锂硫电池用硫复合阴极材料

Sulfur composites as cathode for lithium-sulfur battery

高学平　邱新平　艾新平　吴锋

X. P. Gao, X. P. Qiu, X. P. Ai, F. Wu

南开大学　清华大学　武汉大学　北京理工大学

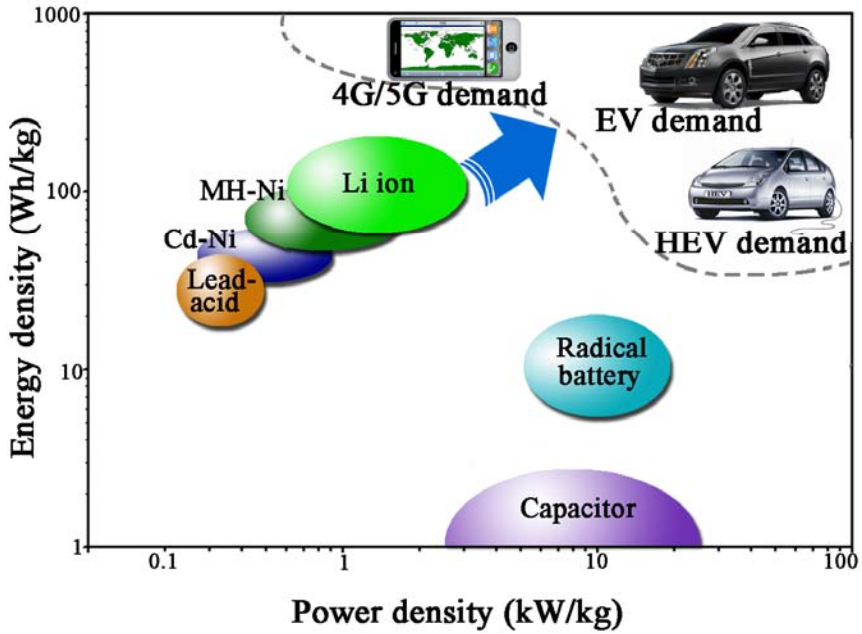
Nankai University, Tsinghua University

Wuhan Univsity, Beijing Institute of Technology

Supported by 973 Program in China

Background

- **Higher energy densities of batteries are required for future applications, such as next generations of communication devices (4G/5G) and electric vehicles (EVs).**
- **In view of the battery development in the past decades, the breakthroughs in battery technology was brought by the development of new materials and battery concept.**

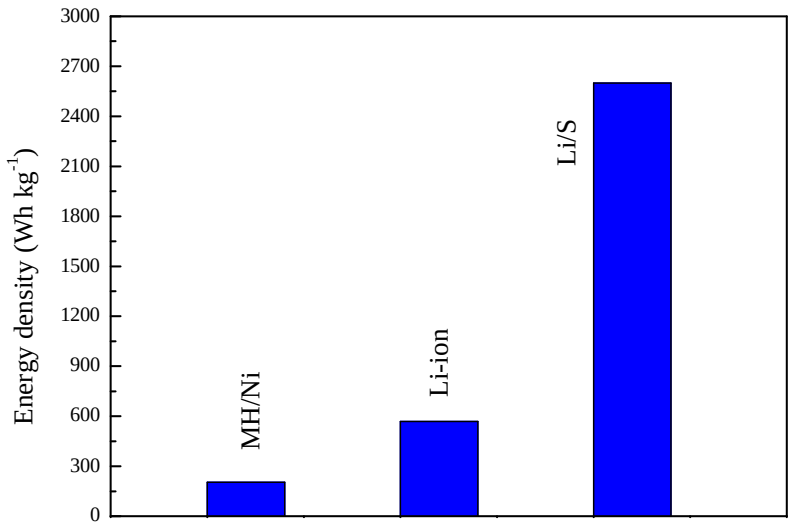


Schematic representation of the different secondary batteries in terms of power density and energy density

Sulfur cathode for lithium-sulfur battery

Advantage

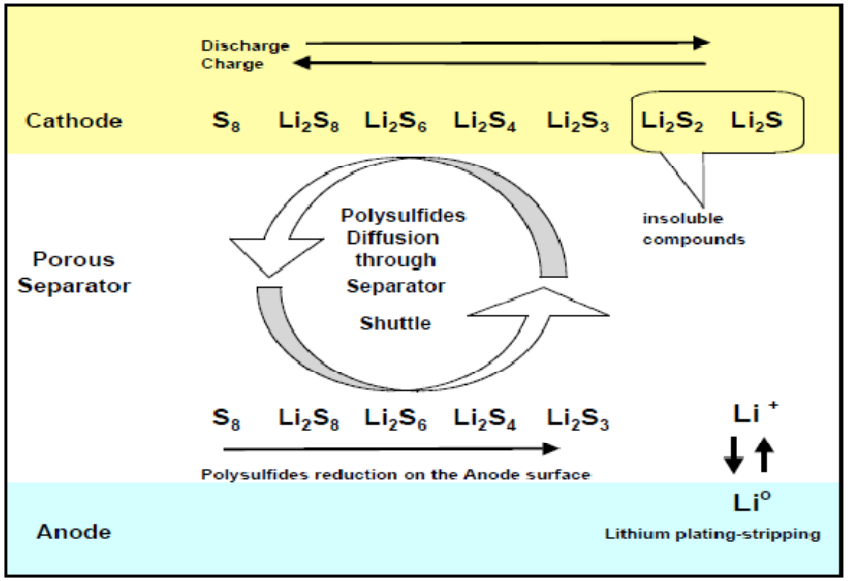
High theoretical capacity (1672 mAh/g, near 6, 11 and 10 times as compared to $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$), **according to 2 electron reaction and lighter weight** of sulfur active material, leading to the high theoretical energy density of 2600 Wh/kg in lithium/sulfur battery.



Theoretical energy density of different batteries based on anode and cathode active materials.

