



# 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

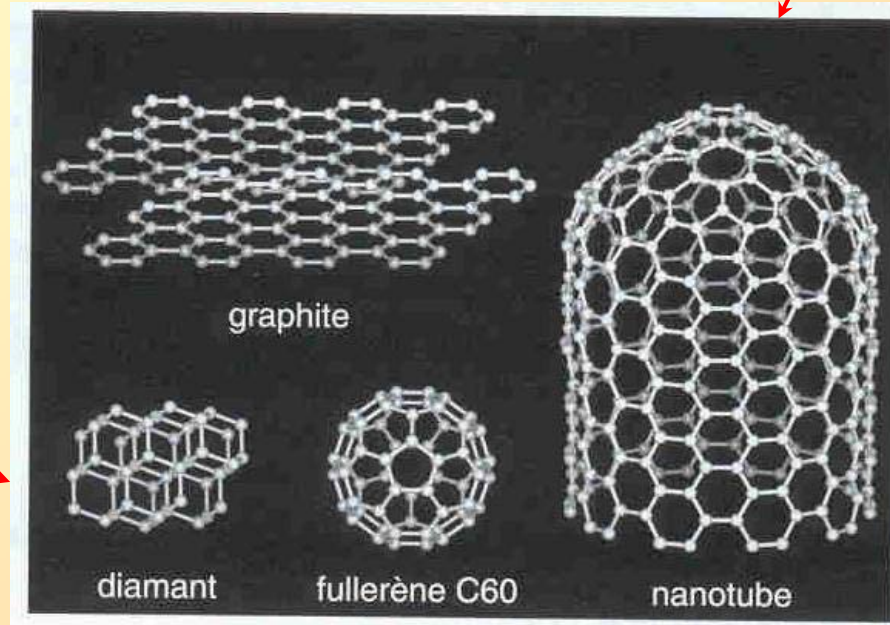
## Graphite :

Exploited since the Middle Ages and used for centuries for writing.

γραφειν : graphein, end 18<sup>th</sup> 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

