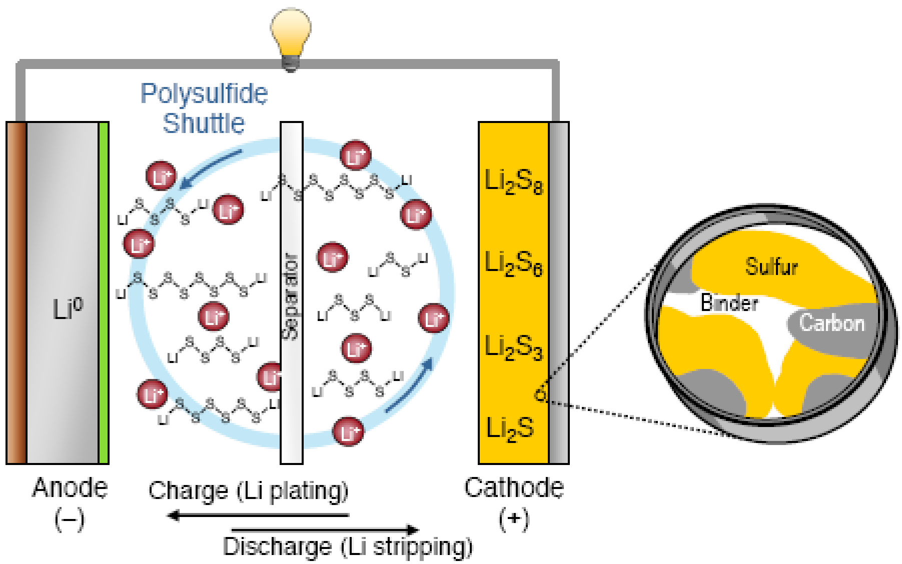
Bateria Litio-Azufre

Working Principle of Li/S System

BASF
The Chemical Company



Model of Lithium/Sulfur battery

Discharging:

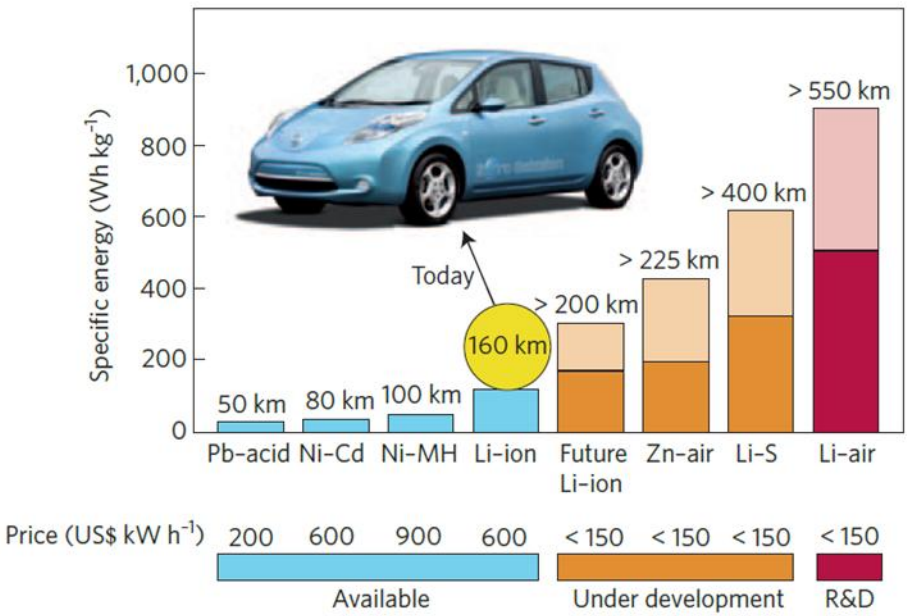
- Li is stripped from anode and lithium sulfides are formed in the cathode

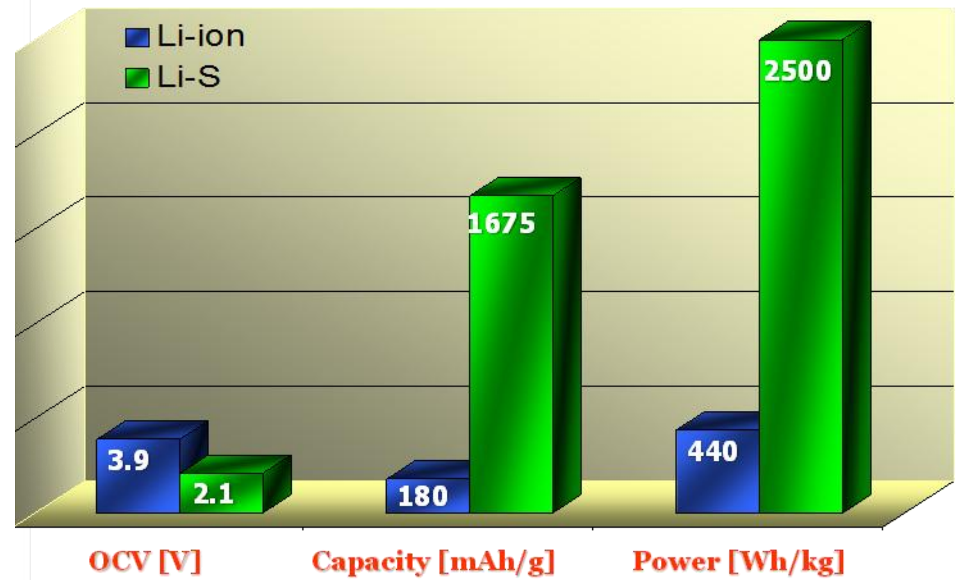
Charging:

- Re-plating of Li and re-formation of elemental sulfur

Speciality of Li/S: (Partly) **dissolving electrodes** during cycling

VENTAJAS DE LITIO-AZUFRE





- Mayor capacidad teorica, densidad de energia y potencia.
- Bajo costo (1$ por 100g) y abundancia de materiales (350 ppm).
- Puede operar a baja temperatura (-40˚C).

Bruce, P. G., Freunberger, S. A., Hardwick, L. J., Tarascon, J.-M.. *Nature materials* **11**, 19–29 (2012).

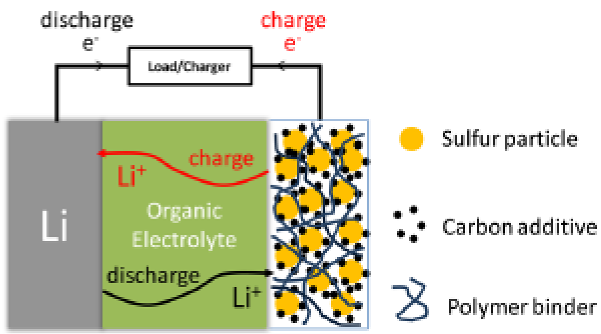


Figure 1. Schematic diagram of a Li–S cell with its charge/discharg operations.

