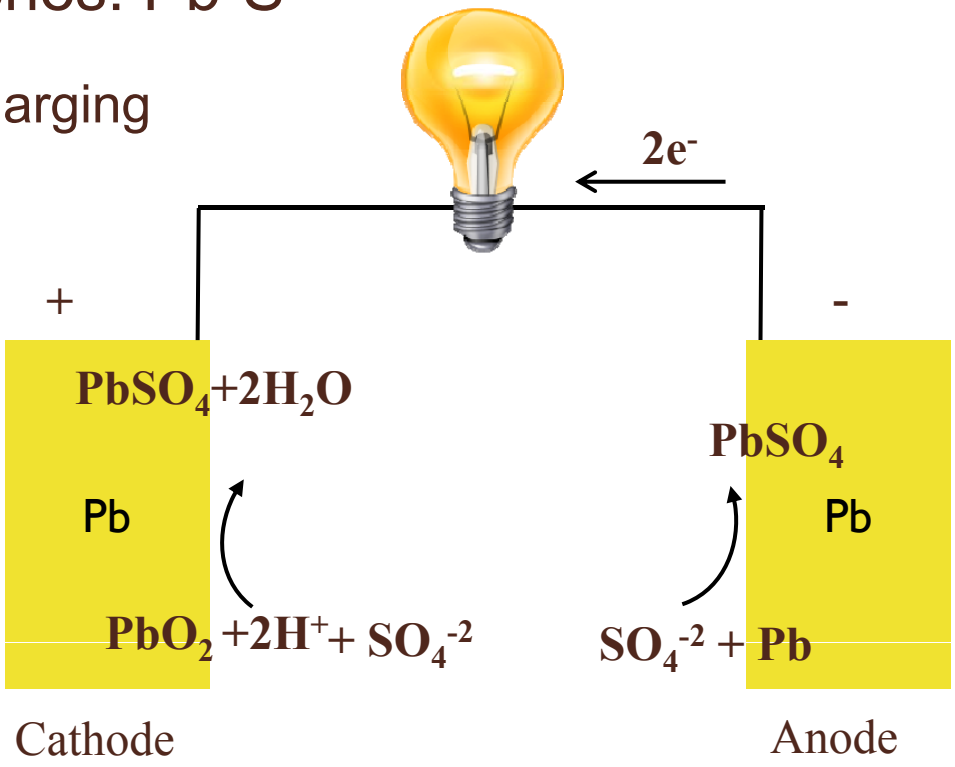
4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors

Batteries: Pb-S

discharging



https://www.youtube.com/watch?v=1Bx5pOajdzg
https://www.youtube.com/watch?v=3zd-rCr8RgE
https://www.youtube.com/watch?v=HhxtfULIO7c

Batteries: the voltage

Cathode	$PbO_2 + 2\,H_2SO_4 + 2\,e^-$	$\xrightarrow{\text{Discharge}}$	$2\,H_2O + PbSO_4 + SO_4^{2-}$	+ 1.69 V
Anode	$Pb + SO_4^{2-}$		$PbSO_4 + 2\,e^-$	- 0.36 V
			V_{max}=	+ 2.05 V

Stored energy: 40 Wh/kg

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors

Batteries: the voltage

Cathode $PbO_2 + 2\,H_2SO_4 + 2\,e^-$ $\xrightarrow{\text{Discharge}}$ $2\,H_2O + PbSO_4 + SO_4^{2-}$ + 1.69 V

Anode $Pb + SO_4^{2-}$ $PbSO_4 + 2\,e^-$ - 0.36 V

V_{max}= + 2.05 V

Stored energy: 40 Wh/kg

Cathode: $Li_{1-x}CoO_2 + xLi^+ + xe^-$ $\xrightarrow{\text{Discharge}}$ $LiCoO_2$ + 0.7 to +1.3 V

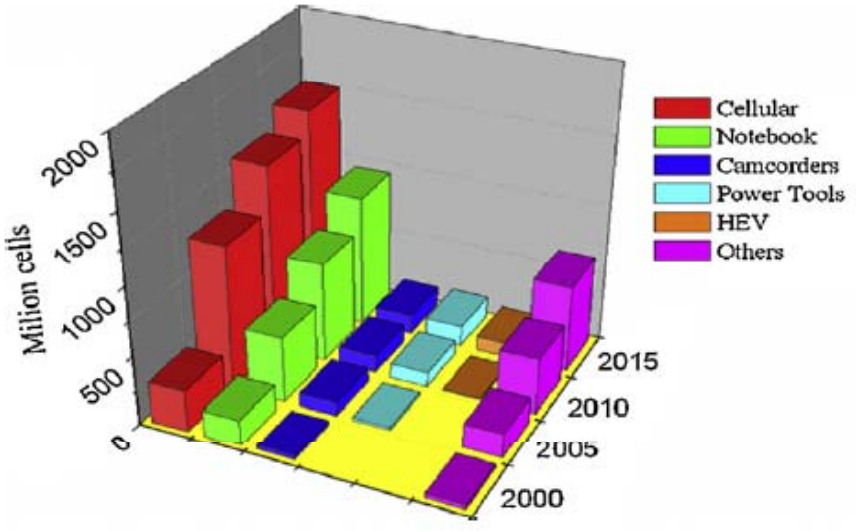
Anode: Li_xC_6 $C_6 + xLi^+ + xe^-$ - 2.8 to -2.9 V

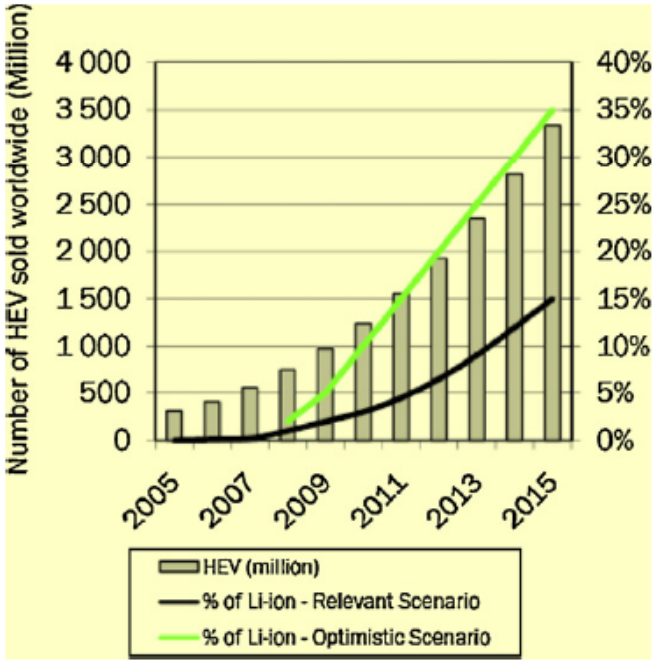
V_{max}= + 3.5 to +4.2 V

Stored energy: 110 Wh/kg

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors





➢ Lithium batteries are the most promising power sources for the exponential growth in portable electronic devices, storage energy from renewable sources and development of electric vehicles.

B. Scrasoti, K. M. Abraham, W. Schalwijk, J. Hassoun Lithium Batteries Advanced Technologies and Applications Wiley **2013**

B. Scrasoti, J. Garche *J. Power Sources* **2010**, 195, 2419-2430

http://www.forbes.com/sites/jeffmcmahon/2015/05/05/why-tesla-batteries-are-cheap-enough-to-prevent-new-power-plants/

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors

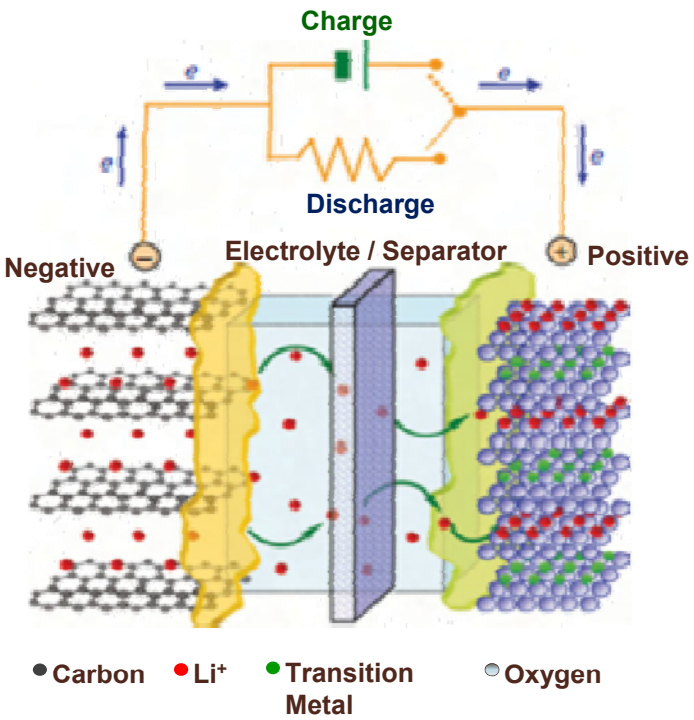
7 kWh daily cycle

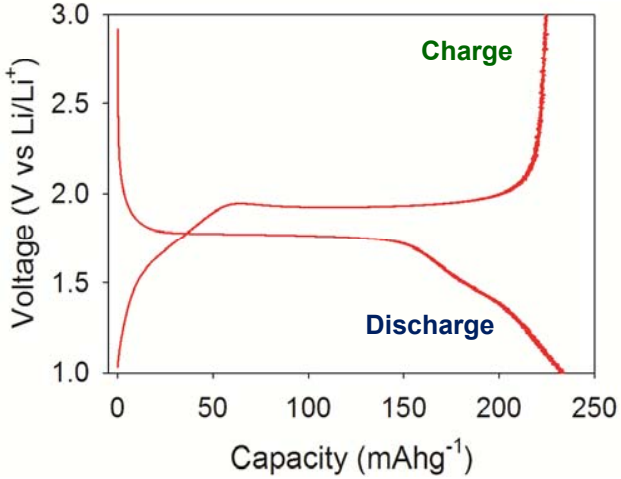
TV_ 0.1 kWh / hr
Light/room_ 0.1 kWh / hr
Laptop_ 0.05 kWh / hr
Fridge_ 4.8 kWh / day
Clothes Washer_ 2.3 kWh / 1use

http://www.teslamotors.com/powerwall
http://www.forbes.com/sites/jeffmcmahon/2015/05/05/why-tesla-batteries-are-cheap-enough-to-prevent-new-power-plants/
http://cincodias.com/cincodias/2015/02/12/motor/1423734040_292448.html
http://www.elmundo.es/tecnologia/2015/05/02/55447d2bca4741a95e8b4570.html

