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# 壳聚糖单体溶胶-凝胶煅烧合成 $LiFePO_4/C$ 正极

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**摘要:** 本文以壳聚糖单体为碳源兼凝胶剂，利用溶胶-凝胶煅烧合成了锂离子电池 $LiFePO_4/C$ 正极材料. 使用 XRD 和 SEM 对合成的材料进行表征，用恒电流充放电测试了 $LiFePO_4/C$ 电极的电化学性能. 当壳聚糖单体与 $LiFePO_4$ 摩尔比为 1:1.2 时,600 ℃煅烧的 $LiFePO_4/C$ 电极性能最佳，其粒径分布均匀(200 ~ 400 nm)，该电极 0.2C 倍率放电比容量为 155 mAh·g$^{-1}$,30 周期循环放电比容量仍保持 152 mAh·g$^{-1}$,库仑效率为 97.9 %.

**关键词:** 壳聚糖; 磷酸亚铁锂; 溶胶-凝胶法; 锂离子电池

**中图分类号:** O611.4 **文献标识码:** A

$LiFePO_4$ 价廉、安全和环保,适用于汽车动力电池[1-4],因此含铁化合物锂离子电池正极材料倍受关注. 但 $LiFePO_4$ 电子电导率低,扩散系数不大,放电比容量不高,高倍率放电容量衰减严重. 因此,急需改善其导电率以期提高其大电流充放电性能[5-8]. 碳包覆及其它金属或金属离子掺杂等的效果较佳[9-12]. 添加碳的种类很多,如炭黑、聚丙乙烯以及蔗糖等[13-16]. 壳聚糖大分子链上分布着许多羟基、氨基或乙酰氨基,可起到络合作用[17-18]. 本文首次以壳聚糖单体为碳源兼胶凝剂，溶胶-凝胶煅烧合成 $LiFePO_4/C$ 材料,并研究煅烧温度及壳聚糖配比对 $LiFePO_4/C$ 电极电化学性能的影响.

## 1 实 验

### 1.1 $LiFePO_4/C$ 材料的制备

将适量的壳聚糖单体溶解于一定量 2% (by volume)的醋酸溶液中，搅拌均匀(2 h). 按 $CH_3COOLi\cdot 2H_2O$: $Fe(NO_3)_3\cdot 9H_2O$:$NH_4H_2PO_4$ = 1:1:1 (by mole)的比例加入到壳聚糖单体的醋酸溶液中[19], 搅拌均匀, 80 ℃水浴下蒸发形成凝胶,再真空 120 ℃下干燥 24 h 得到干凝胶. 该凝胶粉在 $N_2$ 氛围 600 ℃煅烧 12 h，冷却后即可得 $LiFePO_4/C$ 正极材料.

### 1.2 材料表征

采用 X-射线衍射仪 (D/max-TTR III，日本 Rigaku)表征材料的物相,Cu $K_\alpha$ 波长 0.154 18 nm,石墨单色器,扫描速度 5°·min$^{-1}$,阶宽 0.02°($2\theta$),用扫描电子显微镜(JSM-6480A, 日本 JEOL)观察材料的微观结构,20 kV. 材料的碳含量利用化学方法进行分析[8].

### 1.3 $LiFePO_4/C$ 正极的制备

将活性物质、乙炔黑和聚偏氟乙烯(PVDF)按 85:8:7(by mass)比混合均匀,并将其均匀涂敷在铝箔上(厚度 200 μm),真空 120 ℃干燥 10 h,10 MPa 下冲压成极片($\phi$ = 14 mm)即得正极.

### 1.4 电池组装与性能测试

$LiFePO_4/C$ 正极与金属锂箔负极,1 mol·L$^{-1}$ $LiPF_6$ 的碳酸乙烯酯(EC)/ 碳酸二甲酯 (DMC)溶液电解液和微孔聚丙烯膜 (Ceigard-2300) 隔膜，在充满氩气的手套箱(Super1220/750/900,德国 MIKROUNA)中用手动封口机组装电池(JH-80,深圳美森). 采用电池性能检测仪(BTS-5V5mA,深圳新威尔士) 进行电池充放电及循环寿命曲线测试，0.2C、0.5C 和 1C 倍率充电,截止电位 4.2 V,静置 10 min,放电至 2.4 V.