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

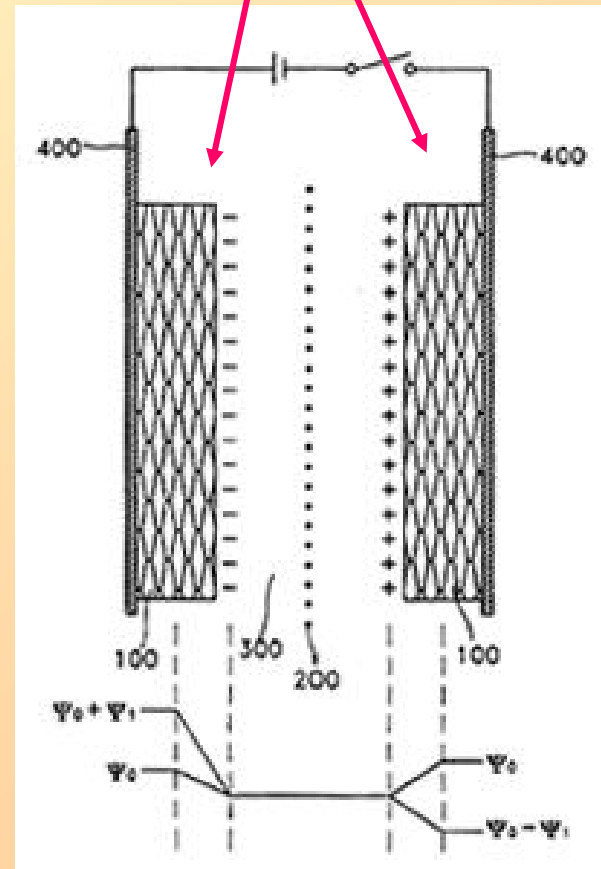
## Advantages

- relatively unlimited cycle life
- rapid charging time

## Limitations

- energy density
- high self-discharge

C electrodes



# Catalyst supports: one example

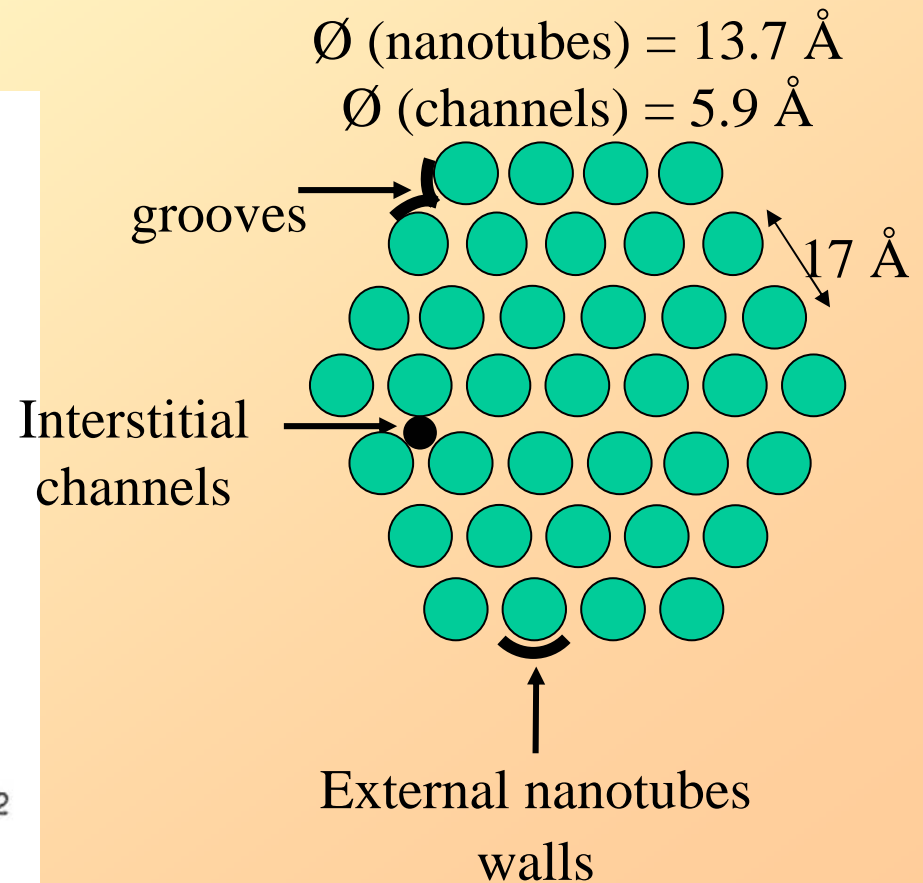
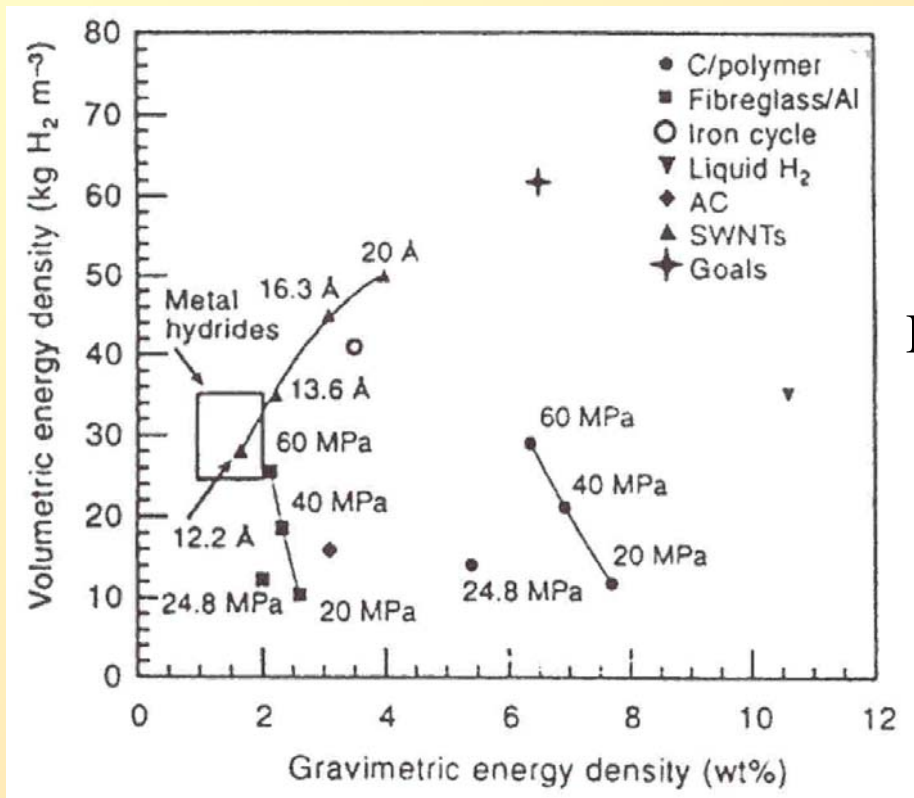
## Succession of steps