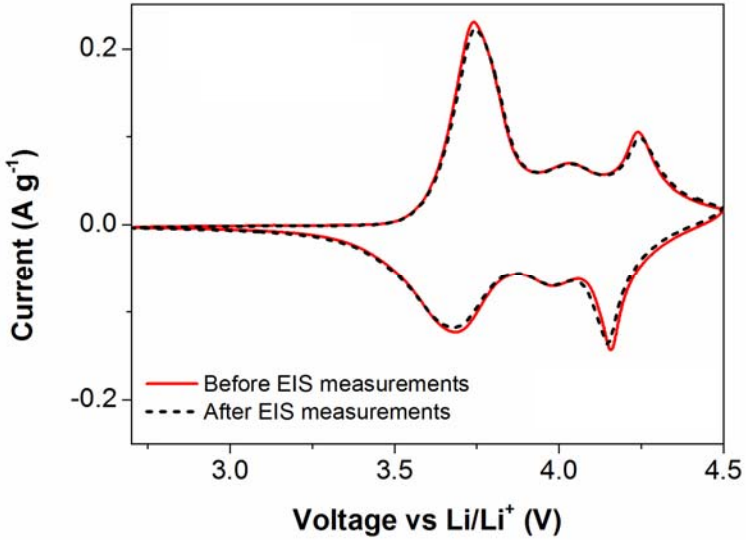
4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors





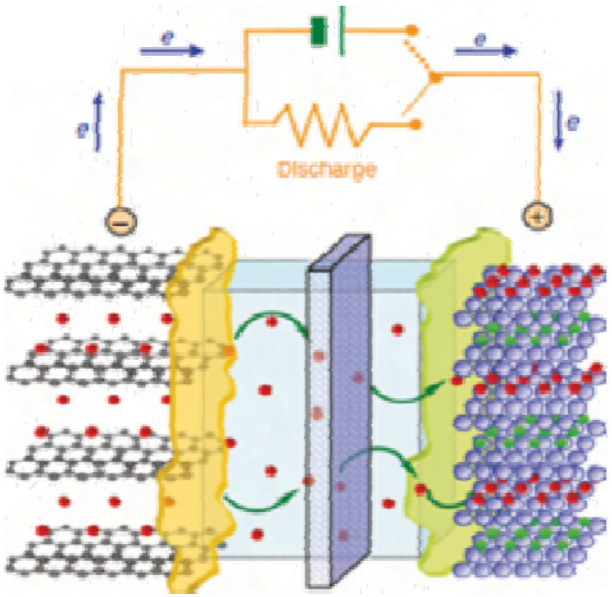
$$yC + LiMO_2 \rightleftharpoons Li_xC_y + Li_{(1-x)}MO_2$$

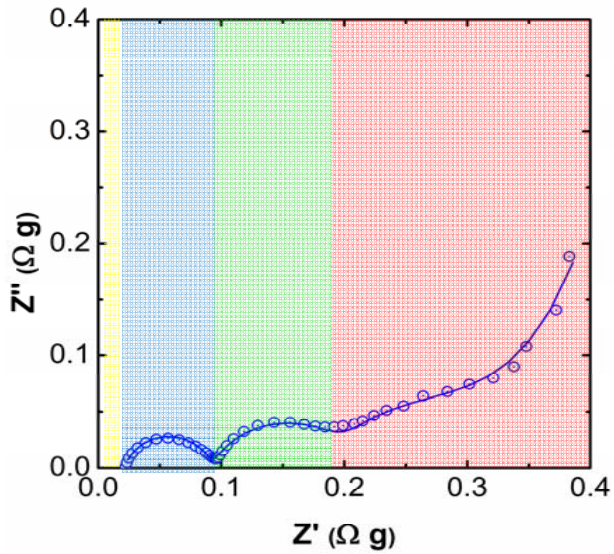


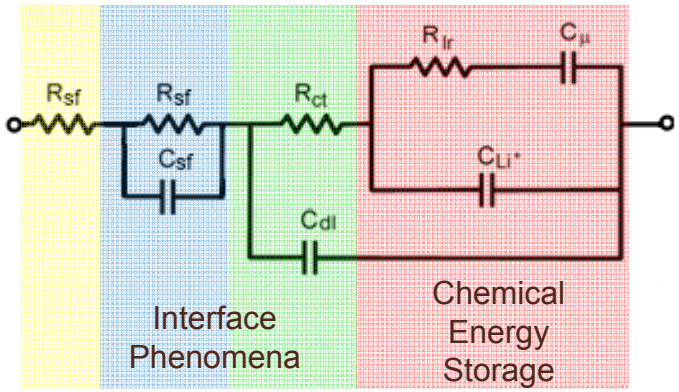
P. G. Bruce, B. Scrasoti, J-M. Tarascon *Angew. Chem. Int. Ed.* **2008**, 47, 2930-2946
J. Chen, F. Cheng *Acc. Chem. Res.* **2009**, 42, 713-723

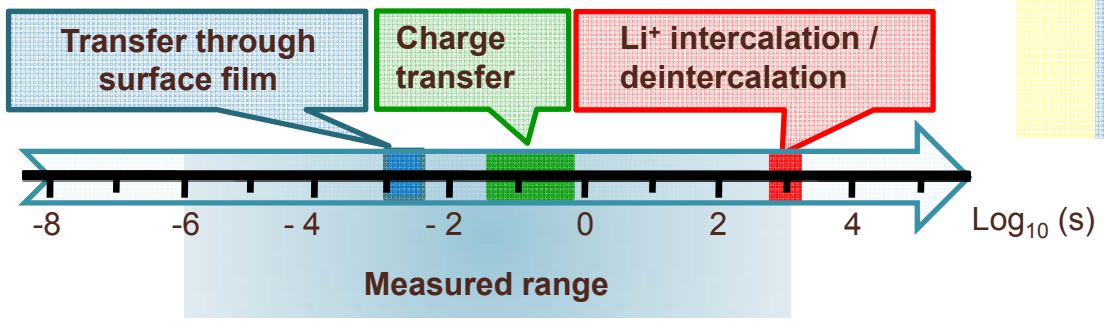
4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors



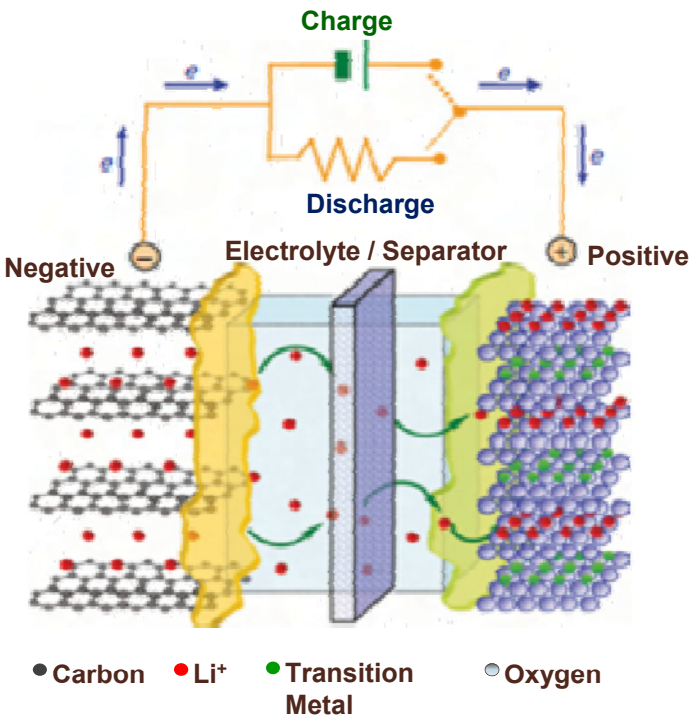






4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors



$$yC + LiMO_2 \rightleftharpoons Li_xC_y + Li_{(1-x)}MO_2$$

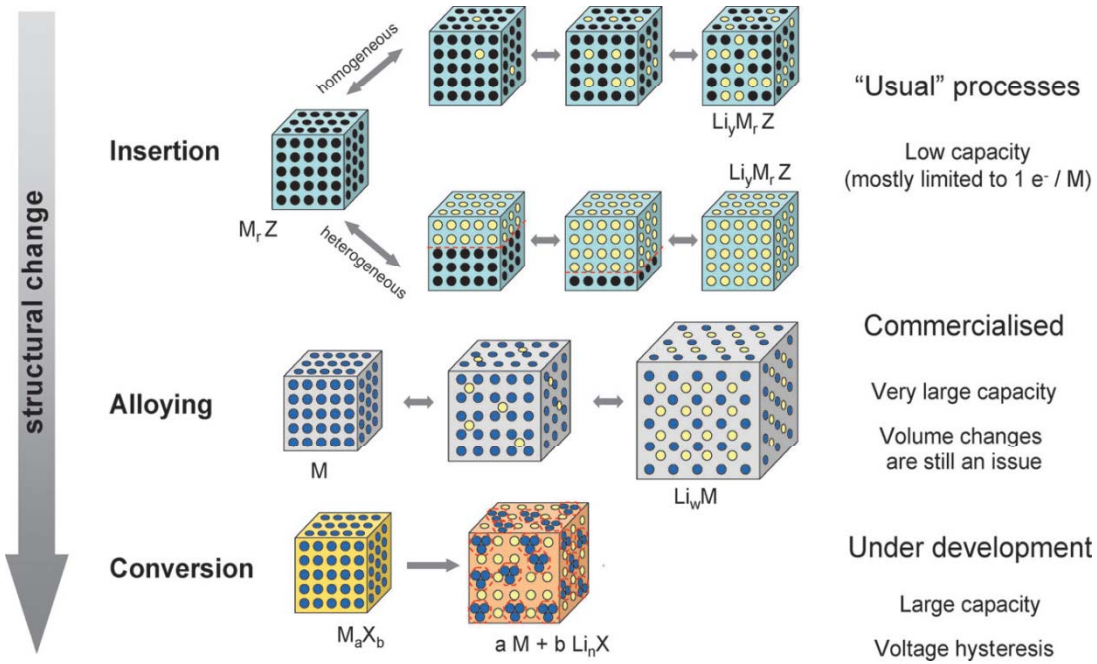
Nanostructured materials

- ☺ Less strains in the structural changes
- ☺ Rate increase in Li insertion/removal and e^- conductivity
- ☺ Change of electrode potential
- ☺ High surface electrolyte/electrode
- χ Difficult synthesis
- χ Lower volumetric energy density
- χ Increase of side reactions with electrolyte

