

# 电沉积乙炔黑/锗材料及其性能研究

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**摘要:** 目的 提高锂离子电池锗基材料的电化学性能。方法 采用电泳和离子液体电沉积制备乙炔黑/锗负极材料, 用 SEM, Raman 和充放电循环等手段表征其结构和性能。结果 乙炔黑/锗负极材料在 0.2C 倍率下循环 100 次, 比容量依然可达到 600 mAh/g 以上。结论 乙炔黑/锗负极材料的电化学性能明显优于单独锗材料和碳材料。

**关键词:** 锂离子电池; 负极; 乙炔黑/锗; 电化学性能

**中图分类号:** O484.4; TM91

**文献标识码:** A

**文章编号:** 1001-3660(2014)06-0011-05

## Research on the Properties of Acetylene Black/Ge Prepared by Electrochemical Deposition

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**ABSTRACT:** **Objective** To improve the electrochemical performance of the germanium materials of lithium-ion batteries. **Methods** Germanium nanoparticles (Ge-NPs) and acetylene black anodes were fabricated through electrodeposition of Ge in the new-generation ionic liquids on the surface of acetylene black which was electrophoretically deposited on a copper current collector. The structure and electrochemical properties were characterized by electron microscopy, Raman spectroscopy and constant current charge-discharge methods. **Results** The acetylene black-Ge nanocomposite exhibited the electrochemical cycling properties of over 600 mAh/g at 0.2C after 100 cycles. **Conclusion** The electrochemical performance of composite was obviously better than Ge or acetylene black by itself as anode electrode material.

**KEY WORDS:** lithium-ion battery; negative electrode; acetylene black/Ge; electrochemical properties

锂离子电池具有工作电压高、比能量大、循环寿命好、工作温度范围宽、自放电率低、无记忆效应及环

收稿日期: 2014-06-14; 修订日期: 2014-09-27

Received: 2014-06-14; Revised: 2014-09-27

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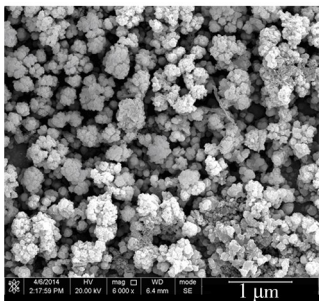


图 2 乙炔黑与锗复合的 SEM 照片

数比约为 1 : 1, Au 来自于 SEM 测试前进行的喷金。复合材料截面(如图 4 所示)的厚度为 5 μm,单独电沉积的锗膜厚度仅为 2 μm,电泳碳层的厚度能够较好地缓解锗的体积膨胀并表现出复合材料的明显优势。

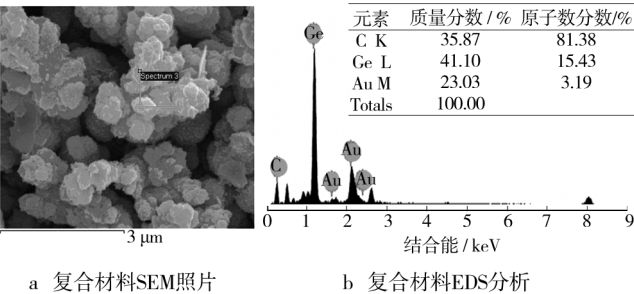


图 3 乙炔黑与锗复合材料的 SEM 照片及能谱分析

Fig.3 SEM image and EDS analysis of the acetylene black-Ge composite

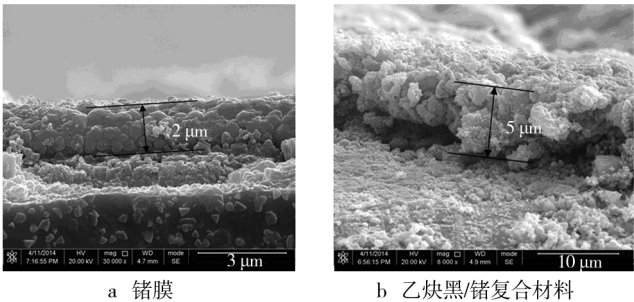


图 4 锗膜与乙炔黑/锗复合材料的横截面形貌

Fig.4 Cross section morphology of the germanium film and the acetylene black/Ge composite

