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锂硫二次电池正极材料的制备、结构与性能
研究

Synthesis, Structure and Electrochemical Performance of
Cathodes for Lithium-Sulfur Batteries

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Synthesis, Structure and Electrochemical Performance of Cathodes for Lithium–Sulfur Batteries



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摘要

目前电动汽车一次充电行驶里程不及传统汽油车的 1/3。为满足电动汽车技术发展需求，必须全面提升动力电池的性能。因此，研制具有更高比容量和更优电化学性能的新型正极材料成为发展下一代锂二次电池的关键。单质硫具有高的理论比容量，同时自然界储量丰富、价格低廉和环境友好等优势，是十分理想的下一代锂离子电池正极材料。虽然硫作为锂离子电池正极材料优点突出，但很多限制因素却阻碍了其大规模的实际应用。一方面，由于硫的不导电性，使硫的利用率很低，循环性能差；另一方面，充放电过程中产生的多硫化锂(S_n^{2-})易溶解在有机电解液中，导致活性材料的流失，及电解液粘度增大，离子迁移困难。同时产生的多硫阴离子(S_n^{2-})会通过电解液在正/负极间来回扩散迁移，分别被还原/氧化，产生所谓“穿梭效应”。随着充放电周期数的增加，正极和负极表面会逐渐生成电子绝缘的 Li_2S 沉积层，一方面阻碍电荷传递，另一方面改变了电极/电解质的界面，增大了电池的内阻。针对锂硫电池体系存在的问题，本论文开展了以下研究：

1. 以棒状石墨为原料，使用改良的 Hummers 法制备氧化石墨，在含有流动保护气氛的管式炉中热处理，制备出了膨胀氧化石墨 (E-GO) 材料。通过红外光谱和 X-射线光电子能谱表征发现，膨胀氧化石墨表面具有多种含氧官能团。 N_2 吸脱附等温线测试结果表明 E-GO 载硫前后的 BET 比表面积的变化，载硫前比表面积为 $296.53 \text{ m}^2/\text{g}$ ，载硫之后为 $21.55 \text{ m}^2/\text{g}$ ，说明硫已经进入到 E-GO 的间隙。同时通过 E-GO 材料的 SEM 图像表明棒状石墨虽然发生了剥离，但它的层状结构并不是单层的。膨胀氧化石墨的 XRD 测试也证实了该实验结果。

2. 亚硫酸钠作为硫的高价盐，硫化钠作为硫的低价盐， $1 \text{ M H}_2\text{SO}_4$ 溶液为 pH 调节剂，利用归中化学反应的原理，生成纳米尺度的硫颗粒，使其嵌入到膨胀氧化石墨的内部，制备了膨胀氧化石墨-硫 (E-GO/S) 复合材料。通过 XRD、XPS、SEM、TEM、BET 等测试手段对含硫复合材料的结构进行了全面的考察。将含硫量为 $75.13 \text{ wt}\%$ 的复合材料作为正极活性物质，Li 金属为对电极，在充满 Ar 气的手套箱中组装 2025 型扣式电池，并对其电化学性能测试，结果表明 E-GO/S 复合材料具有优异的电化学性能，该复合正极材料在 0.1 C 电流密度

下,首次放电容量为 1020 mAh/g,100 周循环之后其容量还保持在 650 mAh/g 左右;材料的倍率性能和库伦效率优异,这可能得益于小尺寸的硫在材料中均匀分布,以及表面官能团对硫的固定化作用。

3. 采用具有极佳导电性和高比表面的商业导电炭黑——科琴黑(Ketjenblack EC600JD) 作为纳米硫吸附导电载体,使用简单热复合的方法,制备了不同硫载量的复合材料: KJ600-xS, x=0.4, 0.5, 0.6, 0.7, 0.8。BET 比面积测试表明 KJ600 表面积高达 1941.1 m²/g,热复合 40% 的硫之后比表面积下降至 446.8 m²/g。XRD 结果表明 KJ600 对硫具有良好的分散性,这主要得益于它具有的极大的比表面积值。当硫载量为 40 wt% 时,电池性能最佳。在 0.1C 倍率下恒电流充放电,由于其极佳的导电性能,首次放电容量达到 1686.8 mAh/g,接近理论容量,100 周循环之后,还保持 767.7 mAh/g 的容量。

