Pitch-Based Carbon Materials

Conchi Ania

Instituto Nacional del Carbón, CSIC.
Oviedo, Spain

ITA Annual Conference, Palma de Mallorca, June 2007
• Introduction
• Carbon/Carbon composites
• Carbon fibres and synthetic graphites
• Materials for energetic applications
• Concluding remarks
Carbon materials. Applications

Genesis, 6, 14:
“Make for yourself an ark of gopher wood; you shall make the ark with rooms, and shall cover it inside and out with pitch”

Painting (charcoal)

Gunpowder (wood based carbons)

Writing (graphite / carbon black)

Composites C/C

Anodes in batteries

Fission /Fussion reactor

Prosthesis and implants
Carbon materials. Applications

- Aluminum production (anodes)
- Electric arc furnace (graphite electrodes)
- Refractories (ladles)

High-tech applications

- Aeronautic industry
- Aerospace industry
- Competition

Saturn V Rocket – Johnson Space Center
HIGH TEMPERATURE MATERIALS!

CARBON MATERIALS

STRUCTURAL PROPERTIES
• Graphite-like microstructure

MECHANICAL PROPERTIES
• High resistance

ELECTRICAL PROPERTIES
• Excellent conductivity

CHEMICAL PROPERTIES
• Inertness (except oxygen)

THERMAL PROPERTIES
• Superb thermal conductivity
  • Low CTE
  • Temperature tolerance

High Temperature Materials!
# Carbon precursors and materials

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Intermediate</th>
<th>Final product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaseous hydrocarbons</td>
<td>Carbon black, VGCF, pyrolytic carbon, fullerenes</td>
<td></td>
</tr>
<tr>
<td>Petroleum</td>
<td>Petroleum pitch</td>
<td>Needle coke, carbon fibers, Mesophase microspheres, carbon fibers, foams</td>
</tr>
<tr>
<td>Mesophase pitch</td>
<td>Mesophase microspheres, carbon fibers, foams</td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>Coal- tar pitch CTP</td>
<td>Needle coke, carbon fibers</td>
</tr>
<tr>
<td>Coal</td>
<td>Charcoal</td>
<td>Activated carbons</td>
</tr>
<tr>
<td>Biomass</td>
<td>PAN</td>
<td>Carbon fibers</td>
</tr>
<tr>
<td>Polymers and prepolymer</td>
<td>Resins</td>
<td>Vitreous (glassy) carbon</td>
</tr>
<tr>
<td></td>
<td>Polyimides</td>
<td>Monoliths, graphite films</td>
</tr>
</tbody>
</table>
Carbon precursors and materials: gas phase

Carbon: 1s², 2s², 2p²
Flexible coordination chemistry (sp, sp², sp³), allowing infinite 3D architectures

- Synthetic diamond
- Pyrolytic carbon
- Hydrocarbon
- Graphite

Carbon black, SWNT, Nanotubes

Electric discharge, Laser, He ions

VGCF, Carbon films
Carbon precursors and materials: liquid-solid phase

Pitch
Polymers
Biomass
Coal

Organic precursor

Graphitizable (Anisotropic)

Mesophase

Non graphitizable (Isotropic)

Activated carbons

Vitreous carbons

Fibers

Cokes

Foams

graphites

Diamonds

Fibers

Vitreous carbons
Carbon precursors

Pitch: A carbon rich source

Pitch

Mesophase

Mesophase pitch

Carbon material
• Introduction
• Carbon/Carbon composites
• Carbon fibres and synthetic graphites
• Materials for energetic applications
• Concluding remarks
C/C composites

C/C Composites Advantages

- High temperature materials
- Thermally stable solids
- High resistance to thermal shock due to their thermal conductivity and low thermal expansion
- Retain and even improve their mechanical properties at high temperature
- Chemical inertness
- Low weight
- Optimum fatigue resistance
- Corrosion resistance
- Biocompatibility

C/C Disadvantages

- Sensitive to high temperature oxidation
- Price

High temperature materials

- Titanium 35% - Fibres SiC (0°)
- 35% B₄C (particles) - Ti
- 35% B₄C (particles) - Ni
- Carbon - Carbon
- Carbon - CSi
- Columbium (Nb) C129Y
- Titanium
- Ni
- SiC - SiC