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  $\text{MoCl}_5$  then reduction by  $\text{H}_2$
7. Carburisation using  $\text{CH}_4 \rightarrow \text{Mo}_2\text{C}$  5 nm nanoparticles

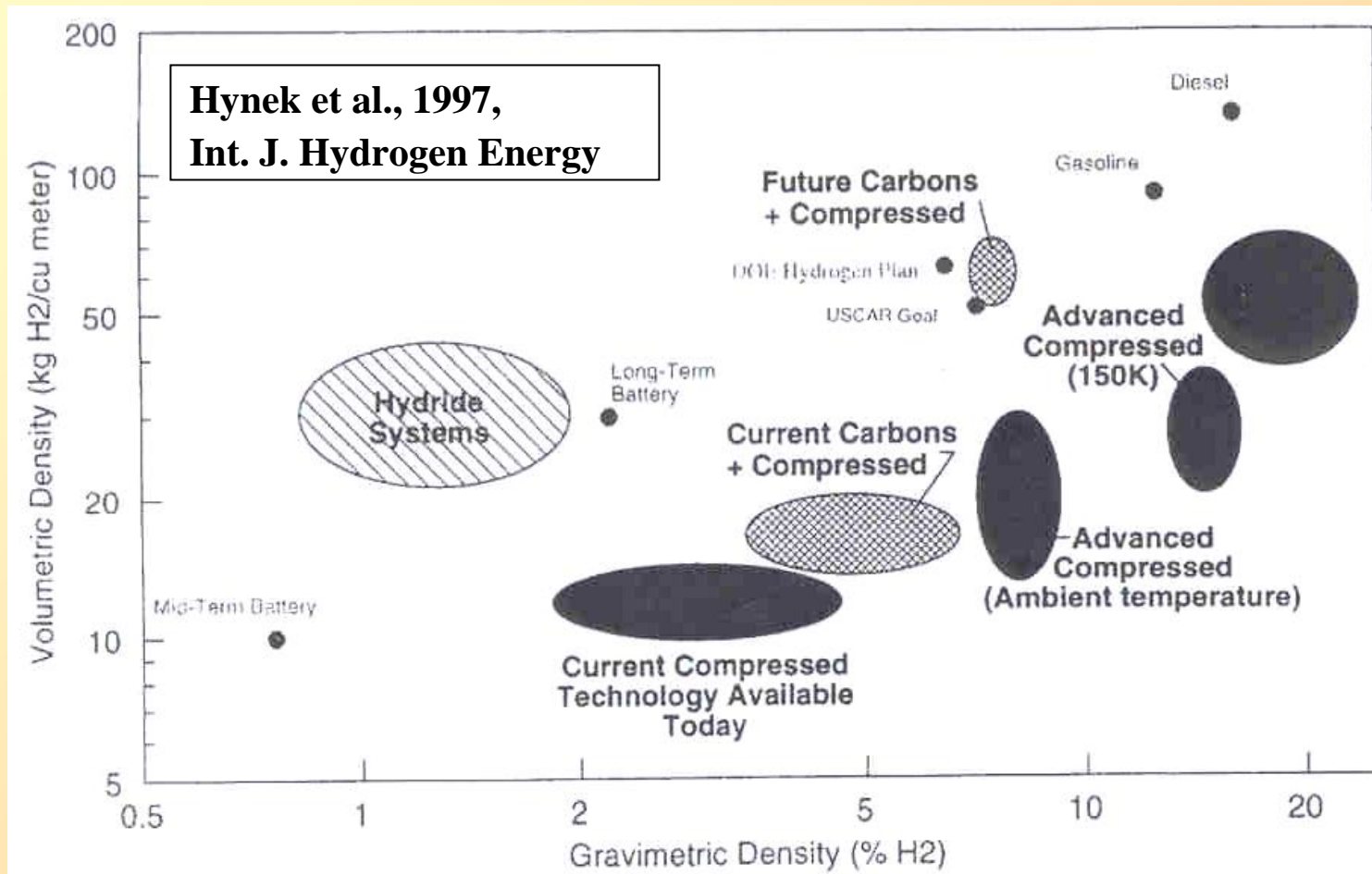
$\text{MoCl}_5$  is an interesting precursor for obtaining hexagonal  $\text{Mo}_2\text{C}$  nanoparticles (diameter < 5 nm)