图 5 为复合材料的拉曼光谱,在约 1343 cm<sup>-1</sup>和 1597 cm<sup>-1</sup>处的两个峰分别对应的是碳的无序态 D 峰和石墨态 G 峰<sup>[18]</sup>,位于 298 cm<sup>-1</sup>处的拉曼峰代表纳米晶锗的光学模式<sup>[19]</sup>,118 cm<sup>-1</sup>和 165 cm<sup>-1</sup>处的不明显小峰代表的是非晶态锗。分析结果与 EDS 结果相

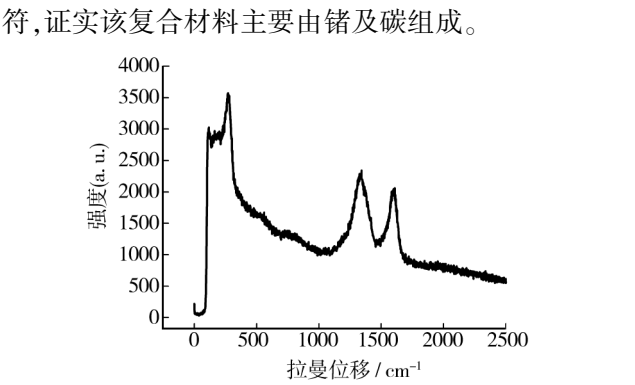


图 5 乙炔黑与锗复合材料的拉曼光谱图

Fig.5 Raman spectra of the acetylene black-Ge composite

2.2 电化学测试及分析

图 6 为乙炔黑/锗复合材料的循环伏安、充放电性能、循环性能、库伦效率和倍率性能变化曲线。从充放电循环可以看出乙炔黑和锗的复合材料首次放电比容量高达 2000 mAh/g,由于形成 SEI 膜,其充电比容量降为 1200 mAh/g。从图 6a 可知,在 2 ~ 5 次循环测试中,曲线能够保持较高的重合性且氧化还原电位保持一致。从 0.4 V 开始出现一段坡度较缓的曲线,对应一个轻度的嵌锂过程;在 0 V 附近出现较强的还原峰,对应 Li<sup>+</sup>嵌入锗和碳中的反应;0.6 V 附近的氧化峰对应着 Li<sup>+</sup>从不同嵌锂态的锂锗化合物和碳中脱出的反应。从图 6b 可知,0.25 ~ 0 V 的平台是锂锗合金化和 Li<sup>+</sup>嵌入碳中的过程,0.4 ~ 0.6 V 处出现的平台则是 Li<sup>+</sup>从碳材料和合金中脱出的过程。

如图 6c 所示,该复合材料循环 50 次后放电比容量降到 900 mAh/g,100 次之后依然可达 700 mAh/g。单独锗薄膜材料首次放电比容量为 1700 mAh/g,第二次已降到 800 mAh/g,经过 100 次循环比容量只为 300 mAh/g,与单独碳材料相近。经过测试,该复合材料在循环性能上与单纯锗材料相比有明显的提高,不仅在初始循环中,复合材料的比容量要比单纯锗材料高 300 mAh/g,而且这种优势在 100 次循环之后依然存在。

对传统锂离子电池负极的碳材料来说,其库伦效率可以达到 95% 以上,100 次循环后依然如此,表现出明显优势,这也是采用碳材料作为组成复合材料成分的主要原因。单独锗材料的库伦效率在前 40 次与碳材料类似,但之后急剧下降。复合材料前 50 次的稳定性与碳材料持平甚至更高,可以达到 98% 以上,但 50 次之后因电极材料结构的坍塌,减少电接触,导致出现下降的状态,不过依然比单纯锗材料高,保持



