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Graphene based supercapacitors : results perspectives and potential industrial implementation

Paolo Bondavalli, PhD, HdR
In charge of transversal topic Nanomaterials
Thales Research and Technology

The Thales Group

Date /Référence

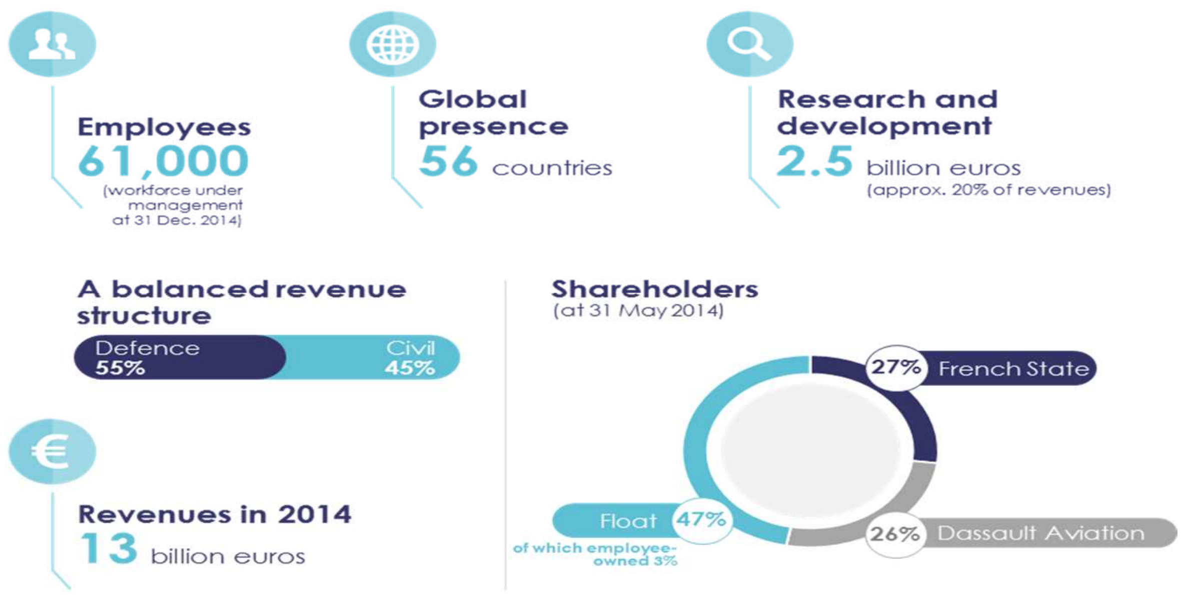
Research & Technology

Thalesgroup

Collective intelligence for a safer world

Whenever critical decisions need to be made, Thales has a role to play.
In all its markets - aeronautics, space, ground transportation, defence and security - **Thales solutions help customers to make the right decisions at the right time and act accordingly.**

World-class technology, the combined expertise of **61,000 employees** and operations in **56 countries** have made **Thales a key player in keeping the public safe and secure,** guarding vital infrastructure and protecting the national security interests of countries around the globe.



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Thales Research & Technology

An international network of research laboratories ...

Excellence
External recognition
~500 researchers ~200 PhDs

Partnerships
Common laboratories
Labs located close to / on campuses

High visibility
Strongly present within
national & European R&D networks

... strongly contributing to the overall competitiveness and attractiveness of the Group

France
Palaiseau

UK
Reading

Netherlands
Delft

Singapore

Canada
Quebec

A global player

Global reach, local expertise

68,000 employees in 50 countries

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THALES RESEARCH &TECHNOLOGY France (Palaiseau)


THALES
Thales R&T
Reading


Thales R&T
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Thales R&T
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ONERA
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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

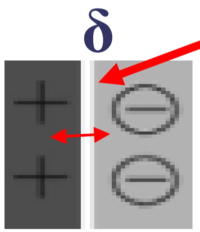
THE JOINT LABS

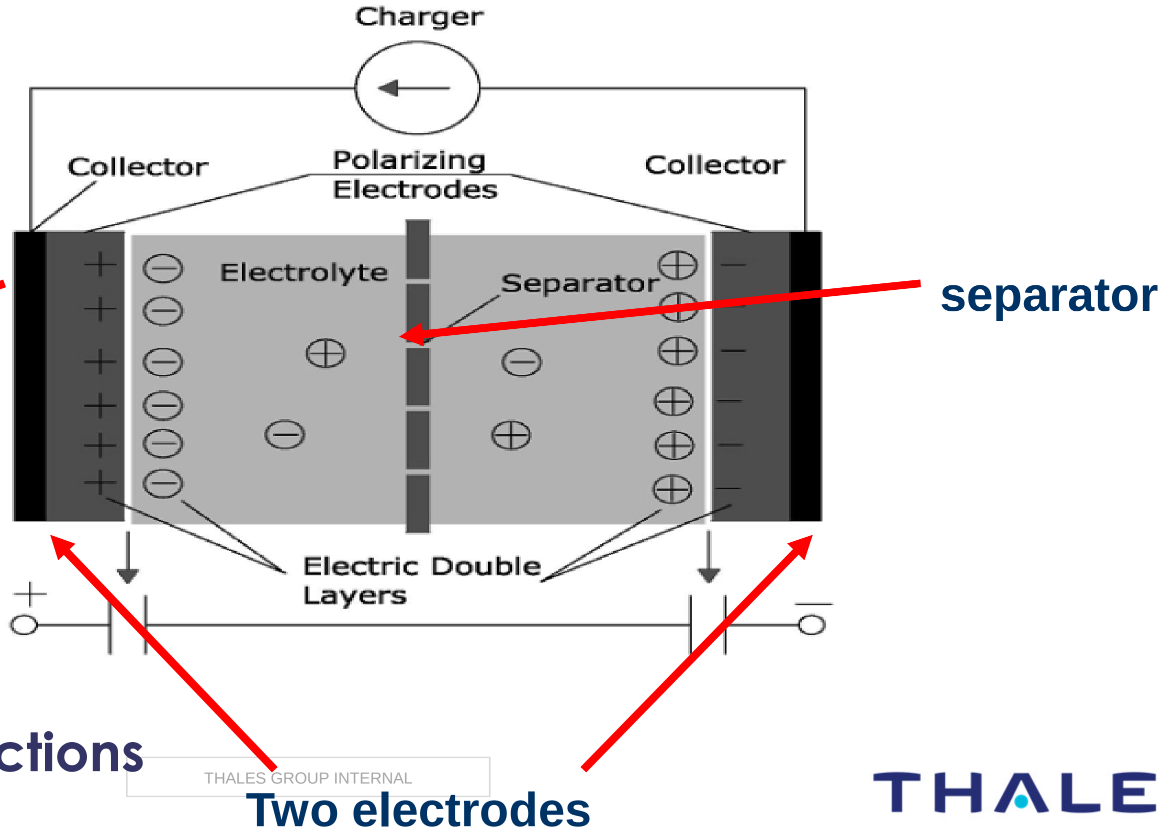
TRT	**INNOVATION PLATFORMS** Work on concrete cases of technology implementation in the products of the group.	DIVISIONS
TRT	**ACADEMICS JOINT LABS** Those common labs have common personnel, common equipment and shared research agenda	ACADEMICS CNRS-Ecole Polytechnique…
TRT	**INDUSTRIAL JOINT LABS** Those common labs have common personnel, common equipment and shared research agenda	INDUSTRIALS ALCATEL

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

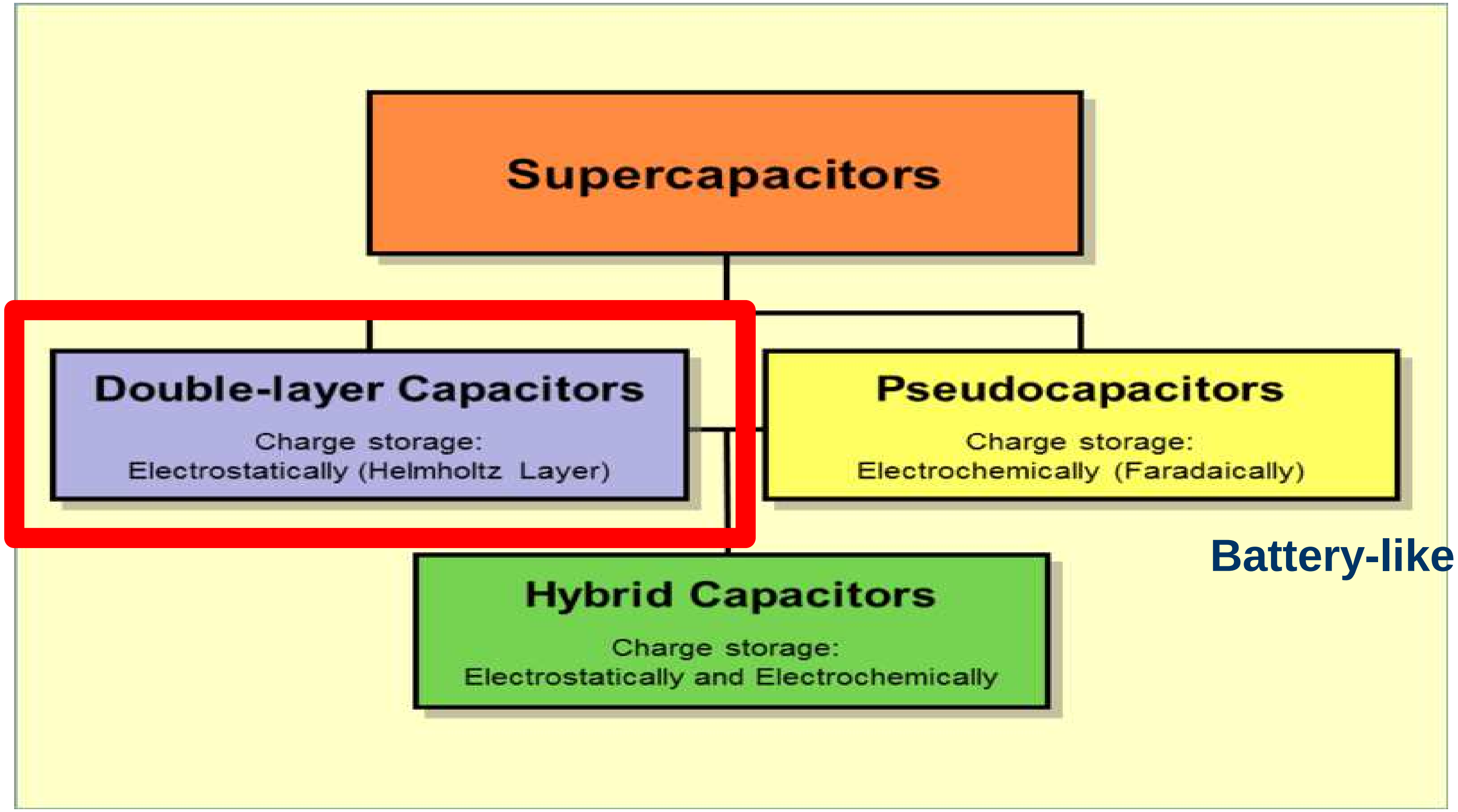
$$C=(\varepsilon/\delta)A$$
$$E=(1/2)CV^2$$
$$P=V^2/(4R)$$

Helmotz's model





Only non faradic reactions



Battery-like devices

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)

Some visible supercap applications

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 ($3000 m^2/g$)
- Low-cost material

Non-faradic carbon nanotubes based supercapacitors : state of the art, **P.Bondavalli,** et al. , Eur. Phys. J. Appl. Phys. 60,10401, 2012

