Synthesis and Characterization of $LiFe_{0.7}Mn_{0.3}PO_4/C$ Cathode Material for Lithium Ion Batteries

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Abstract: $LiFe_{0.7}Mn_{0.3}O_4/C$ was synthesized at 650℃ by solid-state reaction. Structure, surface morphology and electrochemical properties of $LiFe_{0.7}Mn_{0.3}O_4/C$ were characterized by X-ray diffraction, scanning electron microscopy and electrochemical measurement, respectively. Results show that $LiFe_{0.7}Mn_{0.3}O_4$ shares a single olivine structure. The morphologies of $LiFe_{0.7}Mn_{0.3}O_4$ are greatly affected by the addition of carbon. The $LiFe_{0.7}Mn_{0.3}PO_4/C$ has a small particle size of 100~200 nm and carbon is coated on the surface of $LiFe_{0.7}Mn_{0.3}O_4$ uniformly. $LiFe_{0.7}Mn_{0.3}O_4/C$ demonstrates high reversible capacity and perfect cycling performance, and excellent rate capability: the reversible capacity of about 141 mAh·g^{-1} at a current rate of 0.1C and the capacity loss per cycle is only 0.19% after cycling 60 times, while that of $LiFe_{0.7}Mn_{0.3}PO_4$ is 0.53%, suggesting the electrochemical performance of $LiFe_{0.7}Mn_{0.3}PO_4$ is improved effectively by addition of carbon.

Key words: lithium iron phosphate; lithium ion batteries; carbon doping
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Olivine $LiFePO_4$ has attracted significant interest as a good candidate positive electrode in next generation of Li-ion batteries for the hybrid electric vehicle application[1].

In addition to $LiFePO_4$, a series of olivine structure $LMPO_4$ (M = Mn, Co, Ni) have been considered as attractive cathode materials recently because of their high theoretical capacity of about 170 mAh·g^{-1} and high equilibrium potential based on the M^{3+}/M^{2+} couple[2]. Among these materials, $LMnPO_4$[3] seems to be one of the most attractive candidates because of the 4.1 V high potential of Mn^{3+}/Mn^{2+} versus Li/Li^+, which is compatible with the electrolytes presently used in lithium ion batteries. However, the low conductivity[3] of the $LMnPO_4$ makes the insertion or extraction of lithium into or from the lattice difficult to be realized. Some researchers[2] have tried the doping of iron to enhance the conductivity of this composite and synthesized the $LiFe_xMn_{1-x}PO_4$ material. Padhi et al. noticed that the extraction of lithium from $LiFe_xMn_{1-x}PO_4$ occurred at 3.4 and 4.1 V (versus Li/Li^+), which correspond to the redox of Fe^{3+}/Fe^{2+} and Mn^{3+}/Mn^{2+} couples, respectively. It would generate high energy density providing that higher capacity can be achieved at high Mn content.

In this paper, we chose the x value of 0.7 and synthesized the pure and carbon-containing $LiFe_{0.7}Mn_{0.3}PO_4$ by solid-state reaction. The influence of the addition of carbon black to the performance of the material was discussed.

1 Experimental

The pure and carbon-containing $LiFe_{0.7}Mn_{0.3}O_4$ compounds were prepared by solid-state reaction. The raw materials of Li_2CO_3 (99.9%), $MnCO_3$ (AR), $NH_4H_2PO_4$ (99.5%), and $FeC_2O_4\cdot 2H_2O$ (98%) were mixed in a stoichiometric ratio. $LiFe_{0.7}Mn_{0.3}PO_4/C$ was synthesized by adding carbon black to the synthetic mixture. The mixture was firstly ground for 12 h by ball milling under Ar atmosphere. Then the samples were reground for 8 h by ball milling after they were sintered at 300℃ for 4 h. Finally, the materials were annealed at 650℃ for 24 h in a purified Ar atmosphere to prevent the formation of Fe(III) compounds as impurities and the final product of pure $LMn_{0.7}Fe_{0.3}PO_4$ and $LMn_{0.7}Fe_{0.3}PO_4/C$ were obtained.