anodo

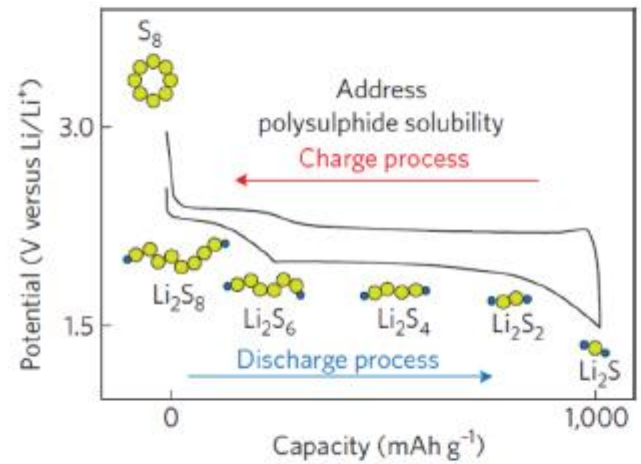
$$2Li \rightarrow 2Li^{+} + 2e$$

cathodo

$$S + 2Li^{+} + 2e \rightarrow Li_2S$$

Reaccion global

$$2Li + S \rightarrow Li_2S$$



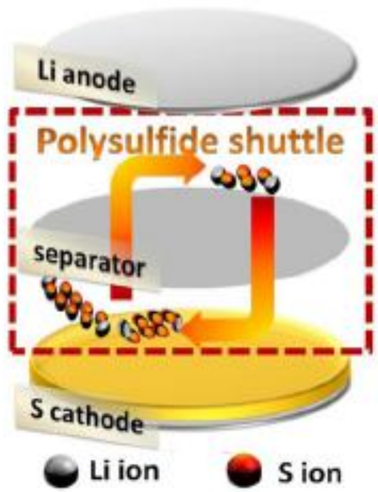
3.861 Ah/g (litio) 1.672 Ah/g (azufre), 1.167 Ah/g (celda Li-S) a 2.15 V, densidad de energia2,51 W.h/g

Reducción en la descarga: $Li_2S \rightarrow Li_2S_2 \rightarrow Li_2S_3 \rightarrow Li_2S_4 \rightarrow Li_2S_6 \rightarrow Li_2S_8 \rightarrow S_8$

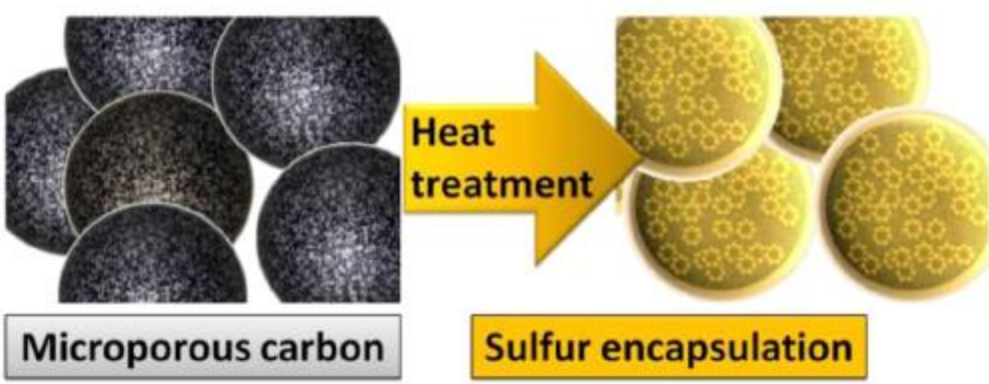
Oxidacion en la carga, $S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_3$

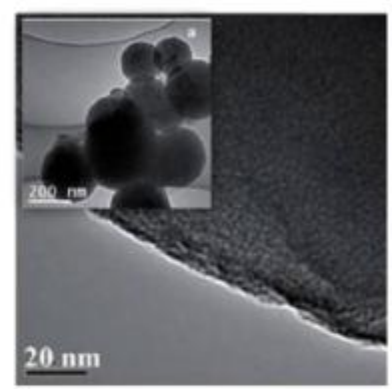
Transporte por polisulfuro

$Li_2S_x\ (6 < x \leq 8)$,



Alta resistencia del Azufre ($\sim 10^{-30}$ S cm^{-1}





PROBLEMAS

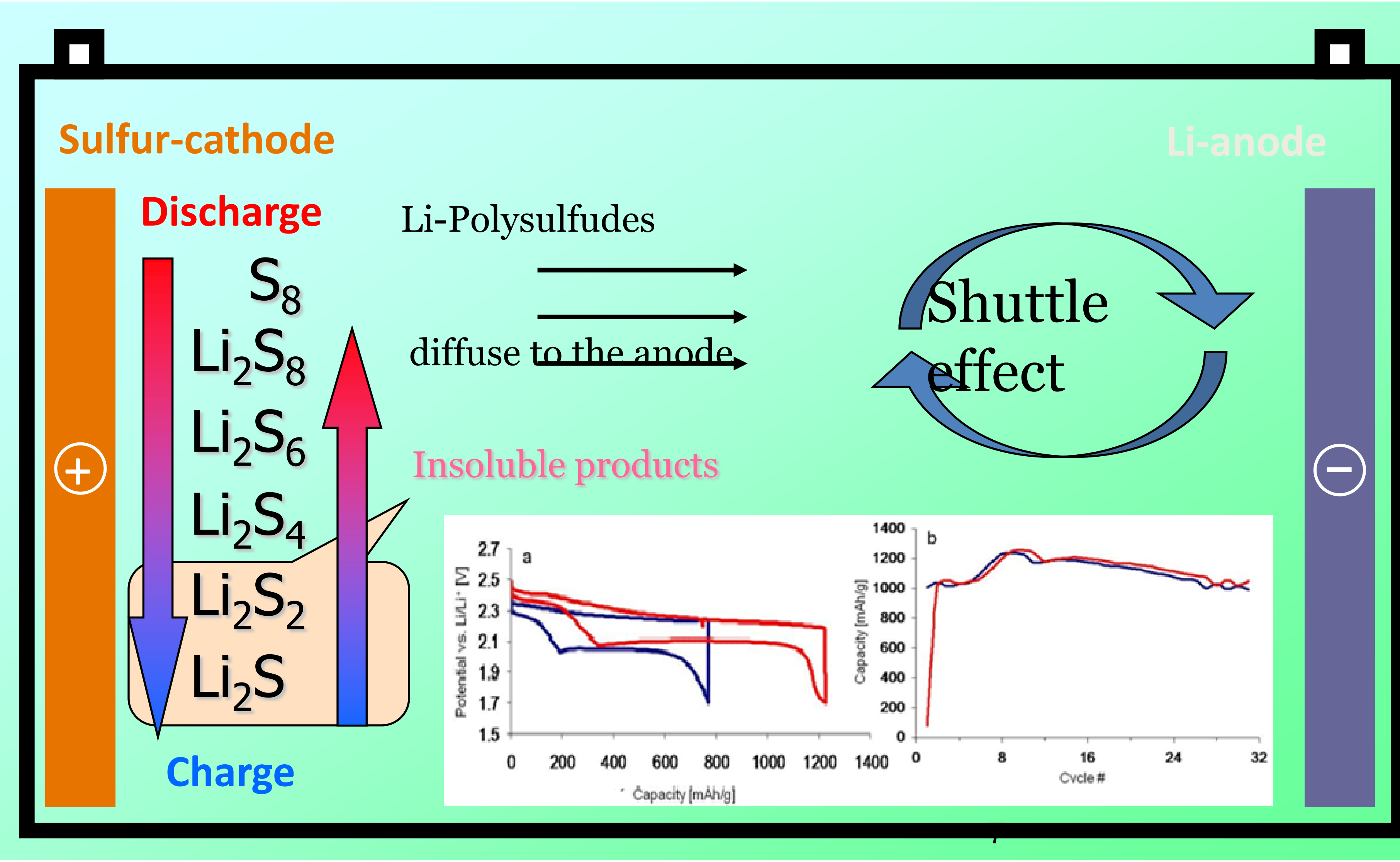
- Que origina la caida de capacidad de la bateria Li-S?
  - Analisis de la superficie de litio metalico.
  - Cambios morfologicos del composito S-C en el catodo.

