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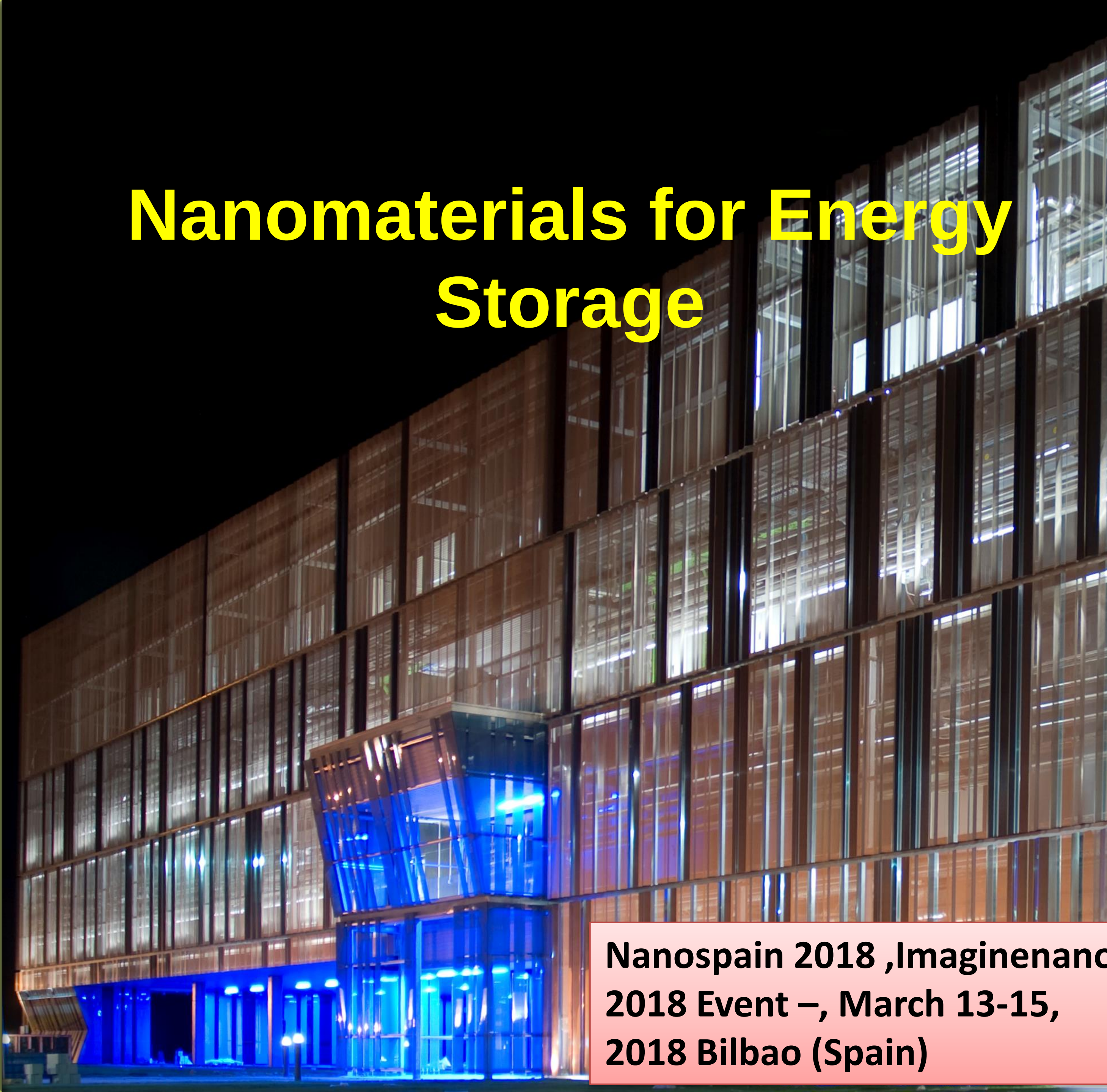

Nanomaterials for Energy Storage

Nanospain 2018 ,Imaginenan
2018 Event –, March 13-15,
2018 Bilbao (Spain)

2018

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Nanomaterials for Energy Storage

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Nanospain 2018 ,Imaginenano 2018 Event –, March 13-15, 2018 Bilbao (Spain)

- **Introduction**
- **Batteries:**
    - ☐ Nanostructured Anodes
        - Volumetric expansion
        - Critical particle size
        - Active materials aggregation.
- **Supercapacitors:**
    - ☐ Double Layers
    - ☐ Hybrid
- **Conclusions**

Key Energy Storage Technologies

Pumped hydro power energy storage

Water is pumped to a reservoir at a higher elevation as potential energy

Compressed air energy storage

Electricity is used to compress air into an air reservoir to operate an air generator later

Flywheels

Electric energy is converted to mechanical energy in a flywheel that spins at a very high velocity which can be converted back to electric energy at a later time

Batteries and capacitors

Electrochemical way to store energy

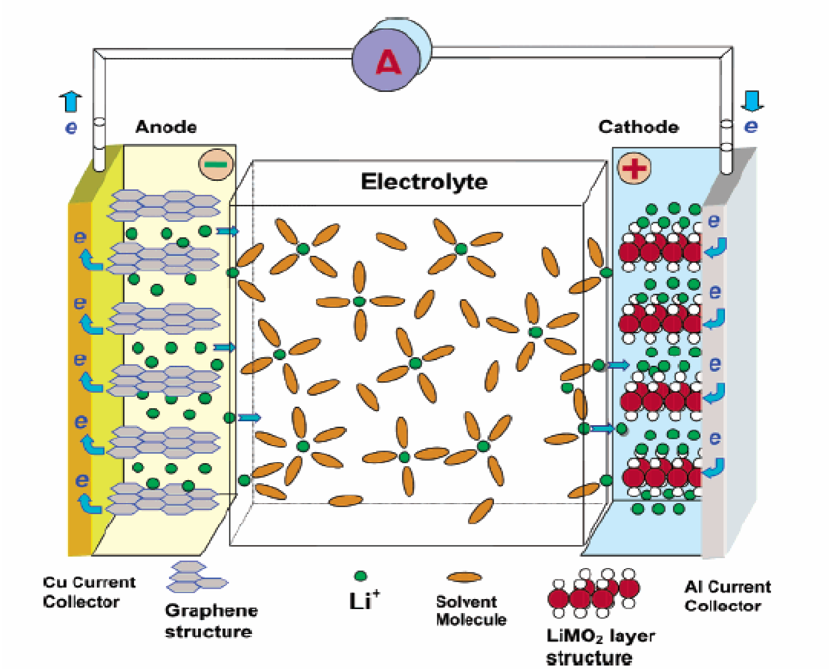
Superconducting magnetic energy storage

Energy is stored in a magnetic field created by the flow of direct current in a superconducting coil

Electrochemical Energy Storage

Advanced Batteries

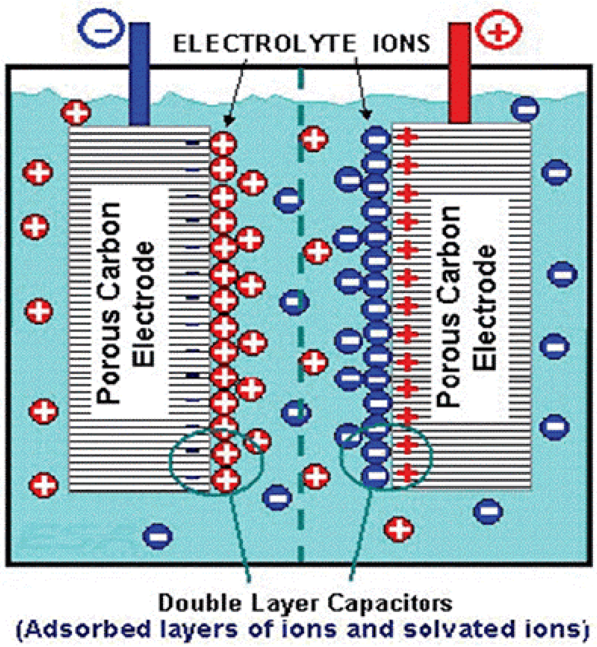
Electric energy is stored by the conversion of chemical energy through redox reactions between the anode and cathode.



US Department of Energy, 2007

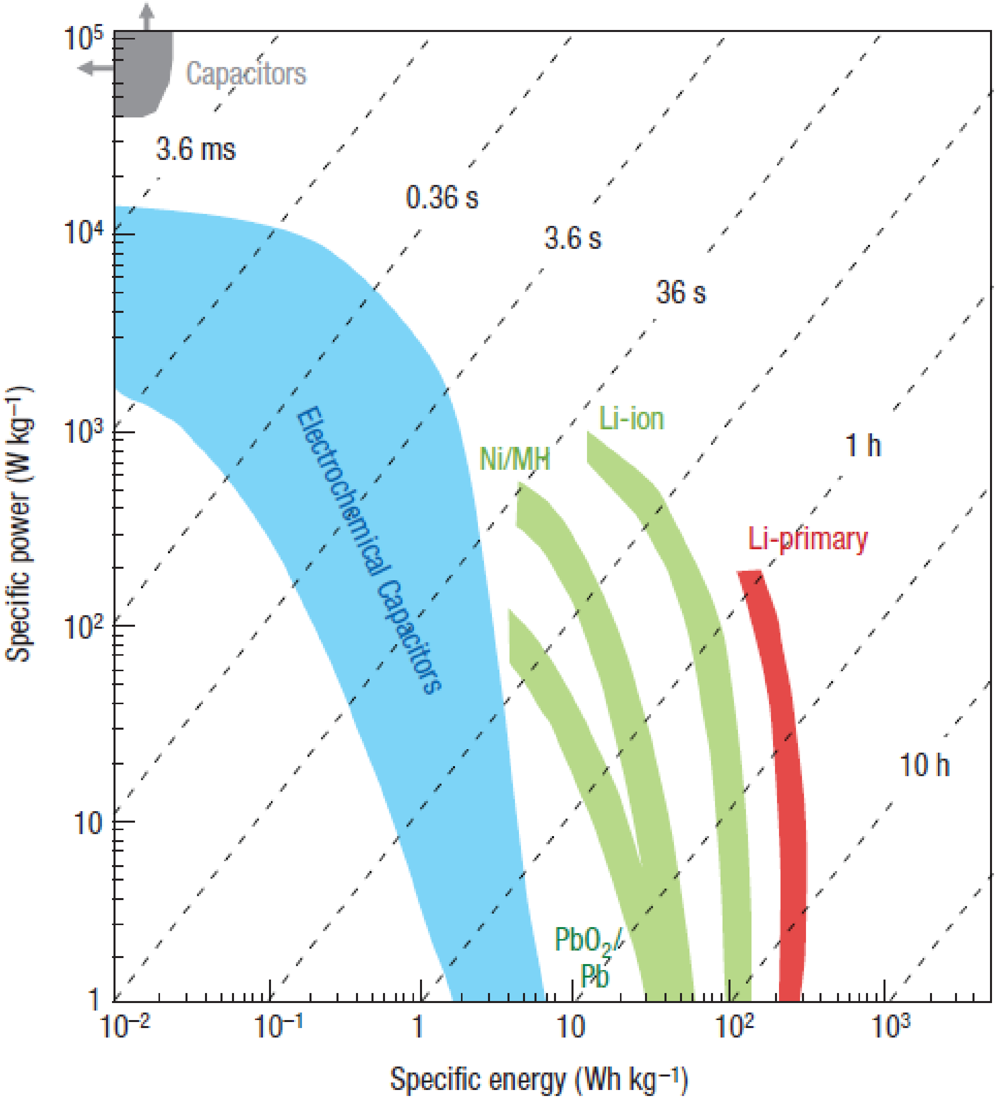
Supercapacitors

Electric energy is stored physically in the electrochemical double layer at the electrolyte-electrode interface.



http://www.ic.gc.ca/eic/site/wei-iee.nsf/eng/00177.html

Electrochemical Energy Storage



Advanced Batteries

- Higher energy density
- Lower power density
- Short cycle life
- Low self discharge

Supercapacitors

- Higher power density
- Lower energy density
- Long cycle life
- High self discharge

Nanostructured materials

Advantages

- May conveniently modify the chemical potential and ***facilitate the alkali ion insertion***
- An increased surface to volume ratio ***enhances electron transfer rates*** and decreases ion diffusion length
- An increased surface area available for contact with the electrolyte ***increases the charge transfer***
- Shorter diffusion length leads to increased ion diffusion ability, thus remarkably ***improved reaction kinetics***, i. e. rate capability
- The nanostructured morphology is ***less affected by the volume expansion***, it can accommodate morphological and structural changes

Disadvantages

- High surface area results in <u>**remarkably increased reactivity towards electrolyte decomposition**</u>
- Nanoparticles have <u>**low density**</u>, which **negatively affects the volumetric density** of the battery
- <u>**Nanoparticle aggregation (clustering)**</u> due to the van der Waals interactions is a challenge that has to be overcome for promoting uniformly distributed nanostructured materials for battery applications
- The inability to control the size and shape of the nanoparticles leads to an <u>**increase in the manufacturing cost**</u>

