



Remarkable enhancement of the electrode performance of nanocrystalline LiMn_2O_4 via solvothermally-assisted immobilization on reduced graphene oxide nanosheets

Kyung-Yeon Jo^a, Song-Yi Han^a, Jang Mee Lee^a, In Young Kim^a, Sahn Nahm^b, Ji-Won Choi^c, Seong-Ju Hwang^{a,*}

^a Center for Intelligent Nano-Bio Materials (CINBM), Department of Chemistry and Nano Sciences, Ewha Womans University, Seoul 120-750, Republic of Korea

^b Department of Materials Science and Engineering, Korea University, Seoul 136-701, Republic of Korea

^c Electronic Materials Center, KIST, 39-1 Hawolkkok-dong, Seongbuk-gu, Seoul 137-791, Republic of Korea

ARTICLE INFO

Article history:

Received 18 September 2012

Received in revised form 4 January 2013

Accepted 4 January 2013

Available online 10 January 2013

Keywords:

Nanocomposites

Nanoparticles

Graphene

Cathode materials

Lithium secondary batteries

ABSTRACT

A facile solvothermal way to immobilize nanocrystalline LiMn_2O_4 on the surface of graphene nanosheets is developed to improve the functionality of lithium manganate as lithium intercalation electrode. A solvothermal treatment for the colloidal mixture of graphene oxide (GO) nanosheets and LiMn_2O_4 nanocrystals gives rise not only to the reduction of GO to reduced graphene oxide (RGO) but also to the immobilization of lithium manganate nanoparticles on the surface of RGO nanosheets. According to powder X-ray diffraction and electron microscopic analyses, the crystal structure and morphology of spinel lithium manganate remain intact upon the composite formation with the RGO nanosheets. The application of larger aldehyde molecule as a reductant leads to the increase of crystallinity and the lowering of Mn oxidation state for the pristine LiMn_2O_4 and its nanocomposite with the RGO nanosheets. The present LiMn_2O_4 -RGO nanocomposites display promising cathode performances for lithium rechargeable batteries, which are much superior to those of the pristine LiMn_2O_4 nanocrystals. The observed enhancement of electrode performance upon the composite formation with the RGO nanosheets is attributable both to the improvement of the surface ion transport of nanocrystalline lithium manganate and to the increase of electrical conductivity. The present experimental findings demonstrate that the solvothermal treatment with RGO nanosheets provides an effective way of improving the electrochemical activity of nanocrystalline lithium metal oxides.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Many economic and ecological merits of manganese element evoke intense research interest on lithium manganese oxides as alternative electrode materials for lithium secondary batteries [1–11]. Among various polymorphs of lithium manganese oxides, spinel-structured LiMn_2O_4 phase boasts many advantages such as a fast Li^+ diffusion in 3D connected diffusion paths, a high tunability of chemical composition, and facile synthesis [2,11–14]. For the optimization of the electrode performance of this spinel phase, a great deal of researches are carried out with the control of Li/Mn ratio, chemical substitution, surface coating, morphology control, nanostructure formation, composite formation, and so on [2,13–19]. The composite formation with highly conductive carbon species can provide a powerful way of improving the electrochemical performance of electrode materials especially under

high current density condition [20–22]. As an effective support for immobilizing electrode material, graphene, an exfoliated 2D sheet of graphite, attracts prime attention because of its high electrical conductivity and its unique 2D morphology providing many surface sites for the anchoring of metal oxide crystals [23–26]. Since the graphene is synthesized in the form of the colloidal suspension of reduced graphene oxide (RGO) nanosheets via the chemical reduction of precursor graphene oxide (GO) [27–29], most of metal oxide-graphene nanocomposites are prepared by the crystal growth of metal oxide crystals on the surface of RGO nanosheets [30,31]. Such a direct crystal growth method is not readily applicable for multicomponent metal oxides like LiMn_2O_4 . Alternatively, the presence of many hydrophilic functional groups on the surface of GO nanosheets would render an anchoring of presynthesized lithium metal oxide on the surface of GO nanosheet a useful method to prepare lithium metal oxide-graphene nanocomposites.