- Como podemos mejorar la ciclabilidad de celdas Li-S?
  - Encapsular al azufre dentro de estructuras porosas.
  - Solventes a base de carbonato para baterias Li–S.
  - Carbon activado o tela de carbon impregnada de azufre
  - El efecto del nitrato de litio como aditivo para electrolito basado en DOL:DME electrolyte en el catodo.

- Es posible tener baterias de Li-ion-Azufre en lugar de Li-S para resolver problemas de seguridad?
  - Baterias Sn-S ion litio.
  - Prototipos de baterias de silicio litiado-azufre (SLS).

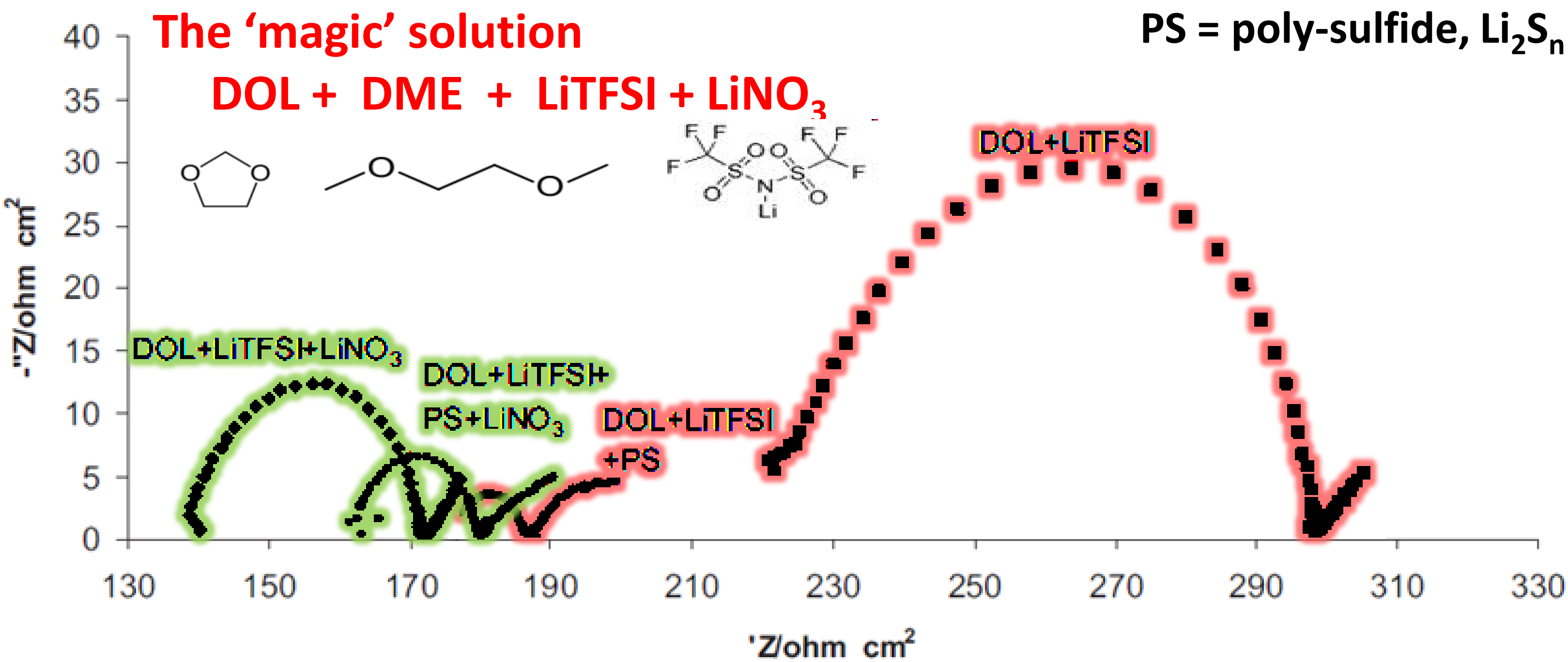
Mecanismo de la bateria

Formacion y re-oxidacion de Li_2S_n



El efecto de $LiNO_3$ en la quimica de superficie y la impedancia de anodos de Li.

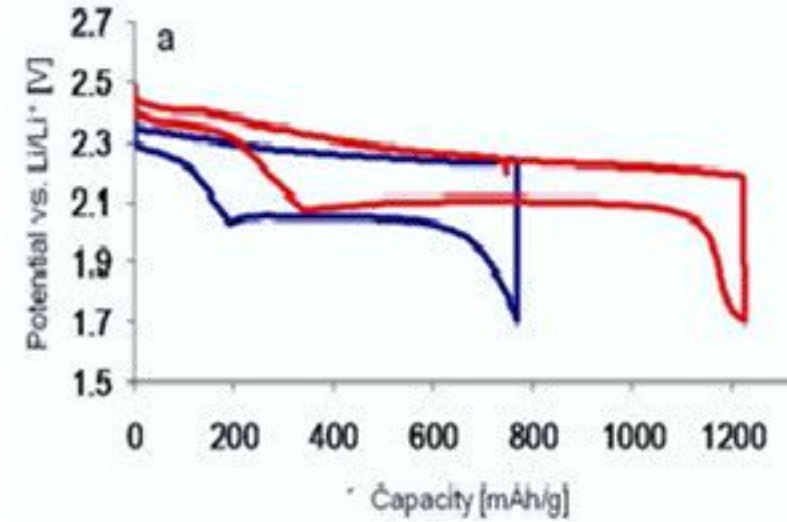
Adicion de nitrato de litio disminuye la impedancia.



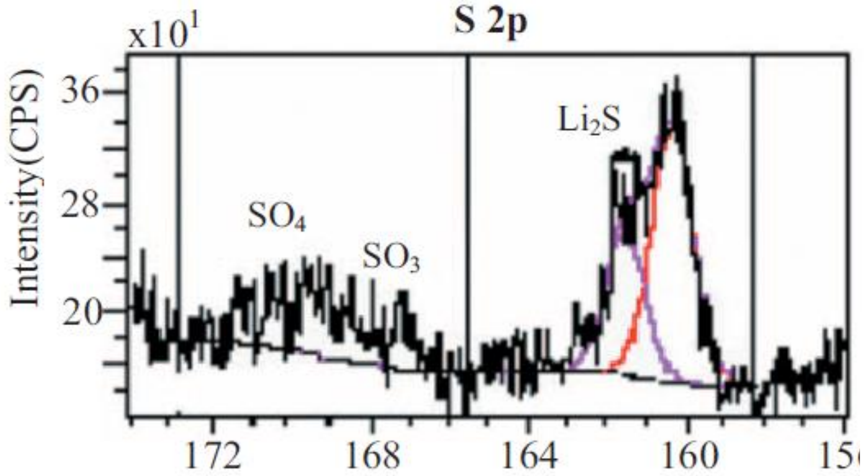
• Espectro de impedancia de electrodos de Li luego de 18h almacenado a OCV en varias soluciones electroliticas.

