锂硫电池及相关材料的研究进展

Research in Lithium-Sulfur Batteries and Key Materials

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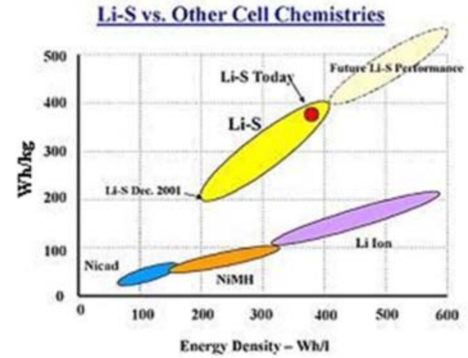
锂硫电池机理与研究背景

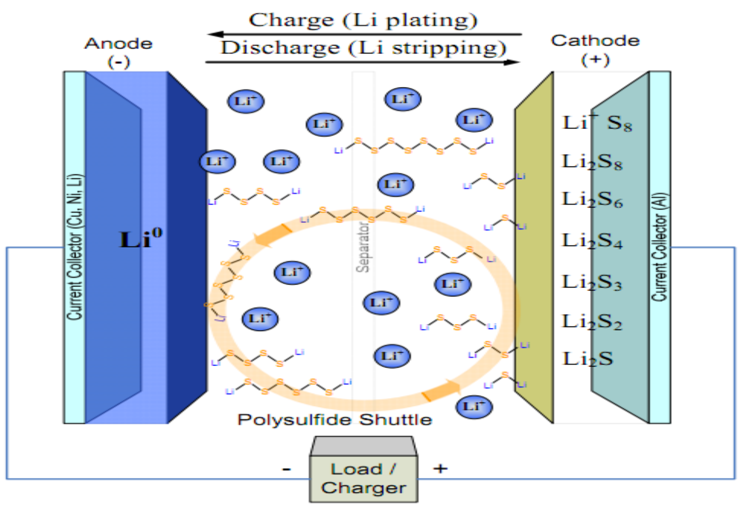
Mechanism and context of Li/S Battery

负极反应（Anode reaction）：$2Li \rightarrow 2Li^{+} + 2e^{-}$

正极反应（Cathode reaction）：$1/8S_8 + 2Li^{+} + 2e^{-} \rightarrow Li_2S$

总反应（Overall reaction）：$2Li + 1/8S_8 \rightarrow Li_2S$





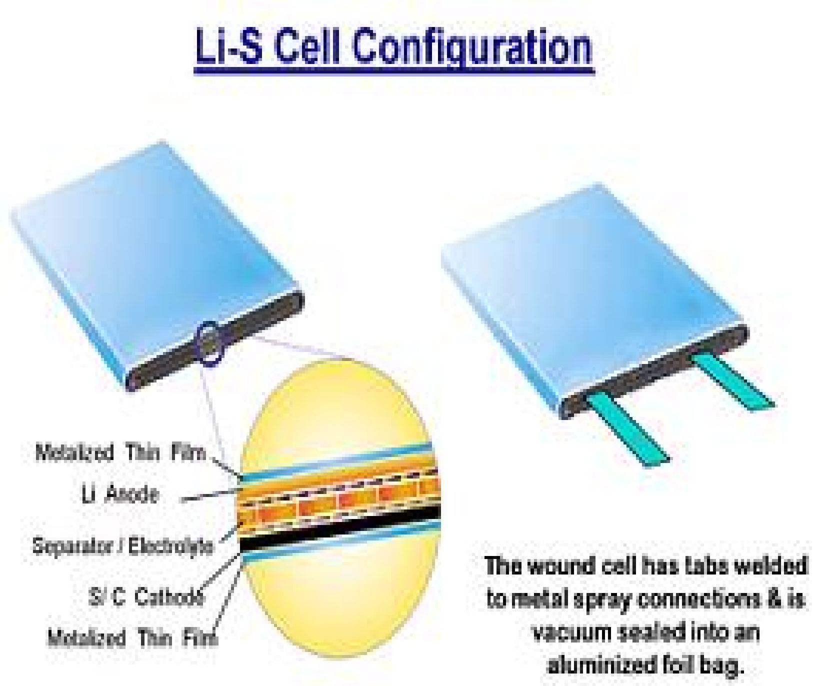
锂硫电池电化学过程

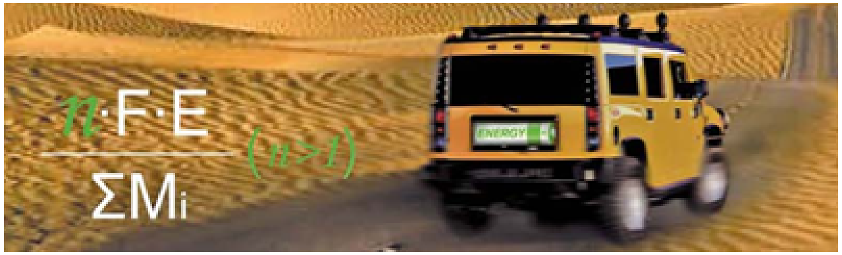
Electrochemical processes in Li/S cell

多电子体系 Multi-electrons reactions system	• n=2
理论工作电压 theoretical working voltage	• 2.287V
理论能量密度 theoretical energy density	• 2600 Wh/kg

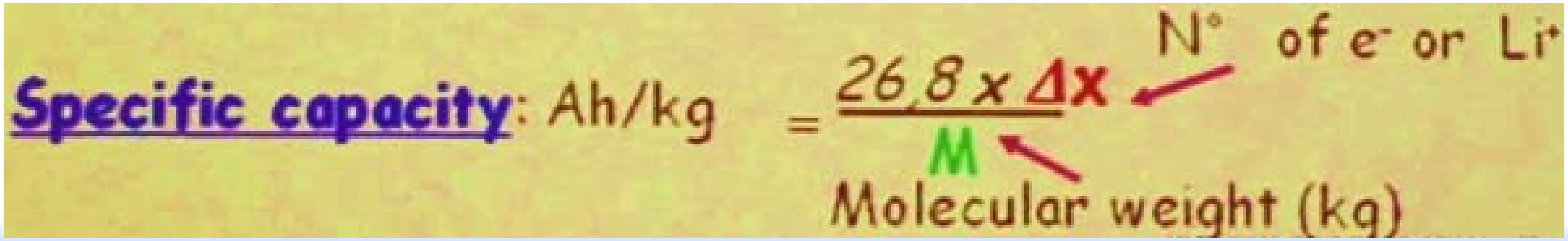
锂硫电池机理与研究背景

Mechanism and context of Li/S Battery





- 比容量高
- 耐过充
- 工作温度范围宽
- 资源丰富
- 价格低廉
- 设计多样
- **High theoretical capacities (n>1)**
- **Resistance to overcharge**
- **Wide operating temperature range**
- **Resource-rich**
- **Environment- friendly**
- **Design diversity**



