Nanostructured Carbon: What Roles in Energy Storage ?

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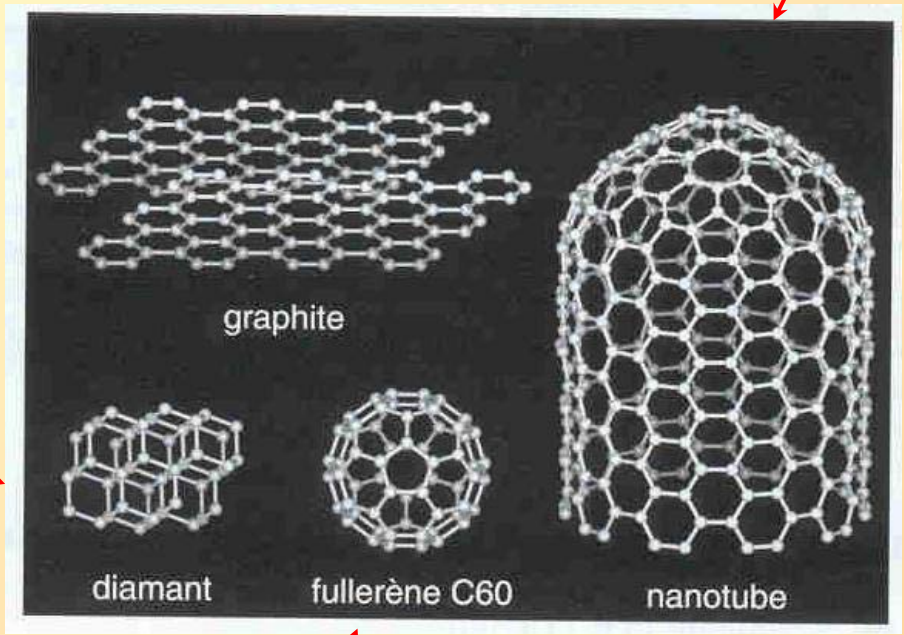
- Why carbon? ➔The specifics of such structures
  - What is nanostructured? Why is it useful?
    - Fields in which it can be of use
      - Reality versus fiction
    - What does the future hold ?

The “ordered” carbons

Graphite :
Exploited since the Middle Ages and used for centuries for writing.
γραπειν : graphein, end 18^{tcc} century..

Nanotubes :
Iijima, 1991, NEC Corp., Japan



Diamond :
Impurity level < 10 ppm in best materials. Classified according to optical absorption.

Fullerenes :
1985 : synthesis of grams by Kroto, Curl, Smalley
1990 : Kratschmer et al., electric arc synthesis
1996 : Nobel Prize in Chemistry

Diversity of “all-carbon” materials

	Dimensionnalité	Coordination	Caractère électronique
Diamant	3D	sp^3	Isolant, $E_{gap} > 5V$
Graphite	3D anisotrope ou quasi-2D	sp^2	Semi-métal
Graphène	2D	sp^2	Semi-conducteur, $E_{gap} = 0$ V
Nanotube monoparoi	1D	$Sp^2 + sp^3$	Semi-conducteur ou métallique
Fullerite, C_{60}	0D		isolant

The world of less-ordered carbons

- activated carbons
- amorphous carbons
- carbon fibres
- exfoliated graphite
- turbostratic carbons

- pyrolysed polymers
- cokes
- carbon black
- aerogels
- coals, anthracite

• chemical & structural heterogeneity
• numerous possible treatments : chemical, thermal

➔range of functional groups,
➔ wide possible range of porosities

The specifics of « nano »

- **Changes in dimensionality, physical properties, the laws that govern the physics and chemistry**
  - Discretisation of energy levels
  - High ratio of surface energy to total energy
- **The solid**
  - Increasing ratio of number of surface atoms to bulk atoms
    - Catalysis, adsorption, functionalisation,
- **The porous structure**
  - Confinement
  - Increased passage per unit area
  - Increased surface area
    - templates

How is nanotechnology often seen to improve things ?

- increased surface area
  - ➔ Increased surface reactivity per mass,
  - ➔ increased dispersion,
  - ➔ optimisation of channel dimensions and accessibility

Many synthesis routes and characterisation tools

What is always required: a close mixture of experimentation – characterisation – simulation

The immense literature

From SciFinder Scholar data base, Nov 10, 2005:

"Exact fits" / "containing the concept"

- Nanotechnology 5800 / 345000
- Energy storage 9000 / 29000
- Fuel cells 51000
- Carbon electrodes 5000 / 97000
- Carbon nanostructures 2500
- Carbon nanotubes 17800

Real-world applications to which nano-structured carbon is – or may be - applied

- Supercapacitors
- Catalyst supports
- Gas storage (H_2, CH_4, …)
- Electrodes for fuel cells
- Lithium ion batteries

What features common to all ?