D. Aurbach

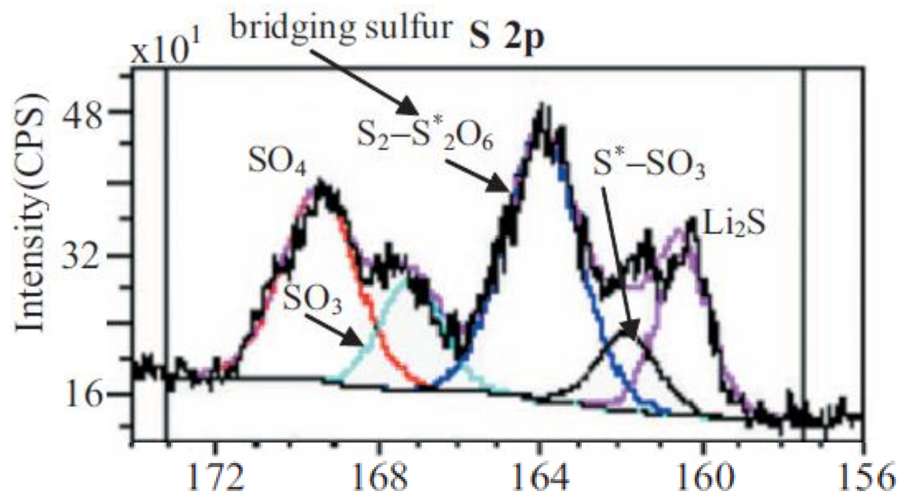
NO_3^- en solucion oxida el sulfuro hasta sulfato (6^+)



Solution containing only Li_2S_6



Solution containing both Li_2S_6 and $LiNO_3$



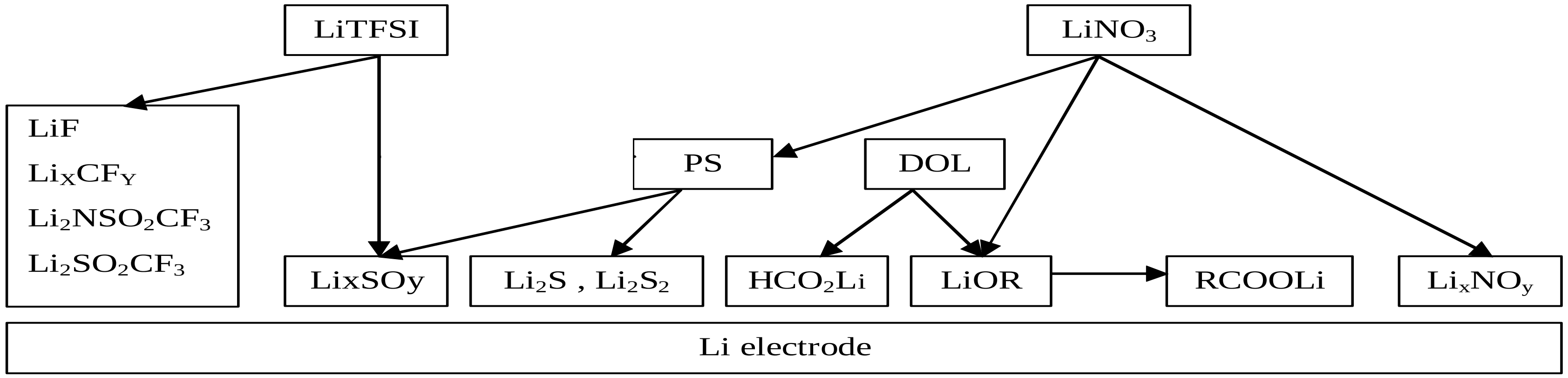
- Espectros XPS de azufre en electrodos de Li preparados y almacenados en soluciones de 1,3-dioxolane.

D. Aurbach

Efecto de $LiNO_3$

- La presencia de $LiNO_3$ en solucion afecta la quimica de superficie de electrodos de litio.
- Por reduccion forma Li_xNO_y . Oxida Li_2S_n (PS) a Li_xSO_y en superficie.
- Afecta el mecanismo de transporte que evita la carga completa de los electrodos de azufre en celdas Li–S.

