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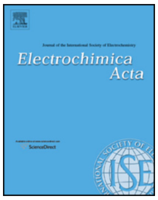

Nanospherical-Like Manganese Monoxide/Reduced Graphene Oxide Composite Synthesized by Electron Beam Radiation as Anode Material for High-Performance Lithium-Ion Batteries

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ABSTRACT

Nanospherical-like manganese monoxide/reduced graphene oxide (MnO/rGO) nanocomposites are synthesized by using an electron beam radiation approach in an aqueous solution containing potassium permanganate and graphene oxide in the presence of acetone as radical scavenger and subsequently calcining in flowing Ar atmosphere. SEM and TEM observations show that nanospherical-like MnO with average size of 20 nm are firmly anchored onto the rGO to form MnO/rGO nanocomposites. The typical MnO/rGO nanocomposite exhibits a high initial reversible capacity (977.1 mAh g^{-1}) at a current density of 150 mA g^{-1} and delivers 648.4 mAh g^{-1} at a rate of 750 mAh g^{-1} with excellent cycling performance (89% of capacity retention over 50 cycles), which indicates that the MnO/rGO nanocomposite is a promising anode candidate for Li-ion batteries. Furthermore, the facile synthetic strategy by using an electron beam radiation provides a novel avenue for making high-performance metal oxide/graphene nanocomposites for energy storage applications.

1. Introduction

Lithium-ion batteries (LIBs) are now extending their territory from portable electronic market to large scale energy storage applications due to their high capacity, long-term cycle life and fast charge–discharge rate [1,2]. With the demand of higher energy-density LIBs, various transition-metal oxides have been widely investigated as the anode materials for lithium-ion batteries due to their higher energy densities based on conversion reactions than intercalation reactions of commercial graphite anode, such as manganese oxides SnO_2, CuO, Fe_2O_3, and so on [3–11]. Among these transition-metal oxides, manganese oxides are proven to be a promising candidate for the new generation of anode materials because of their high storage capacity (MnO: 755 mAh g^{-1}, Mn_3O_4: 936 mAh g^{-1}, Mn_2O_3: 1018 mAh g^{-1}), natural abundance, environmental benignity and low cost [12,13].

However, drastic volume change destabilizes the structure of manganese oxides during the phase transformation in the conversion reaction, resulting in poor cycling stability. Besides, the poor electronic conductivity leads to the inferior rate capability [3,14,15]. Recently, many efforts have been made to overcome these challenges. One of the effective strategies is to reduce the particle size of manganese oxides to nanometer scale to accommodate the large volume variation and shorten Li^+ diffusion pathways [15–17]. A large number of nanosize manganese oxide anode materials such as MnO, MnO_2 and Mn_3O_4 have been investigated [18–20]. Another alternative strategy is to disperse manganese oxides into carbon-based matrix which not only improves the electrical conductivity of the composite, but also buffers eventual volume variation and reduce the aggregation of nanoparticles during cycling [3,21–24]. Graphene, carbon nanowires, carbon nanofibers and carbon nanorods have been used to fabricate the manganese oxide-carbon nanocomposite as the anode material [3,23,25–28]. Lin et al. investigated the electrochemical performance of carbon nanofiber-supported MnO_x composites via electrodepositing to give the reversible capacity of 444 mAh g^{-1} at 50 mAh g^{-1} after 50 cycles [27]. Pang et al. showed a Novel MnO_x@Carbon hybrid

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nanowires prepared by hydrothermal process can deliver a reversible capacity of 541 mAh g^{-1} at 100 mAh g^{-1} after 54 cycles [3]. Among these conducting and structure-buffering supporters, graphene has an excellent electrical conductivity, an extremely high specific surface area and superior thermal conductivity, thus, it is an excellent substrate to host active nanomaterials for energy storage applications [26,29]. On the other hand, the addition of electroactive materials in graphene-based composite can in turn hinder re-stacking by lowering the van der Waals forces among the layers and keeping their high active surface area and increasing the lithium storage performance [23,29]. For instance, Mai et al. reported that the MnO/RGOS hybrid electrode have a reversible capacity of 665.5 mAh g^{-1} at 100 mA g^{-1} after 50 cycles which is much better than that of bare MnO electrode [23].

Recently, ionizing radiation has been developed as a new method to prepare various inorganic nanocompounds such as metals, metal oxides, metal sulfides et al. [30–33]. Radiation-induced processes have a number of distinctive advantages compared with common chemical methods, such as: (1) fast production of materials; (2) narrow size distribution of products; (3) no trick control of experimental conditions required [34]. Moreover, ionizing radiation is a highly efficient, facile, cost-efficient and eco-friendly method for the production of reduced graphene oxide [35–37]. Therefore, nanosized metal oxide anchoring on graphene is capable to be prepared by in situ deposition utilizing ionizing radiation.

In this present work, MnO/rGO oxide nanocomposite was synthesized by electron beam radiation in a mixture solution of $KMnO_4$ and graphene oxide, followed by calcination of the precursors in the oven. The MnO/rGO nanocomposites exhibit significantly high Li^+ storage property and superior rate capability compared with the bare MnO nanoparticles.