现存的主要问题 Major Problems

活性物质利用率低
low active material utilization

- 单质硫的电子绝缘性
  electrical insulating nature of sulfur
- 可溶性中间产物造成飞梭机理
  solutable polysulfides that cause shuttle mechanism

循环寿命差
Poor cycle performance

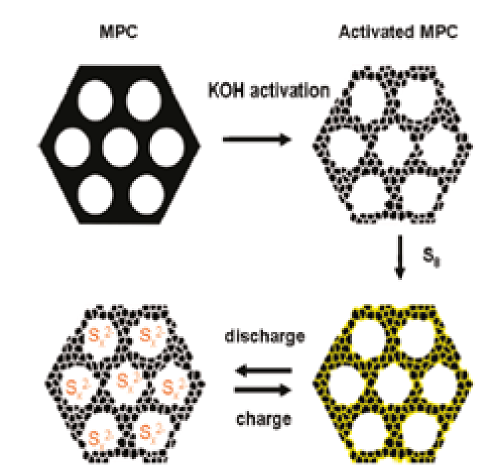
- 不溶性最终产物Li_2S_2，Li_2S在正极表面沉积
  Insulating Li_2S and Li_2S_2 deposition on the surface of cathode

研究思路 Solution1:

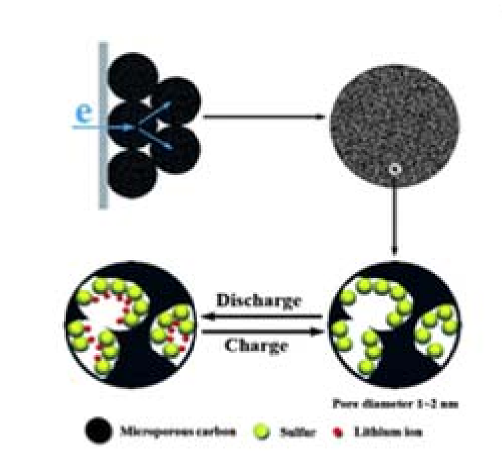
硫活性物质复合添加剂要求具有良好导电性能和适宜结构以保证硫活性物质的有效担载

Maintaining the active material in an intimate contact with an electron conductive Matrix

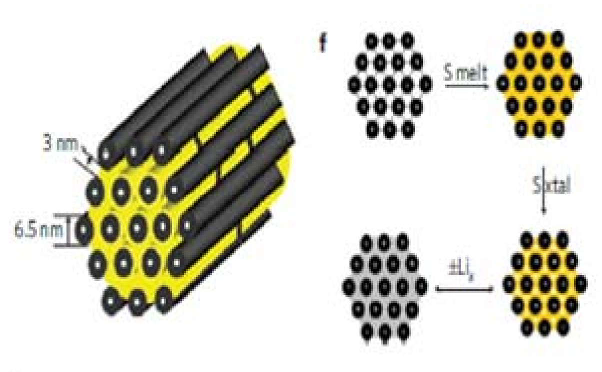
介孔碳
Mesoporous carbon



微孔碳球
Micropores of carbon spheres



碳纳米管
Carbon nanotubes



研究思路 Solution2:

选择适宜的溶剂、添加剂或是应用聚合物电解质以改善电解液与电极材料间的电化学兼容性

Different solvents and additives or using polymer-type of electrolyte to improve the electrochemical compatibility

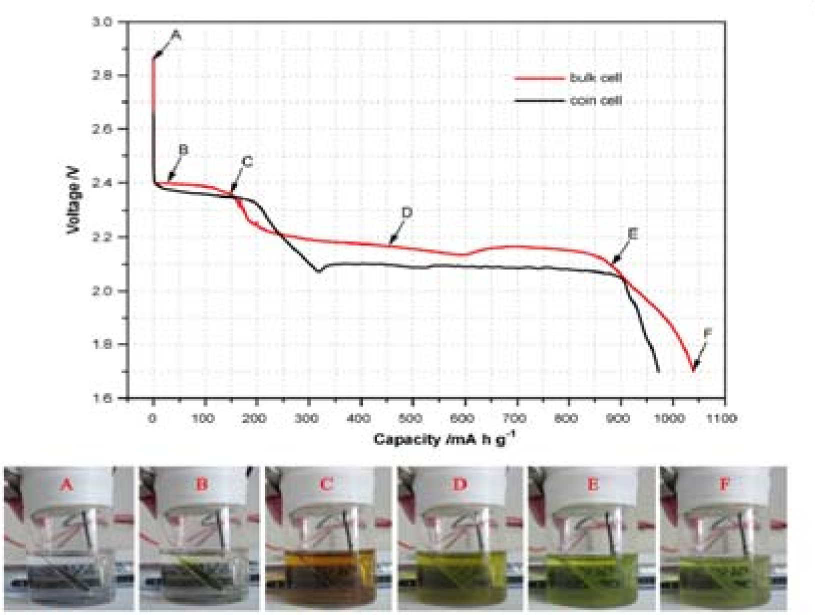
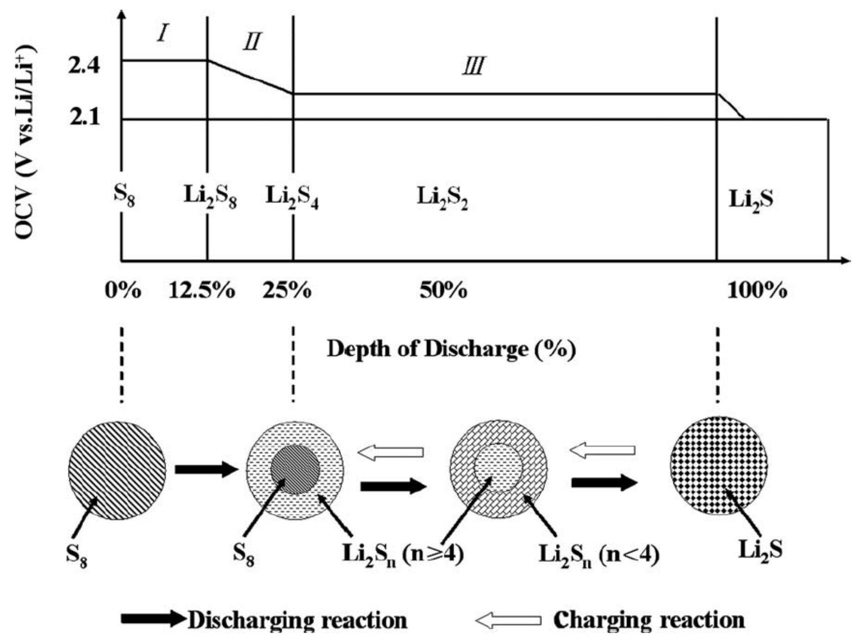


Fig. 1. Discharge profiles of lithium sulfur coin cell and bulk cell at 20 mA g^{-1} and photos as the bulk cell discharged to varying depth.