Mapa de la quimica de anodos de Li en DOL/LiTFSI/PS/$LiNO_3$



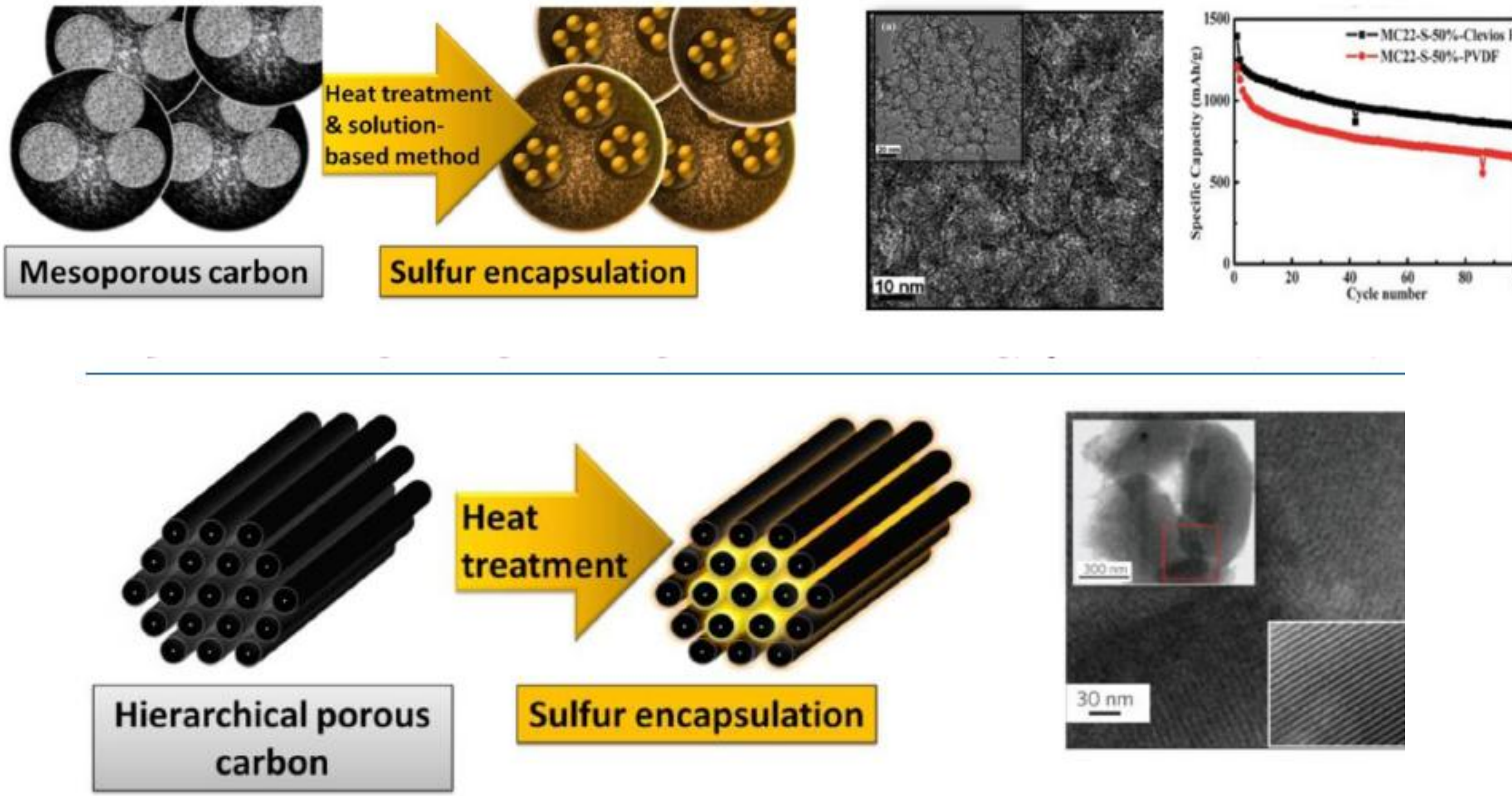


Figure 9. Schematic models, SEM observation (the SEM image of the carbon host is also shown), and cell

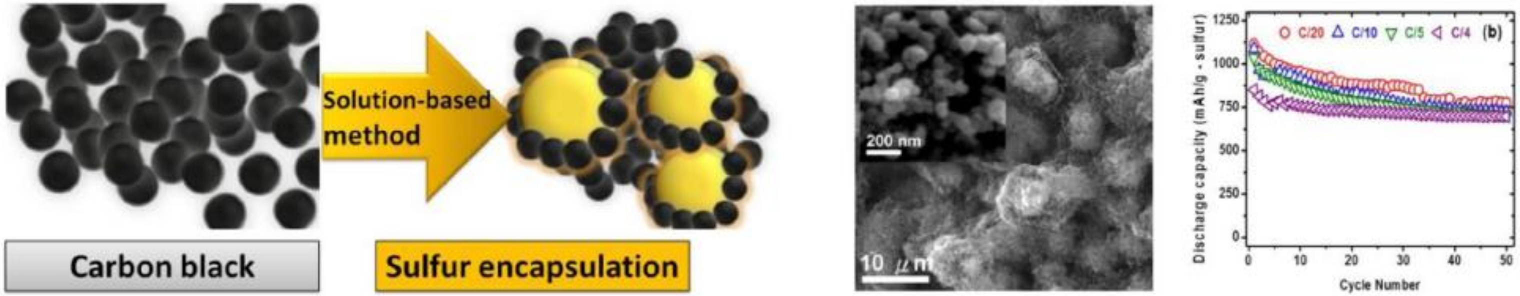


Figure 10. Schematic models, SEM observation (the SEM image of the carbon host is also shown), and cell performance of a representative S–carbon black composite. Reprinted with permission from ref 29c. Copyright 2012 Elsevier.

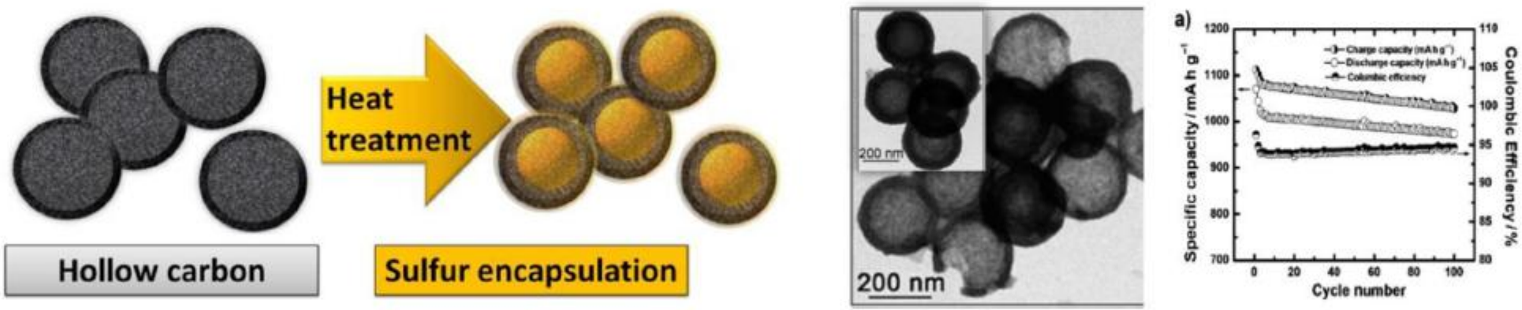


Figure 11. Schematic models, SEM observation (the SEM image of the carbon host is also shown), and cell performance of a representative S–hollow carbon sphere composite. Reprinted with permission from ref 30a. Copyright 2011 Wiley-VCH Verlag GmbH & Co. KGaA.

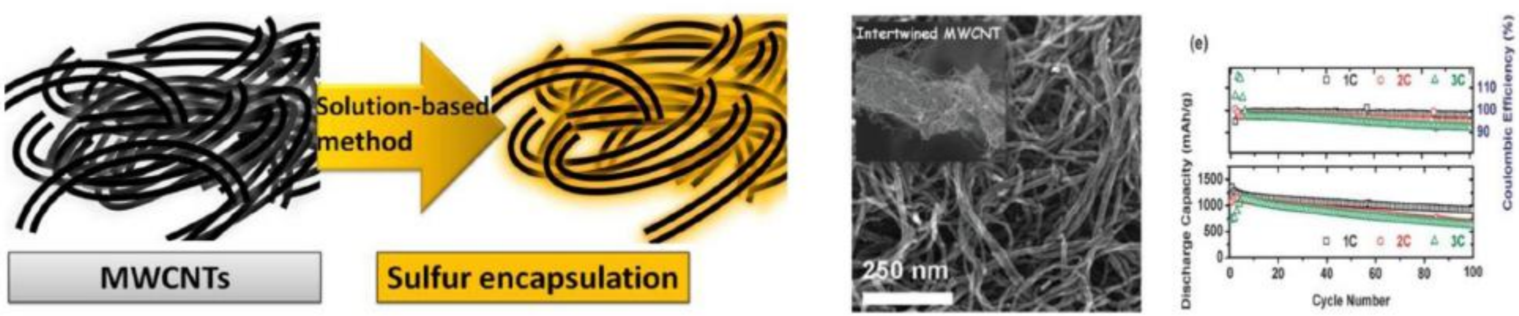
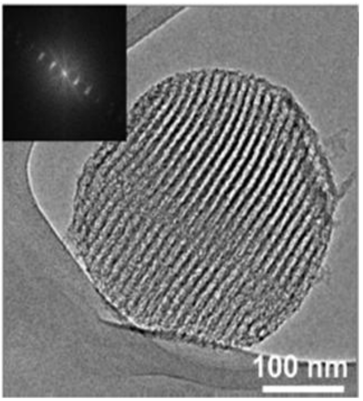
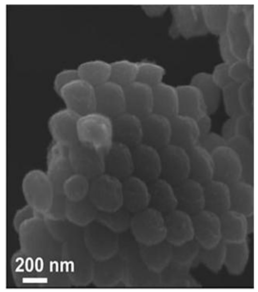