2. Experimental

2.1. Synthesis of MnO/rGO nanocomposites

All the chemicals are analytical grade and used as purchased without further purification. Graphene oxide (GO) was purchased from Institute of Coal Chemistry (Taiyuan, China). Typically, 200 mg GO was dispersed in 200 ml deionized water by sonication for 60 min to form GO suspension. Then a $KMnO_4$ solution (50 mL, 0.1 mol/L) was added into the GO suspension. 3 mL of acetone was added into the resulting mixture as a radical scavenger followed by sonication for 10 min. After that, the mixture was transferred into a PE package and radiated by an electron beam at doses of 250 kGy (1 Gy = 1 J kg^{-1}) at a dose rate of 50 kGy/pass at room temperature by a 1 MeV electron accelerator (Wasik Associates, USA). The resulting black solid products were washed several times with deionized water and then freeze-drying to prevent reaggregation of graphene. Finally, the precursor was annealed at 450 °C in Ar for 5 h to remove the water and form MnO by reductive reaction with the graphene matrix. For comparison, bare MnO nanopartcle was synthesized by using the similar procedure above, but the GO suspension was replaced by deionized water and the precursor was annealed at 450 °C in H_2/Ar (10% H_2) for 5 h.

2.2. Materials characterizations

The crystal structures of the products were characterized by X-ray diffraction (LabX XRD-6000, Cu Kα radiation) over the range of 10–80°. The content of graphene in composites was determined by thermogravimetric analysis (Thermo analysis instrument Q 500, Burlington) at a heating rate of 10 °C min^{-1} from 30 to 800 °C in air. The morphology and microstructure were characterized by field-emission scanning electron microscope (FE-SEM, ZEISS Merlin Compact VP, Germany) and field emission transmission electron microscopy (JEOL, JEM-2010F, Japan). Raman spectroscopy was performed with a laser micro-Raman spectrometer (Renishaw in Via, Renishaw, 532 nm excitation wavelength). Surface element analysis was conducted by using energy dispersive X-ray spectroscopy (EDS, Oxford Instruments Link ISIS). The BET surface area and pore size distribution were determined by using Micromeritics ASAP 2020 at liquid N_2 temperature.

2.3. Electrochemical characterization

Electrochemical tests were conducted by using CR2016 type coin cells with Li foil as the counter electrode. The working electrodes were consisted of 80 wt% active material (MnO or MnO/rGO), 10 wt% poly(vinylidene fluoride) (PVDF) and 10 wt.% super P. The loading of the active material in the electrode is about 1.5 mg cm^{-2}. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (1:1:1 v/v/v) with 10 vol% fluoroethylene carbonate (FEC). The cells were assembled in a high-purity argon-filled glove box with water/oxygen content lower than 1 ppm. The cells were galvanostatically cycled on a LAND cycler (Wuhan LAND Electronics Co., China) with a current density of 150 mA g^{-1} in the voltage range of 0.01–3.0 V vs. Li/Li^+. The rate performance was investigated at various current densities in the range of 75–750 mA g^{-1}. Cyclic voltammetric measurements were carried out at a scan rate of 0.1 mV s^{-1} between 0 and 3 V (versus Li/Li^+) using a CHI660a electrochemical workstation (ChenHua Instruments Co, China). For CV test, a small piece of the MnO/rGO electrode was used as working electrode to alleviate the electrochemical polarization. The electrochemical impendence spectroscopy (EIS) tests were carried out using Autolab PGSTAT128 N (Eco Chemie, Netherlands) over the frequency range from 100 kHz to 0.01 Hz with amplitude of 10 mV. The Li^+ storage capability of the MnO/rGO electrode was calculated solely based on the contribution from MnO by deducting the capacity contributions from the rGO.

3. Results and discussion

The in-situ synthesis of MnO/rGO nanocomposites by using electron beam radiation is shown schematically in Fig. 1. In the electron beam radiation process, water molecule first decomposes to form a very strong oxidative ($^{\bullet}OH$) and reductive ($^{\bullet}H$, e_{aq}^{-}) intermediate products which react rapidly with solute species (Eq. (1)) [38], where the numbers are the radiation chemical yields in units of μmol J^{-1}.

$$\begin{aligned} H_2O \overset{\text{EB radiation}}{\rightarrow} & 0.26e_{aq}^{-} + 0.06H^{\bullet} + 0.27OH^{\bullet} + 0.045H_2 \\ & +0.07H_2O_2 + 0.26H_3O^{+} \end{aligned} \tag{1}$$

$$e_{aq}^{-} + H^{\bullet} + OH^{\bullet} + (CH_3)_2C{=}O \rightarrow (CH_3)_2C{-}HO^{\bullet} + OH^{-} \tag{2}$$

$$Mn^{VII}(aq) \overset{(CH_3)_2C-HO^{\bullet}}{\rightarrow} MnO_2(col) \overset{(CH_3)_2C-HO^{\bullet}}{\rightarrow} MnO_x \tag{3}$$

$$GO \overset{(CH_3)_2C-HO^{\bullet}}{\rightarrow} rGO \tag{4}$$

Acetone in the water can scavenge $^{\bullet}OH$, $^{\bullet}H$ and e_{aq}^{-} and changes into the secondary radicals ($(CH_3)_2C$-HO•) to eventually reduce MnO_4^{-} and GO (Eq. (2)) [39]. During radiation, not only the MnO_4^{-} and GO are reduced (Eq. (3) and (4), but also the generation of new