Les Nanomatériaux Carbonés boostent le stockage d’Energie

Paolo Bondavalli
Thales Research and Technology

31 Mars 2016, NanoInnov Saclay
Mission

> THALES Research & Technologies is a portal for emerging technologies into THALES Group

> Open organisation, co-located close to or within some of the best research campus in our fields, according to the Group worldwide map of locations

- France (Palaiseau) : 350 p + 70 PhD + 80 CNRS-Universities
  - Ecole Polytechnique – Plateau de Saclay
- UK (Reading) : 130 p
  - University of Surrey
- Netherlands (Delft) : 15 p
  - Technological University of Delft - University of Twente
- Singapore : 15 p
  - Nanyang Technical University
The actors of research

THE JOINT LABS

INNOVATION PLATFORMS
Work on concrete cases of technology implementation in the products of the group.

ACADEMICS JOINT LABS
Those common labs have common personnel, common equipment and shared research agenda

INDUSTRIAL JOINT LABS
Those common labs have common personnel, common equipment and shared research agenda

DIVISIONS

ACADEMICS CNRS-Ecole Polytechnique

INDUSTRIALS ALCATEL
What’s graphene?  
What are carbon nanotubes?
Allotropic forms of Carbon (until 80s)

These different ways of rearrange themselves, change the properties of the final “macromaterials”. For example graphite is black and quite soft, inversely diamond is transparent and one of the hardest materials discovered up to now.
Diamond

Graphite

4 Bondings

3 Bondings
After 80s....
What's graphene?
The Nobel Prize in Physics 2010

1946 Theoretical Prediction (P. R. Wallace, Un. Ontario)

1961 First observation of “2D Graphite Lamellae” (Hanns-Peter Boehm, Ludwig-Maximilians-Universität in Munich)

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene"
**Figure 1** Mother of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite.
Figure 1 Mother of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionality. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite.
Fullerene: beautiful…but no real application…

It was first generated in 1985 by Harold Kroto, James R. Heath, Sean O'Brien, Robert Curl, and Richard Smalley at Rice University.

1996 Nobel Prize in Chemistry

Buckminsterfullerene C60, where 60 is the number of carbon atoms, is the most known form of the fullerene family.

Richard Buckminster Fuller
The Nobel Prize in Chemistry 1996

Robert F. Curl Jr.
Prize share: 1/3

Sir Harold W. Kroto
Prize share: 1/3

Richard E. Smalley
Prize share: 1/3

The Nobel Prize in Chemistry 1996 was awarded jointly to Robert F. Curl Jr., Sir Harold W. Kroto and Richard E. Smalley “for their discovery of fullerenes”.

[Image of three scientists]
Figure 1 Mother of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite.
1991 Carbon Nanotubes Discovery

Sumio Iijima
Senior Research Fellow, NEC Corporation

新素材の力で
日本のものづくりを
加速したい。
Carbon nanotubes properties: how to roll up graphene?

Graphene
Rolling up Graphene to Obtain Carbon Nanotubes
Carbon nanotubes properties: how to roll up graphene?
MultiWalled Carbon Nanotubes, SingleWalled Carbon Nanotubes

\[ C_h = n.a_1 + m.a_2 \]

**Saito Law:**

\[ n-m \neq 3p \text{ (} p \text{ entier)} \]
Sumio Iijima
Senior Research Fellow, NEC Corporation

新素材の力で
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加速したい。
What’s a supercapacitor?

Supercapacitor is the name done by NEC in 1971
Technically is defined Electrical Double Layer Capacitor (EDLC)

\[ C = \frac{\varepsilon}{\delta} A \]
\[ E = \frac{1}{2} CV^2 \]
\[ P = \frac{V^2}{4R} \]

Helmotz’s model

Only non faradic reactions

Two electrodes

separator
Battery-like devices

- **Supercapacitors**
  - **Double-layer Capacitors**
    - Charge storage: Electrostatically (Helmholtz Layer)
  - **Pseudocapacitors**
    - Charge storage: Electrochemically (Faradaically)
  - **Hybrid Capacitors**
    - Charge storage: Electrostatically and Electrochemically
Advantages

- Very high rates of charge and discharge
- Higher life cycle (>500000, rechargeable batteries can attain 10000)
- Good reversibility
- Low toxicity of material used
- High cycle efficiency
- Low internal resistance (Higher output power)
- Extremely low heating levels

Drawbacks

- Low amount of energy stored (3-5 Wh/Kg vs 30-40 Wh/Kg for batteries)
- It requires sophisticated control and switching equipment (from batteries to supercaps)
1957: the first patent on EDLC (Electrical Double Layer Capacitance) 
General Electric: Electrolytic capacitor with porous carbon electrodes

Two porous graphite electrodes
1966 : SOHIO (Standard Oil company, OHio)

At this time SOHIO acknowledged that “the double-layer at the interface behaves like a capacitor of relatively high specific capacity”.

