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锂硫电池硫膨胀石墨正极材料的电化学性能

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摘要: 应用高温气相扩散沉积法由单质硫制备硫膨胀石墨. 该硫膨胀石墨正极可降低反应界面电荷传递阻抗, 提高扩散阻抗抑制单质硫或多硫化物在充放电过程的穿梭. 其首次放电容量达到 972 mAh·g^{-1}, 容量保持率为 78%, 循环效率在 80%以上.

关键词: 锂硫电池; 正极材料; 含硫膨胀石墨; 单质硫; 电化学性能
中图分类号: TM911 **文献标识码:** A

电子数码产品急需高能量二次电池, 锂硫电池倍受关注. 它由单质硫正极、金属锂负极及 DOL-DME电解液构成, 工作电压 2.1 V, 理论比能量 2600 Wh·kg^{-1}, 具有良好的电倍率性能和耐过充能力[1]. 而在单质硫的放电充电 (氧化)过程中, 由于环状硫硫链还原 (放电)断裂生成 (多)硫化锂, 后又氧化 (充电)生成多硫化锂或单质硫[2-3]. 况且氧化反应时单质硫穿梭效应明显加之还原反应时放电深度浅[4], 这就影响了锂硫电池的放电比容量以及首次容量保持率和循环性能. 为了提高单质硫的电化学性能, 本文利用膨胀石墨的丰富网络空隙结构及良好吸附性能[5], 将单质硫气相扩散沉积在膨胀石墨中制得新型硫膨胀石墨正极, 研究其电化学性能.

1 实验部分

1.1 硫膨胀石墨和电极

将可膨胀石墨 (KH80, 粒度 80目, 晶元石墨公司)放入马弗炉 (800℃)恒温 (3 min)即得膨胀石墨 (膨胀度 200倍). 再将单质硫和膨胀石墨分别放在开口哑铃型玻璃管的两端, 置于管式炉中通入 N_2气加热 (400℃, 2 h), 硫蒸气扩散吸附在膨胀石墨上, 缓慢冷却至室温即可制得硫膨胀石墨 (硫的质量百分含量约为 67.2%).

将硫膨胀石墨和导电剂乙炔黑、粘合剂 LA132按 70∶20∶10比 (by mass)混合加入适量异丙醇 水溶剂, 球磨 (转速 500 r/min, 10 h). 把浆料涂覆铝箔集流体 (面积 1 cm^2)上, 50℃真空干燥 (24 h)即得硫膨胀石墨电极. 另将单质硫导电剂、乙炔黑和粘合剂 LA132按 60∶30∶10比 (by mass)混合, 同上述方法制作单质硫电极.

1.2 纽扣电池和仪器

在充满 Ar气的手套箱 (Unilab, H_2O < 1×10^{-6}, O_2 < 1×10^{-6})中以硫膨胀石墨或单质硫电极作正极组装纽扣电池 (CR2025), 负极金属锂片、隔膜 Cellgard 2400、电解液 1 mol·L^{-1} LiCF$_3$SO$_3$/DOL-DME (1∶1, by volume).

使用武汉蓝电电池测试系统 (LAND2001CT)测试电池充放电性能, 电流密度 0.4 mA·cm^{-2}, 电压区间 1.5~2.8 V, Solartron 1280Z电化学工作站测定系统循环伏安和交流阻抗. 扫描速率为 0.1 mV·s^{-1}, 电压区间 1.5~2.8 V, 交流阻抗测试干扰电位为 5 mV, 频率范围 20 000~0.1 Hz. S4800型冷场扫描电镜观察电极形貌.

将硫膨胀石墨或单质硫电极纽扣电池 (CR2025)静置 22 h, 在 0.4 mA·cm^{-2}电流密度下放电至 1.5 V, 接着再充电至 2.8 V, 然后拆卸电