Problems

- Highly insulating nature (5×10^{-30} S/cm at 25 °C)
- High solubility of lithium polysulfides as intermediate products
- Poor cycle life



JR Akridge, *Solid State Ionics*, 2004, 175 , 243

Possible technological improvements

- **Sulfur-carbon composites**
- **Sulfur-conducting polymer composites**
- **New electrolytes**
- **Binder**

- **To improve conductivity**
- **To restrict dissolution of Li_xS_y**

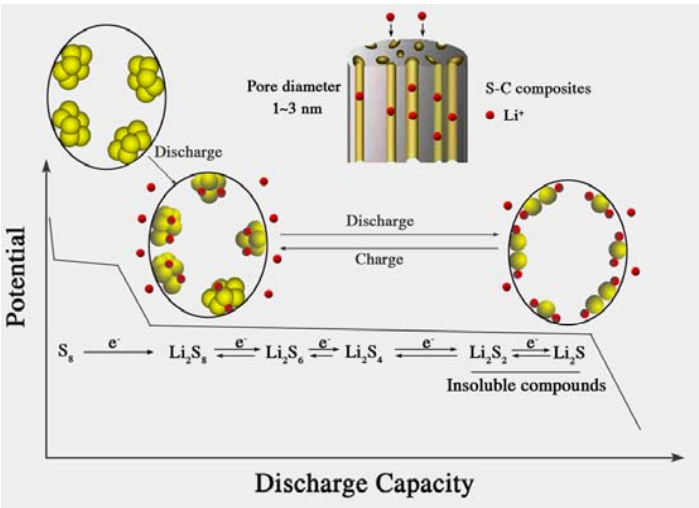
Outline

（1）Sulfur-porous carbon
mesoporous, meso/microporous, microporous carbon

（2）Sulfur-carbon nanotubes

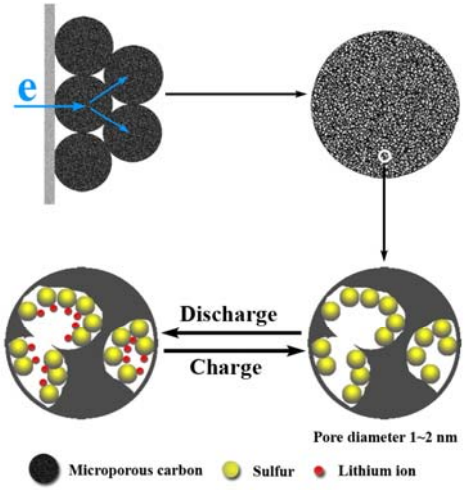
（3）Sulfur-conductive polythiophene

Sulfur-porous carbon



from mesopores

to micropores



Proposed constrained electrochemical reaction inside meso/micropores for S cathode

➢To improve conductivity:

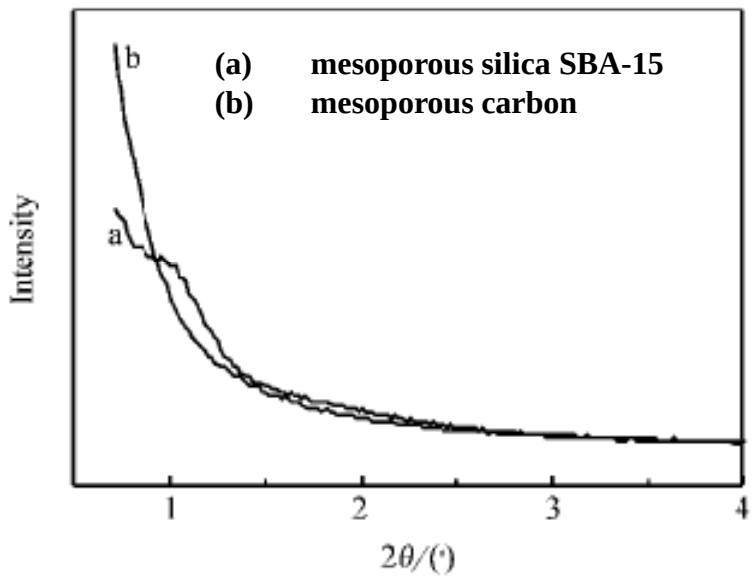
The porous carbon acts as current collectors with high electrical conductivity.

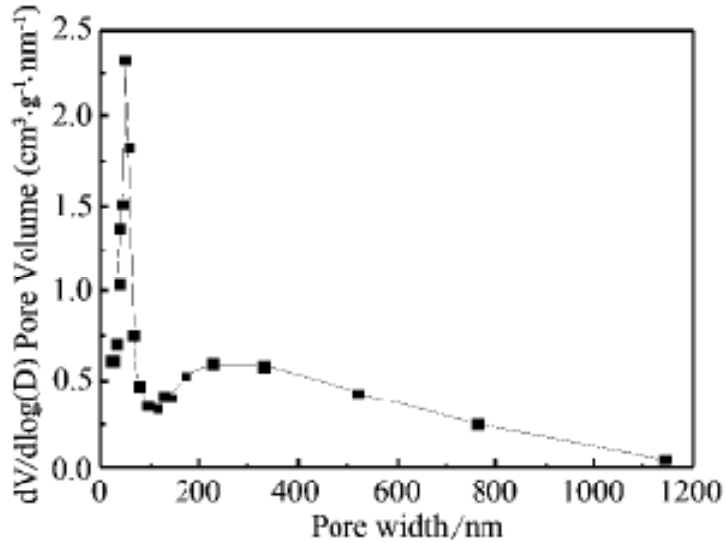
➢To restrict dissolution:

The charge-discharge process, constrained inside meso/micropores of porous carbon, corresponds to transform between high-order polysulfides and low-order polysulfide/lithium sulfide, effectively prohibitting the dissolution of polysulfides in organic electrolytes, due to strong adsorption.