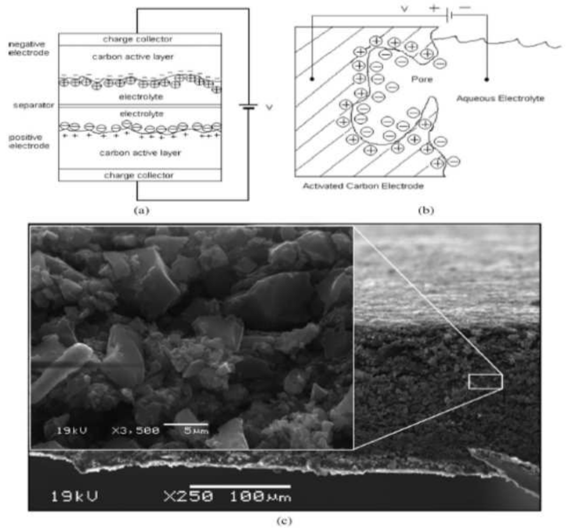
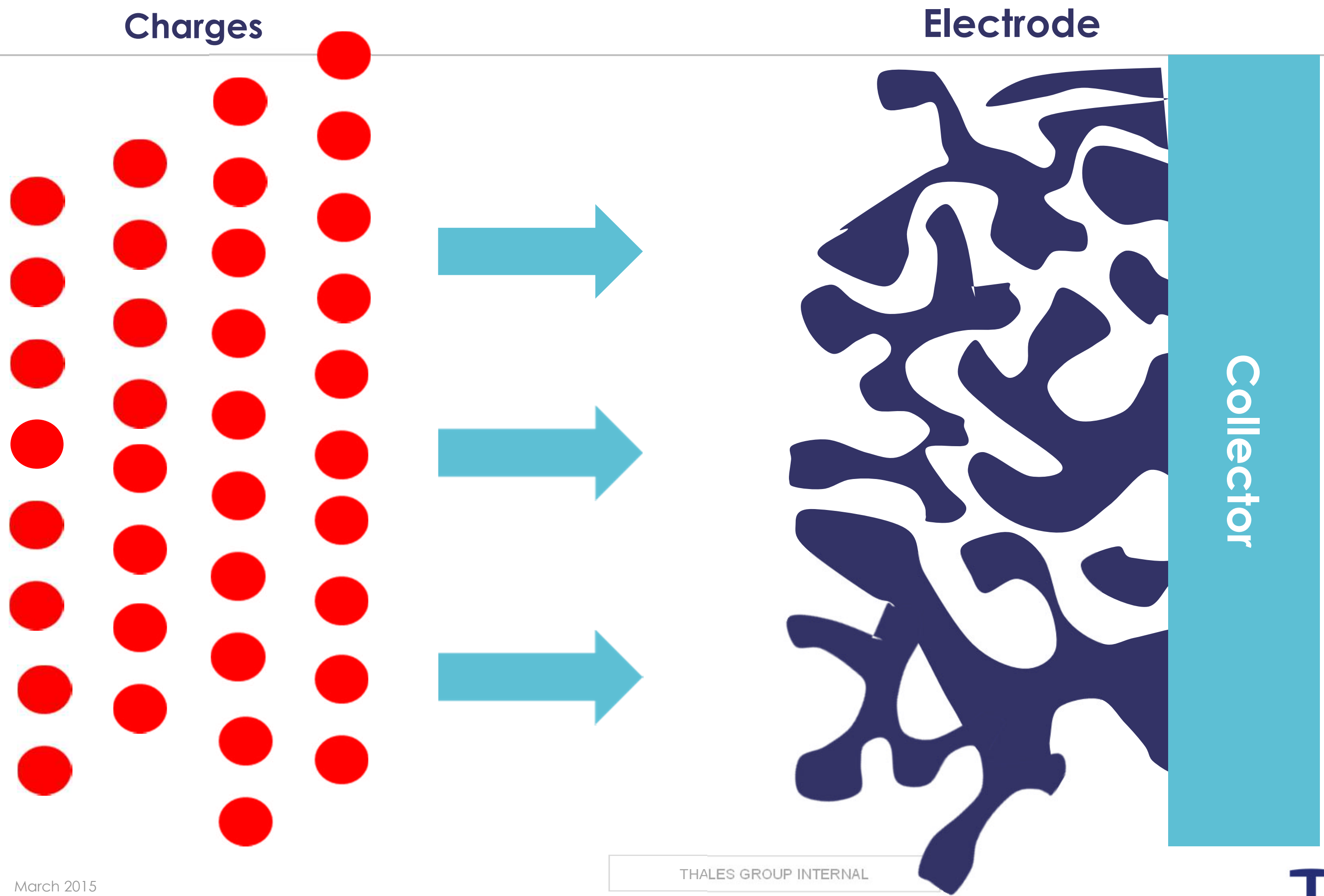


Fig. 1. (a) Schematic of an activated carbon-based EDLC. (b) Representation of pore in carbon electrode active layer. (c) Electron micrograph of activated carbon electrode.

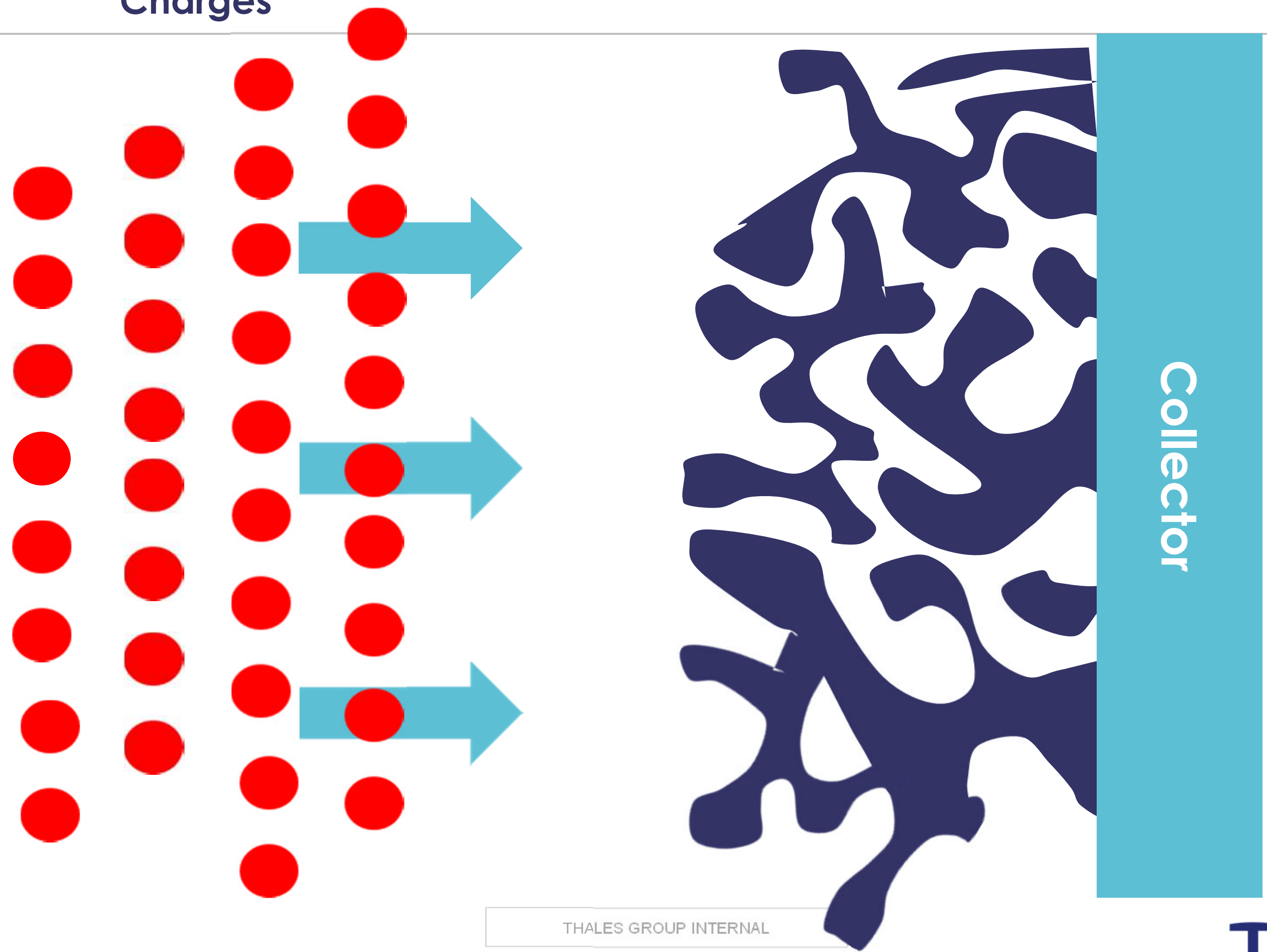
The main issue :

- **Very bad mesoporous distribution!!!**

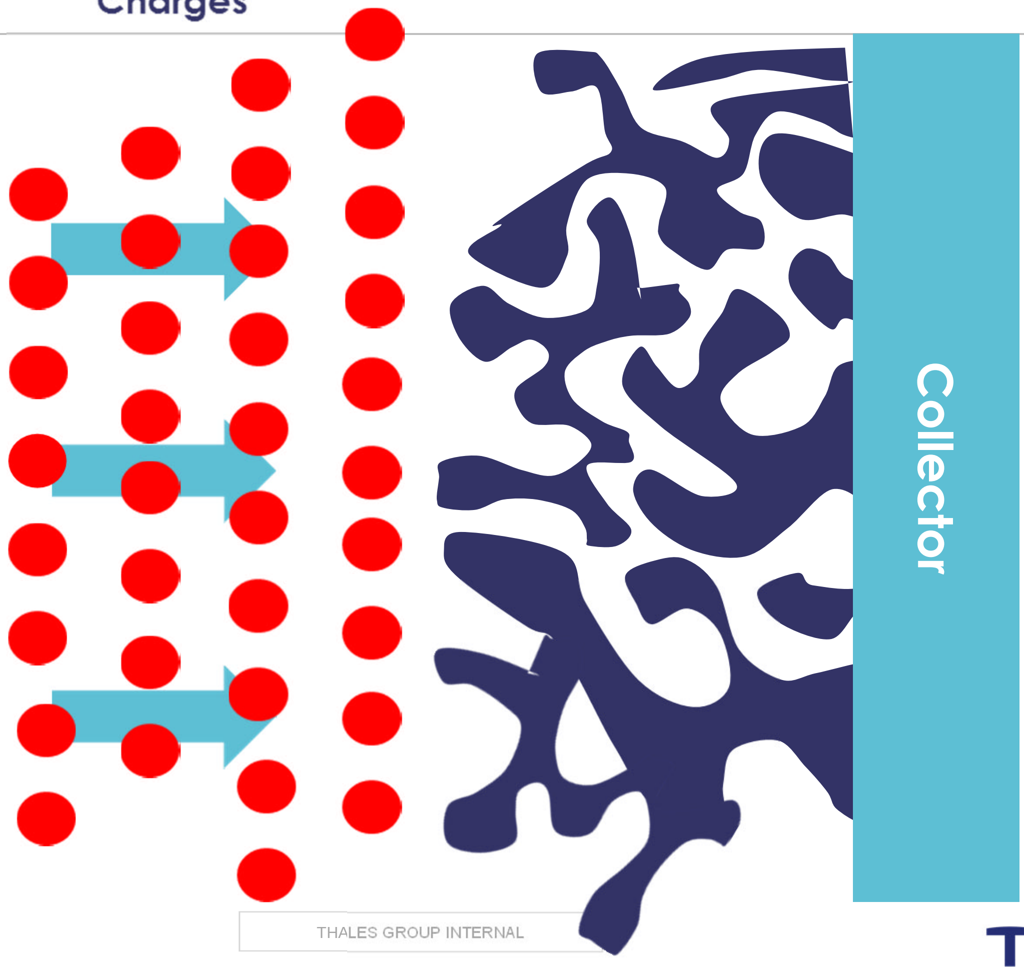
2/3 of the pore size are smaller than 2 nm and so are unpercolated)