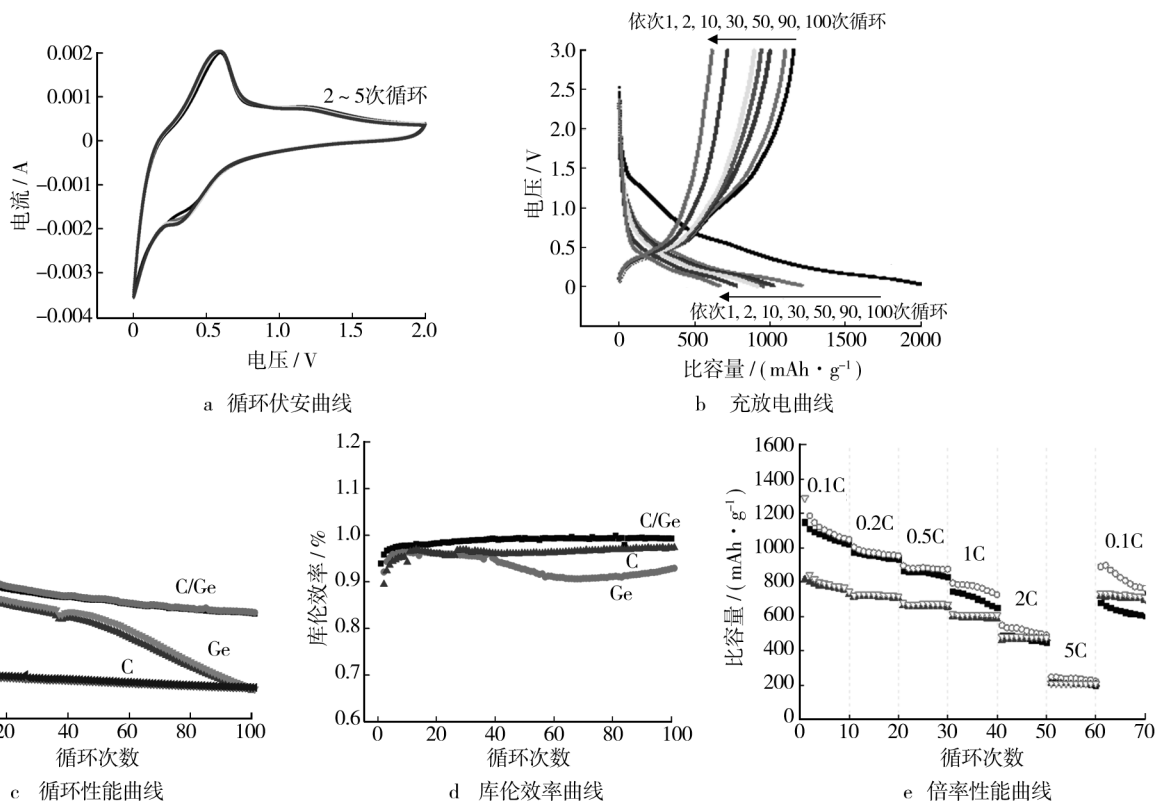


图 6 乙炔黑/锗复合材料的电池性能曲线

Fig. 6 Electrochemical performance curves of the acetylene black-Ge composite

在 93% 以上,说明复合材料结构能在一定程度上缓解体积变化。图 6e 分别为在 0.1C,0.2C,0.5C,1C,2C,5C 这 6 种倍率下进行测试,从 0.1C,0.2C,0.5C 这 3 种小倍率下可以看到复合材料的明显优势,始终比单纯锗材料高约 300 mAh/g,1C 时已出现比容量差值的缩小,在 2C 以上的倍率下,其性能有明显的下降,5C 时基本与纯锗材料相似。分析可知,在小倍率下此复合材料有明显优势。从整体复合材料与单纯锗材料对比可以看出,结构的改变使复合材料在电化学性能上有明显的改善。