## 2 结果与讨论

### 2.1 壳聚糖单体配比

图 1 给出不同配比壳聚糖单体 600 ℃煅烧 $LiFePO_4/C$ 电极 0.2C 进行充放电曲线. 由图 1 可

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知，壳聚糖单体与 $LiFePO_4$ 摩尔比为 1:1.2（碳含量 4.656%）时其电极比容量最高. 壳聚糖摩尔比减小为 1:1.1，热解的碳量也少（碳含量 3.231%），不能有效地提高其电导率；壳聚糖单体配比升高（1:1.4，碳含量 5.698%；1:1.6，碳含量 7.514%），虽可提高其电导率，但 $LiFePO_4$ 的量相对于活性物质减少，反而使其比容量下降，即 1:1.2 的配比最适宜.

## 2.2 煅烧温度

图 2 为壳聚糖单体与 $LiFePO_4$ 摩尔比为 1:1.2 时不同温度煅烧的 $LiFePO_4$/C 电极 0.2C 充放电曲线. 由图 2 可知，煅烧温度升至 600 ℃时（碳含量 4.656%）其比容量最高（充电比容量 158 mAh·g$^{-1}$，放电比容量 155 mAh·g$^{-1}$），库仑效率为 98.4%. 超过此煅烧温度，碳含量减少，电导率降低，其充放电容量和库仑效率均下降. 即煅烧温度 600 ℃最适宜.

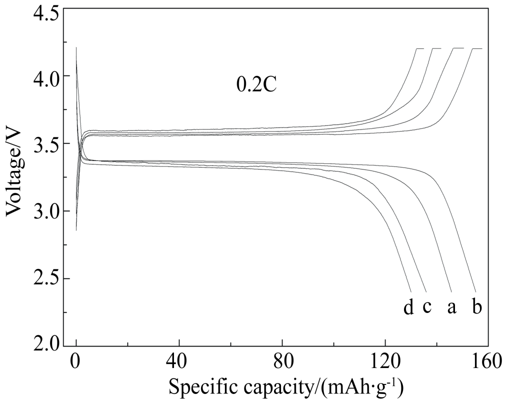

图 1 不同配比壳聚糖单体 600 ℃煅烧合成的 $LiFePO_4$/C 电极 0.2C 倍率首次充放电曲线
壳聚糖单体与 $LiFePO_4$ 摩尔比：a. 1:1; b. 1:1.2; c. 1:1.4; d. 1:1.6

Fig. 1 The first charge/discharge curves of the $LiFePO_4$/C cathode calcined at various molar ratios of chitosan monomer to $LiFePO_4$ at 0.2C rate
Molar ratios of chitosan monomer to $LiFePO_4$: a. 1:1; b. 1: 1.2; c. 1:1.4; d. 1:1.6

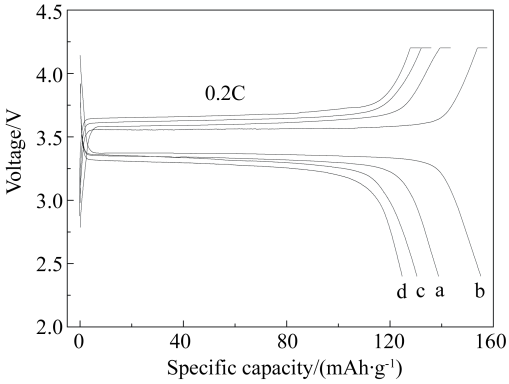

图 2 不同温度煅烧合成的 $LiFePO_4$/C 电极 0.2C 倍率首次充放电曲线
a. 550 ℃; b. 600 ℃; c. 650 ℃; d. 700 ℃

Fig. 2 The first charge/discharge curves of the $LiFePO_4$/C cathode calcined at various temperatures at 0.2C rate
a. 550 ℃; b. 600 ℃; c. 650 ℃; d. 700 ℃

