What impact can graphene have on future batteries

Vittorio Pellegrini

Istituto Italiano di Tecnologia, Graphene Labs, Genova, Italy

Bedimensional S.p.a., Genova, Italy

iit GRAPHENE ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

BEDIMENSIONAL

Battery: basic facts

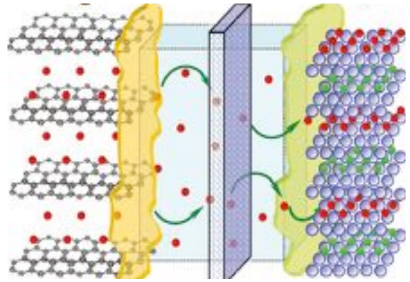
A battery is a device that converts chemical energy into electrical energy and vice versa

Alessandro Volta 1799

ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

BEDIMENSIONAL

The future of Lithium batteries



1 liter of gasoline
6000Wh/Kg

1kg of Li-ion
150-250 Wh/Kg

Lithium Ion Battery,
Cathode - $LiCoO_2$
150 mAh g^{-1}

Lithium Ion Battery,
Cathode – $LiFePO_4$
170 mAh g^{-1}

Lithium Ion Battery,
Anode – Si / carbon
1000 mAh g^{-1}

Lithium Ion Battery,
Cathode – NMC
200 mAh g^{-1}

Lithium Sulfur Battery,
Cathode – Sulfur Carbon
1675 mAh g^{-1}

Lithium/Na Oxygen Battery,
Cathode – Oxygen Carbon
3500 mAh g^{-1}

400 Wh kg^{-1} → 500 Wh Kg^{-1}

1000 Wh kg^{-1} → 3000 Wh Kg^{-1}

ISTITUTO ITALIANO DI TECNOLOGIA
GRAPHENE LABS

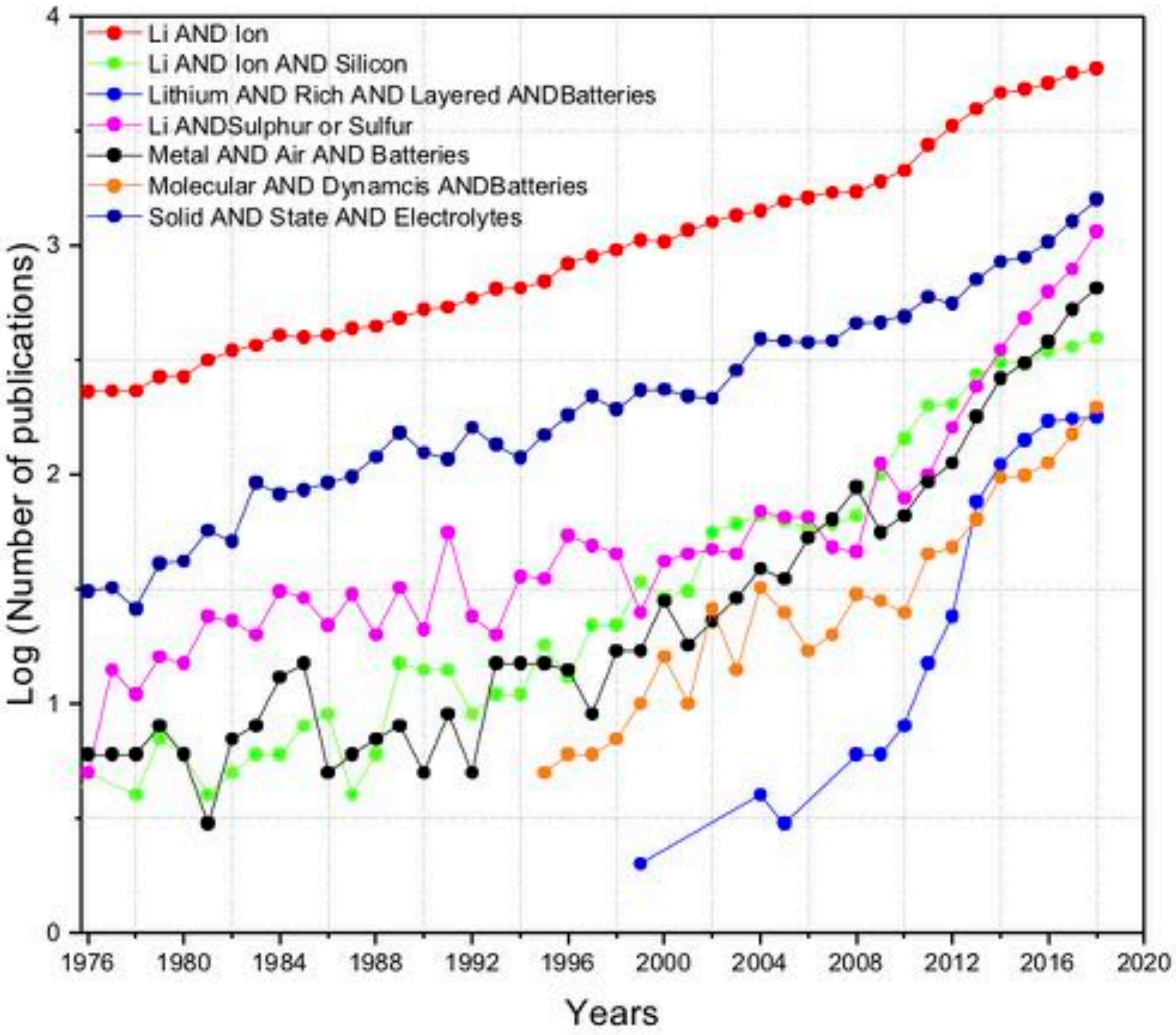
BEDIMENSIONAL

The future of batteries

- New functionalities
- New materials
- New chemistries
- Industrially-scalable and cost effective approaches

<100$/kWh on cell level
<120$/KWh on module level
30$/Kg on active material

The future of Lithium batteries

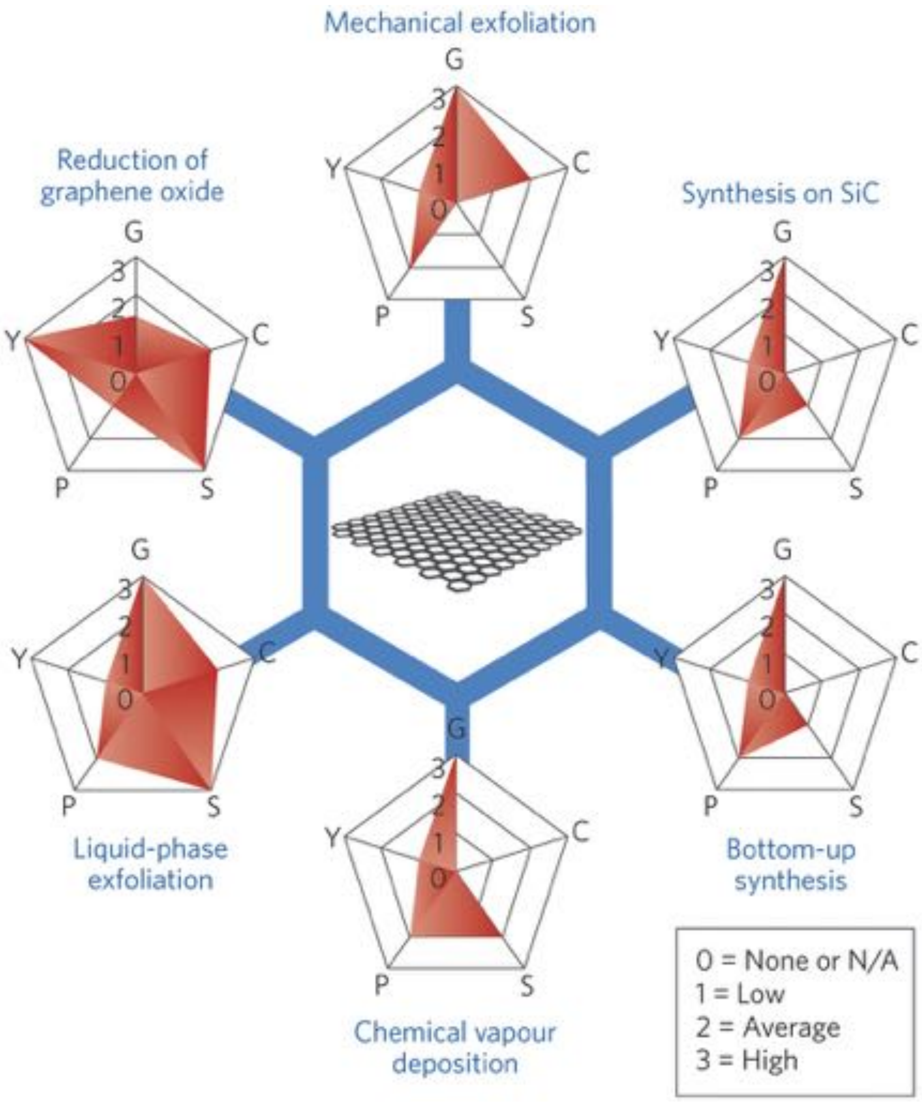


V. Pellegrini, S. Bodoardo, D. Brandell, K. Edstrom Solid State Communications (2019)

What is the role of graphene and other 2D crystals in emerging technologies for energy storage?

F. Bonaccorso et al., Science **347**,1246501 (2015)
E. Quesnel et al., 2D materials, **2** 030204 (2015)
A. Ferrari et al., Nanoscale, **7**, 4598 (2015)
E. Pomerantseva et al., Science **366**, (2019)

Graphene production



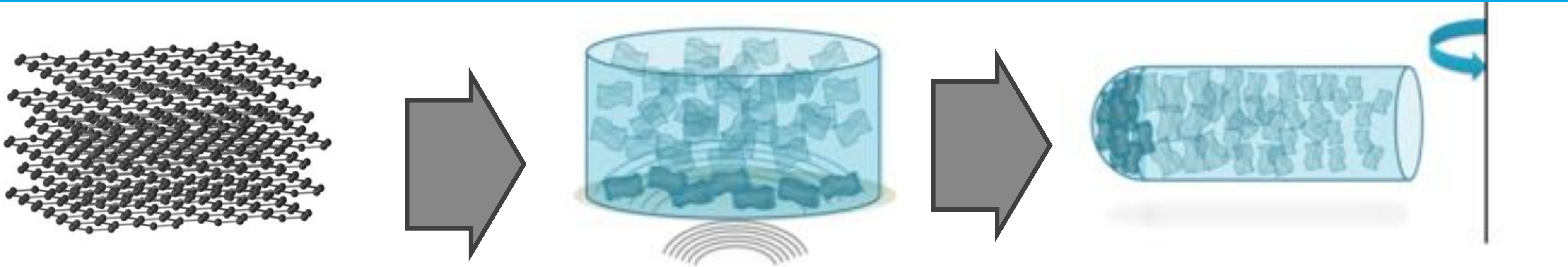
G Graphene quality
C cost aspect
S scalability
P purity
Y yield