# Gas storage: CNTs, ...

**Target : 6.5 mass density and 62 kg H<sub>2</sub>/m<sup>3</sup>**

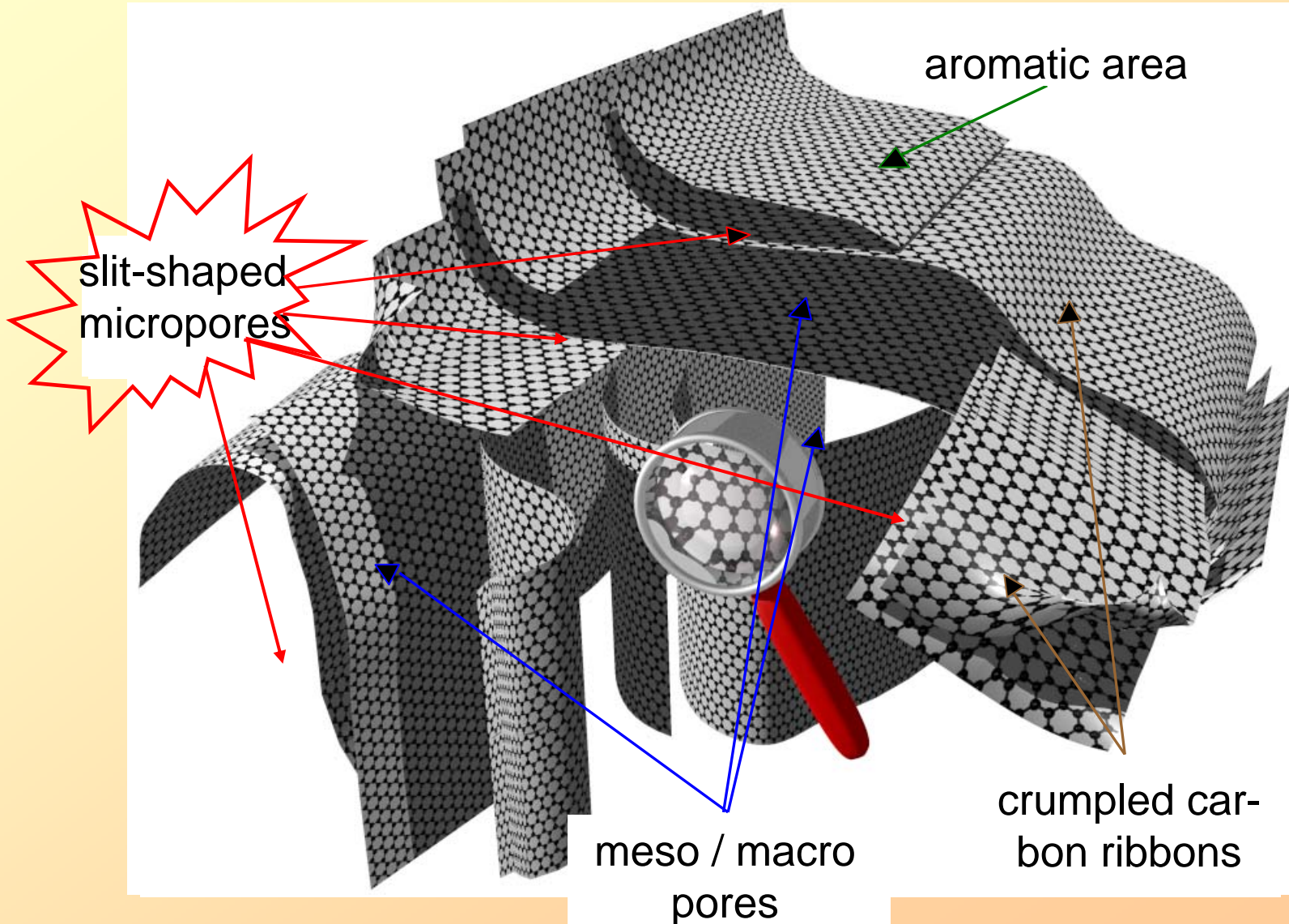


# And the future for hydrogen storage ... ?



# CH<sub>4</sub> storage: why may active carbons be better ?

- Structure of active carbons



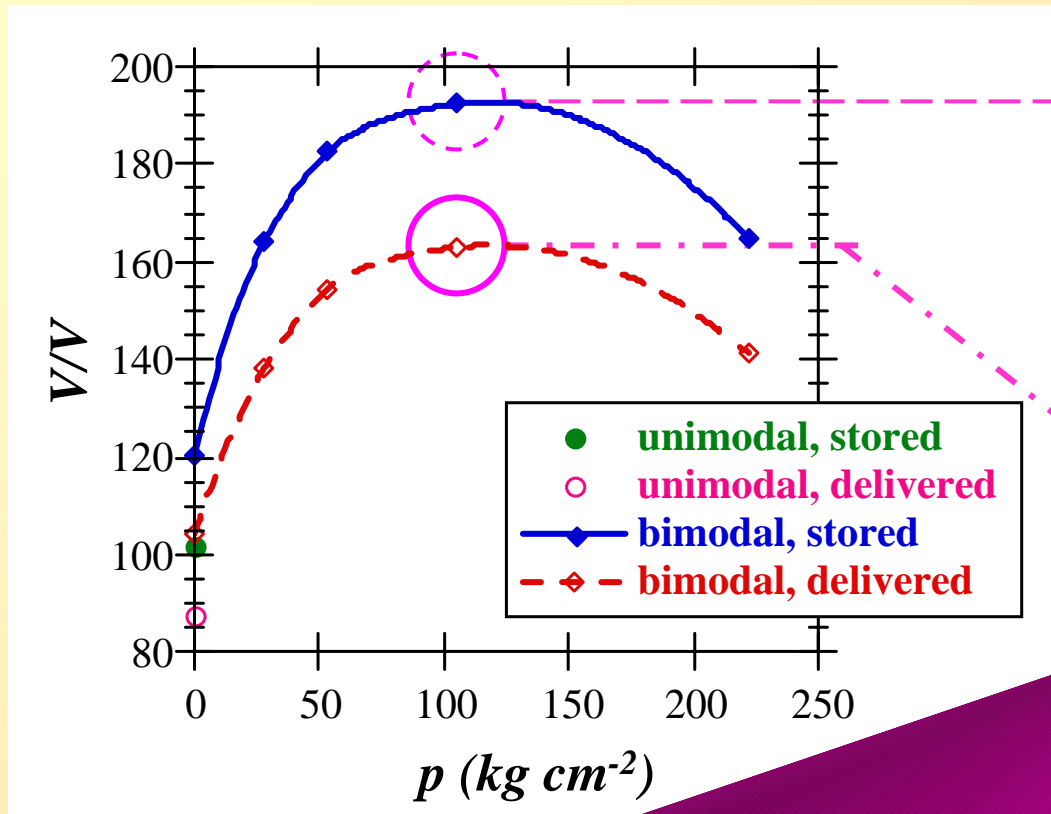
# Methane storage on active carbons

## Irreplaceable properties of active carbons

- slit-shaped micropores  $\Rightarrow$  *more uptake than any other geometry*
- hydrophobic surface  $\Rightarrow$  *low (competitive) adsorption of water*
- higher thermal conductivity than ceramics  $\Rightarrow$  *better heat transfer*
- highest surface areas (up to 3000 m<sup>2</sup> g<sup>-1</sup>)
- highest micropore volumes (above 1 cm<sup>3</sup> g<sup>-1</sup>)
- pore structure may be tailored