## 2.3 材料表征

图 3 为壳聚糖单体与 $LiFePO_4$ 摩尔比为 1:1.2 时 550 ℃ ～ 700 ℃下煅烧 $LiFePO_4$/C 材料的 XRD 谱图. 由图 3 可知，600 ℃下煅烧时，其衍射峰均与 $LiFePO_4$ 标准衍射峰谱图相对应（JCPDS 40-1499），且无明显杂质峰，表明材料具有橄榄石晶型结构. 煅烧温度升高（650 ℃或 700 ℃），各衍射峰位不变，衍射峰增强，结晶度增强，粒径增大. 图

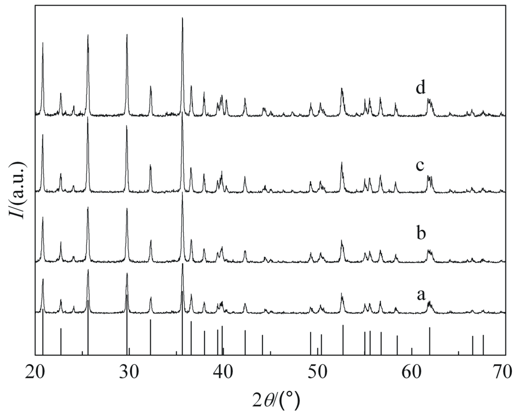

图 3 不同温度煅烧合成的 $LiFePO_4$/C 材料的 XRD 谱图
a. 550 ℃; b. 600 ℃; c. 650 ℃; d. 700 ℃

Fig. 3 X-ray diffraction patterns of the $LiFePO_4$/C samples calcined at various temperatures

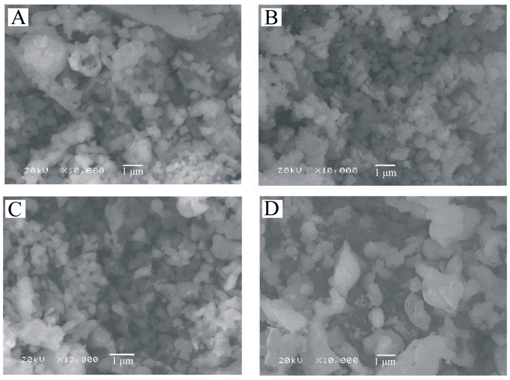

图 4 不同温度合成的 $LiFePO_4$/C 材料的 SEM 照片
a. 550 ℃; b. 600 ℃; c. 650 ℃; d. 700 ℃

Fig. 4 SEM images of $LiFePO_4$/C samples calcined at various temperatures

4 是壳聚糖单体与 $LiFePO_4$ 配比 1:1.2(by mole)不同温度煅烧合成的 $LiFePO_4/C$ 材料的 SEM 照片，由照片可知，煅烧温度升高，$LiFePO_4$ 粒径逐增. 600 ℃煅烧 $LiFePO_4$ 材料粒径分布均匀(约为 200 ~ 400 nm)，颗粒表面光滑，无团聚，$LiFePO_4$ 颗粒可均匀地分布于壳聚糖的分解碳中.

## 2.4　$LiFePO_4/C$ 电极充放电倍率性能

图 5 是壳聚糖单体与 $LiFePO_4$ 摩尔比为 1:1.2 时在 600 ℃下煅烧 $LiFePO_4/C$ 电极不同倍率的首次充放电曲线. 从图 5 中可以看出，$LiFePO_4/C$ 电极首次放电比容量分别为 155 mAh·g$^{-1}$(a)、137 mAh·g$^{-1}$(b)和 127 mAh·g$^{-1}$(c)，大电流充放电过程中的极化加大.

图 6 为壳聚糖单体与 $LiFePO_4$ 摩尔比为 1:1.2 时在 600 ℃煅烧合成的 $LiFePO_4/C$ 电极的循环寿命曲线. 从图 6 可知，0.2C 首周期放电比容量为 155 mAh·g$^{-1}$，30 周期循环其放电比容量仍保持 152 mAh·g$^{-1}$，衰减量为 2.1%，该电极循环寿命较优异.

