Lithium-rich layered oxide nanoplate/carbon nanofiber composites exhibiting extremely large reversible lithium storage capacity

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ABSTRACT

Novel $0.7Li_2MnO_3$–$0.3LiMO_2$ (LMO, M = Co, Ni, and Mn) nanoplates were successfully synthesized on a carbon nanofiber (CNF) matrix using our original ultracentrifugation material processing method (UC treatment). The 2D dimension-controlled LMO nanoplates with a length of 100 nm on a side and a thickness of 5–10 nm coexist with CNF in the as-prepared composite owing to the application of an ultrahigh centrifugal force of 75,000G in combination with the hydrothermal method. This first-reported LMO nanoplate/CNF (70/30 by weight) composite exhibited an extremely large reversible capacity at 0.1 C of 326 mA h g^{-1}, which is close to its theoretical value (327 mA h g^{-1}). This high capacity is due to the hyper dispersed and highly crystalline LMO nanoplates entangled within the CNF matrix. The prepared LMO nanoplates are covered with a thin unidentified layer (2–5 nm in thickness). The composite shows a high capacity of ca. 240 mA h g^{-1} at 1 C as well as stable cycle performance, maintaining 70% of its initial capacity over 100 cycles.

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1. Introduction

There have been a large number of research studies on cathode materials for lithium ion batteries. So far, the conventional cathode material is LiCoO$_2$ [1], which is responsible for half of the total cost and weight of lithium ion batteries. While other materials based on lithium metal oxides such as LiMn$_2$O$_4$, LiFePO$_4$, and LiCo$_{1/3}$Mn$_{1/3}$Ni$_{1/3}$O$_2$ have been proposed and extensively investigated, these materials show capacities of less than 200 mA h g^{-1}. Recently, a new concept for the cathode material has been proposed. Solid solution materials of the form xLi$_2$MnO$_3$–$(1-x)$LiMO$_2$ (LMO, M = Co, Ni, Mn, etc., 0 < x < 1), first reported by Lu and Dahn [2,3] and then investigated by Amine and Thackeray's Argonne national laboratory groups and others, are combinations of the saturated-valence rock salt Li$_2$MnO$_3$ and electrochemically active layered LiMO$_2$. These interesting materials have attractive features such as large discharge capacities of >230 mA h g^{-1} and high operating potentials of >3.5 V vs. Li/Li$^+$ on average, although they require

electrochemical activation at 4.5–4.6 V vs. Li/Li$^+$ during the first charge [2–4]. However, there are several drawbacks of these materials, including (i) crystallographic instability due to the initial activation process followed by oxygen release, (ii) the existence of thermodynamically unstable manganese ions (Mn^{3+}) during discharge, (iii) low electrical conductivity (4.07×10^{-5} S cm^{-1}), (iv) a complicated reaction mechanism that has not yet been fully defined, and (v) limited choice of preparation procedures due to the oxidation that occurs under air at high temperature.

So far, many studies on overcoming these problems with LMO have been reported. One of the proposed solutions is surface treatment of LMO particles in order to stabilize the surface and prevent the dissolution of the released oxygen atoms after the activation process. As reported by Li et al. [5], an AlF$_3$ thin film of 5–7 nm in thickness coated on the particles (≈ 100 nm) suppresses excess Li extraction and oxygen release, yielding a stable capacity of 232 mA h g^{-1} at 0.2 C over 50 cycles. To further improve the rate capability, downsizing the microparticles into nanoparticles is an effective approach. Zheng et al. [6] reported LMO nanoparticles with diameters of 100–200 nm prepared using a sucrose combustion method, which showed a discharge capacity of 172 mA h g^{-1} at 900 mA g^{-1}. However, the prepared nanoparticles had agglomerated, so their initial capacity of 275 mA h g^{-1} was far below the

