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$Li_{1.15-x}N_{i0·33}Co_{0.33}Mn_{0.33}O_{2+\delta}$溶胶-凝胶法合成、表征及合成机理

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摘要 以可溶性盐为原料采用溶胶-凝胶法合成了具有六方层状结构的$Li_{1.15-x}N_{i0·33}Co_{0.33}Mn_{0.33}O_{2+\delta}$(LNCMO)固溶体. 用X射线衍射(XRD)、光电子能谱(XPS)、扫描电镜(SEM)、循环伏安(CV)、充放电测试等表征了其结构、形貌、过渡金属元素的离子价态及电化学性能, 结合热重-差热分析(TG-DTA)及变温过程XRD结果分析了合成机理. 950℃样品以0.1mA/cm^{2}的电流密度在2.5～4.5V间首次放电容量为190mAh/g, 循环10次后为180mAh/g, 表明样品具有较好的电化学性能.
前驱物在较低温度下分解即可形成层状LNCMO主相, 高温焙烧不仅可稳定材料的层状结构, 而且能显著提高其结晶性, 固溶体的形成可分为以下三步: (1)前驱物氧化分解的同时生成Li-Ni-Co-Mn-O固溶体; (2)残余的Li_2CO_3分解产生Li_2O; (3)表面的Li_2O逐步扩散到固溶体内部, 形成单相Li-Ni-Co-Mn-O固溶体.

关键词 Li1.15-xNi0.33Co0.33Mn0.33O2+δ 溶胶-凝胶法 反应机理

分类号 TM911

Characterization and Synthesis Reaction Mechanism of $Li_{1.15-x}N_{i0·33}Co_{0.33}Mn_{0.33}O_{2+\delta}$ Cathode for Li-ion Battery

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Abstract The cathode material for lithium batteries $Li_{1.15-x}N_{i0·33}Co_{0.33}Mn_{0.33}O_{2+\delta}$ with good electrochemical properties was synthesized by the sol-gel method. The synthesis mechanism was examined via X-ray diffraction, X-ray photoelectron spectra, scanning electron microscopy, thermogravimetric analysis and difference thermal analysis and cyclic voltammetry. $Li_{1.15-x}N_{i0·33}Co_{0.33}Mn_{0.33}O_{2+\delta}$ exhibited initial specific discharge capacity of 190mAh/g and tenth of 180mAh/g at 2.5～4.5V by current density of 0.1 mA/cm^2. That $Li_{1.15-x}N_{i0·33}Co_{0.33}Mn_{0.33}O_{2+\delta}$ main phase can be obtained as low as 400℃ is attributed to the short distance among lithium, manganese, cobalt and nickel formed in precursor prepared by the citric acid gel process. The crystallinty and layered structure were improved by sintering at high temperature. The solid solution formation could be a three-step process: (1) formation of small particle Li-Ni-Co-Mn-O solid solution main phase at lower temperature; (2) decomposition of residual lithium carbonate; (3) bulk diffusion of lithium oxide from exterior into the bulk of Li-Ni-Co-Mn-O solid solution.

Key words Li1.15-xNi0.33Co0.33Mn0.33O2+δ sol-gel method reaction mechanism

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