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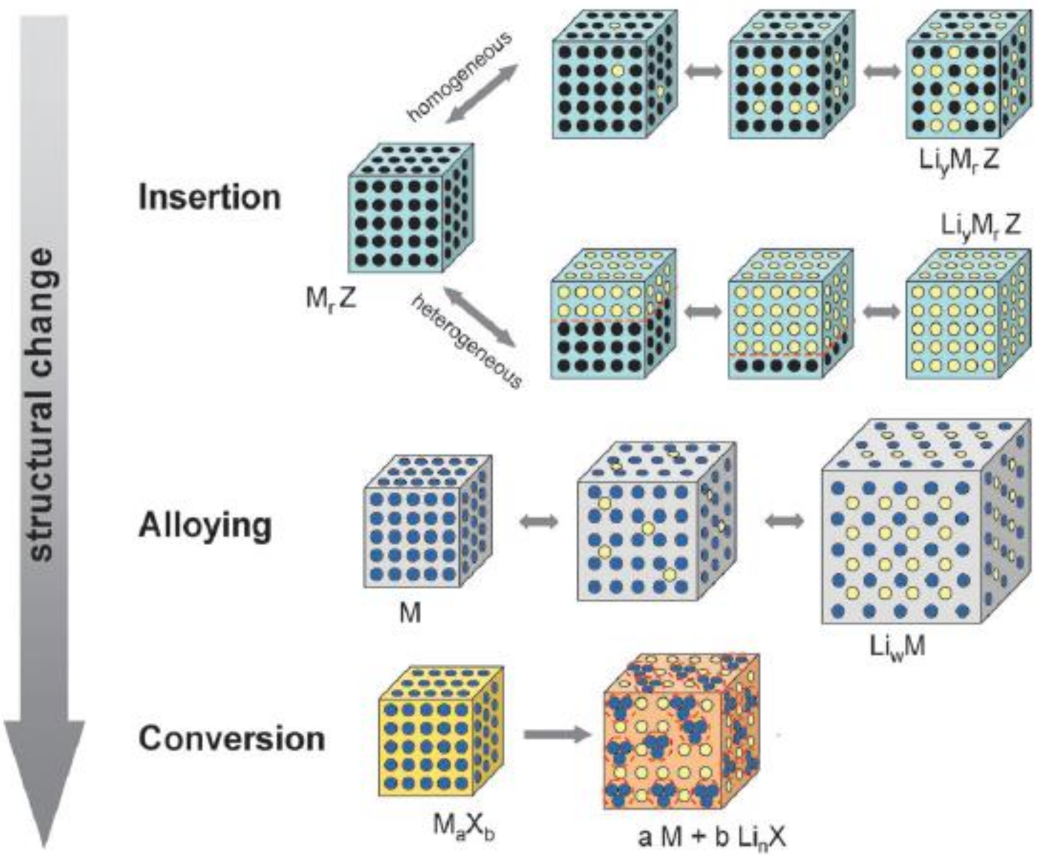
  - ☐ Hybrid
- **Conclusions**

Reaction mechanisms in electrode materials



"Usual" processes

Low capacity
(mostly limited to 1 e^- / M)

Commercialised

Very large capacity

Volume changes
are still an issue

Under development

Large capacity

Voltage hysteresis

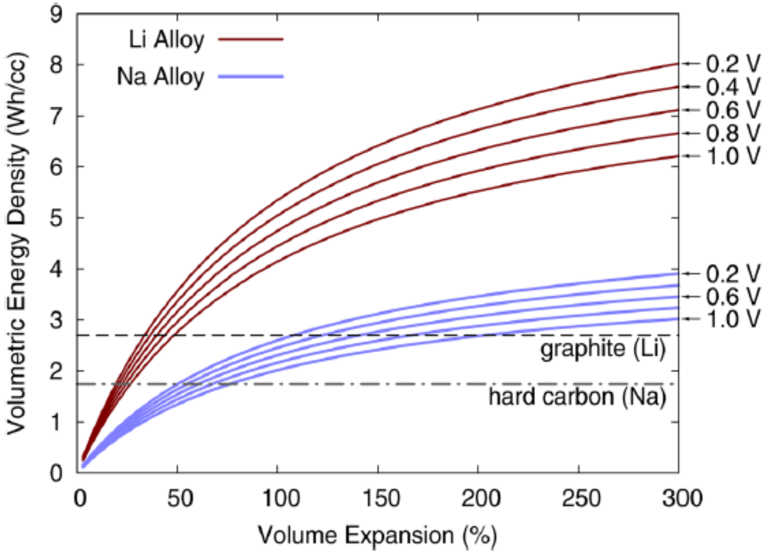
$$n\mathrm{Li}^+ + ne^- + \mathrm{M}^{n+}\mathrm{X} = \mathrm{M}^0 + \mathrm{Li}_n\mathrm{X}$$

R.Palacin , *Chem.Soc.Rev.*, 38,2565 (2009)

Nanostructured Anode Materials

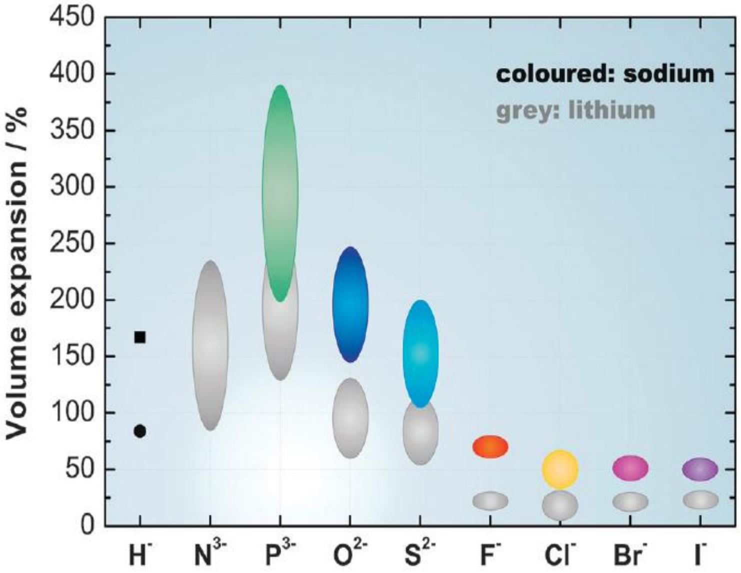
Li and Na alloying and conversion reactions induce large volume changes which cause mechanical stress, particle fracture and cell failure

Alloying materials



- ○ Ionic radius $Na^+ > Li^+$
- ○ Volume changes $Na^+ \sim Li^+$
- ○ Energy density $Na^+ < Li^+$

Conversion reactions



Sodium based materials exhibit somewhat larger expansion than their Li counterparts.

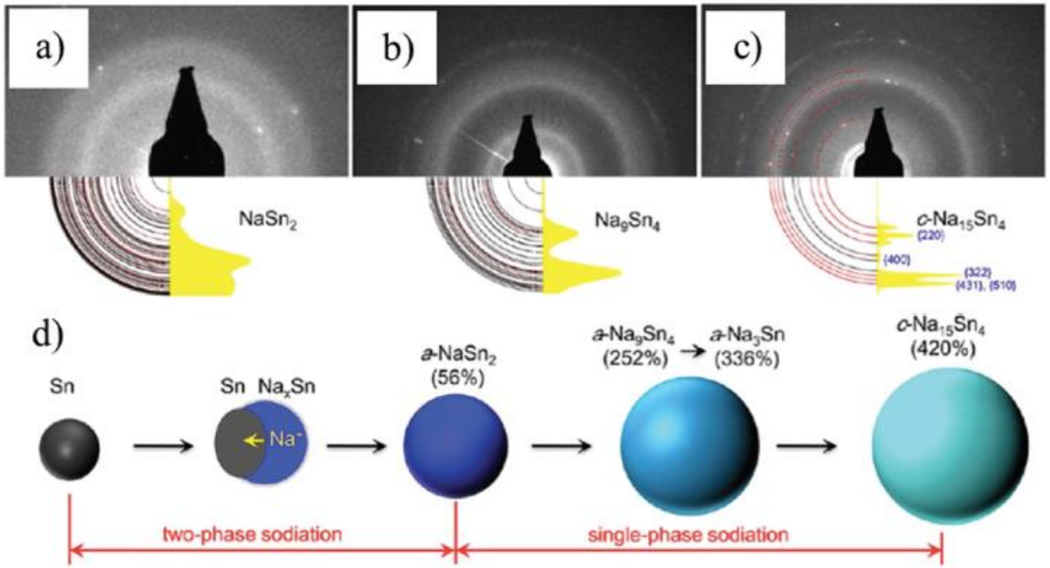
Chevrier V.L., Ceder G., J. Electrochem. Soc., 2011, 158(9), A1011-A1014

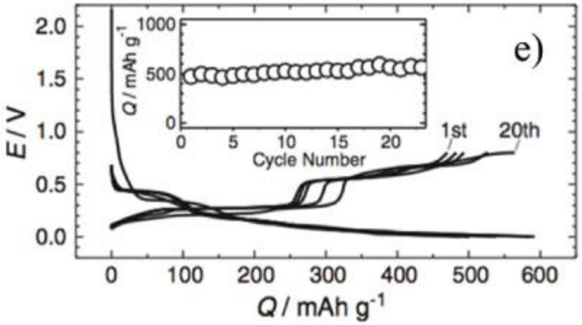
F. Klein et al., Phys. Chem. Chem. Phys., 2013, 15, 15876-15887

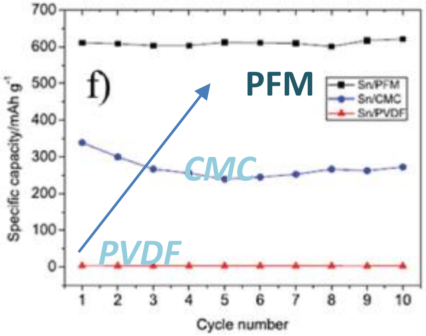
Nanostructured Anode Materials

Overcoming the volume expansion effects: Nanoparticles embedded in C derivatives

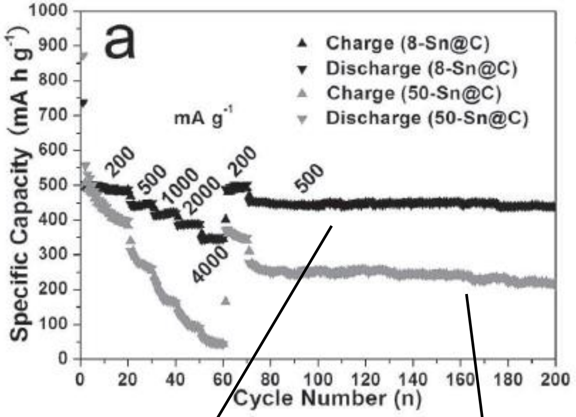
Sodiation mechanism of Sn nanoparticles and accompanying volume expansion

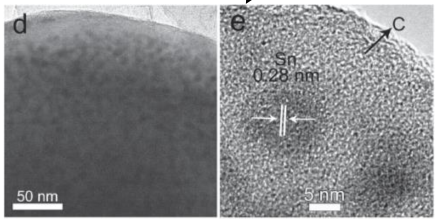


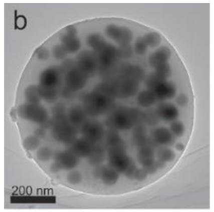




8 nm vs 50 nm Sn nanoparticles embedded in C spheres







J.W. Wang et al., Nano Lett., 2012, 12, 5897

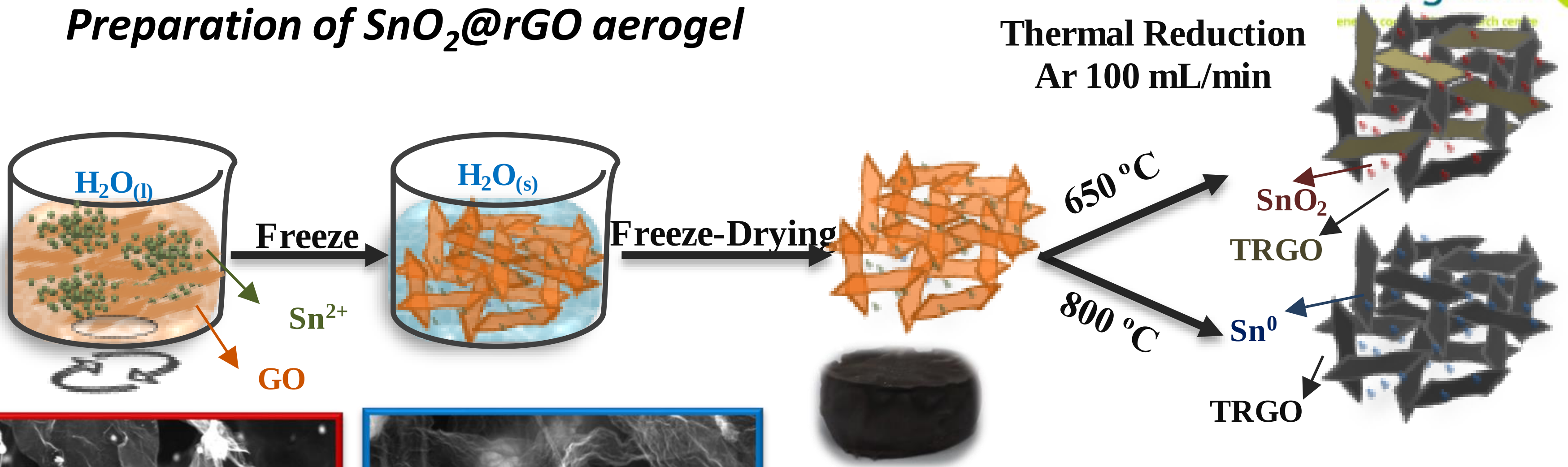
S. Komaba et al., Electrochem. Commun., 2012, 21, 65