R. Raccichini et al., Nature Mat. **14**, 271–279 (2015)

ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

BEDIMENSIONAL

Liquid phase exfoliation of 2d crystals



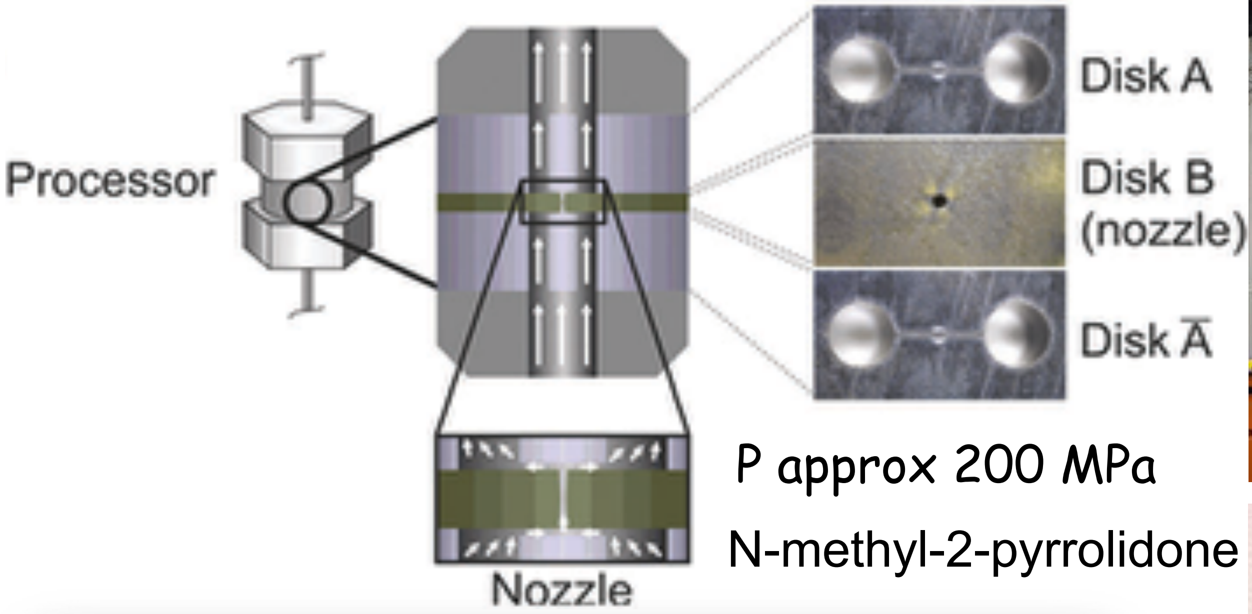
2D bulk materials · Ultrasonication · Ultracentrifugation

Graphene · Bi_2Te_3 · WSe_2 · WS_2 · MoS_2 · BN

ISTITUTO ITALIANO
DI TECNOLOGIA
GRAPHENE LABS

BEDIMENSIONAL

Graphene production



P approx 200 MPa

N-methyl-2-pyrrolidone

Materials Horizons

Patent WO2017089987A1

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal

Check for updates

Cite this: DOI: 10.1039/c8mh00487k

Received 25th April 2018, Accepted 6th July 2018

DOI: 10.1039/c8mh00487k

rsc.li/materials-horizons

High-yield production of 2D crystals by wet-jet milling†

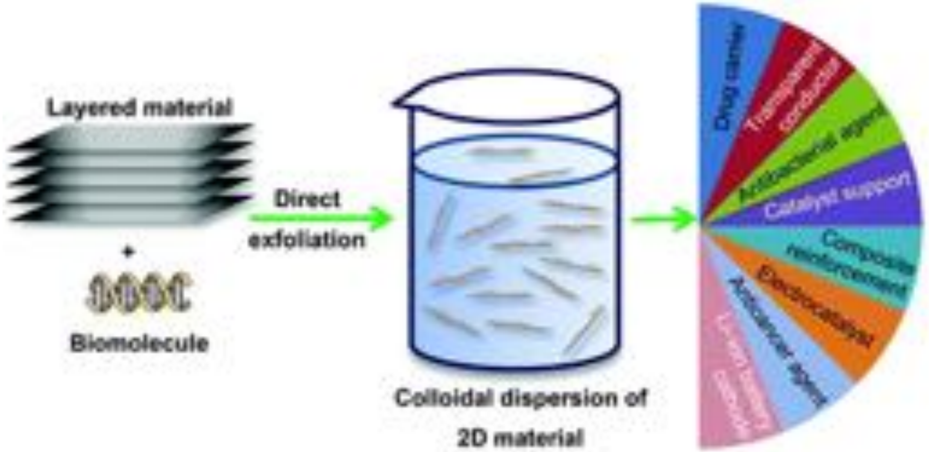
A. E. Del Rio Castillo,[*a] V. Pellegrini,[ab] A. Ansaldo,[a] F. Ricciardella,[a] H. Sun,[a] L. Marasco,[a] J. Buha,[c] Z. Dang,[c] L. Gagliani,[a] E. Lago,[a] N. Curreli,[ad] S. Gentiluomo,[a] F. Palazon,[c] M. Prato,[e] R. Oropesa-Nuñez,[b] P. S. Toth,[a] E. Mantero,[a] M. Crugliano,[a] A. Gamucci,[a] A. Tomadin,[a] M. Polini[a] and F. Bonaccorso[*ab]

ISTITUTO ITALIANO DI TECNOLOGIA
GRAPHENE LABS

BEDIMENSIONAL

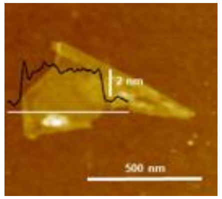
BEDIMENSIONAL

Graphene production



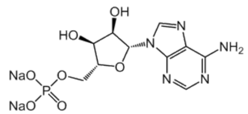
Proteins/peptides, RNA, DNA,
polysaccharides,
plant extracts
bile salts

CIC energiGUNE
energy storage research centre

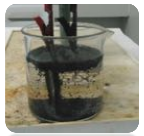


~0.5–1.5 nm of height
≤5 layers

Stable aqueous graphene bio-ink



innocuous molecules



environmental friendly, cheap and easy-to-scale process

3D graphene-derived structures

EASY PROCESSING

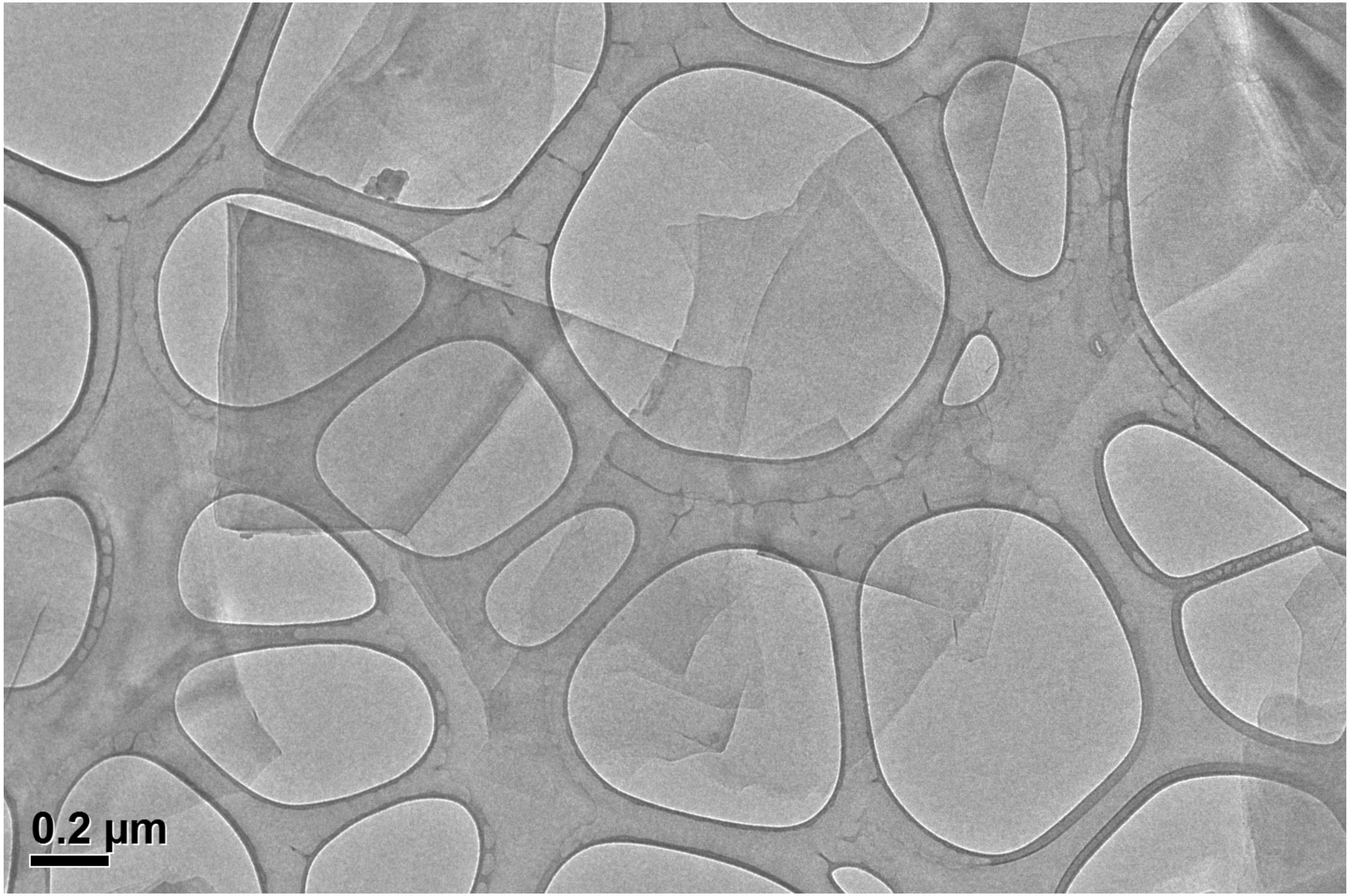
Exfoliation of graphite in water with LiPAA

Solid concentration: 10g/L (solid includes both Graphite and LiPAA)

