掺铬锂锰氧化物的湿化学法合成与性能

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摘要:为了寻求新的合成方法,改善锂锰氧化物的电化学性能,采用湿化学法合成了掺铬尖晶石锂锰氧化物 $LiMn_{2-x}Cr_xO_4$ ($x=0.00, 0.04, 0.08, 0.12$),并通过热重-差热(TG-DTA)、X射线衍射(XRD)、扫描电镜(SEM)与恒电流充放电等测试方法考查了材料的结构、形貌与电化学性能。TG-DTA测试证明:湿化学法所制得的 $LiMn_{2-x}Cr_xO_4$ ($x=0.04$) 前驱体在100~900 ℃之间有一个较大的放热峰,在此温度范围内,前驱体由非晶态向晶态转变。XRD结果表明:合成产物具有尖晶石结构,随掺铬量的增加,样品的晶格常数变小,晶胞体积收缩。SEM观测结果表明:合成材料的颗粒粒度较小,分布均匀,结晶性能良好,掺铬后样品($x=0.04$)的粒径为0.4 μm,大于未掺铬时的0.2 μm。恒电流充放电实验结果表明:随掺铬量的增加,样品的首次放电比容量降低,当掺铬量由 $x=0.00$ 增至 $x=0.12$ 时,初始放电比容量由123.3 mAh/g降至113.6 mAh/g。兼顾比容量与循环性能,以 $LiMn_{1.92}Cr_{0.08}O_4$ 性能最佳。

关键词:掺铬; 尖晶石锂锰氧化物; 湿化学法; 电化学性能

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Synthesis and performance of chromium-doped spinel lithium manganese oxide prepared by wet chemical method

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Abstract: In order to seek a new synthetic method and improve the electrochemical property of lithium manganese oxide, chromium-doped spinel lithium manganese oxides $LiMn_{2-x}Cr_xO_4$ ($x=0.00, 0.04, 0.08, 0.12$) were synthesized by wet chemical method. The structures, morphologies and electrochemical performance of the products were studied by means of modern method, such as thermal gravimetric and differential thermal analysis (TG-DTA), X-ray diffraction (XRD), scanning electron microscope (SEM) and constant current cyclic test. There was a large exothermic peak corresponding to the transition from an amorphous structure to a crystal one within the temperature rang of 100~900 ℃ on the DTA curves of the precursor of $LiMn_{2-x}Cr_xO_4$ ($x=0.04$). The XRD results showed that all the samples had a spinel structure and the lattice parameters decreased with the increasing amount of the chromium-doped. The SEM micrographs of the products revealed that the particle size distribution was narrow and the average grain sizes of $LiMn_2O_4$ and $LiMn_{2-x}Cr_xO_4$ ($x=0.04$) were 0.2 μm and 0.4 μm, respectively. The results of constant current cyclic tests showed that the cyclic performance of the products increased with the amount of chromium-doped, while their initial capacities decreased from 123.3 mAh/g of $LiMn_2O_4$ to 113.6 mAh/g of $LiMn_{2-x}Cr_xO_4$ ($x=0.12$). According to both the special capacity and the cyclic performance, the product with chromium-doped of $x=0.08$ had the optimized performance.

Key words: chromium-doped; spinel lithium manganese oxide; wet chemical method; electrochemical performance

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