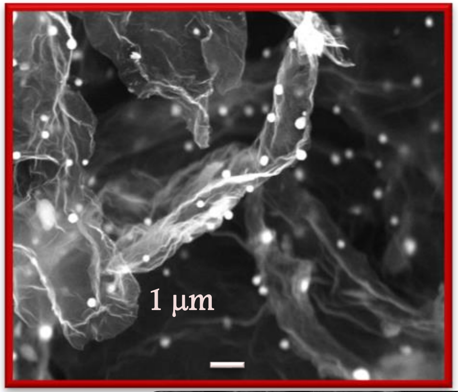
K. Dai et al., J. Power Sources, 2014, 263, 276

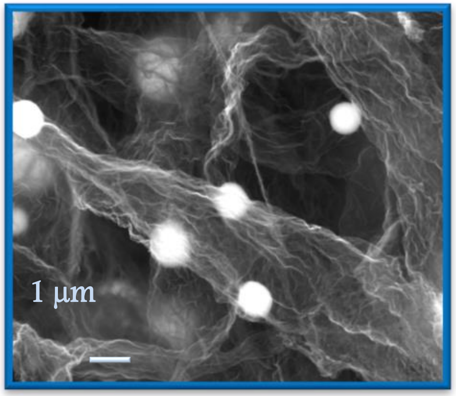
Y. Liu et al., Adv. Funct. Mater., 2015, 25, 214-220

Nanostructured Anode Materials

Preparation of SnO_2@rGO aerogel



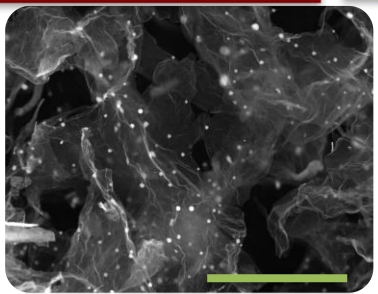




SnO_2 nanoparticles

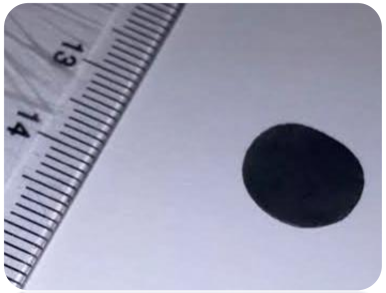
SnO_2@rGO →650

Sn@rGO-800 → 800



Binder-Free
Without additives

Flexible



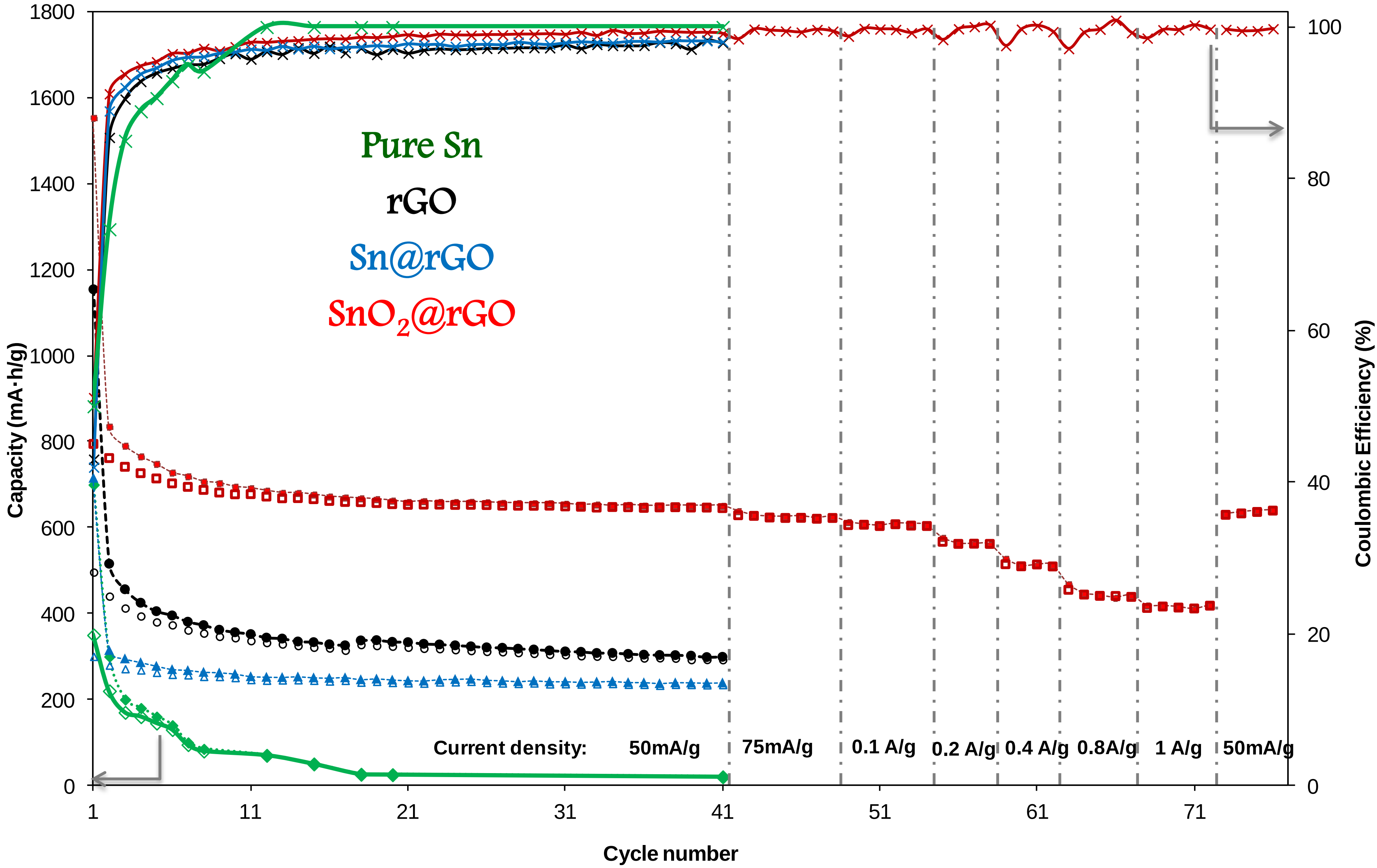
Self-standing
(No Copper)

Without organic
solvents

C. Botas et al. *J Mater Chem A* **2015,3, 13402**

Nanostructured Anode Materials

SnO_2@rGO aerogel as anode for LIBs

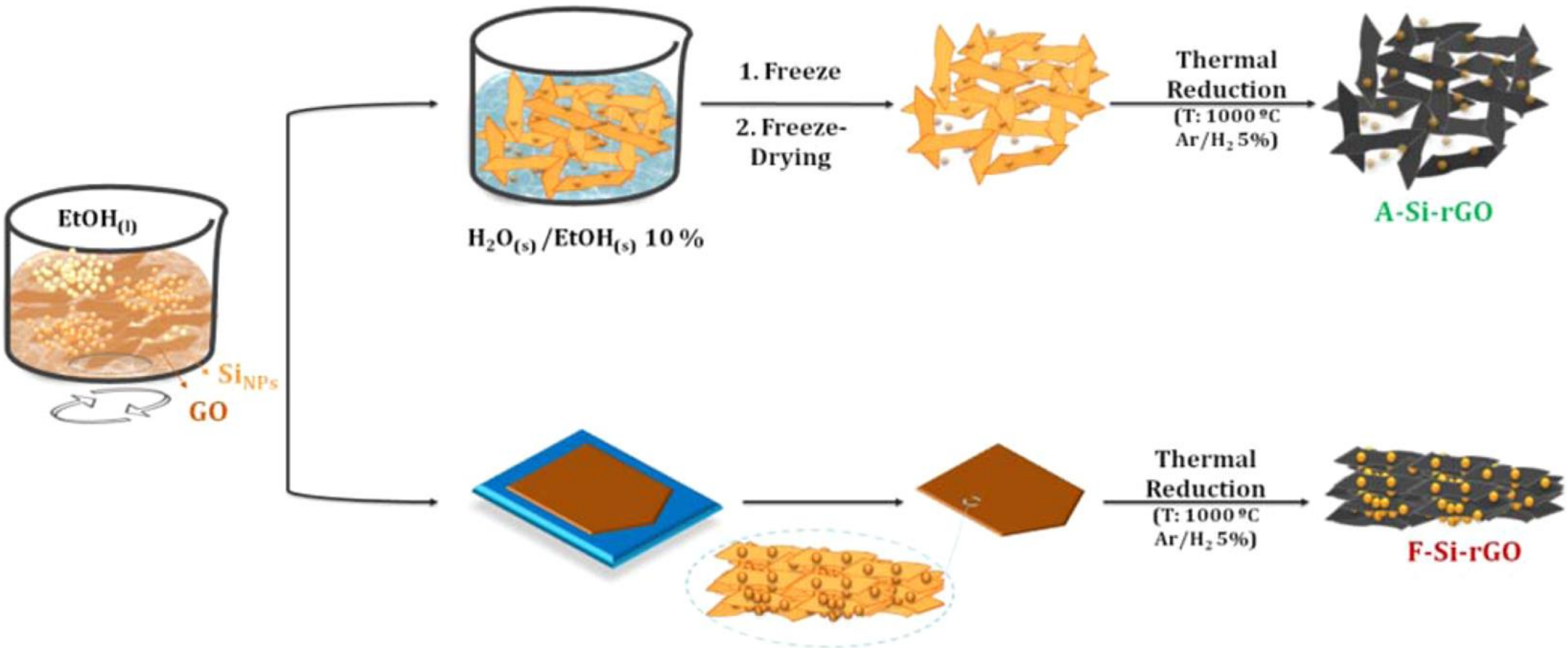


C. Botas et al. *J Mater Chem A* 2015,3, 13402

Nanostructured Anode Materials

Silicon-Reduced Graphene Oxides

Synthetic Routes for the preparation of selfstanding aerogels (A-Si-rGO) and films (F-Si-rGO)

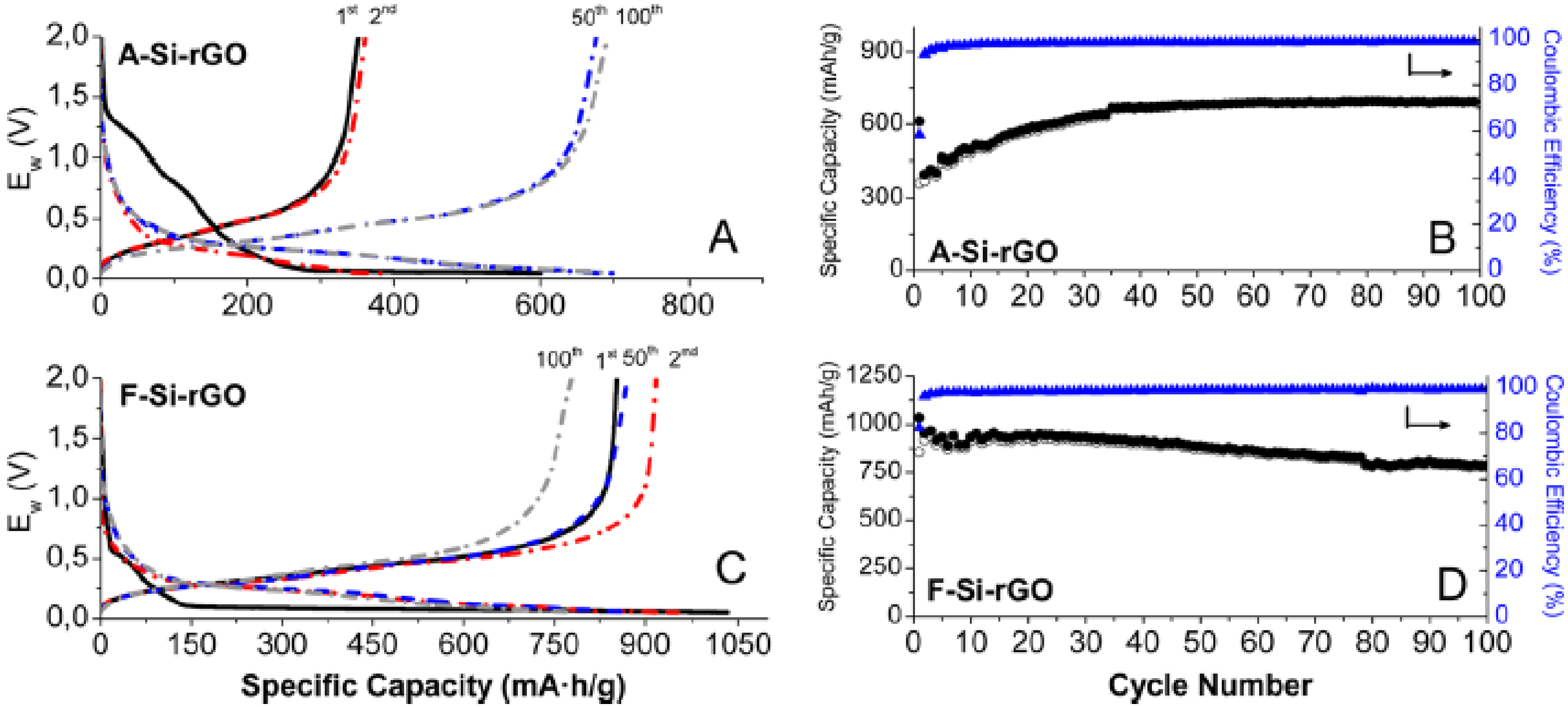


- The composites are formed by rGO sheets homogeneously decorated with 50 nm silicon nanoparticles with silicon contents of appr. 40% wt.
- In the case of the films, a certain amount of suspension was simply casted into a silicon rubber mold and allowed to dry.
- They can be directly assembled into the coin cell without adding any binder or using any metallic support to be tested as an anode for LIBs.