Sulfur-mesoporous carbon

Mesoporous carbon was prepared by a template method using SBA-15 and sucrose

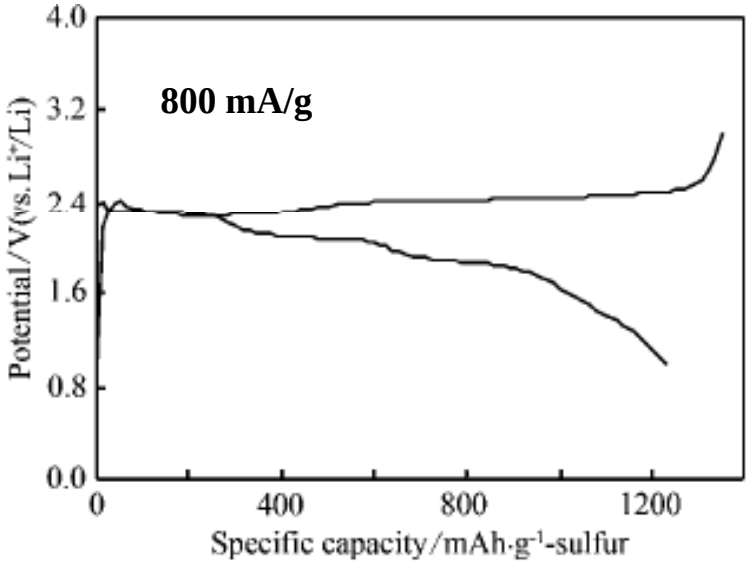


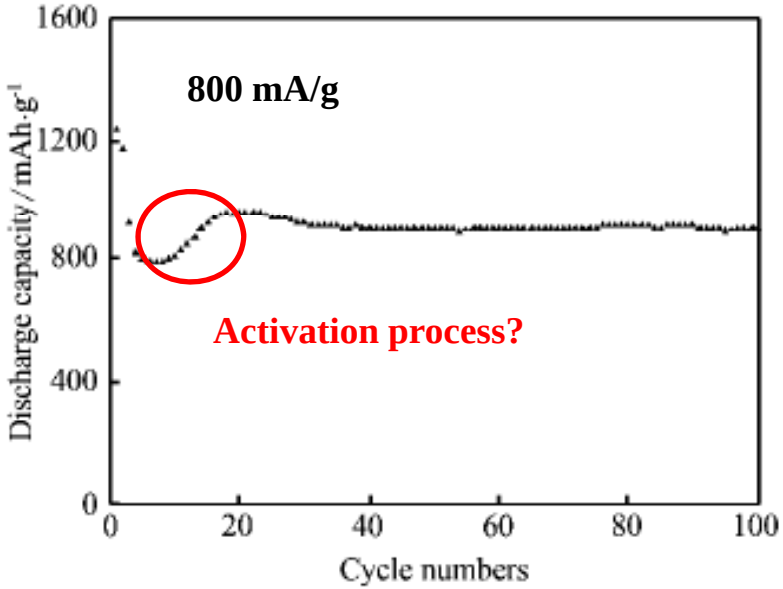


Mesoporous surface area: 975 m^2/g
Pore volume: 1.26 cm^3/g, Pore size: 51 nm

Sulfur/mesoporous carbon composite (48% S) was prepared by thermally treating a mixture of sublimed sulfur and mesoporous carbon.

Electrolyte: 1.0M $LiN(CF_3SO_2)_2$ dissolved in dimethoxyethane (DME) and dioxolane (DOL) (4:1, v/v).



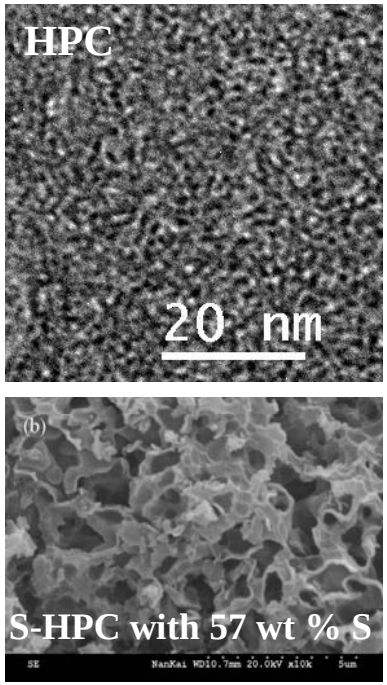


The mesoporous carbon could not only enhance the electrochemical activity of sulfur electrode, but also effectively confine the diffusion of dissolved polysulfides. As a result, the S /C composites showed high capacity, good cycle performance and excellent rate capability.

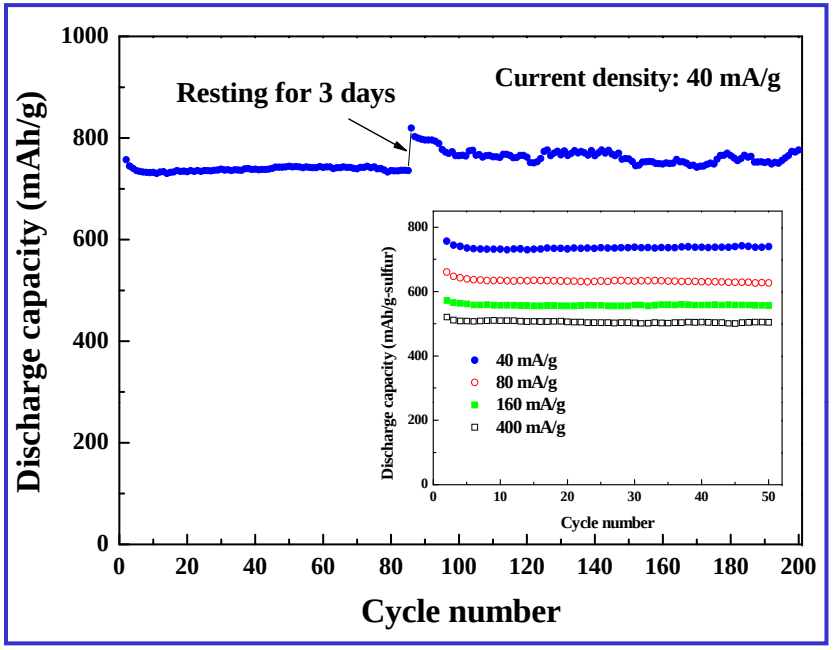
The initial discharge capacity of the S/C composite was more than 1200 mAh/g, and remained at 800 mA /g after 100 cycles at a high current density of 800 mA/g.

X. P. Ai et al., *Electrochemistry (in chinese)*, 2010, 16, 16

Sulfur-meso/microporous carbon



Cycle life and rate capability



S-HPC composite with 57 wt % S

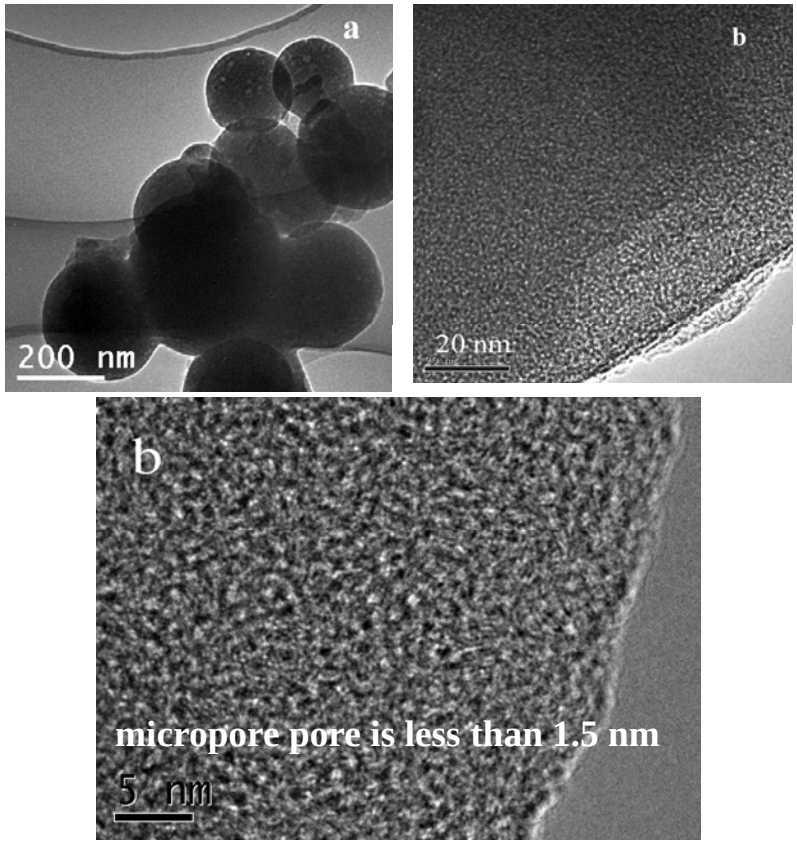
The good cycling stability of the sulfur-carbon composite cathode is maintained for over 200 cycles due to the restricted reaction inside meso/micropores of highly porous carbon.

