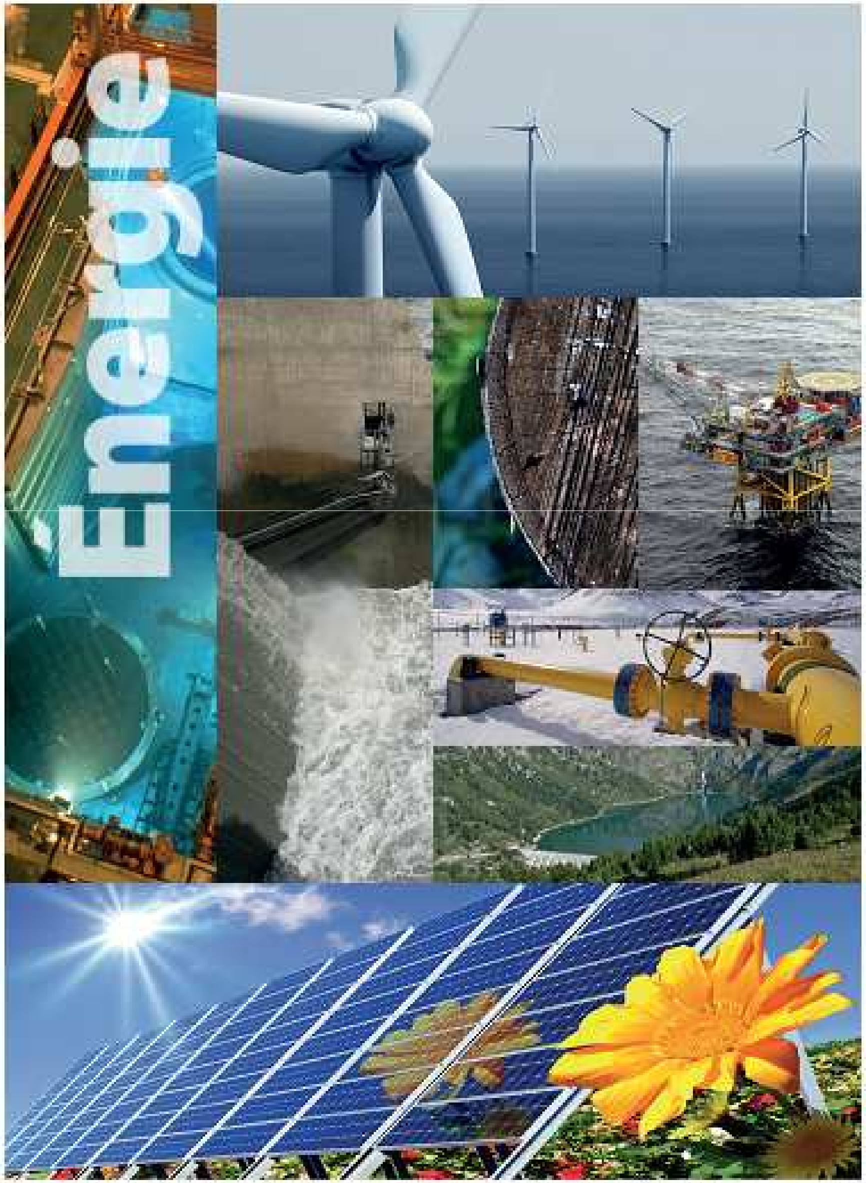
Contexte

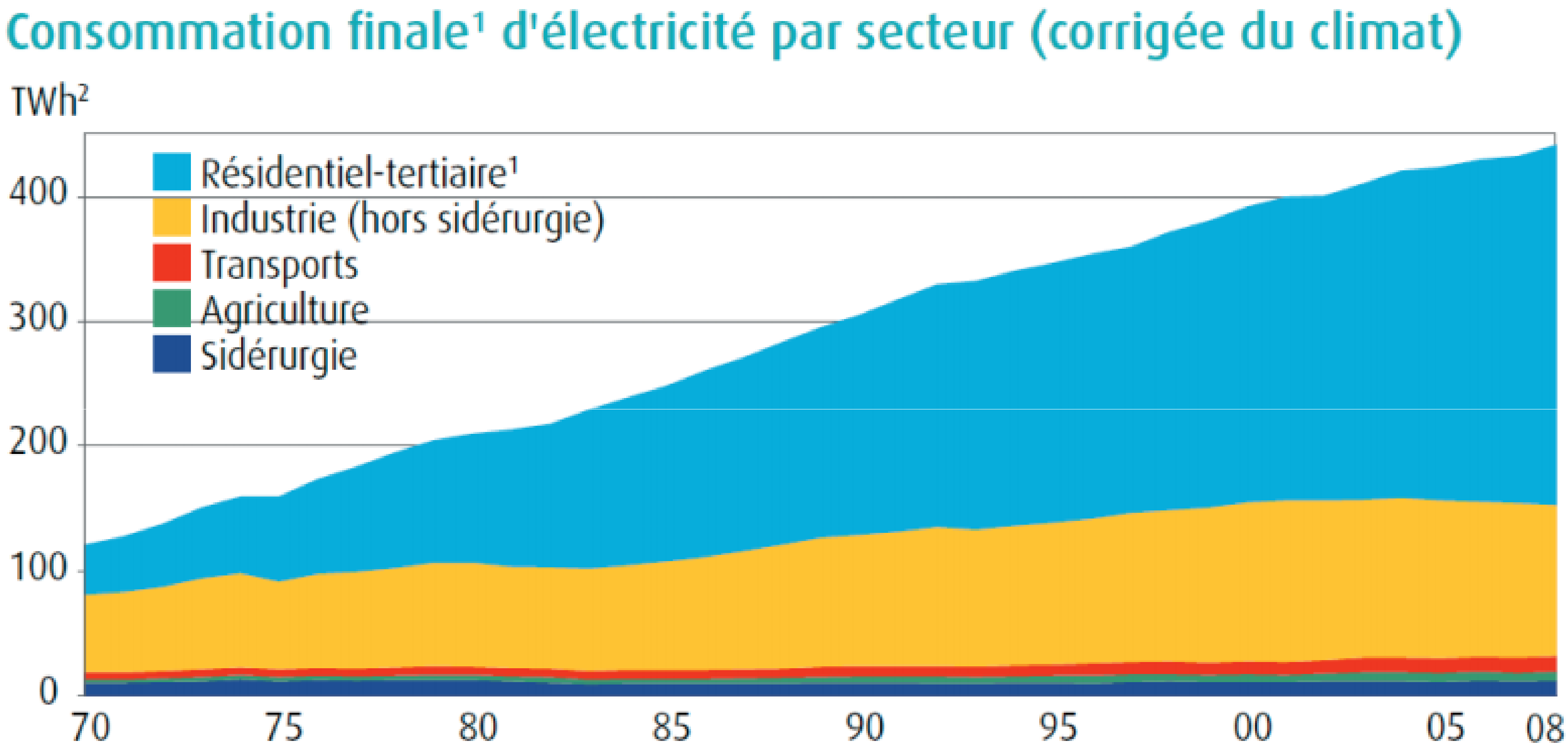
"Technologies clés 2015" , Etude du ministère délégué à l'Industrie

« Fruit du travail de 250 experts du monde de l'entreprise et de la recherche, vise à identifier les technologies qui assureront un avantage de compétitivité et d'attractivité à la France et à ses territoires dans le monde pour les 5 à 10 ans qui viennent »

http://www.industrie.gouv.fr/tc2015/#etu

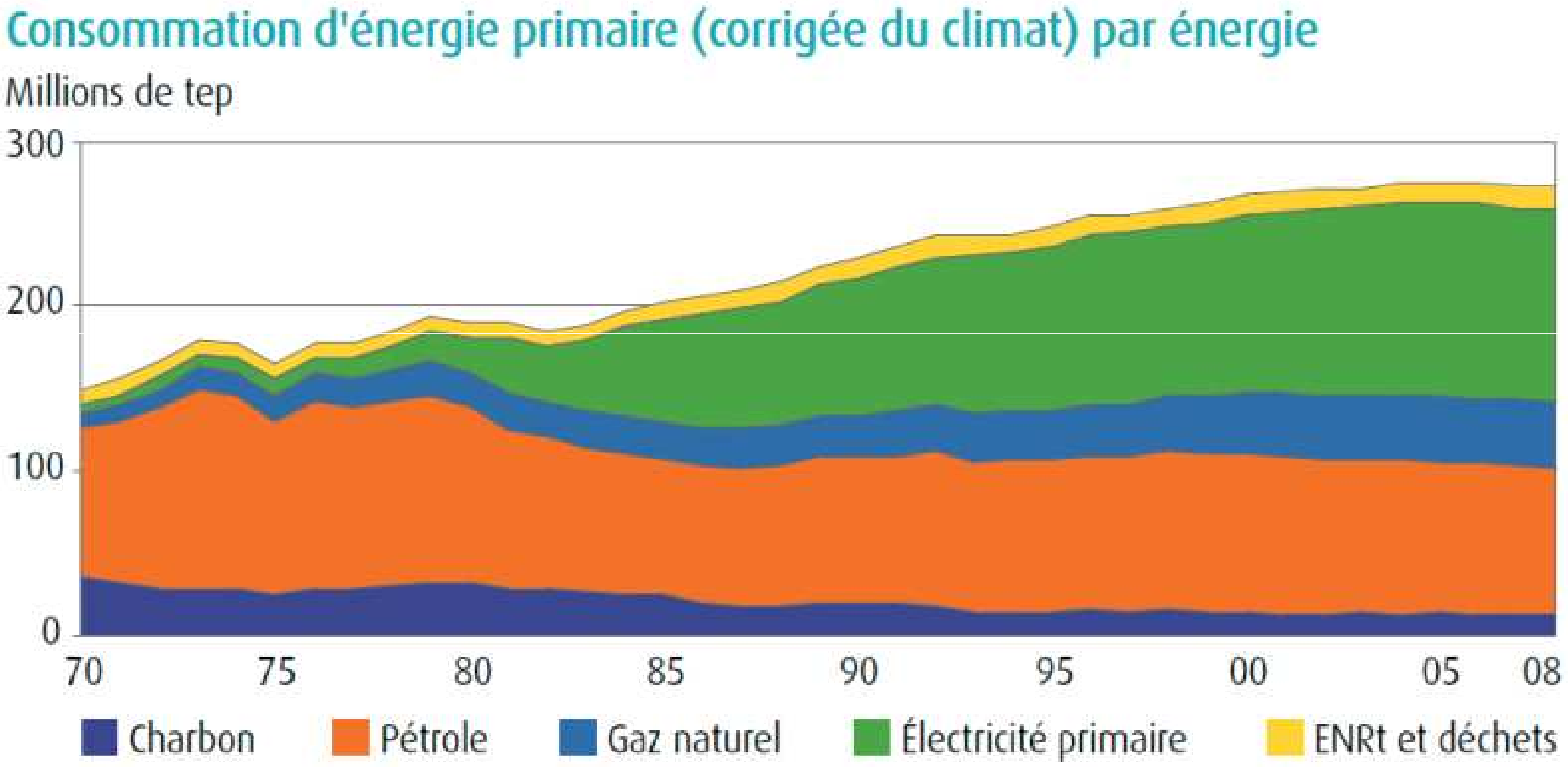


Consommation finale d'électricité (corrigée du climat) en France, par secteur (source : SoeS)

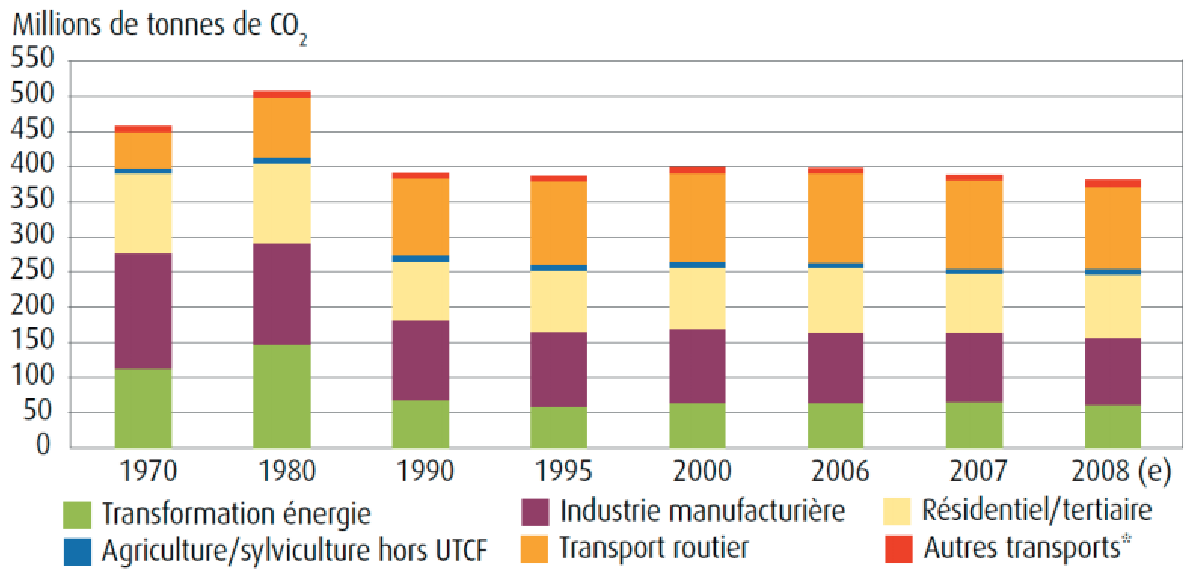


La France est le huitième plus grand consommateur d'énergie au monde

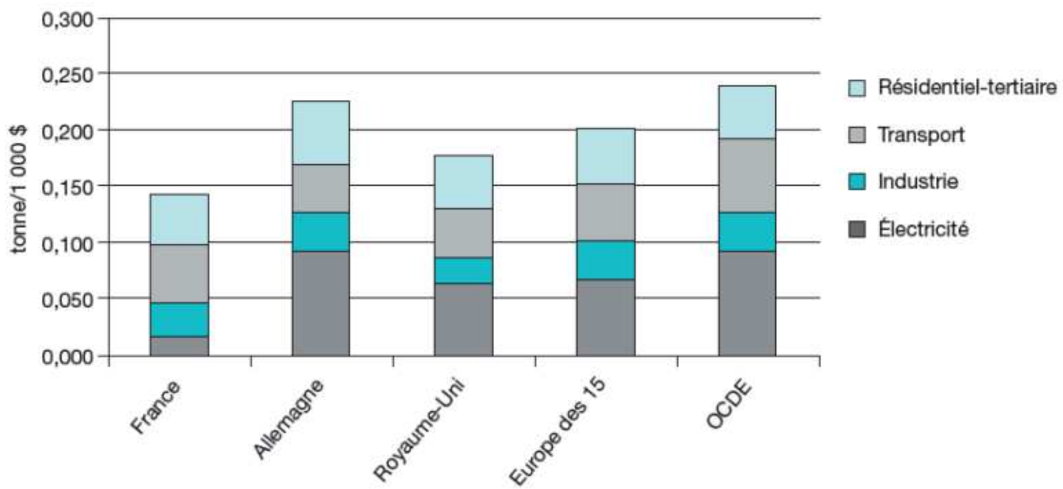
Consommation d'énergie primaire (corrigée du climat) en France, par énergie (source : SoeS)



Émissions de CO_2 pour la France, par secteur (source : SOeS)



Émissions de CO_2 rapportées au PNB en 2005 (source : AIE)

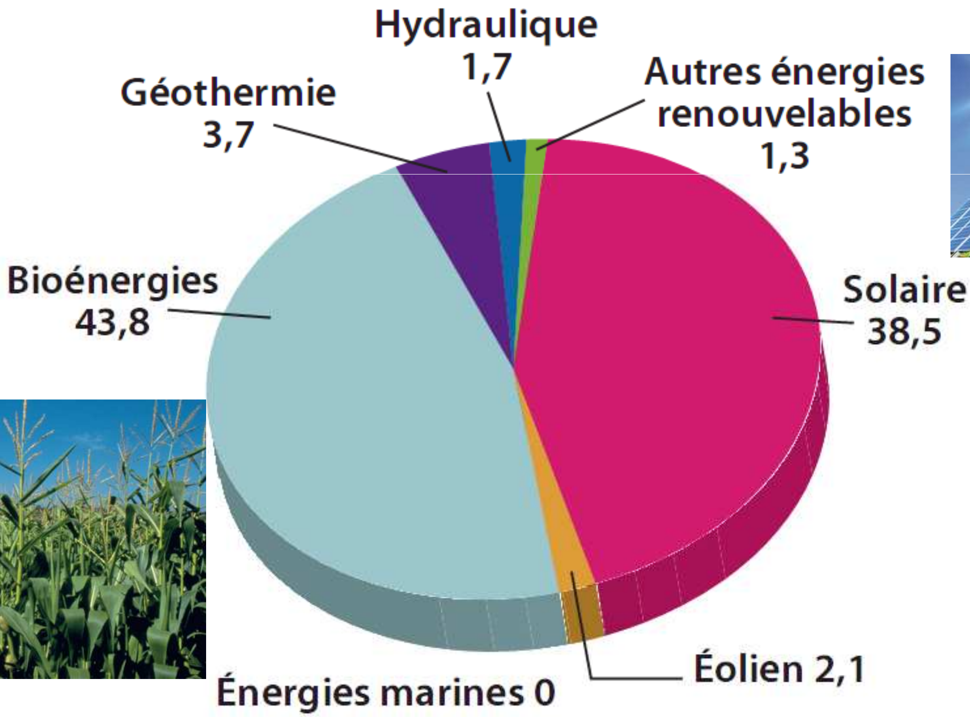


Les voies possibles pour lutter contre le changement climatique :

- Produire de l'énergie en ayant recours à des technologies plus « propres »
- Utiliser l'énergie de façon plus rationnelle

Tendances Technologiques et Technologies clés-I

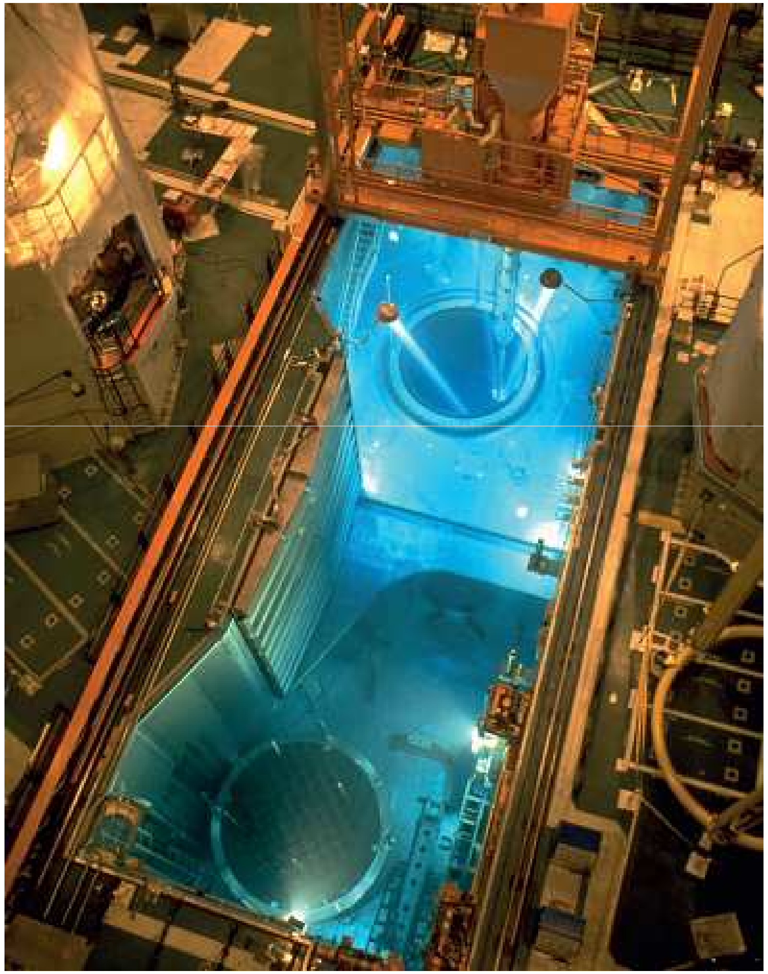
Les énergies renouvelables



Répartition de la dépense publique en recherche sur l'énergie en 2008, en France
(source : DGEC/CGDD)

Tendances Technologiques et Technologies clés-II

L'énergie nucléaire



L'énergie nucléaire est bien adaptée à la production d'électricité en base, avec un impact limité du point de vue des émissions de CO_2.