C.Botas et al, *ACS Appl.Mater.Interfaces* 2016,8,28800-28808

Nanostructured Anode Materials

Electrochemistry behaviour



- ➢ First cycle of the **A-Si- rGO SEI formation** and reaction between **lithium and graphene sheets**.
- ➢ **Subsequent cycles** are characteristic of the **lithiation of amorphous silicon nanoparticles.**

- ➢ First cycle of the **F-Si-rGO SEI formation and the irreversible reaction** between the lithium and the functional groups still present within the graphene sheet.
- ➢ A **long plateau** at ca. 0.08 V, characteristic of the **alloying of crystalline silicon with lithium**.

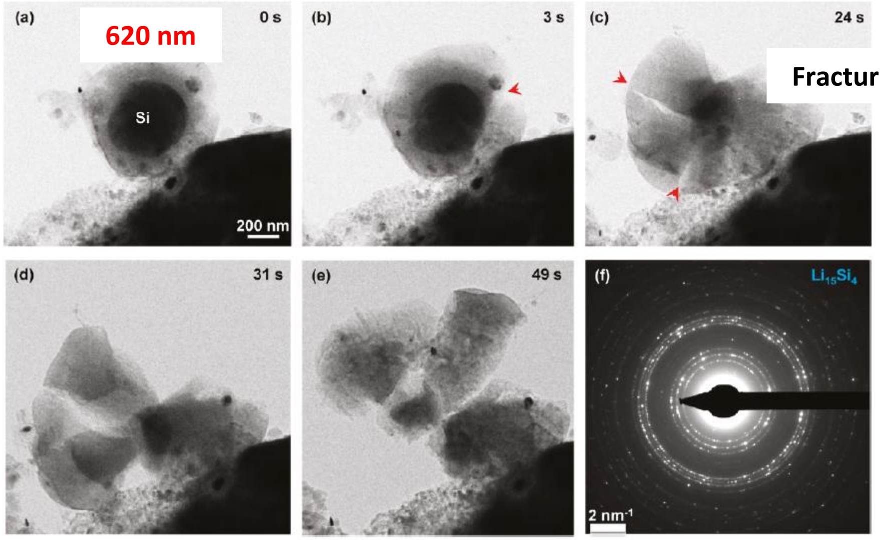
C.Botas et al, *ACS Appl.Mater.Interfaces* 2016,8,28800-28808

Nanostructured Anode Materials

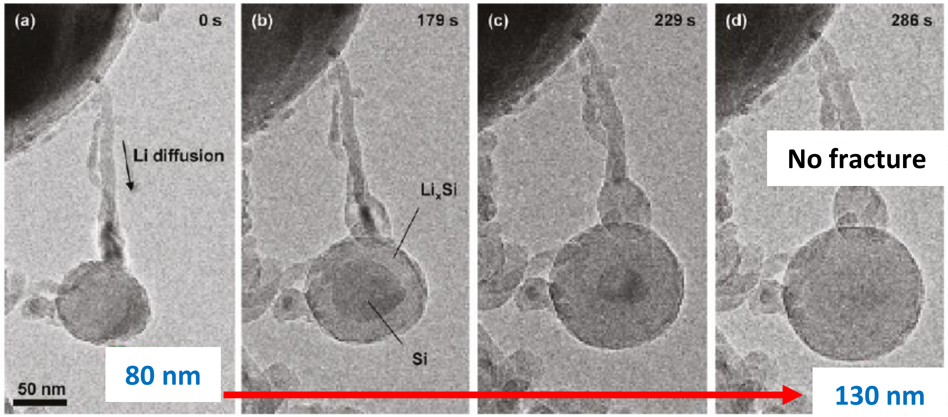
Critical particle size

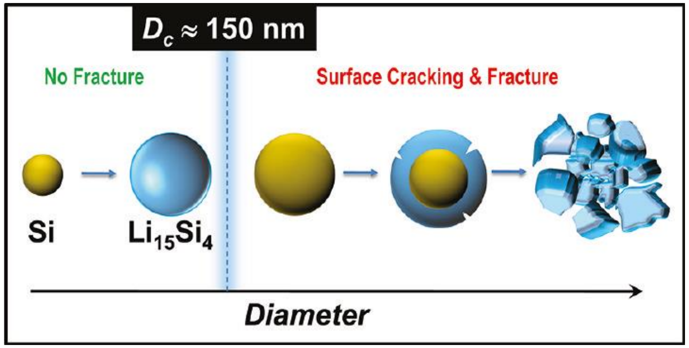
Lithiation of Silicon nanoparticles

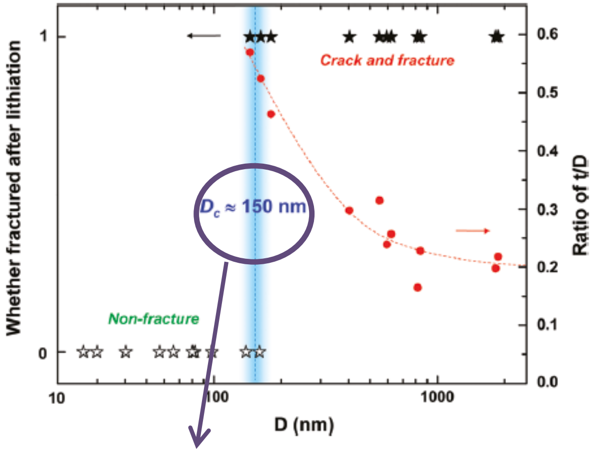
Sub-micrometric



Nanometric







Critical size for Si nanoparticles

Effects of volume changes:

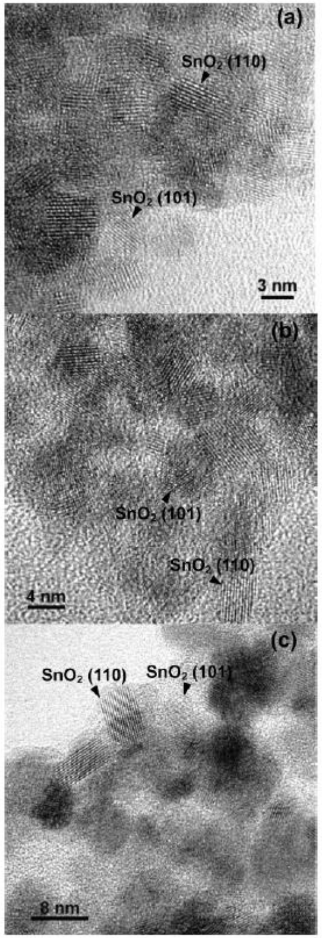
- Morphology and surface evolution
- Particle fracture above a critical size (<u>different for each material)</u>

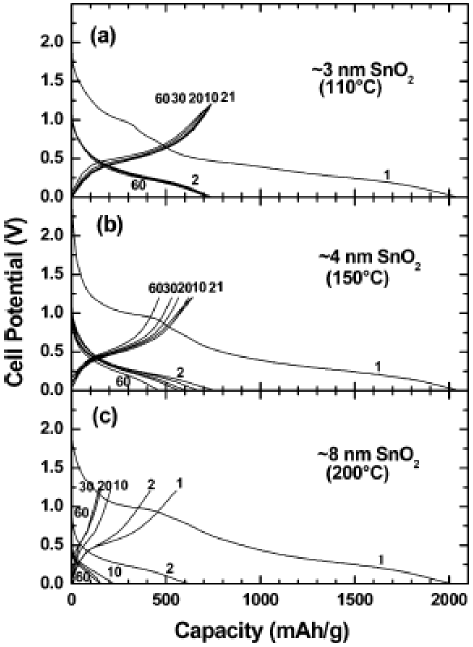
X.H. Liu et al., ACS Nano, 2012, 6(2), 1522-1531

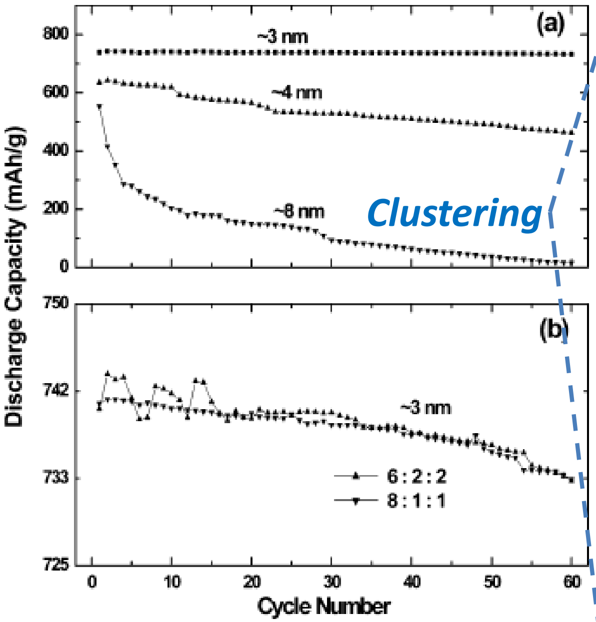
Nanostructured Anode Materials

Active material aggregation

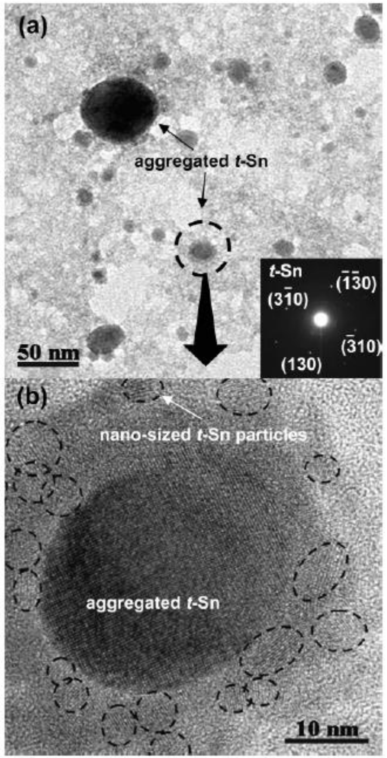
Lithiation of Tin-oxide (SnO_2) nanoparticles







Clustering



$$SnO_2 + 4\,Li \rightarrow 2\,Li_2O + Sn$$

$$Sn + x\,Li \rightarrow Li_xSn$$

- The smaller the tin nanoparticles the better performance
- **Larger Sn nanoparticles tend to agglomerate** due to their surface energy (clustering)
- Poor Electrochemical performance of Sn aggregated

C. Kim et al., Chem. Mater., 2005, 17, 3297-3301

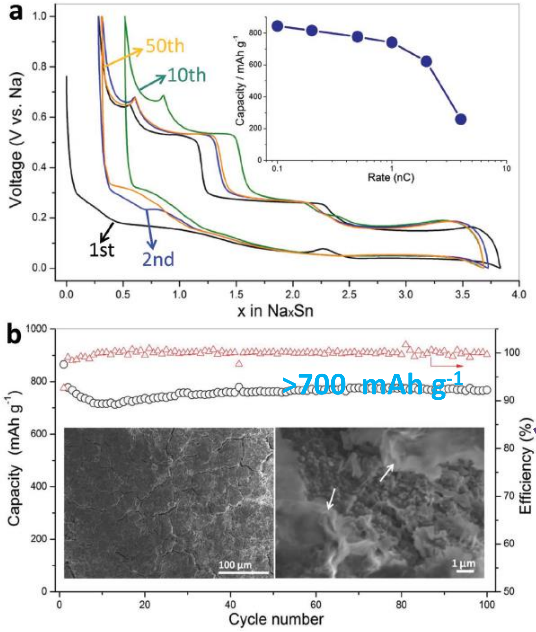
Nanostructured Anode Materials

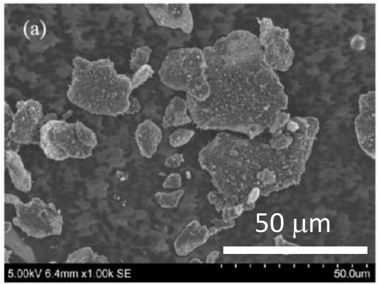
Is the nanostructuration in Batteries really necessary ?