Highly porous carbon (HPC) : thermal decomposition of polyaniline (PAN) at 750 ºC
HPC: 1472.9 m2/g, pore size 1-3nm S-HPC: 24.4 m2/g

Electrolyte: $LiPF_6$ (1 M) in a mixture of propylene carbonate (PC), ethylene carbonate (EC), and diethyl carbonate (DEC) in a volume ratio of 1:4:5

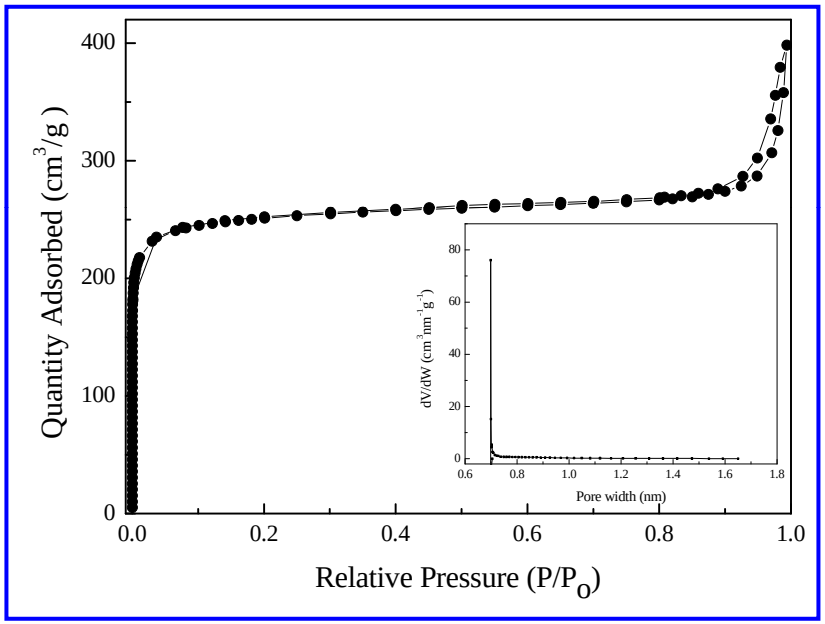
X. P. Gao et al., *J. Phys. Chem. C*, 2009, 113, 4712 and *Energy Environ. Sci*., 2010, 3, 174

Microporous carbon spheres



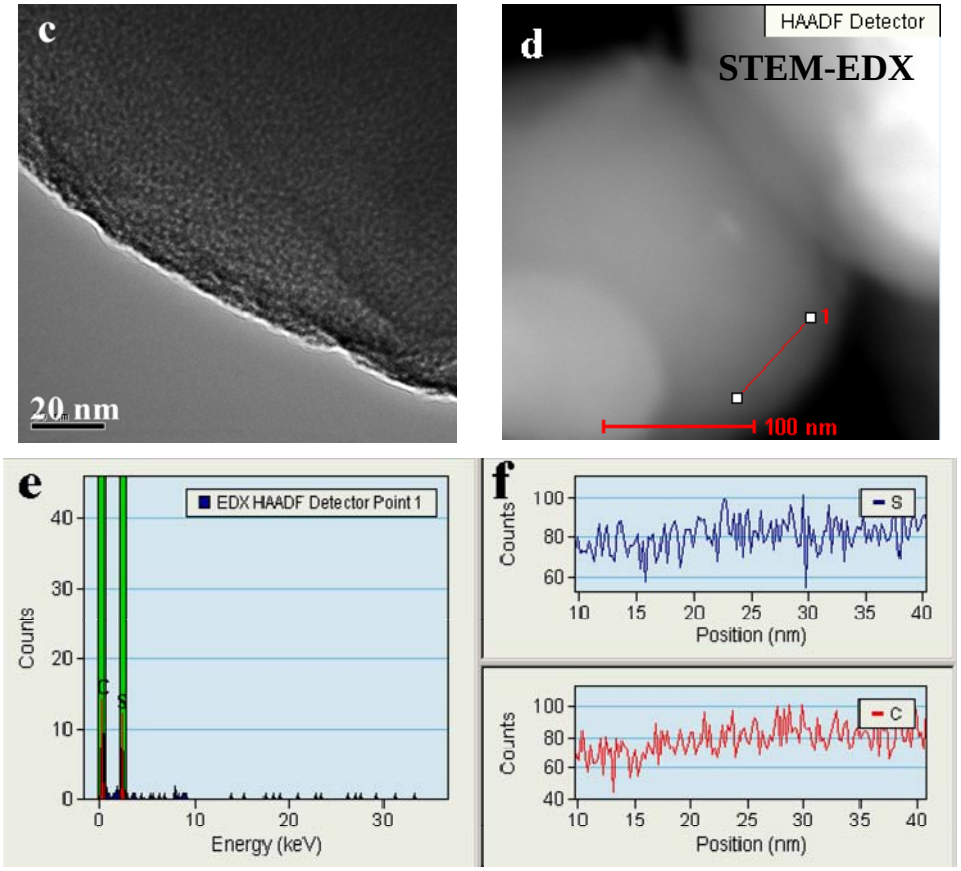
Carbonization from sucrose in 6 M sulfuric acid

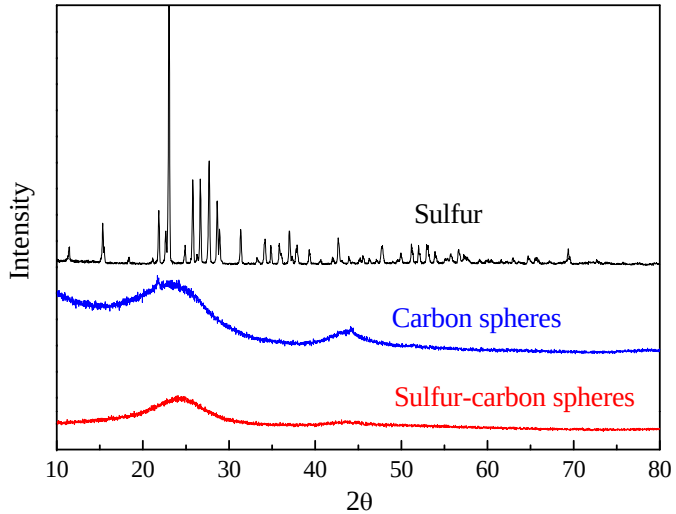
Surface area: 843.5 m^2/g
Narrow micropore: 0.7nm



The pore size distribution curve was obtained from the nitrogen adsorption branch using Horvath-Kawazoe method.