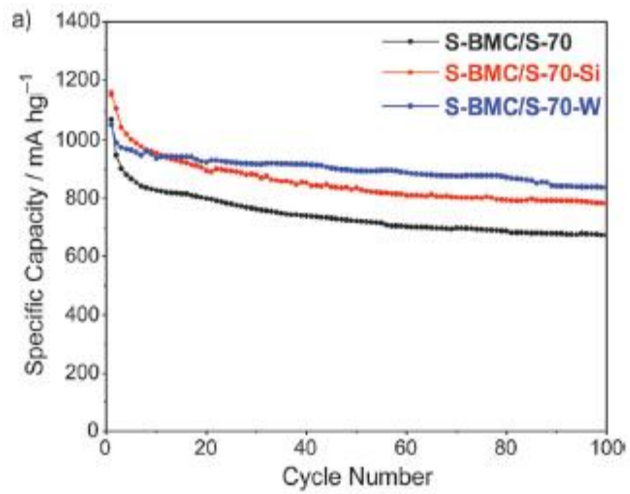
Figure 12. Schematic models, SEM observation (the SEM image of the carbon host is also shown), and cell performance of a representative S–CNT composite. Reprinted with permission from ref 24b. Copyright 2012 The Royal Society of Chemistry.

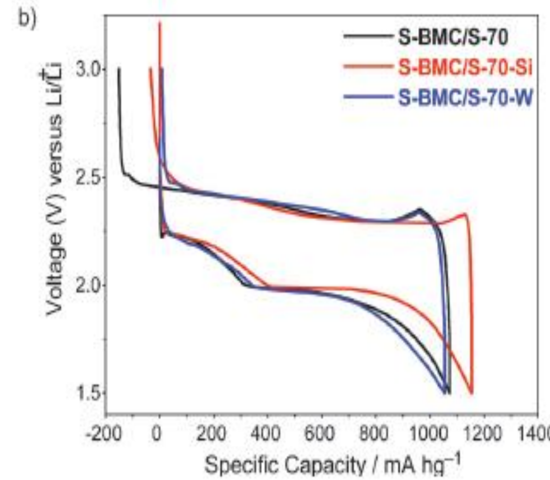
Solucion:
Encapsular al azufre dentro de plantillas porosas

1. **Spherical Ordered Mesoporous Carbon (OMC) Nano particles with high porosity for lithium-sulfur batteries**





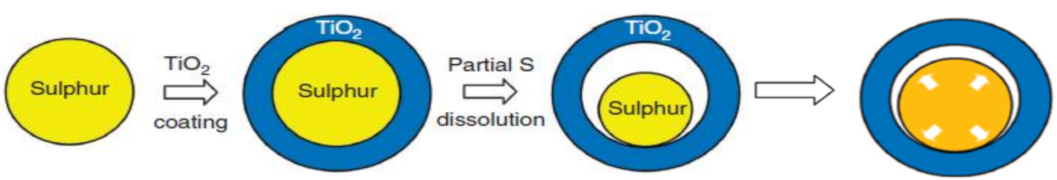


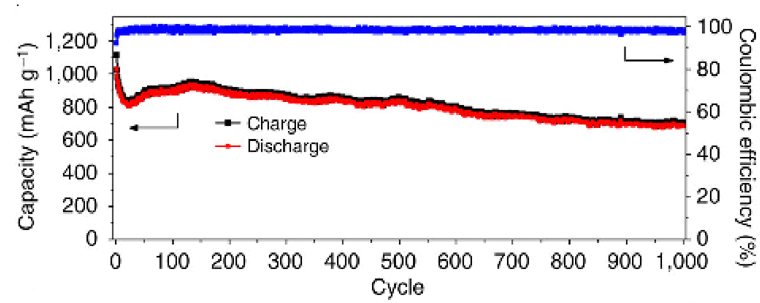


High meso-porous volume >2 cm^3/g; High surface area > 2400 m^2/g;High current density

Schuster, J.; He, G.; Mandlmeier, B.; Yim, T.; Lee, K. T.; Bein, T.; Nazar, L. F. *Angewandte Chemie* 2012, *51*, 3591.

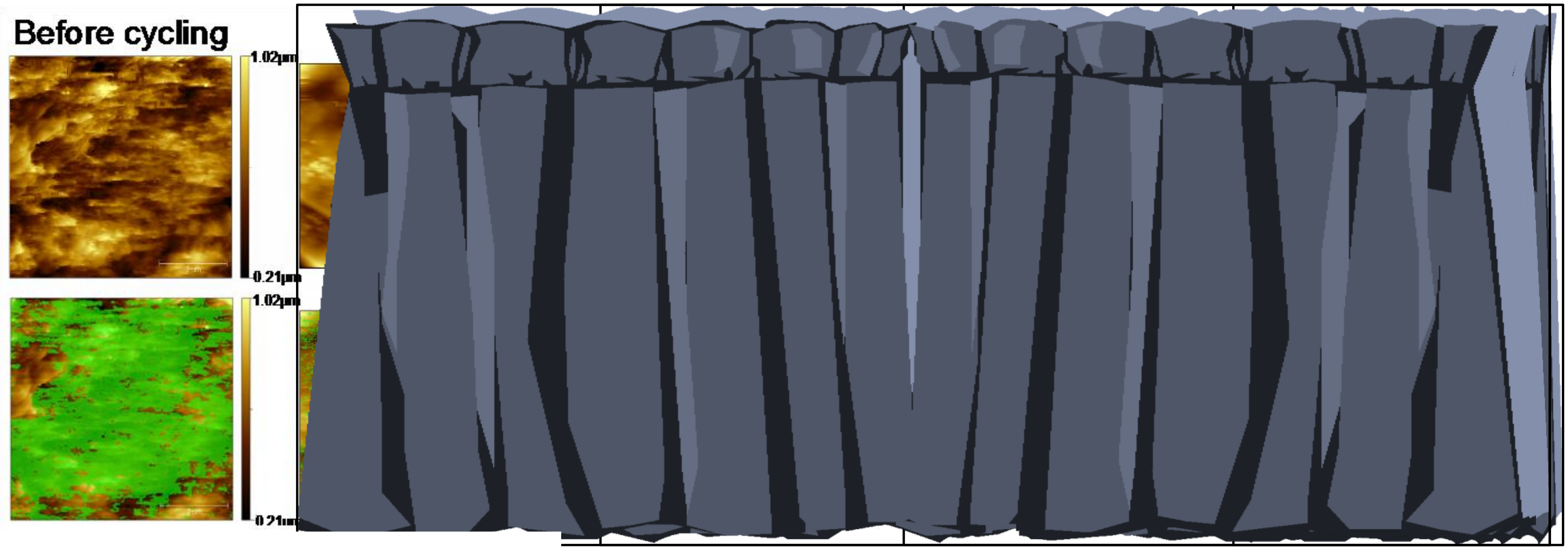
2. **Sulfur–TiO_2 yolk–shell nano- architecture with internal voids**

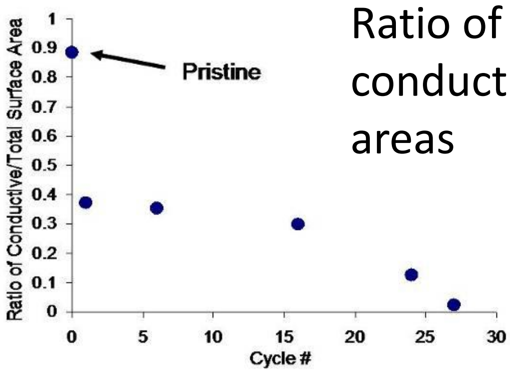




Zhi Wei Seh, Weiyang Li, Judy J. Cha, Guangyuan Zheng, Yuan Yang, Matthew T. McDowell, Po-Chun Hsu & Yi Cui Nature Communications 2013 , 4, 1331

Luego de ciclado, la superficie de los catodos de azufre pierde area y se hace menos conductora.