多孔活性炭-硫复合材料
Activated carbon-sulfur composite materials

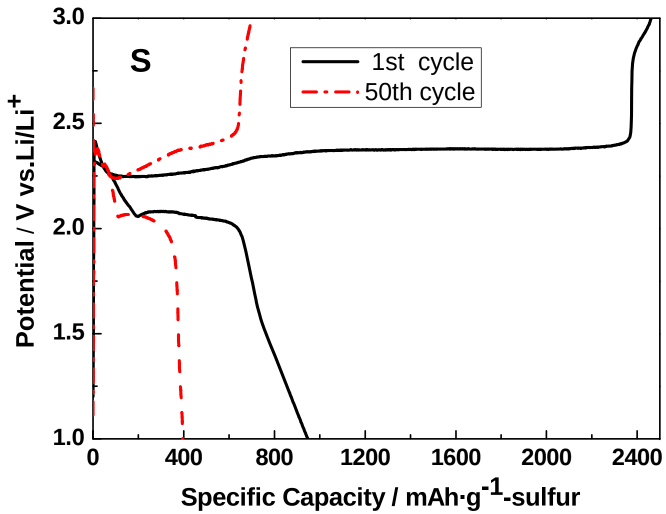
制备方法 Synthesis method	首次放电容量 /mAh·g^{-1} (initial discharge capacity)	第10次放电容量/mAh·g^{-1} (after 10 cycles)	第20次放电容量/mAh·g^{-1} (after 20 cycles)	前20次容量保持率 (capacity remaining after 20 cycles)
直接添加 Adding directly	947.0	631.8	558.7	59.0%
球磨复合 Ball-milling	1057.8	689.7	607.7	57.4%
热复合（70%） Thermal treating	1180.8	942.1	863.3	73.1%

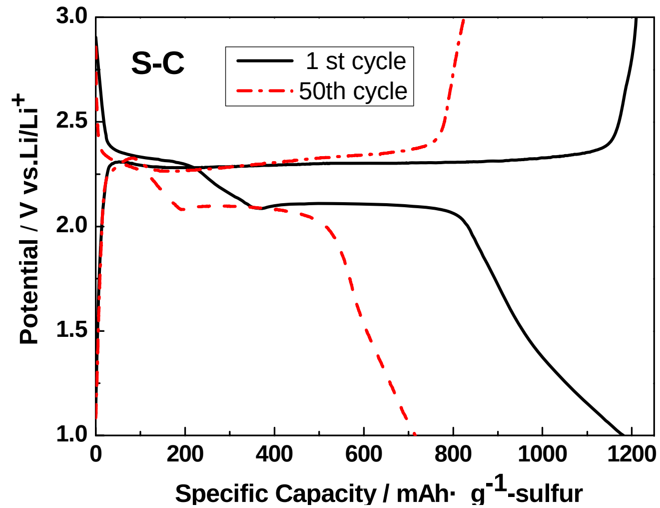
采用密封分段加热方法制备了硫含量为70%的单质硫-活性炭复合材料。单质硫-活性炭复合材料首次放电比容量达1180.8 mAh/g，活性物质利用率为70.5%，循环至第20周时放电容量还保持在863.3 mAh/g。

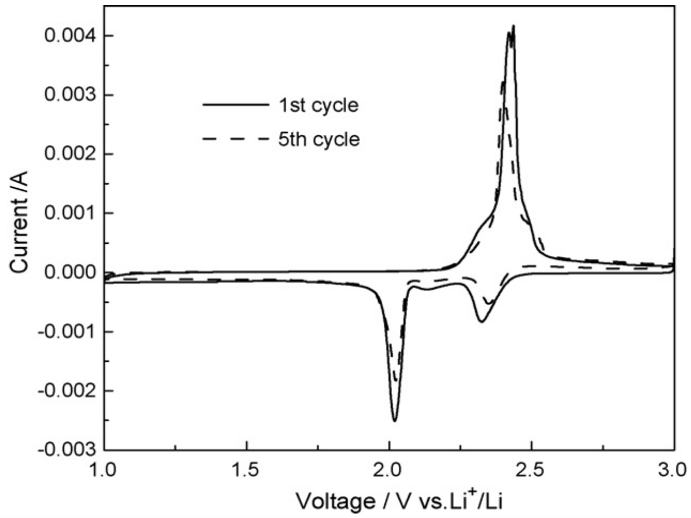
70%Sulfur-actived carbon composite was synthesized via an two-step thermal treating method. The initial discharge capacity of the active material was 1180.8 mAh/g, sulfur, the efficiency of active material was 70.5% and remaining capacity was 863.3 mAh/g sulfur after 20 cycles.

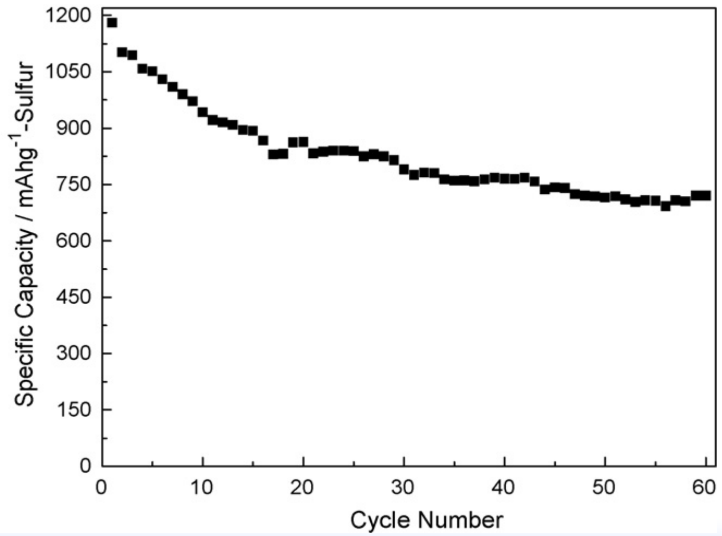
现阶段的研究进展
Current research progress

多孔活性炭-硫复合材料
Activated carbon-sulfur composite materials









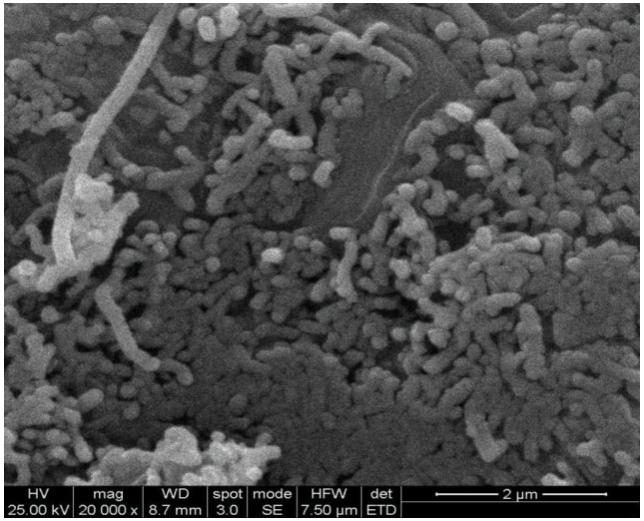
多壁碳纳米管-硫复合材料的制备及表征
MWCNT-sulfur composite materials

