



The beneficial effect of nanocrystalline and amorphous nature on the anode performance of manganese oxide for lithium ion batteries



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ABSTRACT

The effect of the amorphous structure and nanocrystalline nature of metal oxide on its anode performance in lithium ion batteries is investigated with two nanocrystalline and one well-crystallized layered manganese oxides. X-ray amorphous manganese oxide nanocrystals are synthesized by soft-chemical redox reactions using reducing agents of KBH_4 and LiI at room temperature, whereas well-crystallized layered manganese oxide is obtained by solid state reaction at elevated temperature. Although both of the amorphous manganese oxides lack a long-range structural order, they are crystallized with a layered MnO_2 -type local structure, which is nearly identical to the crystal structure of the well-crystallized $\text{K}_{0.45}\text{MnO}_2$. In comparison with the well-crystallized $\text{K}_{0.45}\text{MnO}_2$, both the amorphous manganese oxides commonly possess smaller particle sizes with larger surface areas and better homogeneity of composite structure. The amorphous manganese oxide nanocrystals show better anode performance with greater discharge capacity for lithium ion batteries than does the well-crystallized $\text{K}_{0.45}\text{MnO}_2$, which is attributable to the greater surface area, higher structural and electrochemical stability, more homogeneous composite structure, and better charge-transfer characteristics of the amorphous materials. This result highlights the merit of the nanocrystalline and amorphous nature for optimizing the electrode performance of manganese oxide. The present solution-based redox reaction can provide a facile, economic, and scalable route for synthesizing efficient manganese-based anode materials for lithium ion batteries.

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1. Introduction

Over the past decades, manganese oxides have attracted a great deal of research interest as alternative electrode materials for lithium ion batteries because of their cheap price, rich abundance, and environmentally benign nature [1–9]. Since manganese oxides possess various crystal structures with diverse oxidation states of manganese ions [10,11], these materials can accommodate lithium ions at various potentials. This renders manganese oxides promising electrode materials for lithium ion batteries [11,12]. Among many Mn-based oxides, spinel-structured LiMn_2O_4 and layered LiMnO_2 have been intensively studied as cathode materials [13–16], because the redox couple of $\text{Mn}^{3+}/\text{Mn}^{4+}$ in these materials possesses a high redox potential of near 4 V vs. Li^+/Li . Alternatively many attempts are made to apply manganese oxides as anode materials for lithium ion batteries [17–22], since conversion reactions between manganese oxide and lithium ions occur at a quite low potential of < 1 V vs. Li^+/Li . Taking into account the fact

that the surface adsorption of lithium ions and the subsequent conversion reaction only slightly change the chemical potential of the electrode material, nanostructured manganese oxides with expanded surface area are supposed to accommodate lithium ions at low working potential in terms of conversion and adsorption mechanisms. Many types of nanostructured manganese oxides such as MnO , Mn_3O_4 , Mn_2O_3 , and $\alpha\text{-MnO}_2$ have been investigated as anode materials for lithium ion batteries [12,17–22]. Most of this research on the anode application of manganese oxides has been devoted to well-crystallized materials [23,24], although poorly-crystallized amorphous materials are expected to show better cyclability, because their amorphous structure with short structural coherence length is fairly tolerable for the repeated Li insertion–extraction process [25]. Even though these materials possess distinct structural order in short distance, the absence of long-distance structural order suppresses their Bragg reflections in X-ray diffraction (XRD) pattern, that is, they are X-ray amorphous materials. In addition, X-ray amorphous nanocrystals with expanded surface area promise to deliver large discharge capacity through the provision of many surface sites for the adsorption of lithium ions. For synthesis, amorphous manganese oxides possess

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economic and ecological advantages over well-crystallized materials usually prepared at elevated temperature, since they can be prepared by a solution-based reaction at low temperature ($< 100^\circ\text{C}$) [26,27]. However, no systematic study has investigated the application of amorphous nanocrystalline manganese oxides as anode materials for lithium ion batteries or the effects of nanocrystallinity and amorphous nature on the electrode performance of manganese oxide.

In the present work, X-ray amorphous nanocrystalline manganese oxides are synthesized by a soft-chemical redox reaction of KMnO_4 with KBH_4 [28] or LiI at room temperature whereas a well-crystallized homologue is prepared by conventional solid state reaction [29]. The local crystal structure, chemical bonding nature, and crystal morphology of the obtained X-ray amorphous and well-crystallized manganese oxides are studied with diffraction, spectroscopic, and microscopic tools. Charge–discharge cycling tests are carried out for these manganese oxides to probe the effect of X-ray amorphous nanocrystalline nature on the anode performance of manganese oxide for lithium ion batteries. The effects of electrochemical cycling on the crystal structure and charge-transfer characteristics are investigated with powder XRD and electrochemical impedance spectroscopy (EIS) for the electrochemically cycled derivatives.