Promising results have been shown by using microparticles in combination with

- ✓ Functional binders
- ✓ Electrolyte solvents

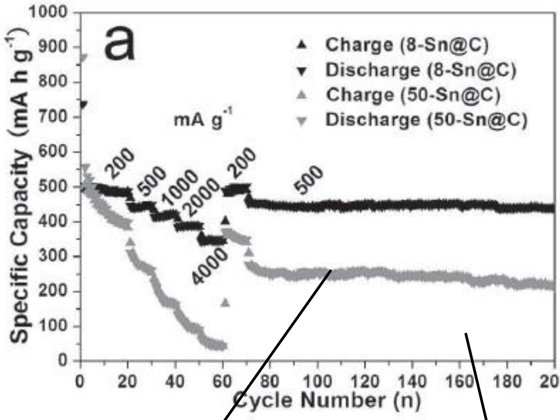
5-50 µm Sn/C cycled in NaPF$_6$/diglyme

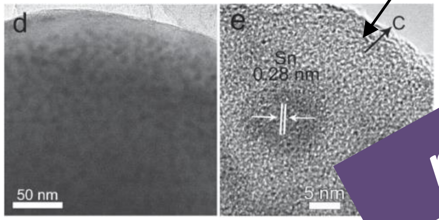




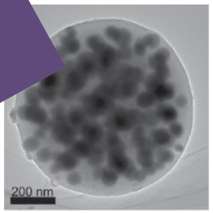
micro

8 nm vs 50 nm Sn nanoparticles embedded in C spheres





nano



Zhang et al., Adv. Mater., 2016, 28(44), 9824-9830

Y. Liu et al., Adv. Funct. Mater., 2015, 25, 214-220

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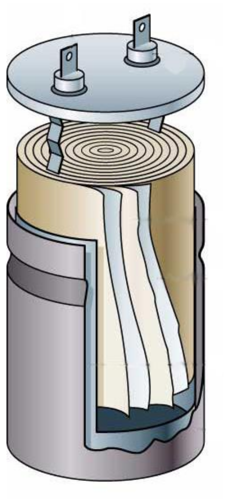
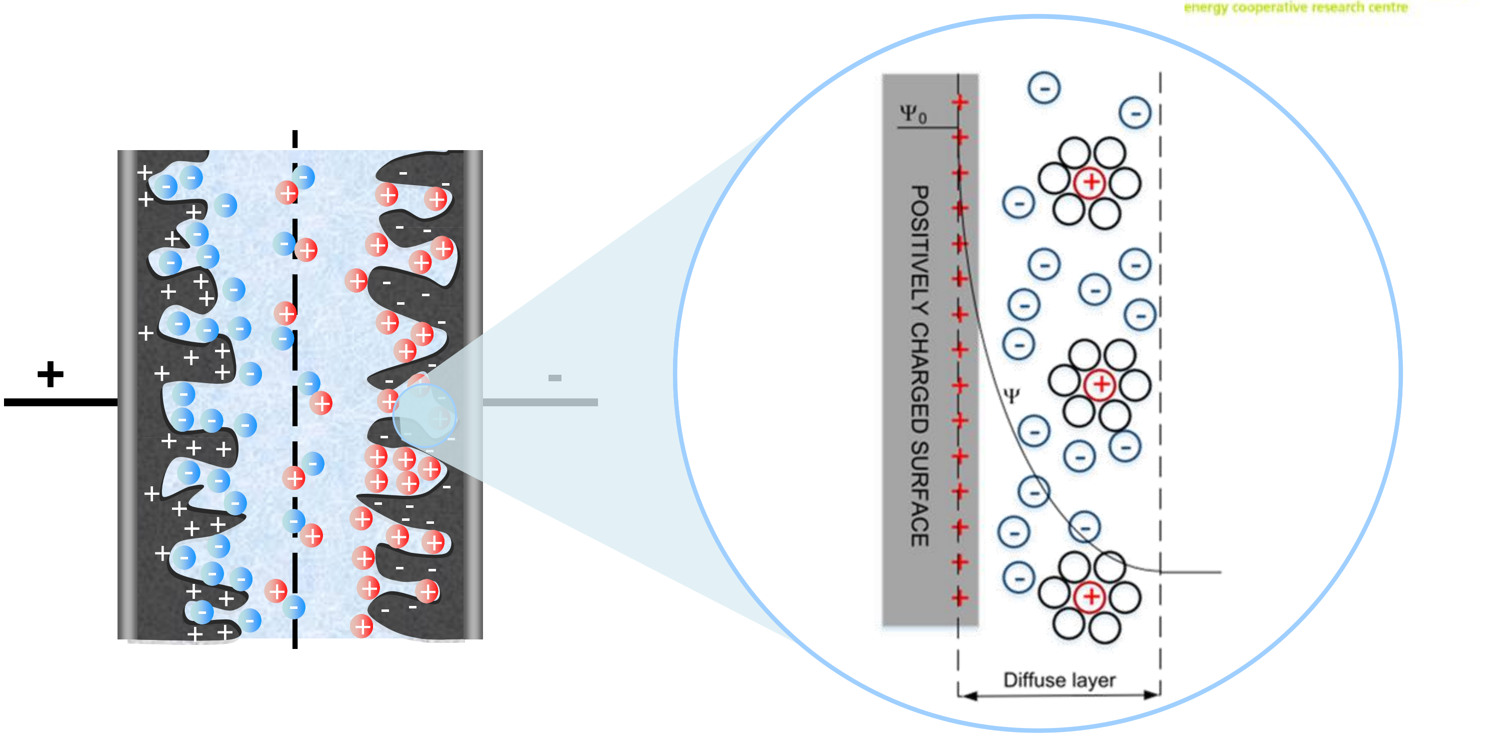
  - ☐ Hybrid
- **Conclusions**

Overview on supercapacitors





Ion adsorption on the surface of the active material – **Physical charge storage**

Electric double-layer formation (C ~ 10 μF/cm^2 on electrode)

$$\boxed{E = \frac{1}{2} C V^2}$$

$$\boxed{C = \frac{\varepsilon_r \varepsilon_0 S}{d}}$$

- **High** values per **volume** or **mass** are required for bulk storage
- **High specific surface area** (SSA) or **surface-to-volume ratio** (SV) materials are needed
- **Pore size similar to the ion size ➔ NANOSCALE**

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Active materials for supercapacitors

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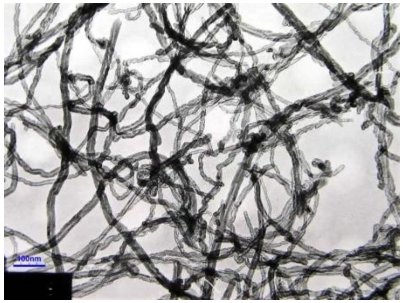
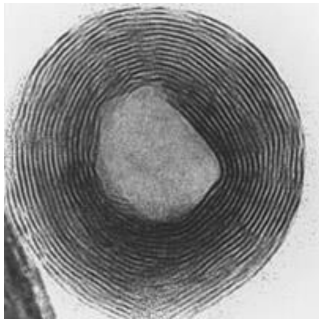
Carbon nanotubes



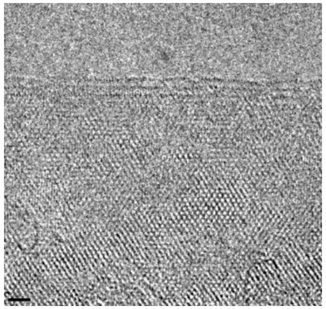
SSA << 500 m^2/g

Carbon onions



SSA << 400-600 m^2/g

Reduced graphene oxides



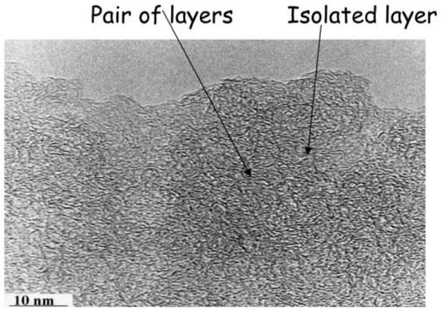
SSA << 400 m^2/g
a-rGO, SSA >> 2000 m^2/g

Low surface-to-volume ratio: Mesopore size interparticle voids in bulk powders and packed electrodes

Lower-density

High electrical conductivity

Microporous carbons



SSA > 1000-2000 m^2/g

Micropores

(< 2 nm, **high surface-to-volume ratio**)

Higher-density

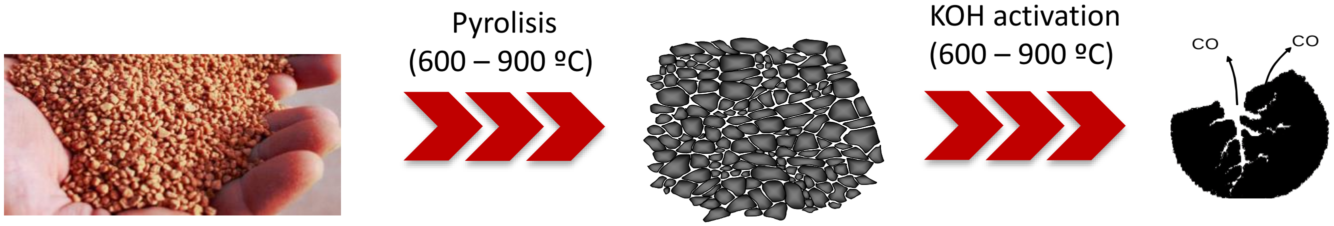
Conductive enough

Not competitive as the main electrode material for bulk storage

Main electrode material for bulk storage

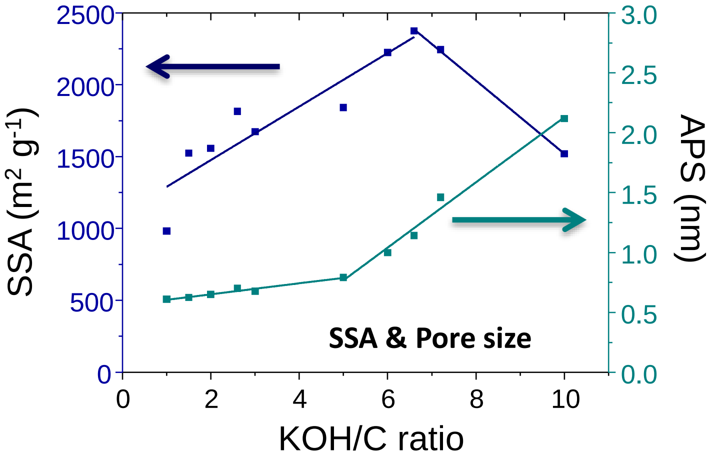
Activated Carbons

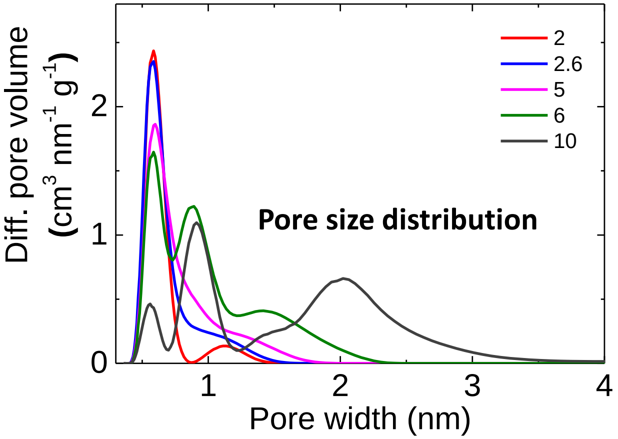
Olive pit derived activated carbons

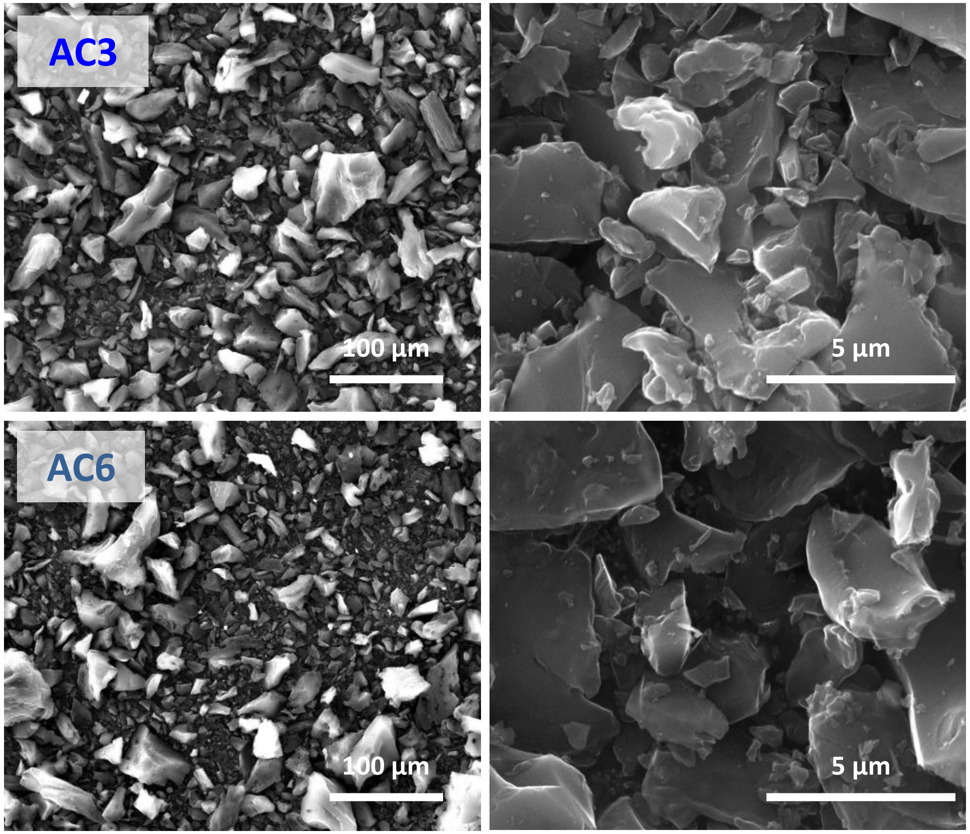


Pyrolisis
(600 – 900 ºC)

KOH activation
(600 – 900 ºC)