Charges
Electrode
Collector

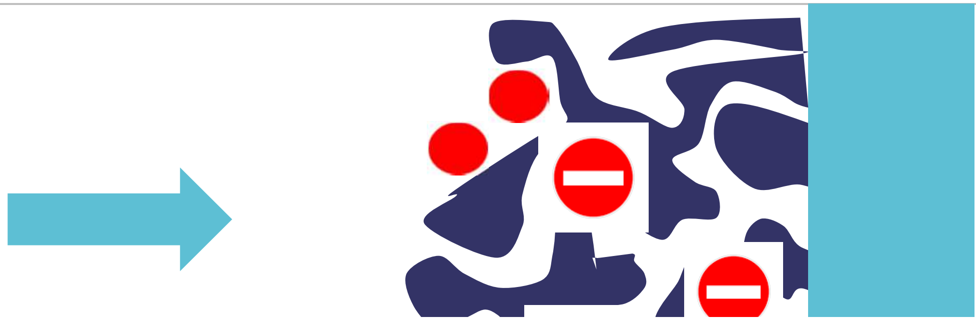
Charges



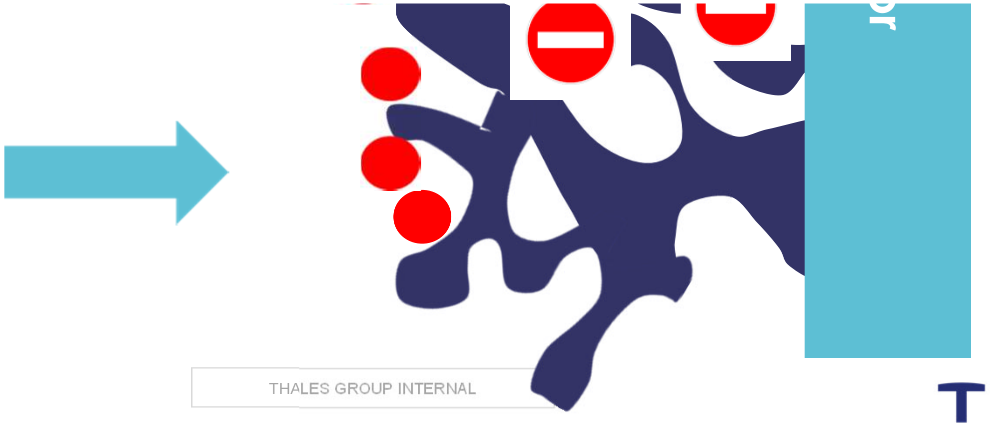
Charges



2/3 of the surface is not exploited

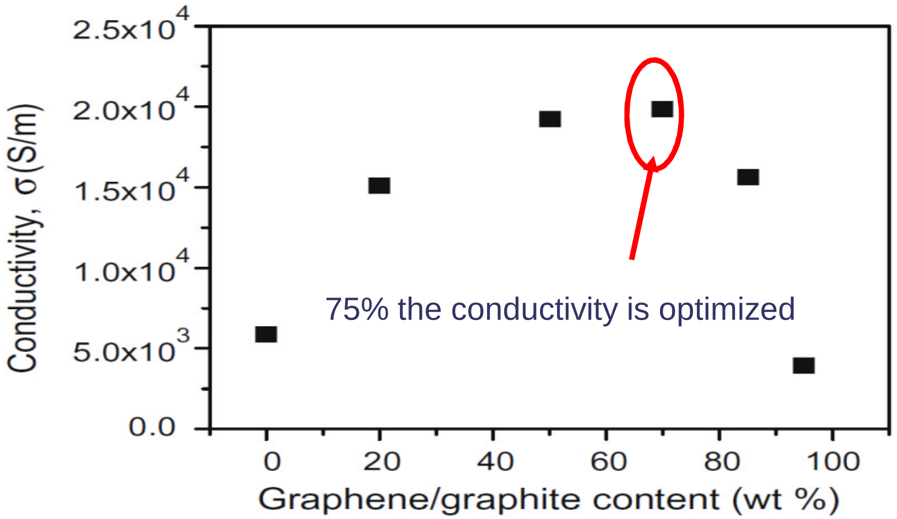


PORE SIZE IS NOT OPTIMIZED AND SURFACE IS NOT ADEQUATELY EXPLOITED

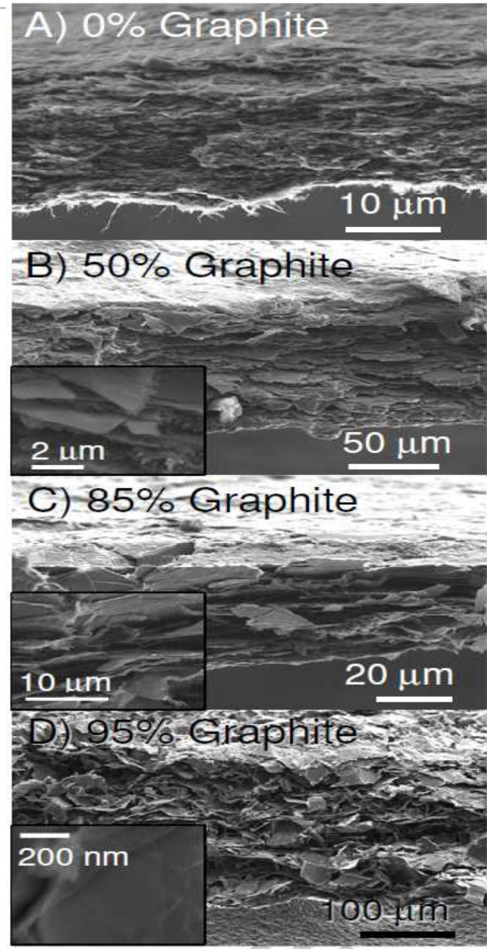


Why to use Graphene related materials and CNTs mixings?

CNT/graphene/graphite composite



U. Khan, J. N. Coleman et al Carbon (2010)



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

Can we improve the Power output (P∝ 1/R)?

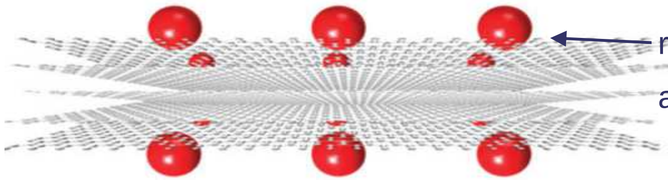
Why to use Graphene related materials and CNTs mixings?

Cite this: *Phys. Chem. Chem. Phys.*, 2011, **13**, 17615–17624
www.rsc.org/pccp

PAPER

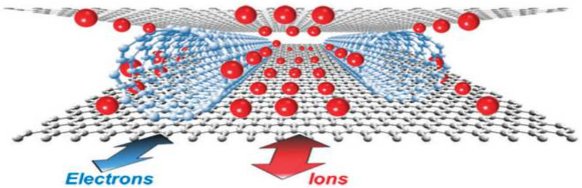
Graphene and carbon nanotube composite electrodes for supercapacitors with ultra-high energy density

Qian Cheng,[ab] Jie Tang,*[ab] Jun Ma,[a] Han Zhang,[a] Norio Shinya[a] and Lu-Chang Qin[c]



reduced charge diffusion and surface

Pristine graphene/graphite



Graphene/graphite/CNTs mixing

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

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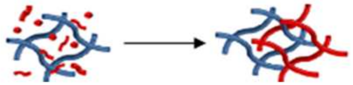
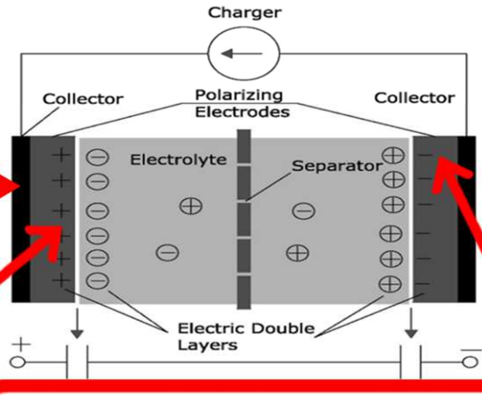
Thales approach and strategy : technological differentiators

Liquides ioniques

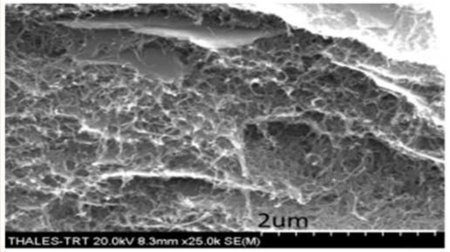
+ solvant et matrice polymère

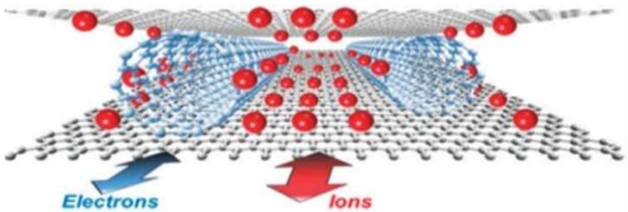


Electrolytes



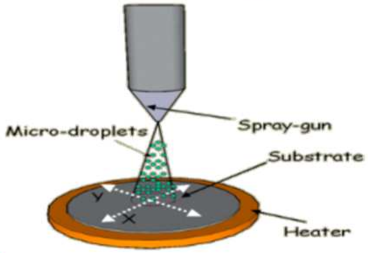
Nanostructured electrodes





Graphene/CNTs

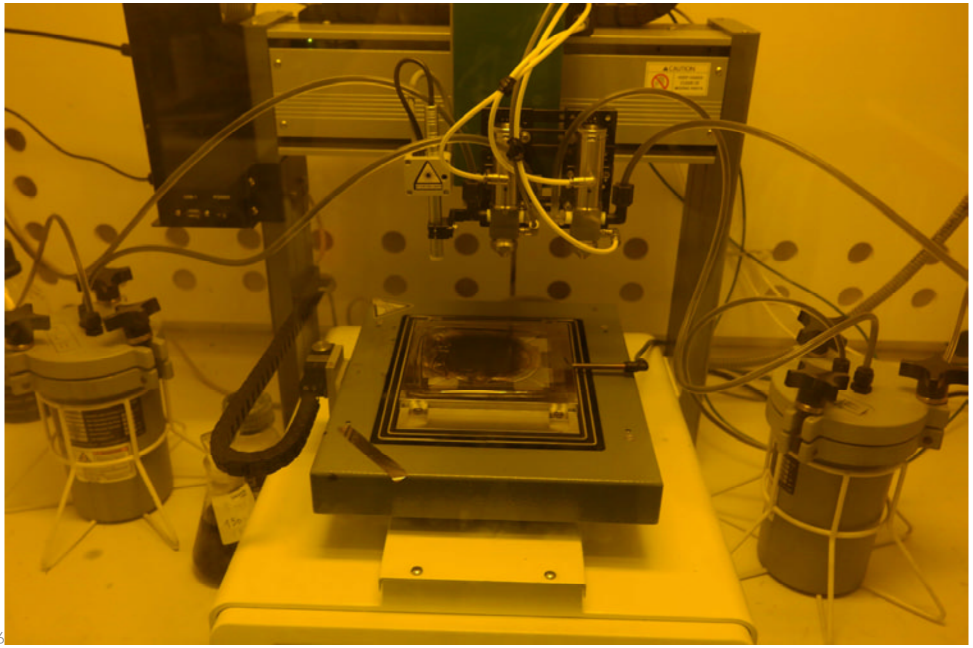
Spray-gun deposition method

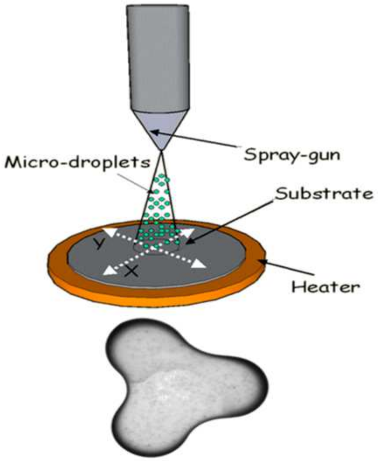


Final sonication of the mixture :
18h low power

Deposition method

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

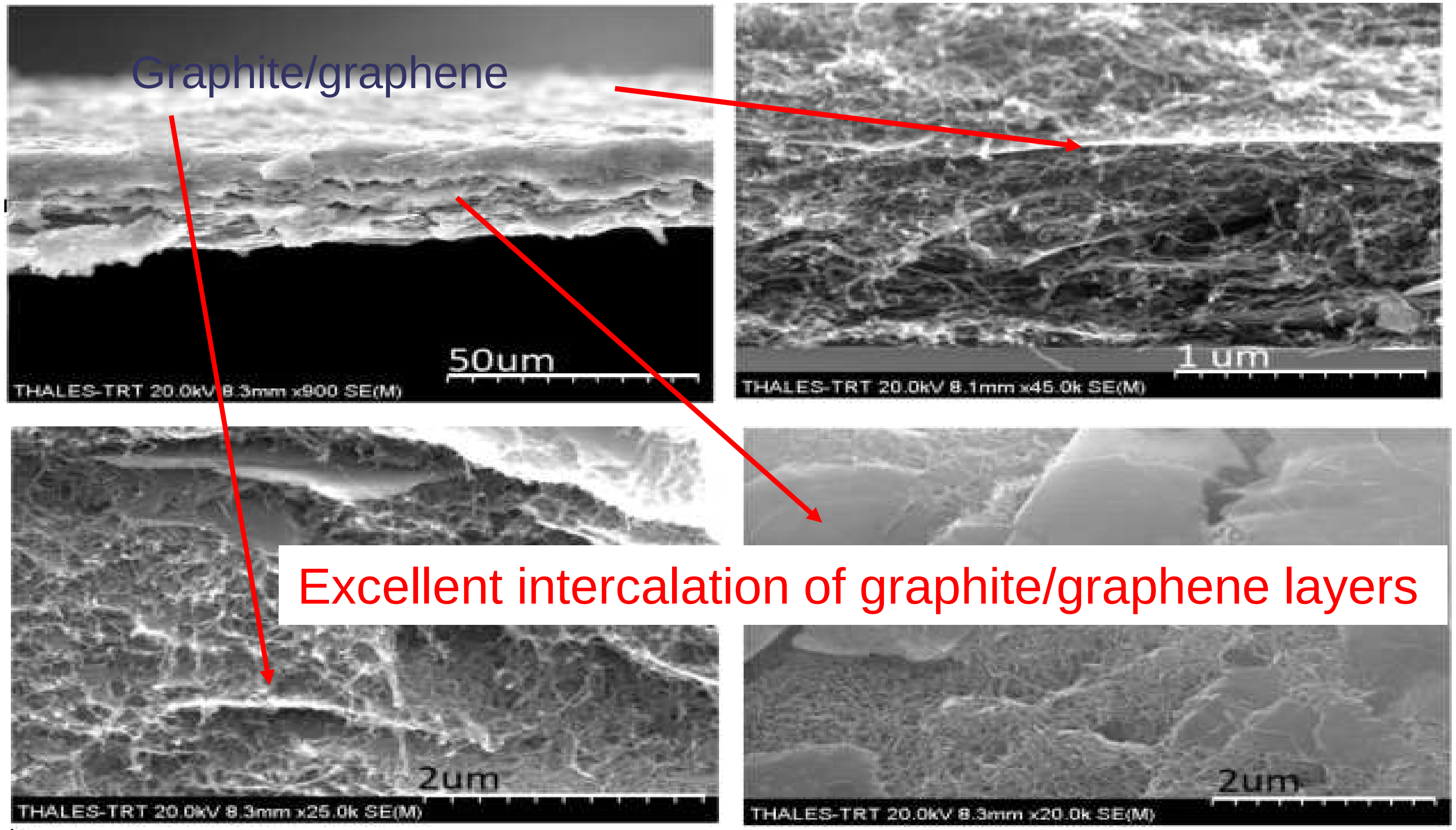




Process patented

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

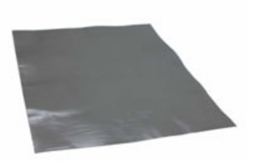


Electrode design and cell fabrication

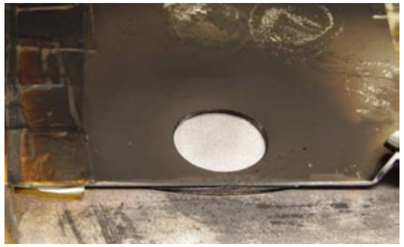
Supercapacitor electrode based on mixtures of graphite and carbon nanotubes deposited using a new dynamic air-brush deposition technique, **P Bondavalli,** JECS 160 (4) A1-A6, 2013