In the present study, the LiMn_2O_4 -RGO nanocomposites are synthesized by the solvothermal treatment of the precursor LiMn_2O_4 spinel oxides with aqueous/ethanolic GO suspension.

* Corresponding author. Tel.: +82 2 3277 4370; fax: +82 2 3277 3419.
E-mail address: hwangsj@ewha.ac.kr (S.-J. Hwang).

The structural, morphological, and bonding characteristics of the resulting nanocomposites are investigated with the combination of diffraction, microscopic, and spectroscopic tools. The evolution of the electrode performance of lithium manganate nanocrystals upon the composition formation with RGO is also examined.

2. Experimental

2.1. Synthesis

The cubic spinel LiMn_2O_4 nanocrystals were prepared by hydrothermal reaction of KMnO_4 and LiOH in the presence of reductant organic molecule, i.e. formaldehyde or isobutyraldehyde, at 200°C for 3 h in Teflon-lined 100 mL hydrothermal vessel [32,33]. The resulting powdery materials were thoroughly washed with distilled water. The molar ratio of KMnO_4 /organic reductant was adjusted to unity commonly for both the aldehydes. The obtained LiMn_2O_4 materials prepared with formaldehyde and isobutyraldehyde were denoted as **LMOF** and **LMOB**, respectively. The nanocomposites of LiMn_2O_4 -RGO were synthesized by the solvothermal treatment for the colloidal mixture of 0.3 g of lithium manganate nanocrystals and 60 mL of water:ethanol (2:1 in mole ratio)-based GO suspension at 120°C for 3 h in the 100 mL-hydrothermal vessel. The molar ratio of RGO/ LiMn_2O_4 was fixed to 5%. After the solvothermal reaction, the reaction vessel was cooled to room temperature. The obtained powders were washed thoroughly with distilled water and dried in oven. During the hydrothermal treatment, GO was reduced to RGO via a redox reaction with ethanol solvent. The nanocomposite materials prepared with the pristine **LMOF** and **LMOB** were denoted as **LMOFG** and **LMOBG**, respectively.

2.2. Characterization

The crystal structures of the precursor LiMn_2O_4 nanocrystals and their nanocomposites with RGO nanosheets were examined with powder X-ray diffractometer (XRD, Rigaku, $\lambda = 1.5418 \text{ \AA}$, 298 K). The crystallite morphologies and chemical compositions of these materials were probed using field emission-scanning electron microscopy (FE-SEM, Jeol JSM-6700F) with an energy-dispersive X-ray spectrometer (EDS). The composite structure of the present nanocomposite materials was probed with high resolution-transmission electron microscopy (HR-TEM, Jeol JEM-2100F microscope, 200 kV). The cation composition of the present materials and their Mn solubility in electrolyte solution were determined with inductively coupled plasma spectrometry (ICP) analysis. X-ray absorption spectroscopy (XAS) experiments were carried out with the extended X-ray absorption fine structure (EXAFS) facility installed at the beam line 7C at the Pohang Accelerator Laboratory (PAL) in Korea. XAS data were collected at room temperature in a transmission mode using gas-ionization detectors. All the present spectra were calibrated by simultaneously measuring the spectrum of manganese metal foil. The data analysis for the experimental spectra was performed by the standard procedure reported previously [34]. Micro-Raman spectra were obtained in a backscattering mode with JY LabRam HR spectrometer. An Ar laser with a wavelength of 514.5 nm was used as an excitation source. X-ray photoelectron spectroscopy (XPS) data were collected with a PHI 5100 Perkin-Elmer spectrometer that adopted a twin source of X-ray beams. The resulting wide spreading of the X-ray beam led to the minimization of the charging effect. All the present XPS data were obtained with a thin layer of the sample loaded on highly conductive copper foil, resulting in the suppression of charge accumulation.