En France le nucléaire représente 76 % de la production d'électricité.
Au niveau mondial (30 pays)14 % de la production d'électricité globale.

Tendances Technologiques et Technologies clés-III

L'hydrogène en tant que vecteur énergétique

Avantages:
•35 kWh/kg contre 15 kWh/kg pour l'essence
• sa combustion produit que de l'eau (« propre »)

Secteurs principaux d'application:

• Production d'énergie (électricité et chaleur) dans des installations stationnaires ;
• Véhicules à piles à combustible (avec stockage embarqué d'hydrogène) ;
• Applications portables (appareils électriques).

Désavantages:
L'ensemble des maillons de la chaîne (production, stockage, transport et distribution) ne sont pas encore maitrises.

Tendances Technologiques et Technologies clés-IV

Les infrastructures électriques

Les évolutions technologiques concernent:

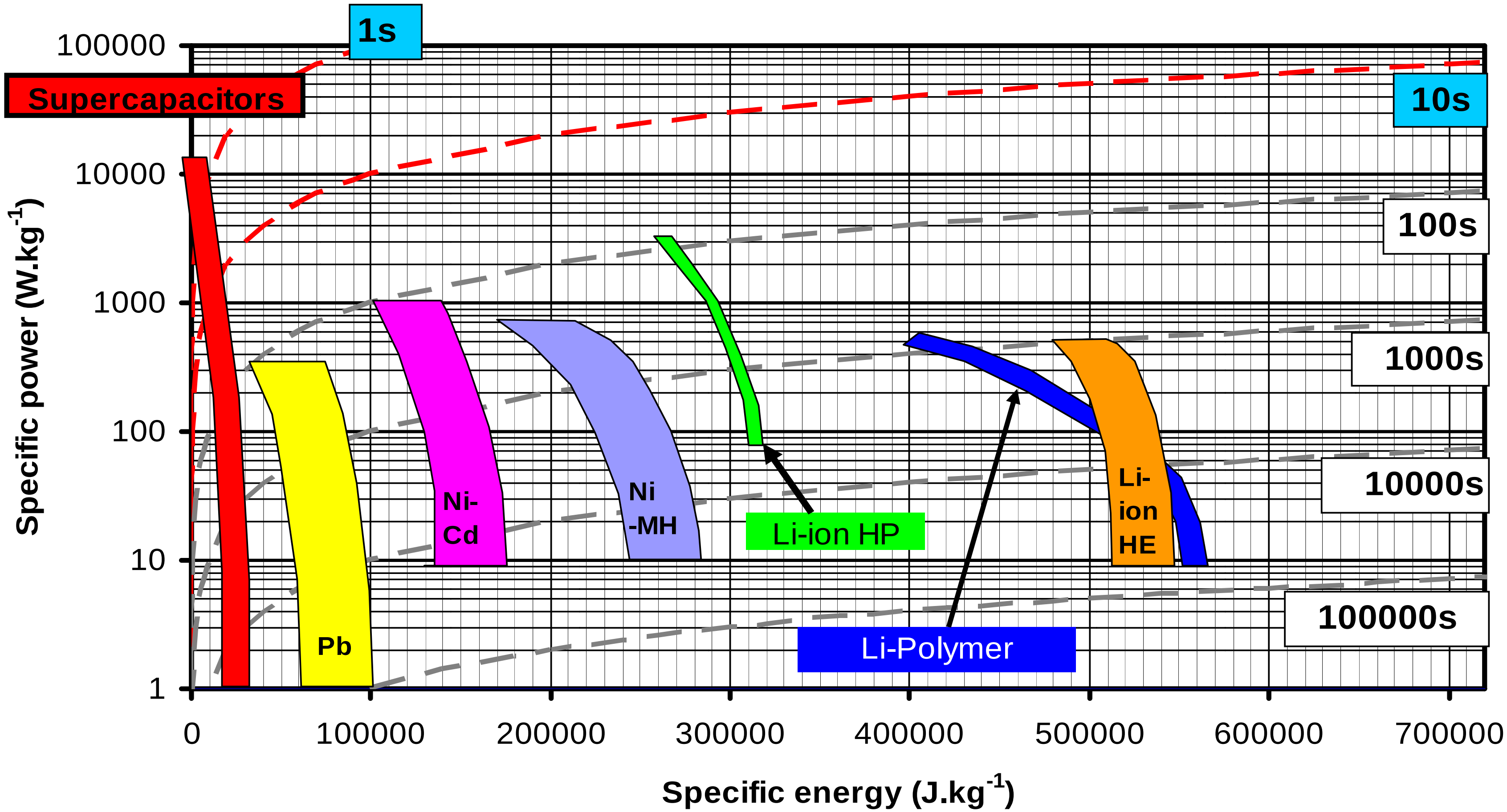
- Les équipements pour gérer efficacement le transit d'énergie sur le réseau
- Les moyennes de **stockage de l'électricité** pour faire face aux fluctuations de la production et de la consommation

Technologies pour le stockage de l'électricité

- Stockage à très grande échelle (plusieurs dizaines à plusieurs centaines de MWh): stations de transfert d'énergie par pompage ou par compression d'air.
- Stockage à grande échelle (plusieurs MWh à plusieurs dizaines de MWh): accumulateurs électrochimiques (plomb-acide, li-ion,…), le stockage de chaleur
- Stockage à moyenne échelle (quelques kWh au MWh): **Supercondensateurs**, accumulateurs électrochimiques, le volants d'inertie, la pile à combustible,…

Supercapacitors

Ragone plot for different electrochemical energy storage systems



➡ Energy density of supercapacitors must be enhanced

Applications of supercapacitors

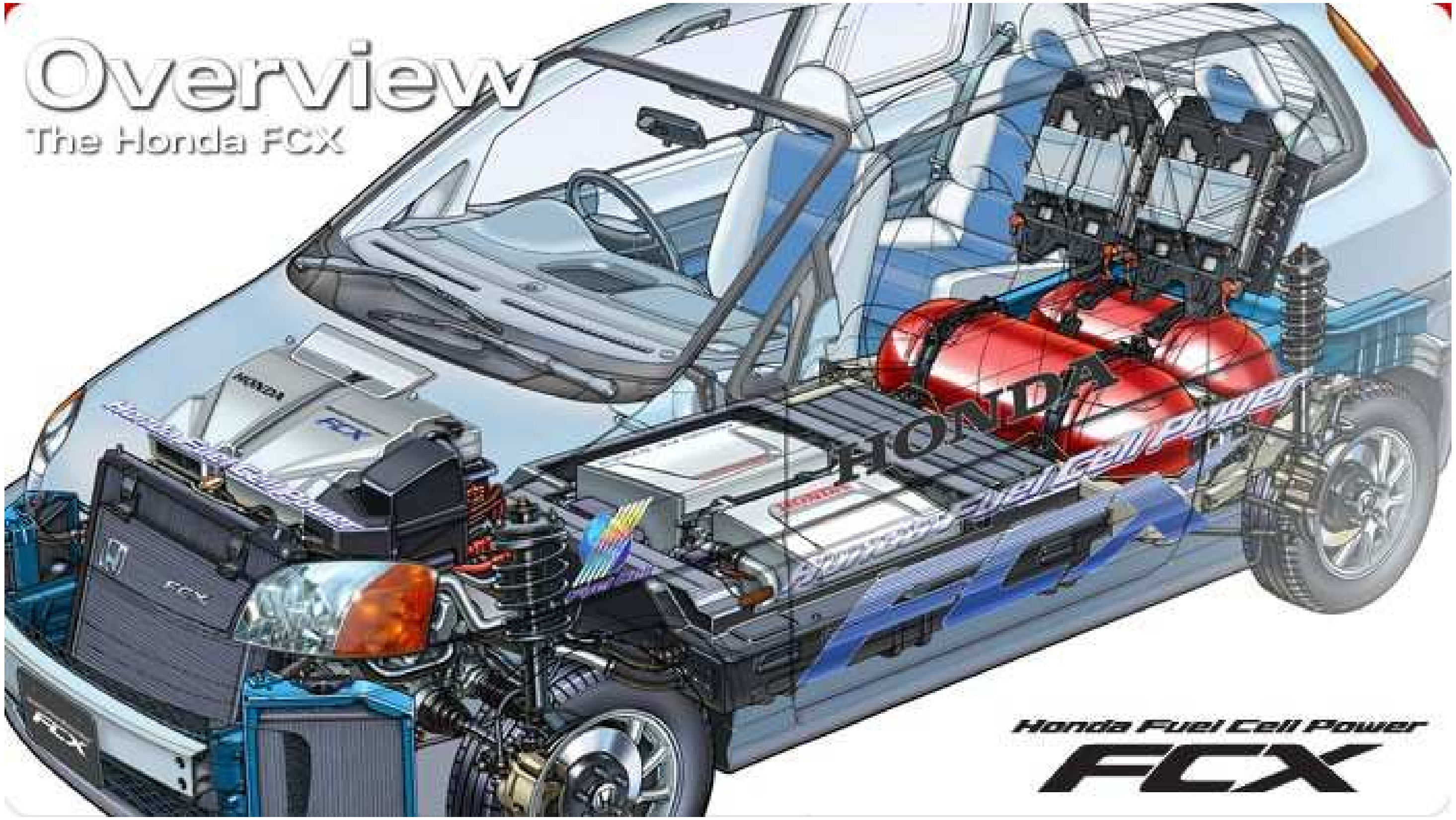
- Used when a high power is requested for a short time

- Electric and hybrid vehicles, telecommunication systems, tramways, computers, cordless tools, wind turbines, cranes, fork-lifts, diesel engine starting, emergency systems, …

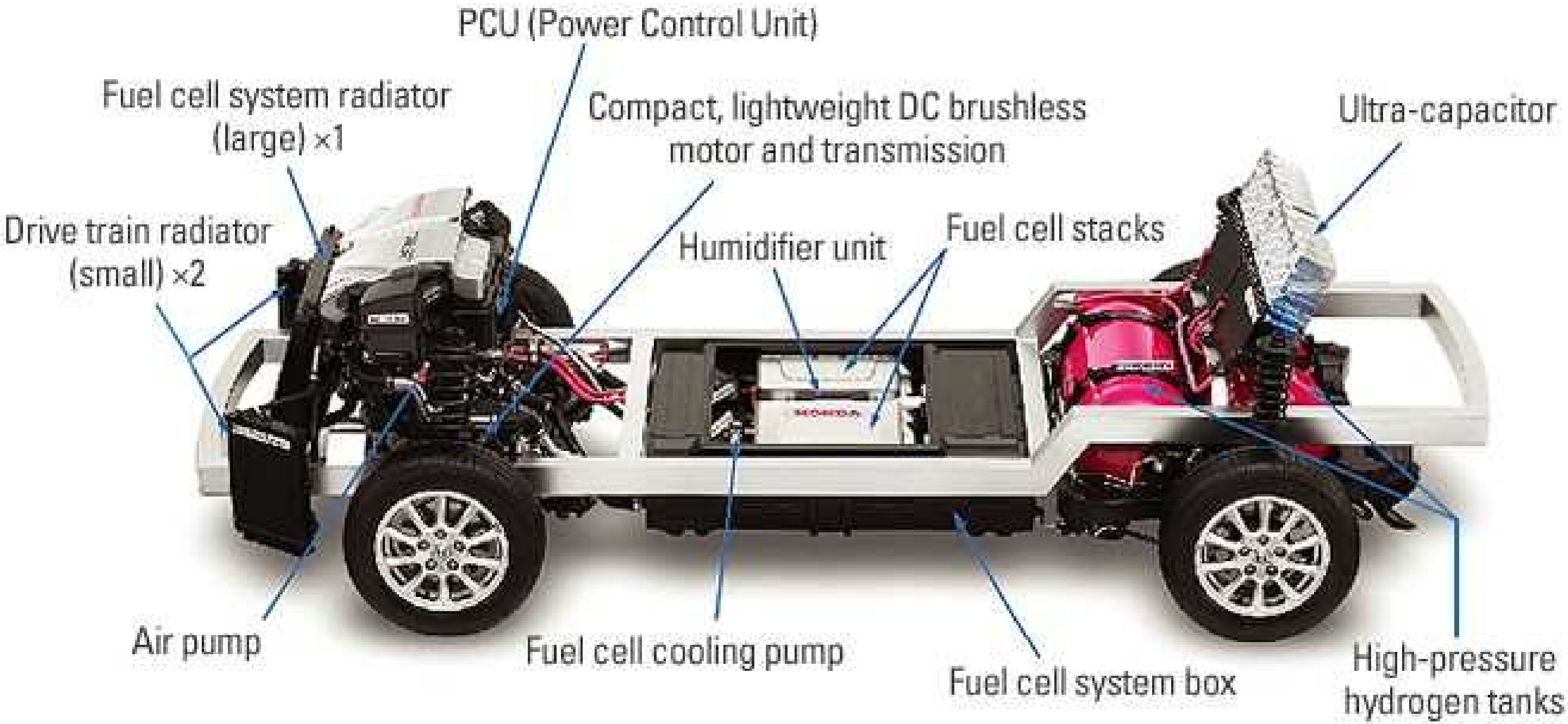
Application of supercapacitors

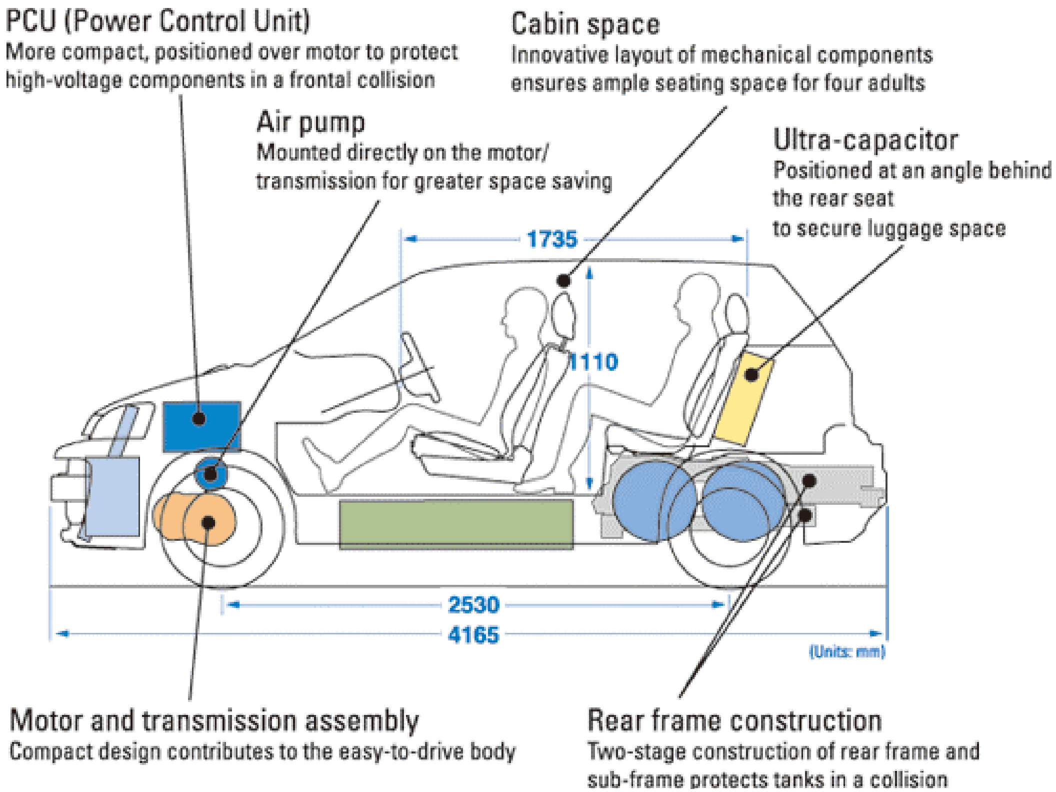
Energy device of high power, e.g., for hybrid electric vehicle

Honda car equiped with supercapacitor



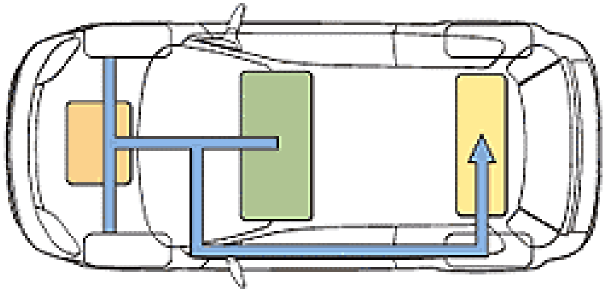
Detailed energy system for the Honda car



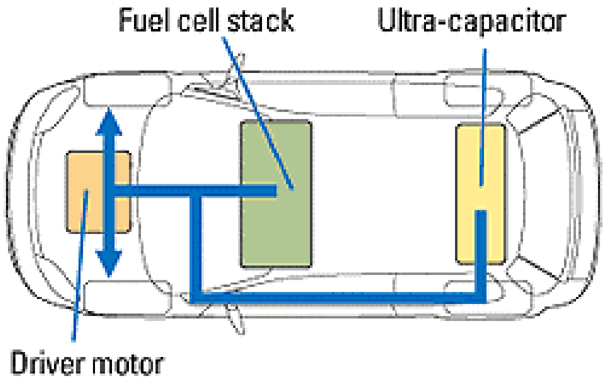


The supercapacitor recovers energy released during braking - using it when a peak power is demanded.