Air-brush deposition

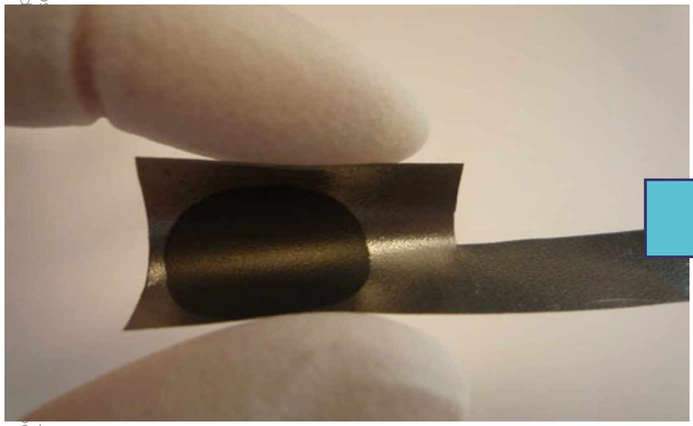
- **Gun spraying**
- **Masking**
- **Several samples fabricated at the same time**



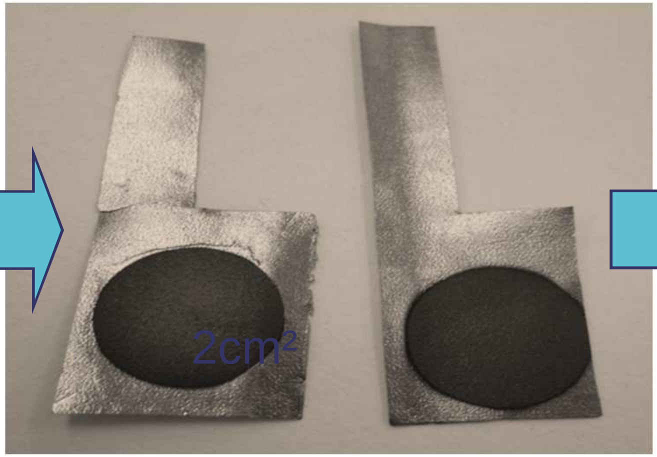
Panasonic
Graphite bucky paper



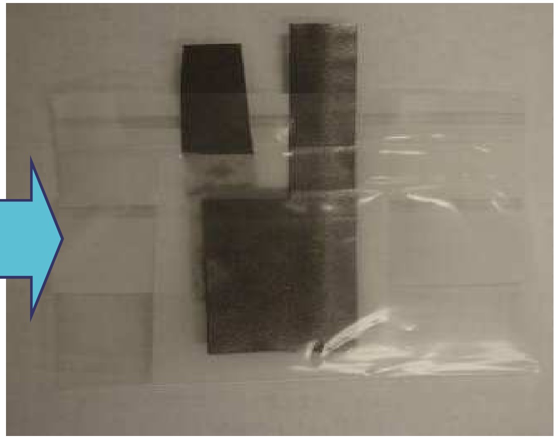
Flexible electrodes



Electrode design



Supercapacitor Cell

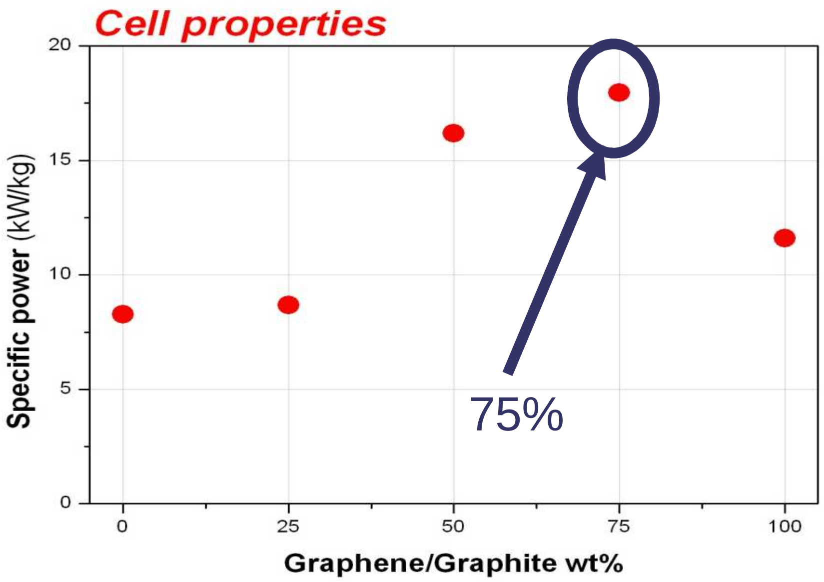


Results : Energy and Power as a function of the concentration

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**, JECS 160 (4) A1-A6, 2013

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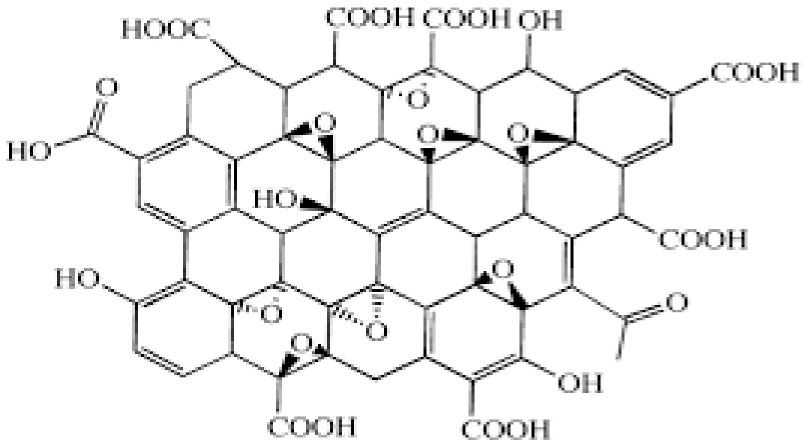
Last measurements : new option for green suspensions using GO

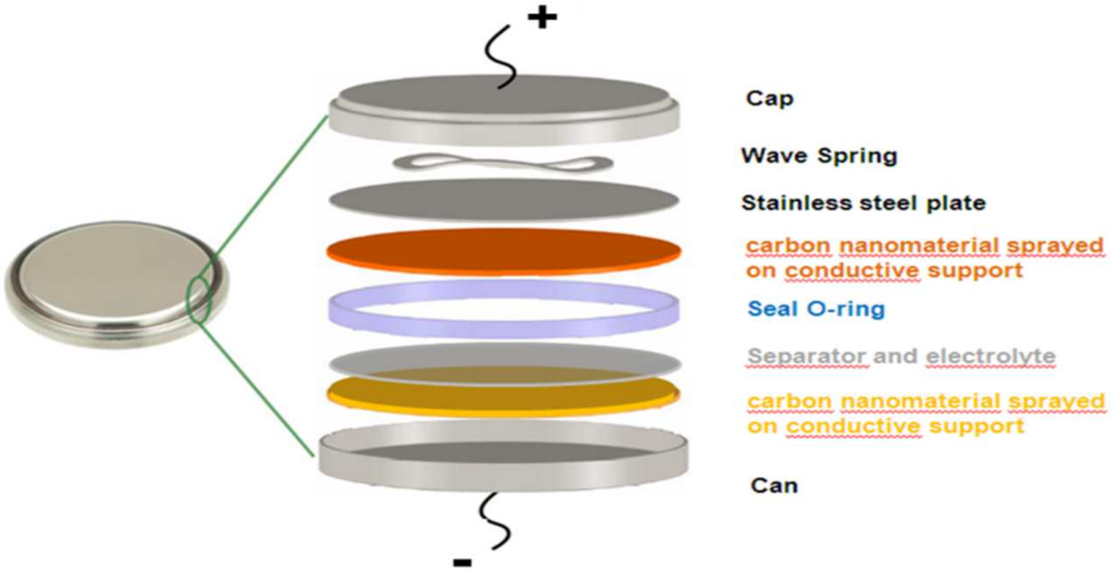
Mixing of Graphene Oxyde and Oxydised Carbon Nanotubes in water

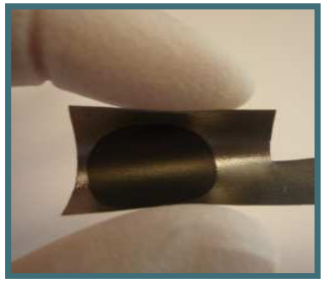
Advantages

- Aqueous based supensions
- Very stable suspensions
- Low temperature process (120°C)