关键词: 单质硫 归中化学反应 锂硫电池 膨胀氧化石墨 科琴黑 热复合

Abstract

At present, electric vehicles on a single charge mileage is less than 1/3 of the conventional gasoline vehicles. To meet the demand for the development of electric vehicle technology, it is necessary that raise the overall performance of the power battery. Therefore, development of new type cathode materials with higher capacity and better electrochemical performance becomes the key to progressing the next generation lithium secondary battery. The elemental sulfur cathode has an extremely high theoretical specific capacity, natural abundance, low cost and environment friendliness, which identify it as a very suitable positive electrode materials. Its superiority is remarkable when sulfur as lithium battery cathode material, but there is many limiting factors hindering its large-scale practical application at the same time. The first one is the insulativity of the sulfur, it will result in low utilization of active material and severe capacity fading. What's more, the dissolution of polysulfide anions (S_n^{2-})-intermediate reaction species formed on charge and discharge, which will result in loss of active material, electrolyte viscosity increased, and ions migration become difficult. The soluble intermediate S_n^{2-} can diffuse through the electrolyte to the Li negative electrode where they are reduced, and to the positive electrode where they are oxidized. We call this process is "shuttle effect". With the increase of charge and discharge cycles, the insoluble precipitate Li_2S adhere to the surface of anode electrode and cathode electrode, which hinder the charge transfer, on the other hand, change the electrode/electrolyte interface, contributes to increase the internal cell resistance. Aiming at the existing problem of lithium sulfur batteries system, this thesis carried our the following study:

(1) In this thesis, we synthesize graphite oxide by the modified Hummers' method, rodlike graphite as raw material. Expanded-graphite oxide (E-GO) is fabricated through heat treatment in the tube furnace with flow protective atmosphere. The results of Fourier transform infrared spectroscopy and X-ray photoelectron

spectroscopy show the existence of functional groups on the surface of the expanded-graphite oxide. N₂ adsorption/desorption isotherms illustrate the change of Brunauer-Emmett-Teller (BET) specific surface area of E-GO before and after sulfur loading from 296.53 m²/g to 21.55 m²/g. It indicates elemental sulfur has gotten into the gaps of E-GO. The SEM images of E-GO indicate the rodlike graphite has been expanded and the layer structure are not single sheet but consist of nanosheets. On the other hand, the XRD results of E-GO can also prove the truth.

(2) The way of fabricate S-C composites is the chemical reaction on the acidic aqueous solution base on comproportionation. On our experiments, sodium sulfide as reductant, sodium sulfite as oxidant, 1M H₂SO₄ as pH regulator. The generated nano-scale sulfur particles get into the interior of the expanded-graphite oxide, then the E-GO/S composites are generated. The composites subsequently are test by XRD, XPS, SEM, TEM and BET for researching its comprehensive physicochemical property. The sulfur content of 75.13 wt% of the composite material as a positive electrode active material, the 2025 coin cells would be fabricated in an argon-filled glove box with lithium metal as anode, and we test the electrochemical performance of the cells. The results show that the E-GO/S composite has a outstanding electrochemical performance of discharge capacity of 1 020 mAh/g at the first cycle and keeps the capacity of ca. 650 mAh/g after 100 cycles with the current density of 0.1C, in addition, the Li-S cells have outstanding coulombic efficiency and rate performance. That may benefit from the small size of sulfur uniformly distributed in the composites, as well as immobilization effect by functional groups on the surface.

(3) In this thesis, we select the commercial conductive carbon black(Ketjenblack EC600JD) with an excellent conductivity and good adsorption as nanoadditive and electronic carrier, the different sulfur content nanocomposites are prepared by the way of simple heat treatment, denoted KJ600-xS, x=0.4, 0.5, 0.6, 0.7 ,0.8. BET specific area measurement show that the specific surface area is 1941.1 m²/g, and the value decrease to 446.8 m²/g after sulfur loading. XRD results show that KJ600 can disperse sulfur very well, because of its high surface area. It has demonstrated that the

cathode of nano-composite with 40% sulfur content exhibits the highest capacity. Its initial discharge capacity is 1 686 mAh/g at 0.1C, close to theoretical capacity, and retains as high as 767 mAh/g after 100 cycles.

Keywords: Elemental sulfur; Comproportionation; Lithium-Sulfur batteries; Expanded-graphite oxide; commercial conductive carbon black

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