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doi: 10.3866/PKU.WHXB201602192

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## 兼具高负载量和高性能的碳/硫复合材料的低成本合成

季恒星<sup>1</sup> RUOFF Rodney S.<sup>2</sup>

(<sup>1</sup>中国科学技术大学材料科学与工程系, 中国科学院能量转换材料重点实验室, iChEM, 合肥 230026; <sup>2</sup>韩国蔚山科学技术大学(UNIST)化学与材料科学学院及韩国基础科学研究所(IBS), 多维碳材料中心(CMCM), 韩国蔚山 689-798)

单质硫能够与锂离子在正极发生多电子反应, 使得锂硫电池具有高达  $2567 \text{ W} \cdot \text{h} \cdot \text{kg}^{-1}$  的理论能量密度, 因而锂硫电池也成为了目前锂离子电池的研究焦点<sup>1</sup>。然而, 要实现锂硫电池的大规模应用仍面临诸多挑战, 包括: 锂枝晶的形成导致电池安全性降低, 硫的低导电能力 ( $5 \times 10^{-30} \text{ S} \cdot \text{cm}^{-1}$ ,  $25 \text{ }^\circ\text{C}$ ) 使得电池倍率性能不够, 充放电过程中形成的可溶性多硫化锂 ( $\text{Li}_2\text{S}_x$ ,  $4 \leq x \leq 8$ ) 产生“穿梭”效应降低电池寿命, 另外在充放电过程中硫也会发生体积膨胀和收缩 (~80%) 影响电池稳定性<sup>2</sup>。碳材料由于其结构多样性、优异的导电能力、卓越的化学稳定性以及廉价易得, 被普遍做为单质硫的载体用于解决锂硫电池正极材料的问

题<sup>3</sup>。负载硫纳米颗粒的碳可以传输电化学反应过程中产生的电子, 限制多硫化物的溶出, 容纳硫的体积变化, 从而提高电池比容量, 改善倍率和循环性能。然而, 这些性能还与硫在碳硫复合物中的质量比及单位面积电极中硫的负载量密切相关。更高的硫含量和高单位面积硫负载量对于锂硫电池的实际应用具有极其重要的意义, 但通常也伴随着硫的低利用率, 从而降低电极材料的比容量、倍率性能与循环性能。

中国科学院理化技术研究所耿建新团队在最近的 *Nature Communications* 上发表研究论文报道他们通过一种新型的合成路径获得了硫含量高达 90%(w, 质量分数) 的碳硫复合材料。当以这

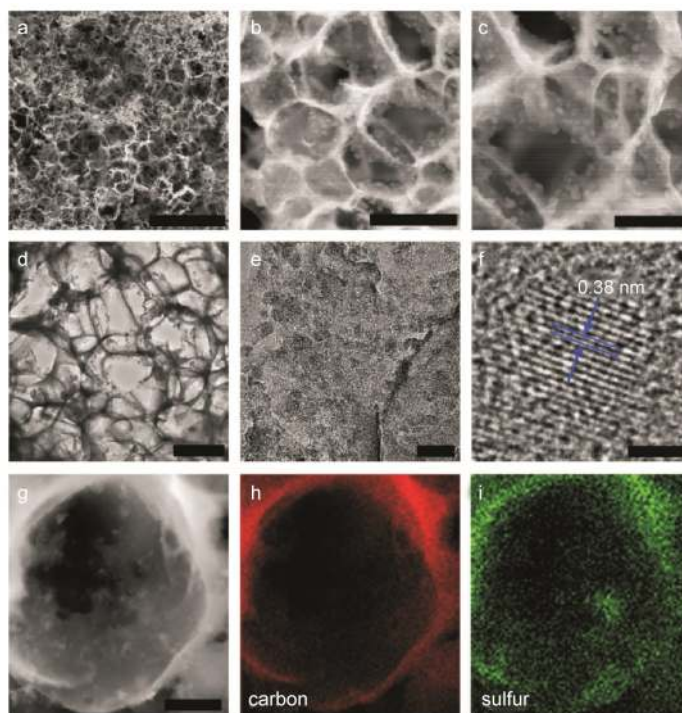


图1 含硫质量分数达90%的碳/硫复合电极材料的形貌

**Fig.1 Morphology of the porous graphitic carbon loaded with sulfur with a sulfur content of 90%**

The SEM images (a, b, c) and TEM images (d, e, f) show the porous structure of the carbon with sulfur nanoparticles uniformly distributed on the pore surface, which is confirmed by the EDAX study (g, h, i). Scale bars in a, b, and c: 20; 1; and  $0.5 \mu\text{m}$ . Scale bars in d, e, f, and g: 500; 50; 2; and 200 nm. Fig.1 from reference 4. Copyright Nature Publishing Group.