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



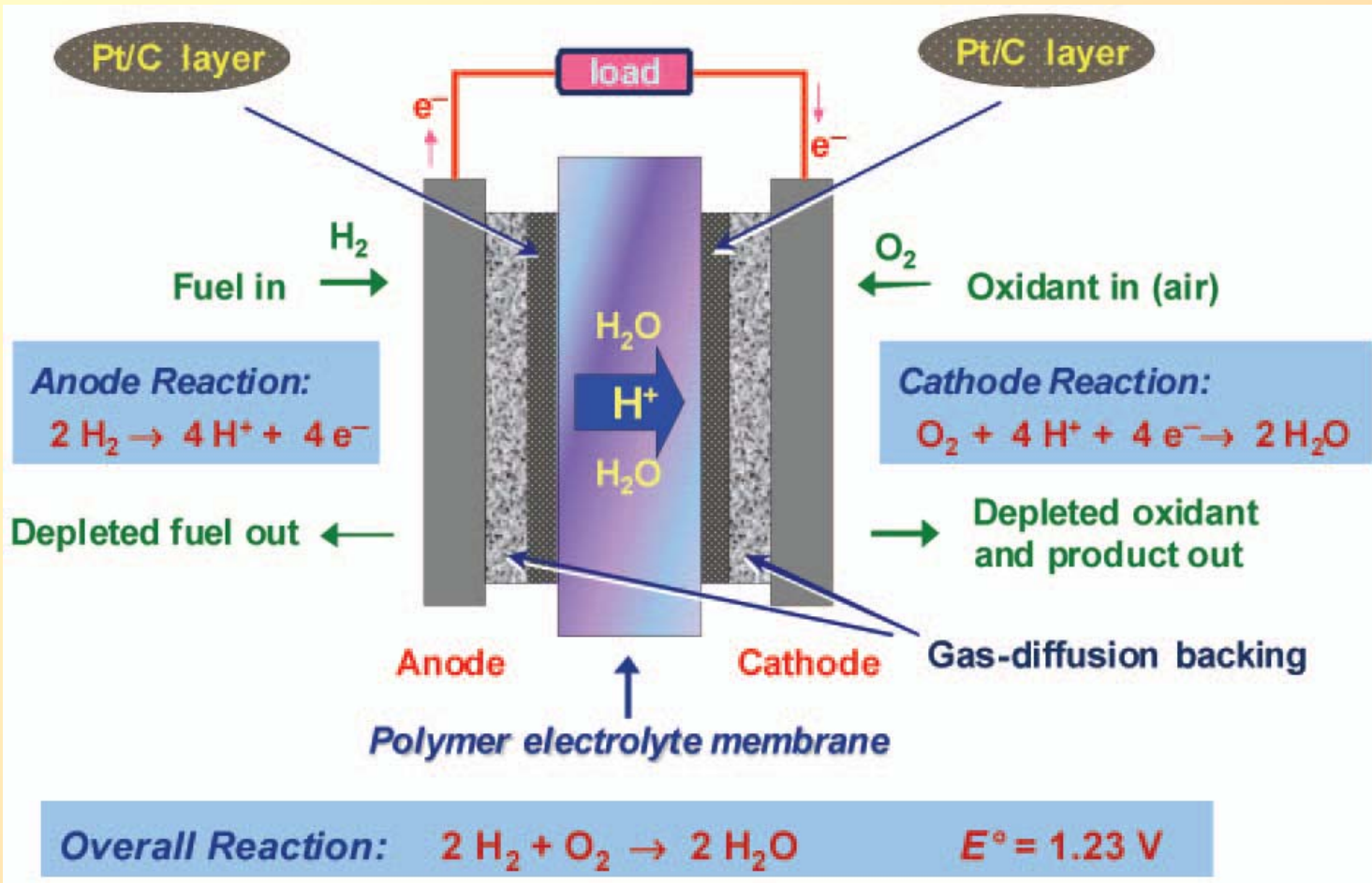


193 V/V  
stored !

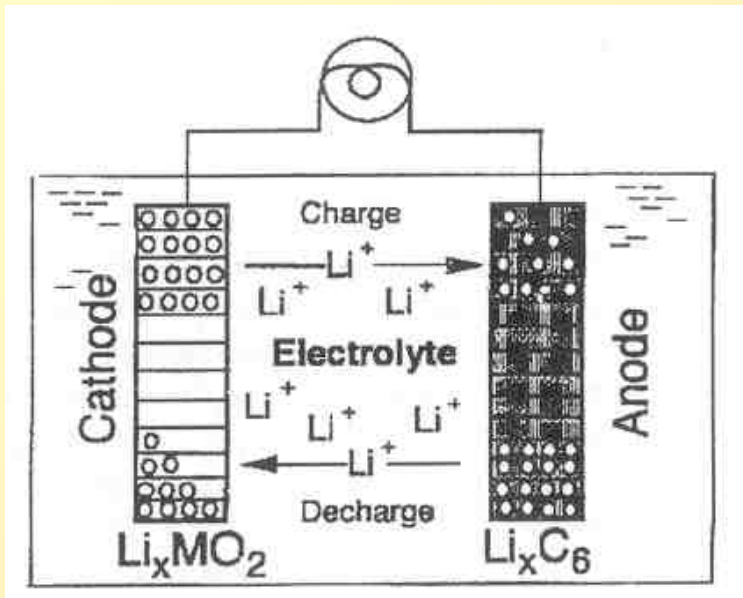
163 V/V  
delivered !!!

**Target value of  
150 V/V delivered  