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors

- Li-ion
  - Intercalation
  - Alloy
  - Conversion
- Batteries of future
  - Li-S
  - Li-O_2

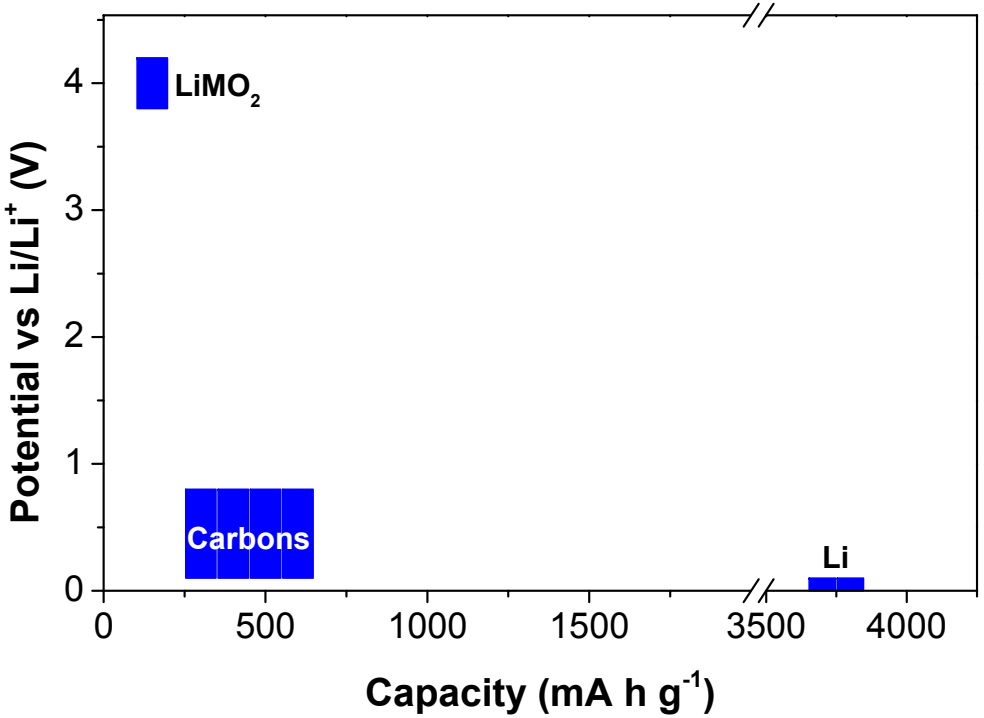


R. Palacín Chem. Soc. Rev. **2009**, 38, 2565

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors

- Li-ion
  - Intercalation
  - Alloy
  - Conversion



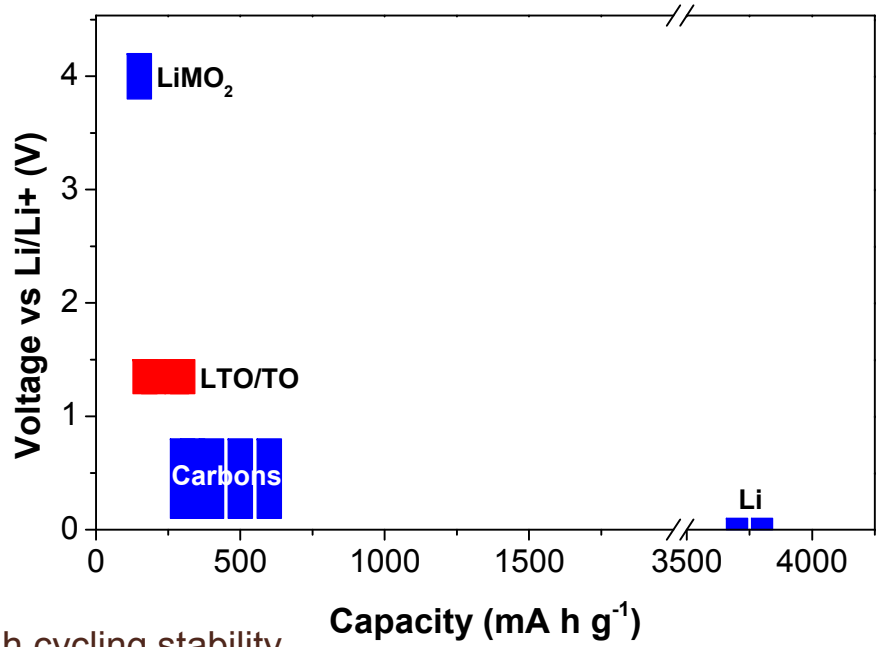
$$V_{oc} = \frac{\mu_{Li(c)} - \mu_{Li(a)}}{F}$$

R. Palacín Chem. Soc. Rev. **2009**, 38, 2565

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors

- Li-ion
  - Intercalation



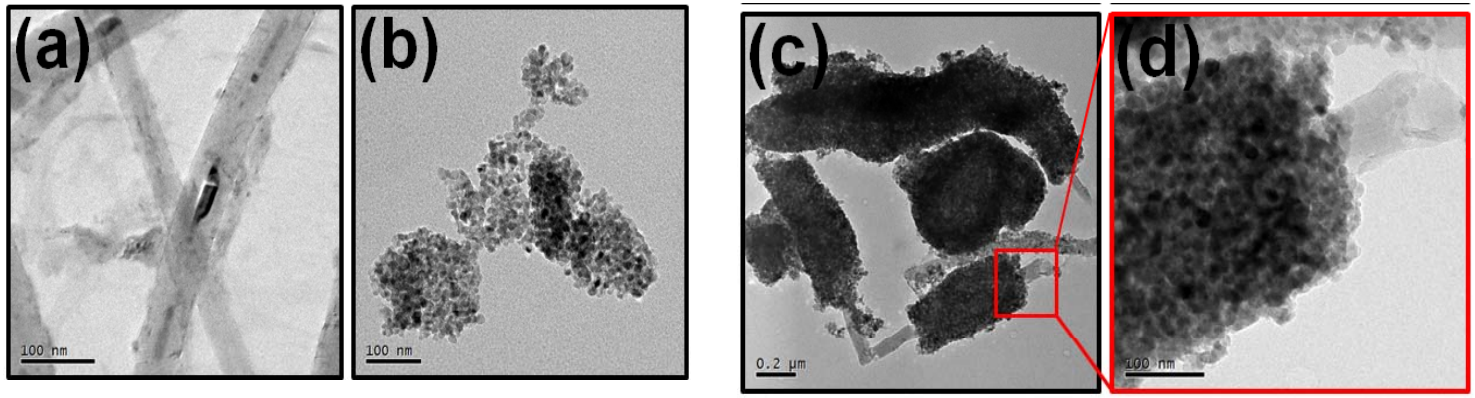
☺ Low V changes (< 1%) → High cycling stability
☺ High thermal stability
☺ No electrolyte decomposition → Low SEI formation

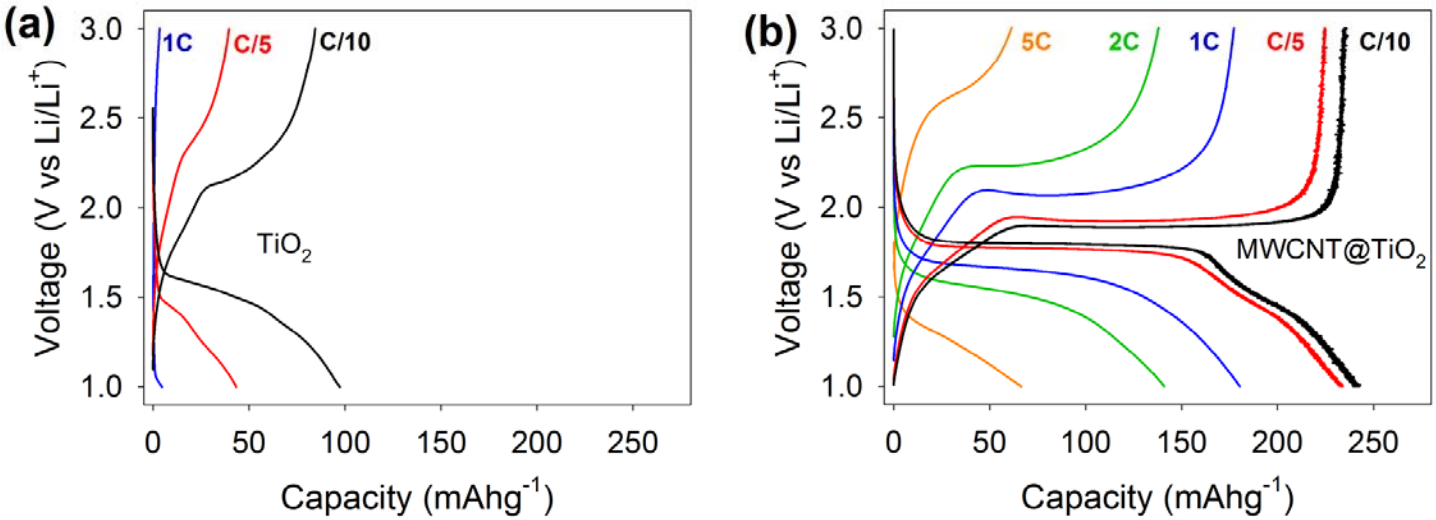
χ Low conductivity → Loss of capacity and poor rate capability