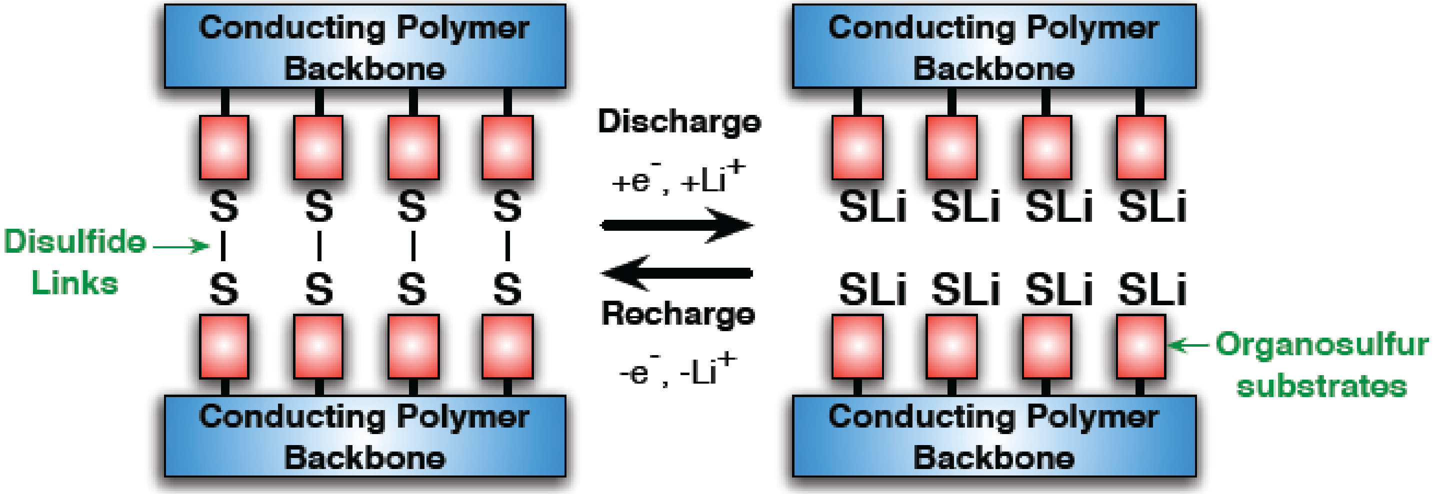




Ratio of conductive areas

- Non conductive layers comoposed of granular features, such as Li_2S and Li_2S_2, are accumulated on of electrode surface.

New Hybrid Compounds: Thiolates with Conducting Polymer π-Backbones



GOALS:

- *Improve* charge/discharge cyclability.
- *Accelerate* redox reactions of disulfide segments with conducting polymer π-backbones.
- *Design* conducting electroactive materials.

Y. Kiya and Jay C. Henderson *et al.*, IMLB2006, Biarritz France, Abstract #224 &225
Y. Kiya, J. C. Henderson, G. R. Hutchison, and H. D. Abruña, *J. Mater. Chem.*, (2007), 17(41), 4366-4376

Aromatic Redox System for Fast Charge/Discharge Reactions

Thiolate/Disulfide System

$$2R\text{-}S^{-}(Li^{+}) \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} R\text{-}S\text{-}S\text{-}R + 2Li^{+} + 2e^{-}$$

- High Gravimetric Capacity (2-Electron Process)
- Easy to Incorporate in Rocking-Chair Type System

Sulfide System

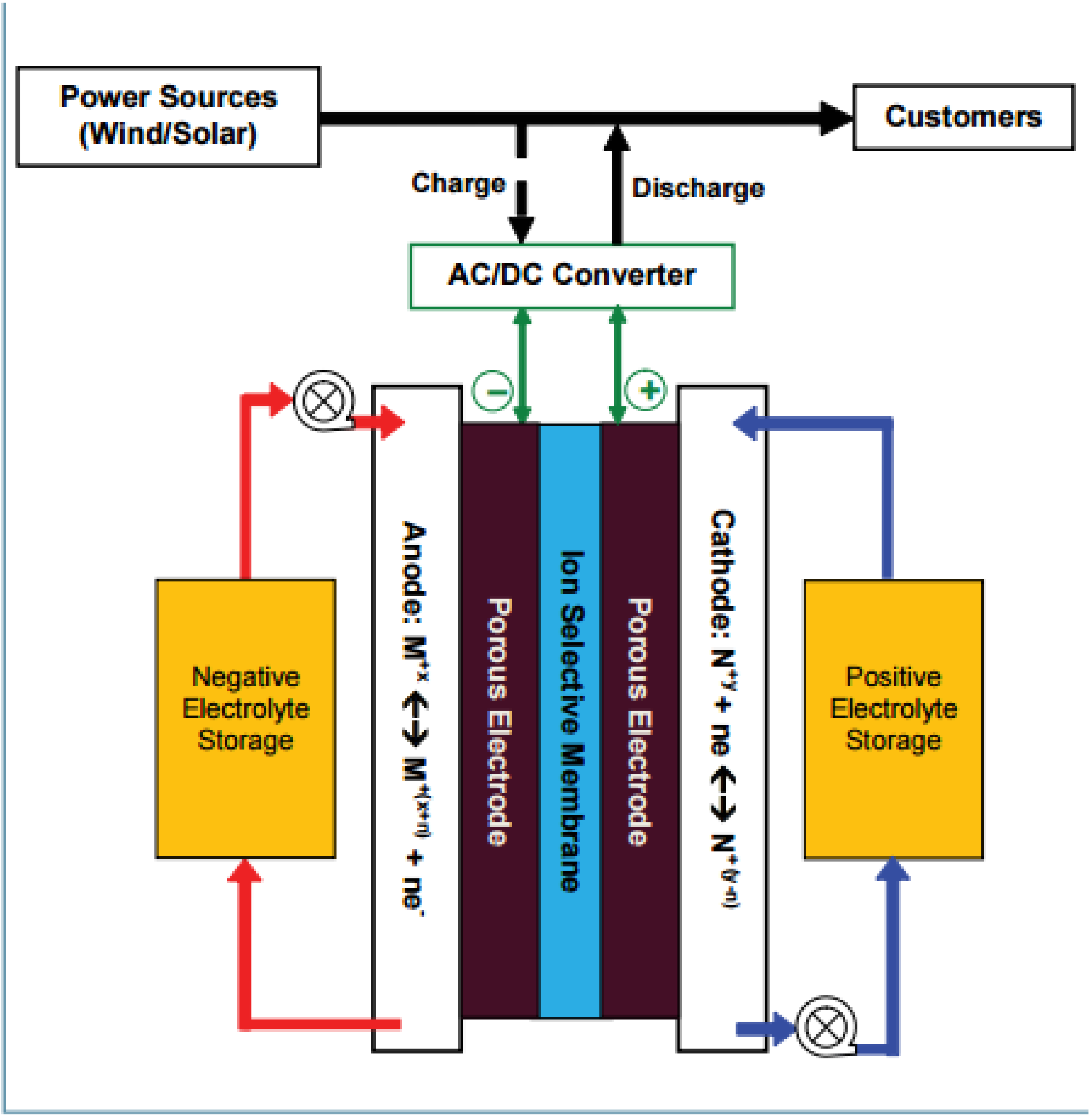
$$RS\text{-}Ar\text{-}SR' \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} [RS\text{-}Ar\text{-}SR']^{2\oplus} + 2e^{-}$$

