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Electrochemically deposited nanowires of manganese oxide as an anode material for lithium-ion batteries

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Abstract

Nanowires of manganese oxide are electrochemically synthesized on nickel substrate by manganous acetate solution at room temperature without any template or catalyst. The synthesized electrode of high porosity is composed of 8–12 nm nanowires after 300 °C annealing. These manganese oxide nanowires show low crystallization. The synthesized anode material has a much higher capacity than the traditional graphite materials for lithium storage. The electrode's reversible capacity reaches 1160 mAh g^{-1} at the first cycle; the specific capacity retention after 50 charge–discharge cycles remains 61% of its initial capacity. During cyclic voltammetric measurements, the linear relationship between peak current and square root of the scan rate suggests that the reaction is controlled by a semi-infinite diffusion of lithium. The diffusion coefficient of lithium in the synthesized manganese oxide is estimated to be in the order of 10–13 $cm^2\ s^{-1}$.

Keywords: Manganese oxide; Lithium storage; Anode material; Diffusion coefficient; Lithium-ion batteries

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1. Introduction

Lithium-ion battery materials of high specific capacity and high rate dischargeability have attracted great attention. Graphite materials are currently the dominating anode materials because graphite offers high capacity, high safety, high electronic conductivity and low electrochemical potential with respect to lithium metal [1]. Nevertheless, graphite materials can hardly meet the high-energy-density demand of the electronic devices today; therefore researches on alternative anodes of higher lithium storage capacities continue.

Transition-metal oxides have attracted attention due by their advantageously high capacities [2–10]. Poizot et al. proposed new anode materials, the nanosized transition-metal oxides, for lithium-ion batteries [2,3]. Electrodes made of nanoparticles of transition-metal oxides (MO, where M is Co, Ni, Cu or Fe) demonstrate high electrochemical capacities (about 700 mAh g^{-1}), great capacity retention, and high discharging rates. More importantly, the mechanism of Li reactivity in such electrodes differs from the classical Li insertion/deinsertion in graphite anodes or Li-alloying processes in alloy electrodes [2]. The mechanism involves the formation and decomposition of Li_2O, accompanying the reduction and oxidation of metal nanoparticles, respectively [2].

Wang et al. reported that the nickel oxide showed a high reversible capacity similar to that of anode materials (transition-metal oxides) for lithium-ion batteries [4,5]. The nanocrystalline NiO thin-film electrode prepared by pulsed laser ablation showed a reversible capacity of 700 mAh g^{-1} in the range of 0.01–3.0 V vs. Li/Li^+[4]. A high capacity retention up to 100 cycles may be achieved by optimizing the NiO films [4]. Improved specific capacity, discharge rate, and cycling performance of the NiO thin-film electrode have all been attributed to its nanosized characteristics [4]. Wang et al. reported that cobalt oxides (Co_3O_4)

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synthesized by chemical decomposition of cobalt octacarbonyl in toluene at low temperature is nanosized and demonstrates a stable reversible lithium storage capacity of 360 mAh g^{-1} within 30 cycles [6]. On the other hand, a much higher capacity of nanoCo_3O_4 electrode was found to be approximately 700 mAh g^{-1} [7]. Morales et al. reported an excellent method in obtaining Cu_2O films for lithium-ion batteries; also indicating that for films of the same thickness, the discharge capacity increased with a decrease in particle size [8]. Gao et al. showed that the fine and polycrystalline CuO nanorods as anode material for lithium-ion battery exhibit a high electrochemical capacity of 766 mAh g^{-1} compared to 416 mAh g^{-1} for the nanorods with single crystalline structure due to their large surface area and numerous structural defects [9].

Therefore, the particle size of anode materials has a crucial effect on the electrochemical behavior of these transition-metal oxides toward lithium, i.e. nanosized transition-metal oxides play an important role in facilitating the reduction and oxidation between Li_2O and metal nanoparticle during charging/discharging. Therefore, synthesis of nanosized anode materials has become important. Until now, nanosized manganese oxide material has rarely been reported as an anode material for rechargeable lithium-ion batteries. In this work, we synthesized the nanowires of manganese oxide electrochemically as a new anode material without any template or catalyst, in which the production cost is low and fabrication is easy.