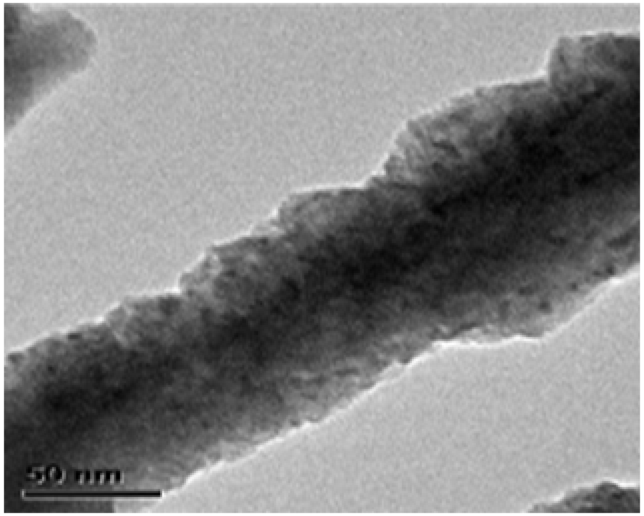
硫含量 Sulfur containing	首次放电容量 /mAh·g^{-1} (initial discharge capacity)	第10次放电容量/mAh·g^{-1} (after 10 cycles)	第20次放电容量/mAh·g^{-1} (after 20 cycles)	前20次容量保持率 (capacity remaining after 20 cycles)
70%	1189.1	942.5	892.7	75.1%
75%	1205.7	781.8	715.9	59.4%
80%	1099.5	790.8	787.4	71.6%
85%	1272.8	1035.4	912.6	71.7%
90%	1222.8	1001.3	896.1	73.3%

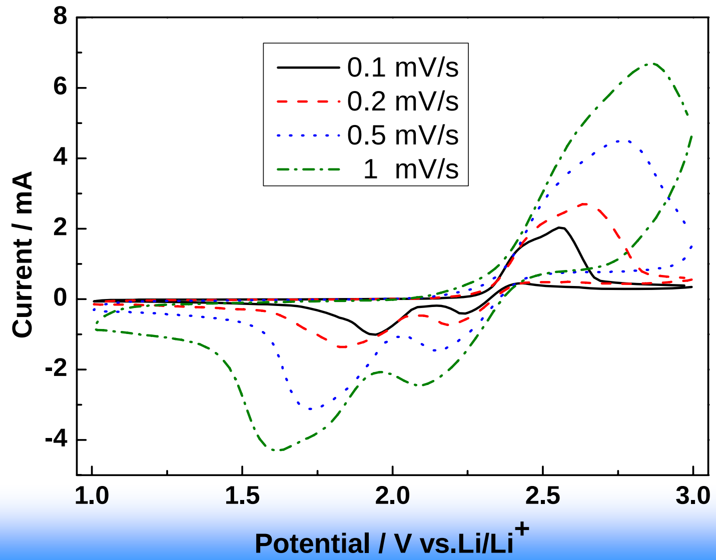
采用密封分段加热方法制备了硫含量为85%的单质硫-多壁碳纳米管复合材料。复合材料首次放电比容量达1272.8 mAh/g，活性物质利用率为76.0%，循环至第20周时放电容量还保持在912.6 mAh/g，容量保持率达71.7%。

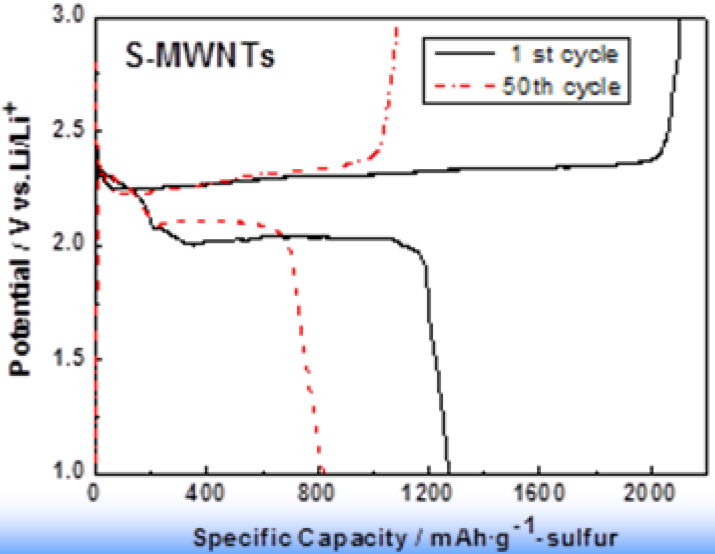
85%Sulfur-MWCNT composite was synthesized via an two-step thermal treating method. The initial discharge capacity of the active material was 1272.8 mAh/g, sulfur, the efficiency of active material was 76% and remaining capacity was 912.6 mAh/g sulfur after 20 cycles.

多壁碳纳米管-硫复合材料的制备及表征
MWCNT-sulfur composite materials



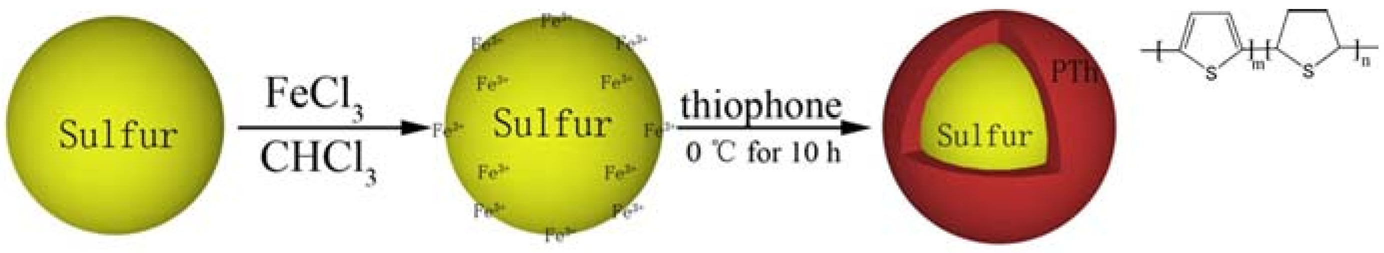






硫聚噻吩核壳结构

Sulfur/polythiophene with core/shell structure



硫聚噻吩球壳结构合成机理

Synthesis of the S-PTh composites.