IIT GRAPHENE ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

BEDIMENSIONAL

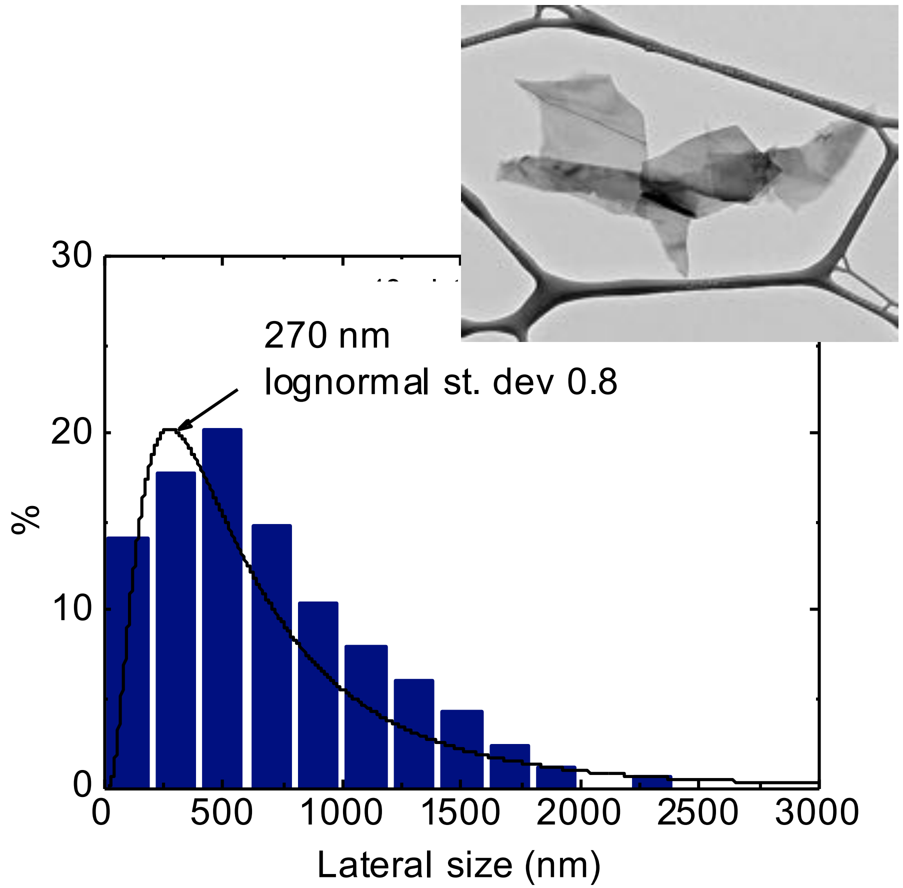
Graphene production

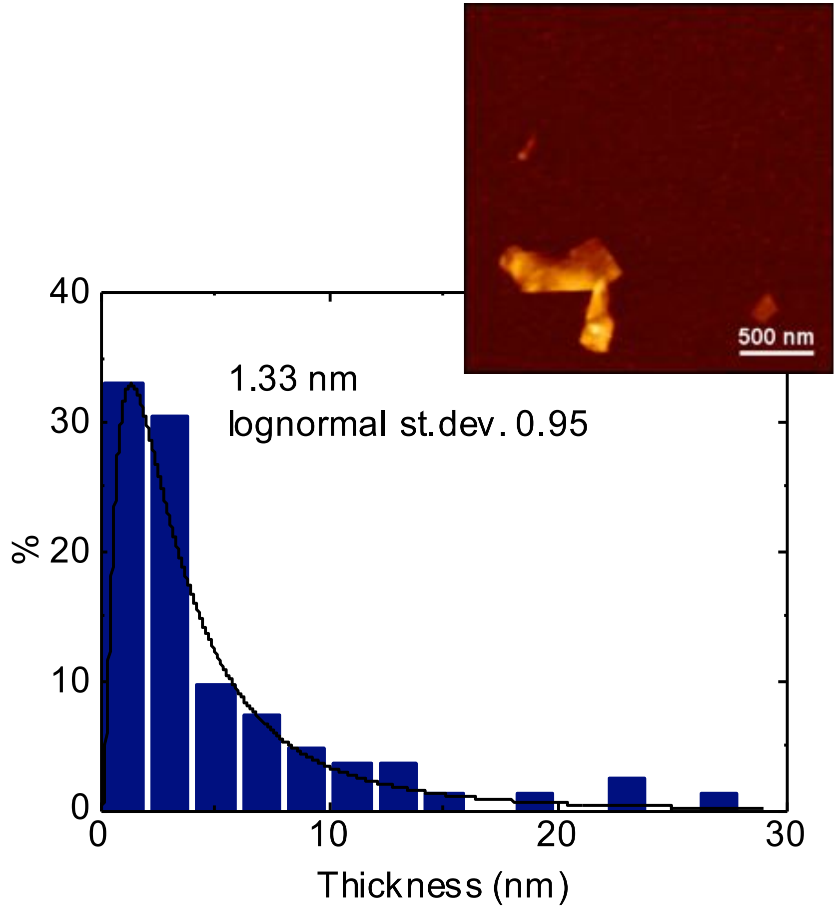


ISTITUTO ITALIANO
DI TECNOLOGIA
GRAPHENE LABS

BEDIMENSIONAL

Graphene production





FLG flakes have tunable lateral size 1µm-300 nm and down ~1.3 nm in thickness.

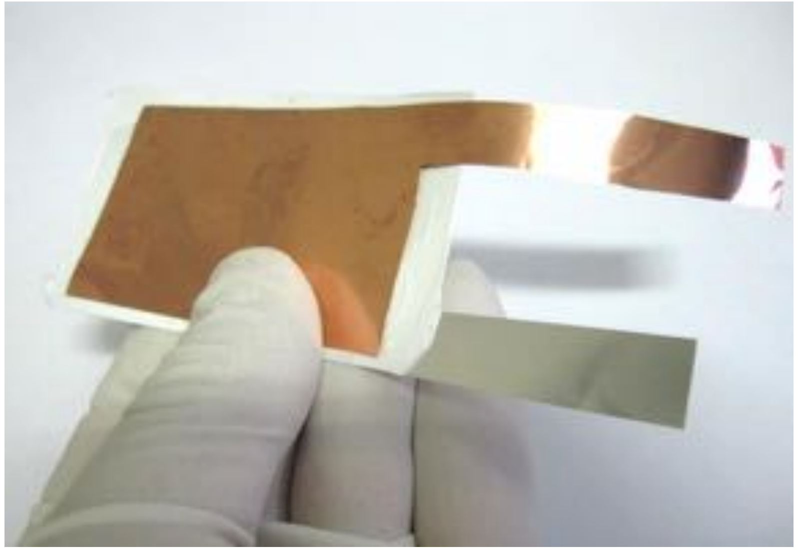
Target : Exfoliated layers < 10 layers 100%
Today: 50%

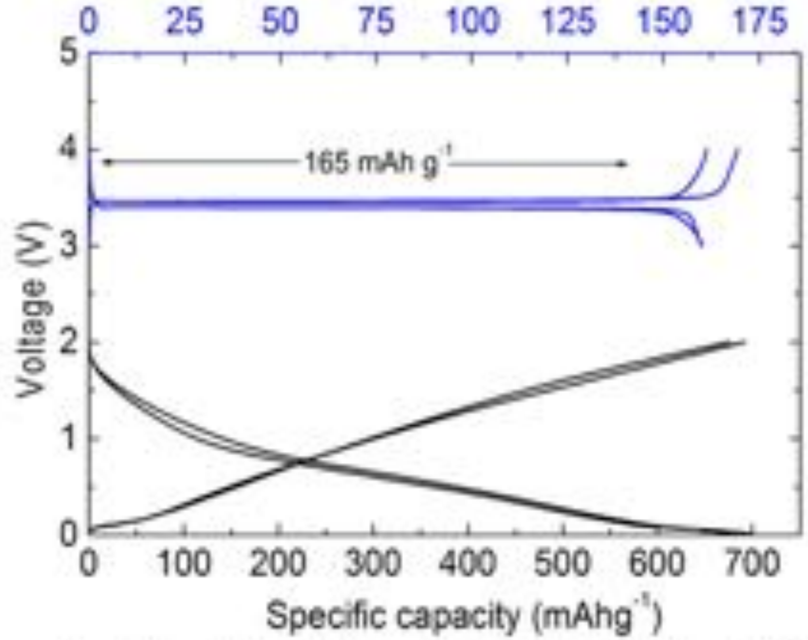
ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

