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锂离子电池锰基氧化物负极材料合成、性质
及转化反应机理的 XAFS 研究

**Mn-based oxides anode materials of lithium ion battery:
synthesis, property and the mechanism of conversion
reactions studied by XAFS**

苏航

指导教师姓名: 孙世刚 教授

专 业 名 称: 能 源 化 工

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**Mn-based oxides anode materials of lithium
ion battery: synthesis, property and the
mechanism of conversion reactions studied
by XAFS**



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Hang Su

Directed by

Prof. Shi-Gang Sun

College of Energy, Xiamen University

Xiamen, Fujian, P.R.China

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摘要

虽然锂离子电池被广泛应用于移动电话、笔记本电脑及便携式电子等设备，但远不能满足电动汽车等大型移动设备的需求。发展高能量、高功率和高安全的电极材料成为研究前沿。由于较高的理论比容量、储量丰富、环保、对锂电位低、原料廉价等优点，锰基过渡金属氧化物成为新型高容量锂离子电池负极材料的研究热点。然而，电导率较低及储锂过程中体积效应较大，导致电化学反应动力学缓慢，比容量较低，循环性能和倍率性能较差。本论文主要从电池材料的结构设计入手，合成出分级、核壳、空心等多种结构的锰基氧化物，缓解其储锂过程中的体积效应，显著提高电化学性能。另一方面，运用 X 光吸收光谱(XAFS)研究锰基氧化物在充放电过程中的价态及结构变化，阐释其转化反应机理。主要内容如下：

1. 在溶剂热合成过程中，通过控制 PVP 的添加，合成出 6 ~ 10 μm 的分级空心 Mn_2O_3 微米球及 Mn_2O_3 微米片，并运用扫描电子显微镜 (SEM)、X 射线衍射 (XRD) 及透射电子显微镜 (TEM) 详细表征其结构。电化学研究结果指出，分级空心 Mn_2O_3 微米球具有较为优异的电化学性能，在 500 mA g^{-1} 的电流密度下充放电循环 140 周后可逆比容量保持为 580 mAh g^{-1} ，在 1600 mA g^{-1} 高电流密度下，给出 422 mAh g^{-1} 的可逆比容量，体现出较好倍率性能。分级结构允许电解液充分的浸润材料，多孔空心的结构则保证了材料在转化反应中的稳定性，从而显著提高了电化学性能。

2. 以共沉淀法合成 CoMn_2O_4 负极材料，通过改变沉淀剂 NH_4HCO_3 的滴加速率，分别合成出核壳结构及多孔微米球结构的目标材料。用 SEM、TEM、XRD、EDS、电池充放电等方法分别对其表面形貌、元素分布、晶体结构、充放电循环及倍率性能进行表征分析。结果表明，核壳结构对转化反应中体积效应有显著的缓解作用，给出较好的电化学性能。作为锂离子电池负极材料时，在 200 mA g^{-1} 下充放电循环 100 周，可逆比容量保持 500 mAh g^{-1} ，在 1600 mA g^{-1} 高电流密度下，比容量保持在 385 mAh g^{-1} 。

3. 利用溶剂热法合成出蛋黄壳结构 ZnMn_2O_4 负极材料，并对其结构及电化

学性能进行了详细表征。对比前驱体及目标材料的 SEM 数据，发现蛋黄壳结构在前驱体时就已经形成。经过煅烧之后，产生了多孔结构。作为锂离子电池负极材料，在 200 mA g^{-1} 下充放电循环 100 周，可逆比容量保持 675 mAh g^{-1} ，在高电流密度 1600 mA g^{-1} 下，比容量高达 502 mAh g^{-1} ，体现出优异的电化学性能。