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theoretical capacity because of the low particle utilization ratio. In order to disaggregate the nanoparticles and overcome the low electronic conductivity of the material, forming a composite of LMO and conductive carbon is the easiest solution. However, to our best knowledge, such a carbon composite has never been reported so far, because the preparation of this material would generally require calcination under air above 700 °C, whereas the carbon can combust under air above 400 °C. Therefore, in order to overcome the poor rate capability, poor cyclability, and low initial discharge capacity of LMO nanoparticles, in this study, a novel nanocrystalline LMO composite with carbon nanofiber (CNF) was prepared using a unique mechanochemical reaction technique under an ultrahigh centrifugal force field (75,000G), followed by a hydrothermal (HT) treatment [7]. This so-called UC-method enables the *in situ* production of a hyperdispersed LMO precursor on the CNF surface, and the subsequent HT treatment facilitates the growth of highly crystalline LMO without combusting the carbon matrix [8–10]. In 2010, we prepared a nc-$Li_4Ti_5O_{12}$/carbon nanofiber (LTO/CNF) composite exhibiting ultrafast lithium insertion by UC treatment [8]. Of particular interest is that the method produced nanoscale LTO crystals with a unique 2D-nanosheet-like morphology entangled within various carbon matrices with a high surface area [9,10]. Moreover, UC treatment is superior to other methods in terms of mass production and manufacturing cost. Here we have adopted this UC method to prepare a novel material consisting of nano-LMO hybridized with CNF. The UC method

simultaneously induces both the formation of the nano-LMO precursors and their anchoring and grafting onto the functional groups of the CNF. The HT method is then used to induce a high degree of crystallization of the LMO below the temperature where CNF oxidation decomposition starts. The coexistence of the CNF promotes the dimension-controlled crystal growth of highly dispersed LMO owing to the layer-by-layer synthesis, and very thin LMO nanoplates are thus achieved. In this paper, we present the first-reported data on this unique LMO nanoplate/CNF composite as a cathode material for lithium ion batteries.