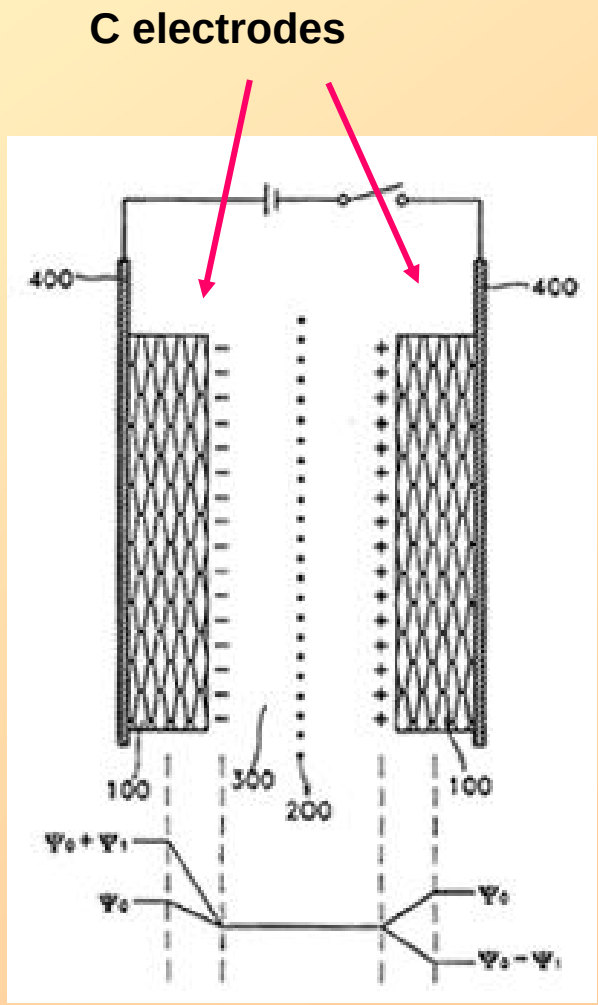
Supercapacitors

Advantages

- relatively unlimited cycle life
- rapid charging time

Limitations

- energy density
- high self-discharge



Catalyst supports: one example

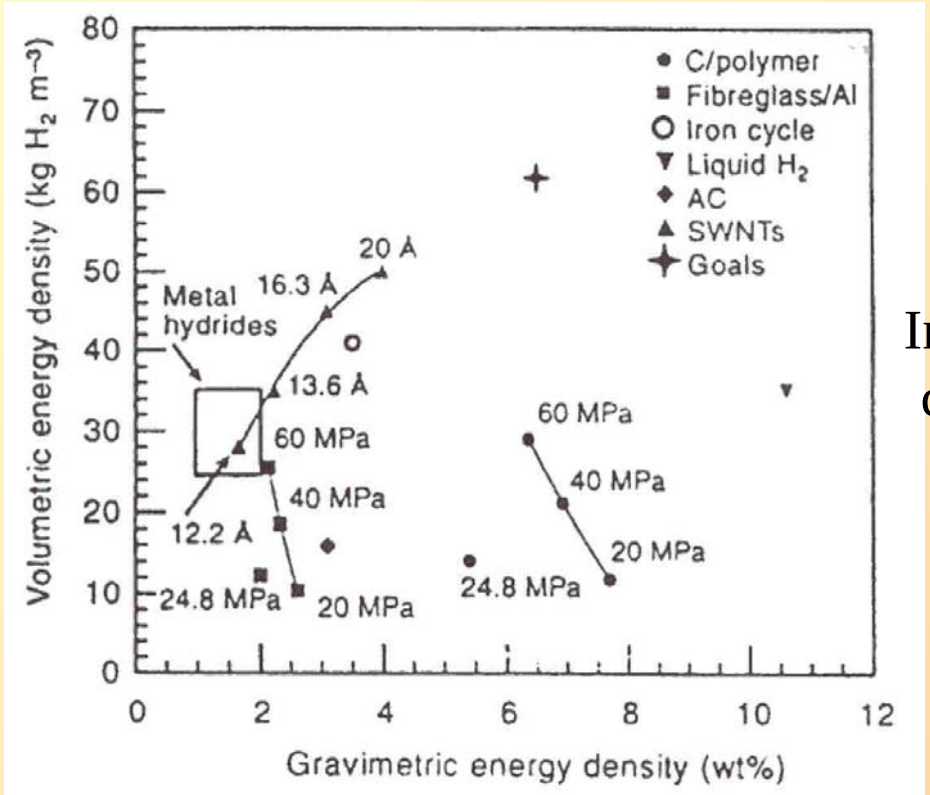
Succession of steps

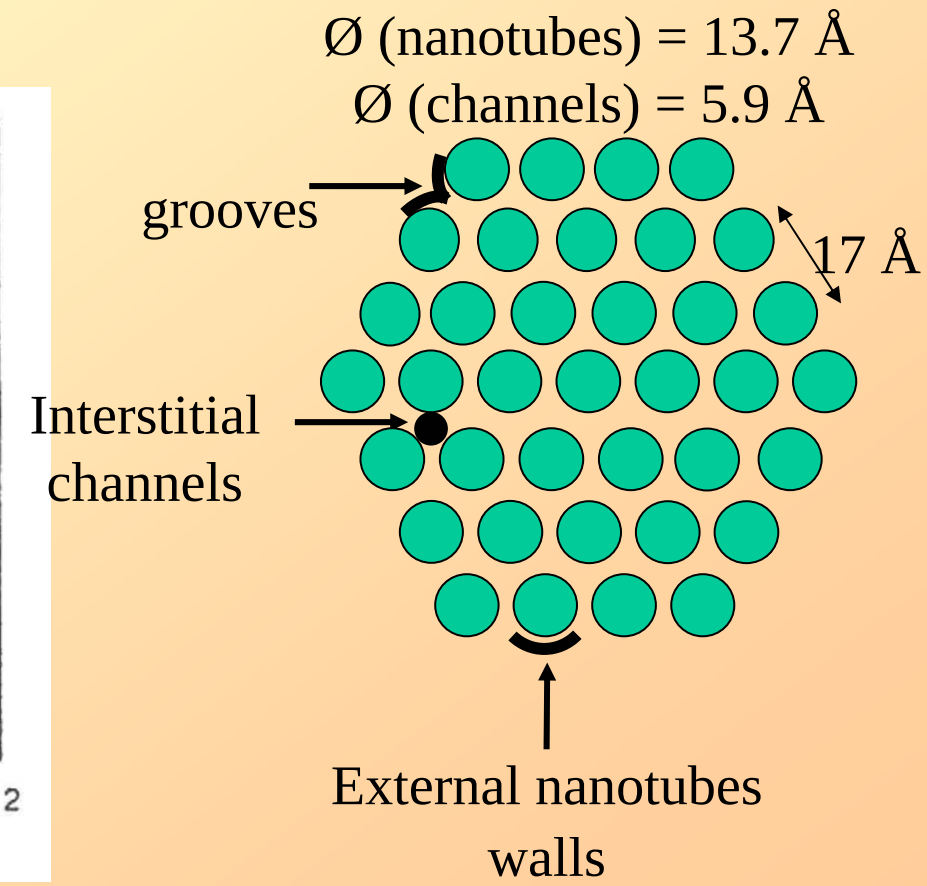
1. axial compression of a column of exfoliated graphite (95% pore volume)
2. Impregnation of block with furfural alcohol
3. Polymerisation
4. Pyrolysis of the composite
5. Activation with steam at 800 °C
6. Vapour phase doping by $MoCl_5$ then reductionby H_2
7. Carburisation using CH_4 ➔ Mo_2C 5 nm nanoparticles

$MoCl_5$ is an interesting precursor for obtaining hexagonal Mo_2C nanoparticles (diameter < 5 nm)