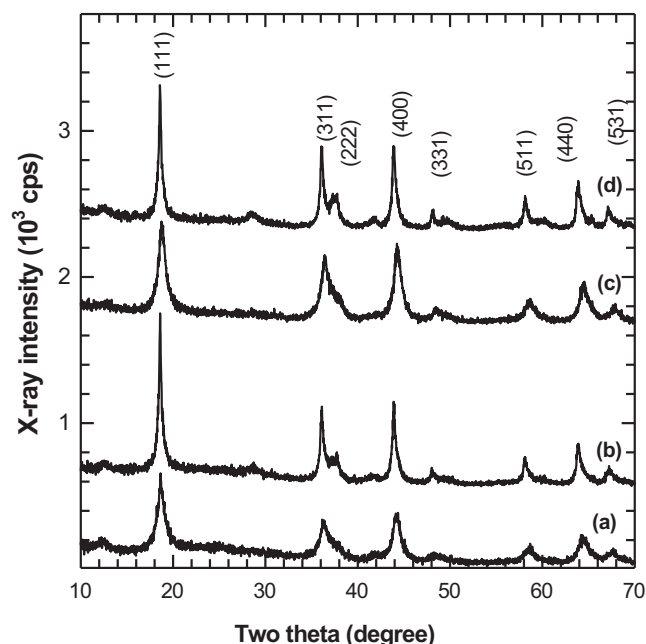


Fig. 1. Powder XRD patterns of the pristine spinel LiMn_2O_4 nanocrystals of (a) **LMOF** and (b) **LMOB**, and their nanocomposites with RGO nanosheets of (c) **LMOFG** and (d) **LMOBG**.

2.3. Electrode performance analysis

The electrochemical measurements were performed with the cell of $\text{Li}/1\text{M LiPF}_6$ in ethylene carbonate (EC):diethyl carbonate (DEC) (50:50, v/v)/composite cathode, which was assembled in Ar-filled glove box. Since this 2016 coin-type cell had two-electrode configuration, the lithium metal acted as both counter and reference electrodes. The composite cathode was prepared by mixing thoroughly active electrode material with super *P* conductor and polyvinylidene fluoride (PVDF) binder in the ratio of 80:10:10. The load of active material in the composite electrode was $\sim 1.2\text{--}1.4 \text{ mg cm}^{-2}$. All the experiments were carried out in a galvanostatic mode with a WonA Tech multichannel galvanostat/potentiostat. The measurements were performed in the voltage range of 3.5–4.3 V at current density of 0.1 C–2 C. Electrochemical impedance spectroscopy (EIS) data were collected with IVIUM impedance analyzer with the frequency region of $0.1\text{--}10^5 \text{ Hz}$.

3. Results and discussion

3.1. Powder XRD analysis

The effect of the molecular weight of reductant aldehyde molecules on the crystal structures of the pristine LiMn_2O_4 nanocrystals is examined with powder XRD analysis, together with the evolution of their crystal structures upon the composite formation with RGO nanosheets. Fig. 1 represents the powder XRD patterns of the pristine **LMOF** and **LMOB** nanocrystals and their nanocomposites with RGO nanosheets (**LMOFG** and **LMOBG**). Both the pristine lithium manganese oxides display typical XRD patterns of cubic spinel LiMn_2O_4 phase [12,13]. In comparison with the **LMOF** material, the **LMOB** one exhibits stronger intensity of XRD peaks with narrower peak width, indicating the higher crystallinity and larger particle size of the latter material than the former one. This observation can be understood from the fact that a larger isobutyraldehyde molecule is more slowly oxidized by MnO_4^- ions than a smaller formaldehyde one, leading to the

Download English Version:

<https://daneshyari.com/en/article/6618187>

Download Persian Version:

<https://daneshyari.com/article/6618187>

[Daneshyari.com](https://daneshyari.com)