### 3 结论

通过离子液体电沉积法在已电泳乙炔黑薄膜的铜箔上电沉积锗,制备出乙炔黑/锗的复合材料电极,该复合电极比单纯锗材料表现出较好的电化学性能。其首次放电可以达到 2000 mAh/g,并且在 0.2C 倍率下循环 100 次依然可以达到 700 mAh/g,同时库伦效率始终保持 90% 以上。乙炔黑不仅可以增强导电性,还具有一定的储锂容量,其蓬松的结构可有效缓解锗在充放电过程中的体积膨胀,为电子传输提供了

一个快速通道,增强了能量密度,具备良好的电化学性能。该复合电极在高能锂离子电池的产业中具有较好的应用前景。

### 参考文献

- [1] 李继红,何建新,张先勇. 某型军用锂离子电池低温环境适应性[J]. 装备环境工程,2014,11(1):111—115.  
LI Ji-hong, HE Jian-xin, ZHANG Xian-yong. Environmental Worthiness Evaluation of a Certain Type of Military Lithium-ion Battery at Low Temperature[J]. Equipment Environmental Engineering, 2014, 11(1): 111—115.
- [2] 张汉平,付丽君,吴宇平. 锂离子电池负极材料的研究进展[J]. 电池,2006,35(4):274—275.  
ZHANG Han-ping, FU Li-jun, WU Yu-ping. Research Progress of Lithium-ion Battery Anode Materials[J]. Battery, 2006, 35(4): 274—275.
- [3] KASAVAJJU L A, WANG U C. Appleby, Nano and Bulk-Silicon-based Insertion Anodes for Lithium-ion Secondary Cells[J]. Journal of Power Sources, 2007, 163(2): 1003—1039.
- [4] OBROVAC M, CHRISTENSEN L. Structural Changes in Silicon Anodes during Lithium Insertion/Extraction[J].