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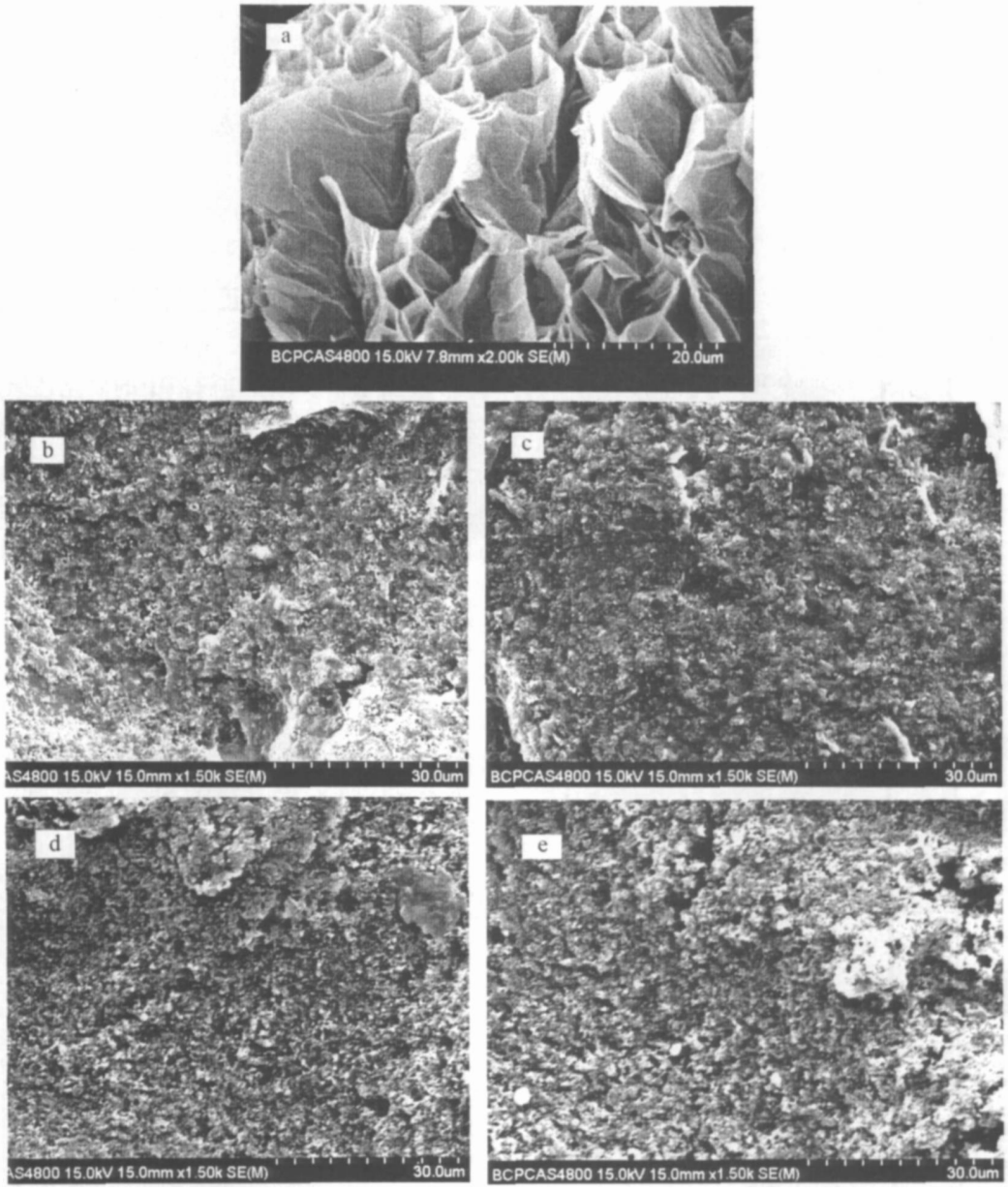

图 1　硫膨胀石墨(a),硫膨胀石墨电极静置 22h(b)首次充电后(c)和硫电极静置 22h(d)首次充电后(e)的扫描电镜图

Fig 1　SEM images of exfoliated graphite containing sulfur(a), exfoliated graphite containing sulfur electrode set for 22h (b) and after initial charged (c), sulfur electrode set for 22h (d) and after initial charged (e)

池、DME溶剂冲洗电极表面,晾干备作测试之用.