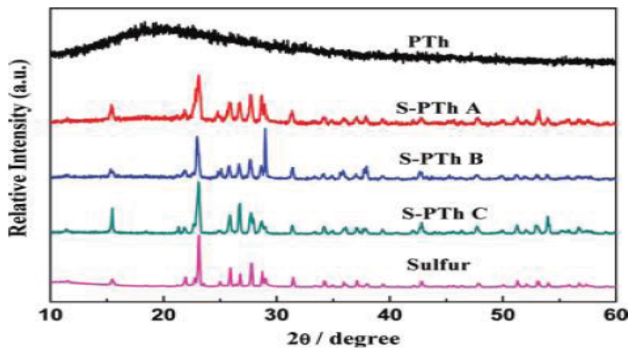
采用原位氧化聚合的方法，合成具有球壳结构的硫聚噻吩活性材料。

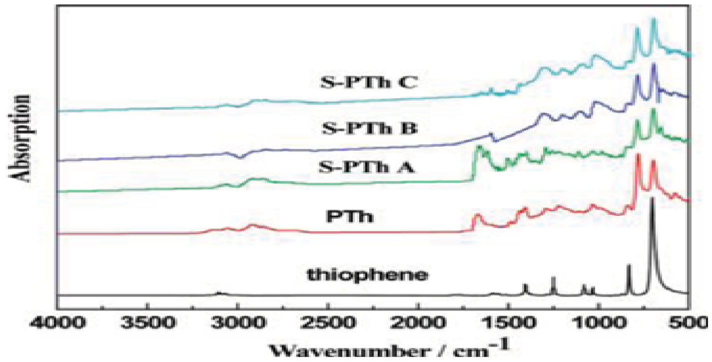
Novel sulfur/polythiophene composites with core/shell structure composites were synthesized via an in situ chemical oxidative polymerization method.

Electrochemical and Solid-State Letters, 13 4 A29-A31 2010

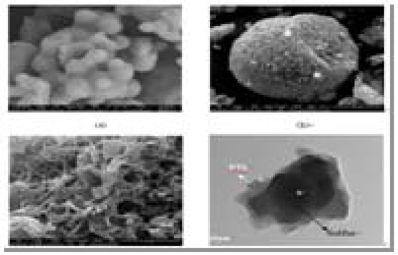
J. Phys. Chem. C 2011, 115, 6057–6063

现阶段的研究进展
Current research progress





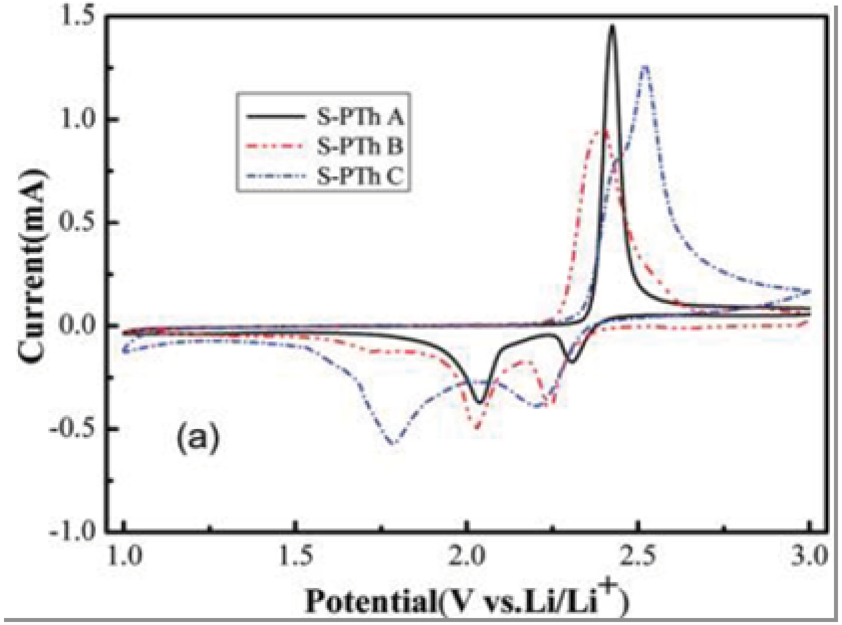
Composite	Element Weight Percentage			Elemental Sulfur	Polythiophene
	C	H	S		
PTh	57.21	4.42	38.37	0	100
S-PTh A	21.75	1.68	76.57	62.0	38.0
S-PTh B	16.16	1.21	82.63	71.9	28.1
S-PTh C	6.25	0.47	93.28	82.5	17.5

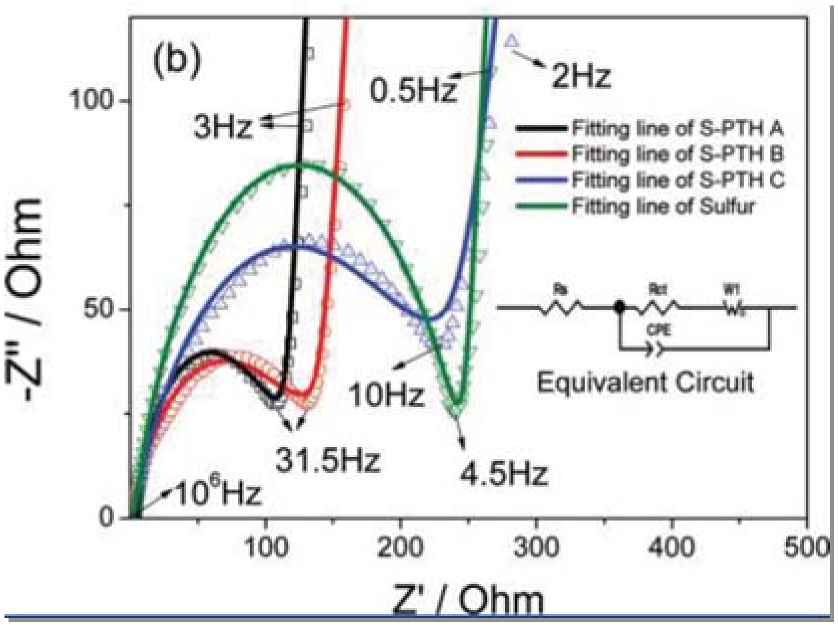


通过元素分析，红外，X射线衍射，扫描电镜，透射电镜等电化学方法对不同比例的硫聚噻吩活性物质进行结构表征，证实聚噻吩被均匀的包覆在单质硫的表面。

Different ratios of the sulfur/polythiophene composites were characterized by elemental analysis, FTIR,XRD, SEM, TEM, and electrochemical methods conforming that polythiophene was uniformly coated onto the surface of the sulfur powder to form a core/shell structure