now exceeded**

# Fuel cell electrodes



# Lithium ion batteries



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

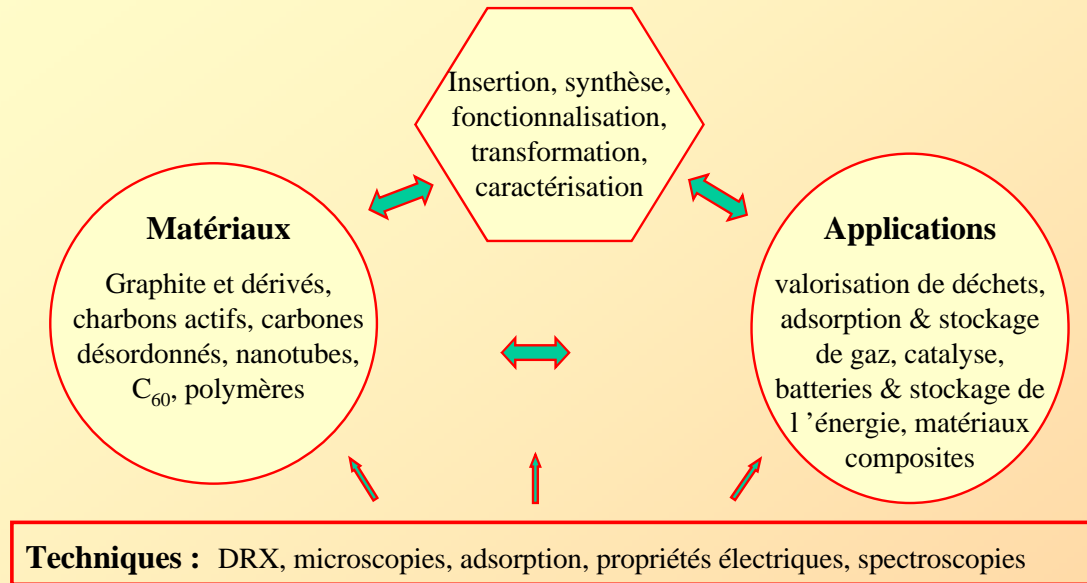
Still required improvements :