- Electrochemical and Solid-state Letters, 2004, 7(5): 93—96.
- [5] YOON S. Electrochemical Characterizations of Germanium and Carbon-coated Germanium Composite Anode for Lithium-ion Batteries[J]. Electrochemical and Solid-state Letters, 2008, 11(4): 42—45.
- [6] CUI G, GU L. A Novel Germanium/Carbon Nanotubes Nanocomposite for Lithium Storage Material[J]. Electrochimica Acta, 2010, 55(3): 985—988.
- [7] LIU W R, GUO Z Z, YOUNG W S, et al. Effect of Electrode Structure on Performance of Si Anode in Li-ion Batteries; Si Particle Size and Conductive Additive[J]. Journal of Power Sources, 2005, 140(1): 139—144.
- [8] WANG Y. Synthesis of Ge/C Core-shell Nanocomposites for High-performance Lithium Storage in Lithium-ion Batteries[J]. Chemistry, 2013, 8(12): 3142—3146.
- [9] CHENG J. Synthesis of Germanium-Graphene Nanocomposites and Their Application as Anode Materials for Lithium Ion Batteries[J]. CrystEngComm, 2012, 14(2): 397.
- [10] 范长岭, 徐仲榆. 乙炔黑在锂离子电池负极中的贮锂功能[J]. 炭素技术, 2007, 26(1): 19—21.
- FAN Chang-ling, XU Zhong-yu. Lithium Storage Function of Acetylene Black in the Negative Electrodes of Lithium-ion Batteries[J]. Carbon Techniques, 2007, 26(1): 19—21.
- [11] DILEO R A, GANTER M. Germanium-single-wall Carbon Nanotube Anodes for Lithium Ion Batteries[J]. Journal of Materials Research, 2010, 25(8): 1441—1446.
- [12] KIM B C, UONO H, SATO T. Li-ion Battery Anode Properties of Si-carbon Nanocomposites Fabricated by High Energy Multiring-type Mill[J]. Solid State Ionics, 2004, 172(1): 33—37.
- [13] DILEO R A, FRISCO S. Hybrid Germanium Nanoparticle-single-wall Carbon Nanotube Free-standing Anodes for Lithium Ion Batteries[J]. The Journal of Physical Chemistry, 2011, 115(45): 22609—22614.
- [14] LEE J K, SMITH K B, HAYNER C M, et al. Silicon Nanoparticles-Graphene Paper Composites for Li Ion Battery Anodes[J]. Chemical Communications, 2010, 46(12): 2025—2027.
- [15] ENDRES F. Air and Water Stable Ionic Liquids in Physical Chemistry[J]. Physical Chemistry Chemical Physics, 2006, 8(18): 2101—2116.
- [16] 赵运伟, 黄巍, 田海燕, 等. 电泳-电沉积 Ni-金刚石复合镀层及其耐磨性能研究[J]. 表面技术, 2013, 42(2): 77—79.
- ZHAO Yun-wei, HUANG Wei, TIAN Hai-yan, et al. Research on the Ni-diamond Composite Coating by Electrophoretic-Electrochemical Deposition and Its Wear Resistance[J]. Surface Technology, 2013, 42(2): 77—79.
- [17] 刘小勤, 曾冬铭, 徐钦建, 等. 电沉积聚 8-羟基喹啉膜及其耐蚀性的研究[J]. 表面技术, 2013, 42(2): 84—88.
- LIU Xiao-qin, ZENG Dong-ming, XU Qin-jian, et al. Electrodeposition of Poly-8-hydroxyquinoline Films and Its Corrosion Resistance Performance[J]. Surface Technology, 2013, 42(2): 84—88.
- [18] REN J G, WU Q H, TANG H, et al. Germanium-Graphene Composite Anode for High-energy Lithium Batteries with Long Cycle Life[J]. Journal of Materials Chemistry, 2013, 1(5): 1821—1826.
- [19] CUI G, GU L, ZHI L, et al. A Germanium-Carbon Nanocomposite Material for Lithium Batteries[J]. Advanced Materials, 2008, 20(16): 3079—3083.

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- and Application of Tungsten Plated Alloy Oil Well Pipe[J]. Oil Field Equipment, 2012, 41(11): 46—49.
- [11] 雷丹, 林琳, 张国超, 等. 电沉积钨合金镀层的研究现状与应用进展[J]. 全面腐蚀控制, 2012, 26(6): 1—6.
- LEI Dan, LIN Lin, ZHANG Guo-chao, et al. Progress in Research and Application of Electro-deposited Tungsten Alloy Coatings[J]. Total Corrosion Control, 2012, 26(6): 1—6.
- [12] 杜贵平, 李雄涛, 姜立军. 基于电流密度在线监控的电镀工艺工程控制系统[J]. 表面技术, 2010, 39(1): 93—96.
- DU Gui-ping, LI Xiong-tao, JIANG Li-jun. Control System for Electroplating Process Based on On-line Current Density Monitoring[J]. Surface Technology, 2010, 39(1): 93—96.
- [13] 陈月华, 刘永永, 江德凤, 等. 化学镀镍施镀过程稳定性分析[J]. 表面技术, 2013, 42(2): 74—76.
- CHEN Yue-hua, LIU Yong-yong, JIANG De-feng, et al. Evaluation on Plating Stability in Electroless Nickel Deposition[J]. Surface Technology, 2013, 42(2): 74—76.
- [14] 万小波, 张林, 周兰, 等. 镍钨合金镀层结构的研究[J]. 材料保护, 2005, 38(5): 8—10.
- WAN Xiao-bo, ZHANG Lin, ZHOU Lan, et al. Structure of Nickel-Tungsten Alloy Electroplating[J]. Materials Protection, 2005, 38(5): 8—10.
- [15] ISO 7539—2. Corrosion of Metals and Alloys — Stress Corrosion Testing—Part 2 Preparation and Use of Bent-beam Specimens[S].