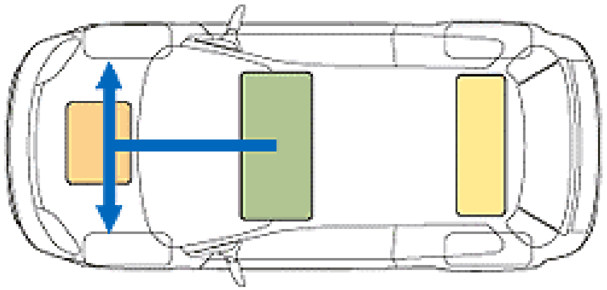
Charge of super-capacitor



Acceleration



Motor powered by fuel cell

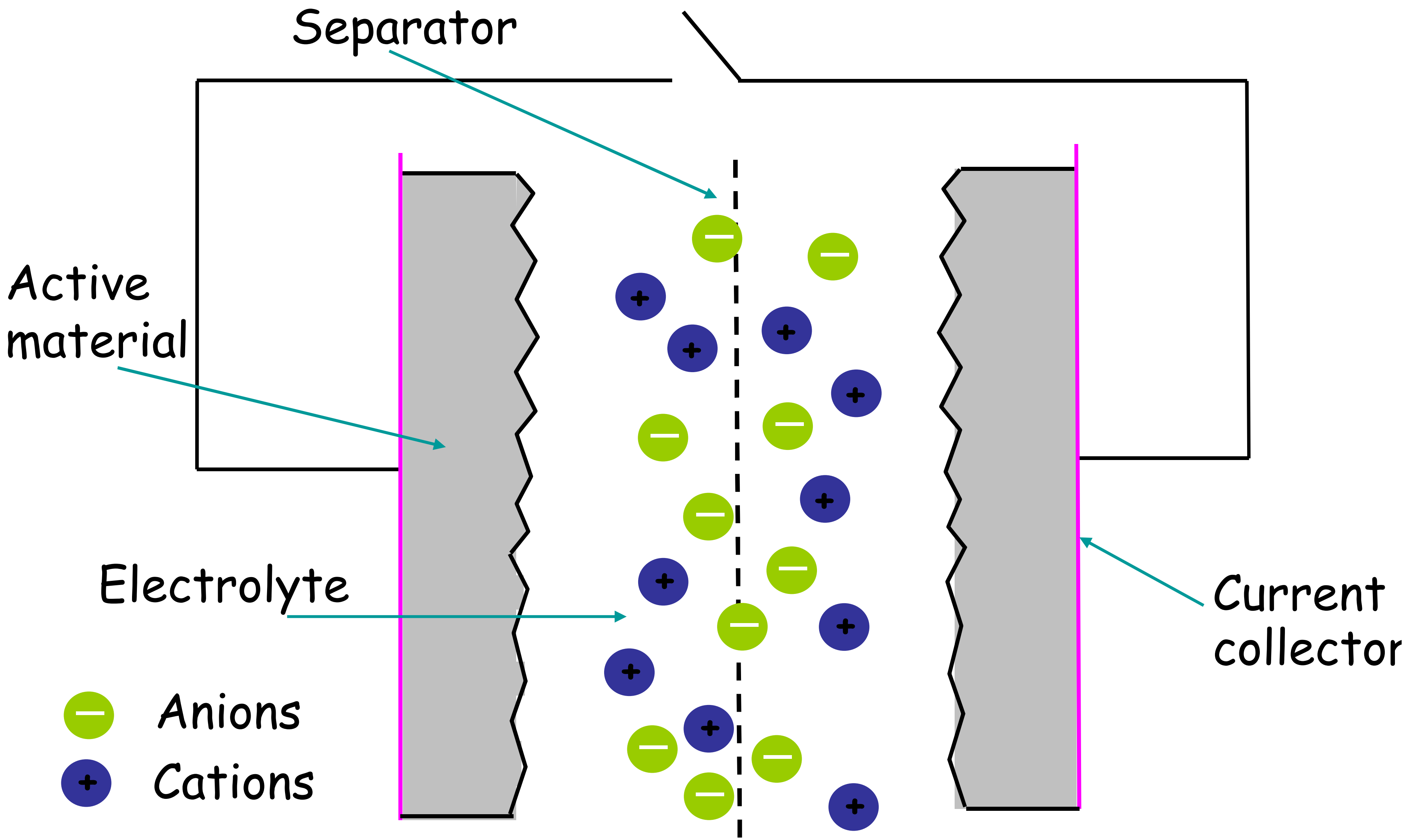


Supercapacitors have been selected to power emergency actuation systems for doors and evacuation slides in the new Airbus 380

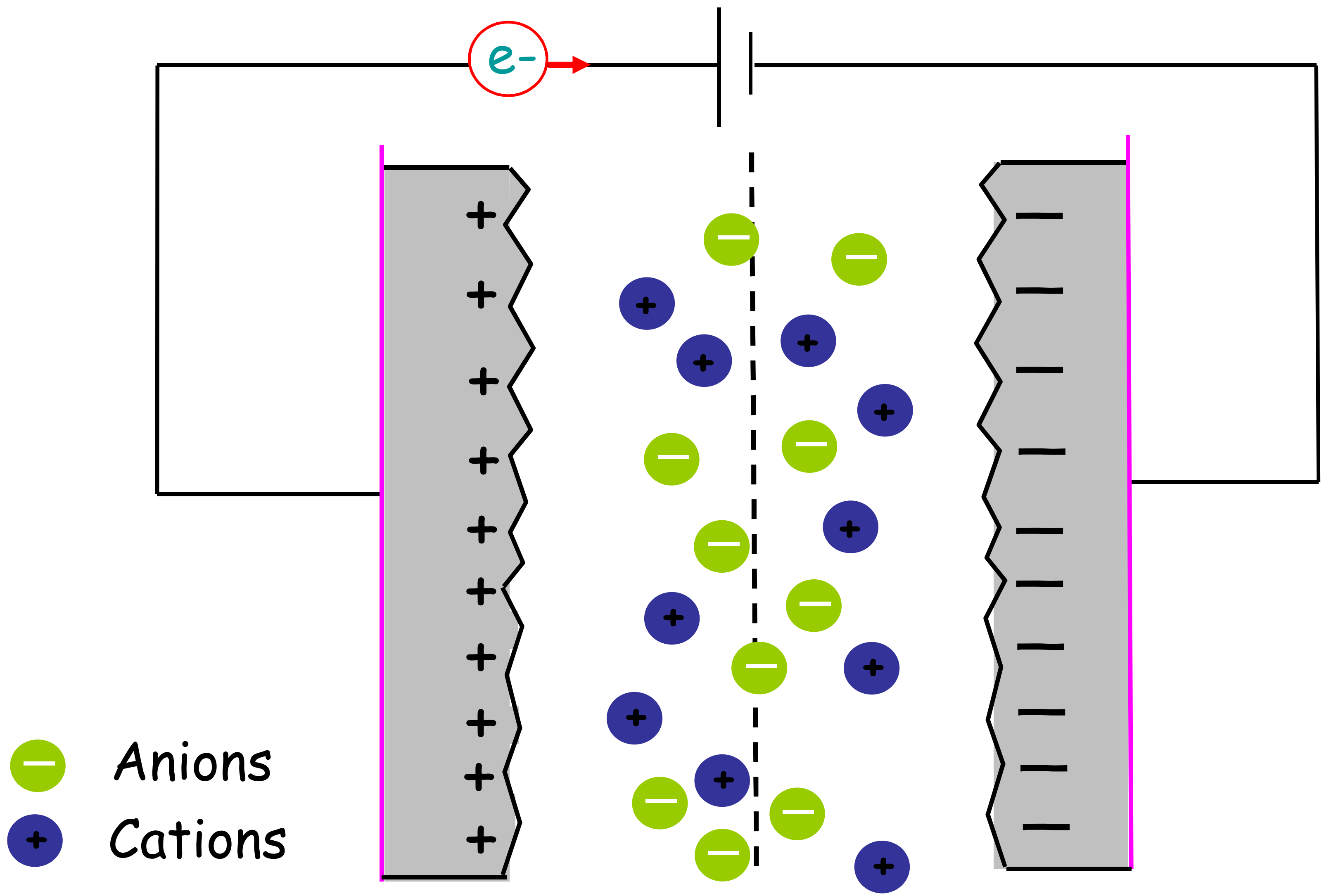
ECs at work. Hybrid diesel/electric rubber-tired gantry crane with DLCAP electro-chemical capacitor energy storage system (fuel savings of 40% are typical).

Sources : John Miller (JME Inc. jmecapacitor@att.net), batSCap (www.batscap.fr), Oshkosh (www.oshkoshcorporation.com),

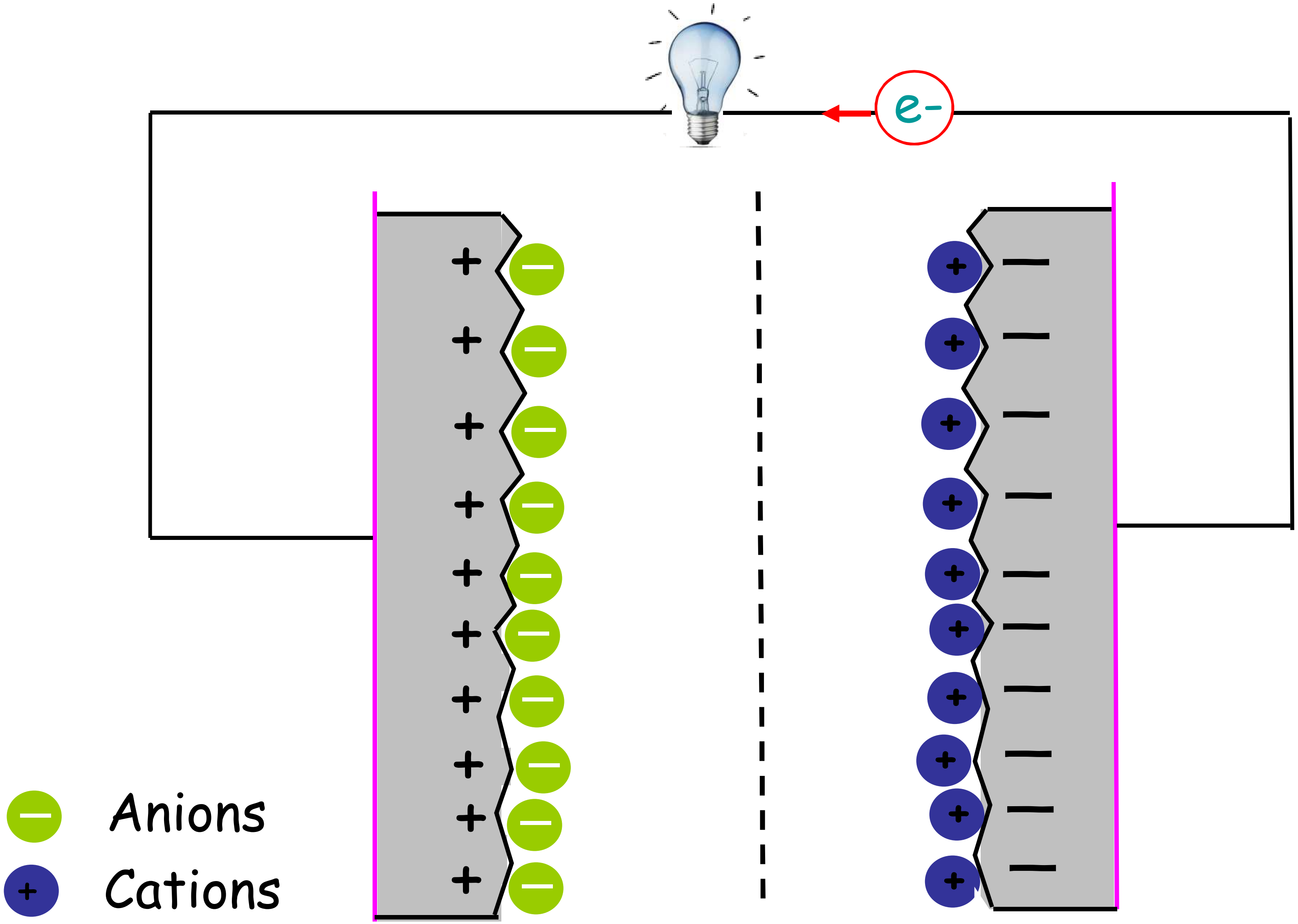
Principle of energy storage in supercapacitors



Charge of supercapacitor

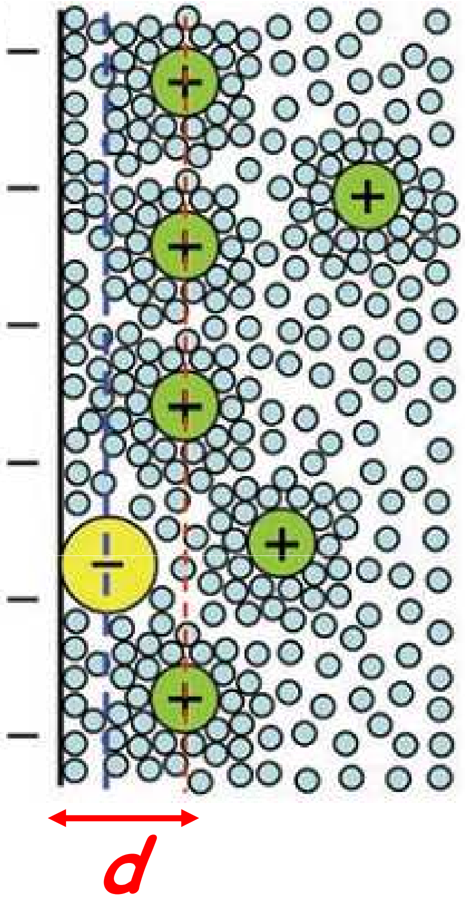


Discharge of supercapacitor



Electric Double Layer Capacitors (EDLCs)

The Electrical Double Layer



$$C_e = \frac{\varepsilon S}{d}$$

Distance d of the layer ~ 1nm

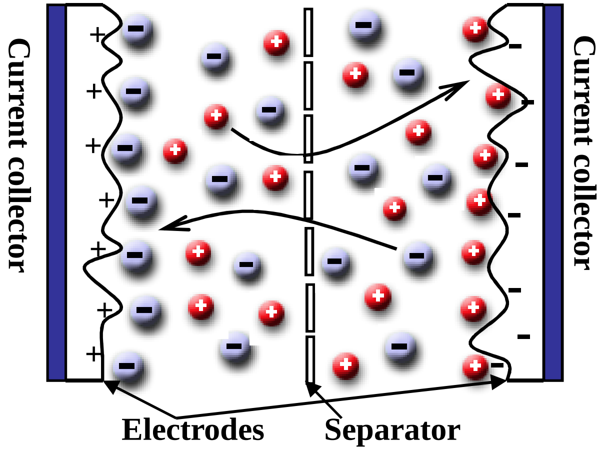
↓

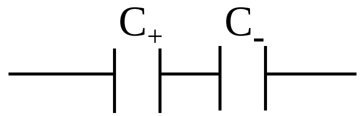
Capacitance ~ 0.1 F m^{-2}

S surface area of the electrode/electrolyte interface

S ~ 1000 m^2 g^{-1} → ~100 F g^{-1}

Principle of Supercapacitors





$$\frac{1}{C} = \frac{1}{C_+} + \frac{1}{C_-}$$

➔ ***Power density:*** *$P = V^2/4R_s$*

➔ ***Energy density:*** *$E = 1/2\,(CV^2)$*

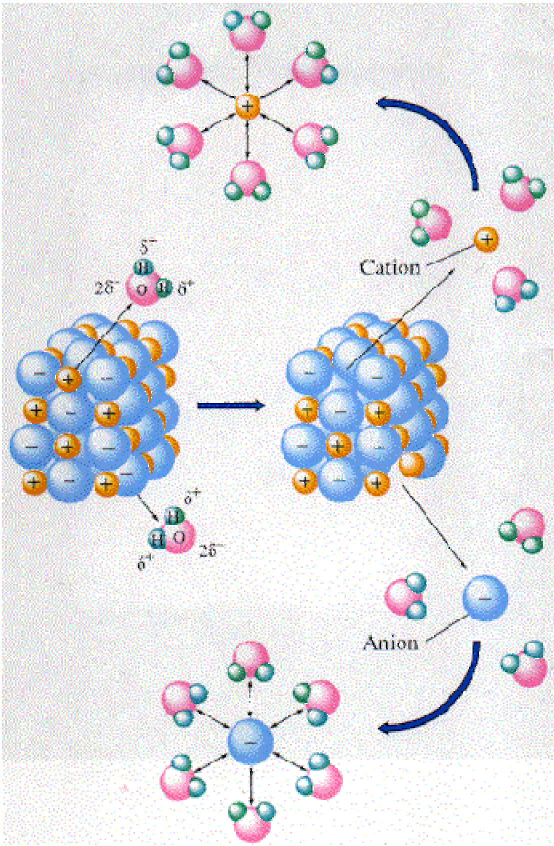
- *Voltage= f (electrolyte stability)*

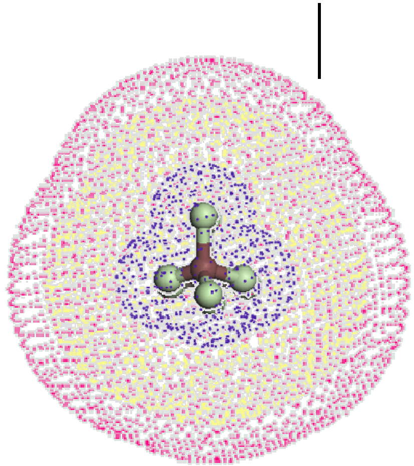
Electrolytes

Classical electrolytes:

Aqueous:1M H_2SO_4, 6M KOH

Organic: TEA BF_4 in AN/PC





Ions are solvated

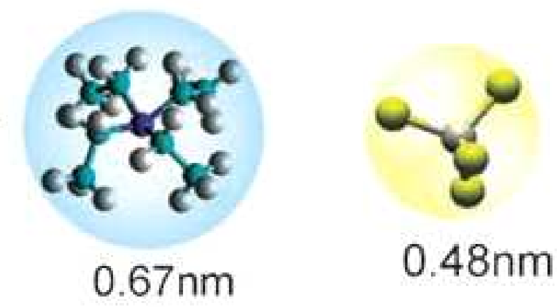
Electrolyte Potential Window

Electrolyte		*Conductivity mS cm^{-1}*	*Electrochemical stability*	
			Anodic Limit (V)	*Cathodic Limit (V)*
Aqueous	H_2SO_4/H_2O (5M)	810	1.23-0.059pH	0.059pH
Organic	$ET_4N\ BF_4$ in AN (0.6M)	50	3.3	-2.8

The electrochemical stability window also depends on the electrode material.
Example: Activated Carbon:

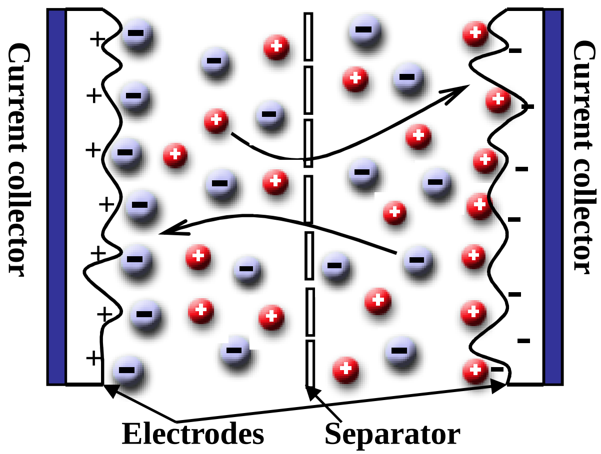
Aqueous: 0.7 - 1.0 V

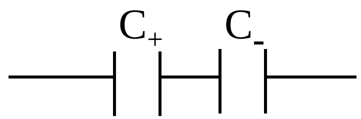
Organic (ET_4NBF_4 in AN): 2.5 -2.7 V



The one chosen for industrial devices

Principle of Supercapacitors





$$\frac{1}{C} = \frac{1}{C_+} + \frac{1}{C_-}$$

➔ ***Power density:*** $P = V^2/4R_s$

➔ ***Energy density:*** $E = 1/2\,(CV^2)$

- ***Voltage= f (electrolyte stability)***

Aqueous medium: ~0.7-1.0 V   Organic medium: ~ 2.5-2.7V

- ***R_s (ESR=Electrical series resistance) = f (electrode conductivity, …)***

- ***Capacitance = f (material)***

Electrical double layer (EDLC):

Surface phenomena

$$C = \varepsilon \frac{S}{d}$$

Electrodes for EDLC

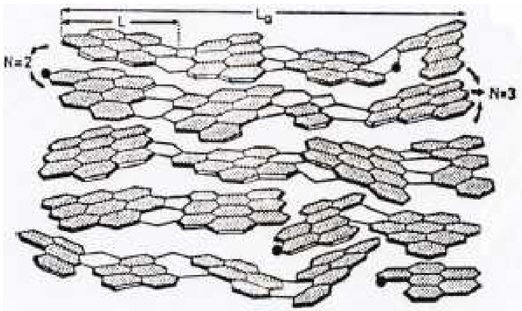
In EDLC, C is controlled by the surface area of the interface