2. Experimental

Nanostructured manganese oxide electrodes were deposited onto nickel foils (1×1 cm^2) by applying a current density of 0.25 mA cm^{-2} in a solution bath of 0.1 M manganous acetate and 0.1 M sodium sulfate for 10 min at room temperature [11–13]. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum foil with dimension 2×2 cm^2 was used as the counter electrode. The plating solution was stirred continuously by a Teflon stirrer during the entire deposition. After deposition, plated foils were rinsed several times in deionized water and dried at 300 °C for 1 h in air. The amount of deposited manganese oxide was measured by a microbalance.

Surface morphology of the electrochemically deposited electrode was examined with a scanning electron microscope (FE-SEM, JEOL JSM-6500 F) with an accelerating voltage of 10 keV. Nanostructure of the manganese oxide was examined with a transmission electron microscopy (FE-TEM, JEOL JEM-2100 F) with an accelerating voltage of 200 kV. TEM specimen were prepared by the following procedure: nanowires were stripped off and dispersed in anhydrous ethanol with ultrasonic vibration for 5 min, a drop of the supernatant was then transferred onto a standard holey carbon-covered-copper TEM grid. An X-ray photoelectron spectroscopy (XPS, Perkin–Elmer, PHI Quantera SXM) with a focused monochromatic Al Kα radiation (1486.6 eV) was used to analyze the composition of the deposited manganese oxide electrode. Crystal structures of the deposited manganese oxide were identified by X-ray powder diffraction (XRD, Philips PW1700) with a Cu Kα target (wavelength = 1.54056 Å). Samples were stripped from a nickel substrate. Diffraction data were collected for 1 s at each 0.04° step width over 2θ, ranging from 30° to 80°.

Batteries were assembled in a dry room (temperature 25 °C, relative humidity 0.22%). The electrochemical cell comprised a working electrode (manganese oxide electrode), a counter electrode (lithium metal), and a reference electrode (lithium metal). A working electrode wrapped with separator (Celgard 2320, 20 μm in thickness, USA) was placed between two counter electrodes and then inserted into an aluminum-plastic laminated film case. Electrolyte was injected into the case and the case was then sealed off at a reduced pressure of 60 mmHg. The electrolyte was 1 M lithium hexafluorophosphate ($LiPF_6$, Tomiyama Pure Chemical, Japan) in ethylene carbonate /propylene carbonate/diethylene carbonate (EC/PC/DEC = 1/1/2, by volume).

Electrochemical tests were performed on a charge/discharge unit (Maccor model series 4000). Cells were charged at a constant current (85 mA g^{-1}) to a cutoff voltage of 10 mV vs Li/Li^+. Discharge was performed at the same rate to a cutoff voltage of 3.0 V vs Li/Li^+. Cyclic voltammetric (CV) measurements were taken by means of a potentiostat/galvanostat (Schlumberger SI 1286). The voltage was cycled in the range of 0.01–3.0 V vs Li/Li^+, with different scan rates.

3. Results and discussion

According to Preisler, γ-manganese dioxides, which exhibit a marked growth orientation and a fibrous structure as well as cleavability, are deposited on the anodes during electrolysis of manganous salt solutions in sulfate bath [14,15]. As a result, the γ-manganese dioxides are fibrous or wires in nature. Fig. 1a shows the SEM micrograph of a manganese oxide electrode after 300 °C annealing. Electrode is highly porous and is of nanowire structure. Nanowires are 8–12 nm in diameter as shown in Fig. 1b (TEM image). In general, the electrochemically deposited manganese oxide contains structural water in the solid phase of manganese oxide [14]. According to Preisler, only a small percentage of water in electrodeposited manganese dioxide is volatile at 120 °C, and a predominant portion of water is desorbed in a relatively smooth manner up to 350 °C [14]. The electrodeposited manganese oxide decomposes rapidly to form Mn_2O_3 at temperatures beyond 500 °C [16]. The water content within is known to affect the electrochemical reactivity and the thermodynamic stability of various manganese oxide phases, as it causes variations in crystal lattice and consequently in electrical conductivity and electrode potential [17,18]. Moreover, water in the structure creates challenges in lithium