Sulfur is loaded into narrow micropores of carbon spheres in the highly dispersed state



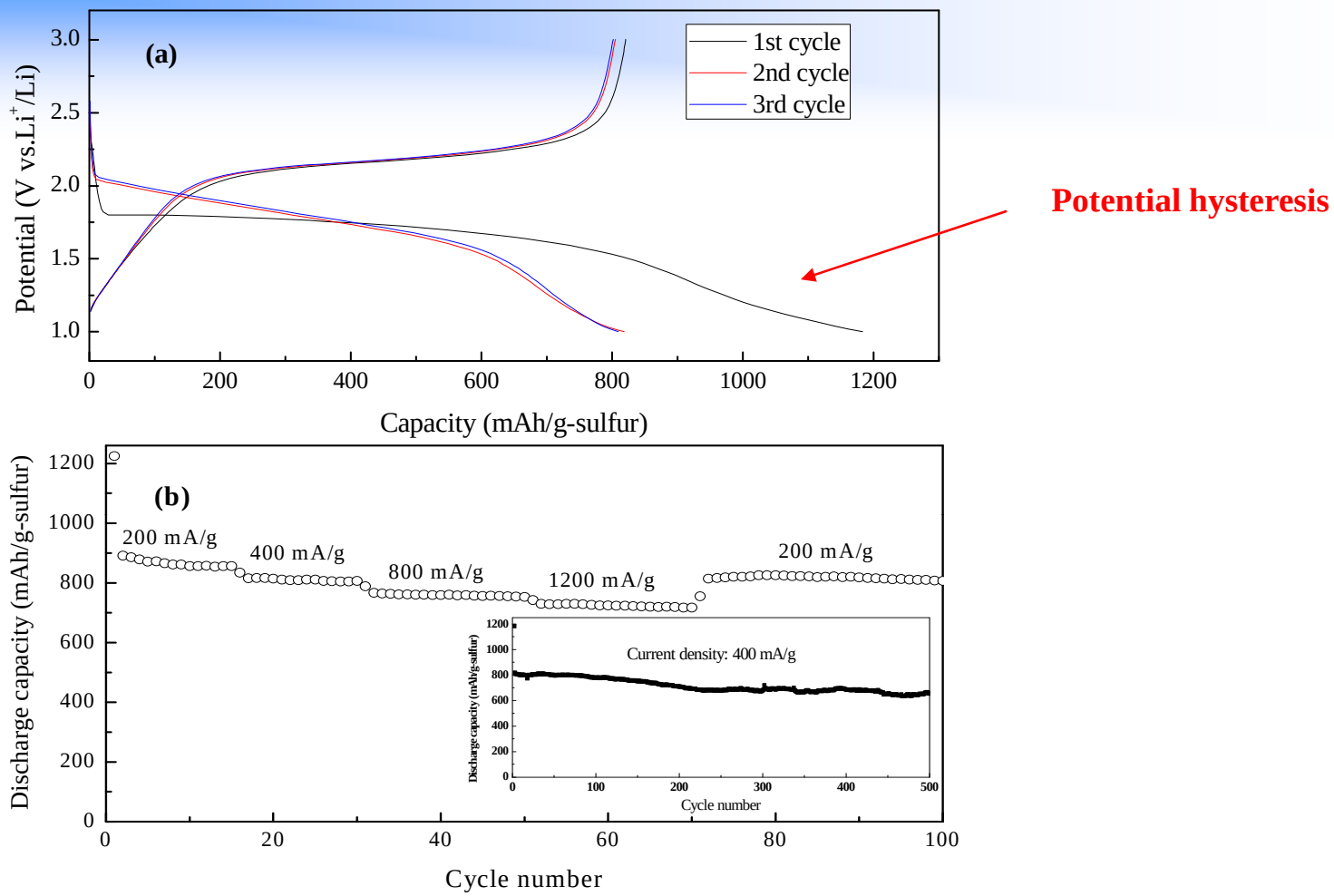


Sulfur exists as a highly dispersed and amorphous state with a monolayered coverage inside the micropores of carbon spheres

S-C with 42 wt % S (6.5 m^2/g)

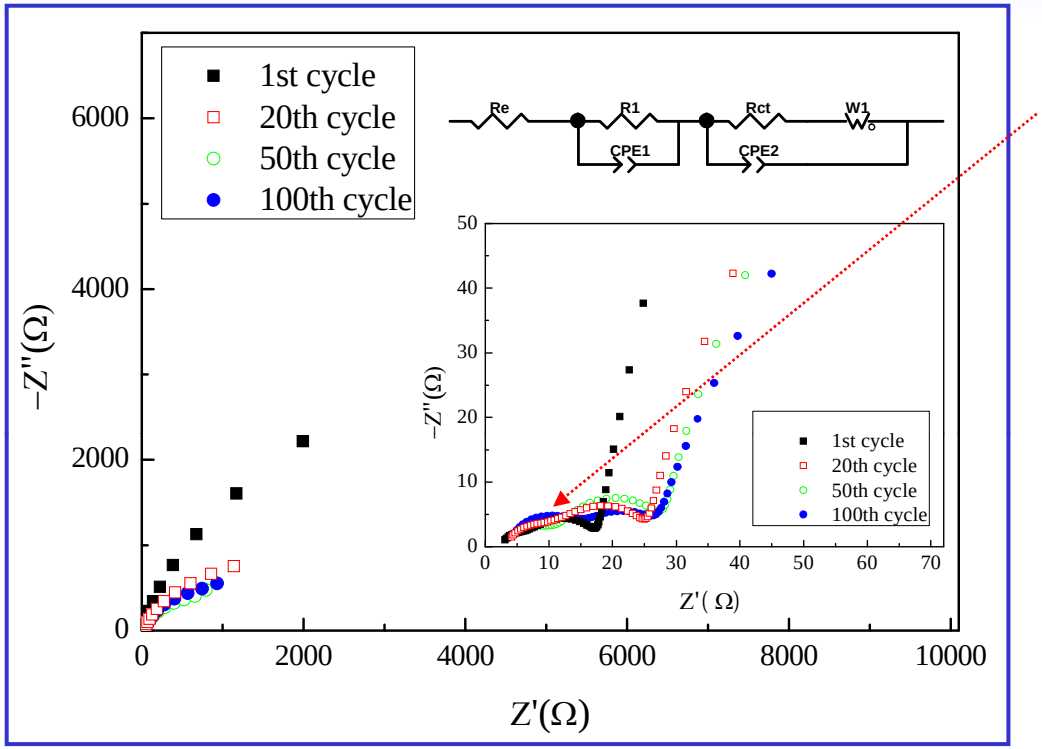
The serious surface deposition and aggregation of sulfur with a particle size larger than 1.5 nm is negligible

S-C preparation: S/C sphere mixtures were heated at 300 ºC for 3 h under Ar atmosphere in a sealed vessel.