Nanotechnology produces hybrids with superior properties than its individual constituents

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors

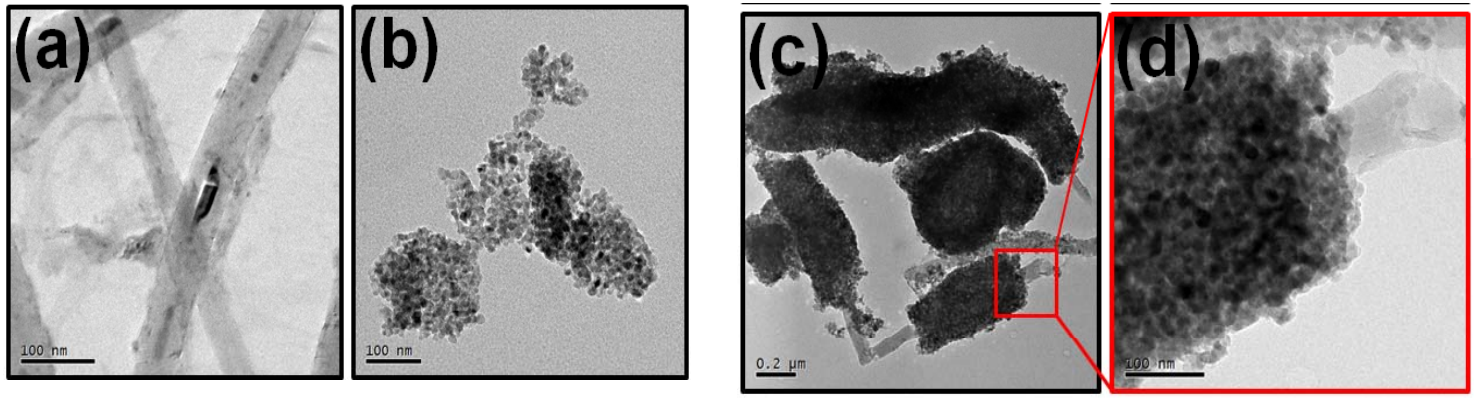


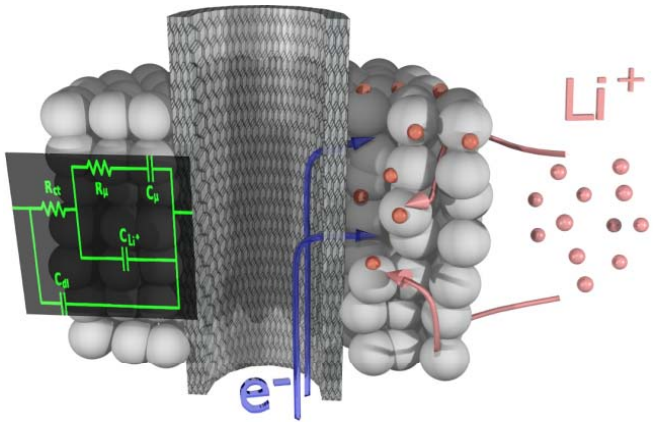


P. Acevedo-Peña, M. Haro, M. E. Rincón, J. Bisquert, G. Garcia-Belmonte *J. Power Sources* **2014**, 268, 397-403

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors



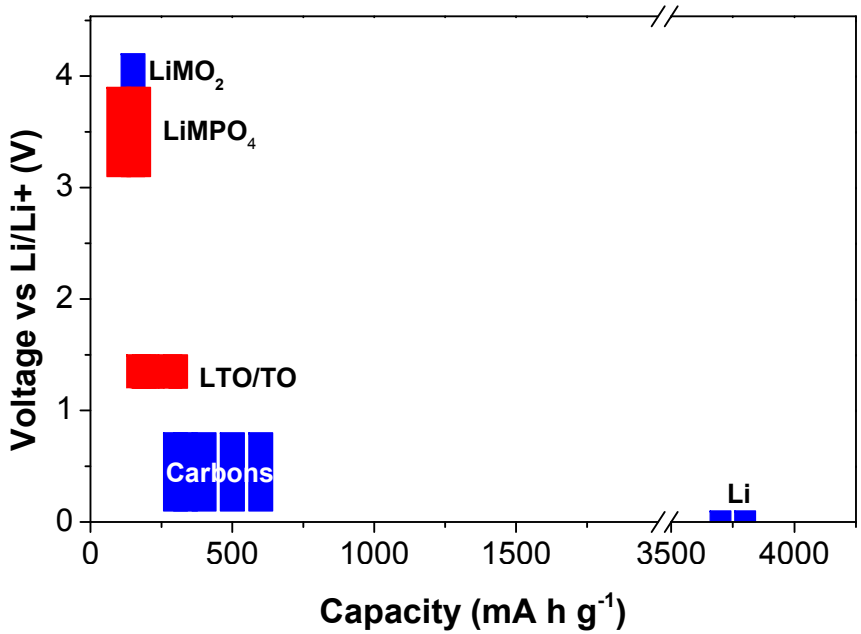


P. Acevedo-Peña, M. Haro, M. E. Rincón, J. Bisquert, G. Garcia-Belmonte *J. Power Sources* **2014**, 268, 397-403

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors

- Li-ion
  - Intercalation



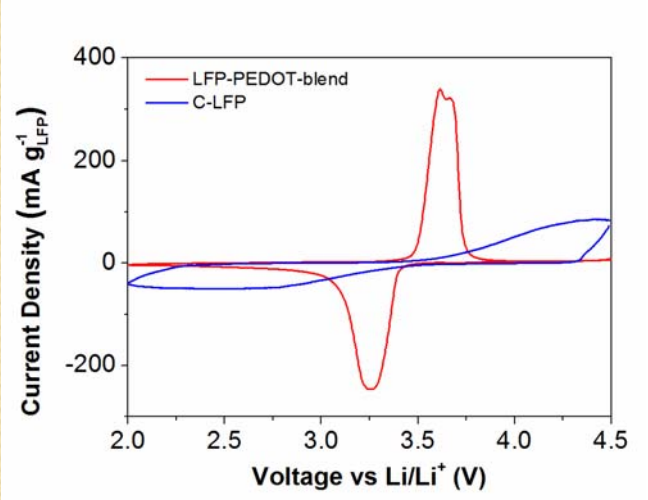
Theoretical capacity: 170 mA h g^{-1}

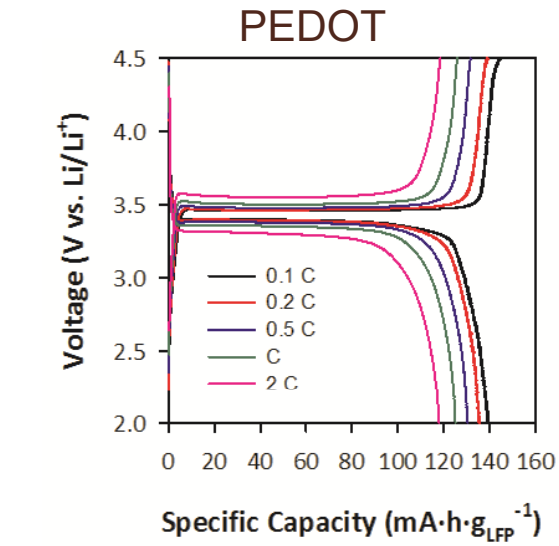
☺ Low cost
☺ High stability
☺ Small amount of O_2 generation at the fully charged state
ϰ Low conductivity → Loss of capacity and poor rate capability

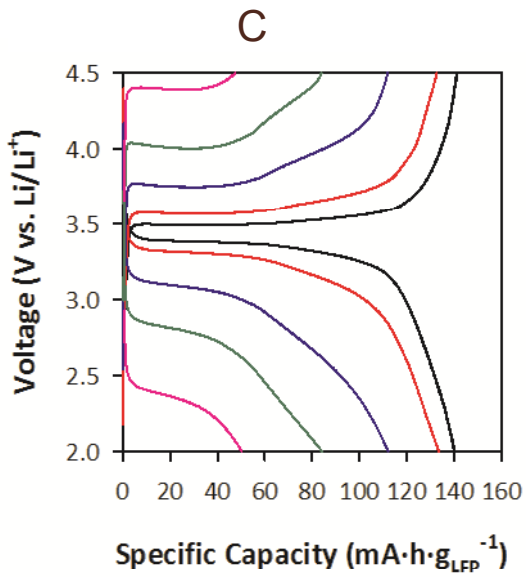
Coating with electric conductors: carbon and PEDOT

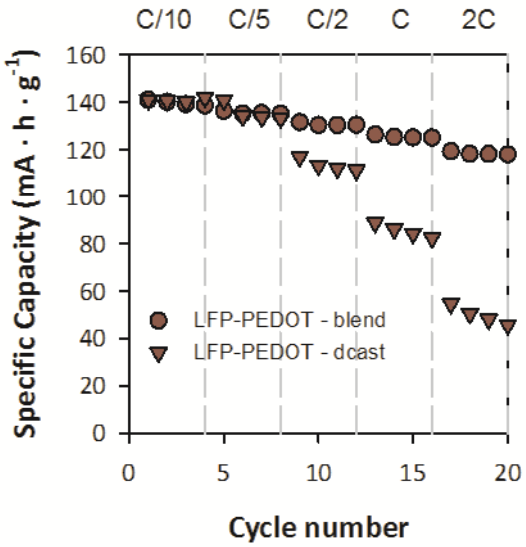
4. Applications with organic, inorganic and hybrid materials