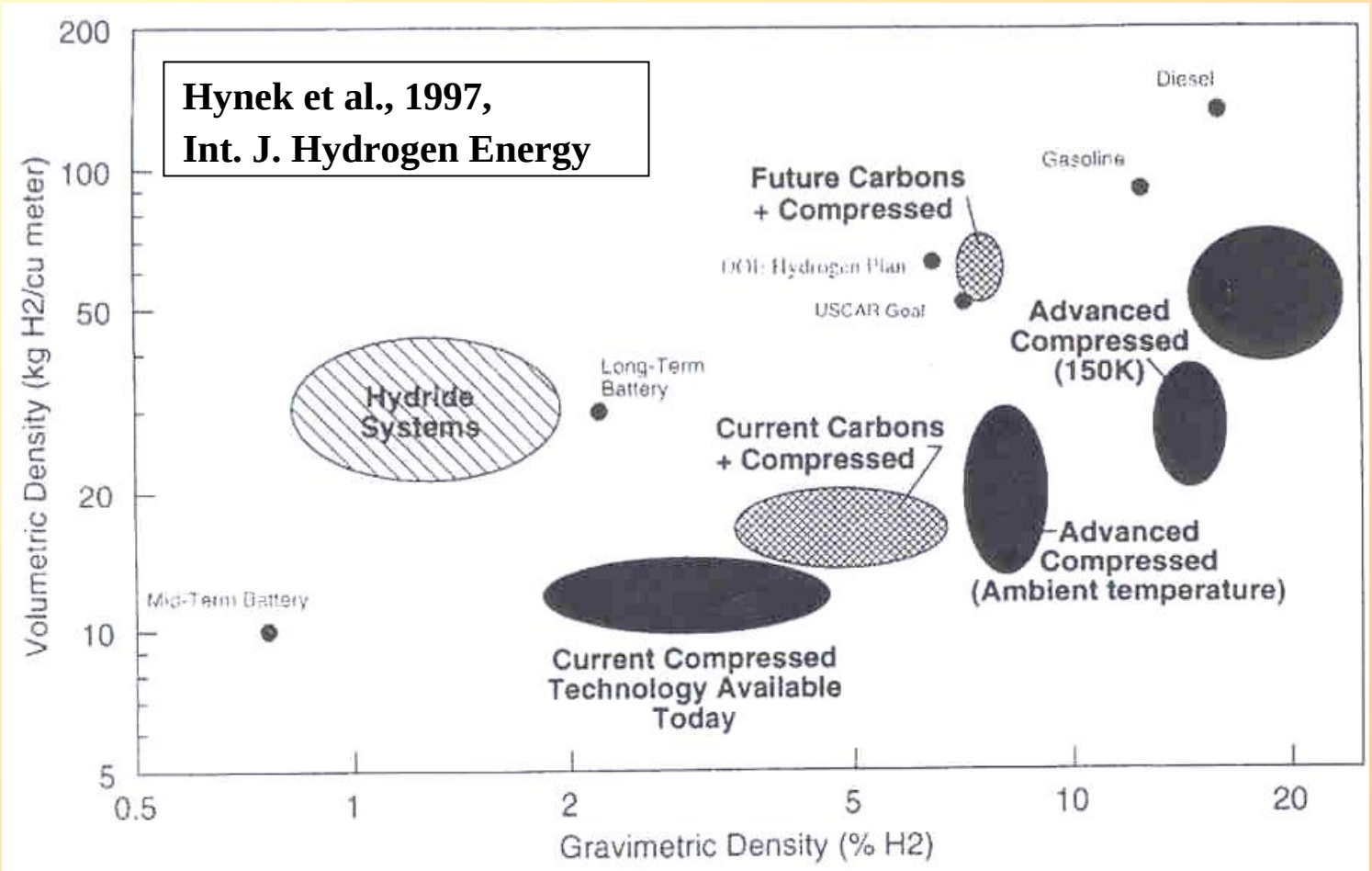
Gas storage: CNTs, …

Target : **6.5 mass density and 62 kg H_2/m^3**



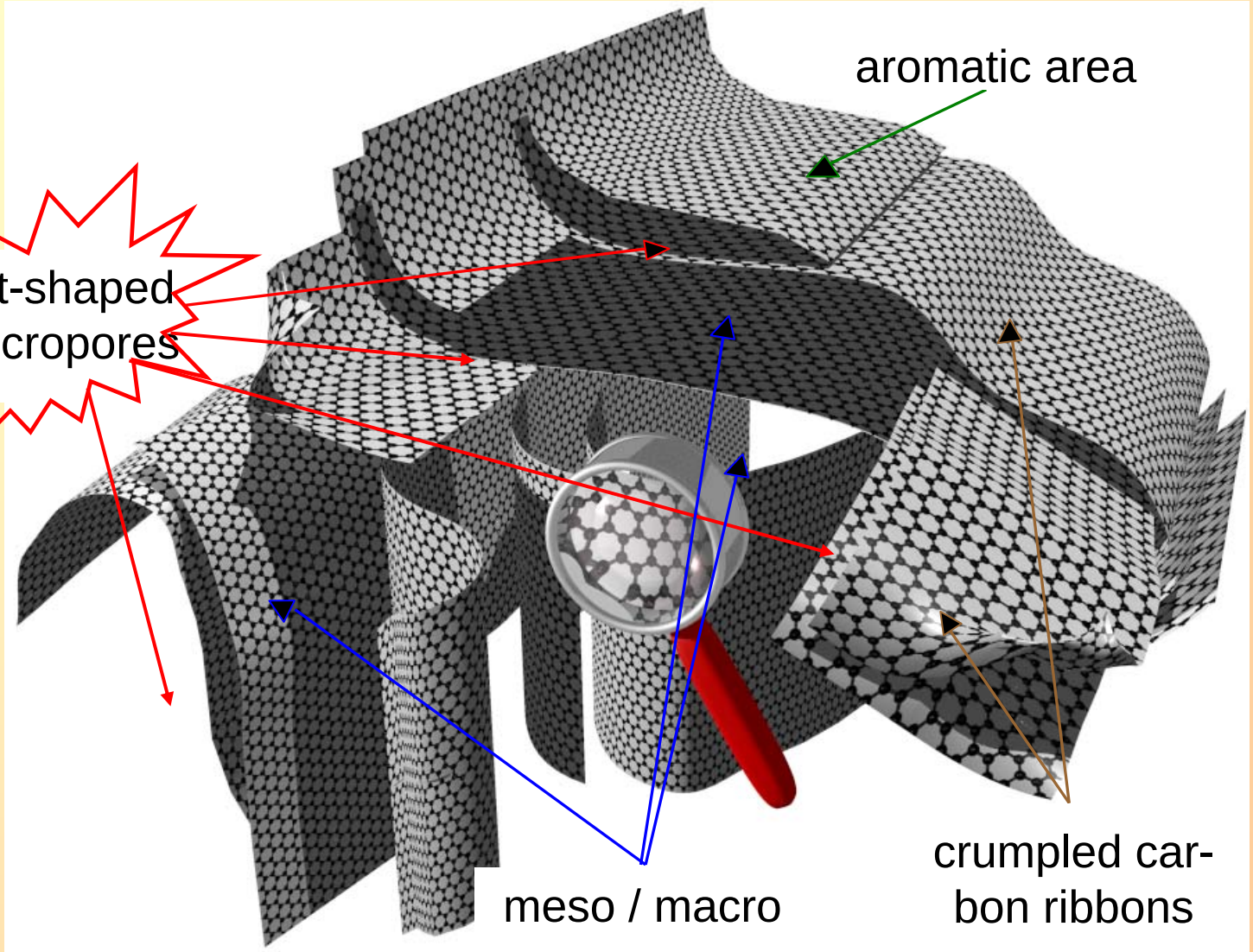


And the future for hydrogen storage ... ?



CH_4 storage: why may active carbons be better ?

- **Structure of active carbons**

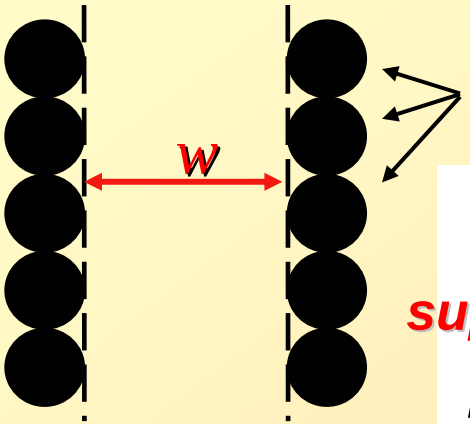


Methane storage on active carbons

Irreplaceable properties of active carbons

- **slit-shaped** micropores ⇒ *more uptake than any other geometry*
- **hydrophobic** surface ⇒ *low (competitive) adsorption of water*
- higher **thermal conductivity** than ceramics ⇒ *better heat transfer*
- highest **surface areas** (up to 3000 m2 g-1)
- highest **micropore volumes** (above 1 cm3 g-1)
- pore structure may be **tailored**

