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锂离子电池 FeO_x/GNS 负极材料的制备与电
化学性能研究

Preparation and Electrochemical Performances of
 $\text{FeO}_x/\text{graphene}$ Composites as Anode Materials for Lithium
Ion Battery

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摘要

基于转化反应机理的过渡金属氧化物(TMOs)由于具有高的理论容量(≥ 1000 mAh/g)倍受研究者的关注。在众多 TMOs 中,铁氧化物(Fe_3O_4 和 $\alpha\text{-Fe}_2\text{O}_3$)由于低成本,制备工艺简单,无毒且分布广泛等优点,成为新型高容量锂离子电池负极材料的研究热点之一。然而铁氧化物在循环过程中大的体积变化导致颗粒发生粉化碎裂,从集流体上脱落,因此造成循环过程中容量的急剧衰减。本文通过液相法合成具有高分散的 $\text{Fe}_3\text{O}_4/\text{GNS}$ 复合材料,通过溶剂热法合成具有特殊形貌的 $\alpha\text{-Fe}_2\text{O}_3/\text{GNS}$ 复合材料,并研究材料形貌结构与电化学性能之间的关系。主要内容如下:

1. 采用水热法将 Fe_3O_4 与石墨烯进行复合。材料首周放电容量为 1563 mAh/g, 2 A/g 电流密度下容量还有 619 mAh/g。0.5A/g 的电流密度下,容量高达 1108 mAh/g, 100 周循环后,容量还有 838 mAh/g(以纯的 Fe_3O_4 计算其容量)。

2. 以 $\text{Fe}(\text{AC})_3$ 和氧化石墨烯为原料,以乙二醇为溶剂和还原剂,合成 $\text{Fe}_3\text{O}_4/\text{GNS}$ 复合材料。通过引入表面活性剂 PVP,研究材料复合分散情况与电化学性能之间的关系。研究表明:引入 PVP 后得到的样品颗粒大小均一,且在石墨烯表面均匀分散。因此不仅具有好的倍率性能,在 2A/g 的大电流密度下,样品仍保持着 672 mAh/g 的高容量,而且具有好的循环性能,在 0.5A/g 的电流密度下循环 100 周,容量保持率仍高达 100%。

3. 采用溶剂热法合成 $\alpha\text{-Fe}_2\text{O}_3/\text{GNS}$ 复合材料,研究材料形貌与电化学性能之间的关系。研究表明:合成的 $\alpha\text{-Fe}_2\text{O}_3/\text{GNS}$ 纳米球颗粒大小为 70 nm,上面均匀的分布着 4 nm 左右的介孔。这种特殊的 3D 介孔球形貌表现出了优异的电化学性能,0.1 A/g 电流密度下首周容量高达 1442 mAh/g, 50 周循环后,容量稳定在 975 mAh/g。在 10 A/g 的大电流密度下,可逆容量仍高达 473 mA/g。2 A/g 电流密度下循环 250 周,容量保持率高达 92%。

关键词: 负极材料 石墨烯 3D 介孔纳米球 铁氧化物 锂离子电池

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Abstract

Recently, transition metal oxides (TMOs) based on the reaction mechanism of “conversion reaction” have attracted numerous attentions as anodes materials for lithium ion batteries due to their high specific capacity ($\geq 1000\text{mAh/g}$). Among TMOs, iron-based oxides (Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$) were considered as the most promising candidates due to their low cost, resource abundance and environmental friendliness. However, these high-capacity materials were still plagued with a problem of large volume change during cycling, which leads to the breakdown of electrical connection of active materials from current collectors.

In this thesis, highly dispersed $\text{Fe}_3\text{O}_4/\text{GNS}$ nano-composites were synthesized by hydrothermal method and refluxing method while the $\alpha\text{-Fe}_2\text{O}_3/\text{GNS}$ nanocomposites with special nanostructure were prepared via solvothermal method. And the electrochemical performances of as-prepared composites were investigated.

1. Combining the Fe_3O_4 nanoparticles with graphene through hydrothermal method. The nanocomposites showed a high initial reversible capacity of 1563mAh/g at the current density of 0.1A/g . It could also deliver a reversible capacity of 619mAh/g at the current density of 2A/g . At the current density of 0.5A/g , the capacity maintained 838mAh/g up to 100 cycles. All the capacities were based on the mass of pure Fe_3O_4 .
2. $\text{Fe}_3\text{O}_4/\text{GNS}$ nanocomposites were synthesized using $\text{Fe}(\text{AC})_3$ and graphene oxides (GO) as raw materials and ethylene glycol as solvent and reductant. The relation between the dispersion of Fe_3O_4 on the GNS and their electrochemical performances was investigated when using the PVP as surfactant. The results showed that the homogeneous Fe_3O_4 nanoparticles were uniformly and densely dispersed on the surface of the GNS with the presence of PVP. As a result, the as-prepared material exhibited high rates capability (delivering a reversible capacity of 672mAh/g at 2A/g) and excellent cyclic performances (delivering a high capacity of 892mAh/g up to 100

cycles which is almost 100% of the initial capacity).

3. α -Fe₂O₃/GNS nanocomposites were obtained via solvothermal method. The relation between the morphology and electrochemical performances was investigated. The results showed that spherical mesoporous (~3nm) α -Fe₂O₃ particles anchored on the GNS were obtained,. Such a unique 3D mesoporous nanocrystalline structure displayed superior electrochemical performance. The nanocomposites showed a high initial reversible capacity of 1442 mAh/g. It could also deliver a reversible capacity of 473 mAh/g at the high current density of 10 A/g. At the current density of 2 A/g, the capacity retention was still up to 92 % after 250 cycles .

Keywords: anode materials; graphene; 3D mesoporous nanosphere; α -Fe₂O₃/GNS; Fe₃O₄/GNS; lithium ion battery

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