2　结果与分析

2.1　硫膨胀石墨电极形貌

由图 1可见,硫膨胀石墨保持了膨胀石墨丰富的网络孔隙结构(a),孔隙结构的元素硫含量为 54.5%,表面元素硫含量 7.0% (by mass),这说明单质硫主要填充于膨胀石墨的网络空隙中.该电极(静置 22 h)表面形貌结构致密(b),首次放电 充电循环后电极表面形貌仍很致密(c);而单质硫电极首次放电 充电循环后其表面形貌较疏松(e),充电前的电极(静置 22 h, d)可观察到片状硫.致密的硫膨胀石墨电极有利于抑制单质硫或多硫化锂溶解而扩散入电解液里.

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2.2　硫膨胀石墨正极的放电性能

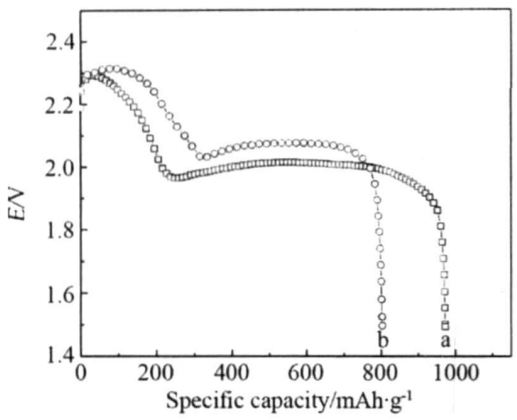

图 2 硫膨胀石墨(a)和单质硫(b)正极的首次放电曲线

Fig. 2 First discharge profiles of the exfoliated graphite containing sulfur (a) and sulfur (b) cathode

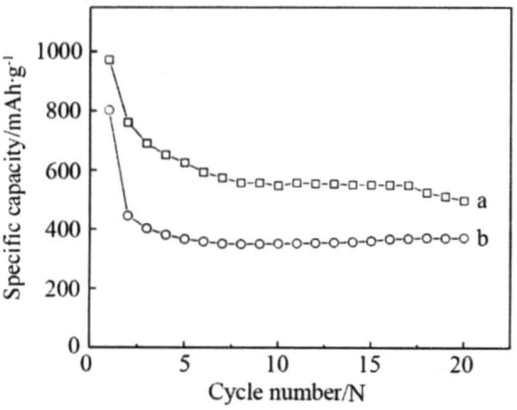

图 3 硫膨胀石墨(a)和单质硫(b)正极的循环寿命

Fig. 3 Discharge profiles of the exfoliated graphite containing sulfur (a) and sulfur (b) cathode materials

从图 2看出,硫膨胀石墨和单质硫正极的首次放电曲线基本相似,均有两个放电平阶,分别对应着高电压(~2.3V vs Li/Li^+)和低电压(2.0~2.1 V, vs Li/Li^+).单质硫电极放电比容量一般为理论放电比容量的 75%,其低电压平阶容量与高电压平阶容量之比约为 2∶1[4].硫膨胀石墨正极的首次放电比容量达到 972 mAh·g^{-1}, 明显大于单质硫电极的放电比容量(803 mAh·g^{-1}),而且低电压平阶容量与高电压平阶容量之比约为 3∶1.从图 3可知,硫膨胀石墨正极循环的首次容量保持率(78%)高于单质硫正极的容量保持率(56%),前者的比容量从第 2次起仅小幅度降低,至第 20次电极放电比容量为 497 mAh·g^{-1}.而单质硫正极从首次放电起比容量即有大幅度衰减,而后经几次循环后逐渐趋于稳定.硫膨胀石墨的首次充放电的库仑效率达到 82%,远远高于单质硫的 29%.据此,设想硫膨胀石墨正极还原反应可能经历如下步骤(分别对应于高电压放电平阶和低电压放电平阶):

$$S_8 + 4e^- \rightarrow 2S_4^{2-} \quad (1)$$

$$8Li^+ + S_4^{2-} + 6e^- \rightarrow 4Li_2S\downarrow \quad (2)$$

2.3 硫膨胀石墨正极循环伏安曲线

图 4示出硫膨胀石墨和单质硫正极循环伏安曲线.由于单质硫在电解液中的氧化还原反应为多电子传递连续步骤,故其循环伏安曲线则出现两个部分重叠的氧化峰,最大氧化峰电位为 2.51V(vs Li/Li^+).而硫膨胀石墨正极伏安曲线仅显示一个氧化峰,峰电位为 2.50 V(vs Li/Li^+)且峰形窄.反向扫描时,硫膨胀石墨和单质硫正极均有两个还原峰,峰值电位均分别处在约 2.35 V和 1.95 V附近.其中前者之第 2还原峰电位距第 1还原峰电位明显小于单质硫电极的两峰距,还原峰电流也明显大于单质硫电极的峰电流,这说明硫膨胀石墨正极第 2还原反应(方程式(2))的可逆性能较好.