1971 : NEC : first commercial device called « supercapacitor » based on technology suggested by SOHIO: Memory backup applications (low voltage, high internal resistance)
1978 : Panasonic : « gold capacitor » : back-up energy source for microprocessors and solar batteries (power failures include video recorders, DVD players, fax machines, telephones, digital still cameras, mobile phones, audio stereo systems, etc.)

1982 : Pinnacle Research Institute : « PRI ultracapacitor » (first time that the term « ultracapacitor » is used) incorporated metal-oxide electrodes

Applications : laser weaponry and missile guidance (military applications)
Some visible supercap applications

- Nuremberg
- Shangai
- Aerial lift
- London
- Forklift Truck
- Emergency issues
- Wind Turbine pitch control
- Rocket ignition
2220mAh  3.8V  8.4Wh

Normal battery for SmartPhone

To charge in 5 minutes....

You need around a supercap of ~90W

The weight of the charger is 0.5kg therefore the density of power is around 200W/Kg....

If we think that only 1/10 of the weight is the electrodes materials... We obtain around 2000W/Kg, 2KW/Kg
Activated carbon: parameters

Main parameters
- Surface (energy)
- High breakdown voltage (energy)
- Pore size (to exploit surface completely and to promote easy ion diffusion)

Activated Carbon
- Large surfaces (3000 m²/g)
- Low-cost material

The main issue:
- Very bad mesoporous distribution!!!
  2/3 of the pore size are smaller than 2 nm and so are unpercolated)
2/3 of the surface is not exploited

PORE SIZE IS NOT OPTIMIZED AND SURFACE IS NOT ADEQUATELY EXPLOITED
What are carbon nanotubes and why carbon nanotubes for Supercaps?

- Randomly entangled nanotubes for electrodes can be fabricated easily
- Highly surface specific surface area (300m²/Kg)
- High mesoporous distribution (2-5nm) and so electrolyte accessibility
- Low resistivity (they can be used as electrode and collector)
- We can fabricate electrodes without binder (higher breakdown voltage)
- Total weight is very low (enhancement energy and power density)
- High stability (long life-time)

CNTs (and Graphene related materials) based Supercapacitors

Considering that supercapacitors bridge the gap of capacitors and batteries performances we have to attain performances in this zone.
Why to use Graphene related materials and CNTs mixings?

- CNT/graphene/graphite composite

![Graphene conductivity graph]

75% the conductivity is optimized


Resistance is reduced by a factor of 4 compared to bare CNTs layers

Can we improve the Power output \( (P \propto \frac{1}{R}) \)?
Why to use Graphene related materials and CNTs mixings?

- CNTs prevent restacking (higher surface, higher energy stored)
- CNTs/graphite/graphene improve conduction (higher power delivered)
- CNTs prevent the disintegration of the composite
Our Approach

**CNTs**

**Separated weighing**

**Separated dispersion** (solvent = NMP)

**Dilution to get** $C_{\text{solide}} = 0.5\text{g/l}$
Initial sonication
- CNT : 10’ high power
- Graphite : 18h low power

Centrifugation
10 minutes x2
Final sonication of the mixture: 18h low power
Dynamic spray-gun deposition method

Deposition method

- Excellent reproducibility
- Versatile, easily scalable for large-area applications
- Extremely uniform deposition with no “coffee-ring” effect

3-axes displacement

Heating plate

Noozle

Process patented
Electrode design and cell fabrication

Supercapacitor electrode based on mixtures of graphite and carbon nanotubes deposited using a new dynamic air-brush deposition technique, P Bondavalli, JEC 160 (4) A1-A6, 2013

Air-brush deposition

Gun spraying

Masking

Several samples fabricated at the same time

Flexible electrodes

Electrode design

Supercapacitor Cell
Sample Morphology (cross section)

Supercapacitor electrode based on mixtures of graphite and carbon nanotubes deposited using a new dynamic air-brush deposition technique, P Bondavalli, JECS 160 (4) A1-A6, 2013