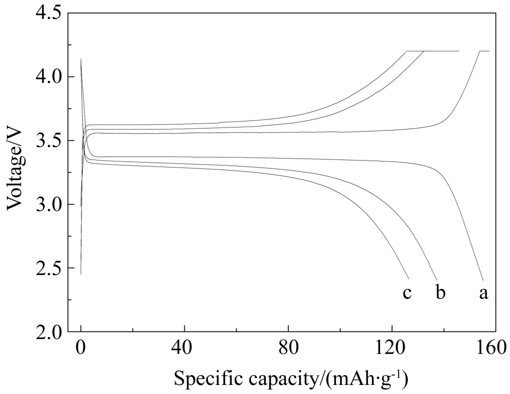

图 5　不同倍率 $LiFePO_4/C$ 电极的首次充放电曲线
a. 0.2C；b. 0.5C；c. 1.0C

Fig. 5　The first charge/discharge curves of the $LiFePO_4/C$ cathode at various rates
a. 0.2C；b. 0.5C；c. 1.0C

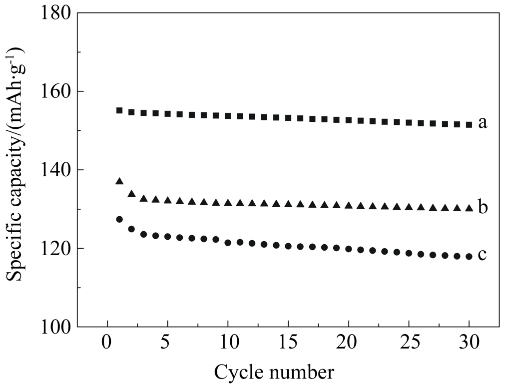

图 6　不同倍率充放电时 $LiFePO_4/C$ 的电极的循环寿命曲线　a. 0.2C；b. 0.5C；c. 1.0C

Fig. 6　The cycling life of the $LiFePO_4/C$ cathode at various rates　a. 0.2C; b. 0.5C; c. 1.0C

## 3　结　论

壳聚糖作为碳源、溶胶 - 凝胶法煅烧合成的 $LiFePO_4/C$ 材料，其粒径分布均匀(200 ~ 400 nm). 壳聚糖单体与 $LiFePO_4$ 配比 1:1.2(by mole)在 600 ℃煅烧 $LiFePO_4/C$ 电极 0.2C 倍率首周期充电比容量为 158 mAh·g$^{-1}$，放电比容量为 155 mAh·g$^{-1}$，库仑效率为 98.4%；30 周期循环其放电比容量为 152 mAh·g$^{-1}$，库仑效率达 97.9%.

## 参考文献(References):

[1] Sabina B, Libero D, Marina M. MW-assisted synthesis of $LiFePO_4$ for high power applications[J]. Journal of Power Sources, 2008, 180(2): 875-879.

[2] Li J(李军), Lai G T(赖桂棠), Huang H M(黄慧民), et al. Preparation and properties of high capacity $LiFePO_4$ [J]. Journal of Electrochemistry(电化学), 2007, 13(4): 403-406.

[3] Fisher C A J, Islam M S. Surface structures and crystal morphologies of $LiFePO_4$: Relevance to electrochemical behaviour[J]. Journal of Materials Chemistry, 2008, 18: 1209-1215.

[4] Park O K, Cho Y, Lee S, et al. Who will drive electric vehicles, olivine or spinel?[J]. Energy & Environmental Science, 2011, 4(5): 1621-1633.

[5] Daiwon C, Prashant N K. Surfactant based sol-gel approach to nanostructured $LiFePO_4$ for high rate Li-ion batteries[J]. Journal of Power Sources, 2007, 163(2): 1064-1069.

[6] Kobayashi G, Nishimura S I, Park M S, et al. Isolation of solid solution phases in size-controlled $Li_xFePO_4$ at room temperature[J]. Advanced Functional Materials, 2009, 19 (3): 395-403.