2. Experimental

2.1. Preparation of the LMO/CNF composite

All chemical compounds were purchased from Wako Pure Chemicals Industries Ltd., except CNF received from Mitsubishi Material Corporation [11]. First, 0.715 g of manganese dichloride tetrahydrate [$MnCl_2\cdot4H_2O$], 0.11 g of nickel dichloride tetrahydrate [$NiCl_2\cdot4H_2O$], and 0.11 g of cobalt dichloride tetrahydrate [$CoCl_2\cdot4H_2O$] were dissolved into 25.0 ml of deionized water. Then, 0.214 g of CNF was added into the solution, which was subjected to ultracentrifugation (UC). The weights for the dosed manganese acetate and CNF have been adjusted so as to sustain a stoichiometric ratio of LMO/CNF of 70/30. During UC, mechanochemical agitation under 75,000G was applied for 1 min to the solution. Next, 5 ml of 7.35 M NaOH (aq.) was added, and a second UC treatment was performed under hyperagitation for 5 min, resulting in a LMO/CNF composite precursor in which the nanoscale LMO precursors hyperdispersed in the carbon matrix all form simultaneously. Subsequently the UC-treated precursor was subjected to hydrothermal reaction with addition of 9 ml of LiOH aq. (3 M) and 0.6 g of $KClO_3$ at 220 °C for 3 h. After drying, a LMO/CNF composite powder was obtained.
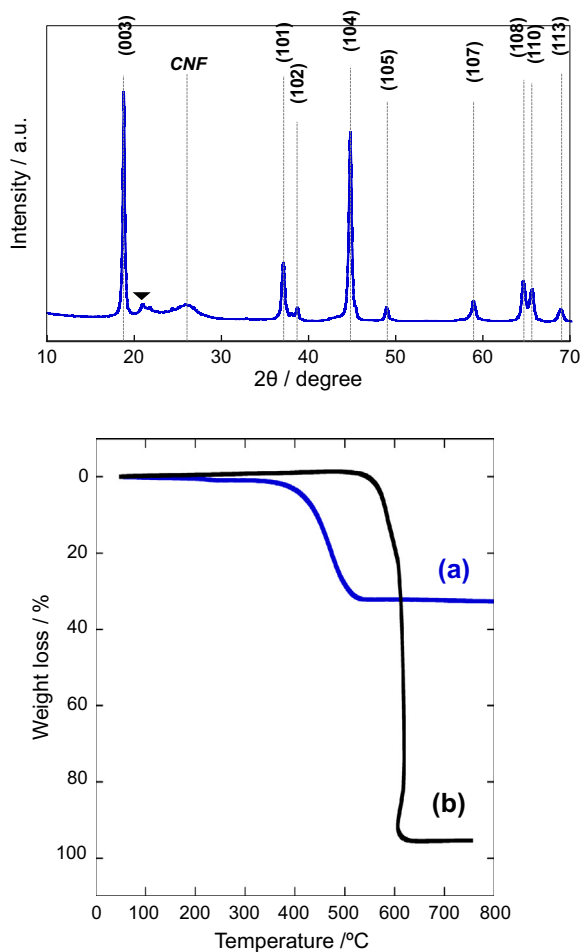
Fig. 1. XRD and TG measurements of a UC-treated $0.7Li_2MnO_3$–$0.3LiNi_{0.3}Co_{0.3}Mn_{0.3}O_2$/CNF composite with a mass ratio of 70/30 and pristine CNF. The XRD measurement was performed at a sweep rate of $0.02°\ min^{-1}$ from 10° to 70°. The TG measurement was performed at a sweep rate of $5\ °C\ min^{-1}$ from ambient temperature to 800 °C under a synthetic air atmosphere.
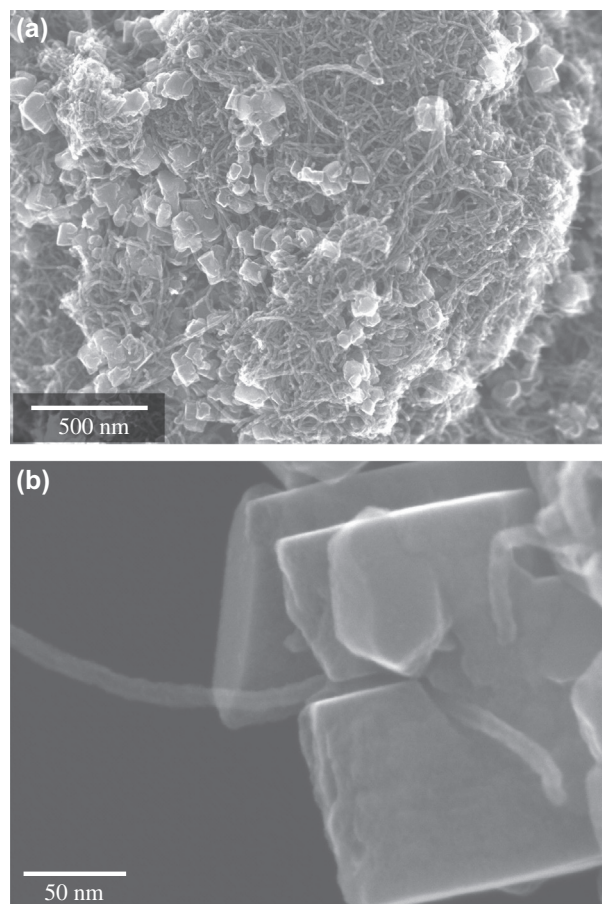
Fig. 2. Low-magnification (top) and high-magnification (bottom) SEM images of UC-treated $0.7Li_2MnO_3$–$0.3LiNi_{0.3}Co_{0.3}Mn_{0.3}O_2$ (LMO)/CNF composites. The UC-treated LMO nanoparticles are hyper dispersed and entangled within the CNF matrix (top). Each LMO particle is a nanoplate and entwined with CNF tubes (bottom).