- Fast Charge/Discharge Reactions w/o Electrocatalysts
- High Operation Voltage (> 3V vs. Li/Li^{+})

H. Abruna, Cornell Univesity

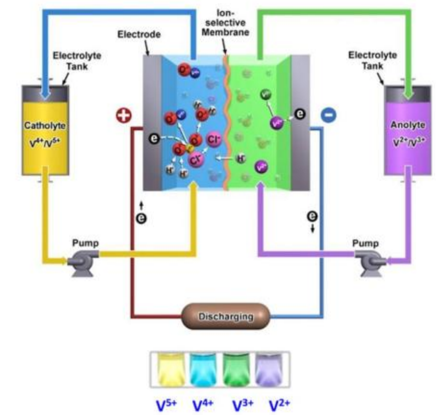
Baterias Redox de Flujo

Flow Battery


Power Sources (Wind/Solar)
Customers
Charge
Discharge
AC/DC Converter
Negative Electrolyte Storage
Anode: $M^{+x} \leftrightarrow M^{+(x+n)} + ne^{-}$
Porous Electrode
Ion Selective Membrane
Porous Electrode
Cathode: $N^{+y} + ne \leftrightarrow N^{+(y-n)}$
Positive Electrolyte Storage

BATERIAS EN FLUJO

International Flow Battery Forum in Karlsruhe
Fraunhofer Institute for Chemical Technology ICT



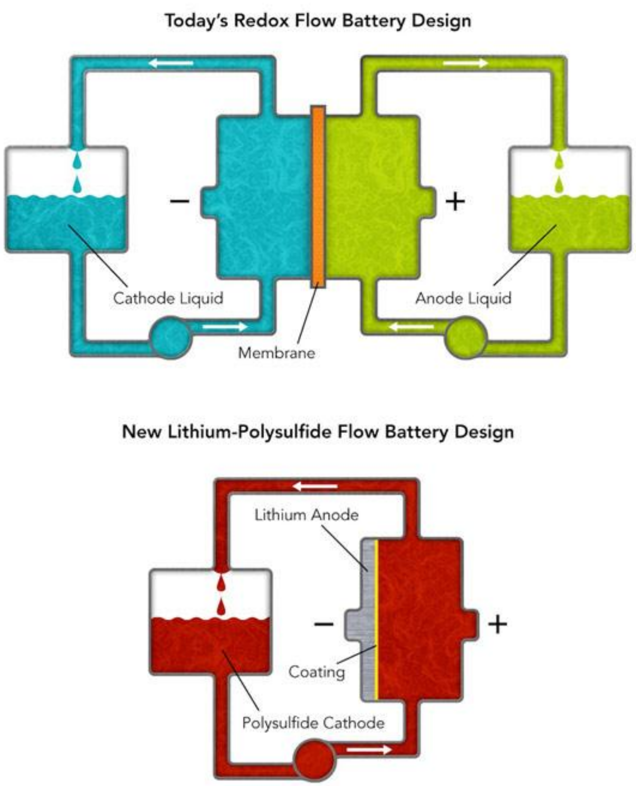
20 MWh all vanadium redox flow cell for stationary applications for 2 MW wind turbine
75% efficiency in current technical solutions
10,000 additional cycles
Cost 0.05 \$us/kWh
UniEnergy Technologies (UET) of Seattle, 2MW/8MWh
Dalian China planned by Rongke, 200MW/800MWh.
Tesla 80 MWh California, 129 MWh Australia (baterías de litio)

Table I. Characteristics of Some Flow Battery Systems.

System	Reactions	E_{cell}^{o}	Electrolyte
Redox			Anode/Cathode
All Vanadium [3]	Anode: $V^{2+} \xleftarrow{charge} \xrightarrow{discharge} V^{3+} + e^-$ Cathode: $VO_2^+ + e^- \xleftarrow{charge} \xrightarrow{discharge} VO^{2+}$	1.4 V	H_2SO_4/H_2SO_4
Vanadium-Polyhalide [5]	Anode: $V^{2+} \xleftarrow{charge} \xrightarrow{discharge} V^{3+} + e^-$ Cathode: $½ Br_2 + e^- \xleftarrow{charge} \xrightarrow{discharge} Br^-$	1.3 V	VCl_3-HCl/NaBr-HCl
Bromine-Polysulfide [6]	Anode: $2 S_2^{2-} \xleftarrow{charge} \xrightarrow{discharge} S_4^{2-} + 2e^-$ Cathode: $Br_2 + 2e^- \xleftarrow{charge} \xrightarrow{discharge} 2 Br^-$	1.5 V	NaS_2/NaBr
Iron-Chromium [7]	Anode: $Fe^{2+} \xleftarrow{charge} \xrightarrow{discharge} Fe^{3+} + e^-$ Cathode: $Cr^{3+} + e^- \xleftarrow{charge} \xrightarrow{discharge} Cr^{2+}$	1.2 V	HCl/HCl
H_2-Br_2 [8]	Anode: $H_2 \xleftarrow{charge} \xrightarrow{discharge} 2H^+ + 2e^-$ Cathode: $Br_2 + 2e^- \xleftarrow{charge} \xrightarrow{discharge} 2Br^-$	1.1 V	PEM*- HBr
Hybrid			
Zinc-Bromine	Anode: $Zn \xleftarrow{charge} \xrightarrow{discharge} Zn^{2+} + 2e^-$ Cathode: $Br_2 + 2e^- \xleftarrow{charge} \xrightarrow{discharge} 2 Br^-$	1.8 V	$ZnBr_2/ZnBr_2$
Zinc-Cerium [9]	Anode: $Zn \xleftarrow{charge} \xrightarrow{discharge} Zn^{2+} + 2e^-$ Cathode: $2Ce^{4+} + 2e^- \xleftarrow{charge} \xrightarrow{discharge} 2Ce^{3+}$	2.4 V	CH_3SO_3H (both sides)

BATERIA DE LITIO-AZUFRE EN FLUJO

Researchers Design a New Low Cost Lithium-Polysulfide Flow Battery
May 24, 2013
Professor Yi Cui., Menlo Park, California (Stanford/SLAC)
Para almacenar energia solar y eolica y alimentar la red



Solucion de polisulfuro, anodo de Li y catodo de S/C

Yuan Yang, Guangyuan Zhengb and Yi CuiA, "A membrane-free lithium/polysulfide semi-liquid battery for large-scale energy storage," Energy Environ. Sci., 2013,6, 1552-1558; DOI: 10.1039/C3EE00072A