[7] Keisuk S, Kaoru D, Kiyoshi K. Formation of impurities on phospho-olivine $LiFePO_4$ during hydrothermal synthesis [J]. Journal of power Sources, 2008, 146(1/2): 555- 558.

[8] Prosini P P , Lisi M , Zane D, et al. Determination of the chemical diffusion coefficient of lithium in $LiFePO_4$ [J]. Solid State Ionics, 2002, 148(1/2):45-51.

[9] Bai Y(白莹), Yang J M(杨觉明), Qing C B(卿春波), et al.

Electrochemical performances of C-coating and co-doping $LiFePO_4$ [J]. Journal of Electrochemistry (电化学), 2011, 17(3): 334-338.

[10] Li T(李婷), Qian J F(钱江峰), Cao Y L(曹余良), et al. Electrochemical performance of $Li_{1-x}M_xFePO_4$ cathode materials synthesized by polymer pyrolysis route[J]. Journal of Electrochemistry(电化学), 2007, 13(2): 136-139.

[11] Zou H L(邹红丽), Zhang G H(张光辉), Shen P K(沈培康). Hydrothermal reduction synthesis of $LiFePO_4$ and its electrochemical performance[J]. Journal of Electrochemistry(电化学), 2010, 16(4): 416-419.

[12] Zhu C, Yu Y, Gu L, et al. Electrospinning of highly electroactive carbon-coated single-crystalline $LiFePO_4$ nanowires[J]. Angewandte Chemie International Edition, 2011, 50(28): 6278-6282

[13] Yu L H(余丽红), Cao Y L(曹余良), Zhang X F(张晓飞), et al. Structure and electrochemical characteristics of $LiFePO_4$ prepared by the polyacrylates pyrolysis reduction method for Li-ion batteries[J]. Journal of Electrochemistry(电化学), 2006, 12(4): 442-444.

[14] Wang L, Liang G C, Ou X Q, et al. Effect of synthesis temperature on the properties of $LiFePO_4$/C composites prepared by carbothermal reduction[J]. Journal of Power Sources, 2009, 189(1): 423-428.

[15] Peng Y Y(彭友谊), Zhang H Y(张海燕), He C H(贺春华), et al. A study on the $LiFePO_4$/ MWCNTs cathode materials for Li-ion batteries[J]. Journal of Electrochemistry(电化学), 2009, 15(3): 331-335.

[16] Lepage D, Michot C, Liang G, et al. A soft chemistry approach to coating of $LiFePO_4$ with a conducting polymer [J]. Angewandte Chemie International Edition, 2011, 50 (30): 6884-6887.

[17] Suh J, Matthew H. Application of chitosan-based polysaccharide biomaterials in cartilage tissue engineering: A review[J]. Biomaterials, 2000, 21(24):2589-2598.

[18] Kumar M. A review of chitin and chitosan applications [J]. Reactive and functional polymers, 2000, 46(1): 1-27.

[19] 王贵领,曹殿学,王博. 壳聚糖改性锂离子电池 $LiFePO_4$ 正极材料[P]. CN200910071245.2.

# Synthesis of $LiFePO_4$/C Cathode by Sol-Gel and Calcining Method with Chitosan Monomer

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**Abstract:** The $LiFePO_4$/C cathode materials for Li-ion battery were synthesized by sol-gel and calcining method using chitosan monomer as a carbon source and a gelating agent. The structures and morphologies were characterized by X-ray diffraction spectroscopy (XRD) and scanning electron microscopy (SEM). The electrochemical performance was investigated by the galvanostatic charge-discharge test. When the molar ratios between chitosan monomer and $LiFePO_4$ were 1:1.2, the $LiFePO_4$/C cathode calcined at 600 °C showed the best performance. The particle sizes ranged 200 ~ 400 nm. The initial discharge capacity of 155 $mAh \cdot g^{-1}$ was achieved at room temperature with discharge rate of 0.2C, while the capacity of 152 $mAh \cdot g^{-1}$ could be maintained after 30 charge-discharge cycles. The coulombic efficiency was 97.9%.

**Key words:** chitosan; $LiFePO_4$/C; sol-gel method; Li-ion battery