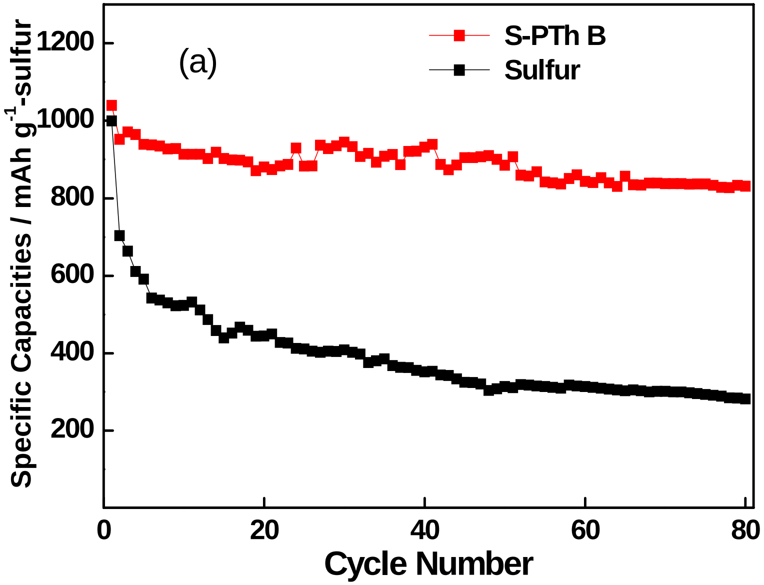
现阶段的研究进展
Current research progress

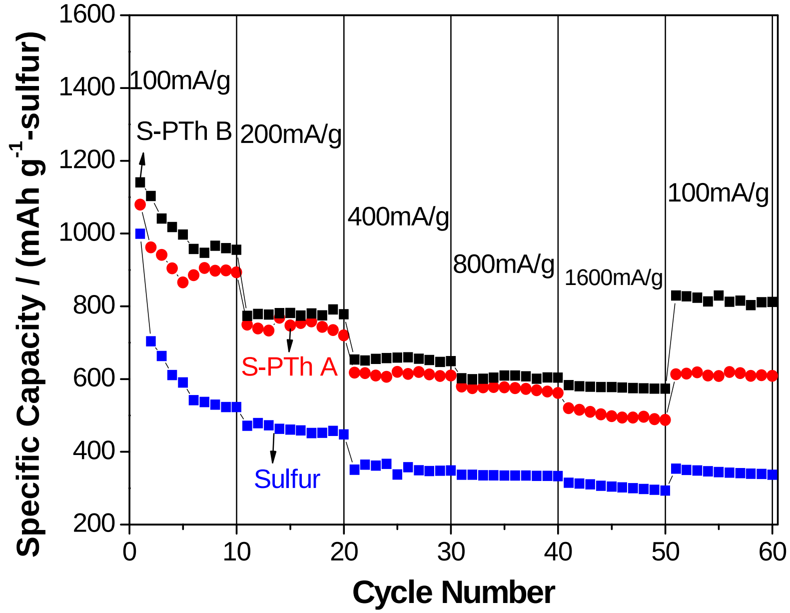




循环伏安和交流阻抗的测试结果表明硫与聚噻吩的组分分别为71.9%，18.1%时，材料的电化学性能最佳。

A suitable ratio for the composites was found to be 71.9% sulfur and 18.1% polythiophene as determined by CV and EIS results.





复合材料首次放电比容量为1119.3 mAh/g，循环80周后放电容量仍保持在830.2 mAh/g 。倍率测试结果表明，以不同倍率循环循环60周后，再以100mA/g的电流密度放电容量仍有811 mAh/g

The initial discharge capacity of the active material was 1119.3 mAh/g, sulfur and the remaining capacity was 830.2 mAh/g sulfur after 80 cycles. After a rate test from 100 to 1600 mA/g sulfur, the cell remained at 811 mAh/g sulfur after 60 cycles when the current density returned to 100 mA/g sulfur.

离子液体新型电解质材料 Ionic liquid-based electrolyte

- 设计合成了锂盐/酰胺基有机物、氨基酯类有机物两系列离子液体电解质材料
- 应用量化计算理论分析方法对离子液体进行构效关系分析、优化功能设计
- 离子液体电解质材料应用于锂二次电池中，有效改善了电池体系的安全性、热稳定性等
- **Novel ionic liquids have been prepared based on lithium bis(trifluoromethane sulfonyl) imide ($LiN(SO_2CF_3)_2$, LiTFSI) and 2-oxazolidinone ($C_3H_5NO_2$, OZO) or organic substances with amide group**
- **Quantum chemistry calculations with nonlocal density function theory have also been performed to have a comprehensive understanding to the structure–activity relationship and make functional design of novel ionic liquids**
- **Ionic liquids have be a promising electrolyte candidate for lithium secondary battery, with high safety and thermal stability.**

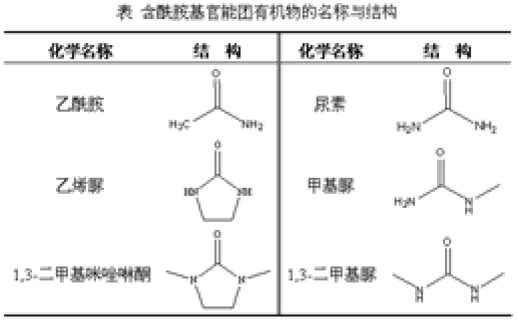
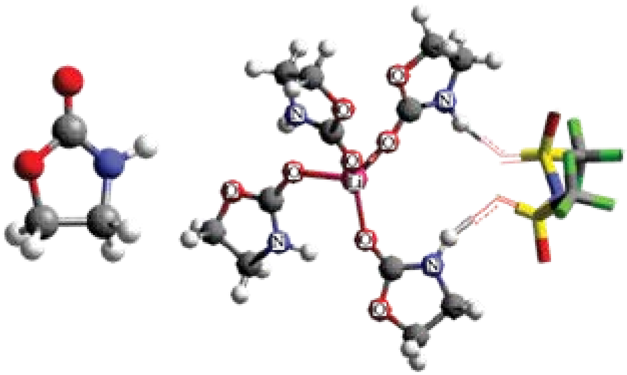
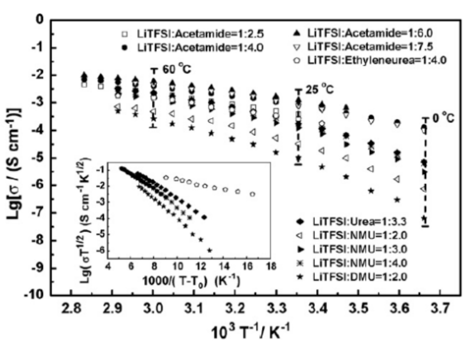