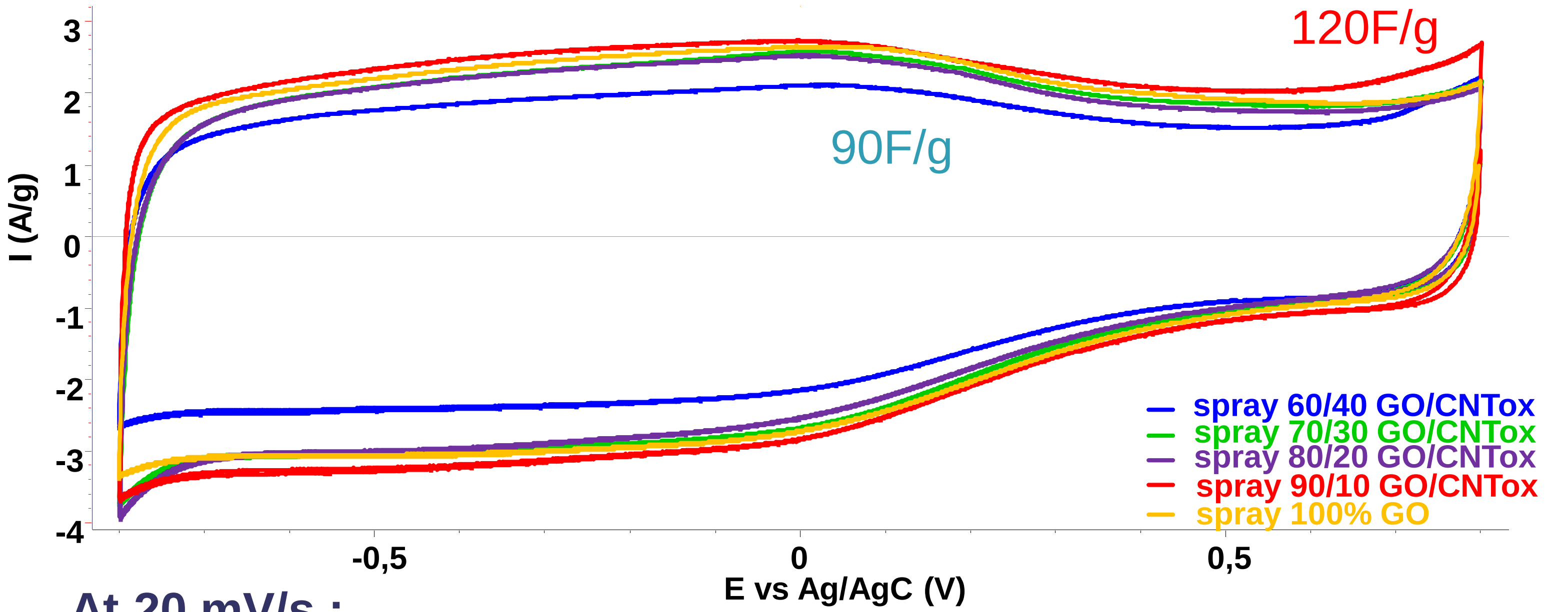


New packaged prototypes





Performances for different GO concentrations

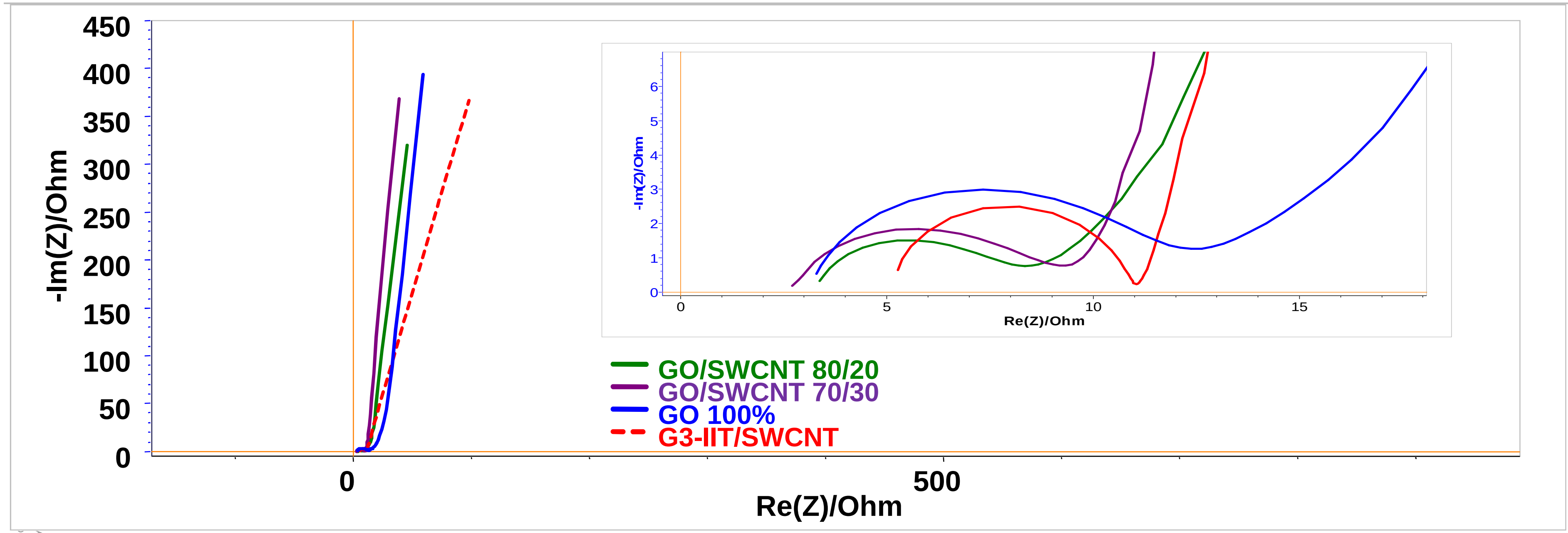


At 20 mV/s :

C = 88 F/g
C = 109 F/g
C = 106 F/g
C = 120 F/g
C = 112 F/g

Graphene based electrodes for high performances supercapacitors, **P.Bondavalli,** G.Pognon, Proceeding of IEEE NANO 2015, 17-20 July, Rome

Power density



Power density :

100 % GO : 14 kW/kg
90/10 : 31 kW/kg
80/20 : 29 kW/kg
70/30 : 21 kW/kg

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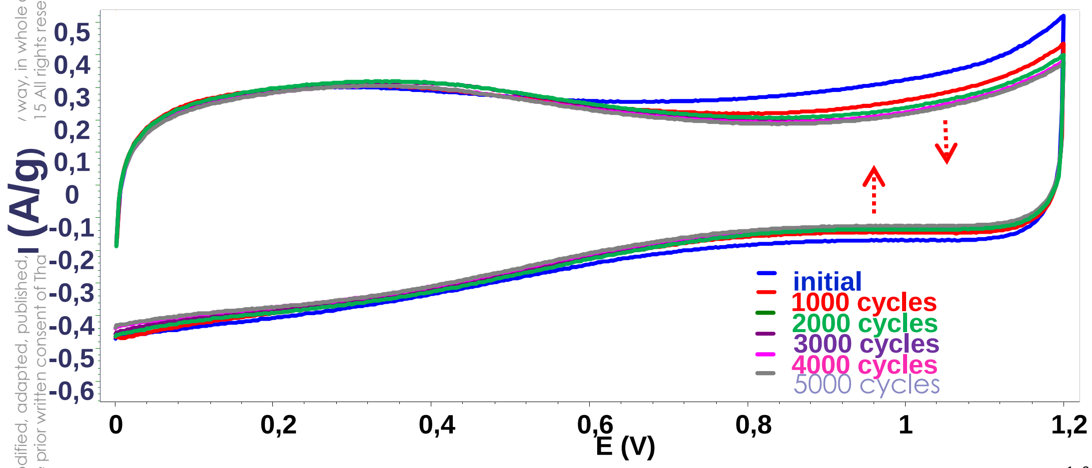
Graphene from IIT : Galvanostatic charge/discharge experiment

Very good stability (same capacitance that using GO)



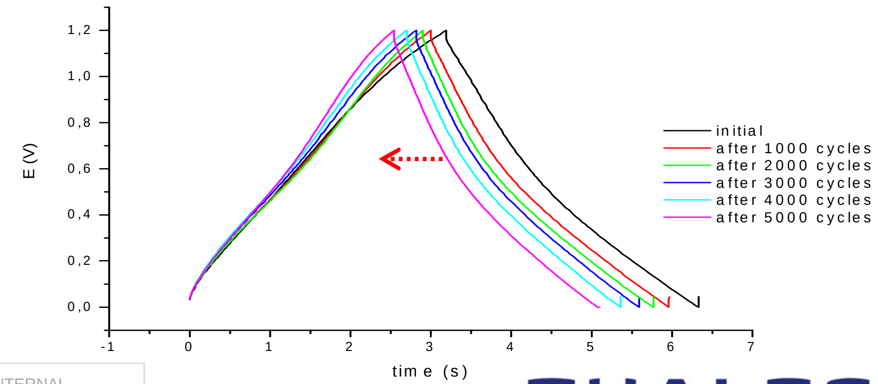
two-electrodes configuration

→ complete system

m = 1,15 mg (x2)

5000 cycles

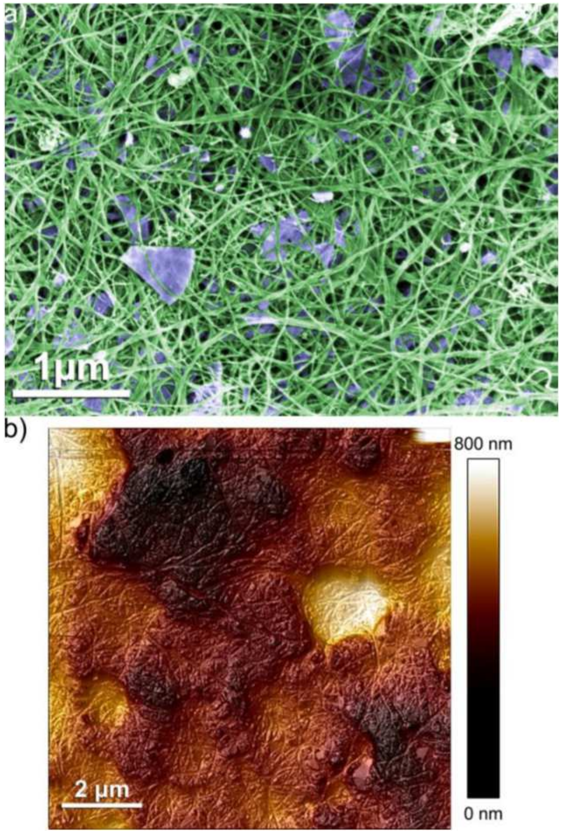
I= 10mA



Graphene exfoliated by IIT :

- Loss essentially during the 1000 first cycles

P= 92,3 kW/kg



FULL PAPER WILEY-VCH

High-power graphene-carbon nanotube hybrid supercapacitors

Alberto Ansaldo,[a] Paolo Bondavalli,[b] Sebastiano Bellani,[a] Antonio Esau Del Rio Castillo,[a] Mirko Prato,[c] Vittorio Pellegrini,[a] Grégory Pognon,[b] and Francesco Bonaccorso*[a]

Thanks to strong collaboration with IIT

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?)

Last developments on nanostructuration

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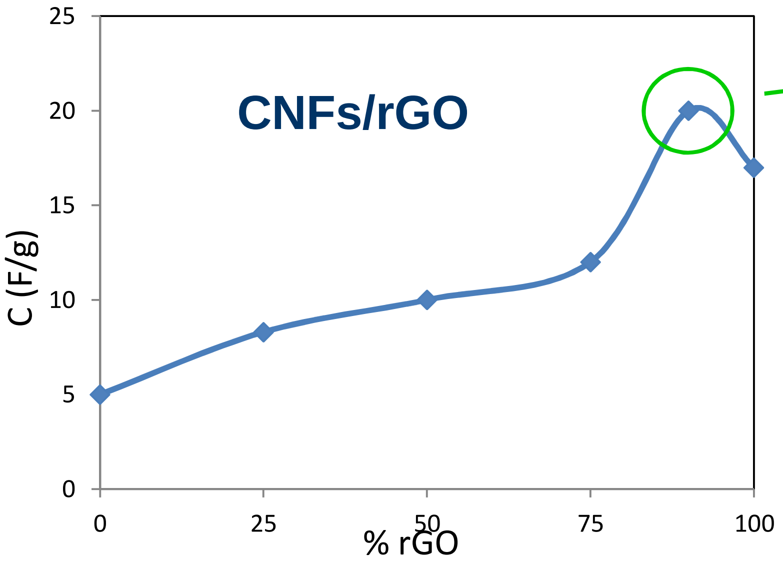
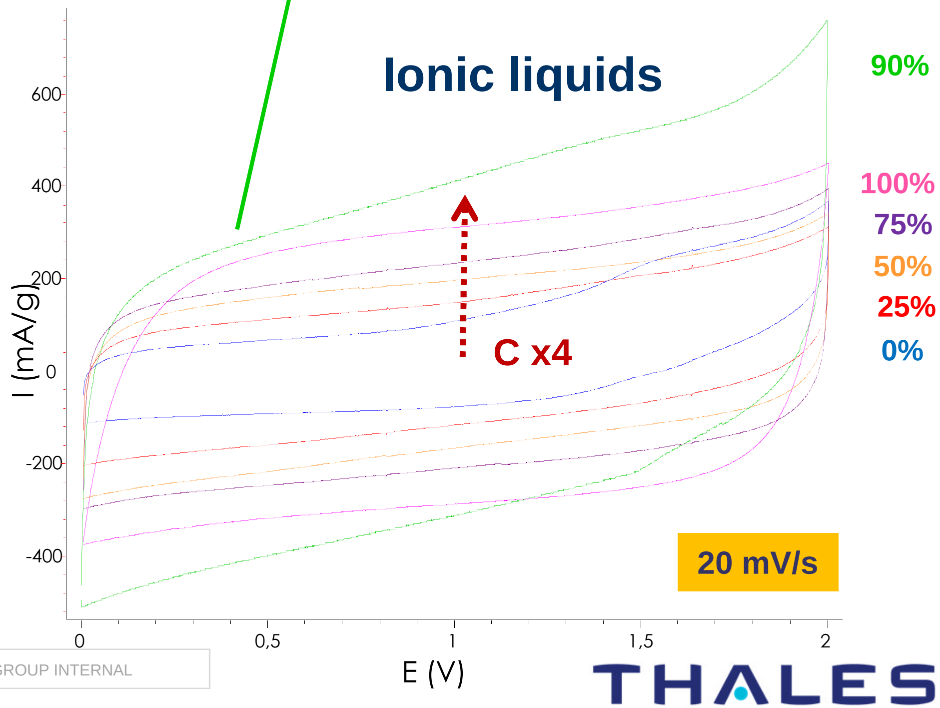
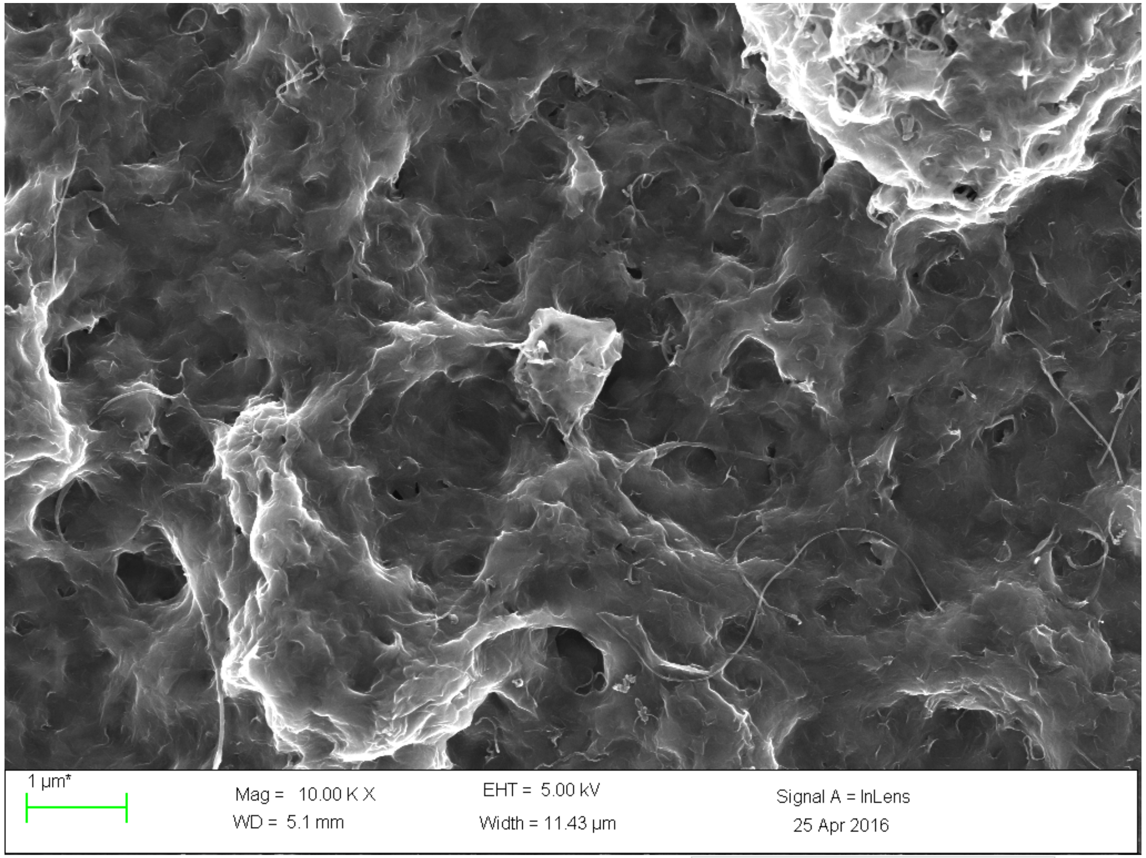
Utilisation of specific ionic liquids : large temperature interval for avionics (-55°C +105°C)