(a) **Discharge/charge curves of the S-C sphere composite with 42 wt % S at 400 mA/g.**
(b) **Cycle life of the composite with 42 wt % S at different current densities.**

The sulfur-carbon spheres with 42 wt % S present the excellent high-rate capability and long stability, based on the constrained electrochemical process inside micropores of carbon spheres. The reversible capacity of 660 mAh/g is obtained at 400 mA/g after 500 cycles.

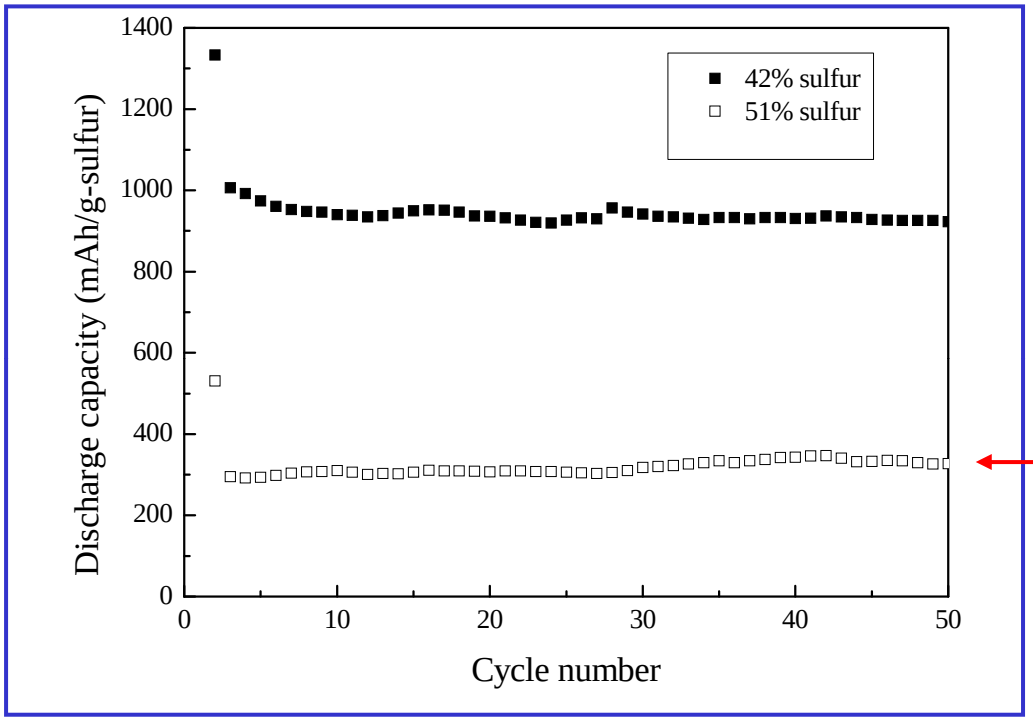


Interface charge-transfer process in the low frequency region is related to the formation of an insulating layer of lithium sulphide (Li_2S)

EIS spectra of the S-carbon sphere composite with 42 wt % S at different cycles after charging to 3 V at 800 mA/g. The inset is the enlarged spectra with two depressed semicircles and a short inclined line

The formation of the insulating Li_2S layer on the composite surface with 42 wt%S is negligible. The electrochemical process can be constrained inside the narrow micropores of carbon spheres without covering of insulated Li_2S on the surface of carbon spheres, while lithium ions freely diffuse in and out the micropores.

Cycle performance of S-carbon spheres with 42 wt % and 51 wt % S at 40 mA/g.



51wt%S

The utilization of the sulfur is much low for the sulfur-carbon sphere with 51 wt % S at low current density (40 mA/g) due to the pore-narrowing and full saturation of the micropores, which prevent passage of solvated electrolyte molecules.

The theoretical loading is 49.5 wt% sulfur based on the total pore volume of carbon spheres (0.474 cm^3/g) and the sulfur density (2.07 g/cm^3 for alpha phase, at RT).

X. P. Gao et al., *Energy Environ. Sci.*, 2010, DOI:10.1039/C002639E

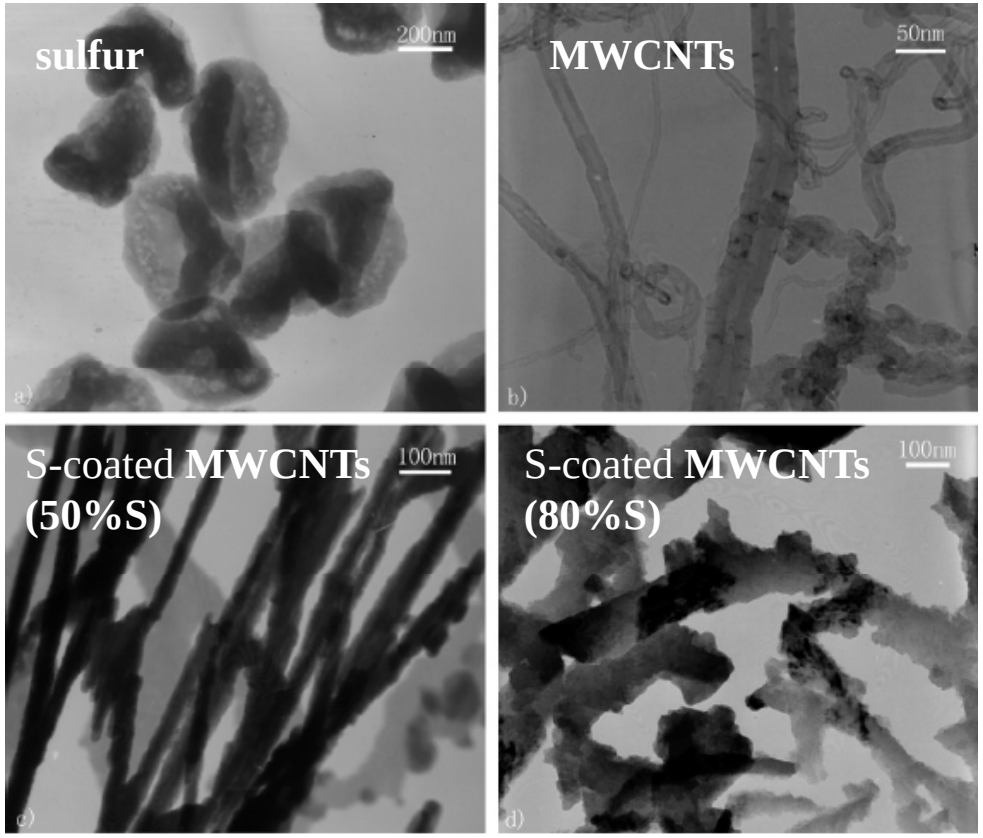
- **Sulfur can be encapsulated into the meso/micropores of carbon in the highly dispersed state.**