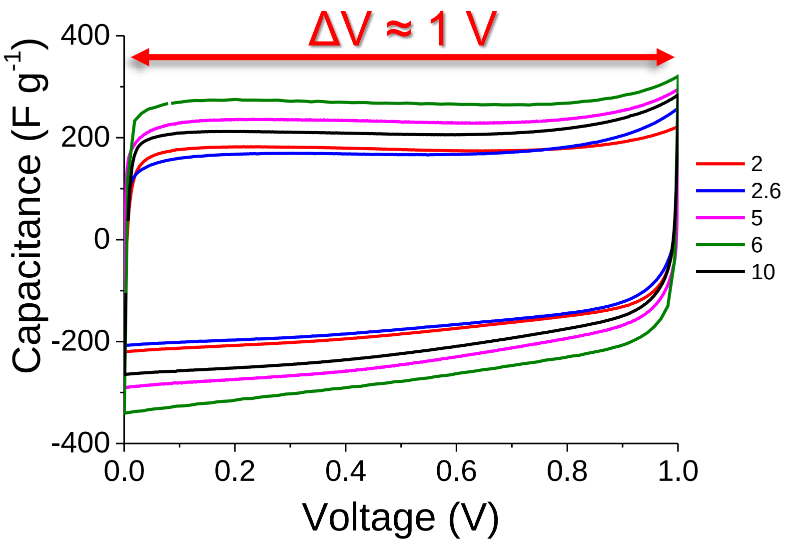


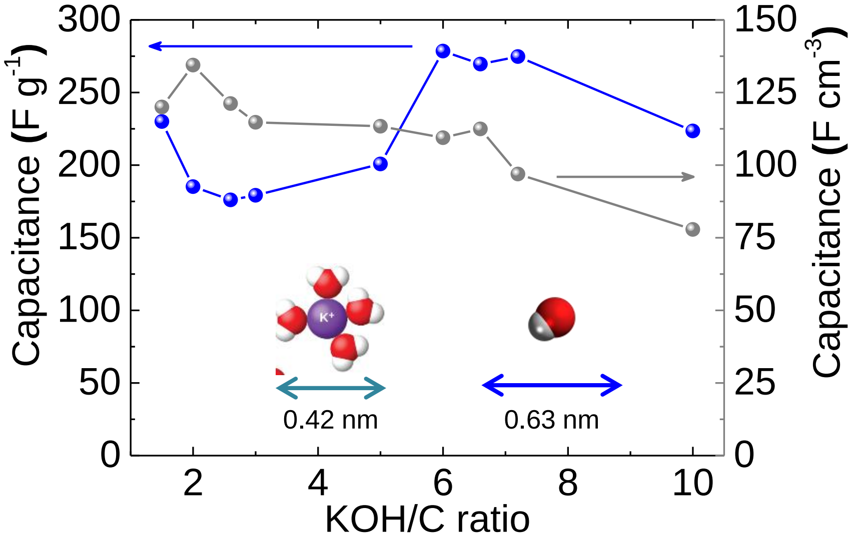


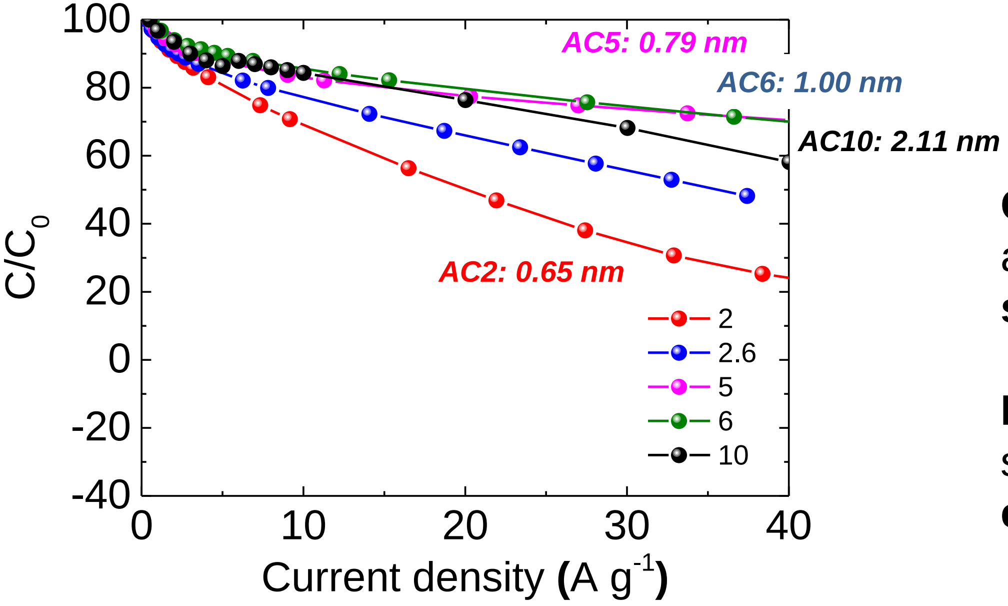
E. Redondo, et al.. *Electrochimica Acta,* 2015, 160, 178-184.

Activated Carbons - Aqueous electrolyte

Capacitance vs Current in KOH (aq)







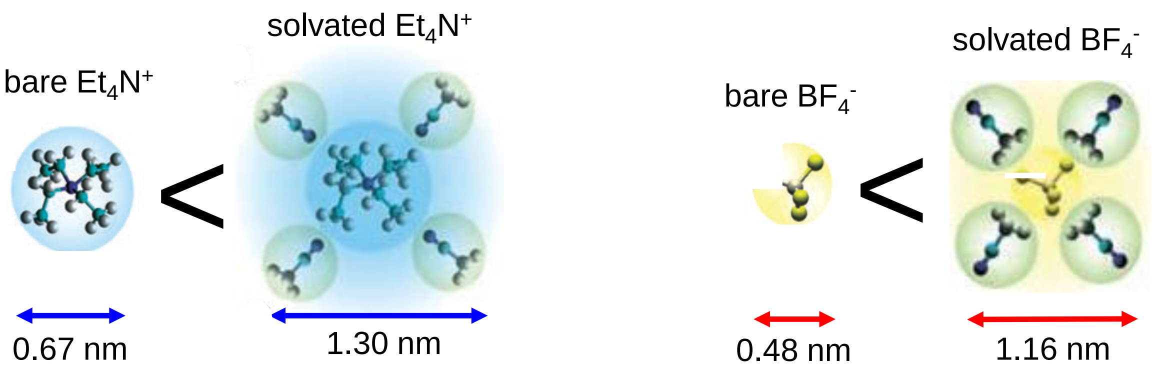
Capacitance retention drops if the accessible **pore size** significantly **surpasses the size of solvated ions**.

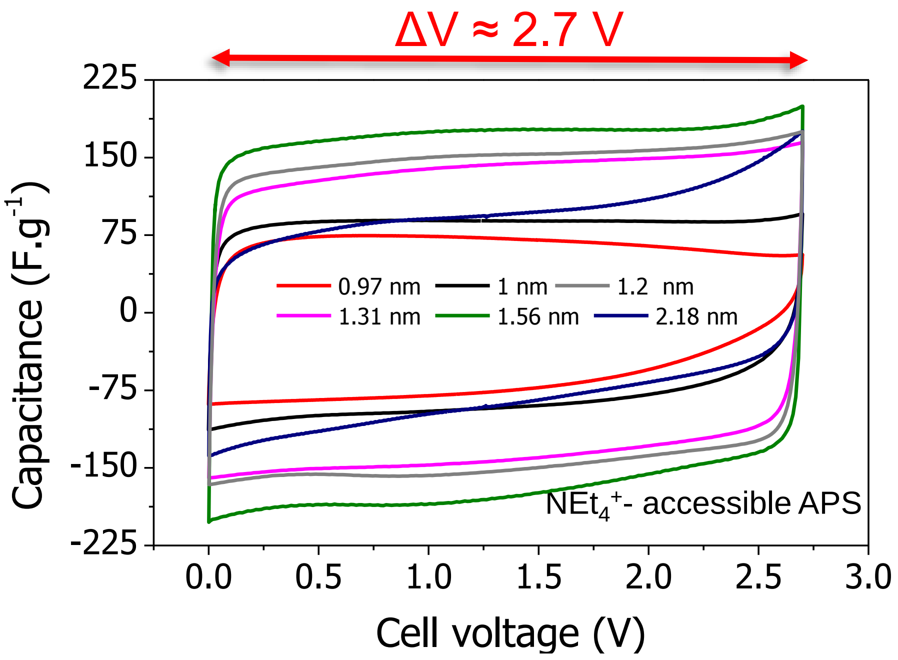
Pores slightly larger than the size of solvated electrolyte ions provide the most **effective high-rate operation** in EDLCs

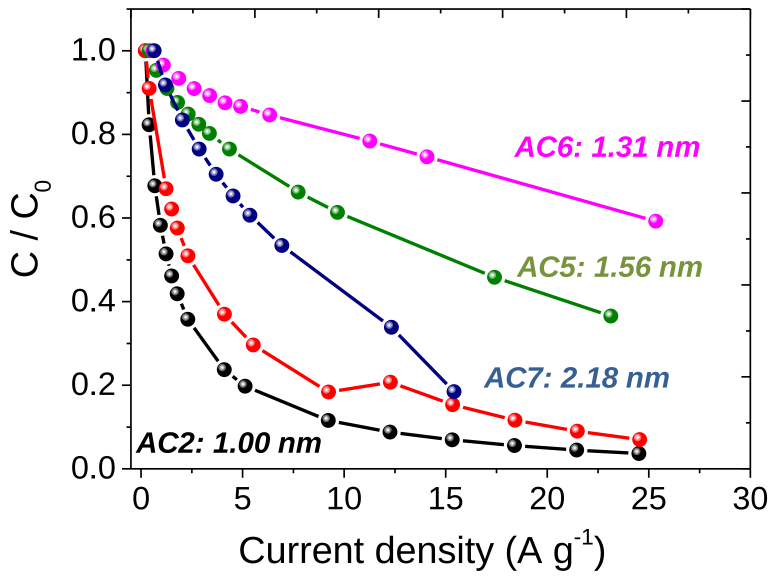
E. Redondo, et al.. *Electrochimica Acta,* 2015, 160, 178-184.

Activated Carbons – Organic electrolyte

Capacitance vs Current in 1.5M Et_4NBF_4 (AN)







- NEt_4^+- accessible average pore size of above 1 nm required for unhindered ion electrosorption
- Rate capability improves as the average pore size approaches the one of solvated cations

Universidad del País Vasco Euskal Herriko Unibertsitatea

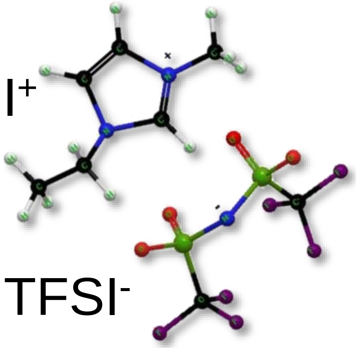
Activated Carbons – RT Ionic Liquids

CIC energiGUNE energy cooperative research centre

Anomalously high capacitance of microporous carbon in solvent-free EMI TFSI

EMI$^+$

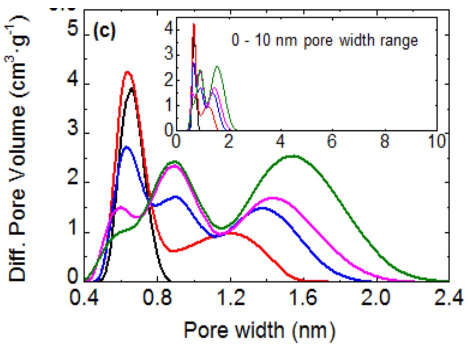
(~0.7 nm)

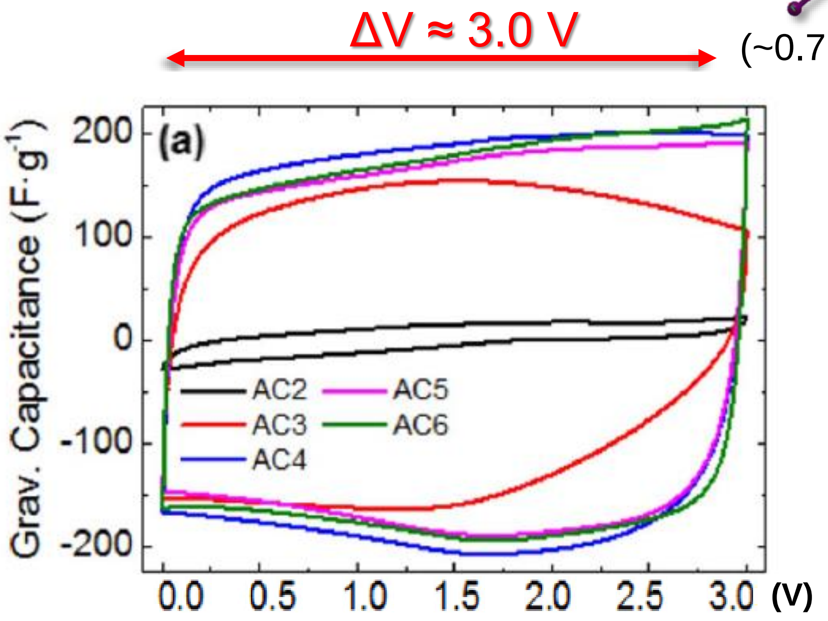


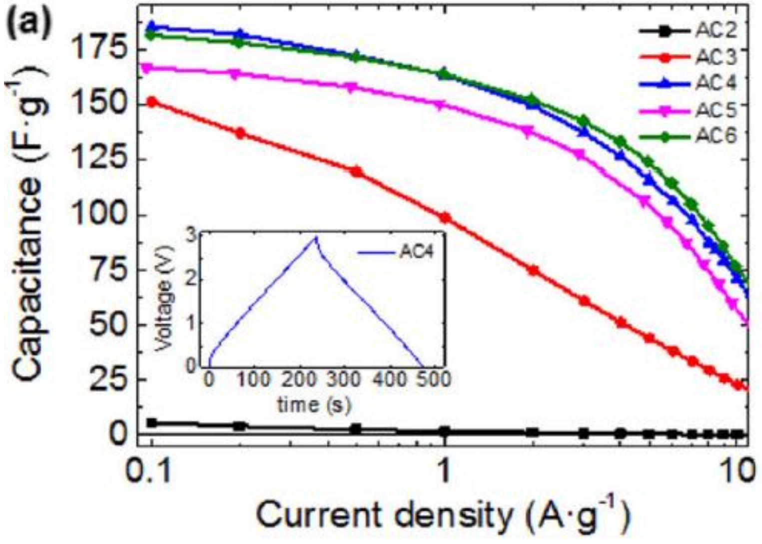
TFSI$^-$

(~0.7 nm)

