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Research Paper

Ball mill assisted synthesis of $Na_3MnCO_3PO_4$ nanoparticles anchored on reduced graphene oxide for sodium ion battery cathodes

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ABSTRACT

$Na_3MnCO_3PO_4$ (NMCP) particles were synthesized via ball milling of $Mn(NO_3)_2.4H_2O$, $Na_2HPO_4.2H_2O$ and $Na_2CO_3.H_2O$ powders. The particles were anchored onto reduced graphene oxide (rGO) sheets during hydrothermal reduction process under stirring. Materials produced were characterized by x-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), thermogravimetric (TG) measurement and galvanostatic charge/discharge tests. Results showed that dissolution of ball milling products in DI water is an effective method for separation of NMCP from byproducts. Best milling time for production of pure NMCP of minimum particle aggregation was 60 min. After preparing the composite, the needle-like NMCP particles of ~15 nm diameter were anchored onto rGO sheets. As a promising cathode candidate for Na-ion batteries, NMCP and NMCP/rGO electrodes displayed initial capacities of 103 and 141 mAh g^{-1} at C/30 rate with capacity retention of 71% and 81% after 15 cycles, respectively. Improvement of the cycling performance at higher rates attributed mainly to the extremely fine NMCP nanoparticles and their almost uniform distribution on rGO conducting network which resulted in electronic and ionic conductivity enhancement and therefore improved the reversibility of intercalation/deintercalation reactions.

1. Introduction

Considerable interest has been paid to Na-based electrode materials due to the low cost and abundance of sodium resources on the earth. $Na_3MnCO_3PO_4$ (NMCP) has been identified as a potential cathode material for Na-ion batteries (NIBs) since the pioneering work of Chen et al. [1] emerged. This material with a monoclinic crystal structure, has a rarely observed capability of delivering two-electron intercalation reaction per formula in which both Mn^{2+}/Mn^{3+} and Mn^{3+}/Mn^{4+} redox couples could be electrochemically active giving rise to the high theoretical capacity of 191 mAh g^{-1} [2–5].

NMCP has low electronic conductivity which results in its poor electrochemical properties [2]. Different strategies could be exploited for electronic conductivity enhancement of cathode materials including reduction of particle size [6], ion doping [7,8], carbon coating [9,10] and combination of the active material with high conductive carbon materials [11]. Among various carbon allotropes, graphene is a highly conductive material which has been well-thought-out for application in electrodes [12–17]. Since graphene has a very high surface/mass ratio, it can interact with the electrode active materials with a high efficiency. Graphene nanosheets with lower addition fractions, can form a more effective electronic conductive network in comparison with conventional carbon additives such as carbon black and graphite [2,4,18].

Ball milling is a simple and energy efficient way [6,19] of applying kinetic energy to break the chemical bonding. Particle fracturing produces new surfaces to which the dangling bonds chemically attach. Ball milling is, hence, widely used as a mechano-chemical synthesis method for fabrication of unique nanostructures [20] required for battery electrodes. Franger et al. [21] have made a comparison between different $LiFePO_4$ synthesis routes such as solid-state reaction, co-precipitation in aqueous medium, hydrothermal method and mechano-chemical (through ball milling) procedure. They have concluded that the mechano-chemical process is superior to the others in achieving the optimum material with good electrochemical performance. To the best of our knowledge, no report has been published on solid-state synthesis of NMCP particles while hydrothermal synthesis has been adopted by many researchers [1–5].

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