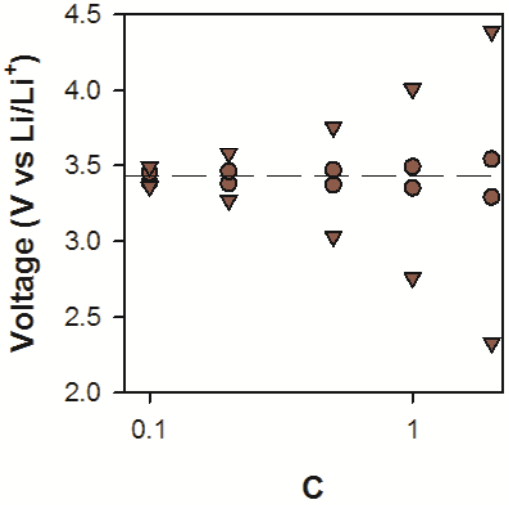
4.5 Batteries and Supercapacitors







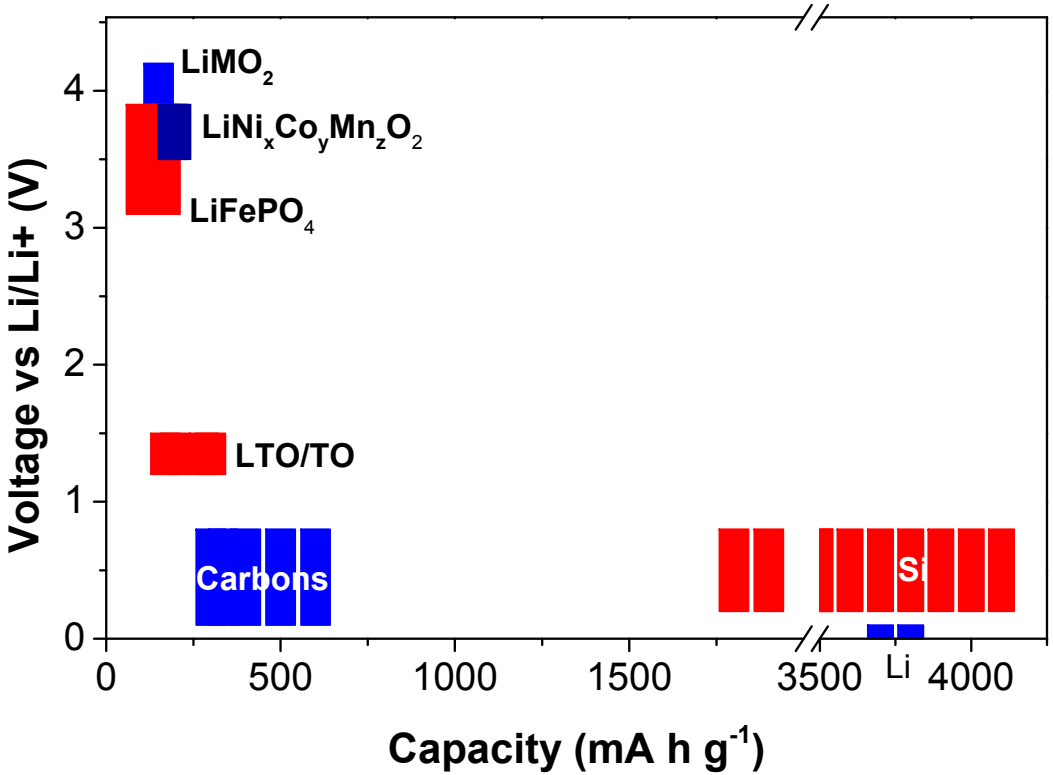




4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors

- Li-ion
  - Intercalation
  - Alloy



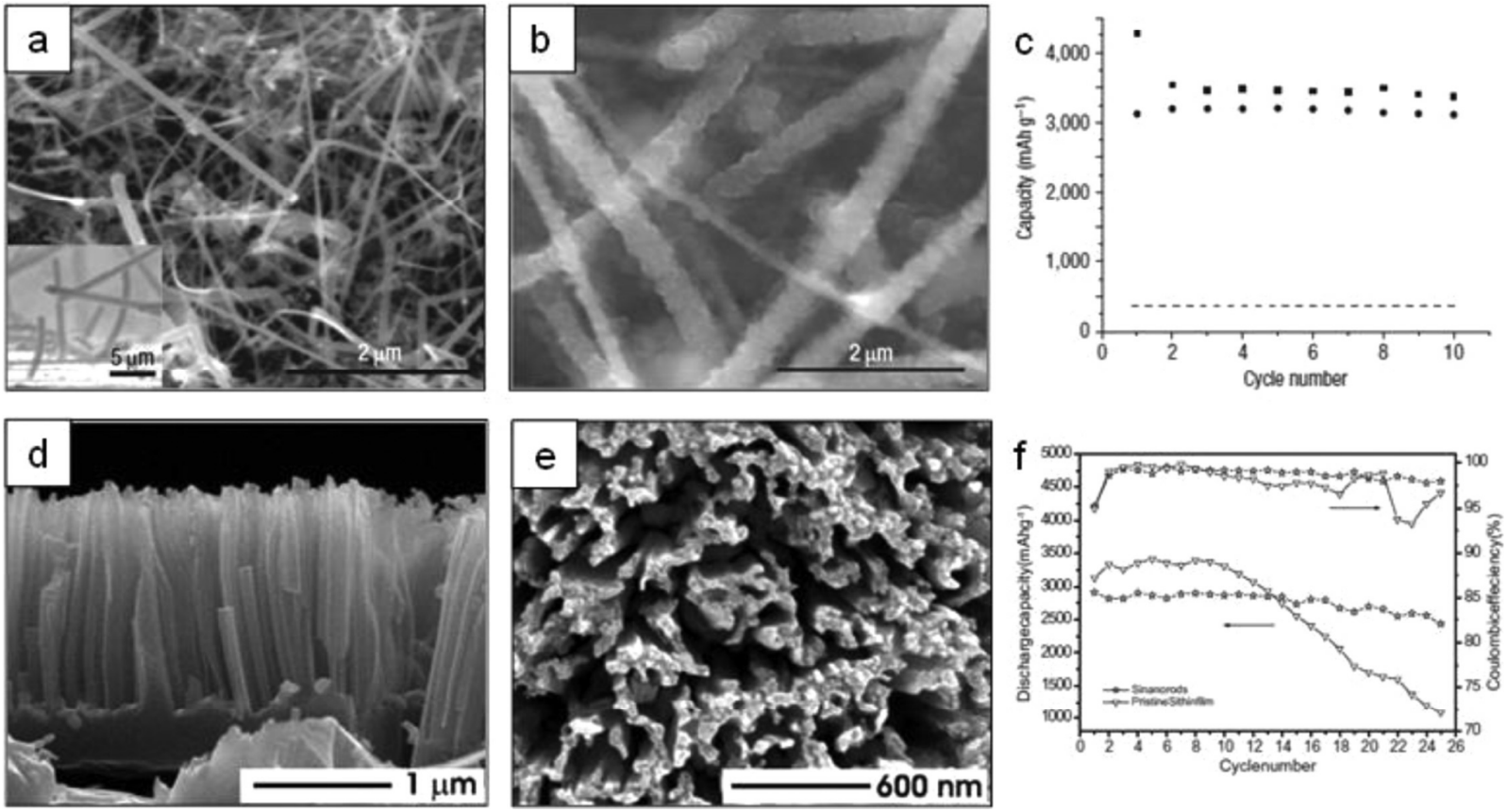
Theoretical capacity: 4200 mA h g^{-1} in the state $Li_{22}Si_5$

- Large V change → Fast capacity fading
- Poor rate capability (low electronic conduction, and ion diffusion)