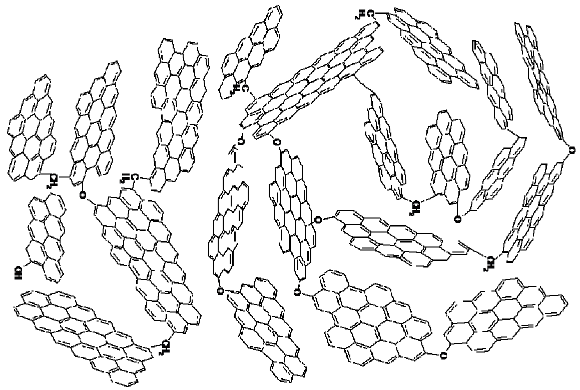
$$C_e = \frac{\varepsilon S}{d}$$

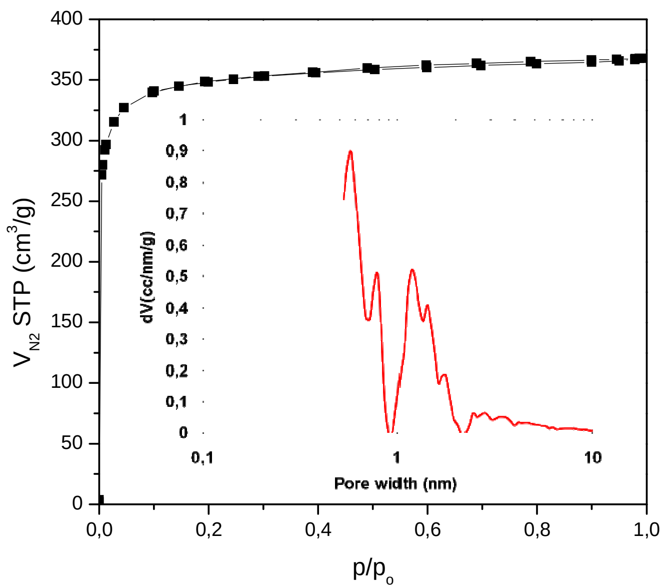
⟹ *Electrodes of EDLCs are based on **nanoporous carbons**:*

- *-Cheap materials*
- *-Good electrical conductivity*
- *-High surface area and pore volume*

Disorder≡ Porosity



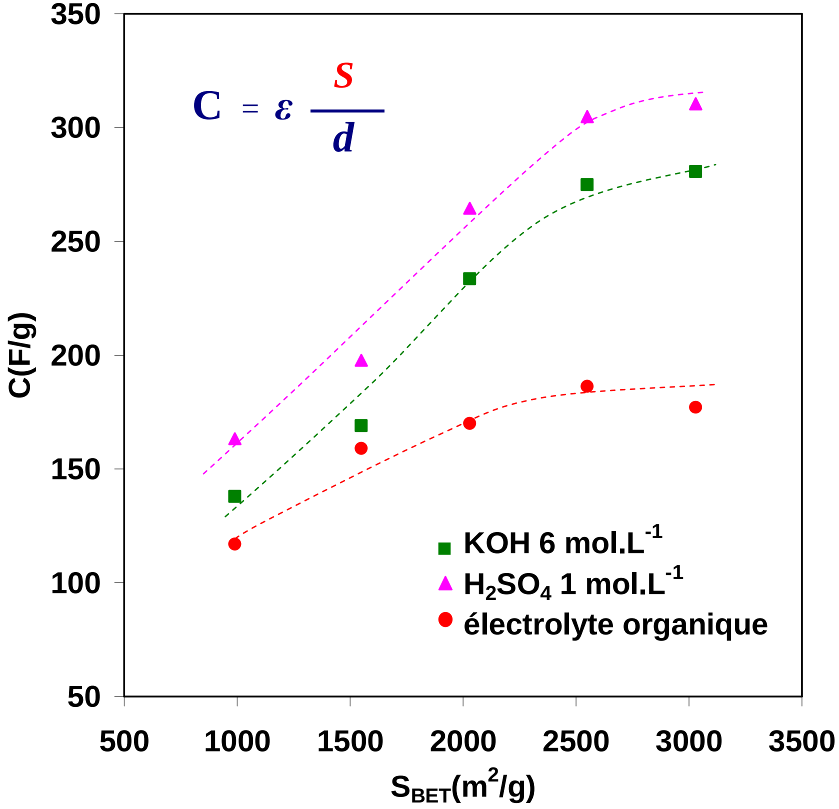




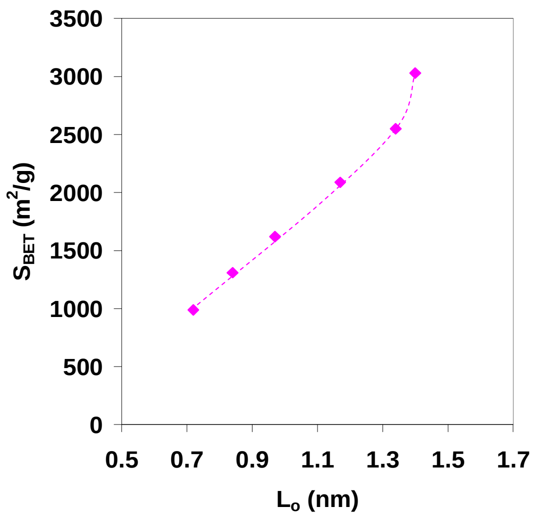
IUPAC pore classification:
Micropore: less than 2 nm
Mesopore: between 2 and 50 nm
Macropore: more than 50 nm

Specific capacitance of a series of carbons vs S_{BET}

Porous carbons with specific surface areas 900-3200 m²/g



- *Heat-treatment of a bituminous coal at 520-1000°C*
- *Activation by KOH at 800°C*

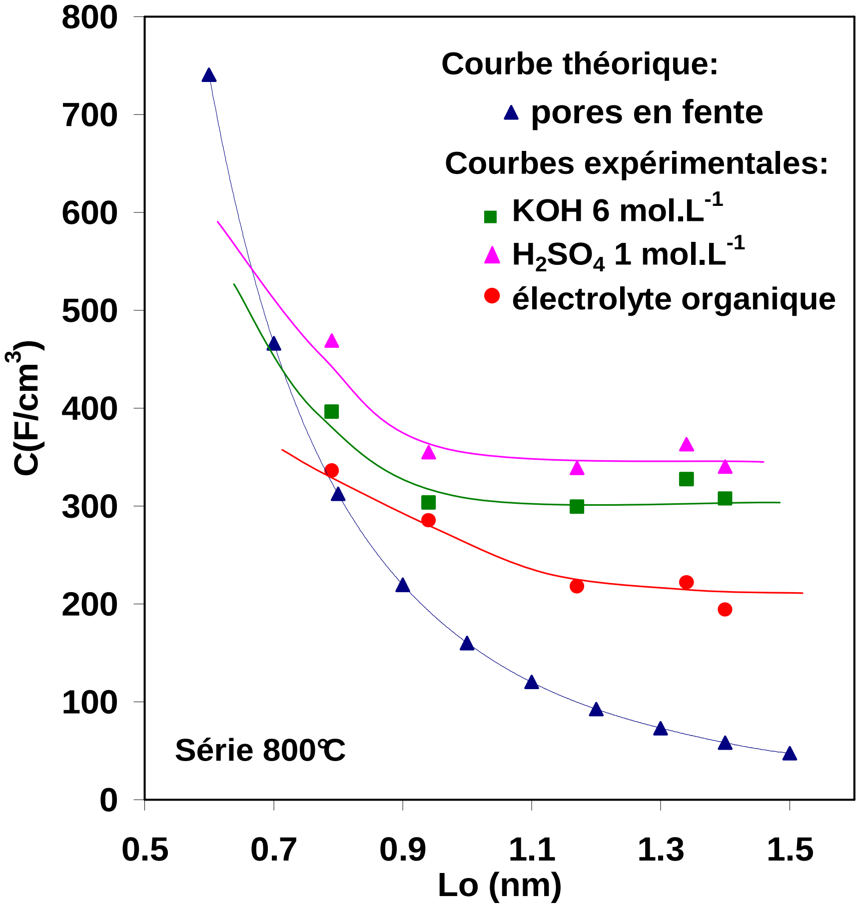


The average pore size L_{0N2} increases from 0.8 to 1.4 nm with S_{BET}

⇨ ***weak interaction of ions in large pores***

Volumetric capacitance of the series of carbons vs L_0

Volumetric capacitance = C / V_{DR}



➡ ***Optimal pore size L_{0N2} : 0.7 nm in aqueous medium***
0.8 nm in organic medium

E. Raymundo-Piñero et al., Carbon 44 (2006) 2498

Conclusion

For an effective formation of the EDL with nanoporous carbons, a good fitting of pores and electrolyte dimensions is more crucial than an extensively developed surface area

Comparison between carbon based supercapacitors in organic and aqueous electrolytes

Organic electrolytes : $TEABF_4$ in AN, $TEABF_4$ in PC
Aqueous electrolytes : KOH, H_2SO_4

$E=1/2(CU^2)$

$P=U^2/4R_s$

	Organic Electrolyte	Aqueous Electrolyte
Operating voltage	2.5-2.7 V	0.7-1.0 V
Conductivity	~ 0.02 S/cm	~ 1 S/cm
Maximum Capacitance	150-200 F/g	250-300 F/g
Technological, economical and safety aspects	Manipulation in inert atmosphere Expensive Environment Unfriendly	Easy manipulation Not Expensive Environment Friendly

Objectives

To develop systems giving high E ($E=1/2(CV^2)$) and keeping a good P ($P=V^2/R_s$) in aqueous medium

- ✓ *Optimize capacitance of Activated Carbon (C)*
- ✓ *Increase the operating voltage window (V)*

Solution for increasing the energy density in aqueous electrolytes:

Improve the capacitance by introducing pseudocapacitance effects

$$E=1/2(CU^2)$$

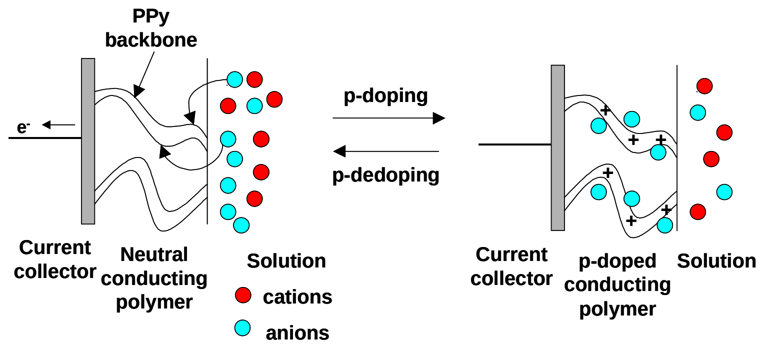
Pseudocapacitance effects in aqueous electrolytes

Pseudocapacitance: additional quick redox charge transfer with a continuous potential charge $dq = C\,dV$

Pseudocapacitance effects are introduced by:

- Conducting polymers (PPy, PANI)

$$[PPy^{+}A^{-}] + e^{-} \leftrightarrow [PPy] + A^{-}$$



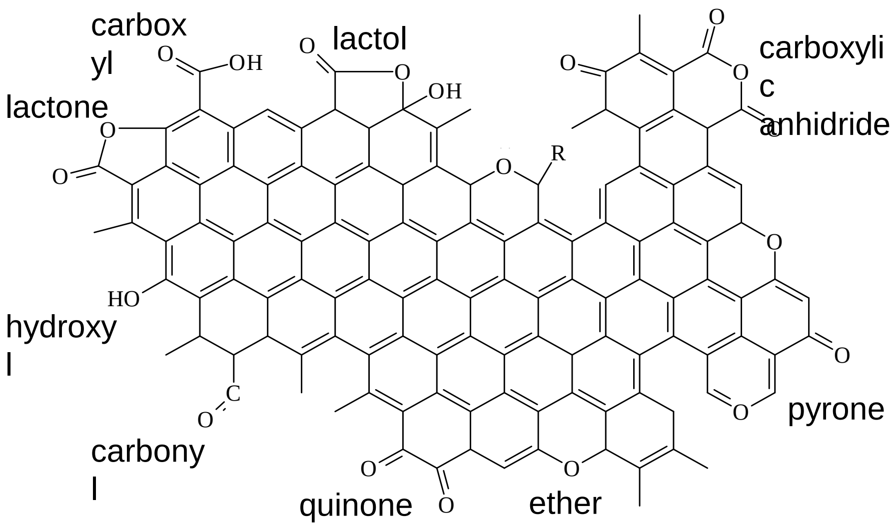
- Oxides (RuO_2, a-MnO_2)

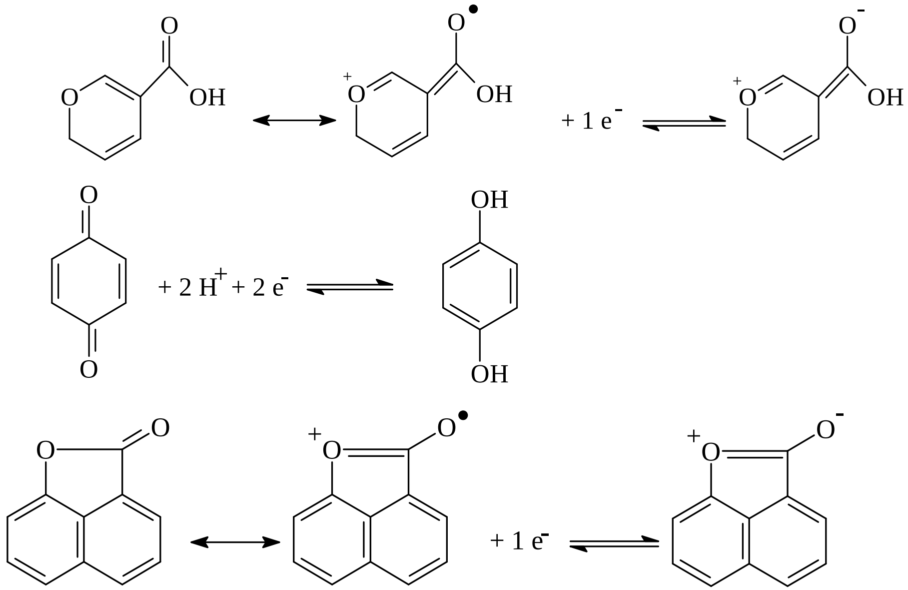
$$MnO_x(OH)_y + \delta e^{-} + \delta H^{+} \leftrightarrow MnO_{x-\delta}(OH)_{y+\delta}$$

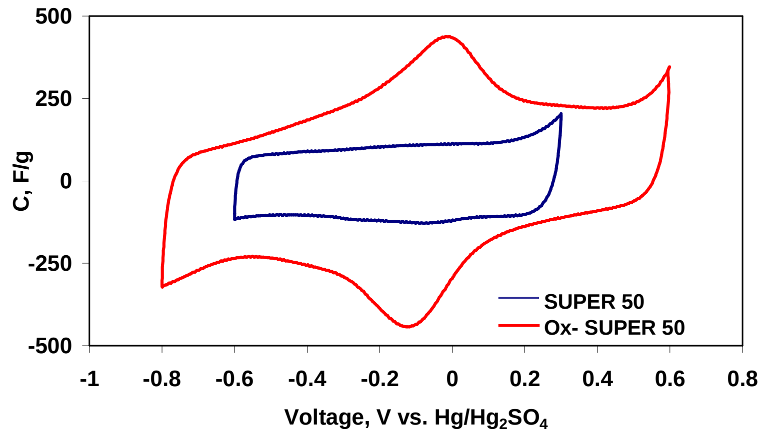
$$RuO_x(OH)_y + \delta e^{-} + \delta H^{+} \leftrightarrow RuO_{x-\delta}(OH)_{y+\delta}$$