Temperature (°C)

UTS/Density × 10⁶ (mm)
Carbon fibres. Variety of architectures

Preform

3-D

2-D

1-D

2-D
**Matrix precursors**

Matrix precursor

- High carbon yield
  - Process efficiency
- Adequate viscosity
  - Effective impregnation
- Affinity to the fibre surface
  - Fibre/matrix adhesion
- Low volume variation on carbonization
  - Material damage

**Pitch vs. Resin Advantages**

- Higher carbon yield
- Graphitizability
- Development of open porosity on carbonization
- Wide variety of structures and properties
- Price

- **Resins**
  - Thermosetting
  - Thermoplastic

- **Pitches**
  - Coal-tar pitch
  - Petroleum pitch
  - Synthetic pitch
Composite preparation

CARBON FIBRE → IMPREGNATION → CARBONIZATION → DENSIFICATION → IMPREGNATION → PITCH → CARBONIZATION → GRAPHITIZATION → C/C COMPOSITE

MATRIX PRECURSOR

Wet-winding

Pultrusion

Injection

Hot-press moulding

1D-PREPREG

1D-PREPREG

nD-PREPREG

2D-PREPREG
Composites. The effect of the precursor

CC-B-CTP

CC-I-CTP

CC-LP

CC-PP

BINDER CTP (BP)

PETROLEUM PITCH (PP)

LIQUEFACTION PITCH (LP)

14 μm
Composites. Pitch densification

n-cycles

UNDENSIFIED C/C COMPOSITE

PITCH LIQUID IMPREGNATION

CARBONIZATION

DENSIFIED C/C COMPOSITE

Impregnating CTP
Modification of the matrix precursor. Pitch thermal treatment

**Impregnating CTP**

- Slight increase in granular microstructures
- Decrease in porosity
- Virtual elimination of microcracks
- Improvement in mechanical properties

**CC-ORIGINAL**
- Density: 1.50 g cm\(^{-3}\)
- Porosity: 16 vol %
- ILSS: 15 MPa
- FS: 416 MPa

**CC-400 °C /5 h**
- Density: 1.60 g cm\(^{-3}\)
- Porosity: 12 vol %
- ILSS: 39 MPa
- FS: 487 MPa

**CC-400 °C /7 h**
- Density: 1.65 g cm\(^{-3}\)
- Porosity: 9 vol %
- ILSS: 44 MPa
- FS: 575 MPa
Modification of the matrix precursor. Pitch oxidative treatment

**CC-I-CTP**

FS = 416 MPa

**CC-250 °C/AIR**

FS = 644 MPa

**CC-275 °C/AIR**

FS = 609 MPa

**CC-300 °C/AIR**

FS = 432 MPa

Impregnating CTP

10 µm
Granular composites

Pitch-based conventional brakes

Friction coefficient vs. time for different types of composites:
- GR
- AT
- ATGR
- Brake B
Pitch infiltration in carbon preforms

**Matrix precursor**
- Fluid
- High carbon yield

**Problems**
- Homogeneity
- Bloating on carbonization

**Anthracene oil-based pitches (mesophase)**
• Introduction
• Carbon/Carbon composites
• Carbon fibres and synthetic graphites
• Materials for energetic applications
• Concluding remarks
Carbon Fibres from pitches

- Isotropic fiber precursor
  - Spinning
  - Green fiber (isotropic)
  - Stabilization
  - Stabilized fiber (isotropic)
  - Carbonization
  - General Purposes Carbon Fiber (GPCF)

- Anisotropic fiber precursor
  - Spinning
  - Green fiber (anisotropic)
  - Stabilization
  - Stabilized fiber (anisotropic)
  - Carbonization
  - Carbonized fiber (anisotropic)
  - Grafitization
  - High Performance Carbon Fiber (HPCF)
Carbon Fibres from pitches - II

