Nanostructured Carbon: What Roles in Energy Storage?

Edward McRae, LCSM UHP-Nancy, France

- 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.

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

**Nanotubes:**
Iijima, 1991, NEC Corp., Japan

**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

<table>
<thead>
<tr>
<th></th>
<th>Dimensionnalité</th>
<th>Coordination</th>
<th>Caractère électronique</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diamant</strong></td>
<td>3D</td>
<td>sp(^3)</td>
<td>Isolant, (E_{gap} &gt; 5) V</td>
</tr>
<tr>
<td><strong>Graphite</strong></td>
<td>3D anisotrope ou quasi-2D</td>
<td>sp(^2)</td>
<td>Semi-métal</td>
</tr>
<tr>
<td><strong>Graphène</strong></td>
<td>2D</td>
<td>sp(^2)</td>
<td>Semi-conducteur, (E_{gap} = 0) V</td>
</tr>
<tr>
<td><strong>Nanotube monoparoi</strong></td>
<td>1D</td>
<td>Sp(^2) + sp(^3)</td>
<td>Semi-conducteur ou métallique isolant</td>
</tr>
<tr>
<td><strong>Fullerite, (C)(_{60})</strong></td>
<td>0D</td>
<td></td>
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# 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 (H₂, CH₄, …)
- 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 reduction by H$_2$
7. Carburisation using CH$_4$ $\rightarrow$ Mo$_2$C 5 nm nanoparticles

MoCl$_5$ is an interesting precursor for obtaining hexagonal Mo$_2$C nanoparticles (diameter < 5 nm)
Gas storage: CNTs, ...

**Target**: 6.5 mass density and 62 kg H$_2$/m$^3$

- Ø (nanotubes) = 13.7 Å
- Ø (channels) = 5.9 Å

Diagram:
- Grooves
- Interstitial channels
- External nanotubes walls
And the future for hydrogen storage...?
CH$_4$ storage: why may active carbons be better?

- **Structure of active carbons**

  - slit-shaped micropores
  - aromatic area
  - meso / macro pores
  - crumpled carbon ribbons
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*

Carbon atoms

- **ultramicropores** $\Leftrightarrow w < 0.7 \text{ nm}$
- **supermicropores** $\Leftrightarrow 0.7 < w < 2 \text{ nm}$
- **mesopores** $\Leftrightarrow 2 < w < 50 \text{ nm}$

Those responsible for the **DELIVERABLE methane capacity**

Those responsible for the **UNDELIVERABLE methane capacity**

Those **USELESS** for methane storage
Target value of 150 V/V delivered now exceeded

(Celzard, Albinia, Jasienko-Halat, Marèché, Furdin, 2005, Carbon, in press)
Fuel cell electrodes

Anode Reaction: \(2 \text{H}_2 \rightarrow 4 \text{H}^+ + 4 \text{e}^-\)

Cathode Reaction: \(\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}\)

Overall Reaction: \(2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}\) \(E^\circ = 1.23 \text{ V}\)
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

Materials:
Graphite and derivatives, active carbons, disordered carbons, nanotubes, C₆₀, polymers

Insertion, synthesis, functionalization, transformation, characterization

Applications:
Valorization of waste, adsorption & storage of gas, catalysis, batteries & storage of energy, materials composites

Techniques: DRX, microscopies, adsorption, electrical properties, spectroscopies

Orientations 2005 – 2008:

Fundamental

- 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

Applied

- Energy & environment: gas storage, supercapacitors, purification adsorbents

Graphite and derivatives, active carbons, disordered carbons, nanotubes, C₆₀, polymers
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!