4. 在本论文的最后一部分，针对 Mn_2O_3 、 CoMn_2O_4 、 ZnMn_2O_4 三种材料转化反应机理，我们运用 X 光吸收光谱(XAFS)分别对其在充放电过程中价态及结构变化进行表征，研究转化反应机理。首先，针对 Mn_2O_3 材料在充电截止电位是否氧化到+3 价进行表征。结果表明，在充电到 3 V 时，Mn 被氧化到+2 价。不同循环周数 Mn 的 K 边 XANES 特征谱图与 EIS 数据表明，随着充放电次数增加，转化反应进行得并不充分，导致金属 Mn 与 Li_2O 累积在电极表面，引起电荷传递阻抗的增加，容量衰减。其次，针对 CoMn_2O_4 材料在首次放电过程中 0.7 V 左右小平台的归属，通过对比元素 Mn 及 Co 的分别在 0.6 V 和 0.8 V 的 XANES 和 EXAFS 谱图可知，在此放电过程中，元素 Mn 与 Co 的价态保持为+2 价，且 Mn 与 Co 原子所处空间结构并未发生改变，说明对应的容量贡献并非活性材料的还原反应，而是电极表面反应，即固体电解质 SEI 膜的形成。最后，为探索 ZnMn_2O_4 材料在储锂过程中是否同时包含转化反应及合金化反应，比较了放电截止电位 0.01 V 下的 Zn 的 EXAFS 与标样 Zn 箔的 EXAFS 谱图。结果指出，两者的 R 空间及 K 空间相同，说明在放电截止时，最终还原产物为单质 Zn，并未形成 LiZn 合金，也即 ZnMn_2O_4 在充放电过程中仅存在转化反应。

综上所述，本论文利用溶剂热法及共沉淀法成功合成出分级、空心、核壳及蛋黄壳结构的锰基氧化物。结果显示，通过调控电极材料的结构可以显著提高电化学性能。运用 XAFS 技术揭示了所制备的三种负极材料的转化反应机理。本论文研究结果揭示了结构对于电极材料的电化学性能的重要性，XAFS 与电化学结合的方法对于研究电极材料的储锂过程、充放电机理和容量衰减机制具有重要意义。

关键词：锂离子电池负极 Mn_2O_3 CoMn_2O_4 ZnMn_2O_4 XAFS 转化反应机理

Abstract

Lithium-ion batteries (LIBs) are widely used in mobile phones, portable electronic devices, and notebook computers, while could hardly fulfill the fast growing demands of development of electric vehicles. Therefore, it's very significant to explore and develop batteries with higher specific energy. Compared with other metal oxides, manganese oxides have been extensively studied as alternative anode materials for LIBs, thanks to high theoretical specific capacity, low operating potential vs. Li/Li⁺, low toxicity and natural abundance. While they have a poor electrochemical performance due to large volume expansion during charge/discharge processes, which hampered its application in rechargeable LIBs. This thesis is aiming at buffering volume expansion to improve the electrochemical performance of manganese oxides through construction of special structures such as hierarchical, yolk-shell, hollow. Besides, X-ray Absorption Fine Structure (XAFS) technique is used in this work to characterize the conversion reaction mechanism of Mn-based oxides anode. The main research work are as follows:

1. In the synthesis process of solvent-thermal, adding PVP K-30 or without it, hierarchical Mn₂O₃ hollow microspheres and Mn₂O₃ microsheets were prepared, respectively. And they were characterized by XRD, SEM, HRTEM to investigate the construction features. Hierarchical Mn₂O₃ hollow microspheres could present a reversible capacity of 580 mAh g⁻¹ after 140 cycles at 500 mA g⁻¹, showing a good cycling performance. A specific capacity of 422 mAh g⁻¹ can be obtained at 1600 mA g⁻¹, showing a good rate capability. The higher electrochemical performance of hierarchical Mn₂O₃ hollow microspheres could be attributed to the hierarchical hollow structural features, which can make each nanosheet contact directly with electrolyte and ensure the structure stability during conversion reaction cycling.