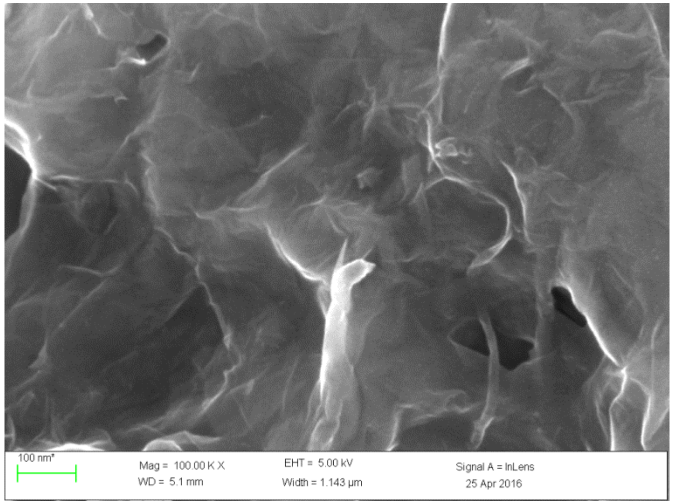


C= 20F/g (whole cell)
P = 40 kW/Kg

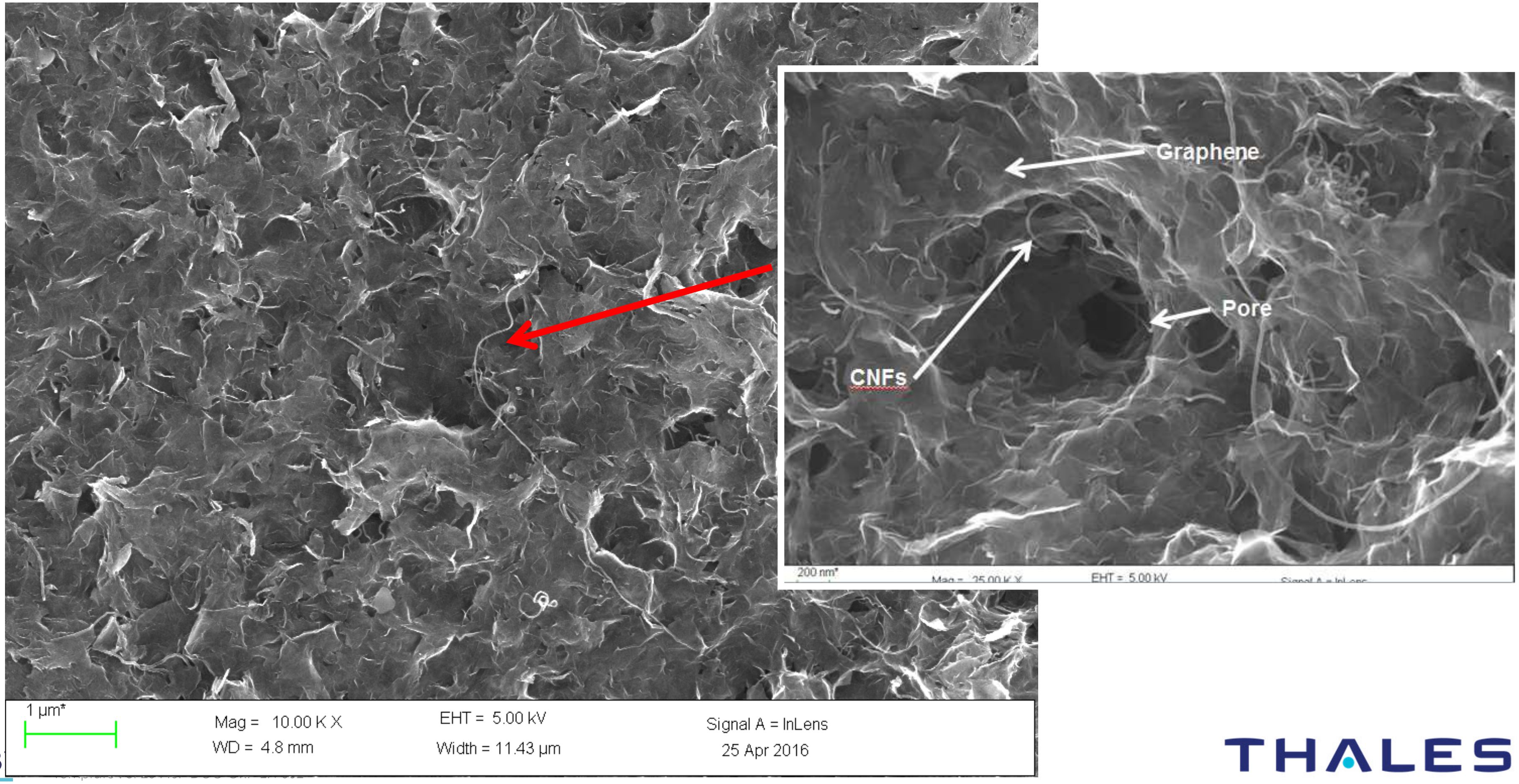


90/10 Cyclohexanone

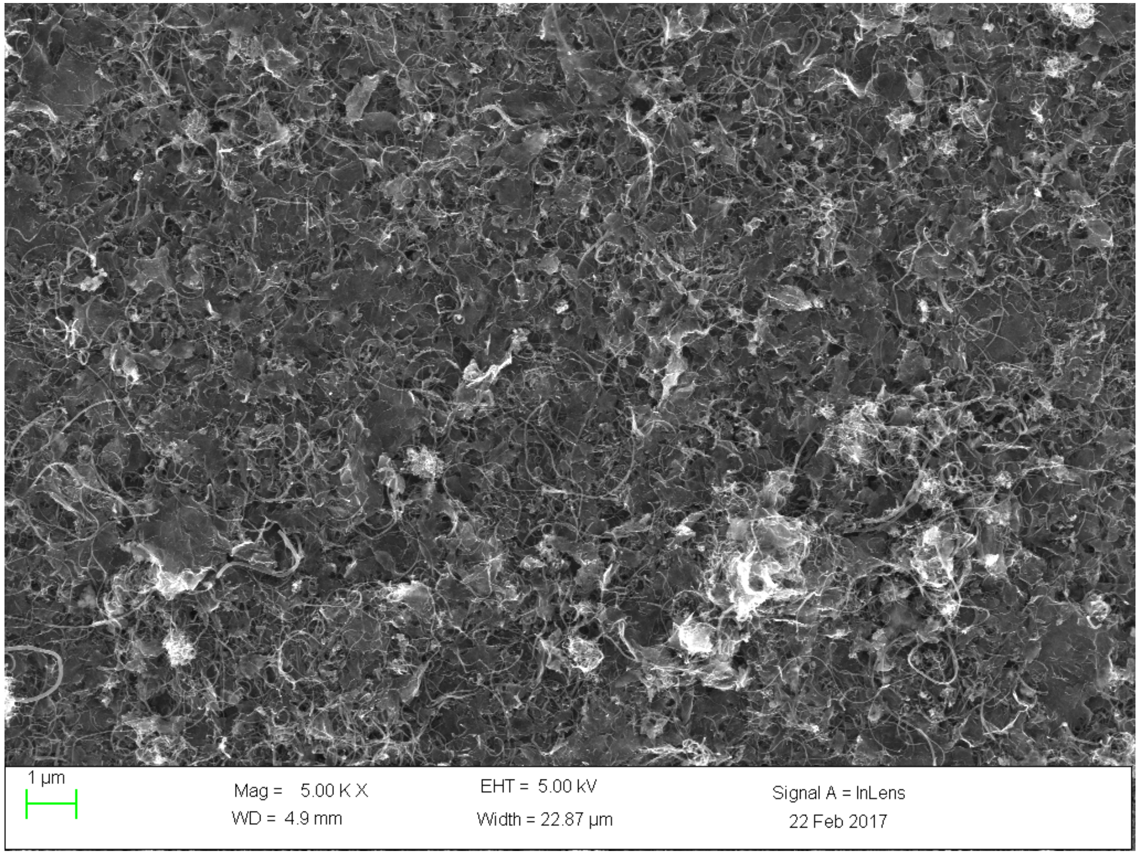


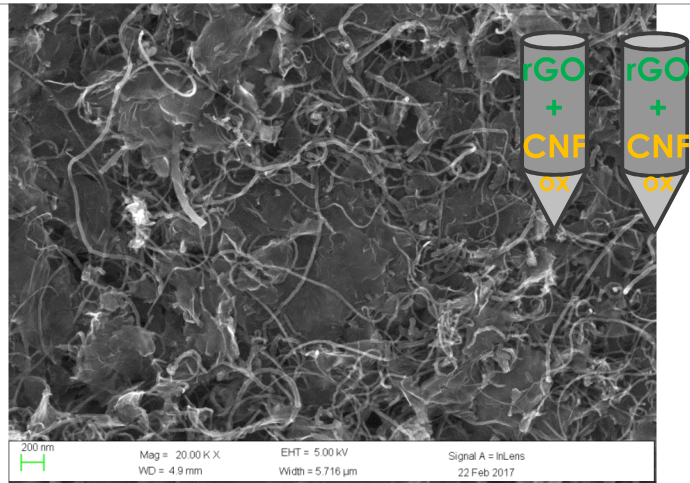


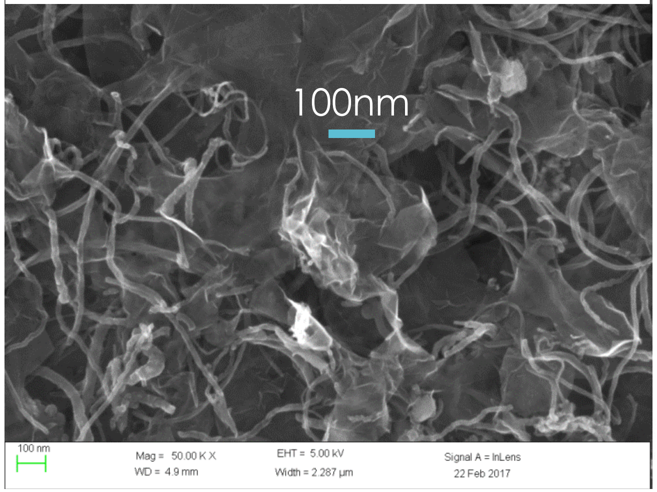
90/10 Dichloroethane (rGO/CNFs)