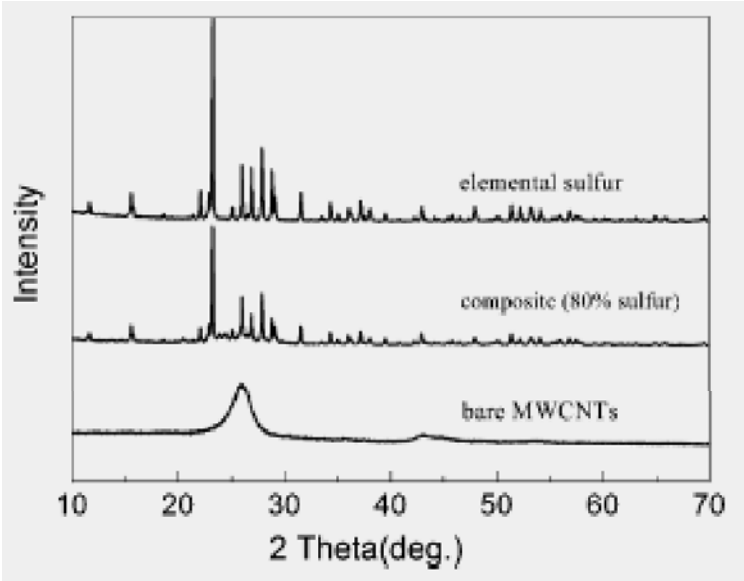
- **The electrochemical process of the sulfur can be constrained inside meso/micropores of carbon, resulting in the good reversibility and excellent high rate discharge capability.**

- **Long electrochemical stability of sulfur cathode can be enhanced by encapsulating sulfur into narrow micropores of carbon spheres.**

- **The same strategy could be helpful to explore and develop new electrode materials with a poor electric conductivity or higher solubility of intermediate products in organic electrolyte.**

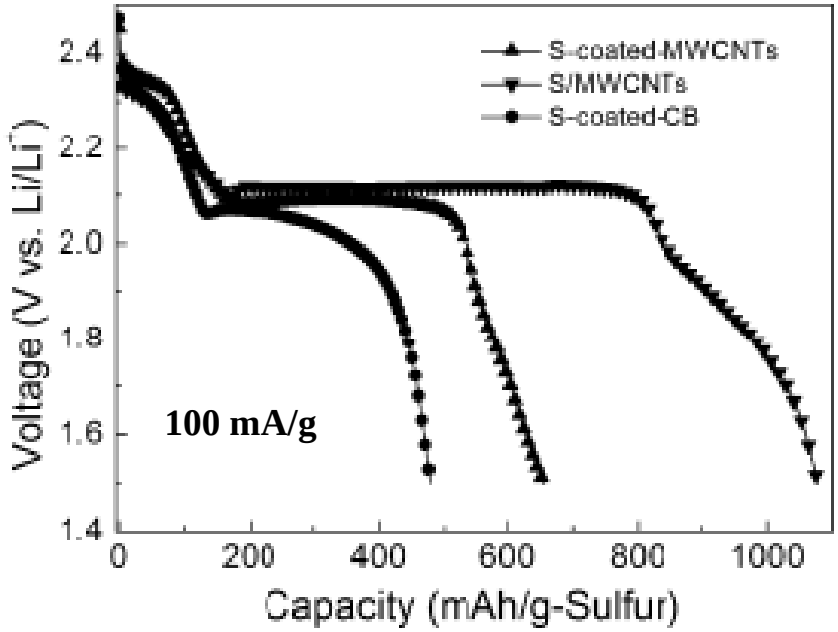
Sulfur–carbon nanotube composite

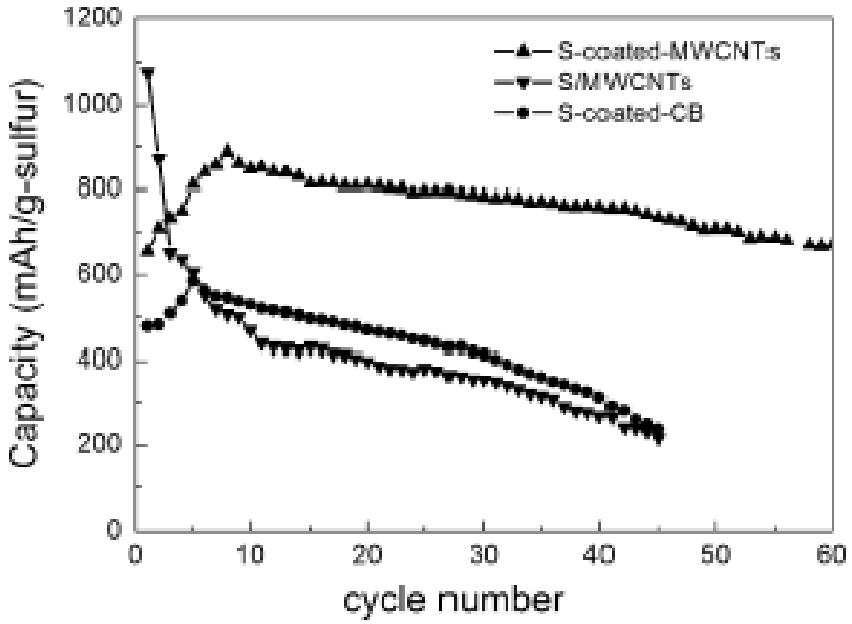




S-coated-MWCNTs have a typical core-shell structure, and the MWCNTs serve as the cores and are dispersed individually into the sulfur matrices.

Sulfur-coated multi-walled carbon nanotube composite (S-coated-MWCNTs) was prepared through capillarity between the sulfur and MWCNTs.