- Functional groups on the surface of carbon

Pseudocapacitance effects of carbon surface functionalities

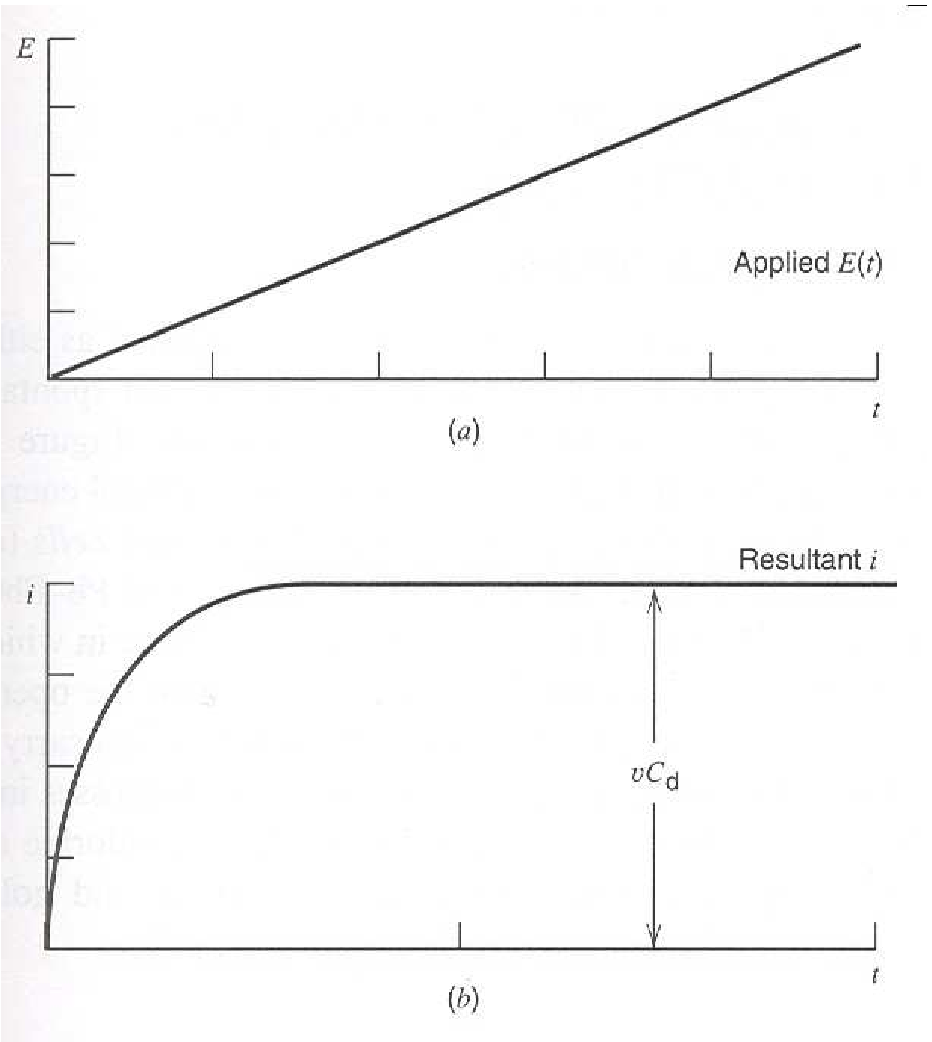






Methods of capacitor investigation

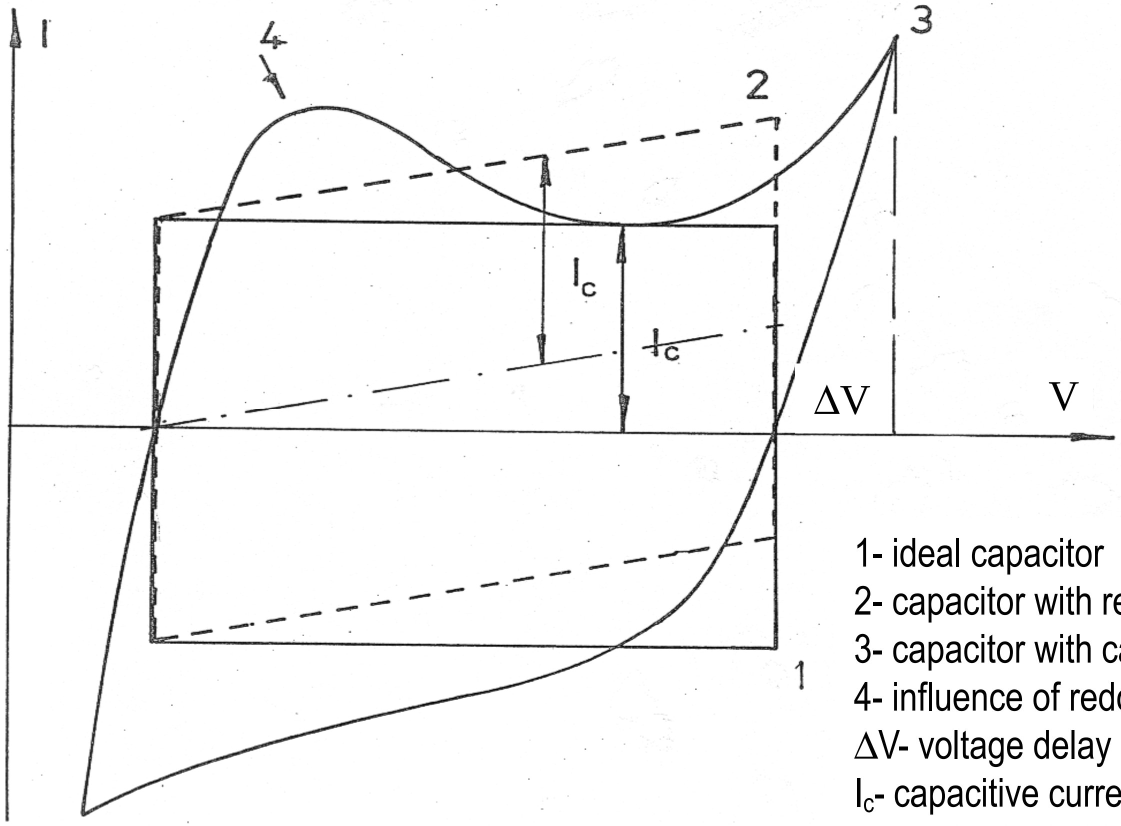
Voltammetry - charging



Voltage is applied with a constant scan rate

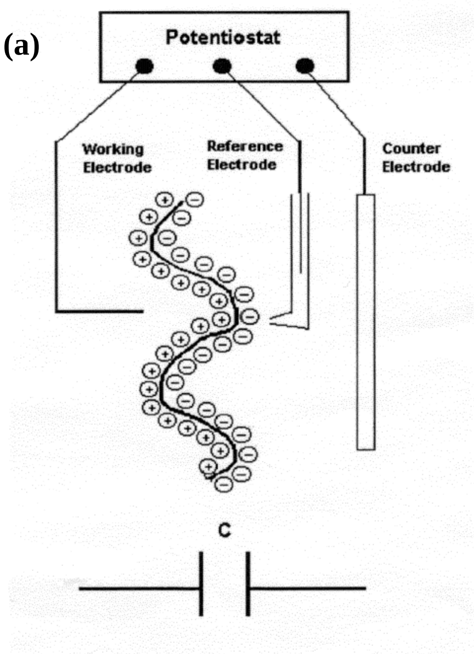
The resulting current through the electrodes is recorded

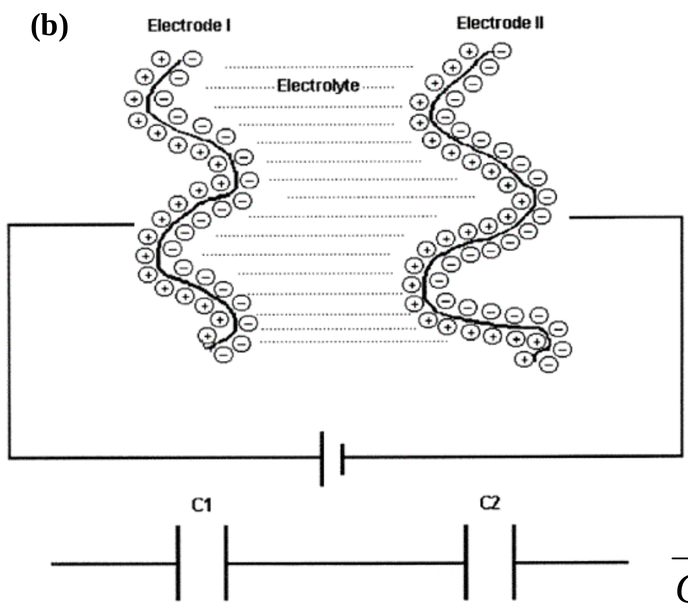
Voltammetry curves of an electrochemical capacitor



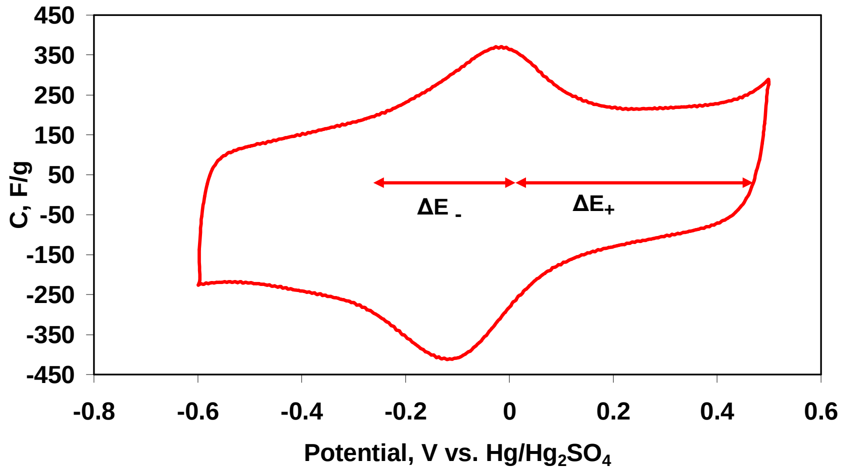
1- ideal capacitor
2- capacitor with resistance
3- capacitor with carbon electrodes
4- influence of redox reactions
ΔV- voltage delay
I_c- capacitive current

Three electrode cell system (a) and two electrode cell system (b) representation and their equivalent circuits

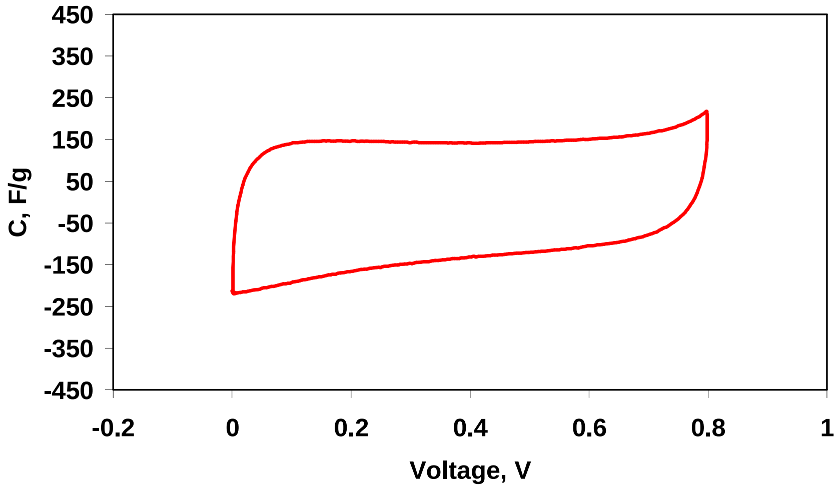




$$\frac{1}{C}=\frac{1}{C_1}+\frac{1}{C_2}$$

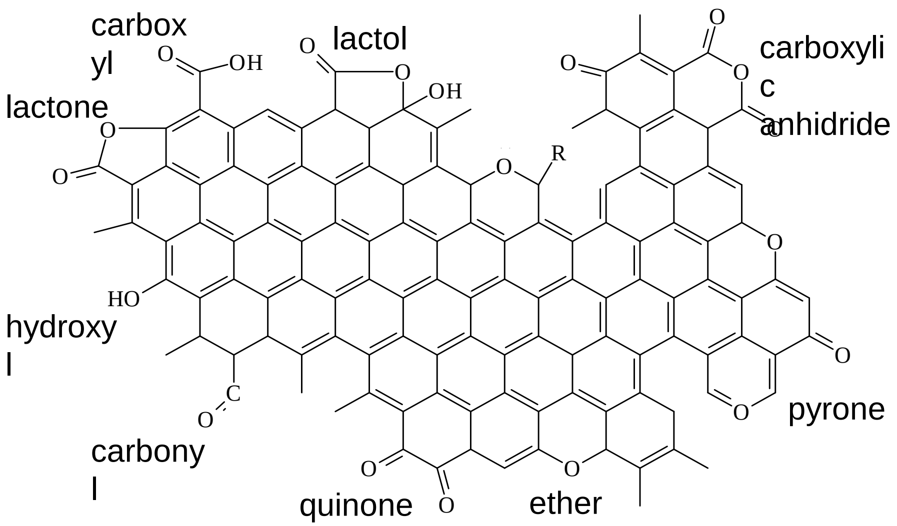


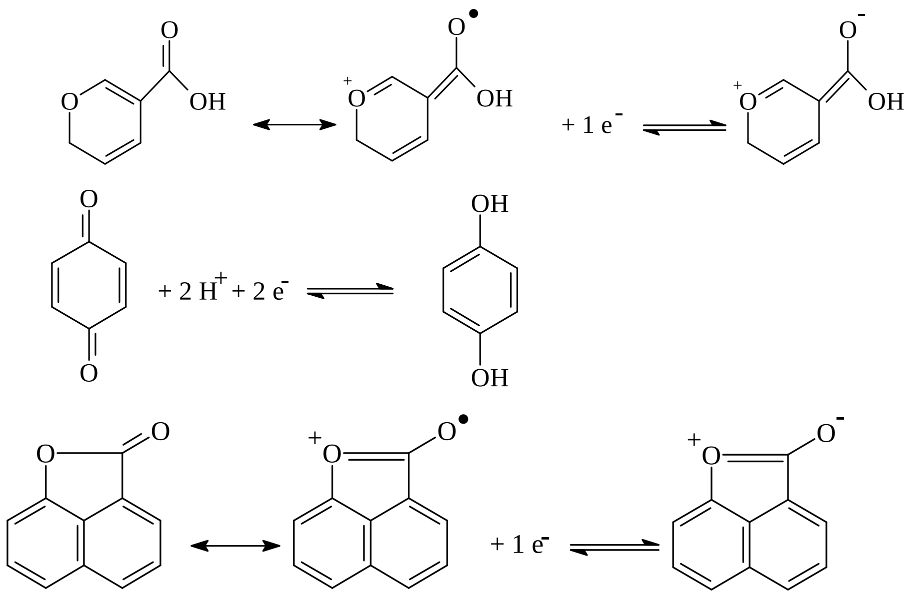
Characterization of the material

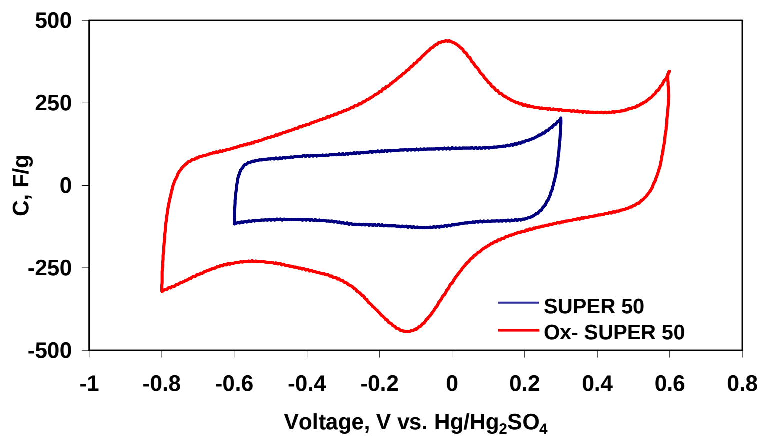


Characterization of the system

Pseudocapacitance effects of carbon surface functionalities

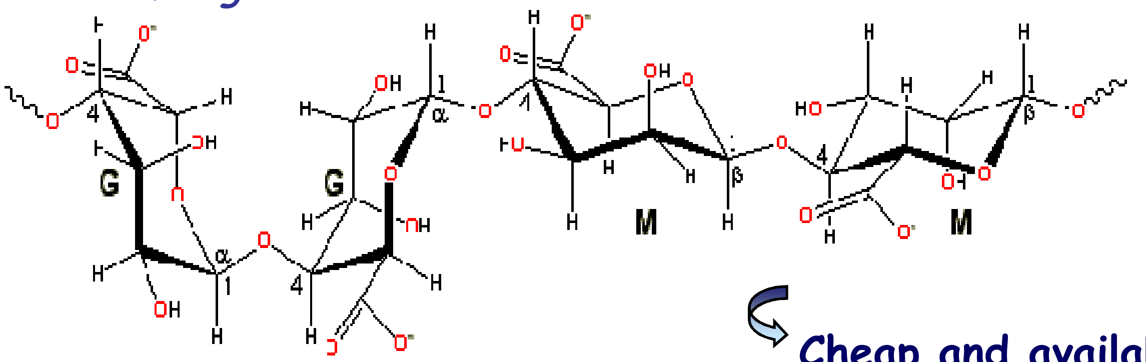






Pseudocapacitive nanotextured carbons prepared by one step carbonization of biopolymers[1]

Sodium Alginate



Emulsifiers, Stabilisers, Thickeners and Gelling Agents

E401	Sodium alginate
E402	Potassium alginate
E403	Ammonium alginate
E404	Calcium alginate
E460	Cellulose

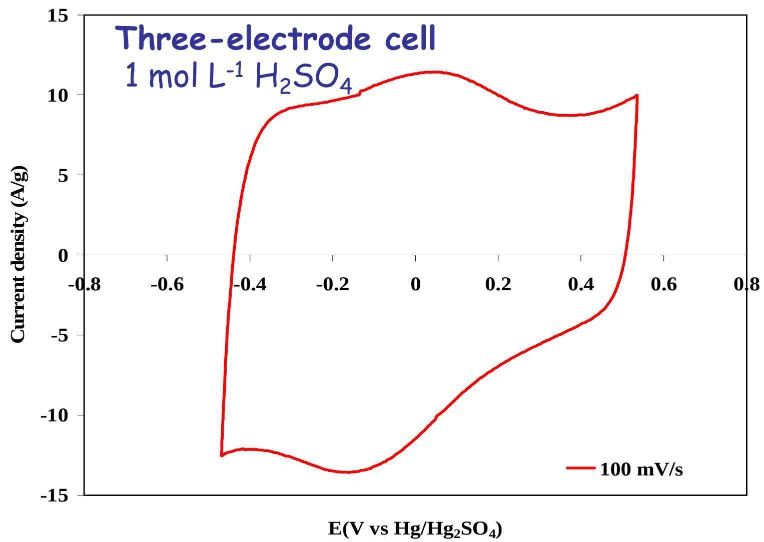
Cheap and available carbon precursors

After one-step carbonization at 600°C:

S_{BET} = 273 $m^2\ g^{-1}$; Oxygen: 15 wt%

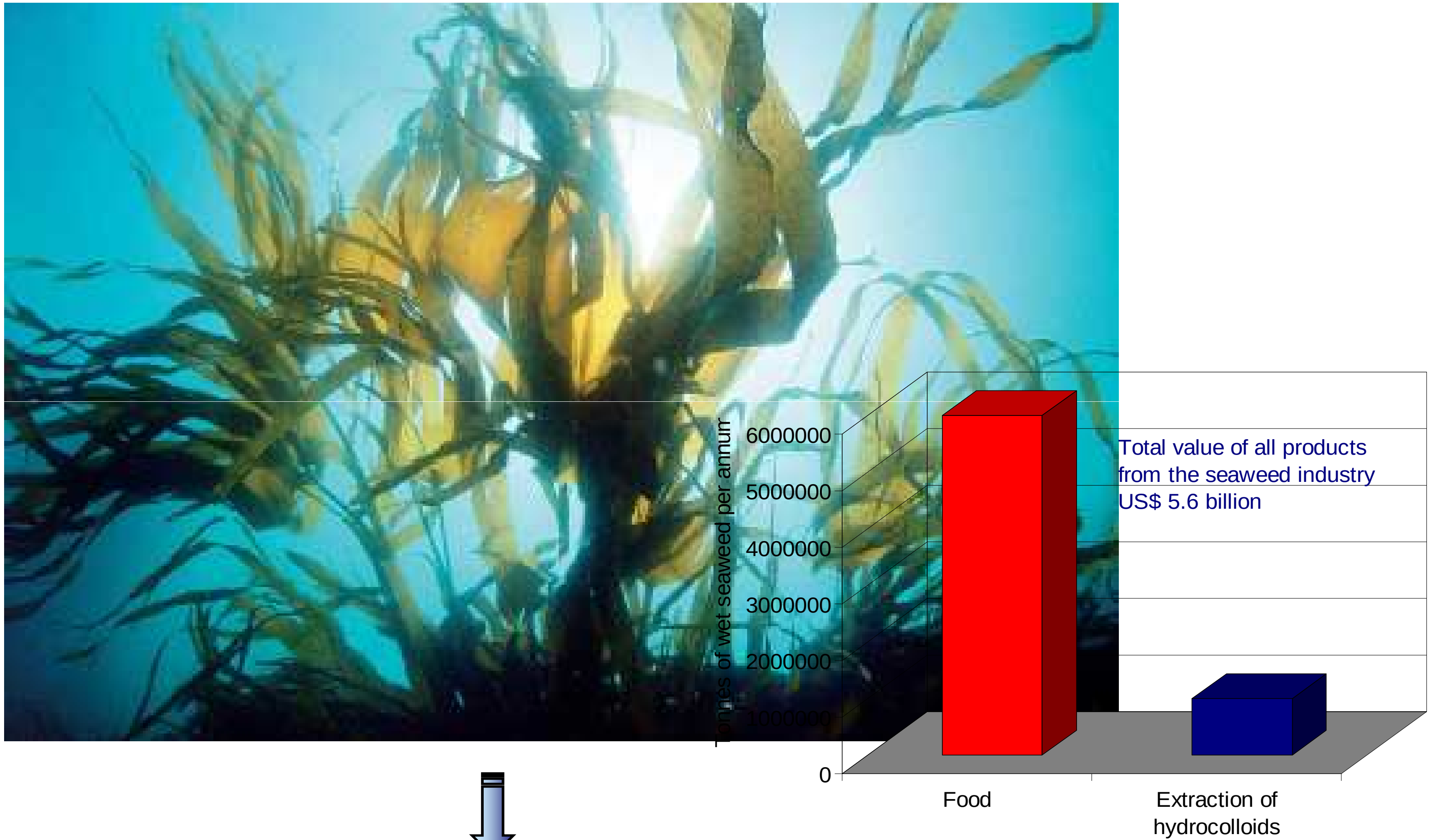
C = 200 F g^{-1} (1 mol L^{-1} H_2SO_4)