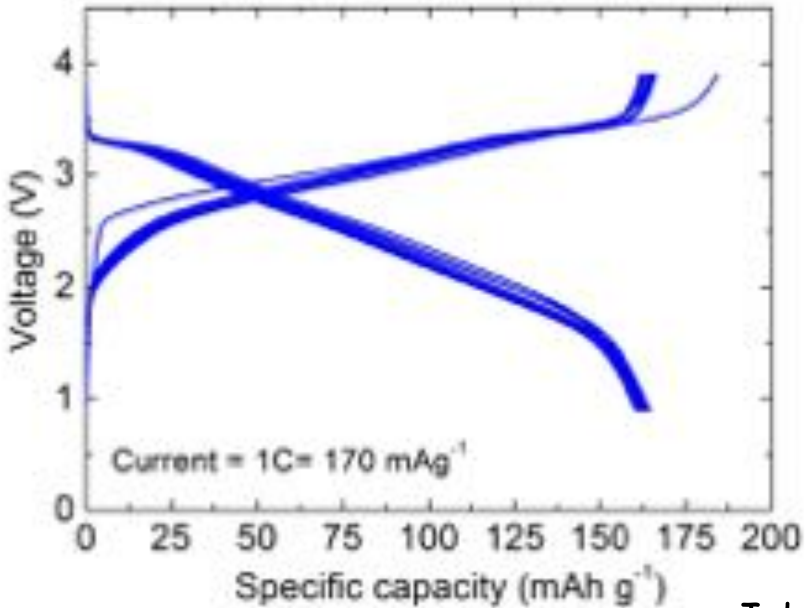
BEDIMENSIONAL

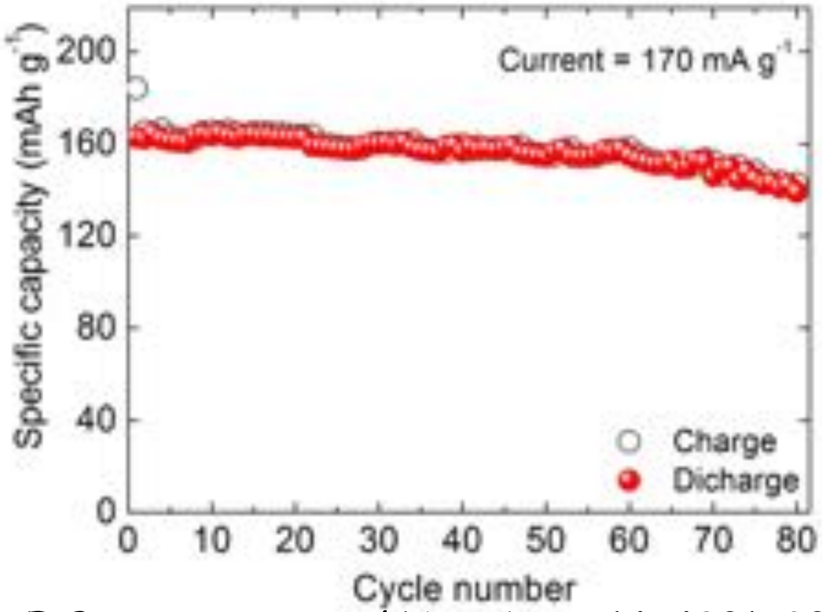
Li-ion full battery with $LiFePO_4$

Coin or Pouch cell configuration



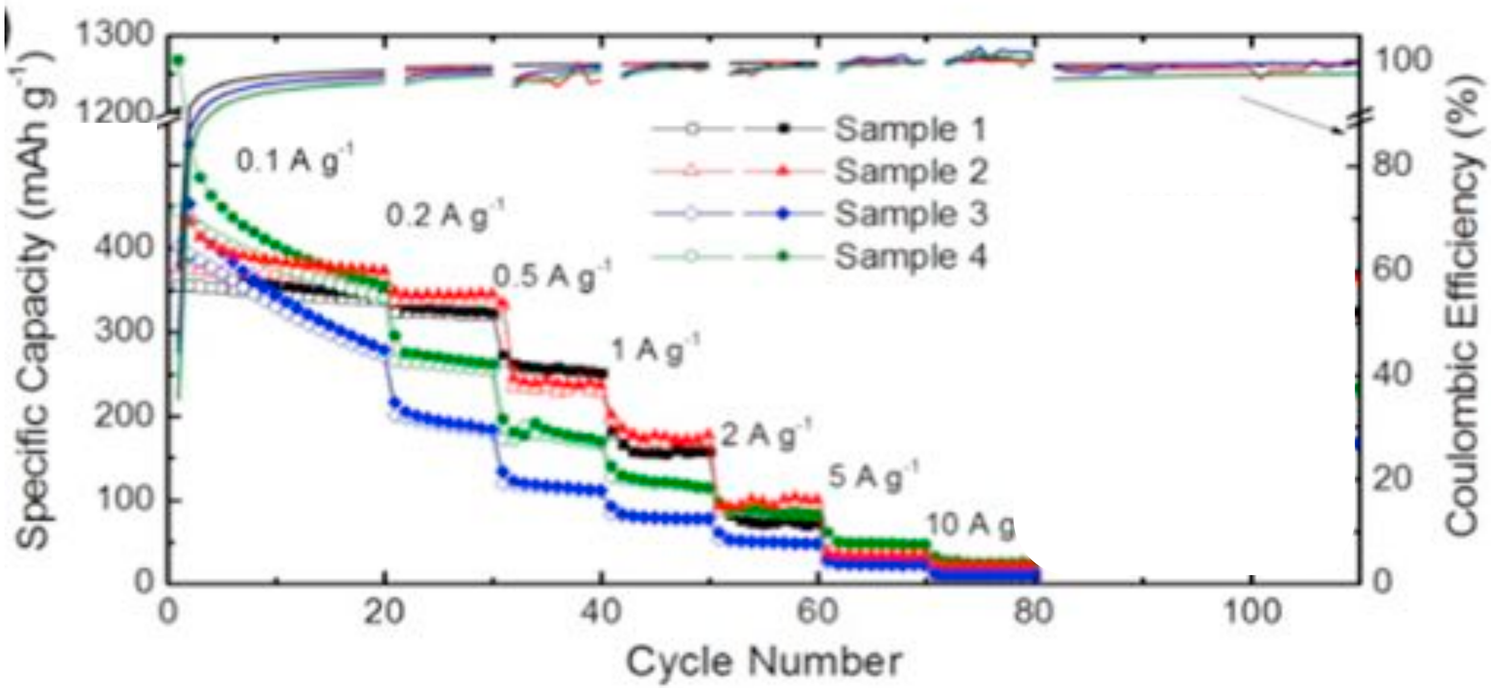






J. Hassoun, F. Bonaccorso, *et al.* Nano Lett. 14, 4901, 2014

Can Graphene replace graphite ?



(anode) oxidation reaction : $Li_2C_6 \rightarrow 2Li^+ + C_6 + 2e-$ **744 mAh/g**

F. Bonaccorso et al., Science (2015)
H. Sun al., Solid State Comm **251**, 88 (2017)
H. Sun et al., Journal of Mater. Chem. A **4**, 6886 (2016)

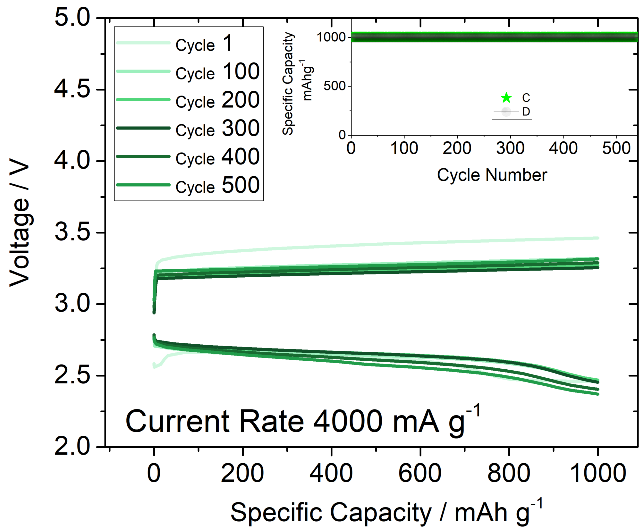
- Marginal improvement vs graphite
- Irreversible processes
- Cost

ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

BEDIMENSIONAL

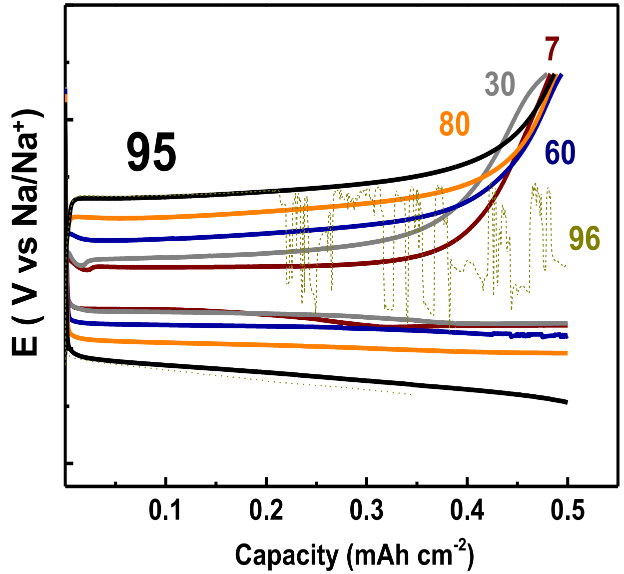
Graphene as active material

Cathodes in metal-O_2



Li-O_2

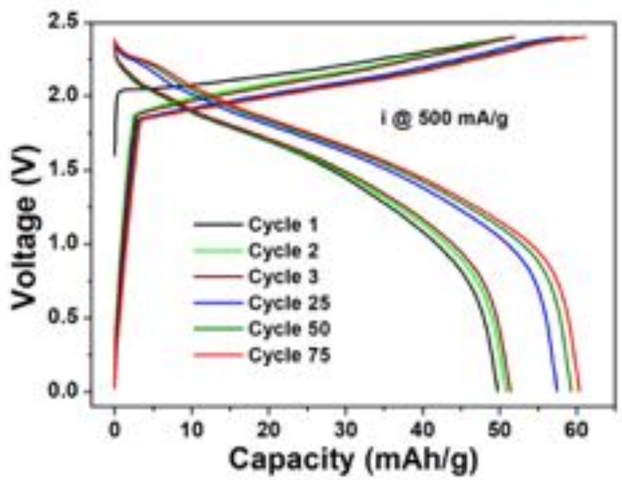
ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

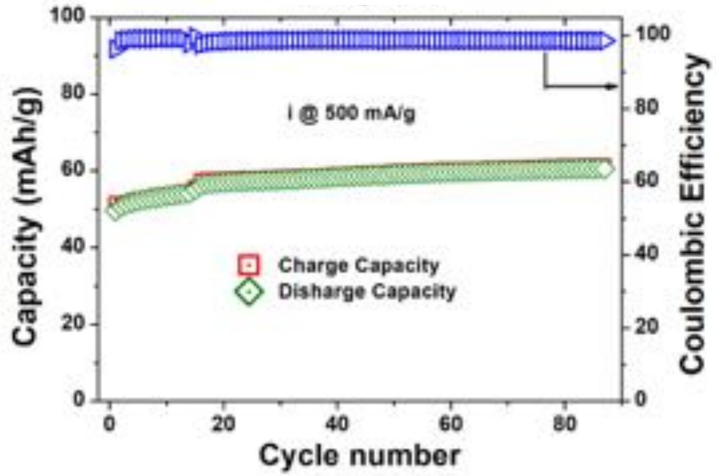


CIC energiGUNE energy storage research centre

Na-O_2

Cathodes in Al-ion



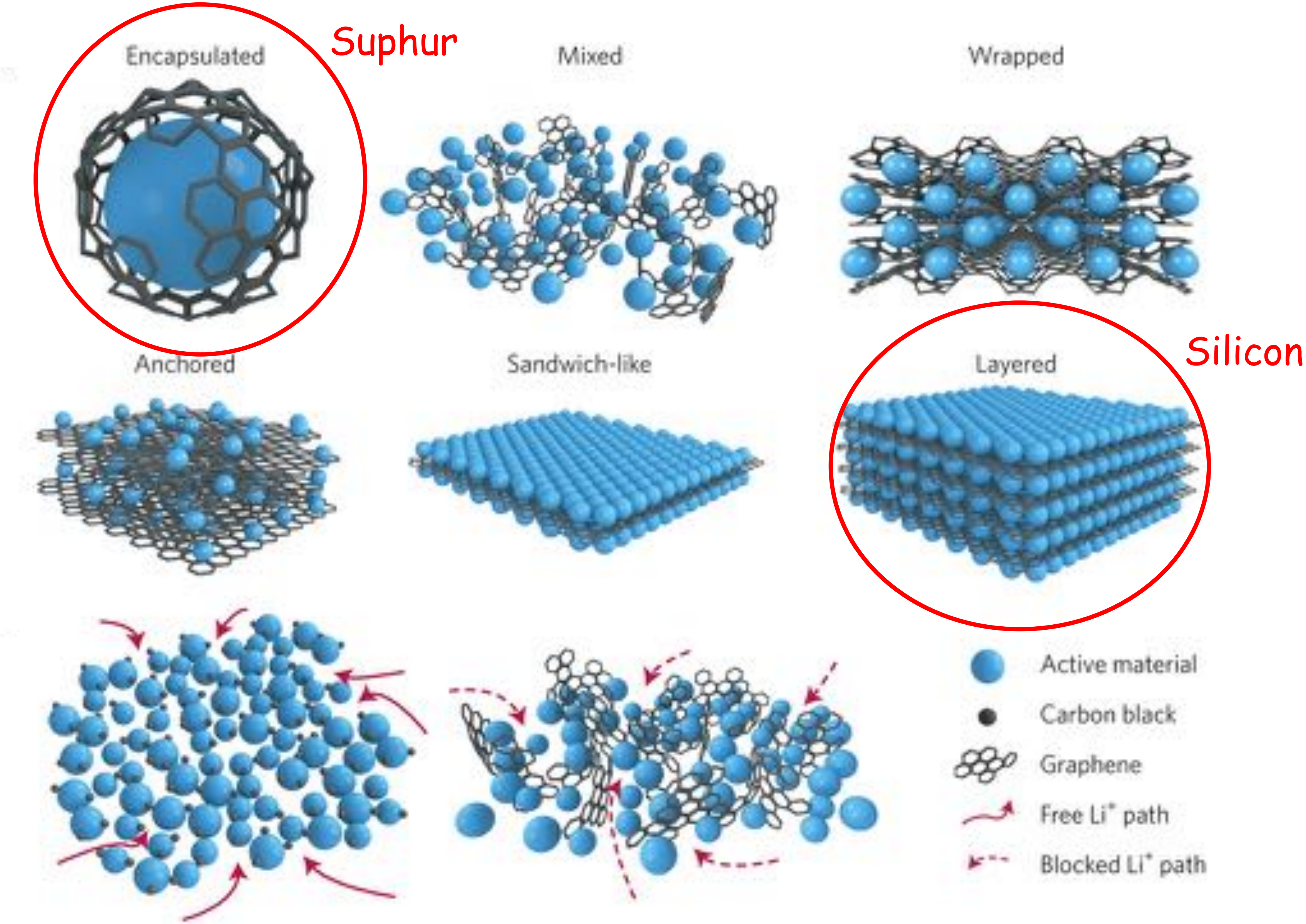


ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

Graphene as additive

- Mechanical flexibility
- Electrical Conductivity
- Tunable morphological properties
- Functionalization
- Price compatible with market requirements (depending on % of electrode mass)