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors

Batteries: Li-Si

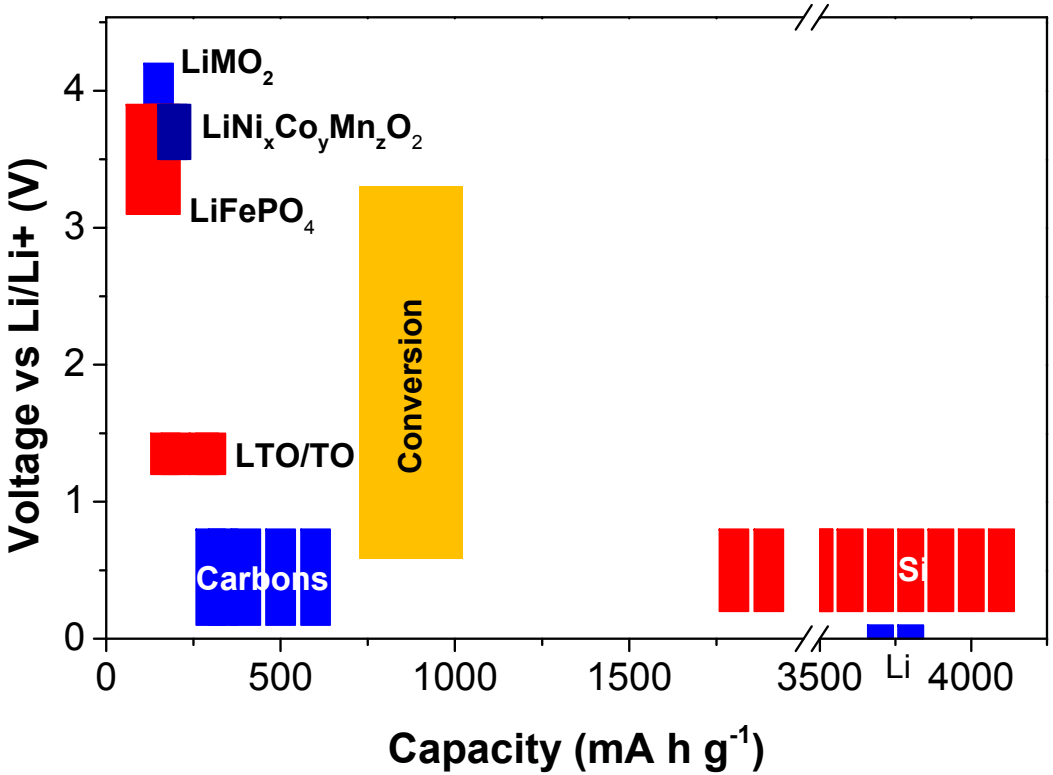


Song et al. J. Phys. Chem. Lett. 2014, 5, 720−731

4. Applications with organic, inorganic and hybrid materials

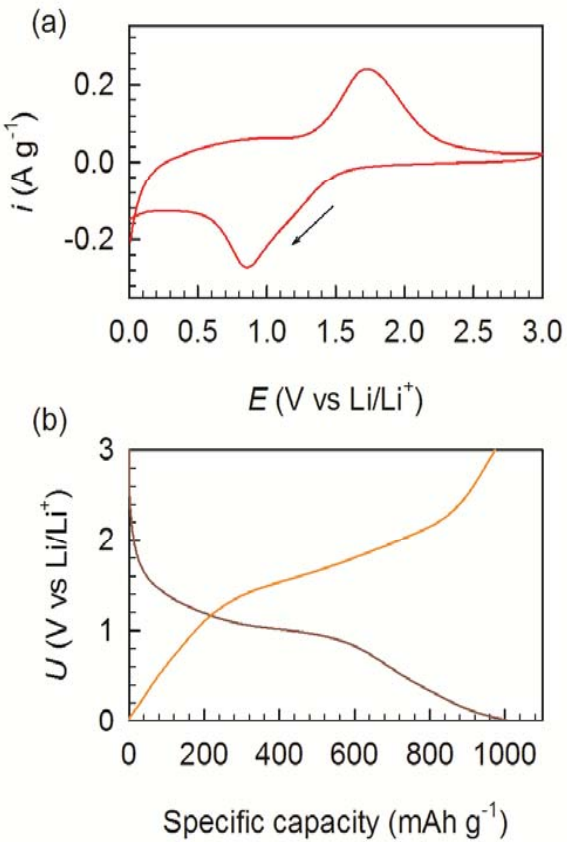
4.5 Batteries and Supercapacitors

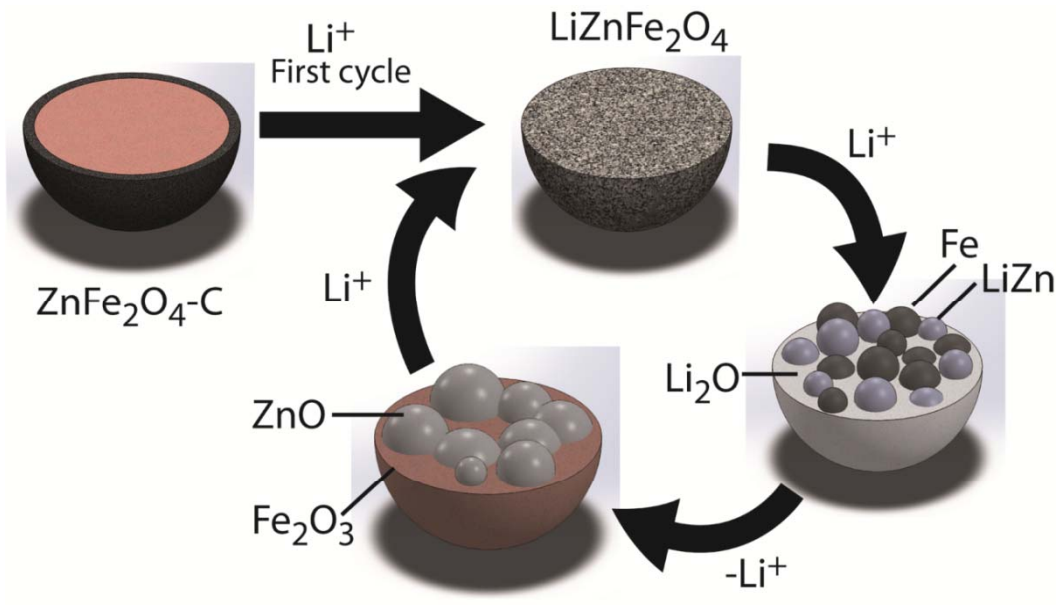
- Li-ion
  - Intercalation
  - Alloy
  - Conversion



4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors



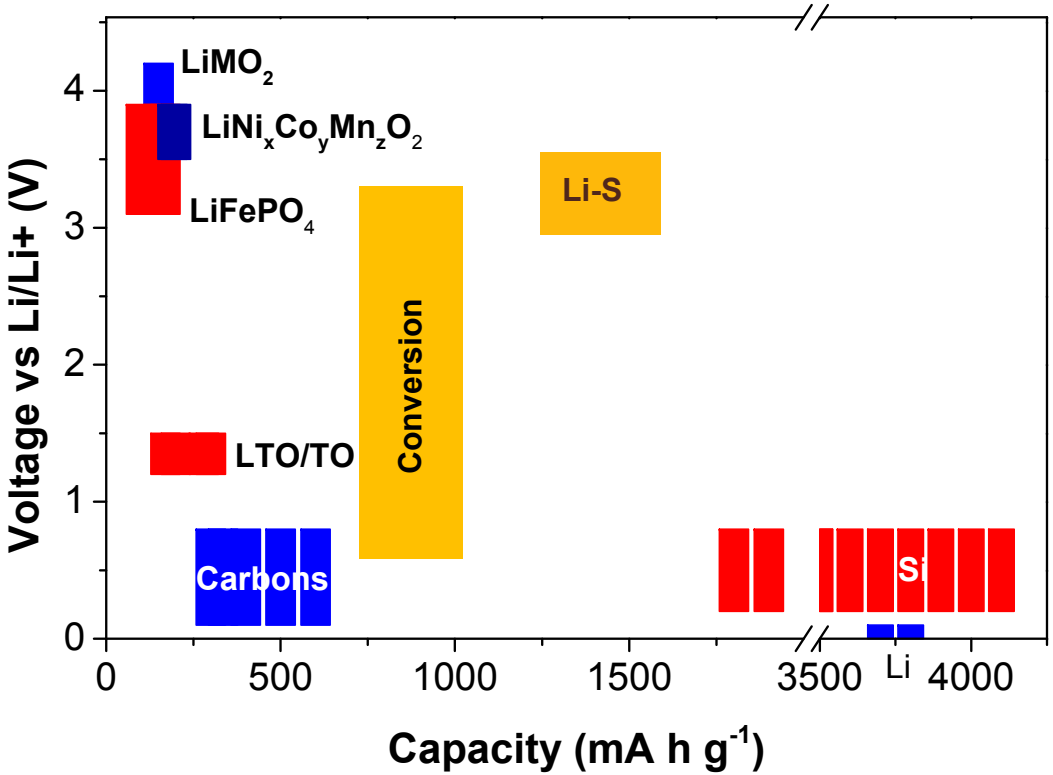


F. Martinez-Julian, A. Guerrero, M. Haro, J. Bisquert, D. Bresser, E. Paillard, S. Passerini G. Garcia-Belmonte *J. Phys. Chem. C* **2014**,

4. Applications with organic, inorganic and hybrid materials

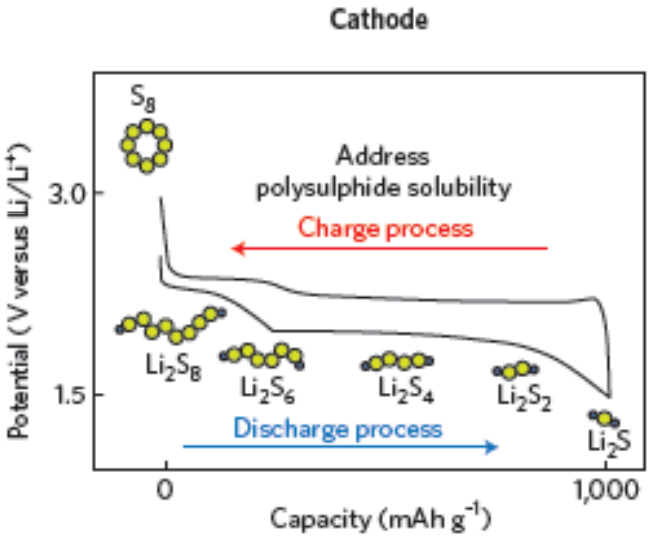
4.5 Batteries and Supercapacitors

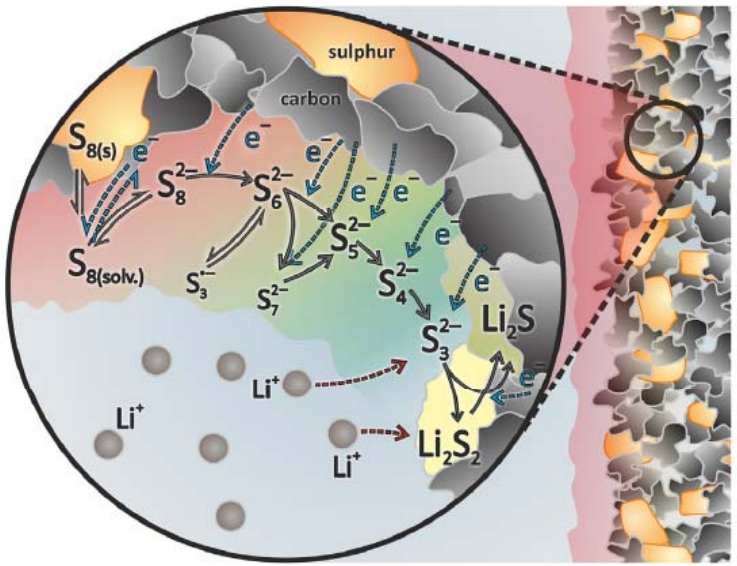
- Li-ion
  - Intercalation
  - Alloy
  - Conversion
- Batteries of future
  - Li-S

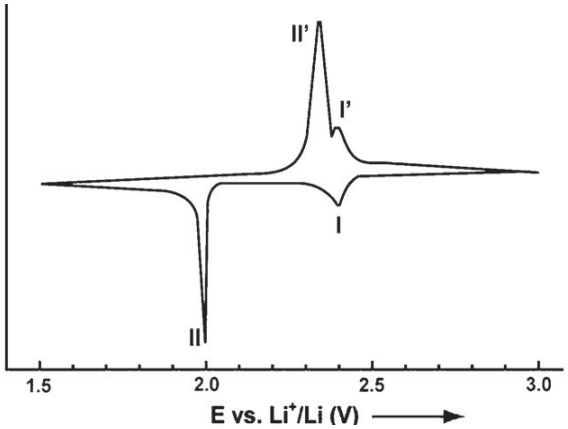


4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors







Theorical capacity: 1,675 mA·h·g $^{-1}$

Discharge:

I: $S_8 \rightarrow Li_2S_n$ ($4 \leq n \leq 8$)

II: $Li_2S_4 \rightarrow Li_2S_2$

III: $Li_2S_2 \rightarrow Li_2S$

Charge:

II': $Li_2S \rightarrow Li_2S_n$ ($2 \leq n \leq 4$)

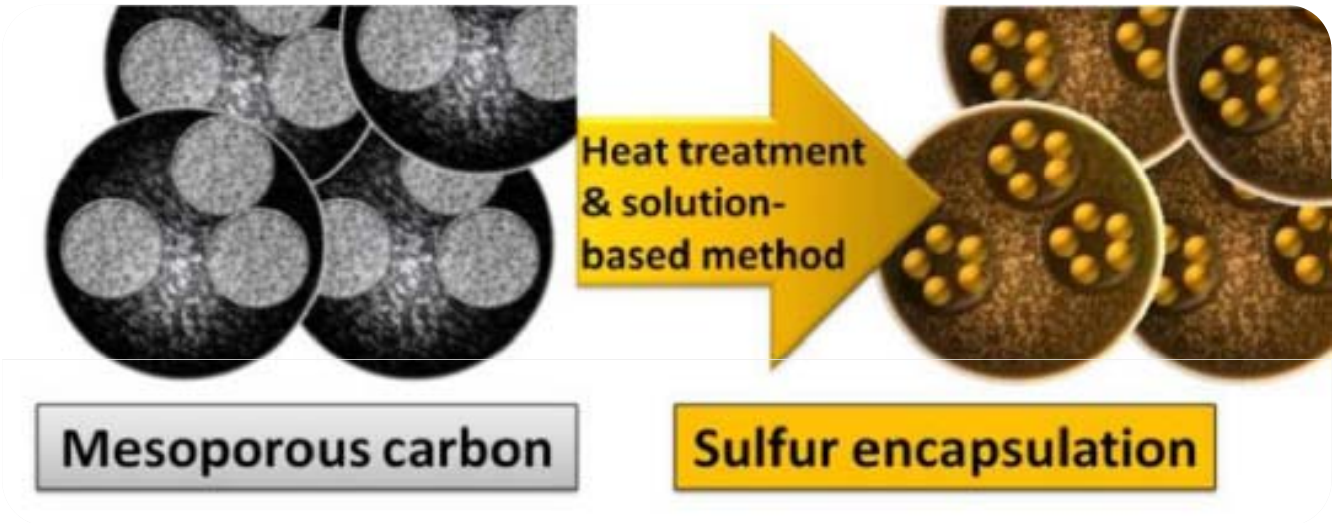
Li_2S_n ($2 \leq n \leq 4$) $\rightarrow Li_2S_n$ ($4 \leq n \leq 8$)