表 含酰胺基官能团有机物的名称与结构

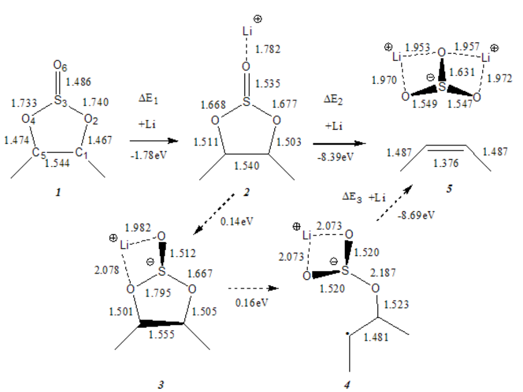
化学名称	结构	化学名称	结构
乙酰胺		尿素	
乙烯脲		甲基脲	
1,3-二甲基咪唑啉酮		1,3-二甲基脲	

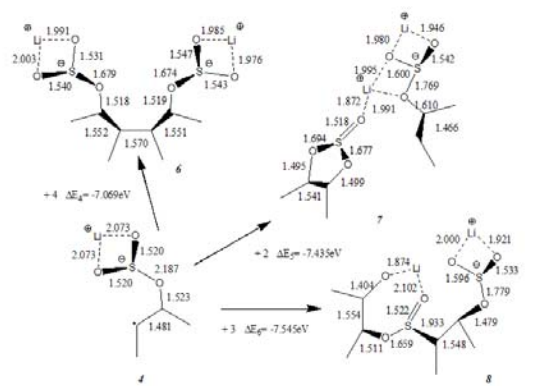


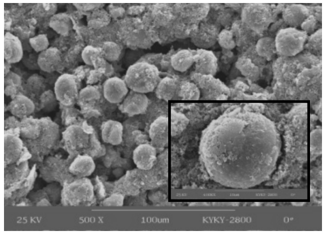


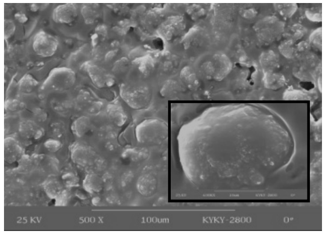
亚硫酸酯类功能添加剂 New Functional Additive – Sulfite

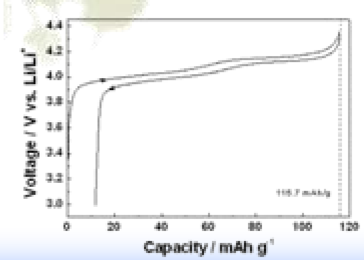
- 物化性能测试表明，以**BS**为基配制不同锂盐的电解液具有较宽的液态温度范围和高的离子电导率。作为添加剂，**BS**分解主要产物在**MCMB**电极表面上形成致密和稳定的**SEI**膜，有效阻止了**PC**和溶剂化锂离子共同嵌入到石墨层间。同时**BS**具有较高的氧化电位，并和正极材料$\mathbf{LiMn_{1.99}Ce_{0.01}O_4}$和$\mathbf{LiFePO_4}$**-C**电极显示出良好的兼容性。
- **The analyses of Physicochemical properties indicate that BS-based electrolyte have been a liquid in a wide range of temperature and own the high ionic conductivity. Even in small additive amounts (5 vol.%) BS is capable of preventing propylene carbonate (PC) co-intercalation into graphite flakes. The formation of a compact and stable SEI film on the graphite flake surface is believed to be the reason for the improved cell performance. In addition, the PC/BS electrolyte has been proved to have a high oxidation stability allowing the cycling of a** $\mathbf{LiMn_{1.99}Ce_{0.01}O_4}$ **and** $\mathbf{LiFePO_4}$**-C cathodes with good reversibility.**