Graphene as additive in Li batteries



ISTITUTO ITALIANO DI TECNOLOGIA
GRAPHENE LABS

Why Silicon

Silicon nanoparticle based anodes for Li-ion batteries

PLUS

Silicon expected capacity at room temperature:

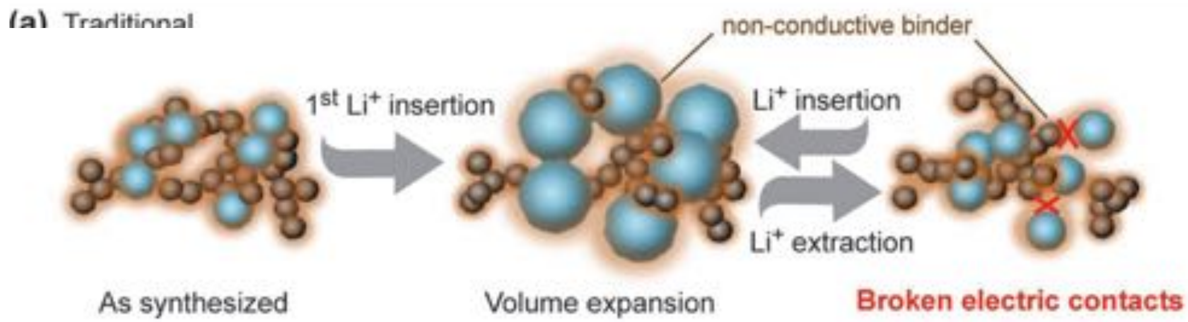
~ 3597 mAh/g ($Li_{15}Si_4$)

Discharge potential is low

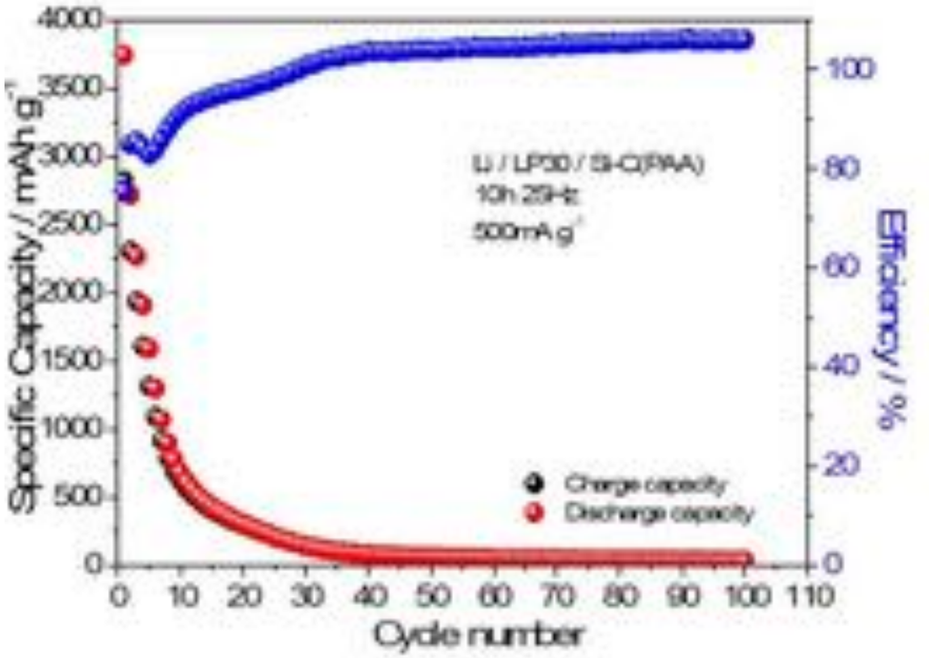
MINUS

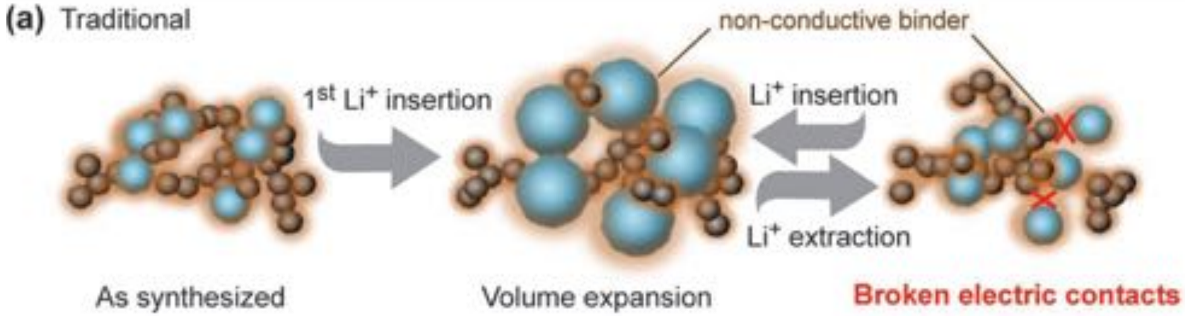
Large volume expansion (300%) → large irreversible capacity