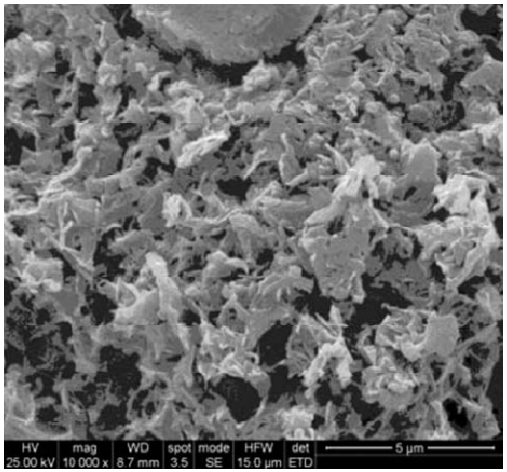


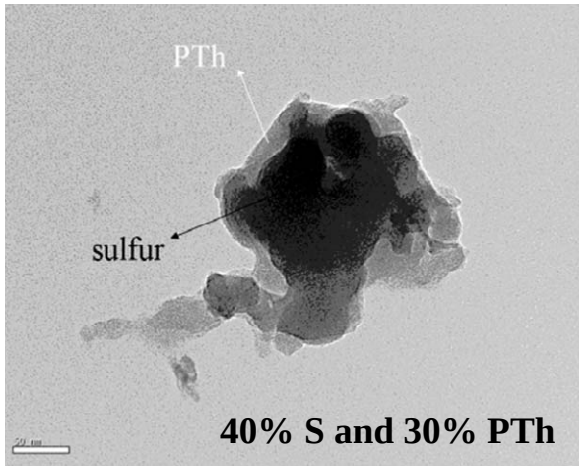
S-coated-MWCNTs cathode could maintain a reversible capacity of 670mAh/g after 60 cycles, showing a greatly enhanced cycle ability as compared with the S/MWCNTs mixture and the sulfur-coated carbon black (S-coated-CB)

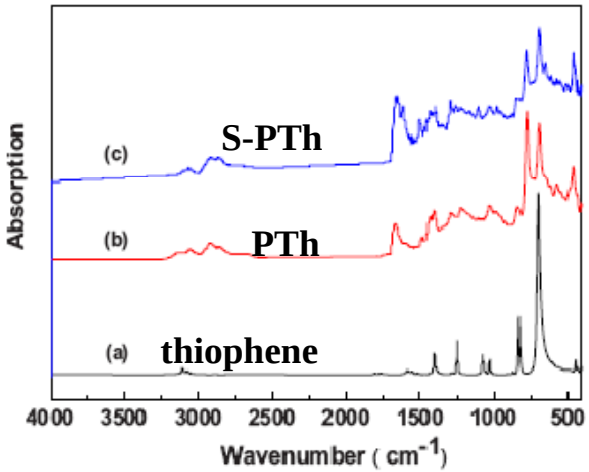
Electrolyte: 1.0M $LiN(CF_3SO_2)_2$ dissolved in dimethoxyethane (DME) and dioxolane (DOL) (1:1, v/v).

X. P. Qiu et al., *J. Power Sources*, 2009, 189, 1141

Sulfur–polythiophene (PTh) composite



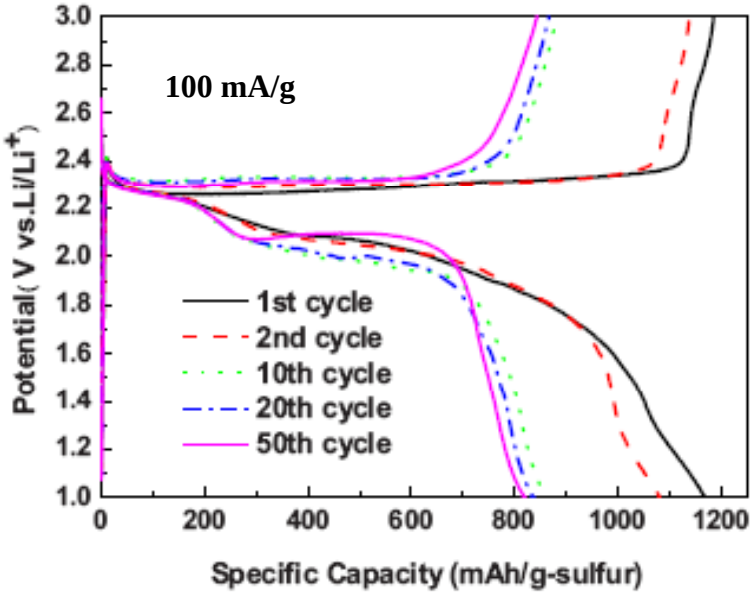


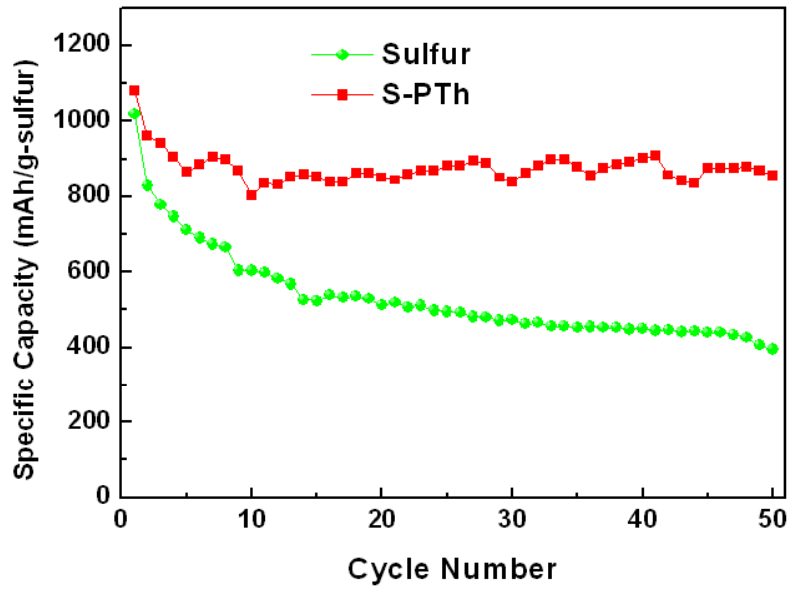


The PTh matrix not only enhances the electrical conductivity of the composite by reducing the particle contact resistance, but also increases the contact area between the electrode and the electrolyte. PTh covers the surface of the sulfur and effectively prevents the sulfur from dissolving in the electrolyte.

S-PTh composite was synthesized by in situ oxidative polymerization method.

Electrolyte: 1 M lithium bis-trifluoromethane sulfonylimide ($LiN(SO_2CF_3)_2$, LiTFSI)/1,3-dioxolane DOL:1,2-dimethoxyethane DME 1:1 (v/v).





To improve the electrochemical performance of Li/S batteries, sulfur coated with conductive PTh was prepared via in situ chemical oxidative polymerization.

The initial discharge capacity was 1168 mAh/g(S) for the S-PTh electrode and the remaining capacity was 819.8 mAh/g(S) after 50 cycles.

The conductive PTh has multiple functions in the cathode: as a conducting additive and as a porous adsorbent.

F. Wu et al., ***Electrochem. Solid-State Lett.,*** 2010, 13, A29

Thank you for your attention!

Financial support from 973 Program is gratefully acknowledged.

(2002CB211800)

(2009CB220100)