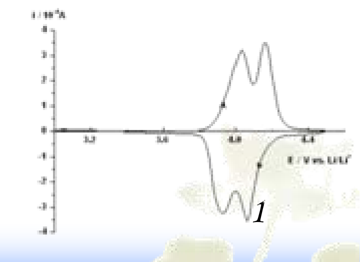






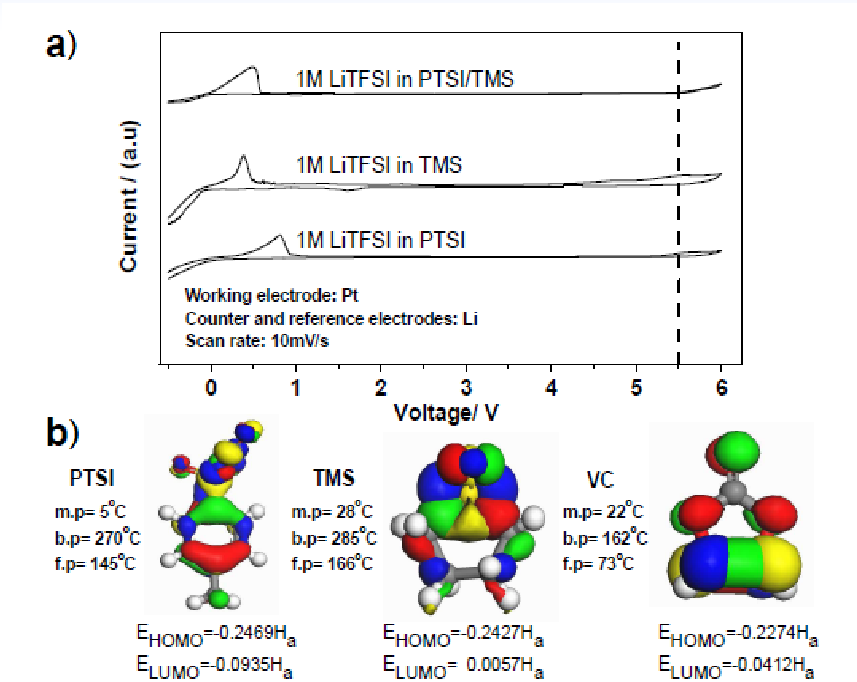


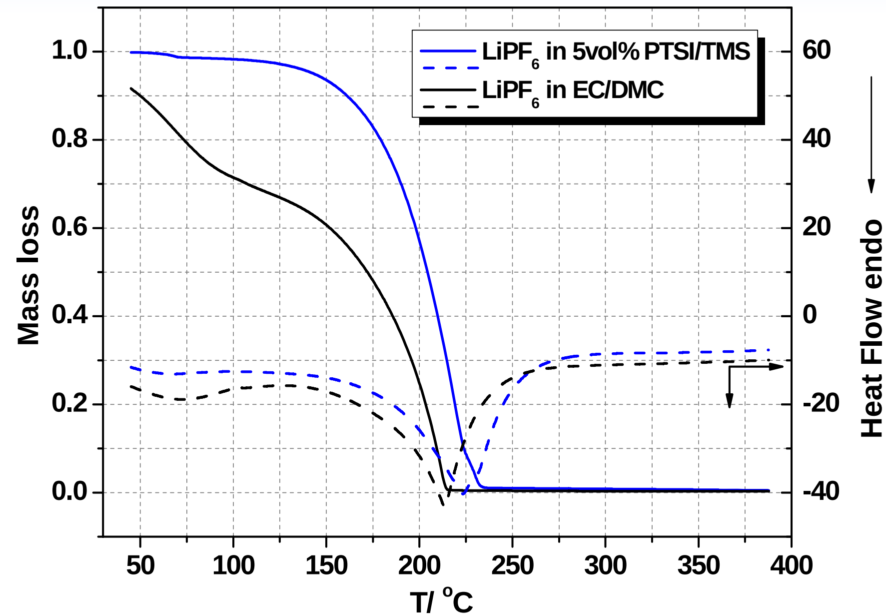




砜/异氰酸酯复合电解质材料(TMS/PTSI电解质体系)

Mixed electrolytes based on sulfone and isocyanate（TMS/PTSI electrolyte system）



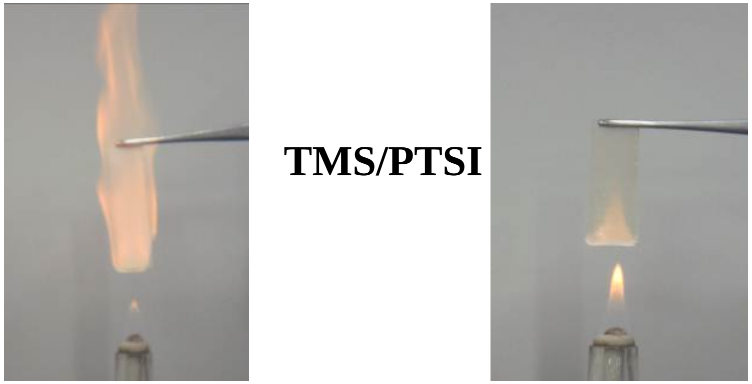


- 高的热稳定性 High thermal stability

- **TMS/PTSI电解质体系具有宽的电化学窗口(5.5V左右)，同时PTSI还具有低的熔点和高的沸点和闪点**

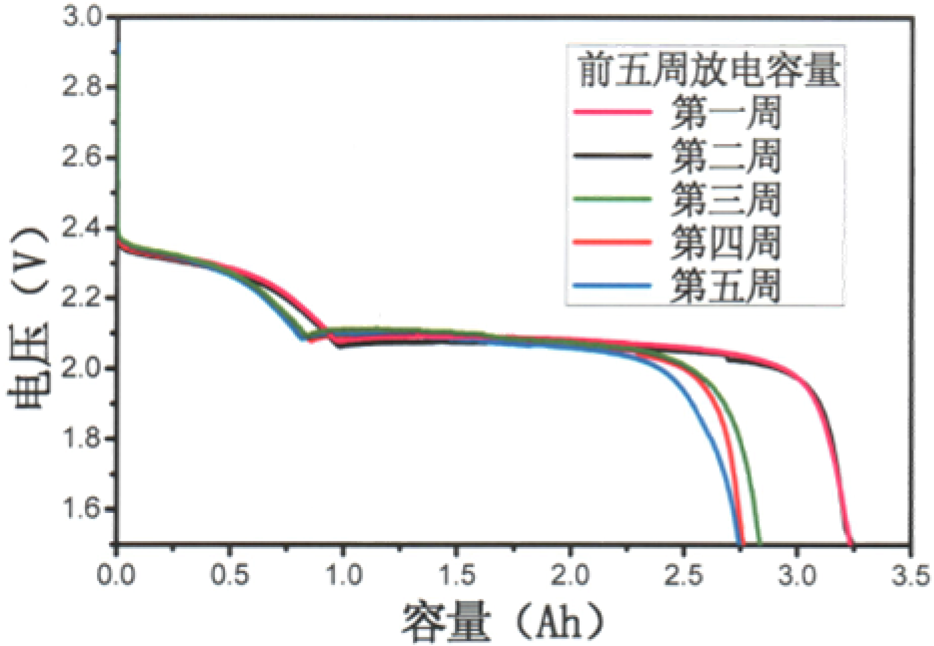
- **The electrochemical stability window of the TMS/PTSI composite electrolyte is around 5.5 V *vs*. Li/Li$^+$, and PTSI also possess relative lower melting point and higher boiling and flash point**

EC/DMC TMS/PTSI



- 低的可燃性 low combustibility

高能量锂硫电池
High energy density Lithium-sulfur battery



Li/S电池的放电曲线
Discharge curve of lithium-sulfur battery

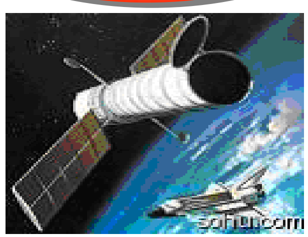
检测报告

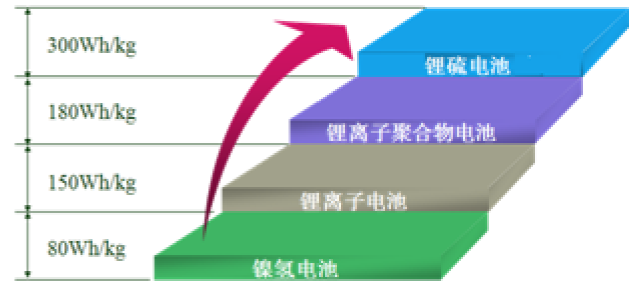
检测项目	电池质量/g	电池尺寸 长×宽×高/mm	平均放电电压/V	放电容量/Ah	放电能量/Wh	能量密度 /Wh·kg^{-1}
结果	18	70×55×5.7	2.1	3.24	6.804	378.88

应用前景
Applications



蓄电池
Secondary battery

各种电池比能量比较

- 硫复合材料的优化
- 锂负极的表面修饰
- 新型电解质体系
- **Sulfur composite optimization**
- **Lithium anode surface modification**
- **New electrolyte system**

安全性　高的功率密度和能量密度

Safety　Higher power and energy density

Thank you all for your attention