Poor electrical conductivity

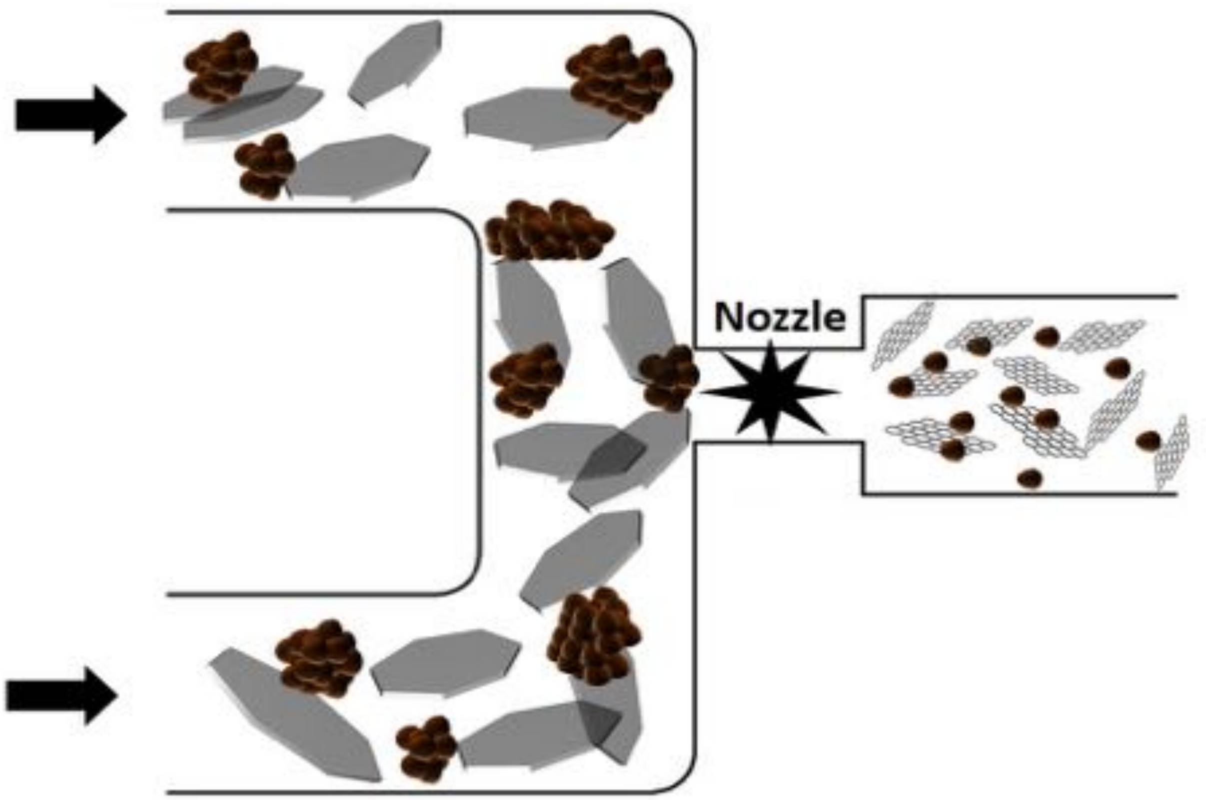


Silicon capacity fading





A new method of production

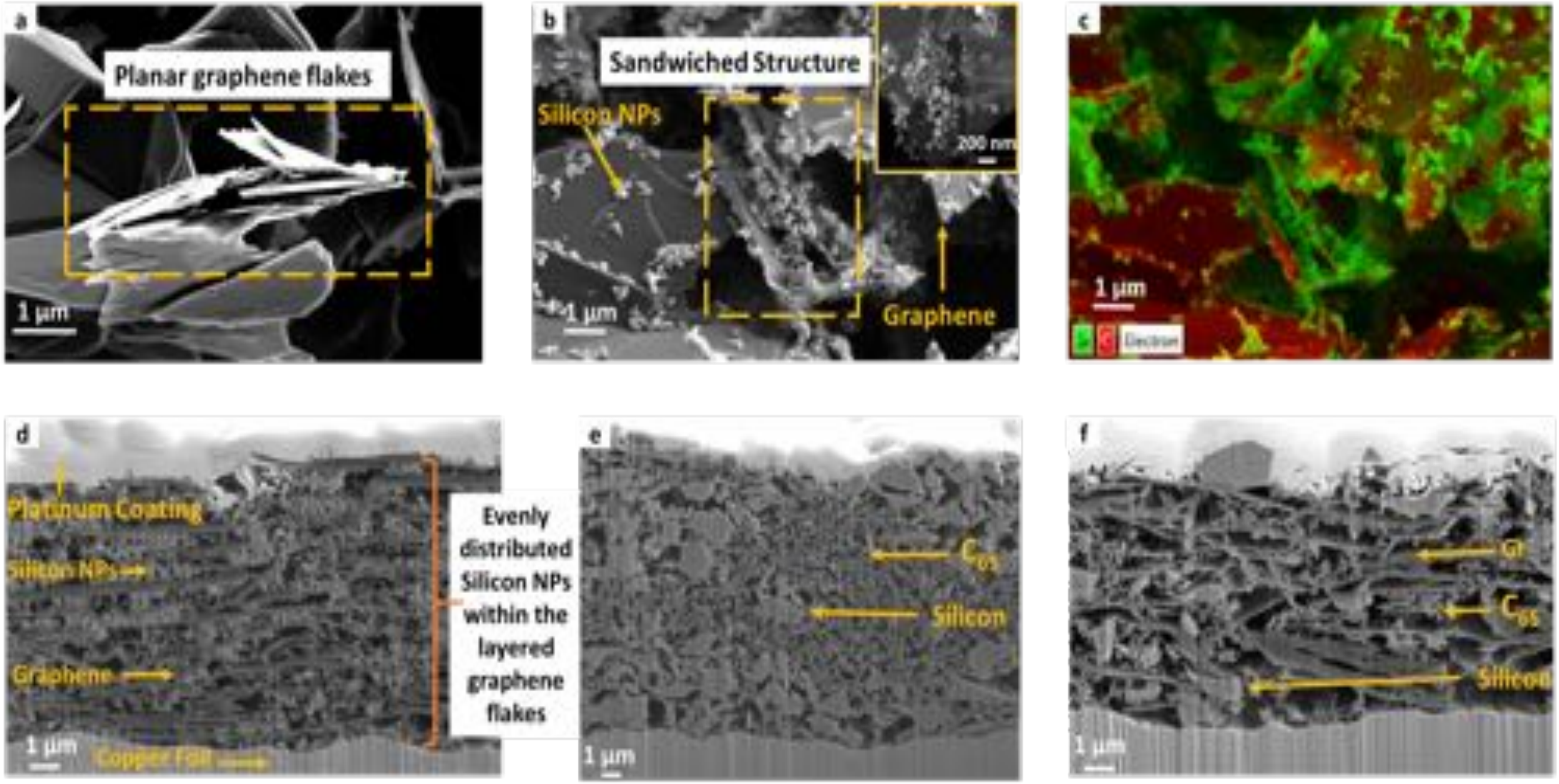


E. Greco et al, J. Material Chemistry A **5**, 19306 (2017)

S. Palumbo, L. Silvestri et al. ACS Applied Energy Materials (2019)

R. Maik, M. Loveridge, V. Pellegrini et al. submitted

Layered structure

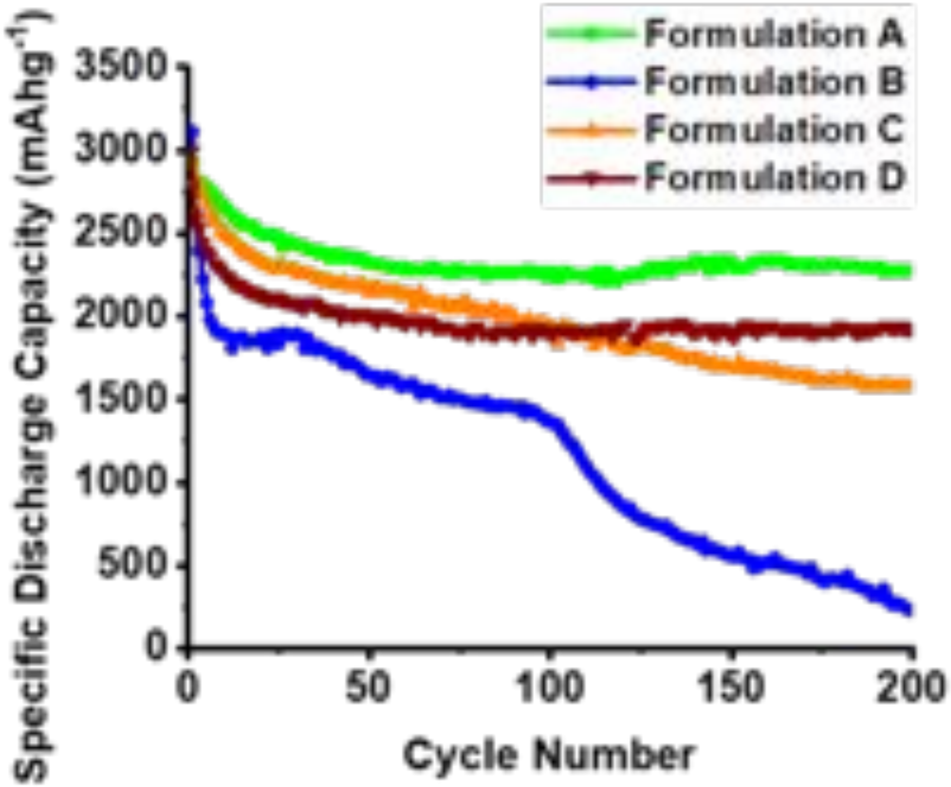


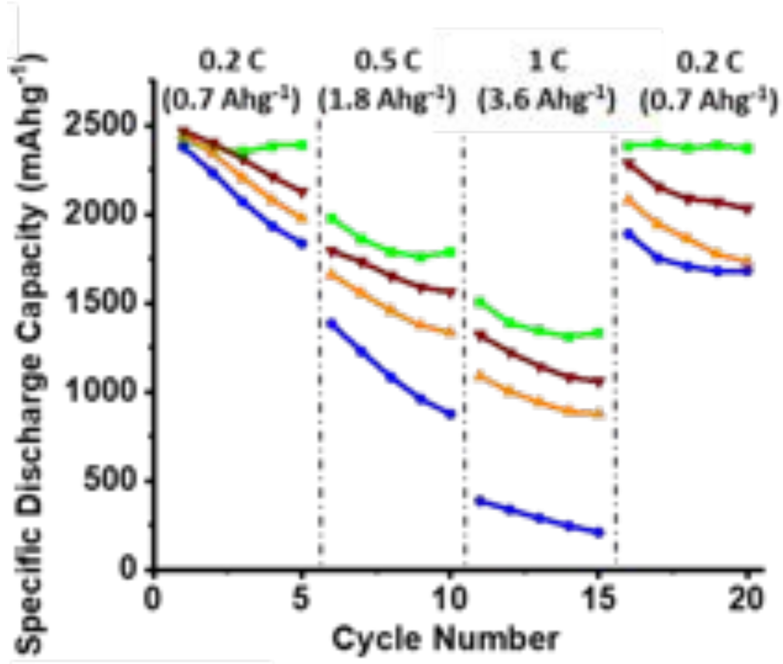
R. Maik, M. Loveridge, V. Pellegrini et al. submitted

ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

BEDIMENSIONAL

Exceptional electrochemical behavior





In collaboration with Melanie Loveridge (WMG)

R. Maik, M. Loverdige, V. Pellegrini et al. submitted

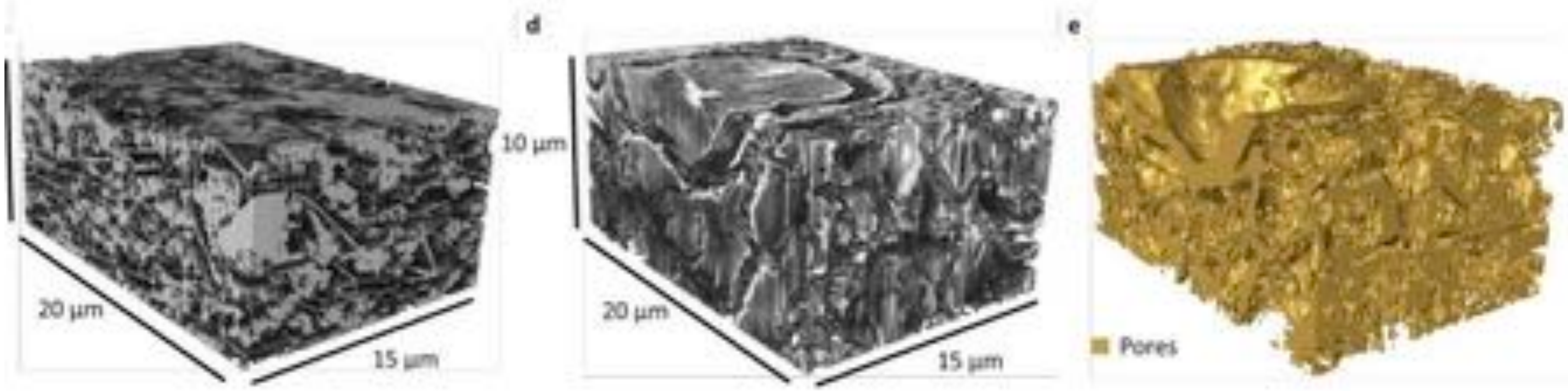
ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

BEDIMENSIONAL

Impact of graphene in silicon electrodes

Stabilization of the electrode's structure

→ facilitate movement of Li+ ions throughout the bulk of the electrode material during cycling



Pristine IIT Si-Gr electrode
Porosity: 34.40%

Cycled IIT Si-Gr electrode
Porosity: 29.21%

Pore volume reconstruction
of cycled IIT Si-Gr electrode

Decrease in porosity:

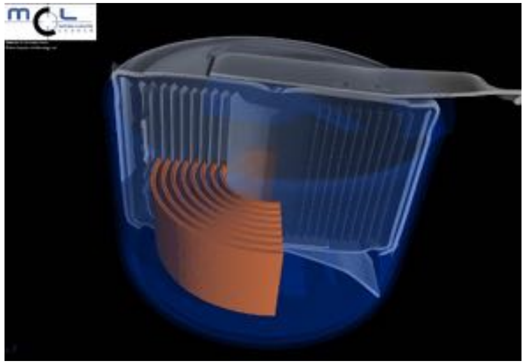
- **Silicon 75%** after 200 cycles
- **Silicon/Graphene 15%** after 200 cycles

ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

BEDIMENSIONAL

Silicon/Graphene - Prototyping

Format



BE DIMENSIONAL

Application

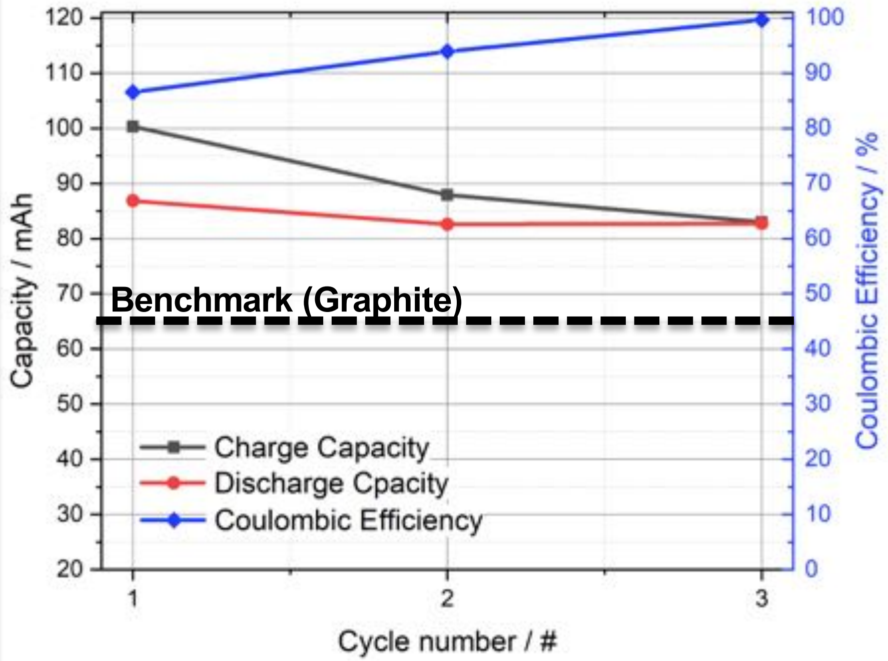
In-Ear Headset

Fitness Tracker

Smart Key

Insulin Patch

Current results



Parameter	Value
Total Capacity*	88 mAh (+35%**)
Total Energy*	300 mWh (+25%**)
Cyclability	tbd