Important pseudocapacitive contribution in aqueous electrolyte



[1]E. Raymundo-Piñero, F. Leroux, F. Béguin, Advanced Materials 18, 1877-1882 (2006)

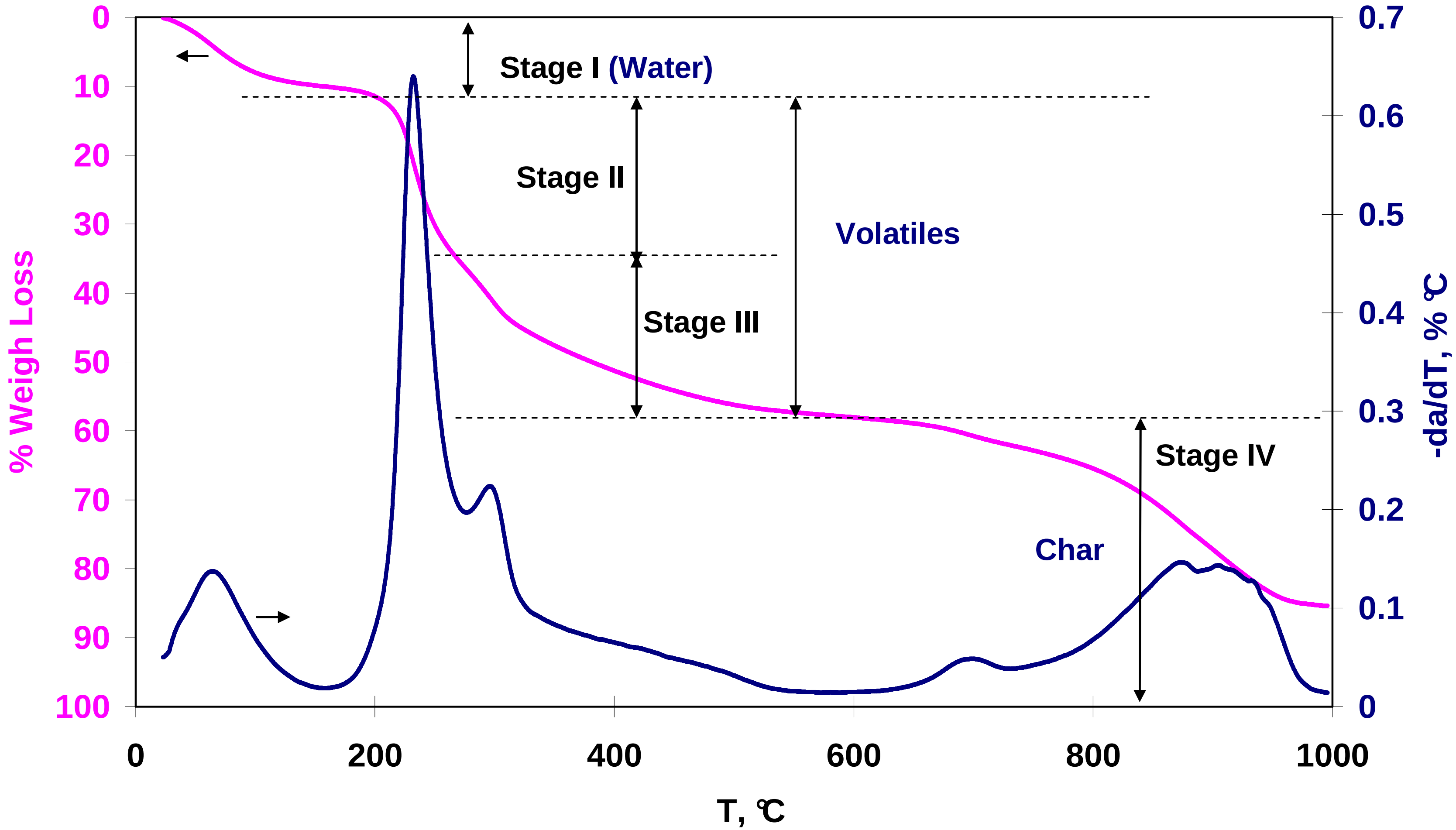
Carbons prepared by direct pyrolysis of seaweeds



Decrease 30 times the price of the precursor

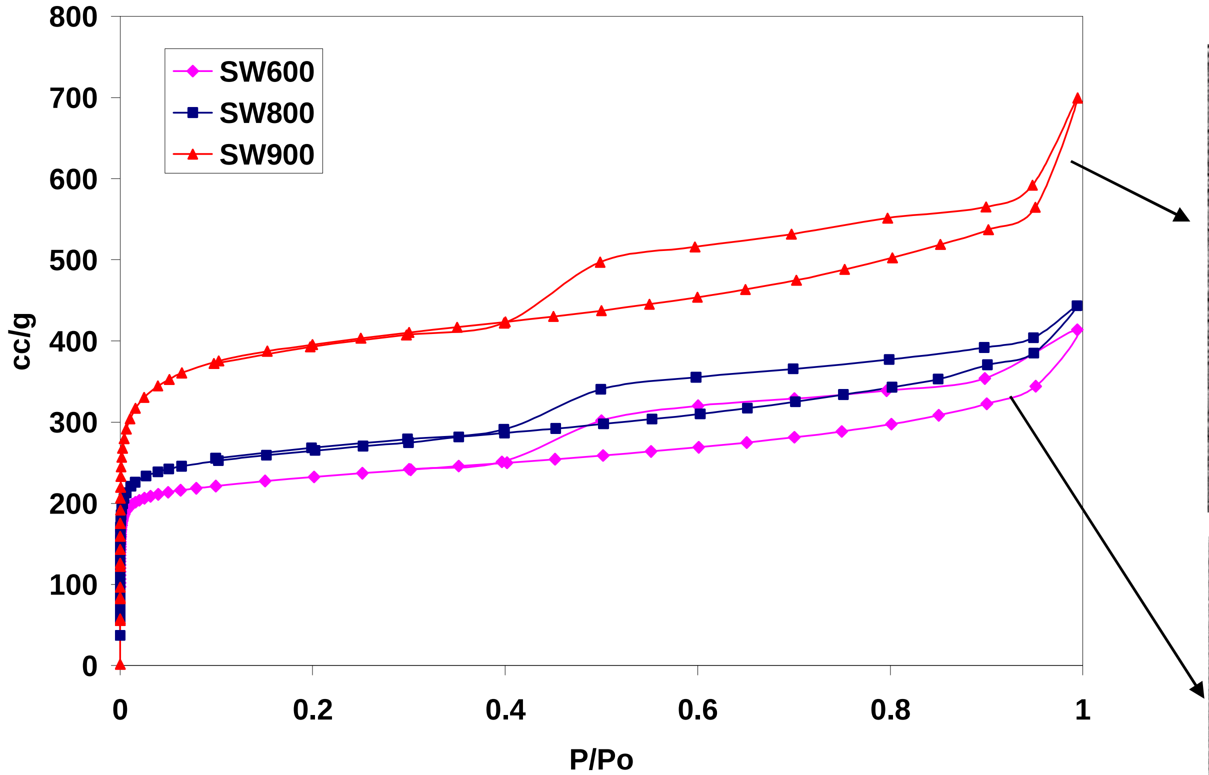
E.Raymundo-Piñero, M. Cadek, F.Béguin, Adv. Funct. Mat., 19 (2009) 1
F. Béguin, M. Cadek, E. Raymundo-Piñero, International Patent SGL Carbon AG/CNRS WO 2008/098841A1
F. Béguin, M. Cadek, E. Raymundo-Piñero, International Patent SGL Carbon AG/CNRS WO 2007/088163A1

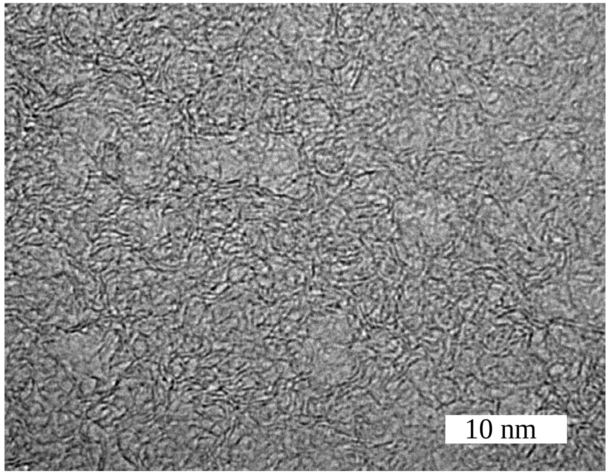
Thermal decomposition of seaweeds (N_2 atmosphere)

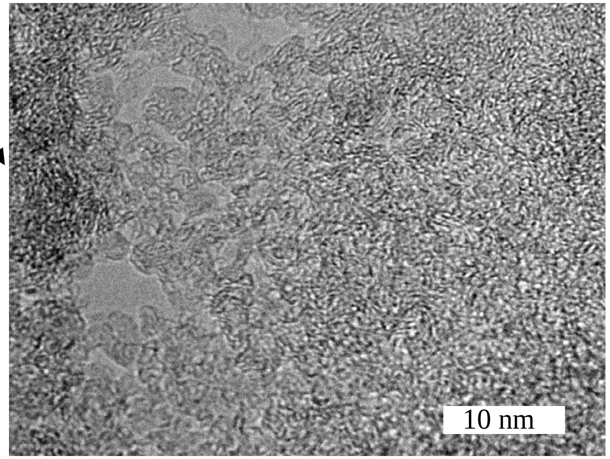


Carbon materials were prepared by carbonizing seaweeds at temperatures from 600°C to 900°C

Properties of seaweeds carbonized at different T°C



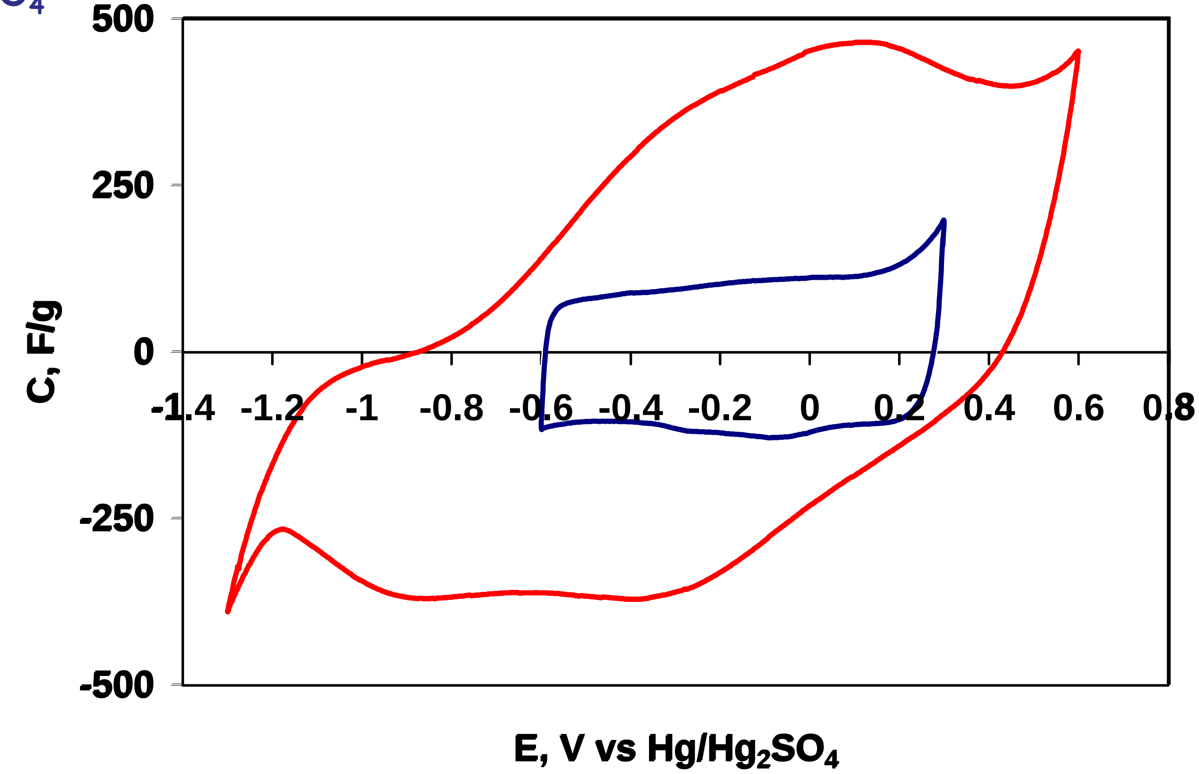




Sample	$S_{BET}(N_2)$ (m^2/g)	$S_{DR}(CO_2)$ (m^2/g)	O at%	N at%
SW 600°C	746	1001	9.6	2.3
SW 800°C	869	1163	8.4	2.1
SW 900°C	1090	1448	7.1	1.6

Three-electrode cell characterization

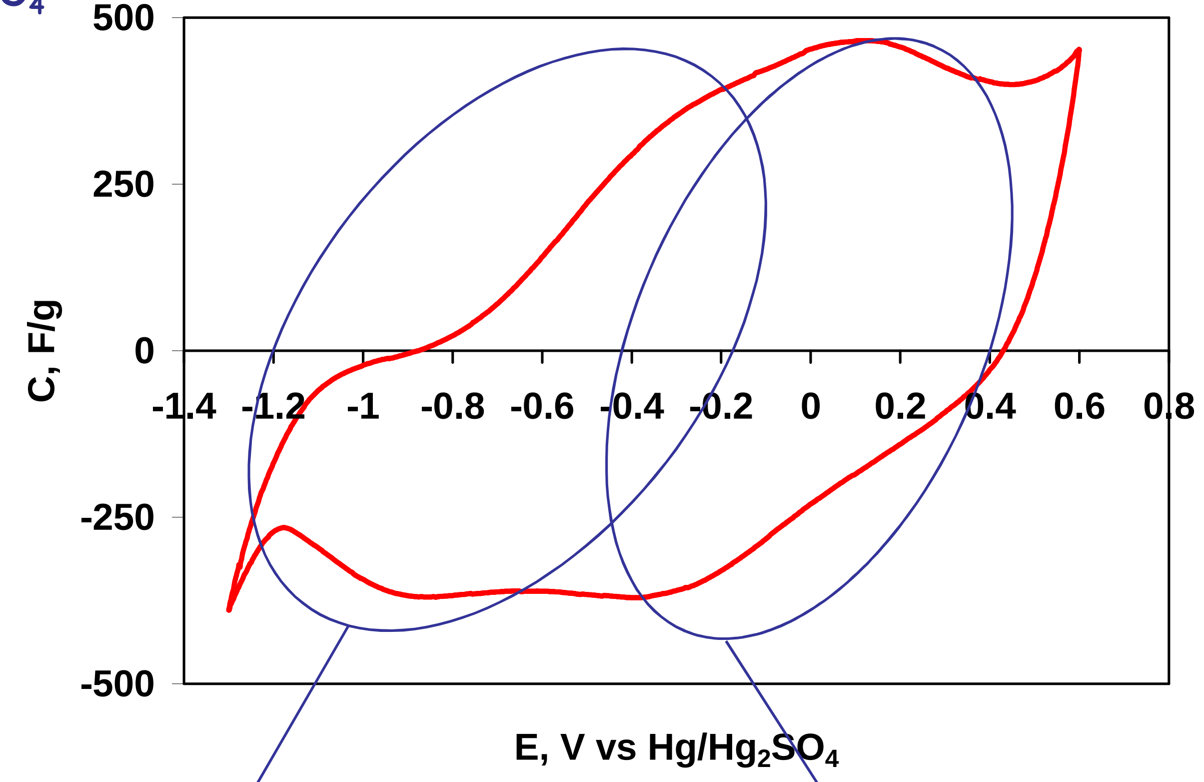
1 mol.L^{-1} H_2SO_4



	S_{BET} m^2/g	O at%	N at%
SW 600°C	746	9.6	2.3
AC1	1402	4.6	-

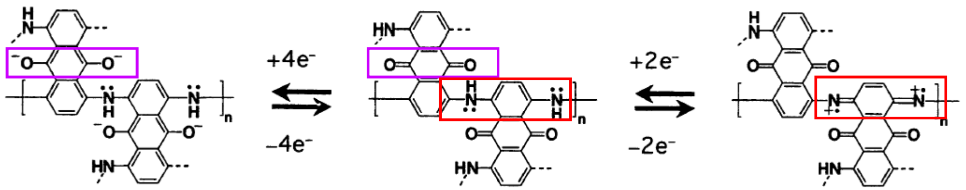
Three-electrode cell characterization

1 mol.L^{-1} H_2SO_4



*$H_3O^+ + e^- \leftrightarrow$ <H> + H_2O

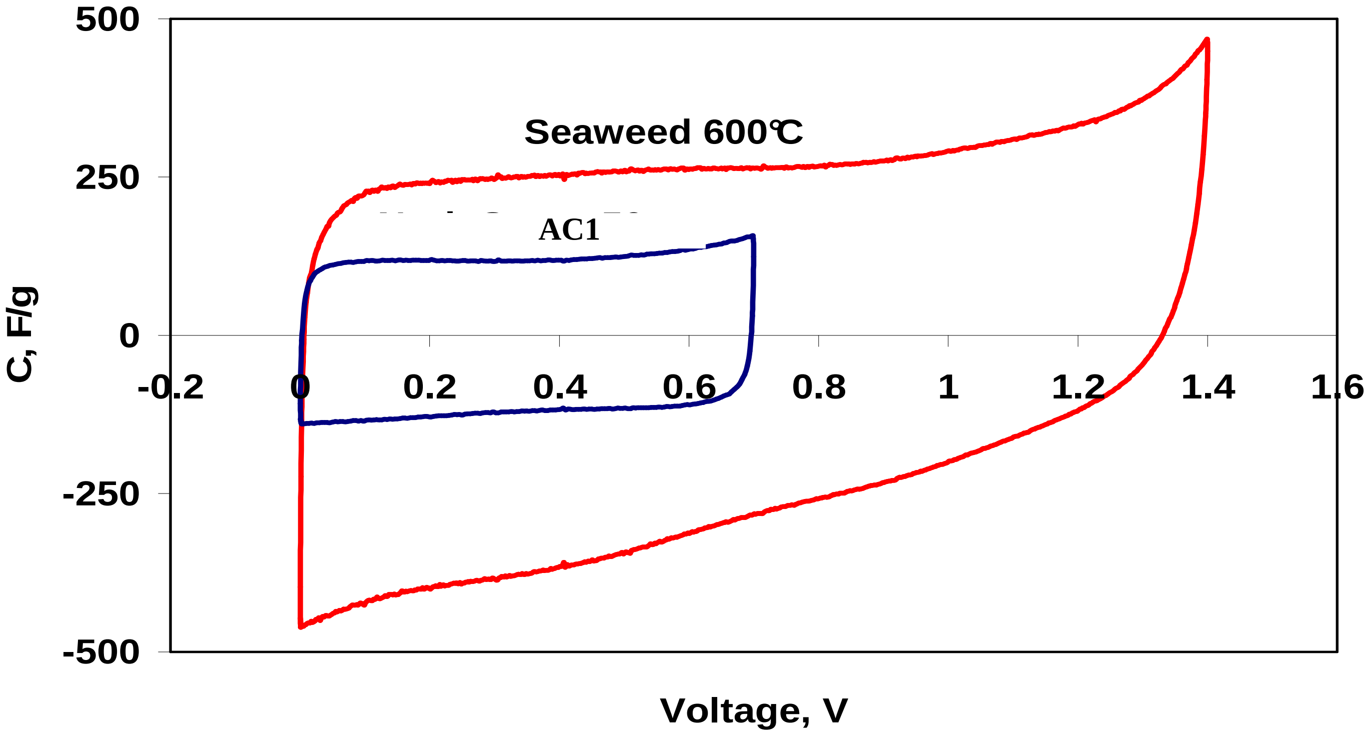
C + <H> $\leftrightarrow$ $\langle H \rangle_{ads}$