2 Results and discussion

The XRD profile of the synthesized $LiFe_{0.7}Mn_{0.3}PO_4$ and $LiFe_{0.7}Mn_{0.3}PO_4/C$ powders show that all peaks

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can be indexed as pure and well-crystallized $LiFePO_4$ phase with an ordered olivine structure and a space group of Pnma [4] given by JCPDS card No. 83—2092. There is no evidence of diffraction peaks for carbon, possibly due to its low content. The amount of carbon in the $LiFePO_4/C$ composite was about 4.8% determined by the weight loss after heating the powder in oxygen, which has been used by Yang et al. [5]. The XRD result demonstrates that the solid-state route developed in the present work could synthesize single-phased product $LiFePO_4$ with no unwanted impurity phases, such as Li_3PO_4 and Fe^{3+}-related compounds. The intensity of diffraction peak for $LiFe_{0.7}Mn_{0.3}PO_4/C$ is a little weaker than that of the pure $LiFe_{0.7}Mn_{0.3}PO_4$. It indicates that the doped carbon plays an important role in restricting the growth of the particles. The small particle size is what we expected because the diffusion coefficient of lithium ion in the olivine cathodes (10^{-14} ~ 10^{-16} $cm^2 \cdot s^{-1}$) is much less than that of the other cathode materials, such as $LiMn_2O_4$ (10^{-9} ~ 10^{-10} $cm^2 \cdot s^{-1}$). The size of particles can be minished by the addition of carbon to improve the diffusion velocity of lithium ion, which is also proved by the measurement of SEM and electrochemical studies. SEM image indicates that the $LiFe_{0.7}Mn_{0.3}PO_4/C$ has a small particle size of 100 ~ 200 nm and carbon is coated on the surface uniformly to reduce the particle-to-particle contact resistance, thus significantly enhancing the electrical conductivity of the composites.

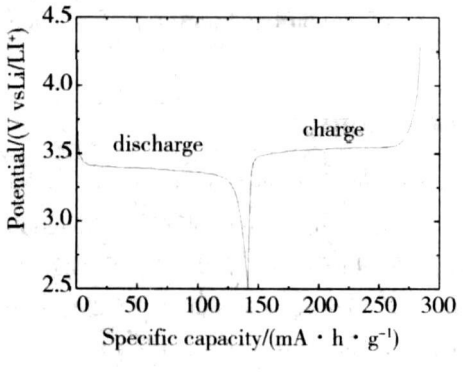

Fig. 1 Charge-discharge curves of $LiFe_{0.7}Mn_{0.3}PO_4/C$ at 0.1 C rate

Charge-discharge tests were carried out to measure the electrochemical properties of the prepared samples. A good plateau at about 3.4 and 3.5 V on the discharge and charge curve can be seen and a reversible capacity of 141 $mA \cdot h \cdot g^{-1}$ can be obtained. Battery with the $LiFe_{0.7}Mn_{0.3}PO_4/C$ has a good cycling performance. The capacity loss per cycle of $LiFe_{0.7}Mn_{0.3}PO_4/C$ and $LiFe_{0.7}Mn_{0.3}PO_4$ is 0.19% and 0.53% after cycling 60 times, suggesting the existing of carbon help improve the cyclability of $LiFe_{0.7}Mn_{0.3}PO_4$.

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锂离子电池用正极材料 $LiFe_{0.7}Mn_{0.3}PO_4/C$的合成与表征

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摘 要: 采用固相反应法在 650℃合成了 $LiFe_{0.7}Mn_{0.3}PO_4/C$, 采用 X—射线衍射、扫描电镜和电化学测试对材料的结构、表面形貌和电化学性能进行了表征. 结果表明, $LiFe_{0.7}Mn_{0.3}PO_4$具有单一的橄榄石结构。碳的加入有效地改变了 $LiFe_{0.7}Mn_{0.3}PO_4$ 的表面形貌。$LiFe_{0.7}Mn_{0.3}PO_4/C$的平均粒度在 100—200nm, 碳均匀地分布在 $LiFe_{0.7}Mn_{0.3}PO_4$的表面。与 $LiFe_{0.7}Mn_{0.3}PO_4$ 相比, $LiFe_{0.7}Mn_{0.3}PO_4/C$具有更高的可逆容量和更好的循环性能以及优秀的倍率性能: 0.1C时 $LiFe_{0.7}Mn_{0.3}PO_4/C$ 的可逆容量达到 141$mAh \cdot g^{-1}$, 60次循环后平均每周的容量损失只有 0.19%, 而 $LiFe_{0.7}Mn_{0.3}PO_4$平均每周的容量损失只有 0.53%, 表明碳的加入有效地改善了 $LiFe_{0.7}Mn_{0.3}PO_4$ 的电化学性能。

关键词: 磷酸铁锂; 锂离子电池; 碳; 掺杂

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