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论文

单斜层状$LiMn_{0.97}Al_{0.03}O_{2-x}(PO_4)_x$材料的合成及其电化学性能

粟智[1], 徐茂文[1], 叶世海[2], 王永龙[2]

1. 新疆师范大学生命科学与化学学院, 乌鲁木齐 830054;
2. 南开大学化学学院, 新能源材料化学研究所, 天津 300071

摘要:

以Na_2CO_3, $(CH_3CO_2)_2Mn·4H_2O$, Al_2O_3, $Na_3PO_4·12H_2O$和$CH_3COOLi·2H_2O$为原料, 通过2次高温固相法和一步水热离子交换法得到一系列铝和磷掺杂的$LiMn_{0.97}Al_{0.03}O_2$, $LiMnO_{1.99}(PO_4)_{0.01}$和$LiMn_{0.97}Al_{0.03}O_{2-x}(PO_4)_x$($x$=0.01, 0.03, 0.05)化合物. 用X射线衍射(XRD)表征了前驱体及交换产物的晶体结构, 用扫描电镜(SEM)测定了晶体的形貌. 通过X射线光电子能谱(XPS)、傅里叶红外光谱及恒电流充放电测试, 研究了掺杂离子对合成材料结构及电化学性能的影响. 研究结果表明, Al-PO_4复合掺杂综合了Al^{3+}掺杂提高材料的电化学反应活性和减低材料的电化学反应阻抗以及PO_4^{3-}掺杂增大材料的晶胞体积的特点, 提高材料中Li^+的扩散能力, 有效地抑制了材料由于Jahn-Teller效应引起的结构畸变, 改性后的$LiMnO_2$正极材料既保持了较高的容量又获得了良好的电化学循环性能.

关键词: 单斜层状LiMnO2; 正极材料; 复合掺杂; 水热离子交换; 电化学性能

Synthesis and Electrochemical Properties of Monoclinic Layered Structure $LiMn_{0.97}Al_{0.03}O_{2-x}(PO_4)_x$ Materials

SU Zhi[1*], XU Mao-Wen[1], YE Shi-Hai[2], WANG Yong-Long[2]

1. College of Life and Chemistry Science, Xinjiang Normal University, Urumqi 830054, China;
2. Institute of New Energy Material of Chemistry, Chemistry College, Nankai University, Tianjin 300071, China

Abstract:

Layered lithium manganese bronze $LiMn_{0.97}Al_{0.03}O_2$, $LiMnO_{1.99}(PO_4)_{0.01}$ and $LiMn_{0.97}Al_{0.03}O_{2-x}(PO_4)_x$($x$=0.01, 0.03, 0.05) with a monoclinic structure were synthesized by the two-step high temperature solid state reaction and a hydrothermal ion exchange method, using Na_2CO_3, $(CH_3COO)_2Mn·2H_2O$, $Na_3PO_4·12H_2O$ and Al_2O_3 as the starting materials. XRD and SEM were used to characterize the structures and morphology of the precursors and products by the ion exchange reaction. The effect of the doping ions on the structure and the electrochemical performances of the samples was investigated by X-ray photoelectron spectroscopy(XPS), Fourier transform infrared spectroscopy(FTIR), electrochemical impedance spectroscopy(EIS) and chronoamperometry techniques. The results showed the co-doping of Al-PO_4 combined the advantages of the improvement of the electrochemical reactivity and the decrease of the electrode reaction resistance by the Al^{3+} doping, as well as enlarging the unit-cell volume by the PO_4^{3-} doping. It benefits for the Li^+ diffusion in the cathode and the suppression of Jahn-Teller distortion. Comparing the pristine one, the Al-PO_4-co-doped $LiMnO_2$ cathode exhibits higher discharge capacity and better cyclic stability.

Keywords: Monoclinic LiMnO2; Cathode material; Co-doping; Hydrothermal ion-exchange; Electrochemical property

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通讯作者: 粟智, 男, 博士, 教授, 主要从事功能材料物理与化学研究. E-mail: suzhixj@sina.com

作者简介:

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