Pseudocapacitive processes are at the origin of large capacitance and high overpotential

Real two-electrode supercapacitor characterization

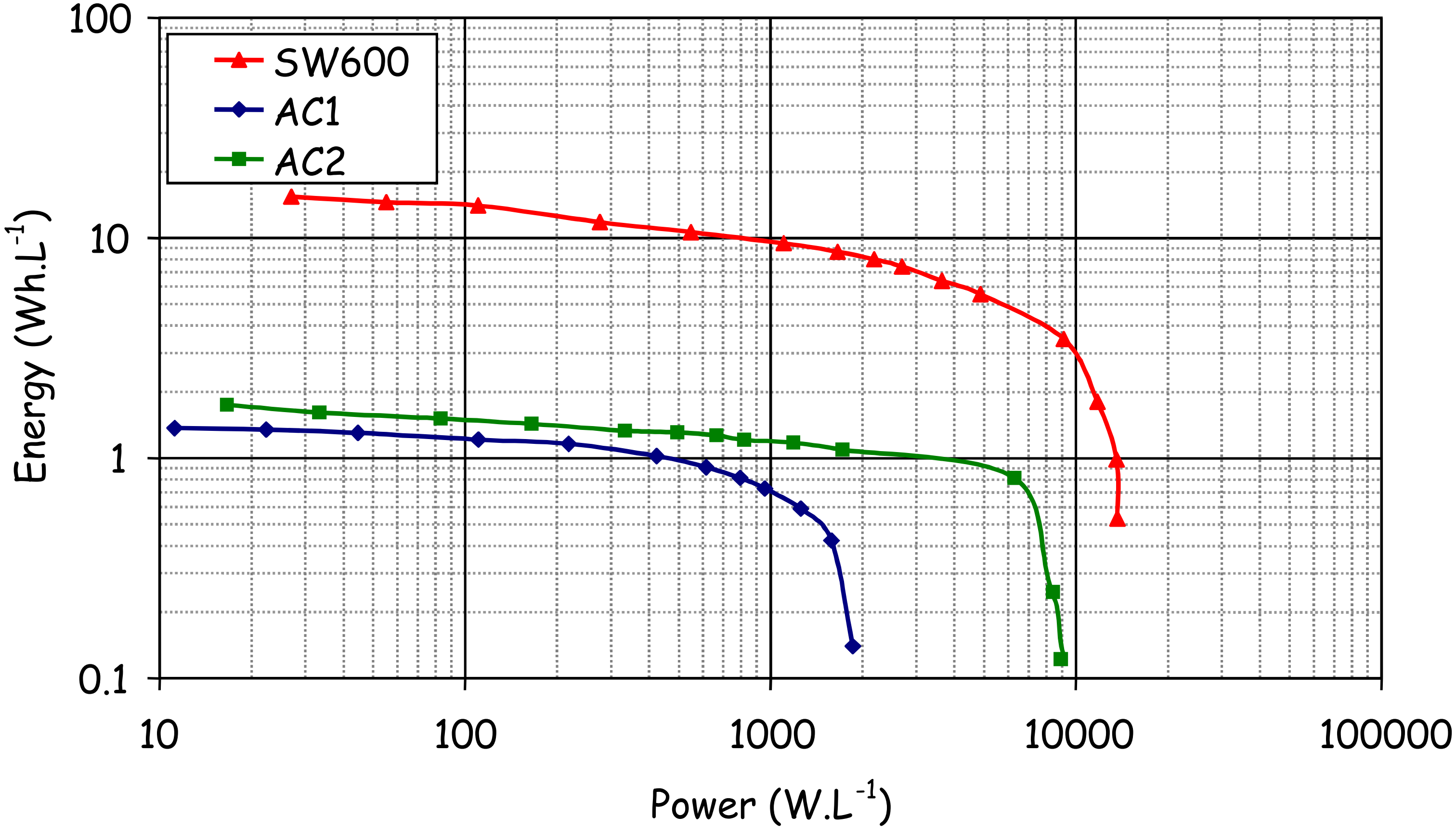
$1\ mol.L^{-1}\ H_2SO_4$



Sample	*C F/g*
SW 600	264
AC1	119

Large capacitance and high voltage window can be obtained for the low temperature seaweed-based carbon ⟹ High Energy Density

Volumetric Ragone Plot



More energy can be extracted from the seaweed based carbon

Summary of performances in 1 mol.L^{-1} H_2SO_4

	S_{BET} m^2/g	O at%	Voltage V	C F/g	E_{max} Wh/Kg	C F/cm^3	E_{max} Wh/L
Seaweed 600°C	**746**	**9.6**	**1.4**	**264**	**19.5**	**208**	**15.4**
AC1	1402	4.6	0.7	119	2.1	77	1.4

High energy density materials with a good cycleability are developed by one-step carbonization of seaweeds at low temperature

Conclusion

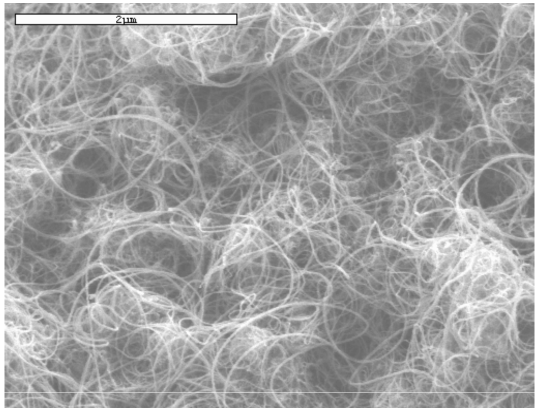
High performance materials can be obtained by one-step carbonization of biopolymers or seaweeds

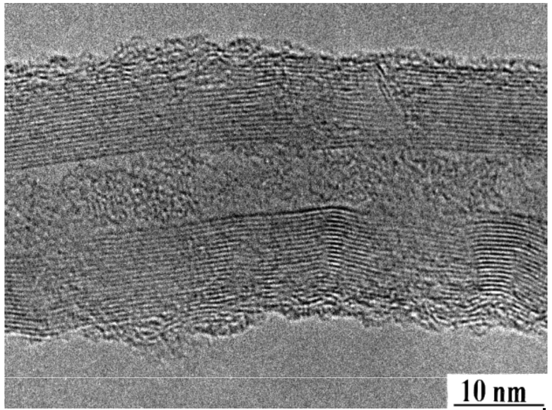
* The functional groups participate to pseudo-faradaic charge transfer reactions, the oxygenated being the most efficient
* The operating voltage is enhanced

High density and electrical conductivity carbons

* High volumetric capacity
* High power density

Composites Seaweed Carbon- Carbon Nanotubes





Carbonization

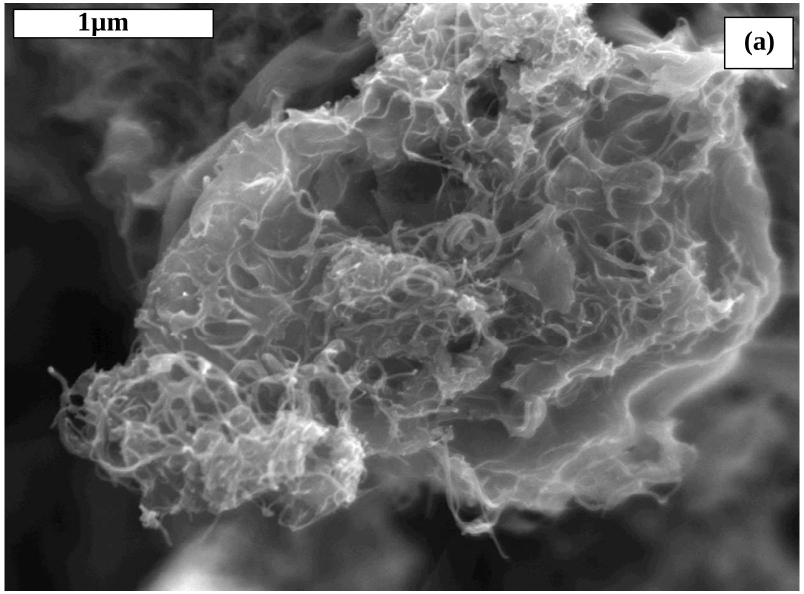
600°C

Seaweed/CNTs nanocomposite

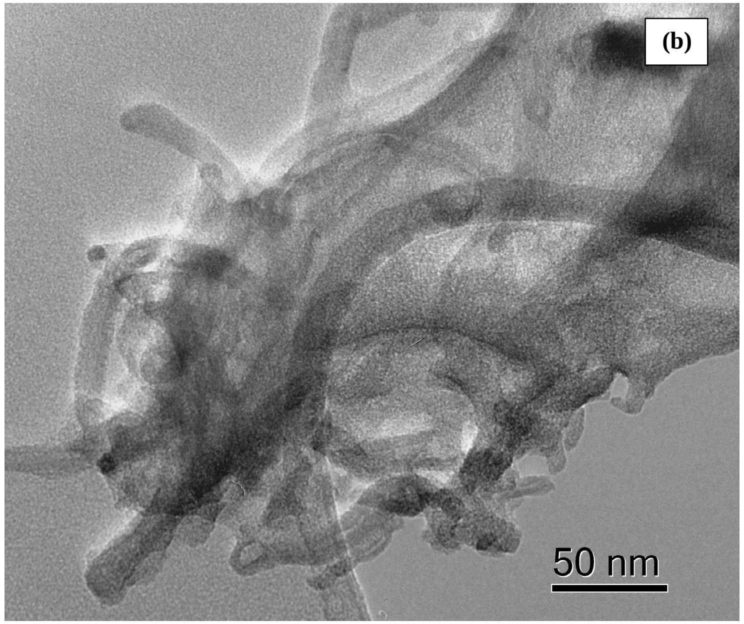
SEM and TEM characterization of the nanocomposite

Example: Seaweed based nanocomposite with 10wt% of CNTs

SEM

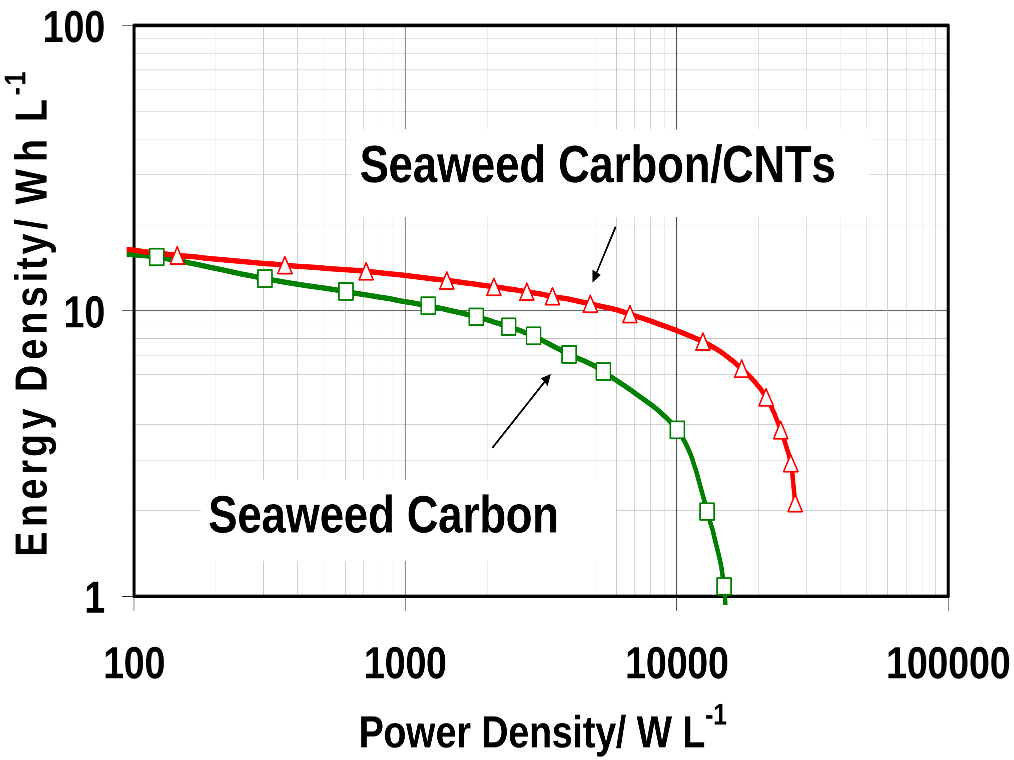


TEM



"Templating effect" of CNTs on the texture of nanocomposites which adopt the mesoporous texture of the nanotubes

Electrochemical data



Sample	*d* *g/cm³*	*C* *F/cm³*	E_{max} *Wh/L*	*E* *(t=10s)* *Wh/L*	*P* *(t=10s)* *kW/L*
SW 600	**0.79**	**208**	**15.4**	**5.9**	**4.3**
SW-10wt%CNT 600	**0.86**	**231**	**17.0**	**9.7**	**6.7**

Conclusions

The carbonization in presence of multi-walled carbon nanotubes adds several advantages :

1) Open mesoporosity of the nanocomposites due to the templating effect of CNTs

2) CNTs drastically increase the conductivity of the materials

The accessibility of ions to the active mass and the charge propagation are improved

More energy can be extracted at high power

Other solution for increasing the energy density in aqueous electrolytes:

Asymmetric systems in order to enhance voltage

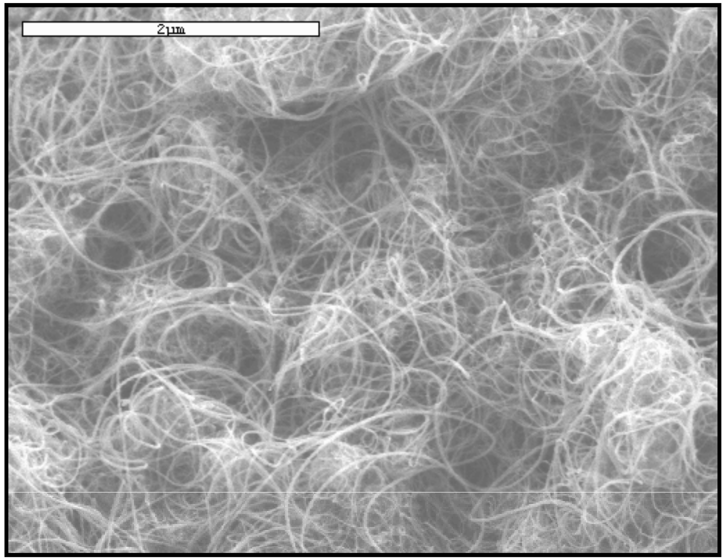
$$E=1/2(CU^2)$$

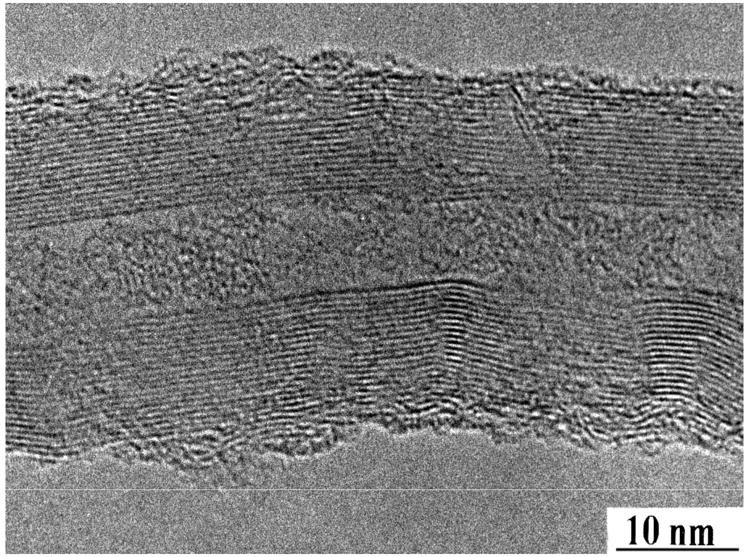
Asymmetric system with :

Positive electrode : *a-MnO_2 / Carbon nanotubes composite*

Negative electrode: *Activated carbon*

Positive electrode: a-MnO_2 / CNTs composite





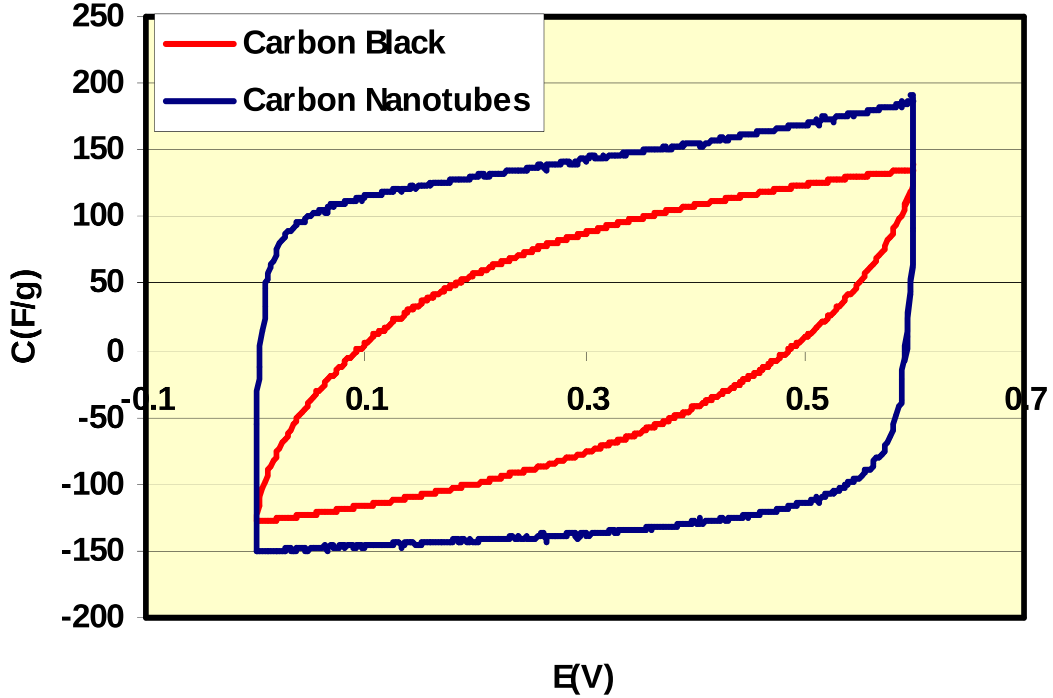
Synthesis of the composite :

$Mn(OAc)_2 \cdot nH_2O$ is added to a $KMnO_4$ solution containing carbon nanotubes