Main feature of an active carbon : *its adjustable porosity*



ultramicropores ⇔ ***w < 0.7 nm***

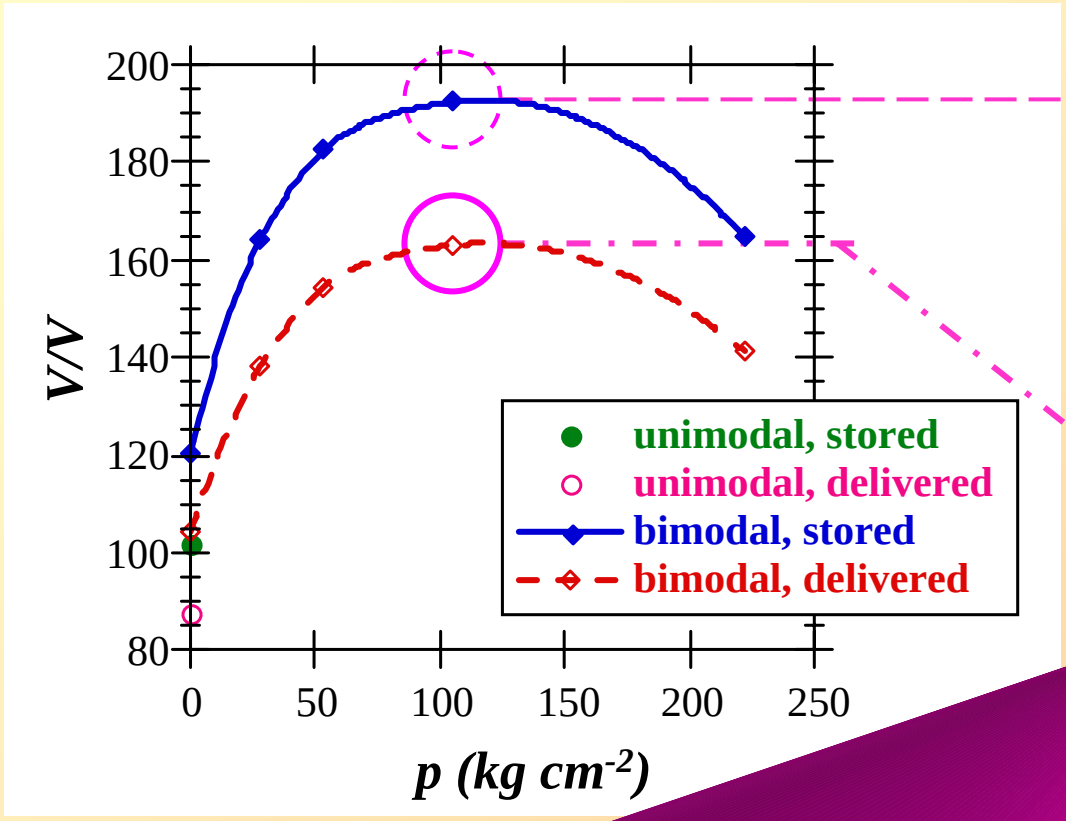
supermicropores ⇔ ***0.7 < w < 2 nm***

mesopores ⇔ ***2 < w < 50 nm***

those responsible for the UNDELIVERABLE methane capacity

those responsible for the DELIVERABLE methane capacity

those USELESS for methane storage



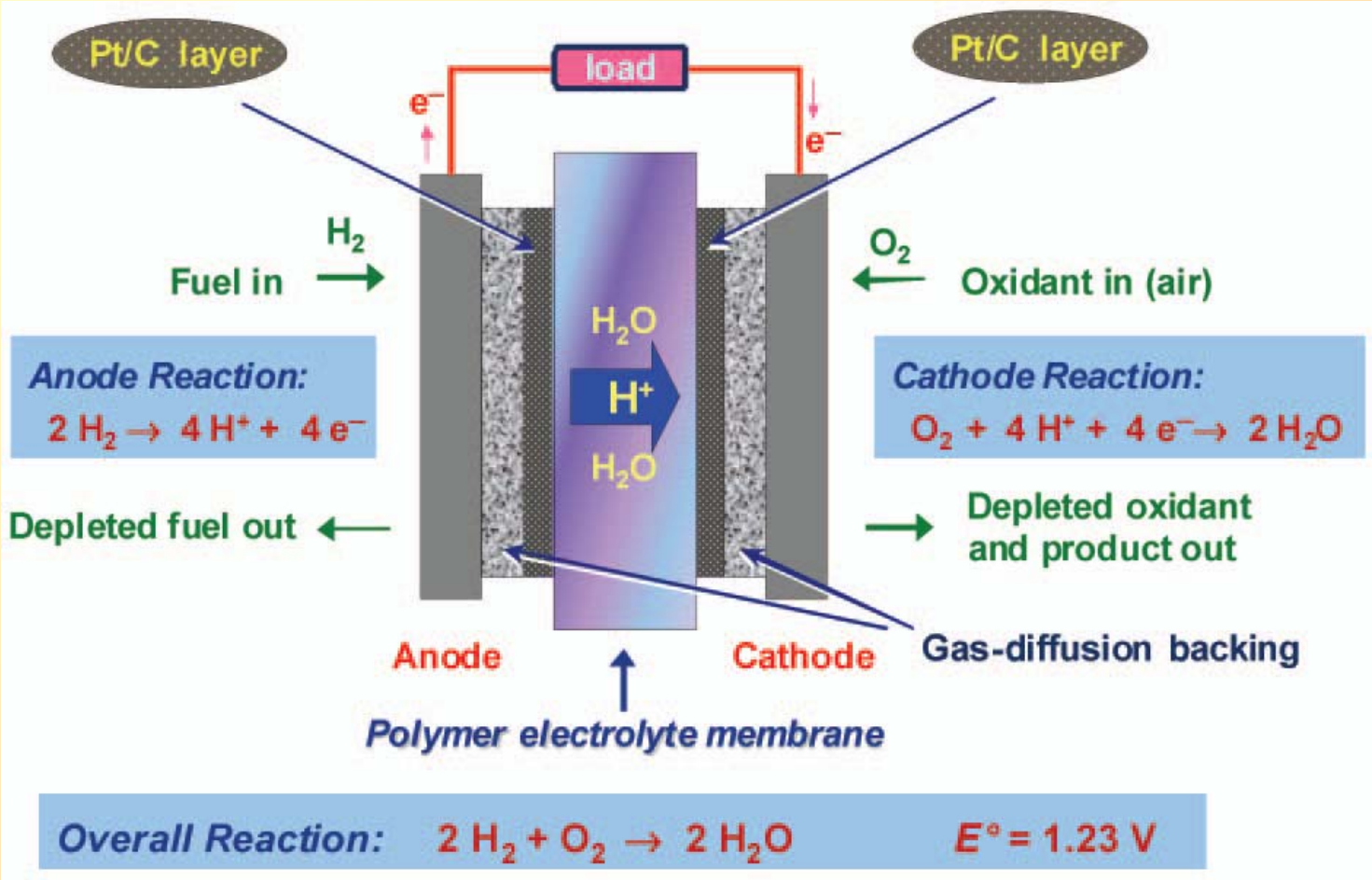
193 V/V stored !