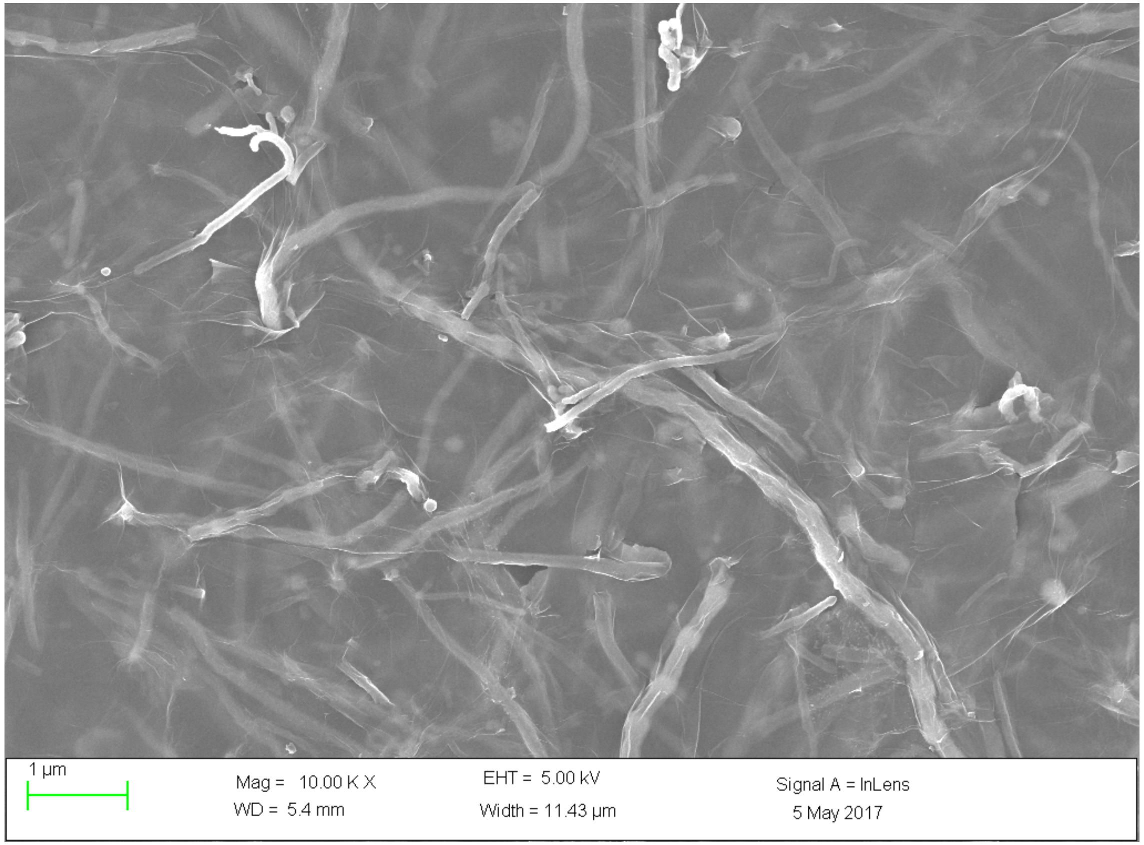
90/10 rGO/CNF two nozzles, $C_2H_4Cl_2$

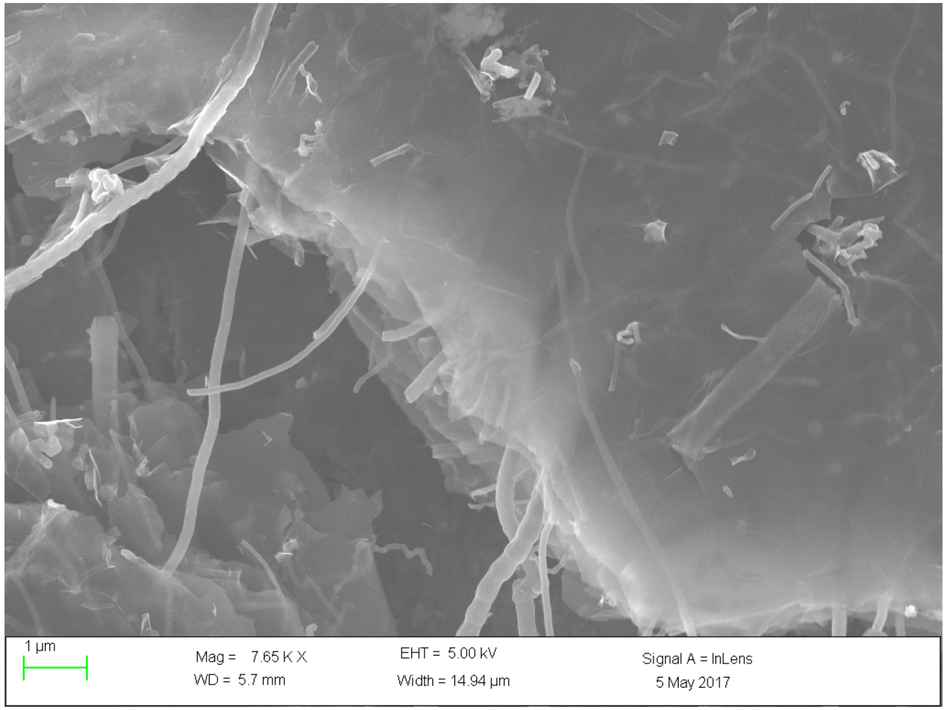


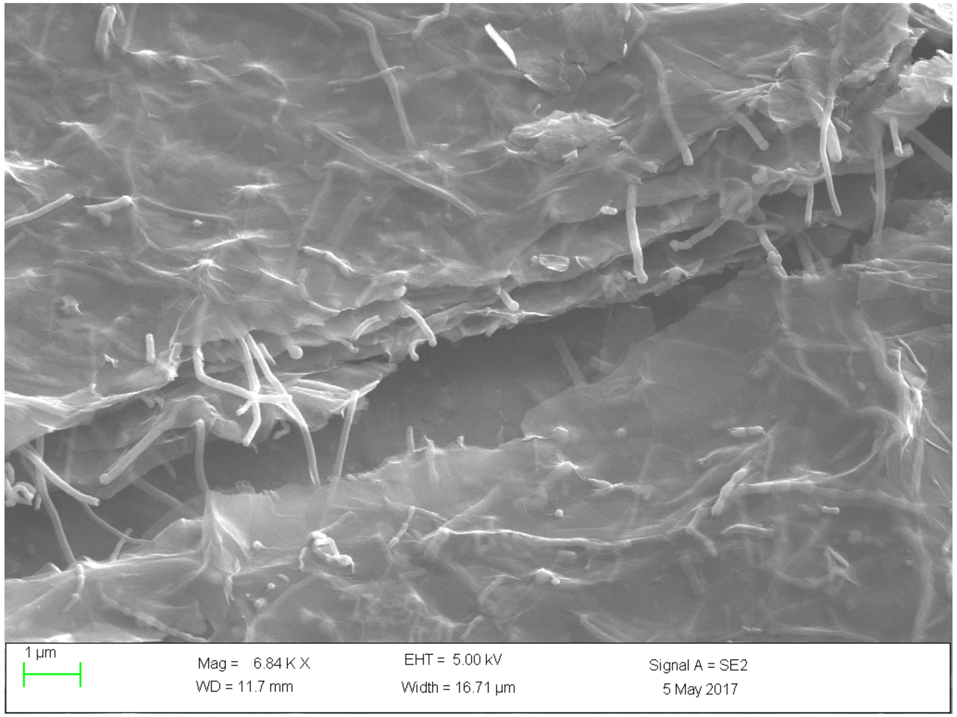




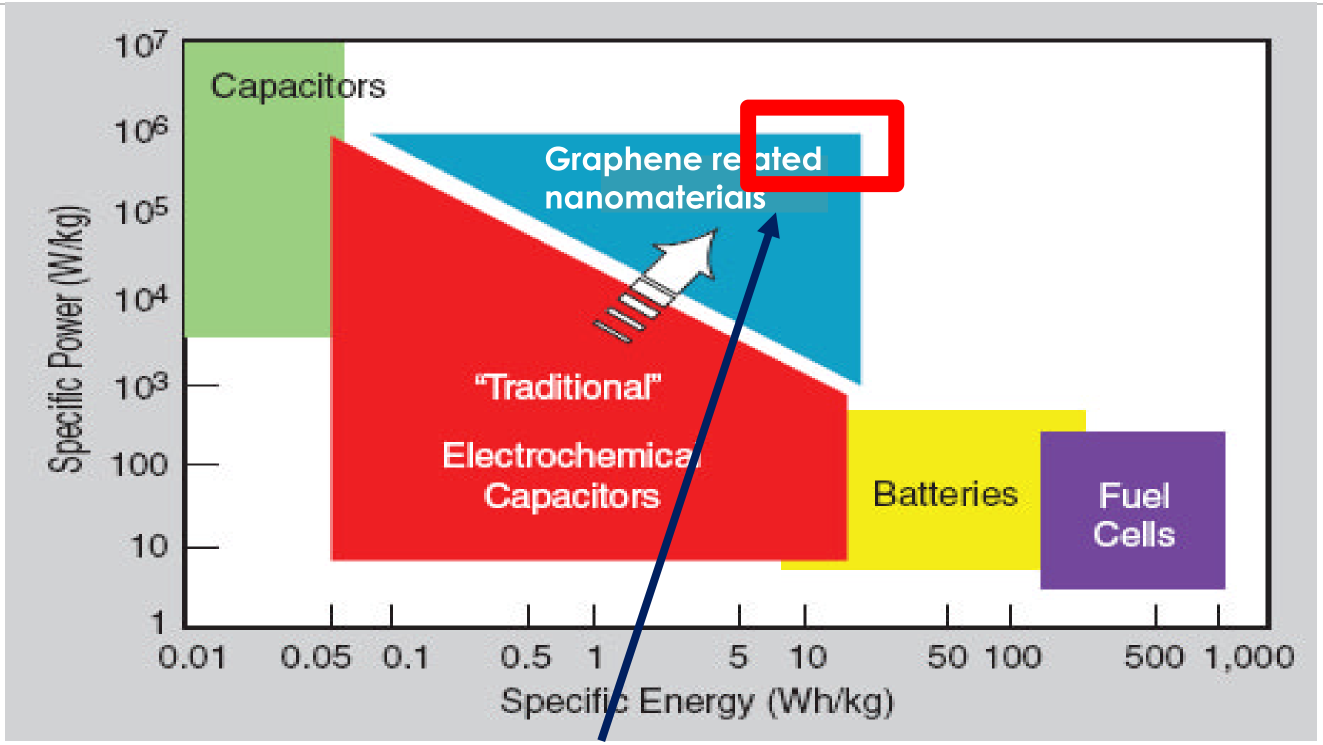
75/25 GO/CNFox




1 µm
Mag = 7.65 K X
WD = 5.7 mm
EHT = 5.00 kV
Width = 14.94 µm
Signal A = InLens
5 May 2017


1 µm
Mag = 6.84 K X
WD = 11.7 mm
EHT = 5.00 kV
Width = 16.71 µm
Signal A = SE2
5 May 2017

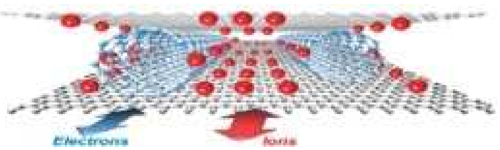
Graphene related nanomaterials based Supercapacitors

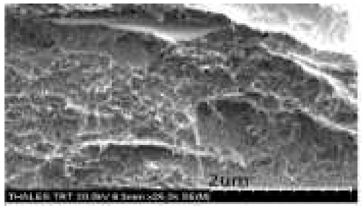


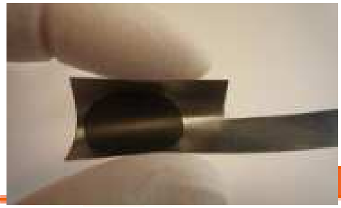
Considering that supercapacitors bridge the gap of capacitors and batteries performances we have to attain performances in this zone

Thales approach and strategy

Electrode fabrication evolution







2012-2014
Nanomaterials structuration

2015
Large surface
Spray on graphite collector

2015
Electrolytes for large interval of temperatures

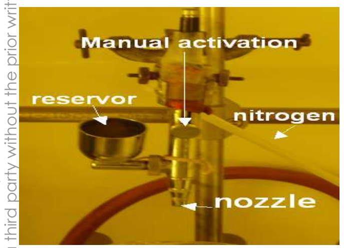
2016
Large surface spray on aluminum

TRL 4

2017
Packaged prototypes

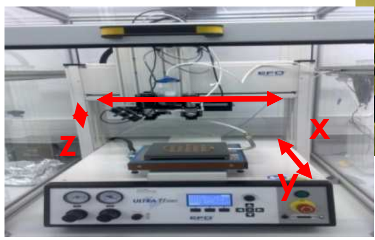
Thales approach and strategy

Deposition method evolution

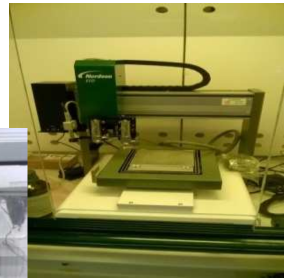


2007
Manual Air- brush

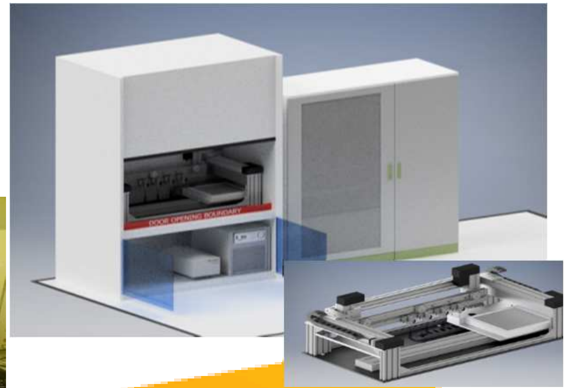
2008
Semi-automatic
Air- brush



2008
Spray-gun robot
with one nozzle



2016
Spray-gun robot
with two nozzles



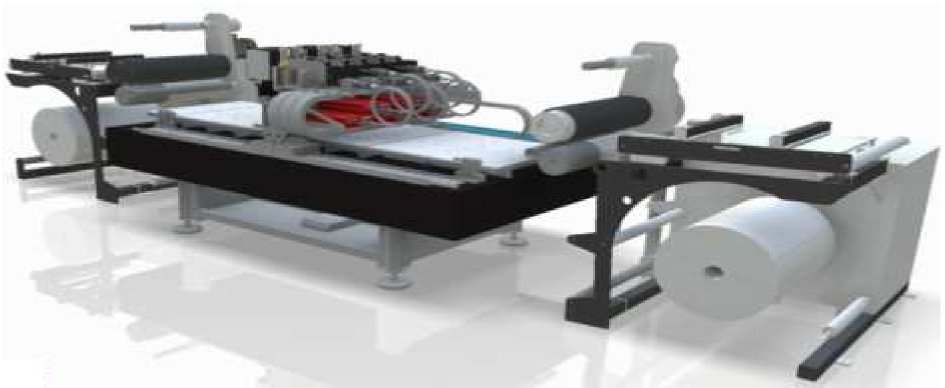
2017
Spray-gun robot
with four nozzles
pre-industrialized
(M-Solv)