2. In the synthesis process of facile co-precipitation, by controlling the speed of distribution droplets of NH₄HCO₃, the core-shell CoMn₂O₄ microspheres and porous CoMn₂O₄ microspheres were synthesized, respectively. SEM, TEM, XRD and

charge/discharge test were used to analyze the morphology, nano-structure, crystal-structure and cycle ability and rate capability. The results indicated that core-shell CoMn_2O_4 microspheres showed a higher electrochemical performance, benefiting from the architectural feature which can buffer the volume expansion during charge/discharge process effectively. The porous core-shell CoMn_2O_4 microspheres can present a reversible capacity of 500 mAh g^{-1} at a current density of 200 mA g^{-1} with a coulombic efficiency of 98.5% after 100 cycles. A specific capacity of 385 mAh g^{-1} are obtained even at a current density as high as 1600 mA g^{-1} , exhibiting a good rate capability.

3. Porous yolk-shell ZnMn_2O_4 microspheres were prepared by solvent-thermal method, and the ability of lithium storage and structural features were characterized adequately. This novel structural feature was obtained during the formation of $\text{Zn}_{0.33}\text{Mn}_{0.67}$ -glycolate by analyzing the SEM images of $\text{Zn}_{0.33}\text{Mn}_{0.67}$ -glycolate precursors and ZnMn_2O_4 . After the calcination of $\text{Zn}_{0.33}\text{Mn}_{0.67}$ -glycolate precursors, the structural feature of porosity was obtained. As served as anode of LIBs, it could present a reversible capacity of 675 mAh g^{-1} at a current density of 200 mA g^{-1} after 100 cycles. A specific capacity of 502 mAh g^{-1} could be obtained even at 1600 mA g^{-1} , exhibiting a good rate capability.

4. In the last part of thesis, aiming at the controversial viewpoints of conversion reactions of Mn_2O_3 , CoMn_2O_4 , ZnMn_2O_4 , X-ray Absorption Fine Structure (XAFS) was employed to characterize the valence evolution and structural transformation, and investigate the mechanism of conversion reactions. Firstly, for the Mn_2O_3 materials, the pristine Mn_2O_3 was reduced to metallic Mn when it was discharged to 0.01 V, and oxidized to MnO when it was charged to 3.0 V. And combining the EIS results with XANES spectra of samples subjected to different cycling numbers, the results indicated that the conversion reaction of Mn and Li_2O to MnO was not a fully reversible reaction, which lead to the accumulation of metallic Mn and Li_2O on the surface of electrodes. As a consequence, the charge transfer resistance (R_{ct}) increased and the capacity decayed. Secondly, for the CoMn_2O_4 materials, aiming at the affiliation of small plateau at 0.7 V in the first discharge process, the results illustrated

that extended X-ray absorption fine structure (EXAFS) spectra of Mn at discharged 0.8 V was same as that at discharged 0.6 V, and the same result could be obtained in the EXAFS spectra of Co. Furthermore, there was no change in the XANES of both Mn and Co at those two stages. Both the results demonstrated that there was no phase transformation and valence evolution on electrode materials, which should be owing to the formation of the solid electrolyte interface (SEI) on the surface of CoMn_2O_4 electrode. In the end, for the ZnMn_2O_4 materials, we compared the k^3 -weighted $\chi(k)$ signals at the Zn K-edge of ZnMn_2O_4 electrodes with the cut-off voltage of 0.01 V with reference Zn foil. There was no obvious change at the Zn K-edge between them. Moreover, The same results were acquired on Fourier transformed k^3 -weighted $\chi(k)$ Zn K-edge EXAFS spectra of them. The results illustrated the there was no alloying reaction during the charge/discharge of ZnMn_2O_4 electrodes.

From the above, this thesis has investigated the electrochemical performances and of Mn_2O_3 , CoMn_2O_4 , ZnMn_2O_4 . We improve the electrochemical performances of manganese oxides by construction of special structure such as hierarchical, yolk-shell, hollow, which can buffer the volume expansion during charge/discharge effectively. And the mechanism of conversion reactions are investigated through both XAFS and EIS data. The study of this thesis is significant to develop high energy batteries and explore the mechanism of conversion reactions of electrode materials.

Keywords: anode materials of lithium ion battery; Mn_2O_3 ; CoMn_2O_4 ; ZnMn_2O_4 ; XAFS; mechanism of conversion reaction

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