163 V/V delivered !!!

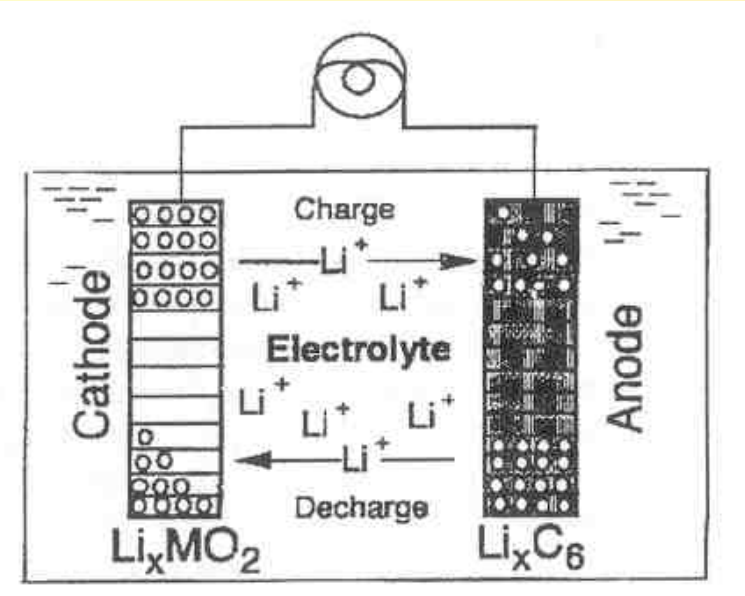
Target value of 150 V/V delivered now exceeded

(Celzard, Albiniak, Jasienko-Halat, Marêché, Furdin, 2005, Carbon, in press)

Fuel cell electrodes



Lithium ion batteries



- Long history of continuous development
- Today's advantages : rechargeable, good energy-to-weight ratio,

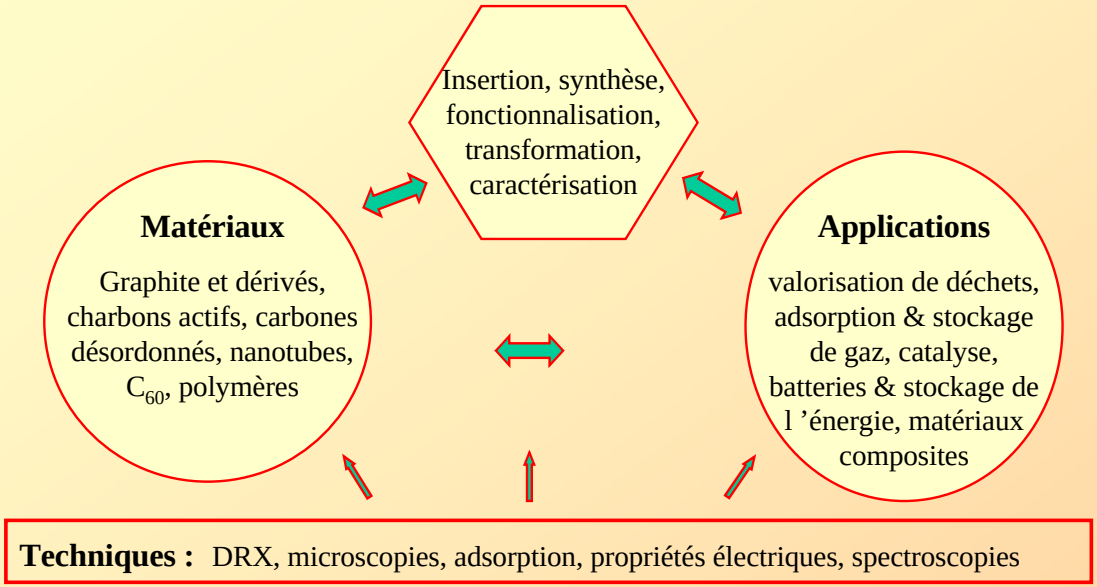
Still required improvements :

- C anodes,
- charge/discharge cycling,
- electrolytes (biomass-based

What features of C have been used?