I': $Li_2S_n \rightarrow S_8$

Angew. Chem. Int. Ed. 2013, 52, 13186 – 13200

4. Applications with organic, inorganic and hybrid materials

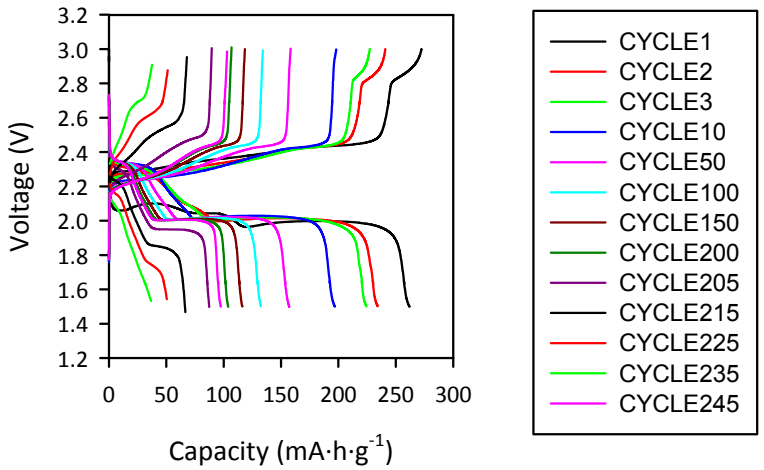
4.5 Batteries and Supercapacitors

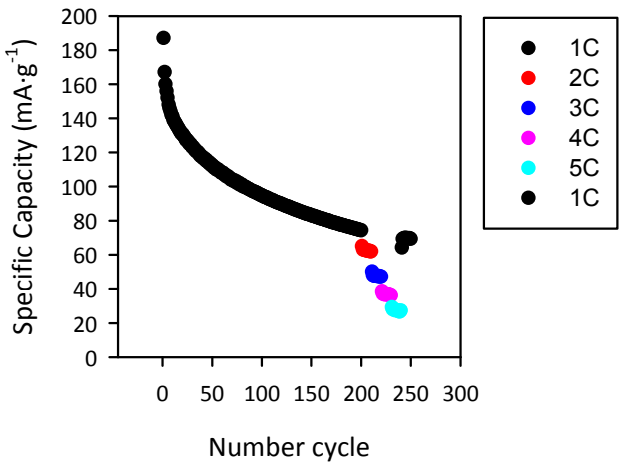


4. Applications with organic, inorganic and hybrid materials

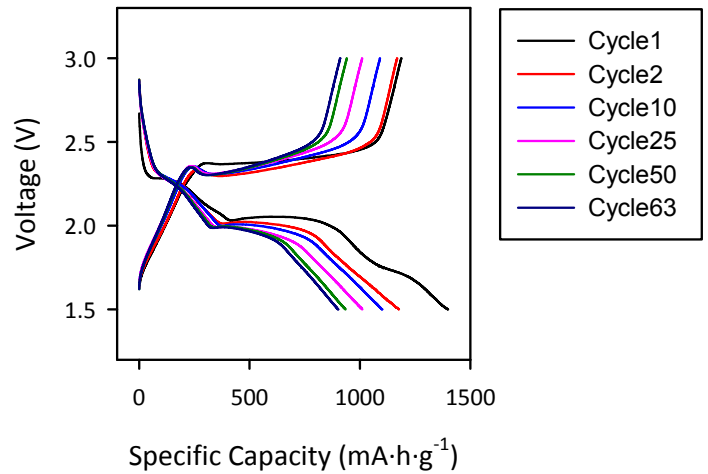
4.5 Batteries and Supercapacitors

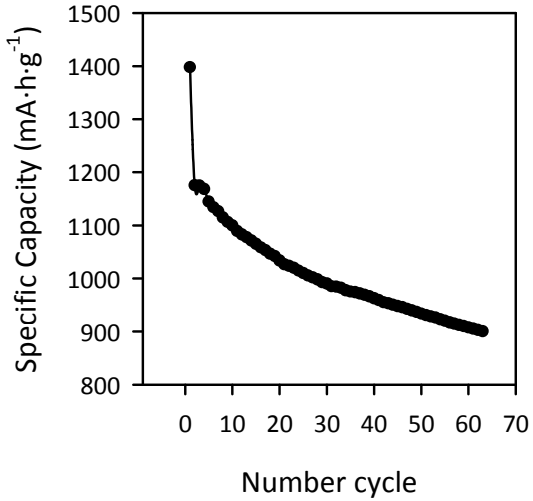
Sample I: Reference





Sample II: Mesoporous matrix

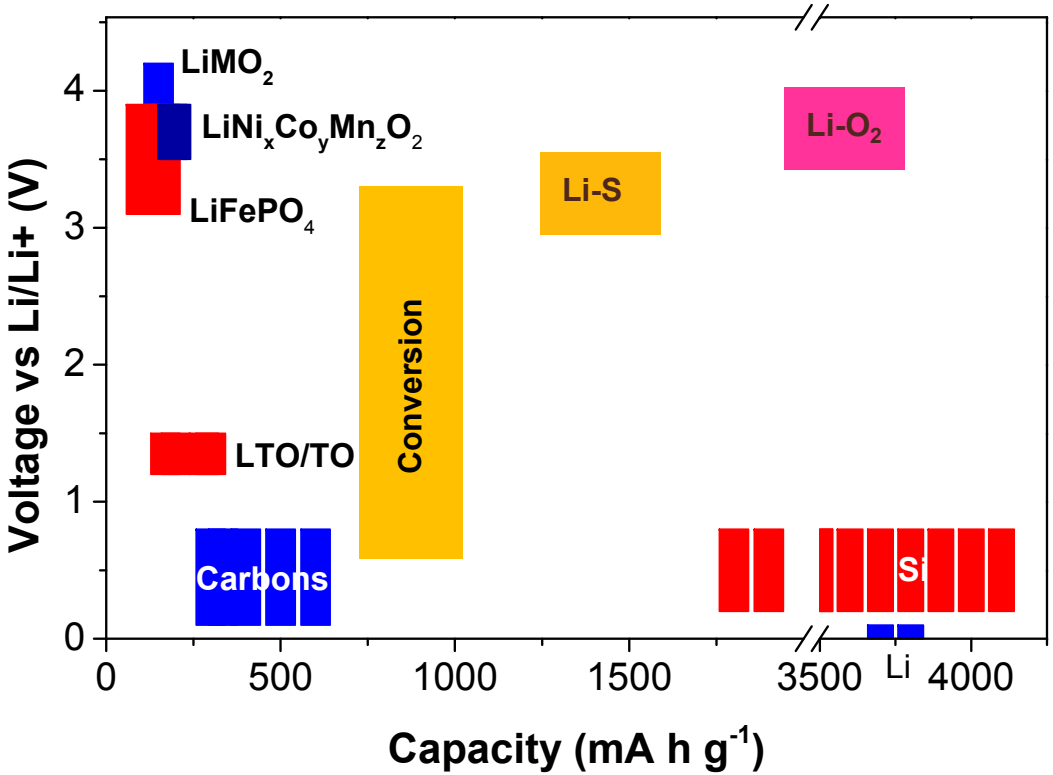




4. Applications with organic, inorganic and hybrid materials

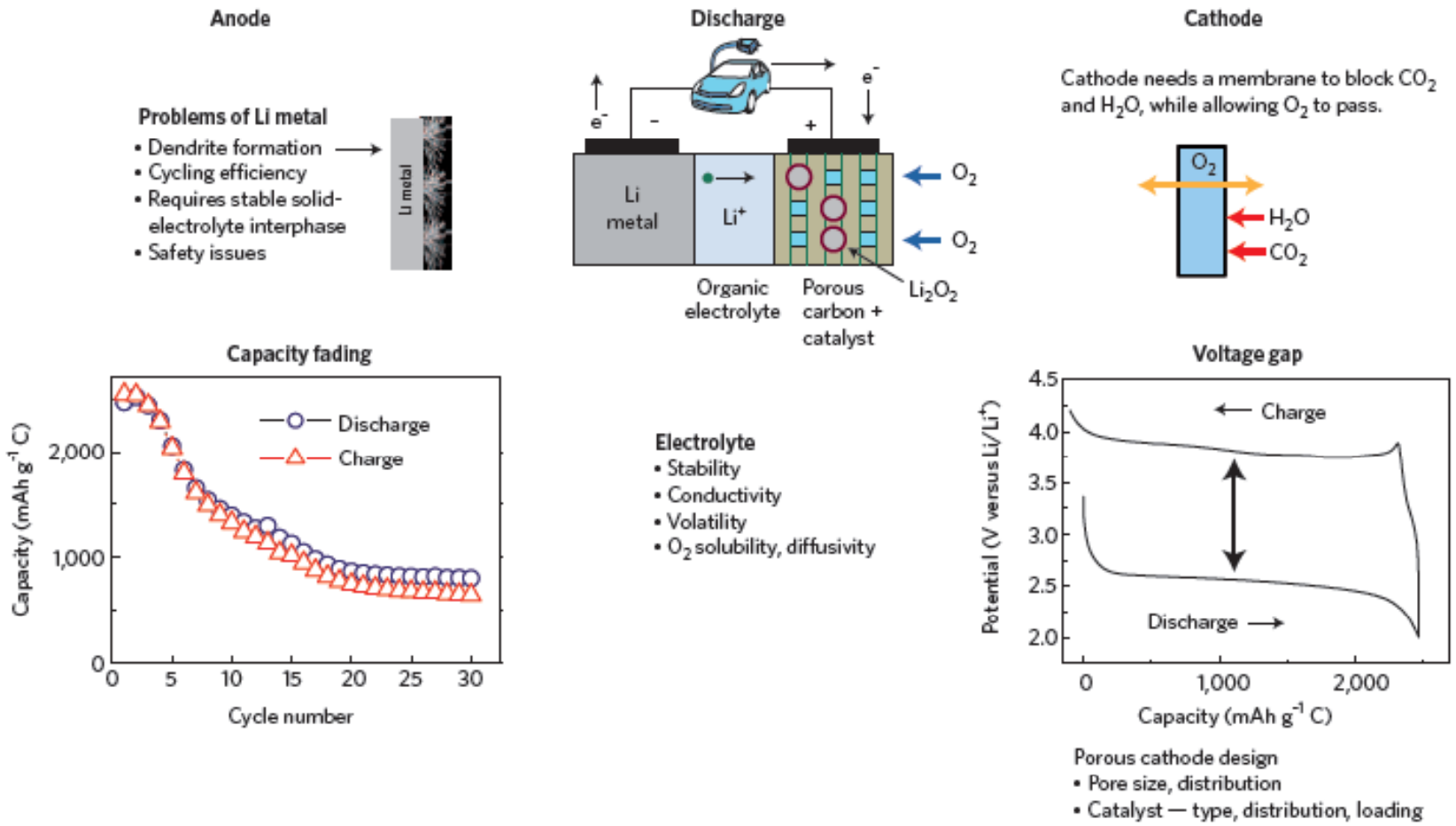
4.5 Batteries and Supercapacitors

- Li-ion
  - Intercalation
  - Alloy
  - Conversion
- Batteries of future
  - Li-S
  - Li-O_2



4. Applications with organic, inorganic and hybrid materials

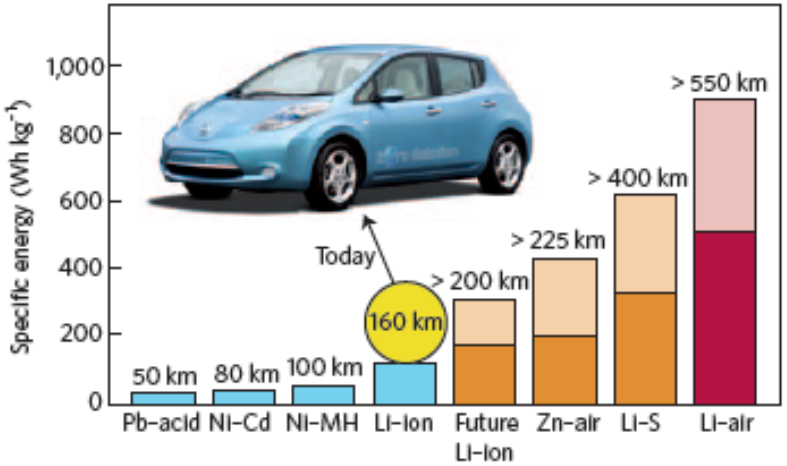
4.5 Batteries and Supercapacitors

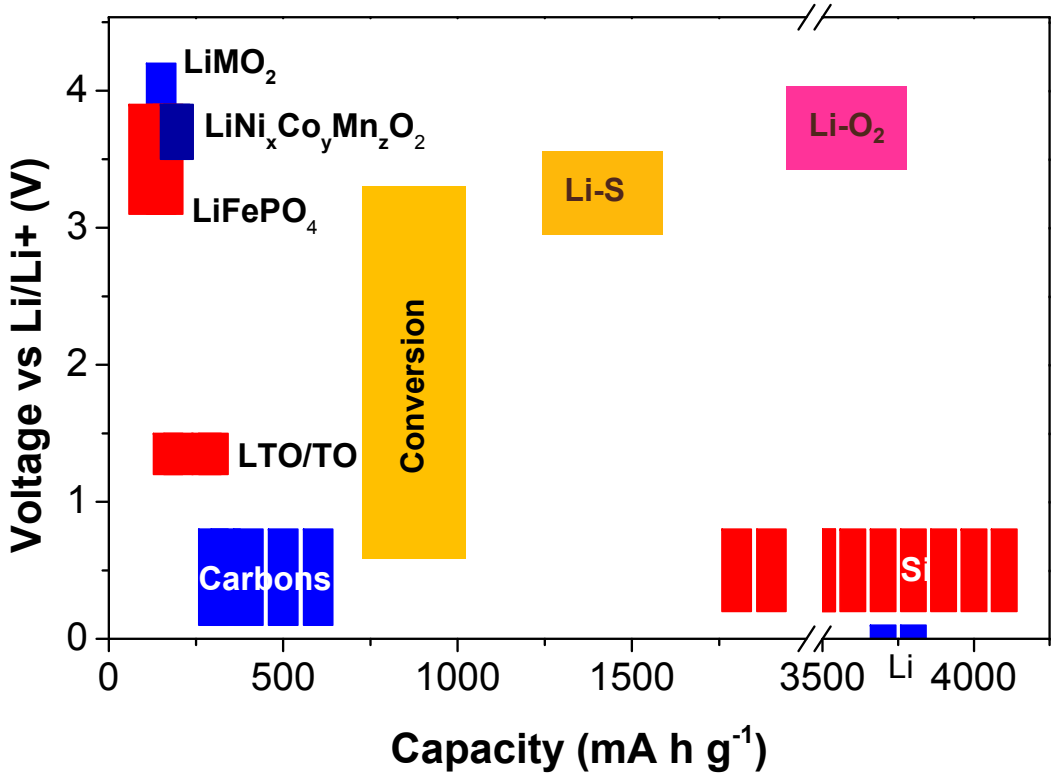


P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J-M. Tarascon Nat. Mater. 2012, 11, 19

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors





4. Applications with organic, inorganic and hybrid materials

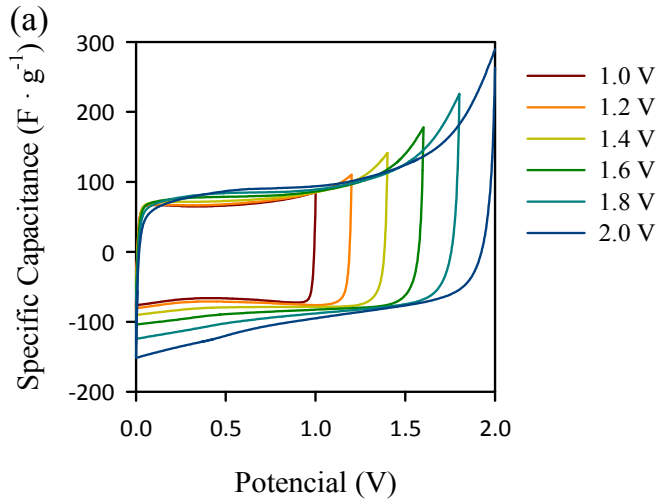
4.5 Batteries and Supercapacitors

Supercapacitors:

Energy storage

$$E = \frac{1}{2} C V_{dc}^2 \rightarrow E = \frac{1}{2} C (V_{\max}^2 - V_{\min}^2)$$

E(y2014) = 15-30 Wh/kg



Power

$$P_{eff} = \frac{1}{8} \frac{V^2}{R_i} \approx 15 \text{ kW/kg}$$

https://www.youtube.com/watch?v=EoWMF3VkI6U
https://www.youtube.com/watch?v=RzGpfi4OkPY
https://www.youtube.com/watch?v=jpy8G3yBeJ4

4. Applications with organic, inorganic and hybrid materials

4.5 Batteries and Supercapacitors

Comparison