Mn(II) + Mn(VII) + CNTs ↔ Mn(IV) + CNTs

Electrodes: Composite film a-MnO_2 / Carbon Additive + 10% Binder

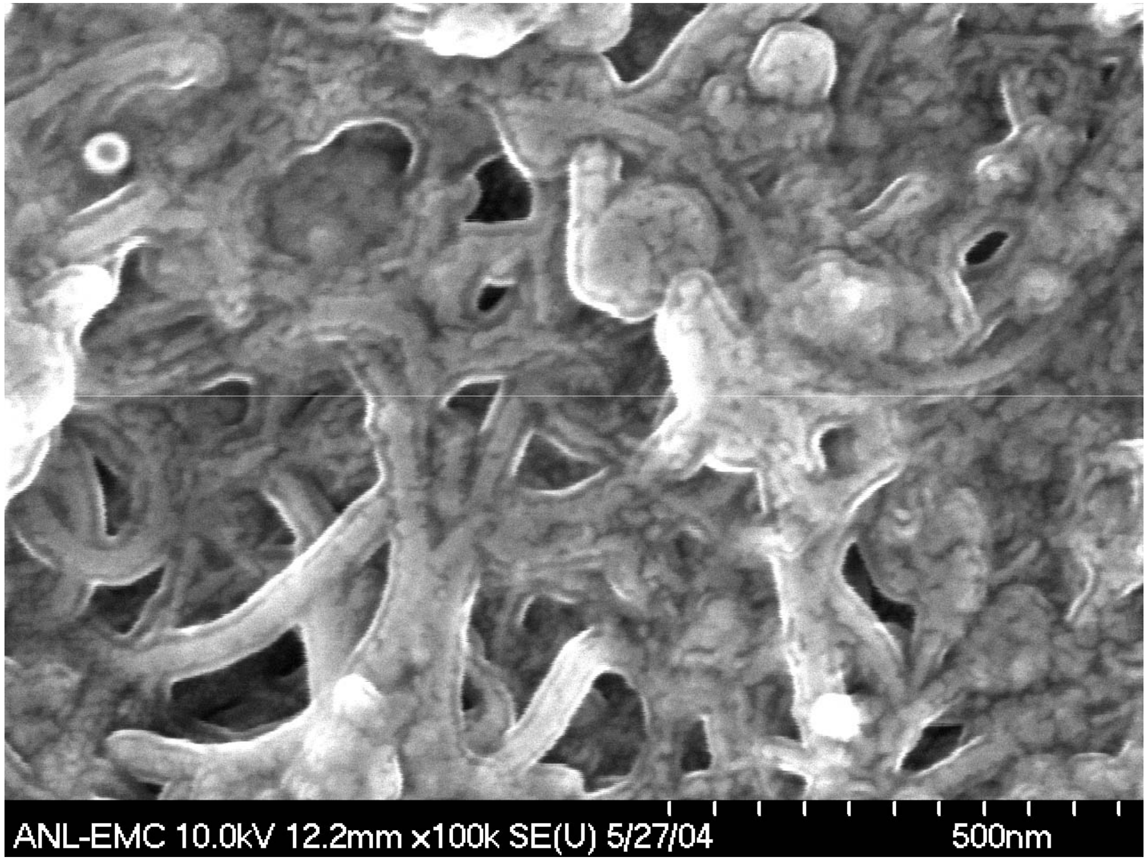
Comparison of MnO_2/CNTs and MnO_2/carbon black composites



Additive to a-MnO_2	C (F/g)	R (Ω)
Carbon Black (15%)	73	50
Carbon Nanotubes (15%)	140	2

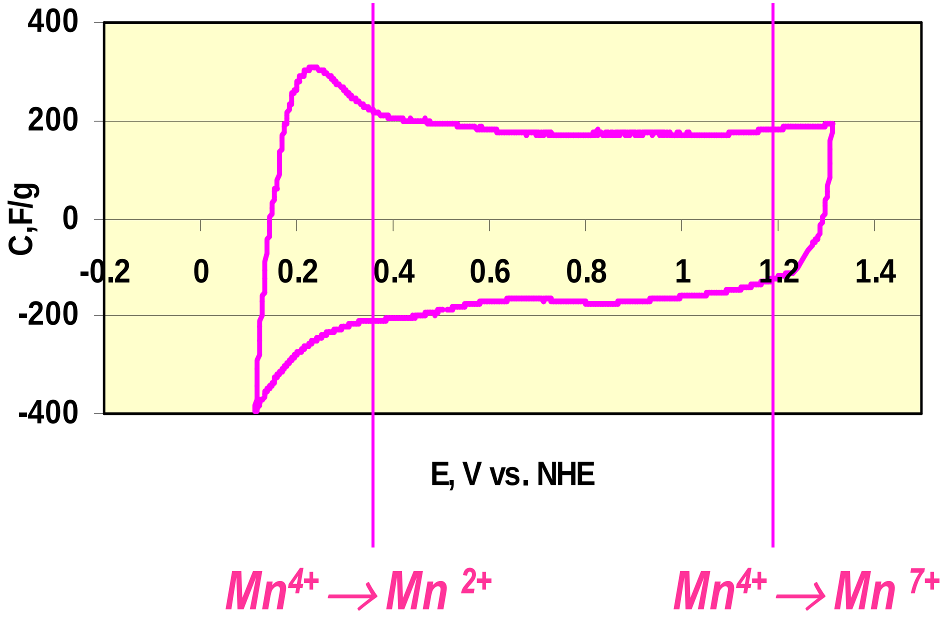
- E. Raymundo-Piñero,V. Khomenko, E.Frackowiak, F. Béguin. J. Electrochem. Soc., 152, A229-A235 (2005)

SEM on a-MnO_2, nH_2O loaded with 15 wt% CNTs



Electrochemical Stability of a-MnO_2 at pH = 6.4

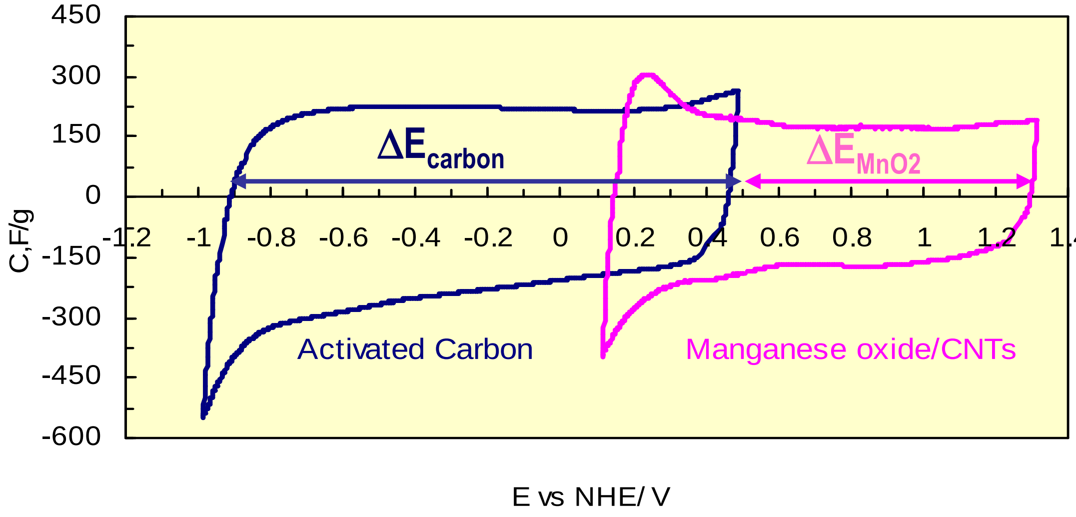
$$MnO_x(OH)_y + \delta e^- + \delta H^+ \leftrightarrow MnO_{x-\delta}(OH)_{y+\delta}$$

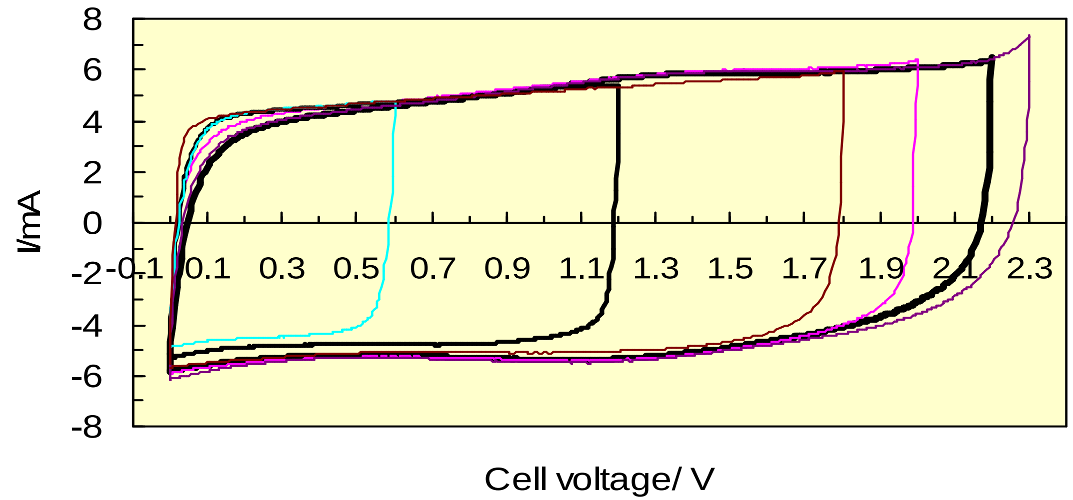


Total potential window: 0.8 V (at pH=6.4)

➡ ***Very interesting for positive polarization***

The activated carbon/a-MnO_2 asymmetric capacitor in 2 M KNO_3





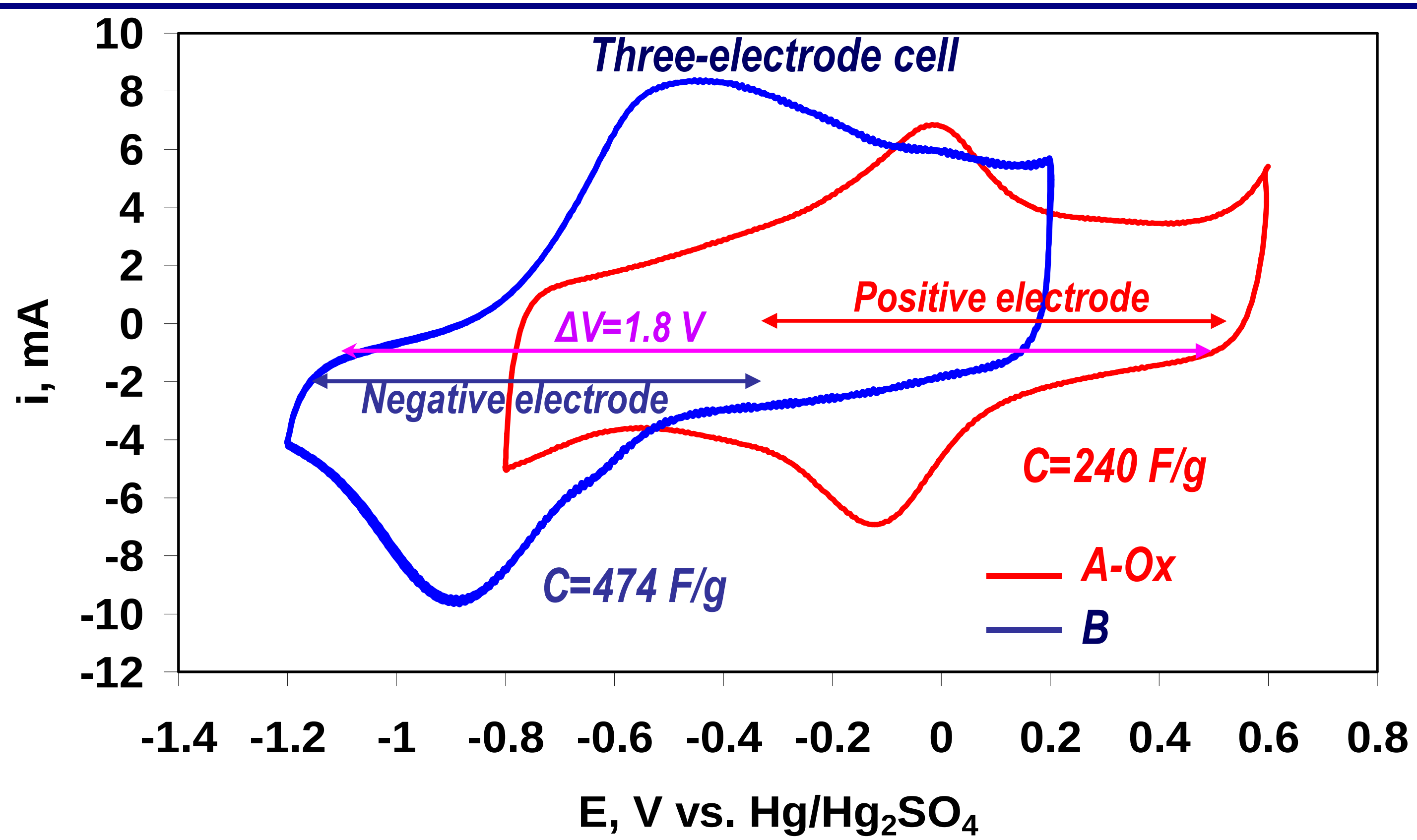
Performance of the asymmetric capacitor in aqueous medium

Supercapacitor type	Electrode Materials	Voltage, V	P_{max} $kWkg^{-1}$	E $Whkg^{-1}$
Symmetric	Carbon / Carbon	0.7	22	3.6
Symmetric	MnO_2 / MnO_2	0.6	3.8	1.5
Asymmetric	Carbon / MnO_2	2.0	62	12.6

-V. Khomenko, E. Raymundo-Piñero, F. Béguin. Journal of Power Sources 153, 183-190 (2006)
-V. Khomenko, E. Raymundo-Piñero, E.Frackowiak, F. Béguin. Journal of Applied Physics A, 82, 567-573 (2006)
-L. Demarconnay, E. Raymundo-Piñero, F. Béguin, Journal of Power Sources 196, 580-586 (2011)

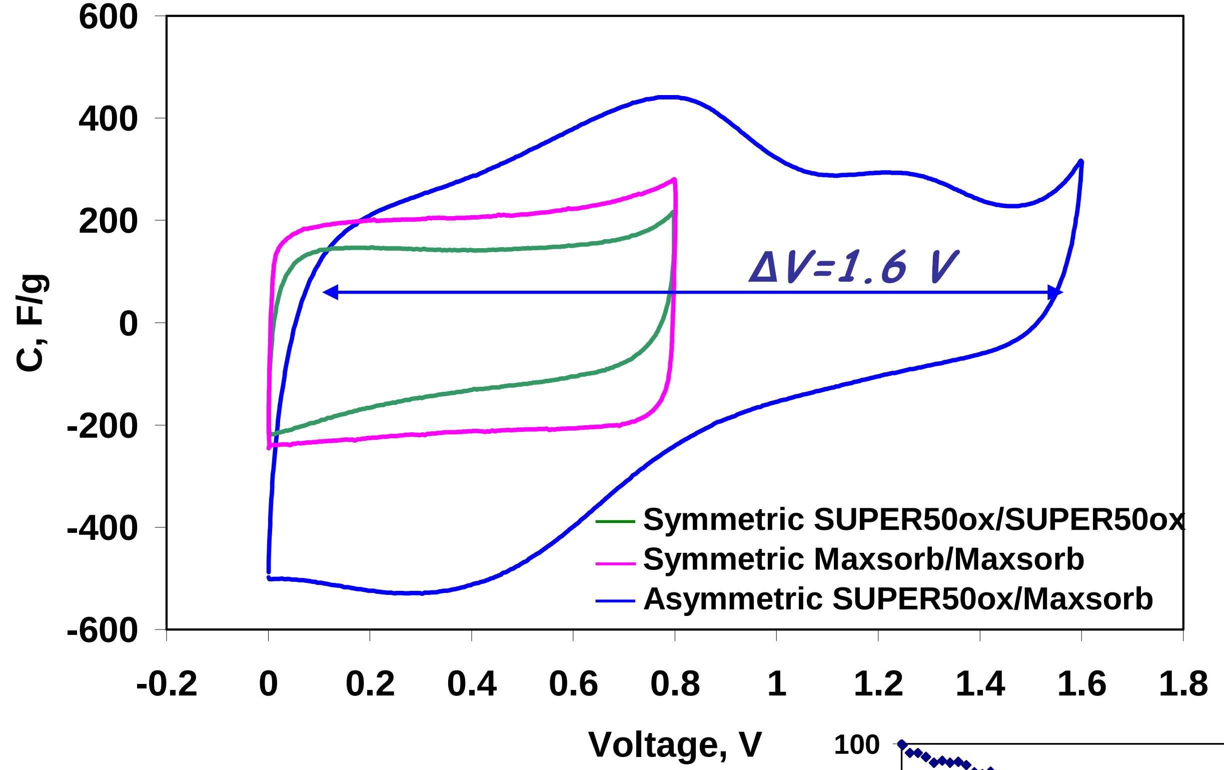
Carbon/Carbon Asymmetric Systems

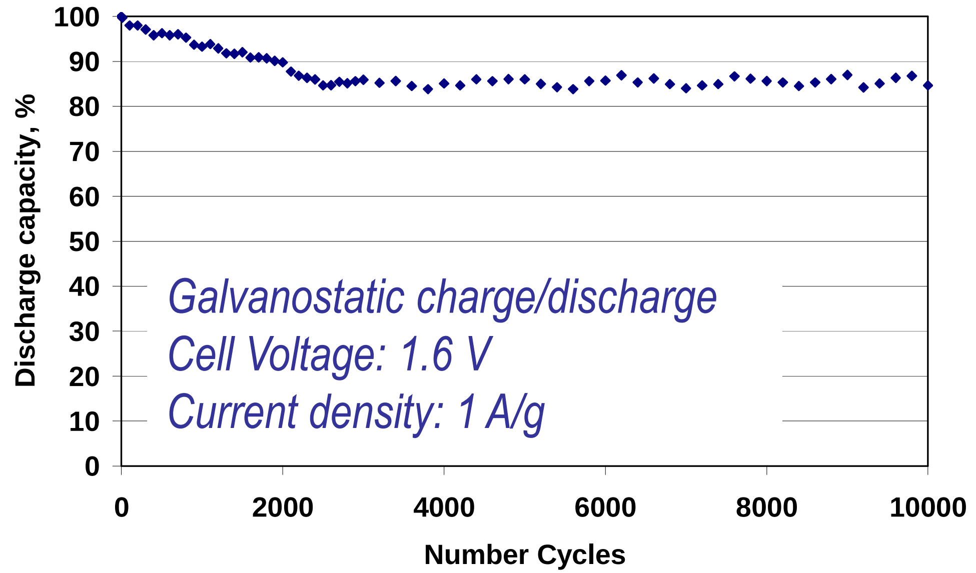
Electrochemical performance of the carbon electrodes of different nature



High capacitance and a theoretical working voltage of 1.8 V should be obtained by assembling the two carbons in an asymmetric system

Asymmetric two-electrode cell





Performance of the Asymmetric System

Material Positive/Negative	System	Cell Voltage V	C F/g	E Wh/Kg
A-Ox/A-Ox	symmetric	0.8	137	3.0
B/B	symmetric	0.8	230	5.1
Ox-A/B	asymmetric	1.6	321	28.6

F. Béguin, V. Khomenko, E. Raymundo-Piñero, International Patent CNRS/Université d'Orléans WO 2008/071888A2
V. Khomenko, E. Raymundo-Piñero, F. Béguin, J. Power Sources. 195, 4234-4241(2010).

Conclusion

- *Asymmetric supercapacitors were developed in aqueous medium by combining two pseudo-faradic carbon based electrodes*

  * *Positive electrode : a-MnO_2 / carbon nanotubes composite, oxidized carbon, …*
  * *Negative electrode : nanoporous carbon*

- *The optimized system gives a practical cell voltage up to 2 V in aqueous medium*

- *Energy density is 5 to 10 times higher than for symmetric systems and comparable to values in organic medium*

Some future directions

EDLCs in organic electrolyte

- Implement more friendly electrolytes

Pseudo-capacitive materials and asymmetric systems in aqueous electrolyte should be implemented

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Stockage de l'énergie dans des supercondensateurs à base de matériaux carbonés

Encarnación Raymundo-Piñero

Centre de Recherche sur la Matière Divisée

CNRS-Université d'Orléans

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