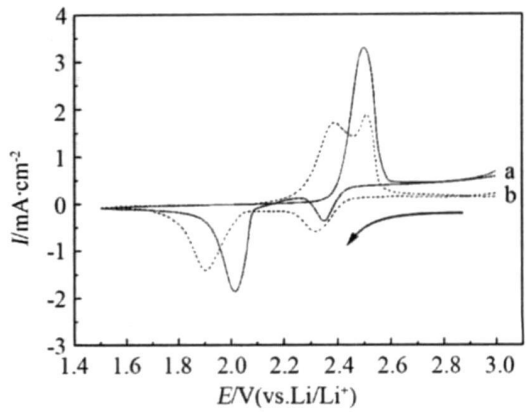

图 4 硫膨胀石墨(a)和单质硫 (b)电极的循环伏安曲线

Fig 4 CVs profiles of the exfoliated graphite containing sulfur (a) and sulfur (b) electrodes

2.4 硫膨胀石墨正极交流阻抗谱

图 5示出硫膨胀石墨和单质硫电极在开路电位下的交流阻抗复平面图谱.如图,两电极的交流阻抗均出现两个半圆,即电极反应都有两个时间常数.高频段的扁平半圆对应着界面电荷传递,低频段的半圆对应着电极表面电活性物质的扩散[6].可以看出硫膨胀石墨正极的界面电荷传递阻抗小

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于单质硫正极的界面电荷传递阻抗,相应的扩散阻抗大于单质硫正极的扩散阻抗.这可能是由于前者良好导电性有利于促进电化学反应速率,同时丰富的网络空隙结构能较好地抑制单质硫或多硫化锂的扩散.

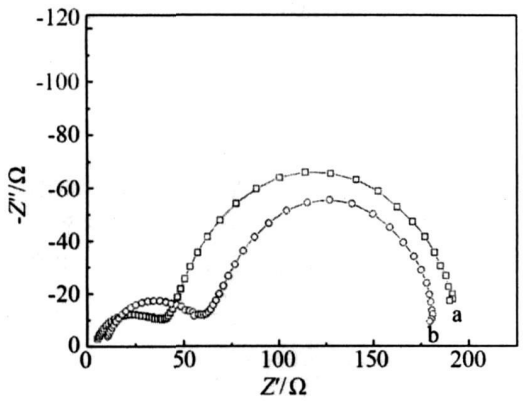

图 5　硫膨胀石墨 (a)和单质硫 (b)电极的交流阻抗图

Fig 5　AC impedance plots of exfoliated graphite containing sulfur (a) and sulfur (b) electrodes

3 结　论

由硫蒸气气相扩散沉积法制备的硫膨胀石墨,其单质硫主要填充于膨胀石墨的孔隙中.此结构能有效抑制单质硫在充放电过程中的溶解.以该材料作锂硫电池正极可降低界面电荷传递阻抗提高扩散阻抗,提高第二还原反应的可逆性能,其首次放电比容量达到 972 mAh·g^{-1},容量保持率为 78%.

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Electrochemical Performance of the Exfoliated Graphite Containing Sulfur Cathode Material for Lithium Sulfur Battery

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Abstract: The exfoliated graphite containing sulfur cathode material was prepared by the high temperature sulfur gas diffusion adsorption method. This cathode material could obtain an initial discharge specific capacity 972 mAh·g^{-1}, capacity retention ratio 78% and cycling efficiency above 80%, respectively. The exfoliated graphite containing sulfur cathode could decrease the reaction interphase charge transfer impedance, and restrain the sulfur or polysulfide shuttle phenomenon during the charge-discharge process through improving the diffusion impedance.

Key words: lithium sulfur battery; cathode material; exfoliated graphite containing sulfur; sulfur; electrochemical performance

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