Excellent intercalation of graphite/graphene layers
Results: Energy and Power as a function of the concentration

Sample characteristics:
- weight = 1.8mg
- surface = 2cm² (circular design)
- thickness ~ 20μm

A - Influence of the CNT concentration (Electrodes)
- Energy max. ~4.5Wh/kg for 75wt% CNT
- Power max. ~15 kW/kg for 25wt% CNT (enhancement of 2.5)

Supercapacitor electrode based on mixtures of graphite and carbon nanotubes deposited using a new dynamic air-brush deposition technique, P Bondavalli, J ECS 160 (4) A1-A6, 2013
Advantages

- Aqueous based suspensions
- Very stable suspensions
- Low temperature process (120 C)
Oxidised CNTs can be put into water based suspensions very easily

Non-oxidised CNTs

Oxidised CNTs
New packaged prototypes
Performances for different GO concentrations

The surface allows to know the capacity of the materials to store energy

Power density

Power density:

100 % GO : 14 kW/kg
90/10 : 31 kW/kg
80/20 : 29 kW/kg
70/30 : 21 kW/kg
Graphene from IIT: Galvanostatic charge/discharge experiment

Very good stability (same capacitance that using GO)

Graphene exfoliated by IIT:

- Loss essentially during the 1000 first cycles

\[ P = 92.3 \text{ kW/kg} \]
2220mAh  3.8V  8.4Wh

Normal battery for SmartPhone

To charge in 5 minutes….

You need around a supercap of ~90W

The weight of the charger is 0.5kg therefore the density of power is around 180W/Kg….

If we think that only 1/10 of the weight is the electrodes materials…
We obtain around 1800W/Kg, 1.8kW/Kg
2220mAh  3.8V  8.4Wh

Normal battery for Smartphone

In this case, we have a density of power of 30kW/Kg for GO (100kW/Kg for graphene)....

In the same conditions (same weight) we have a supercap of 1.5kW (5kW) (compared to the previous 90W).

The meaning is that we can charge the phone in 20 seconds (GO)....

Using our material. And Using Graphene....around 7 seconds....
Conclusions and perspectives
Contracts and Objectives

GRAPHENE FLAGSHIP

> Results published in « 2D Materials » and presented at IEEE NANO 2015

![Figure 1](image_url)

**Figure 1.** (a) Dynamic spray-gun deposition set-up used for the deposition of mixtures of nanomaterial graphite collectors; (b) flexible electrode deposited on graphite collector; (c) SEM cross section of a graphite collector covered with a mixture of sprayed graphene/graphite (50%)/CNTs (50%); (d) typical electrode performance versus composite material.
Contracts and Objectives

GRAPHENE FLAGSHIP

Results published in « 2D Materials » and presented at IEEE NANO 2015 (link2)

![Diagram](image)

**Fig3:** Process to obtain stable suspensions of mixture of GO and oxidised Carbon Nanotubes (ox-CNTs).
**Graphene Oxide based electrodes**

**Advantages**
- Water based suspensions
- Low cost material
- Very stable suspensions (months, years?)
- Capacitance of 120F/g, Power density of 30kW/Kg

**Drawbacks**
- Power lower than for Graphene (factor three)

**Graphene based electrodes**

**Advantages**
- Same capacitance that GO but Larger power density demonstrated (~100kW/Kg)

**Drawbacks**
- NMP based suspensions (toxic and higher boiling temperature than water)
- Stability of the suspensions (weeks?)
Perspectives

- To scale up fabrication

- To transfer the process (Thales Research and Technology is a technology provider)

- To increase the voltage windows by using other kind of electrolytes: organic, ionic liquids...
**Fundings**

**Work Package 9: Energy**

- **Work Package Leader:** Dr. Etienne Quesnel, CEA French Alternative Energies and Atomic Energy Commission, France
- **Work Package Leader:** Dr. Vittorio Pollogrini, Italian Institute of Technology, IIT graphene lab, Italy

The FIBRALSPEC project is supported by the European Commission under the 7th Framework Programme and will run for 48 months from January 2014 to December 2017.

Project coordinator: Costas A. Charitidis
Dissemination activities
Thanks to

In the frame of the Graphene Flagship
- Francesco Bonaccorso of IIT for exfoliated Graphene
- Graphenea for GO in water
- CEA staff: Vincent Derycke, Adrian Balan

My colleague
- Gregory Pognon (Chemistry Lab) Electrochemical characterization and nanomaterial functionalisation
Thank you for your attention!!!