Tailored pore size distribution







Unexpectedly **high capacitance in microporous carbons** (higher than standard organic electrolyte)

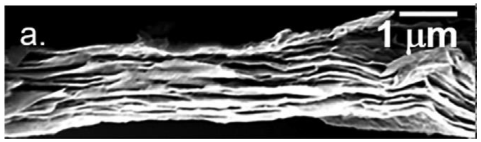
Performance correlates with porosity, but the reasons for high capacitance still have to be understood

E. Redondo *et al. Electrochem. Commun.*, 2017, 79, 5–8.

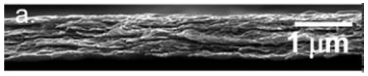
Mxenes: Asymmetric cell

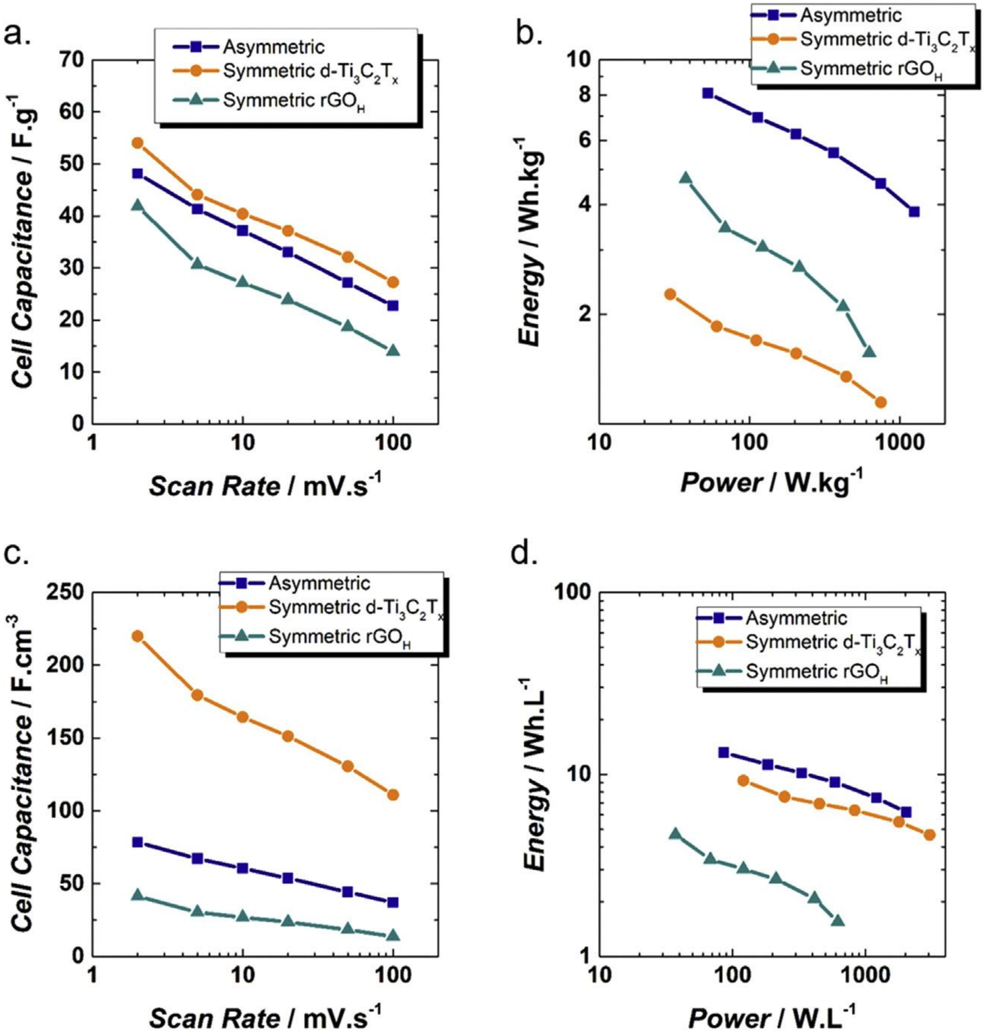
Titanium carbide ($Ti_3C_2T_x$) and reduced graphene oxide (rGO)

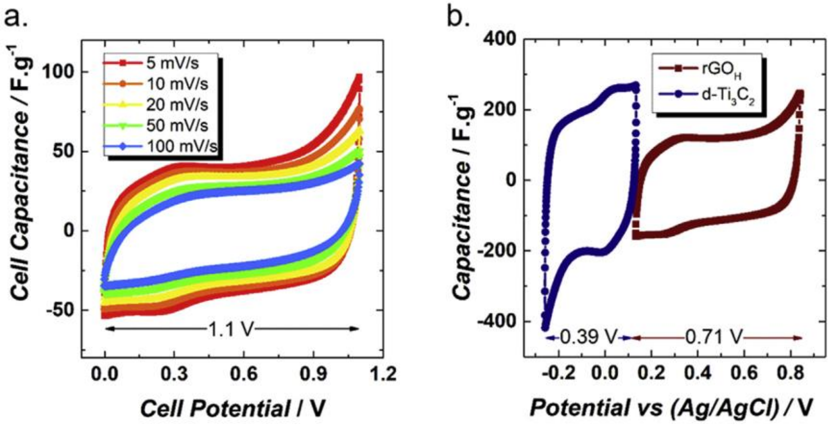
$Ti_3C_2T_x$



rGO







- Lower cell capacitance in the asymmetric cell.
- The increase in the potential window of the **asymmetric cell** resulted in an **increased energy density**.

A.M.Navarro et al *Electrochimica Acta* 259 (2018) 752-761

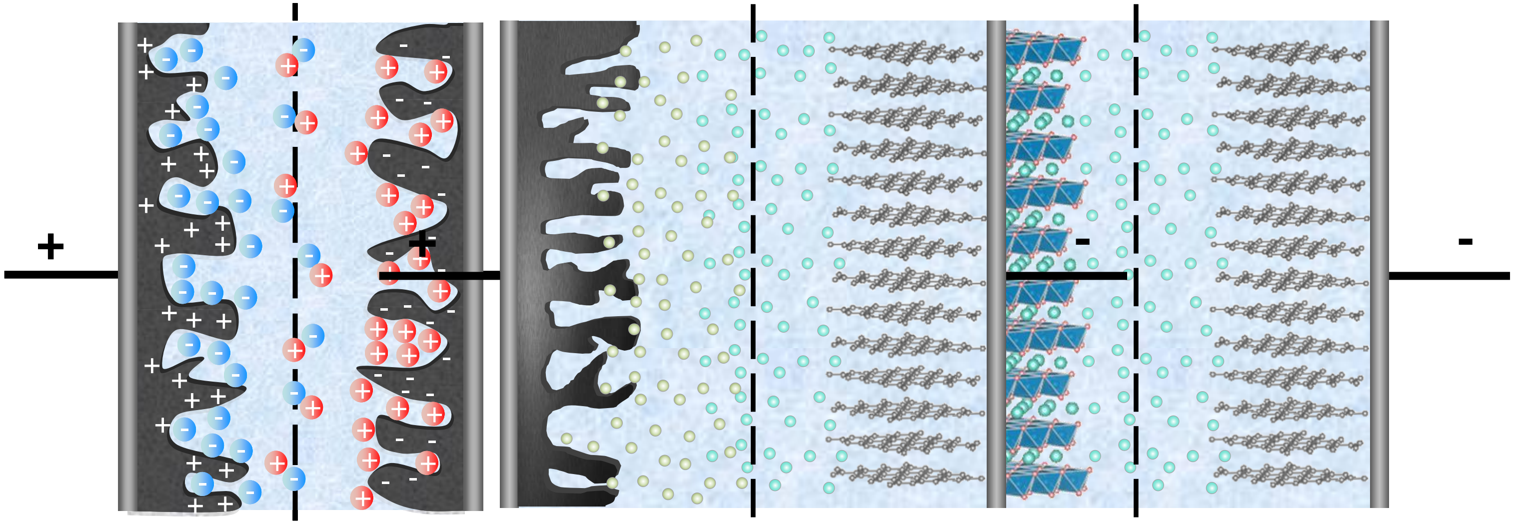
- **Introduction**
- **Batteries:**
  - Nanostructured Anodes
    - Volumetric expansion
    - Critical particle size
    - Active materials aggregation.
- **Supercapacitors:**
  - Double Layers
  - Hybrid
- **Conclusions**

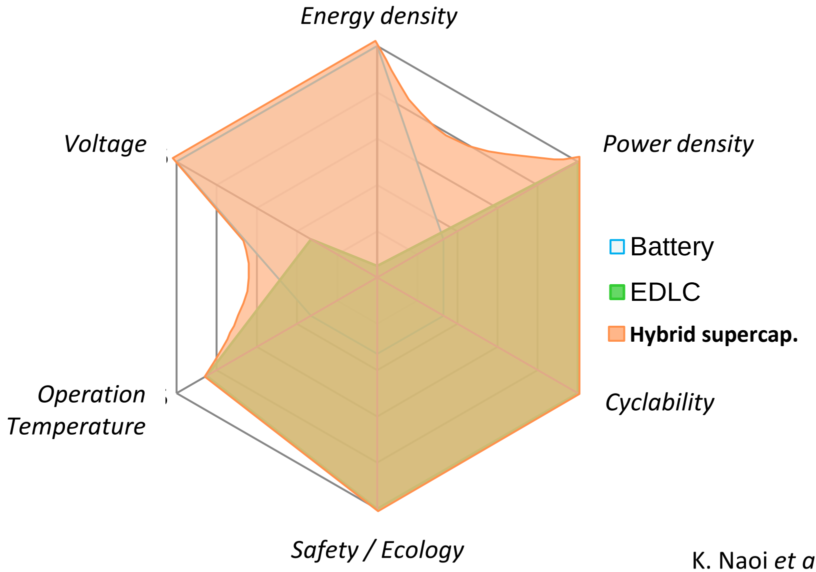
Hybrid Supercapacitors

Supercapacitor

Hybrid Supercapacitor, Li-ion (Na-ion) Capacitor

Battery

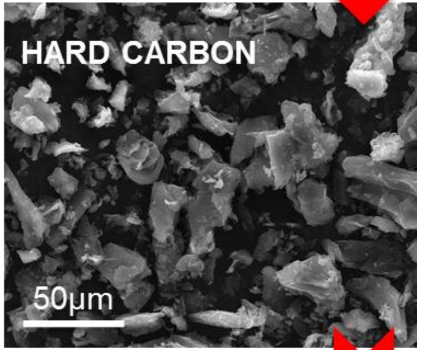




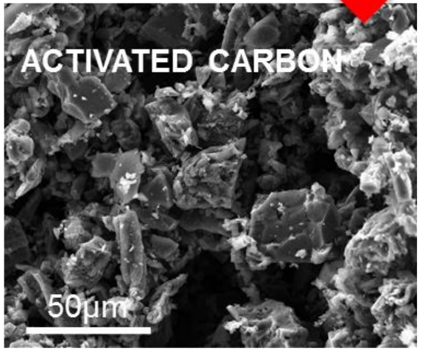
K. Naoi *et al.*, *Energy Environ. Sci.*, 2012, 5, 9363–9373.