- Combination of strong covalent bonding and weak van der Waals bonding
  - ➔ intercalated & **exfoliated graphite**
- Bridgman : “Graphite is nature’s best spring.”
  - ➔ reversible intercalation process in Li-ion batteries
- Processibility ➔ pores and holes covering a vast range of dimensions and sizes.
  - ➔ **activated carbons, CNTs**,
- High thermal and electrical conductivities
- Its amphoteric nature

Carbon Materials Group in Nancy



Orientations 2005 – 2008 :

Fondamental → **Appliqué**

Intercalation:

Huge range of donor and acceptor compounds

Nanotubes :

Adsorption, microscopy, functionalisation, composites

Li ion Batteries

Graphite + metal nanoparticles for negative electrodes, biomass-based solvents

Énergy & environnment :

gas storage, supercapacitors,, purification adsorbents

Fact or fiction: future challenges and some precautionary remarks

An almost unlimited range of commercially fabricated carbon materials

➔ rich but frustrating !

➔ better predictable control of porous structures

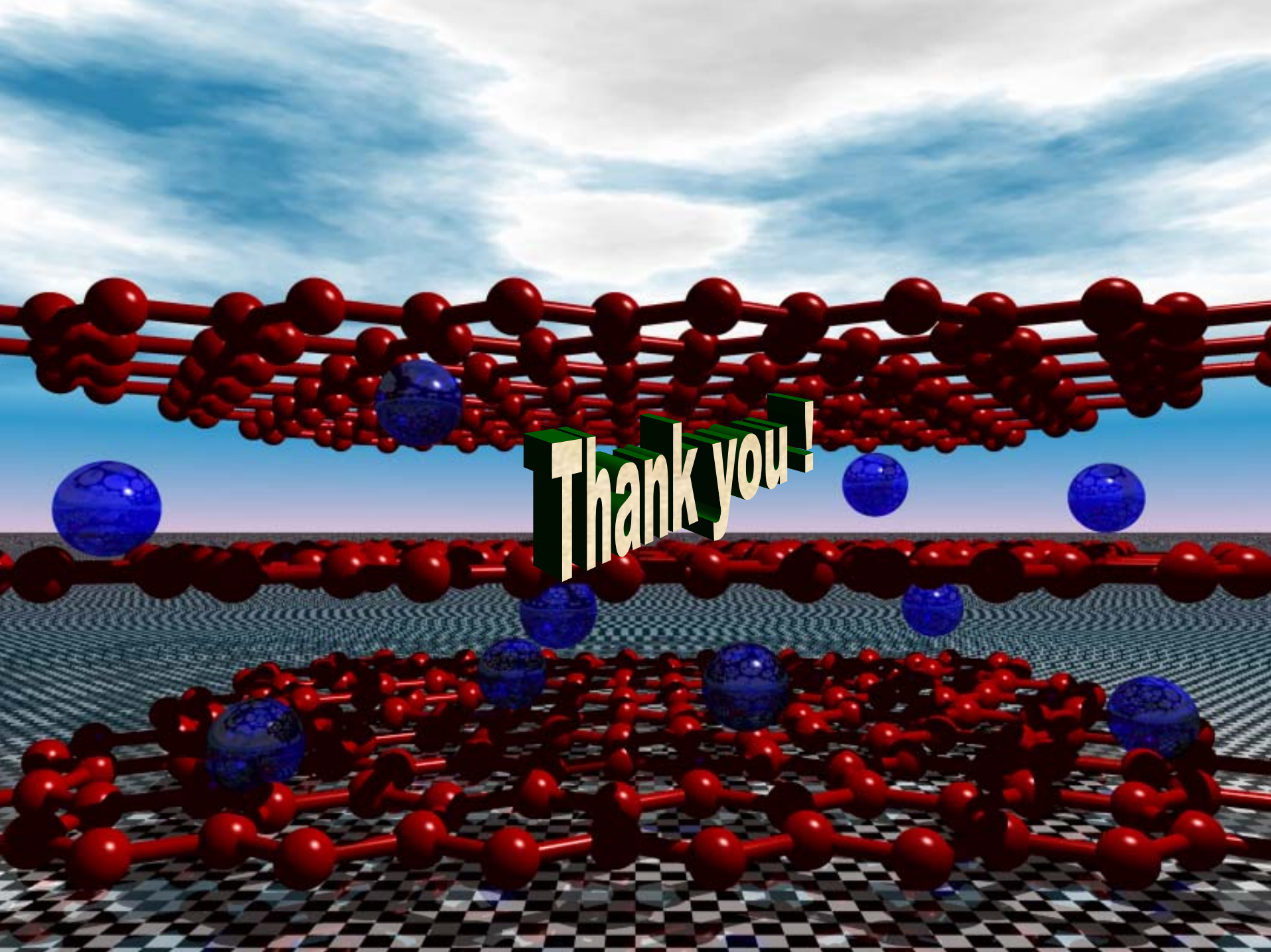
A need to examine the energy expended in the processing techniques before evaluating overall energy benefits !

Thanks to my LCSM colleagues

- A. Celzard
- N. Dupont-Pavlovsky
- G. Furdin
- J.-F. Marêché

…and the numerous PhD students

And the many GFEC, GFECI and GDRE colleagues


Thank you!