2. Experimental

2.1. Synthesis

X-ray amorphous manganese oxide nanocrystals were prepared by reaction between KMnO_4 and two kinds of reductants, KBH_4 and LiI . These reductants were used for the rapid and complete reduction of KMnO_4 precursor, as reported previously [27,28,30]. Another merit of using these reductants is the fine-control of the crystal structure of the obtained amorphous materials via the change of reductant concentration and reaction time [28]. First, 0.1 M aqueous KBH_4 solution was prepared by dissolving KBH_4 powder in 0.01 M KOH solution to prevent the hydrolysis of borohydride. The reductant KBH_4 solution or LiI powder was slowly added into 50 mL of aqueous KMnO_4 solution. The molar ratio of reductant/ KMnO_4 was adjusted to 1. Under mild stirring, the reaction proceeded at room temperature for 2 h. The resulting powdery materials were separated by centrifugation, washed with distilled water, and dried at 180°C under vacuum for the complete removal of water in the electrode materials, since the presence of water has detrimental effect on the electrode performance of the materials through the formation of corrosive HF species. The materials obtained with the reductant KBH_4 and LiI were denoted as **AM-1** and **AM-2**, respectively. For comparison, well-crystallized layered $\text{K}_{0.45}\text{MnO}_2$ was synthesized by solid state reaction using K_2CO_3 and Mn_2O_3 precursors. The sintering process was carried out at 750°C in an O_2 flow for 30 h with intermittent grinding [29].

2.2. Characterization

The crystal structures of the as-prepared manganese oxides and their electrochemically cycled derivatives were examined with powder XRD (Rigaku, $\lambda = 1.5418 \text{ \AA}$, 25°C). The crystal morphology and structure of the present materials were characterized with field emission-scanning electron microscopy (FE-SEM) analysis using a Jeol JSM-6700F electron microscope and transmission electron microscopy (TEM) using a Jeol JEM-2100F electron microscope working at the electrical potential of 200 kV. The composite structures of the present materials were examined by measuring the spatial variation of micro-Raman spectra. The present micro-Raman spectra were measured with micro-Raman spectrometer (Horiba Jobin-Yvon LabRam Aramis), in which the

514 nm line of an Ar^+ laser was used as excitation source. The Raman scanning analysis was carried out for the selected area of $10 \mu\text{m} \times 10 \mu\text{m}$ with the step size of $0.5 \mu\text{m}$. The X-ray absorption near-edge structure (XANES) spectra of the materials under investigation were measured at Mn K-edge and I L_1 -edge with the extended X-ray absorption fine structure (EXAFS) facility installed at beam line 10C at the Pohang Accelerator Laboratory (PAL, Pohang, Korea, 2.5 GeV, and 180 mA). All the XANES data were collected in a transmission mode from the thin layer of powder samples deposited on transparent adhesive tapes using gas-ionization detectors. The measurements were carried out at room temperature with a $\text{Si}(111)$ single crystal monochromator. All the spectra were carefully calibrated by measuring Mn metal foil or KIO_3 simultaneously. The data analysis for the experimental spectra was performed by the standard procedure reported previously [24,31].

2.3. Electrode performance analysis

The anode performance of the obtained manganese oxides was examined by performing galvanostatic charge–discharge cycles. The electrochemical cycling test was done with the button-type half-cell of $\text{Li}/1 \text{ M LiPF}_6$ in ethylene carbonate (EC):diethyl carbonate (DEC) (50:50 v/v)/active material. For preparing the composite electrode, the active material (70%) was thoroughly mixed with Super P (20%) and PVDF (10%) in N-methyl-2-pyrrolidinone (NMP). The resulting slurry was deposited on Cu-foil with the doctor-blade method and dried at 100°C for 3 h. The resulting composite electrode was roll-pressed and cut into disks. The counter lithium electrode and composite electrode were assembled into a 2016 coin-type cell in Ar-filled glove box. The electrolyte of 1 M LiPF_6 solution in EC:DEC (50:50 v/v) was used. All the electrochemical experiments were performed in a galvanostatic mode with a Maccor multichannel battery cycler in the voltage range of 0.01–3.0 V with 100 mA g^{-1} or several current densities. Cyclic voltammetry (CV) measurements were carried out with a Maccor multichannel battery cycler for the electrode materials subjected to the 30th and 50th electrochemical cycling performed at the current density of 200 mA g^{-1} . A scan rate of 0.5 mV s^{-1} was applied for the present CV measurement. The evolutions of the charge-transfer characteristics of the three materials upon the electrochemical cycling were examined by performing EIS analysis using an IVIUM impedance analyzer in the frequency region of $0.01\text{--}10^5 \text{ Hz}$.

3. Results and discussion

3.1. Powder XRD analysis

The crystal structures of the three manganese oxides are examined with powder XRD analysis. Fig. 1 presents the powder XRD patterns of nanocrystalline manganese oxides of **AM-1** and **AM-2**, as compared with that of well-crystallized $\text{K}_{0.45}\text{MnO}_2$. While $\text{K}_{0.45}\text{MnO}_2$ shows well-developed Bragg reflections of layered MnO_2 phase, neither of the nanocrystalline materials (**AM-1** and **AM-2**) exhibits any well-defined XRD peaks, clearly demonstrating the X-ray amorphous nature of these materials. The X-ray amorphous nature of these materials originates from their soft-chemical synthesis route performed at room temperature, in which insufficient thermal energy is provided for the ordering of component ions to construct well-crystallized lattice.

3.2. EXAFS and XANES analyses

Although nanocrystalline **AM-1** and **AM-2** are X-ray amorphous due to the lack of long-range structural order, they still possess

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