CTP (Impregnating) → Thermal Treatment → TREATED CTP

Filtration → MESOPHASE → ISOTROPIC PHASE → ISOTROPIC FIBRE

Limitation factor: QI particles

Free-QI-Pitch (PP, AOP) → Thermal Treatment → TREATED PITCH

Sedimentation → MESOPHASE → GRAPHITIC FIBRE
Isotropic carbon fibres

Ø = 35 \, \mu m
TS = 143 \, MPa
E = 28.9 \, GPa

Ø = 16 \, \mu m
TS = 414 \, MPa
E = 36.6 \, GPa
Graphitic carbon fibres

Partially graphitic carbon fibers
Synthetic polygranular graphites

CTP (Impregnating)
  | Thermal Treatment
  | TREATED CTP
  | Filtration
  | ISOTROPIC PHASE
  | MESOPHASE

Free-QI-Pitch (PP, AOP)
  | Thermal Treatment
  | TREATED PITCH
  | Sedimentation
  | MESOPHASE

Mesophase plasticity (stabilization)
Self-sintering

GRAPHITE
Synthetic polygranular graphites - II

FS ~ 100 MPa  \( \rho \sim 10 \, \mu \Omega \, \text{m} \)  \( d_{H_2O} \sim 2 \, \text{g cm}^{-3} \)
• Introduction
• Carbon/Carbon composites
• Carbon fibres and synthetic graphites
• Materials for energetic applications
• Concluding remarks
Graphite is one of the structural components of the reactors. It acts as “moderator”, protecting the fuel and maintaining fission reaction by converting fast neutrons into low energy ones, that can be absorbed for activating the $^{235}\text{U}$ isotope.

As structural material in the HTGR core, graphite has excellent properties such as low neutron absorption, minimal radiation damage, superb heat resistance and high thermal conductivity.
Materials of high thermal conductivity, low porosity, high mechanical strength and low erosion by hydrogen impact

First reactor wall

H + H → He

‘Endless’ source of energy

Nanotechnology and nanosciences, knowledge-based multifunctional materials, new production processes and devices- ‘NMP’

Integrated Project:
New Materials for Extreme Environments (EXTREMAT)

Consortium of 38 institutions from 13 countries
Methods for introducing dopants

C/C → Doped C/C

Mixture of mesophase pitch with:
- Ti(OBu)₄
- TiC nanoparticles (130 nm)

Decomposition of Ti(OBu)₄ on CF:
- Using an oxidant (H₂O₂)
- Thermal decomposition
**Energy STORAGE**

**Portable electronic devices**
**Electric vehicles**
**Alternative energy sources**

Energy production outside CO$_2$ cycle

\[ \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} \]

Energy storage and production

**Li-ion battery**

**Fuel Cells**

**Supercapacitors**

Li-ion battery diagram:

- Li$_x$C$_6$ (Graphite)
- Electrolyte
- Li$_{1-x}$MO$_2$ (Cathode)
- Li$^+$
- e$^-$

Fuel Cells diagram:

- Individual Fuel Cell
- Hydrogen
- Oxygen
- Electric Power
- Water

Supercapacitors diagram:
Supercapacitors can increase the life of a battery if they are coupled together. Supercapacitor will supply the power peaks. This will enable a significant reduction of batteries size.

### Table: Energy Storage Properties

<table>
<thead>
<tr>
<th>Device</th>
<th>Energy density (Wh/kg)</th>
<th>Power density (W/kg)</th>
<th>Cycle life</th>
<th>Discharge time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supercapacitors</td>
<td>0.5 - 15</td>
<td>$10^2 - 10^3$</td>
<td>$10^5 - 10^6$</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Batteries</td>
<td>50-250</td>
<td>150</td>
<td>1 - $10^3$</td>
<td>&gt; 1000</td>
</tr>
</tbody>
</table>

**Batteries:**
- Higher storage of energy
- Cheaper
- More developed

**Supercapacitors:**
- Higher power
- Free of maintenance
- More environmentally friendly
Energy storage: lithium ion batteries

Anode: graphitic carbon material

\[ C + x \text{ Li}^+ + x \text{ e}^- \leftrightarrow \text{Li}_x\text{C} \]