- 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

### Nanotubes :

Adsorption, microscopy, fonctionnalisation, composites

### Li ion Batteries

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

### Énergie & environnement :

gas storage, supercapacitors,, purification adsorbents

### Intercalation:

Huge range of donor and acceptor compounds

# 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

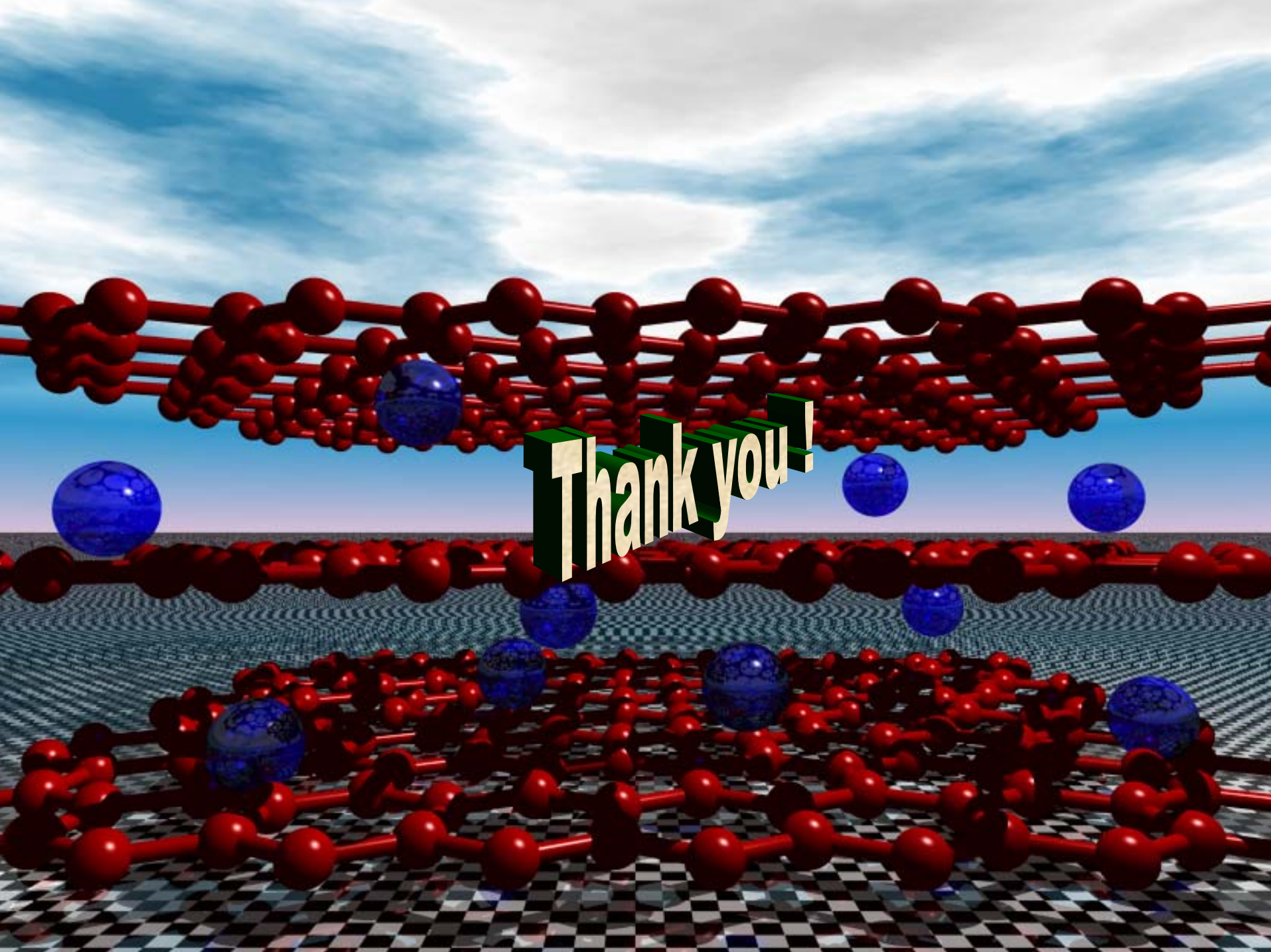
A need to examine the energy expended in the processing techniques before evaluating overall energy benefits !

# Thanks to my LCSM colleagues

- A. Celzard
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  - J.-F. Marêché

...and the numerous PhD students

And the many GFEC, GFECI and GDRE colleagues



Thank you!