*0.1C Discharge
** compared to benchmark

IIT GRAPHENE ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

GRAPHENE FLAGSHIP

VARTA micro innovation

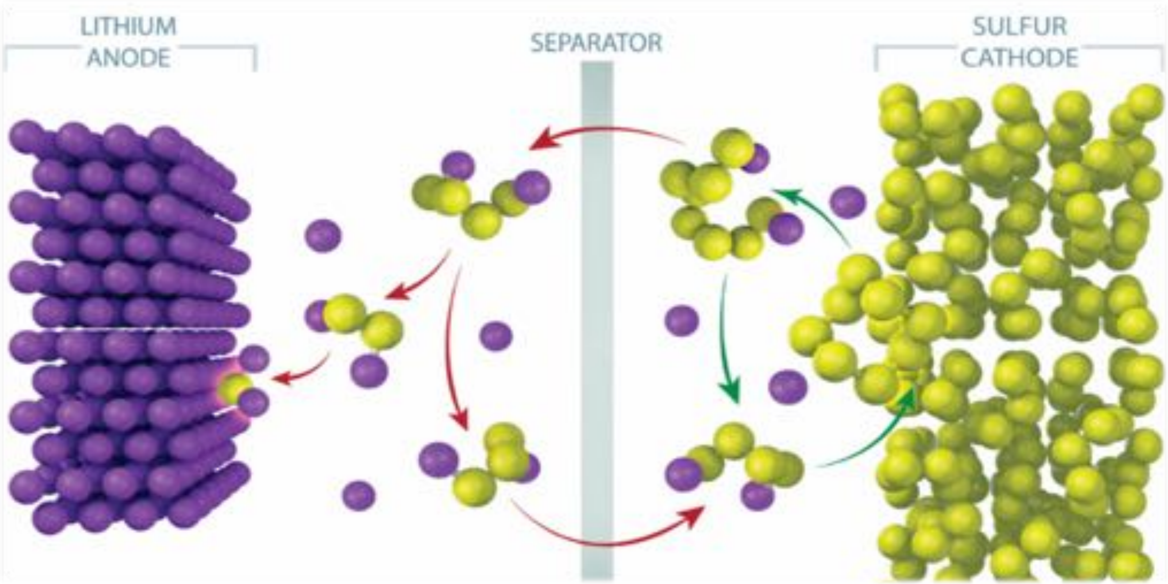
Sulfur rich graphene-based cathode

- Graphene in cathodes in Li-S

$$S_8 + 16Li^+ = 8Li_2S$$

1675 $mAhg^{-1}$ → 3500 $Whkg^{-1}$

Li-S : Drawbacks



Li_2S_8 , Li_2S_6 , Li_2S_4 , Li_2S_2

Li_2S

- Both sulfur and lithium sulfides are intrinsically insulated
- The intermediate discharge products lithium polysulfides are soluble in the organic electrolyte → loss of active materials
- The soluble polysulfide during the charge processes may migrate from the cathode to the anode, reacting on the anode surface producing an electrochemical short circuit well known as polysulfide shuttle effect

Sulfur-graphene cathode

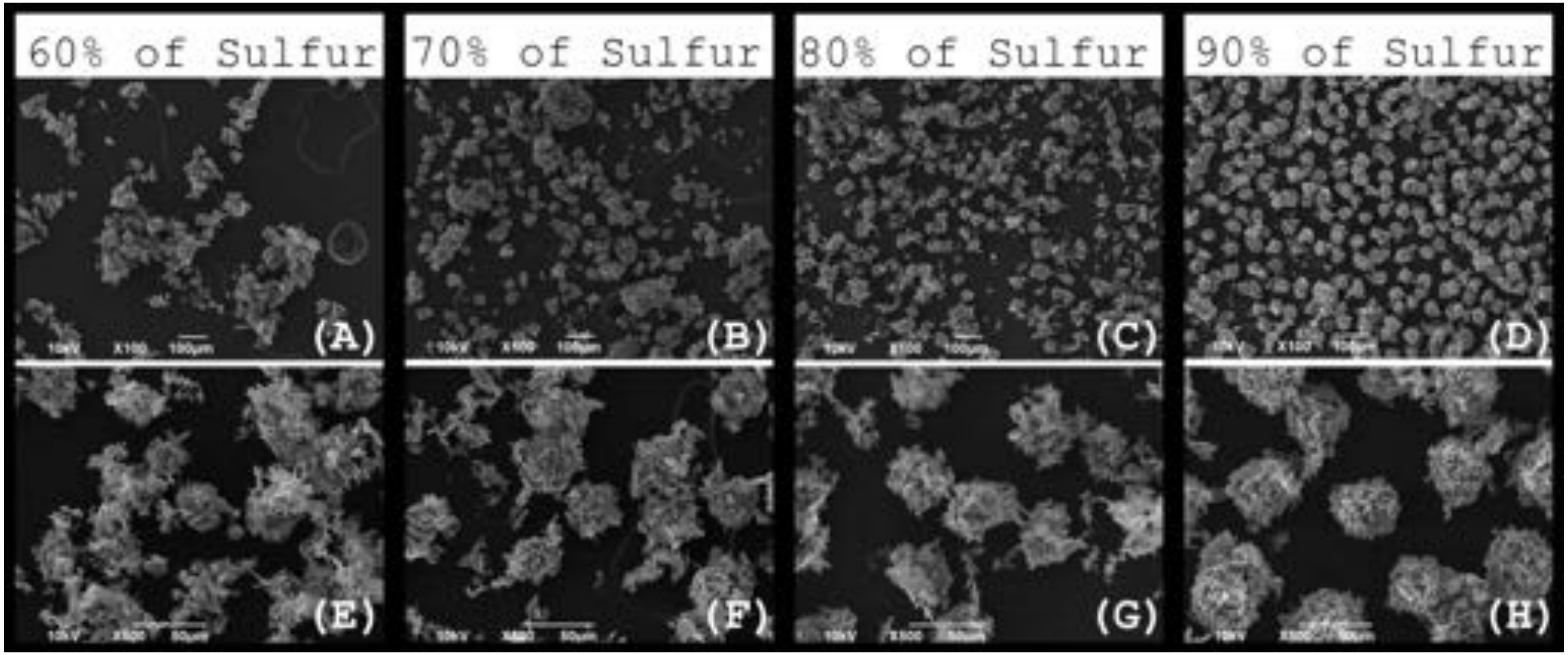
Patent Application
n° IT 102019000016178

- Before mixing, elemental sulfur was totally melted in ethanol solvent. The solution was added by graphene.
- The solution was dried under vacuum at different temperature in order to optimize the composite morphology