Cathode: transition metal oxide (LiMO$_2$)

\[ \text{LiMO}_2 \leftrightarrow \text{Li}_{1-x}\text{MO}_2 + x \text{ Li}^+ + x \text{ e}^- \]

\( M = \text{Mn, Co, Ni} \)

Electrolyte: LiPF$_6$ in PC

In 1991, Sony developed the first commercial Li-ion battery

The capacity to insert Li$^+$ depends on the crystalline structure

Low temperature carbons: higher irreversibility. Pre-treatments required
The addition of a dopant (Sn, Ni, Fe) improves the behaviour of the carbon materials by increasing the cyclability.
Energy storage: supercapacitors

Energy stored = \( \frac{1}{2} (CV^2) \)

Voltage = f (electrolyte)
Capacity = f (electrode material)

\[ C \sim C_{\text{double layer}} + C_{\text{pseudo-capacitance}} \]

Double Layer Capacitance: Non-Faradaic process

\[ C = \varepsilon \frac{S}{d} \]
\[ d \text{ double layer} \sim 1\text{nm} \]
\[ C_{sp} = 10-50 \mu F/cm^2 \]

Example:
\[ S_{\text{BET}} = 1000m^2/g \quad C_{\text{max}} \approx 200 F/g \]

Fast Faradaic redox process

\[ \text{Ox} + n\text{e}^- \leftrightarrow \text{Red} \]
\[ C = \frac{dq}{dV} \]
\[ q = \frac{[\text{Red}] \cdot n \cdot F}{m \cdot \text{w}.} \]
\[ C_{sp}(\text{theoretical}) = 100-400\mu F/cm^2 \]

Example:
\[ S_{\text{BET}} = 250m^2/g \quad C_{\text{max}} \approx 500-1000 F/g \]
Energy storage: supercapacitors

Activated carbon
- High surface area
- Suitable pore size (depending on the electrolyte)
- Suitable surface chemistry
- High electrical conductivity

vs

Pitch-based carbon

Pitch + Stabilization

Chemical activation
6 KOH + 2C → 2K + 3H₂ + 2K₂CO₃

Etching + Washing

Cell assembling
- Electrodes
- Separator
- Current collector

Chemical reaction:
6 KOH + 2C → 2K + 3H₂ + 2K₂CO₃
Energy storage: supercapacitors

Adequate pore size distribution

Suitable surface chemistry

Pitch-based carbon

\[ \text{Energy storage: supercapacitors} \]

\[ +2 \text{H}^+ + 2e^- \rightarrow \text{OH} \]

\[ -1 \text{e}^- \rightarrow \text{O} \]

\[ C=101 \text{ F/g} \]

\[ C=214 \text{ F/g} \]

\[ E, \text{V vs. Hg/Hg}_2\text{SO}_4 \]
Activated carbons obtained by chemical activation of mesophase pitch yield extremely high values of capacitance (~400 F/g compared to 150-200 F/g of best conventional activated carbons and ~50 F/g of carbon nanotubes).
A high electrochemical stability is found up to 10000 cycles indicating that the pseudocapacitance effect introduced by oxygen functionalities is stable with cycling.
**Energy storage: supercapacitors**

Galvanostatic Charge / discharge (200 mA/g)

Voltage : 1.2 V

**CYLEABILITY**

Energy storage: supercapacitors

*H₂SO₄ 1M*

- **1.2V**
- **0.6 V**

Stored energy:

- Y-AN- 4 Wh/kg at 0.6 V
- 15 Wh/kg at 1.2 V
- Norit- 2 Wh/Kg at 0.6 V
Concluding remarks

Multidisciplinary Research

COAL-TAR PITCH

Chemistry

Biotechnology

Friction/lubricants

Industry Al

Energy

Construction

Implants

Carbon Materials

• Immobilization of biomolecules
• Enzyme support
• Carriers in drug delivery

• Hydrogen storage
• Adsorbents
• Molecular sieves
• Catalyst support

• Sportive material
• Civil constructions
• Aeronautic
• Thermal insulators
Thank you for your attention!!!