Activated Carbon (+) / Hard Carbon (-)

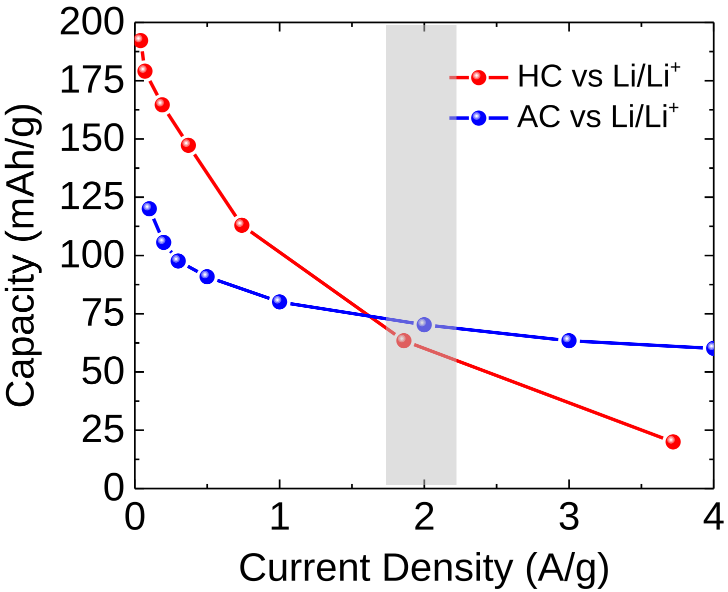
Pyrolisis
(600 - 900ºC)



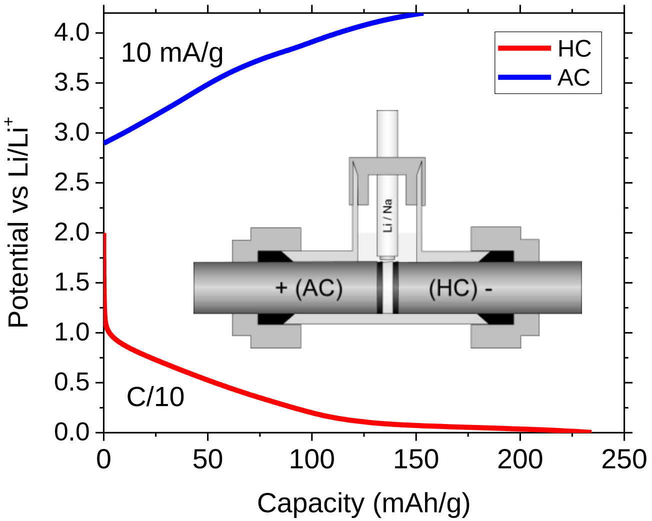
KOH activation
(600 - 900ºC)



Electrode mass balance



Electrode preconditioning

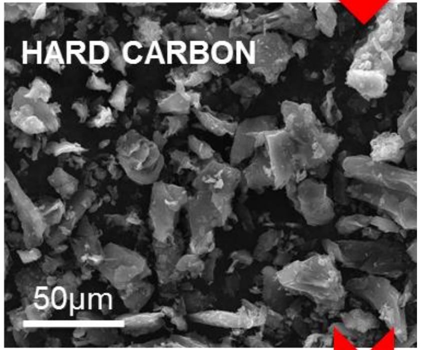


1 to 1 mass balance for an application that requires **charge/discharge** times of ~ **0.5 - 1 minute** (i.e. a current density of ~ 2 A g^{-1})

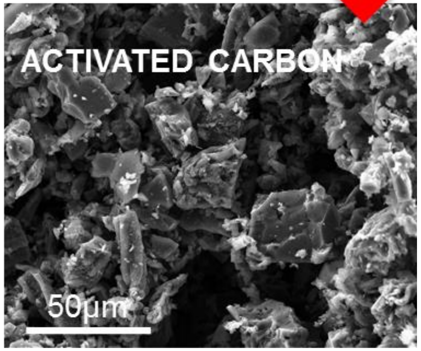
J. Ajuria, et al *J. Power Sources* 2017, 359, 17-26.

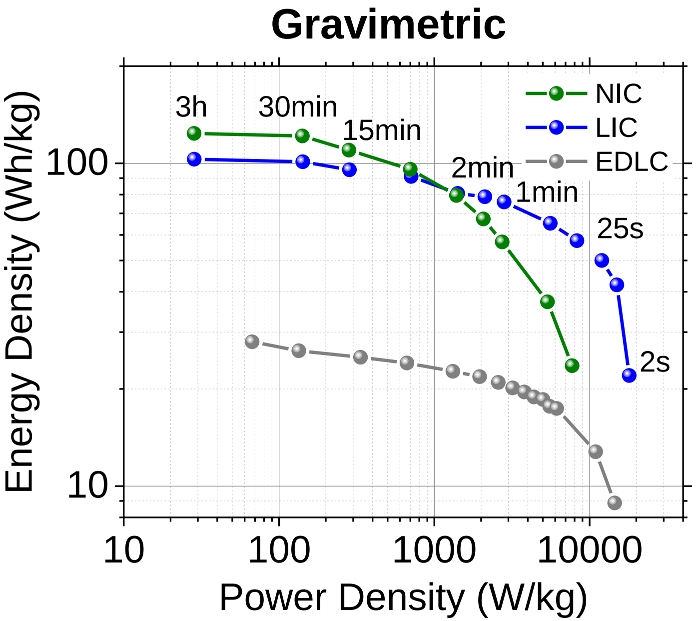
Activated Carbon (+) – Hard Carbon (-)

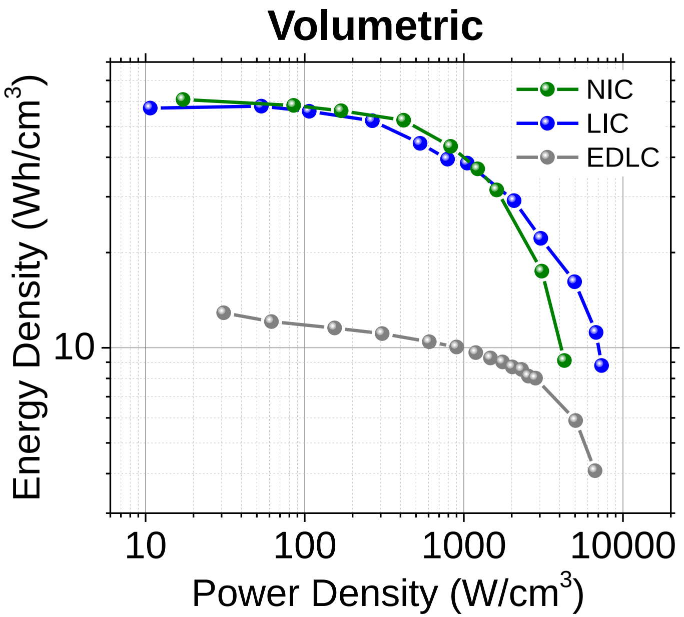
Pyrolisis
(600 - 900ºC)

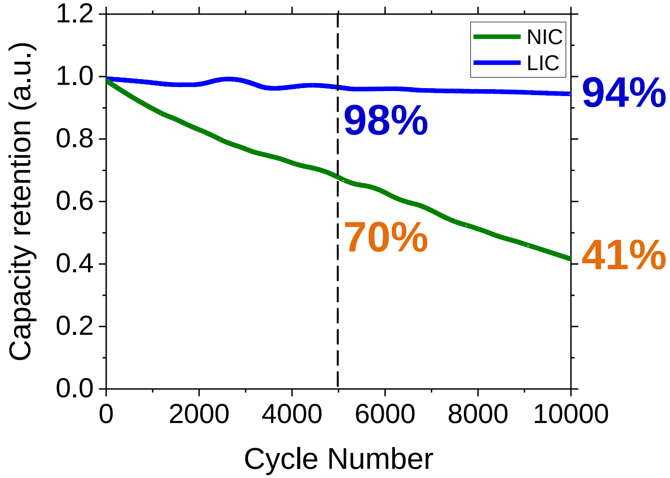


KOH activation
(600 - 900ºC)





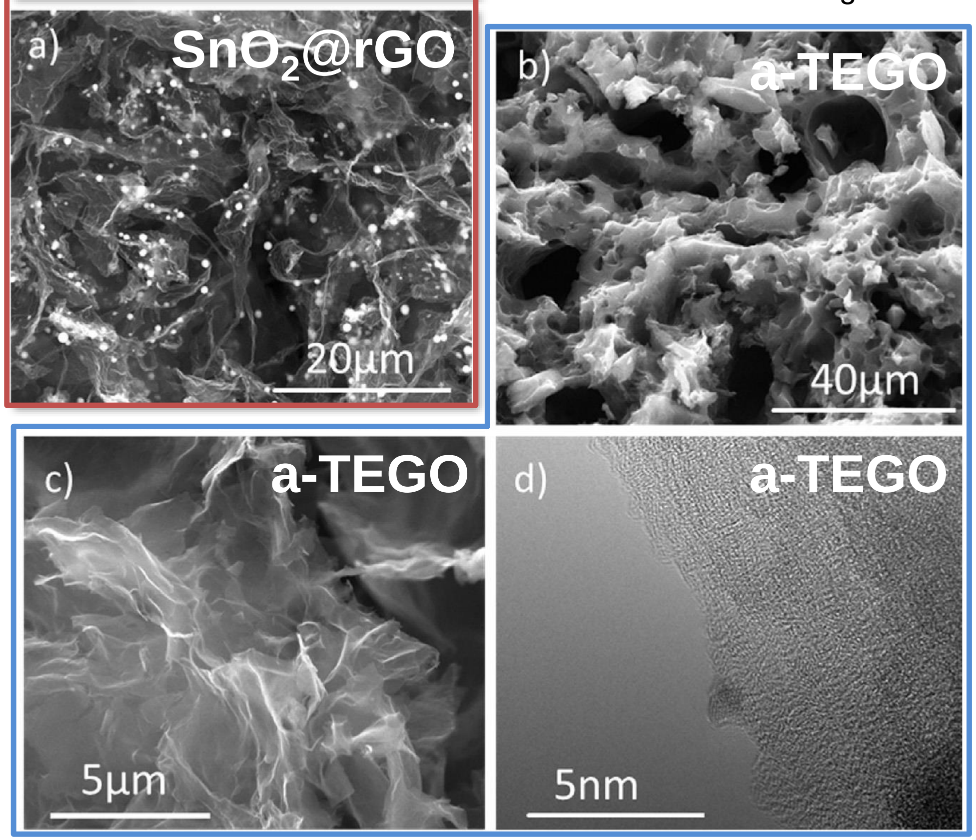


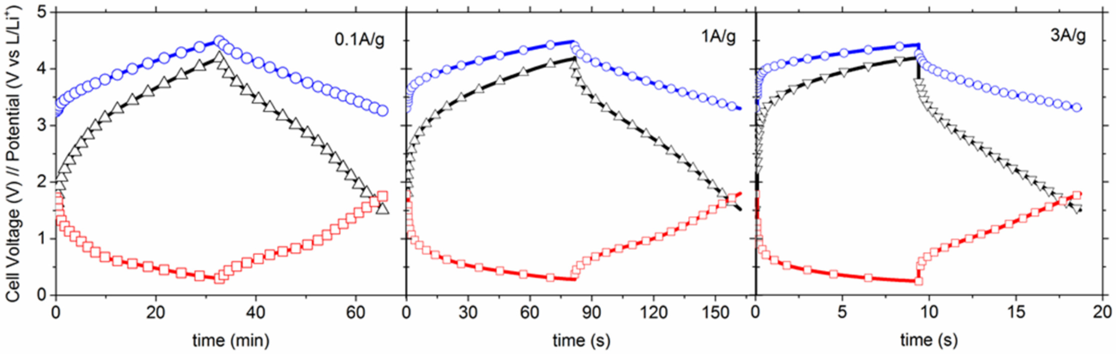


J. Ajuria, et al *J. Power Sources* 2017, 359, 17-26.

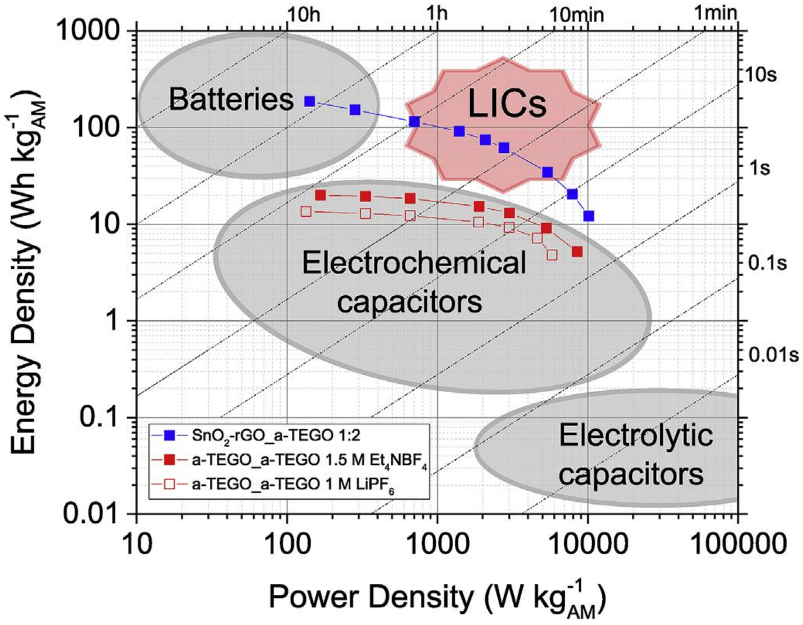
SnO_2@rGO (-) / a-TEGO (+)

SnO_2-rGO 3D foam





GA charge-discharge profiles in 1 M LiFP6 EC:DMC between 1.5 and 4.2 V.



J. Ajuria, et al. *J. Power Sources* 2017, 363, 422-427.

Conclusions

Batteries

- Nanostructured materials **are good candidates to be used as anodes** in Li and Na – ion batteries **with alloying and conversation reactions**.
- Si and Sn nanoparticles embedded in rGO **overcome the volume expansion effects**.
- The negative impact of **particle aggregation** can be mitigated **by embedding nanoparticles** in carbon based materials.

Supercapacitors

- The conditions of chemical activation have been fine-tuned to provide **microporous carbons** (pore size < 2 nm) optimized **for different electrolytes** (aqueous, organic ionic liquids).
- **High gravimetric and volumetric capacitance** and rapid room-temperature capacitive response can be achieved **with only microporous carbons** and **ionic liquid electrolytes.**
- Carbons have been specifically tailored to be used in both **sodium and lithium ion capacitor technologies** overcoming their EDLC counterpart in terms of energy density throughout the whole power density range, **exceeding** the highly challenging **energy density barrier of 100 Wh/kg**$_{AM}$**.**

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Universidad del País Vasco
Euskal Herriko Unibertsitatea

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energy cooperative research centre

Thank for your kind attention!

www.cicenergigune.com