Sulfur-graphene material preparation

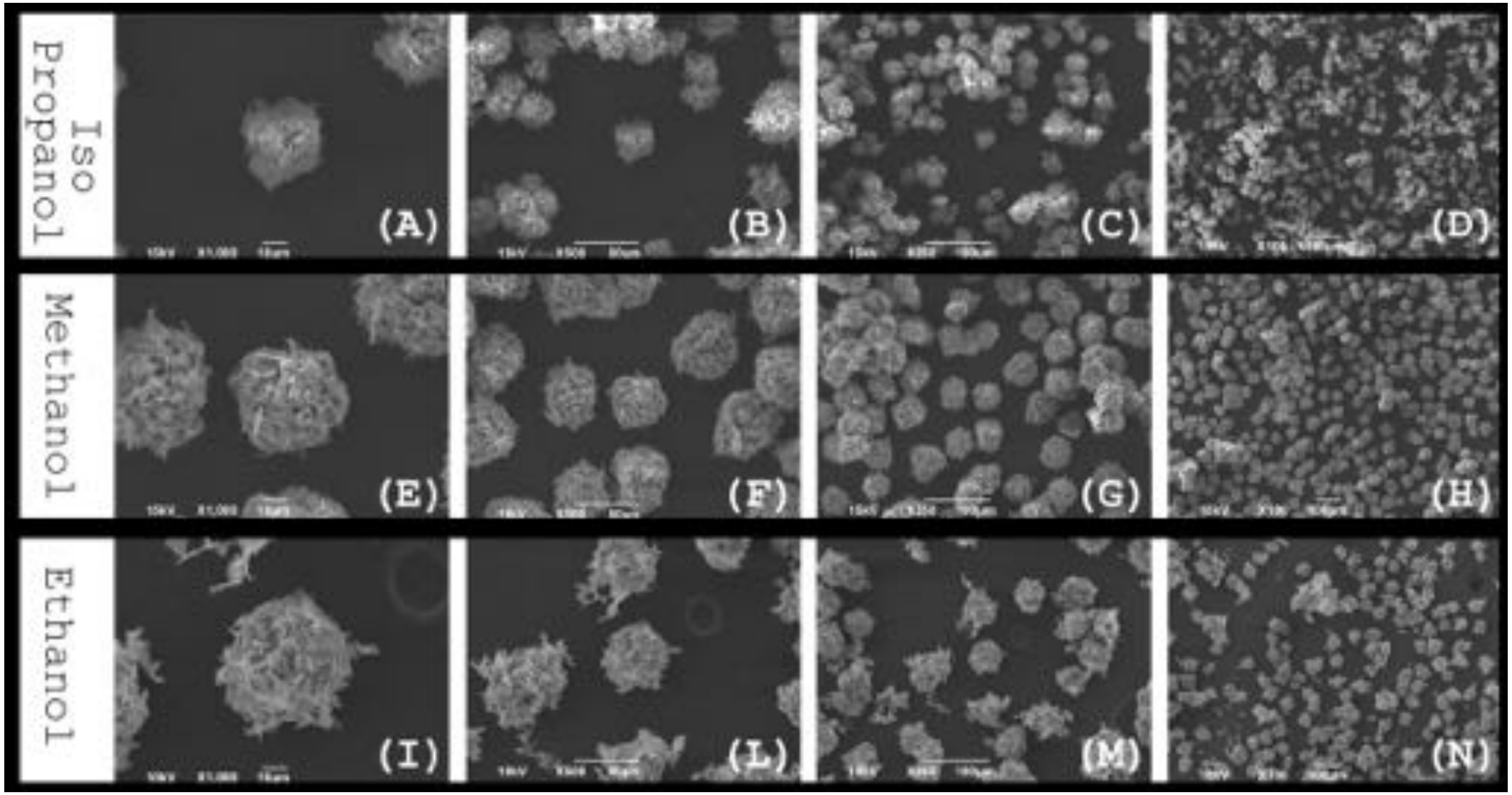
The sample morphology was further

optimized tuning the sulfur – graphene weight ratio



Sulfur-graphene material preparation

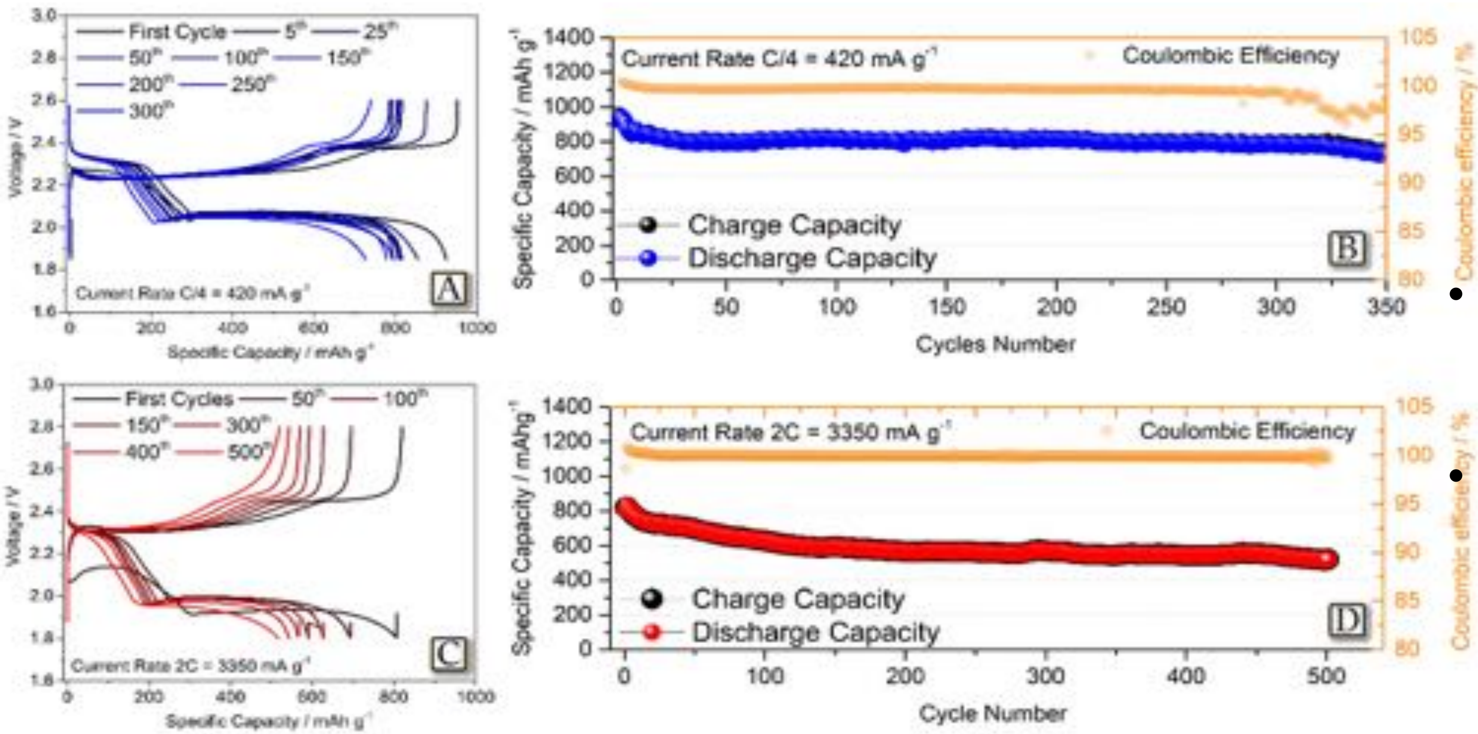
Patent Application
n° IT 102019000016178



ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

BEDIMENSIONAL

S-Graphene cathode



- Galvanostatic cycling 2032-coin cell with Cellgard separator soaked by 30 µl of electrolyte
- Electrolyte = DOL:DME-1:1, LiTFSI 1m, LiNO3 0.5 m
- Current Rate from C/10 = 167.5 mA/g 1.9V – 2.6V to Current Rate of 2C = 3350 mA/g, 1.8V – 2.8V

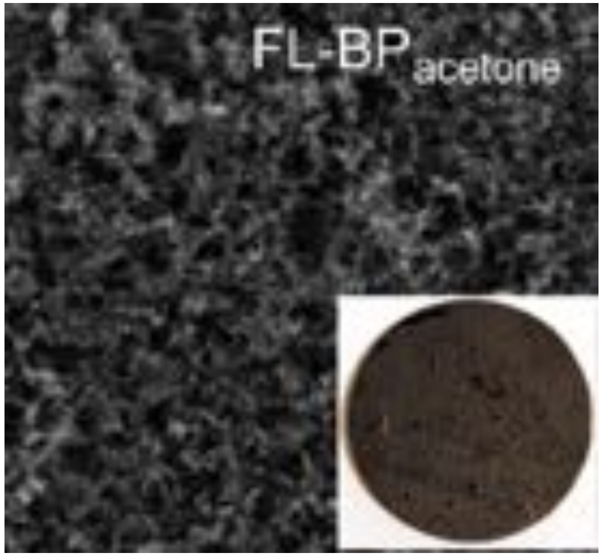
- Electrode = AM:Sp:PvDf = 80:10:10
- Sulfur Loading 2.5mg/cm^2

L. Carbone et al. *ChemSusChem accepted (2019)*

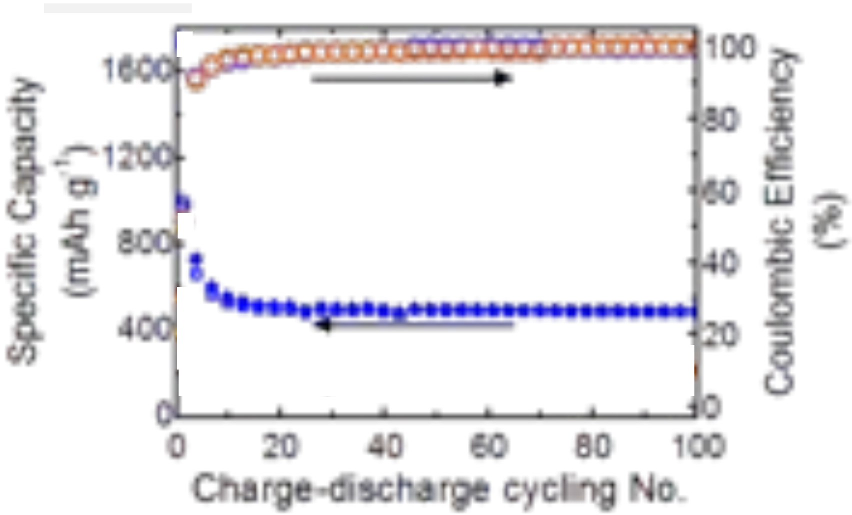
ISTITUTO ITALIANO DI TECNOLOGIA GRAPHENE LABS

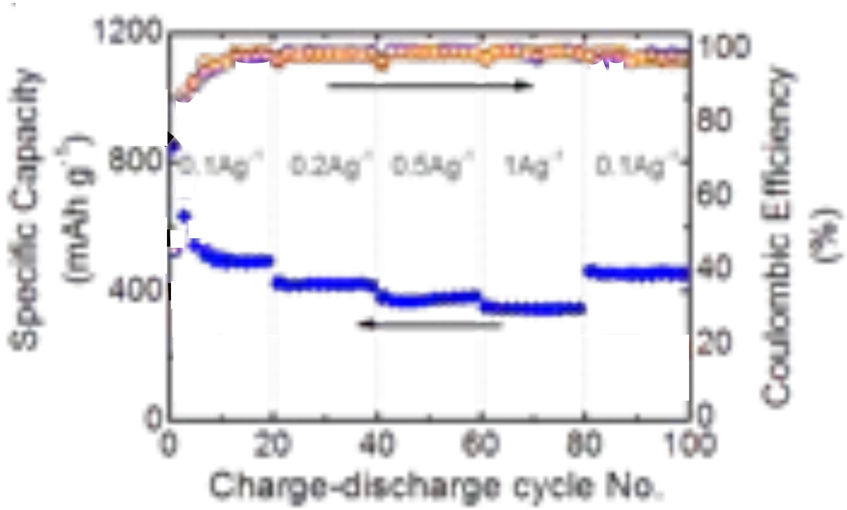
BEDIMENSIONAL

Beyond graphene



BP/Carbon Black/PVdF



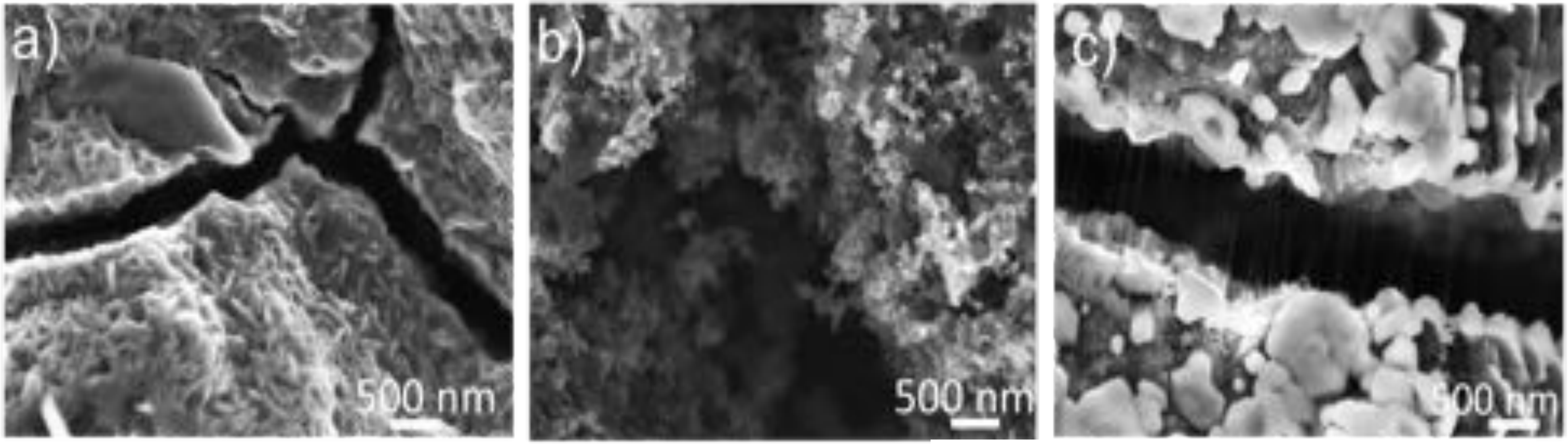


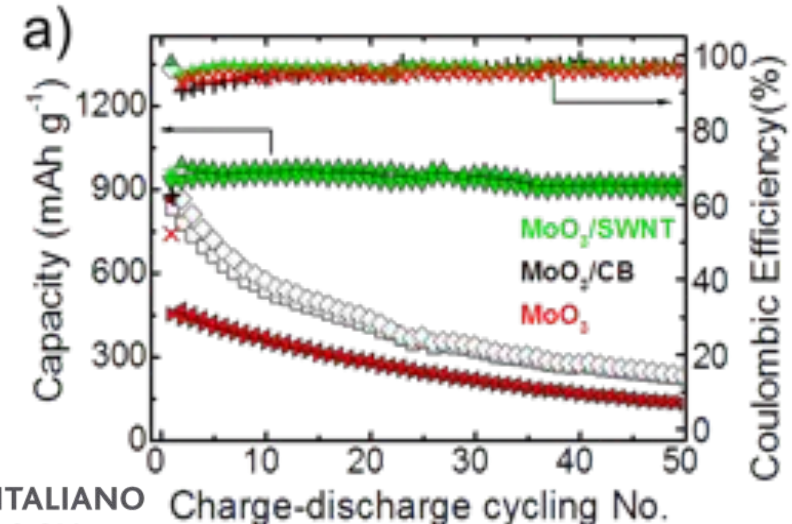
ISTITUTO ITALIANO
DI TECNOLOGIA
GRAPHENE LABS

A.E. del Rio Castillo et al. Chem. Mater. **30** 506 (2018)

Beyond graphene

Carbon nanotubes-bridged molybdenum trioxide nanosheets





In collaboration with
J. Coleman, Dublin

H. Sun et al. 2D materials **5** 015024 (2017)

ISTITUTO ITALIANO DI TECNOLOGIA
GRAPHENE LABS

Laura Silvestri
Stefano Paulumbo
Lorenzo Carbone
Antonio Esau Del Rio Castillo
Alberto Ansaldo
Francesco Bonaccorso
Eugenio Greco
Haiyan Sun
Gianluca Longoni
Sara Abouali
Eleonora Venezia
Shaikshavali Petnikota
Arcangelo Celeste

GRAPHENE FLAGSHIP

Elkem
A Bluestar Company

enel
Green Power

BEDIMENSIONAL


iit
GRAPHENE
ISTITUTO ITALIANO
DI TECNOLOGIA
GRAPHENE LABS