种复合材料作为电极材料，在硫的面负载量为  $\sim 2.3 \text{ mg} \cdot \text{cm}^{-2}$  时，锂硫电池仍显示出卓越的电化学性能。他们应用了低成本的原料，例如氯化钠、硫化钠、硝酸铁、葡萄糖和温和的合成条件，例如常压、氩气保护下  $750 \text{ }^\circ\text{C}$  煅烧<sup>4</sup>。所获得这种复合物(如图1所示)作为锂硫电池正极时，在  $0.5C$ 、 $1C$ 、 $2C$  倍率下的比容量分别为  $1382$ 、 $1242$  和  $1115 \text{ mAh} \cdot \text{g}^{-1}$ ，并且长时间循环测试表明：在  $2C$  倍率下充/放电循环  $1000$  次的容量衰减率仅为每圈  $0.039\%$ 。复合材料的优异性质主要源于合成路径所导致的特殊结构：原位化学沉积过程保证高含量硫纳米颗粒的均匀负载；硫纳米颗粒与碳材料

表面形成的碳—硫键限制了单质硫的聚集与多硫化物的溶出；多孔碳材料载体的高导电性与良好的结构稳定性。

作者同时也提出设计碳硫复合物的几个关键因素：大的孔体积及合适孔径的碳材料载体以确保硫的负载量和电解液的浸渍；高石墨化的碳结构以促进电子传输从而提高导电性；硫纳米颗粒与碳材料表面的强力集合，以及低成本的合成路线。文中提出的这一碳/硫复合材料的合成方法为进一步提升锂硫电池性能以及采用其他碳材料制备锂硫电池提供了可能。

## Low-Cost Synthesis Route for High-Performance S/C Composite with 90% S Content

Ji Heng-Xing<sup>1</sup> RUOFF Rodney S.<sup>2</sup>

(<sup>1</sup>Department of Materials Science and Engineering, CAS Key Laboratory of Materials for Energy Conversion, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), University of Science and Technology of China, Hefei 230026, P. R. China; <sup>2</sup>Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS) Center at the Ulsan National Institute of Science & Technology (UNIST) Campus; and Department of Chemistry and School of Materials Science, UNIST, Ulsan 689–798, Republic of Korea)

Lithium-sulfur (Li-S) batteries offer a high theoretical energy density of  $2567 \text{ W} \cdot \text{h} \cdot \text{kg}^{-1}$  by the multi-electron-transfer cathode reaction between elemental sulfur and lithium ions, and are a focus of post lithium-ion batteries technology<sup>1</sup>. Yet, there are challenging obstacles standing in the way of the large-scale application of the Li-S technology in the market, which include the potential safety risky of Li-dendrite formation, low electrical conductivity of sulfur ( $5 \times 10^{-30} \text{ S} \cdot \text{cm}^{-1}$  at  $25 \text{ }^\circ\text{C}$ ), the dissolution of the charge/discharge intermediates, polysulfides ( $\text{Li}_2\text{S}_x$ ,  $4 \leq x \leq 8$ ) in the electrolyte, and the volume change of the sulfur during lithiation/delithiation ( $\sim 80\%$ )<sup>2</sup>. Carbon materials are commonly used as the host to accommodate sulfur to address the issues relevant to the sulfur-cathode owing to their diversity, conductivity, robust stability and chemistry, and their ready abundance and cost<sup>3</sup>. A carbon host with sulfur nanoparticles adhered can conduct electrons generated by sulfur lithiation/delithiation, limit the dissolution of polysulfides, and withstand the volume change of the sulfur; it therefore can provide an improved specific capacity, rate capability, and cyclic life. However, these improvements are closely connected to both the mass ratio of sulfur in such a sulfur/carbon composite and the areal loading density of sulfur in the cathode. Higher mass ratio and areal loading density of sulfur are favored for practical Li-S battery application, but are usually accompanied by lower ‘sulfur utility’ that yields reduced specific capacity, rate capability, and cycle life.

GENG Jian-Xin and coauthors demonstrated that  $90\%$  (w,

mass fraction) sulfur content in the sulfur/carbon composite and  $\sim 2.3 \text{ mg} \cdot \text{cm}^{-2}$  sulfur areal loading density in the cathode can be achieved without significantly harming the overall performance of the sulfur/carbon cathode; this was achieved, per the recent paper published by the authors, by using a new synthesis route for their sulfur/carbon composite. They used low cost chemicals including sodium chloride, sodium sulfide, iron nitrate, and glucose and moderate conditions of  $750 \text{ }^\circ\text{C}$  at atmospheric pressure in argon gas to generate the composite material shown in Fig.1<sup>4</sup>. This composite material, when tested as a cathode in the Li-S battery, delivered a specific capacity of  $1382$ ,  $1242$ , and  $1115 \text{ mAh} \cdot \text{g}^{-1}$  at  $0.5C$ ,  $1C$ , and  $2C$ , and a long cycle life demonstrated by a small capacity decay of  $0.039\%$  per cycle over  $1000$  cycles at  $2C$ . These results were, per the authors, due to the *in situ* chemical deposition process that allowed for the formation of sulfur nanoparticles uniformly distributed in the porous carbon host with a high content of up to  $90\%$  S; the C—S bonds between the sulfur nanoparticles and carbon surface are stated to limit the agglomeration of sulfur and the dissolution of polysulfides; and the high electrical conductivity and mechanical flexibility of the porous carbon host favor better battery performance.

The authors have addressed several critical factors for rationally designed sulfur/carbon composites: large pore volume with suitable pore size of the carbon host for high sulfur loading and electrolyte impregnation, good conductivity by achieving a relatively high degree of ‘graphitic carbon’ to facilitate electron

conduction, uniformly distributed sulfur nanoparticles with strong adhesion to the carbon surface, and a stated opportunity for scaled and low cost production. One may expect further improvements in Li-S batteries including through the use of this type of approach, and also perhaps with other carbon materials.

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