SMALL SURFACES
MANUAL SYSTEM

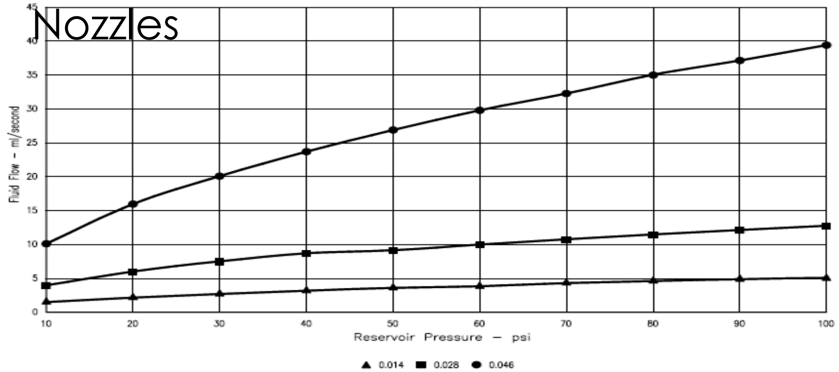
LARGE SURFACES
COMPLETELY AUTOMATISED
SYSTEM
(pre-industrial prototype)

Roll to Roll Core 2 (2020) Pilot Production line using Spray

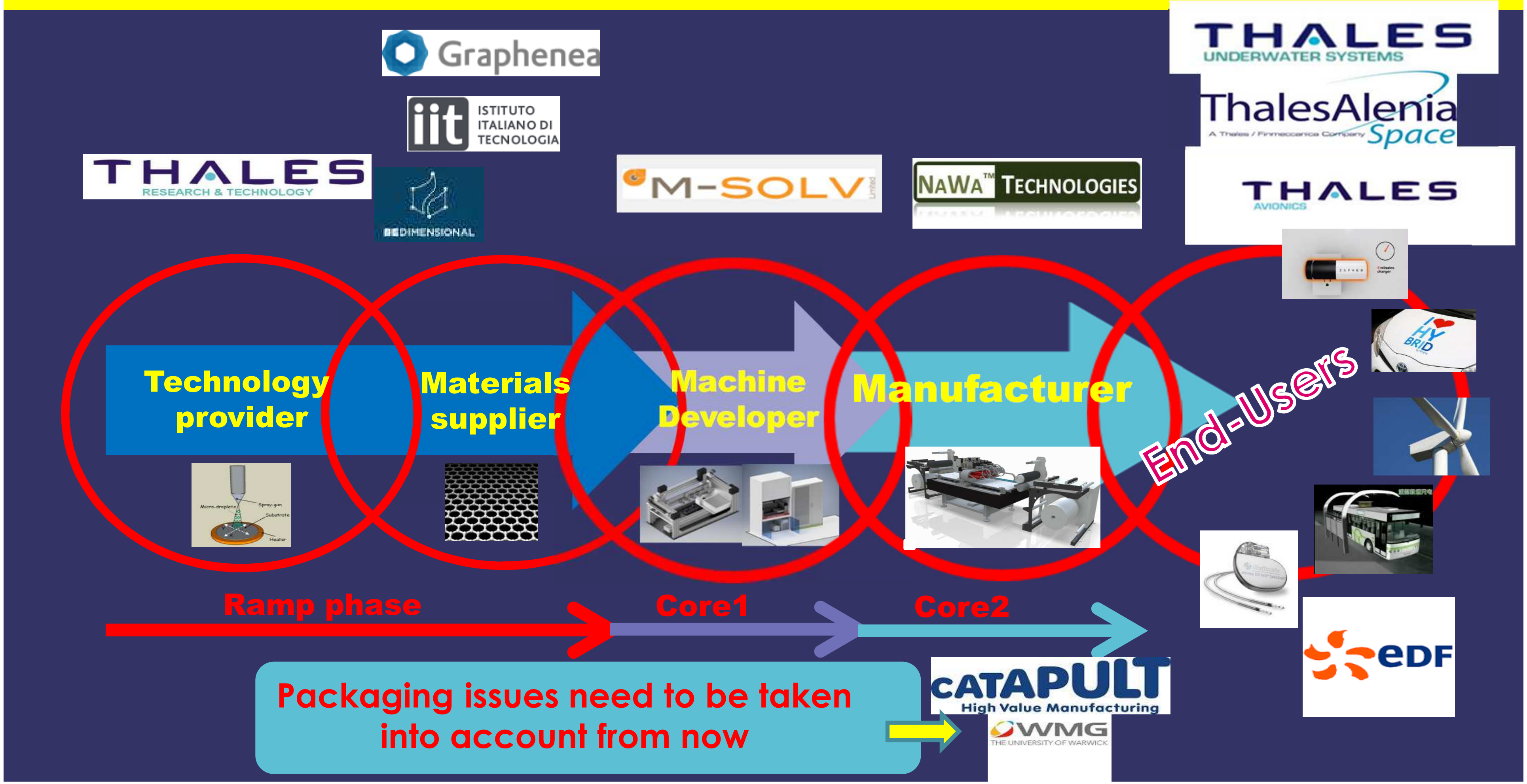
- Scale up deposition further
- Fastest deposition method would have a substrate moving perpendicular to a bank of nozzles
- Faster flow rates could be investigated using higher volume spray heads. May allow deposition of a complete film in one pass



Achievable Flow Rates with Different Nozzles



Value Chain


Graphenea
iit ISTITUTO ITALIANO DI TECNOLOGIA
THALES RESEARCH & TECHNOLOGY
BEDIMENSIONAL
M-SOLV
NAWA TECHNOLOGIES
THALES UNDERWATER SYSTEMS
ThalesAlenia Space
THALES AVIONICS
Technology provider
Materials supplier
Machine Developer
Manufacturer
End-Users
Ramp phase
Core1
Core2
Packaging issues need to be taken into account from now
CATAPULT High Value Manufacturing
WMG THE UNIVERSITY OF WARWICK
eDF

Thales operational units express needs and provide specs to attain

THALES AVIONICS

ThalesAlenia Space
A Thales / Finmeccanica Company

THALES UNDERWATER SYSTEMS

Technology developer and provider of the group

THALES RESEARCH & TECHNOLOGY

Technology moves from TRL1 to TRL4/5

TRT will identify the technical partners to transfer the technology outside the Thales group (technology licensing)

Exclusivity contract for production of subsystems for Thales

Large surface machine developer and provider

M-SOLV Limited

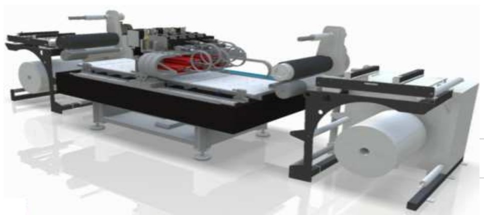
Integration in production line (Start-up/Spin off/Joint venture)

Company producing Supercaps not only for Thales but also for mass-market low-cost applications

Conclusions and perspectives

- **Supercaps can be fabricated by spray-gun deposition method exploiting nanostructuration.**
- **The results are compatible with commercial products but SCs can stay between -50°C and 105°C (no companies are able to do that).**

- **We are improving nanostructuration for ionic liquinds (to increase energy keeping the same lifetime).**
- **Supercaps will be fabricated by roll-to-roll in two years in the frame of the Graphene Flagship (graphene and CNFs seem to be the good option). We are looking for partners for manufacturing (some options)**



Fundings

GRAPHENE FLAGSHIP

Work Package 9: Energy

Work Package Leader - Dr. Etienne Quesnel, CEA French Alternative Energies and Atomic Energy Commission, France

Work Package Leader - Dr. Vittorio Pellegrini, Italian Institute of Technology, IIT graphene labs, 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

SEVENTH FRAMEWORK PROGRAMME

- **High-power graphene-carbon nanotube hybrid supercapacitors.** ChemNanoMat. Accepted Author Manuscript. Ansaldo, A., **Bondavalli**, P., Bellani, S., Del Rio Castillo, A. E., Prato, M., Pellegrini, V., Pognon, G. and Bonaccorso, F. (2017), doi:10.1002/cnma.201700093
- **Graphene-based technologies for energy applications, challenges and perspectives,** Etienne Quesnel, Frédéric Roux, **Paolo Bondavalli** et al., *2D Materials 08/2015; 2(3):030204.*
- **Supercapacitor electrode based on mixtures of graphite and carbon nanotubes deposited using a new dynamic air-brush deposition technique**, **P Bondavalli,** C.Delfaure, P.Legagneux, D.Pribat JECS 160 (4) A1-A6, **2013**
- **Non-faradic carbon nanotubes based supercapacitors : state of the art**, **P.Bondavalli,** D.Pribat, C.Delfaure, P.Legagneux, L.Baraton, L.Gorintin, J-P. Schnell, Eur. Phys. J. Appl. Phys. 60,10401, **2012**
- **Graphene based supercapacitors fabricated using a new dynamic spray-gun deposition technique**, **P. Bondavalli** and G. Pognon, 2015 IEEE 15th International Conference on Nanotechnology (IEEE-NANO), Rome, 2015, pp. 564-567.

- Graphene and Related Nanomaterials 1st Edition, Properties and Applications, **Paolo Bondavalli,** Hardcover ISBN: 9780323481014, Elsevier, Published Date: 1st September 2017

- WO/2016/124756 (A1) - **Method of depositing oxidized carbon-based microparticles and nanoparticles,** Pognon Grégory [fr]; Bondavalli Paolo [fr]; Galindo Christophe [fr]

- WO/2014/166952 (A1) **- Electrode-gel electrolyte assembly comprising a porous carbon material and obtained by radical polymerisation,** Le Barny, Pierre; (FR). Divay, Laurent; (FR).Galindo, Christophe; (FR)

- FR2988900 (A1) **- Electrode pour supercondensateur**, Christophe Galindo, Laurent Divay, Le Barny Pierre

- FR2989215 (A1) - **Electrode hybride pour supercondensateur**, , Le Barny Pierre , Laurent Divay, Christophe Galindo

- FR2989821 (A1) - Electrode hybride nanotubes de carbone-carbonne mesoporeux pour supercondensateur, Le Barny Pierre , Laurent Divay, Christophe Galindo
- FR3011671 (A1) - **Collecteur de courant pour supercapacite**, Bondavalli Paolo [fr]; Legagneux Pierre [fr]; Galindo Christophe

- WO2012049428 (A2) - **Method for depositing nanoparticles on a surface and corresponding nanoparticle depositing appliance**, Bondavalli Paolo [fr]; Gorintin Louis [fr]; Legagneux Pierre [fr]; Ponard Pascal [fr]

- FR2976118 (A1) - **Method for manufacturing collector-electrode assembly that is utilized in supercapacitor, involves forming collector and electrode by spraying suspension comprising nano/microparticles suspended in liquid in substrate,** Bondavalli Paolo [fr]; Schnell Jean Philippe [fr]; Legagneux Pierre [fr]; Gorintin Louis [fr]

- EP2769395 (A1) - **Collector-electrode assembly which can be integrated into an electrical energy storage device,** Legagneux Pierre [fr]; Bergonzo Philippe [fr]; Bondavalli Paolo [fr]; Mazellier Jean-Paul [fr]; Scorsone Emmanuel [fr]

Thanks to

In the frame of the Graphene Flagship **IIT Genova**

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- **Mirko Prato**
- **Vittorio Pellegrini.**

- **Graphenea** for GO in water
  - **A.Zurutuza**
  - **I.Charola**

- Gregory Pognon (Chemistry Lab) Electrochemical characterization and nanomaterial functionalisation

Thank you for your attention!!!