Journal of Power Sources 395 (2018) 92–97

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Self-assembled Mn_3O_4/C nanospheres as high-performance anode materials for lithium ion batteries

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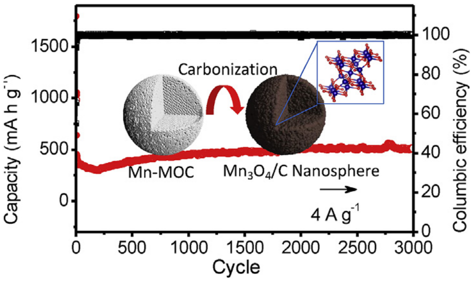
HIGHLIGHTS

- Synthesis of self-assembled spherical Mn based metal organic complex (Mn-MOC).
- Hierarchical porous Mn_3O_4/C nanospheres with high specific surface area.
- Ultrafine Mn_3O_4 nanocrystals with carbon shell.
- Mn_3O_4/C electrode with high reversible specific capacity of 1237 mAh/g.
- Long battery cycle life with no significant capacity fading after 3000 cycles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Mn_3O_4
Self-assembly
Metal organic complex
Hierarchical structure
Lithium ion battery

ABSTRACT

A self-assembled Manganese (Mn) based metal organic complex (Mn-MOC) with spherical structure was synthesized via a solvothermal reaction. The Mn-MOC precursor materials were converted to hierarchical porous Mn_3O_4/C nanospheres through thermal annealing treatment. These nanospheres exhibited a high reversible specific capacity (1237 mAh/g at 200 mA/g), excellent ratability (425 mAh/g at 4 A/g), and extremely long cycle life (no significant capacity fading after 3000 cycles at 4A/g) as an anode in lithium ion batteries. The notable capability for lithium storage is attributed to the unique porous hierarchical structure of the Mn_3O_4/C nanospheres, which consist of homogeneously distributed Mn_3O_4 nanocrystals with thin carbon shells. Such a desired nanostructure not only provided large reaction surface area and enhanced electrical conductivity, but also promoted the formation of a stable solid electrolyte interphase (SEI) and accommodated the volume change of the conversion reaction type electrode.

1. Introduction

Lithium ion batteries (LIBs), as a crucial power source component in electronics and renewable energy generation systems, have been intensively explored in the past few decades [1,2]. The commercial anode for LIBs is based on graphite, which has a theoretical specific capacity of 372 mAh/g. The limited theoretical capacity of graphite cannot satisfy the needs of emerging applications such as electrical and hybrid vehicles, where LIBs with significant higher energy density and power density are required [3]. Therefore, it is necessary to develop advanced

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https://doi.org/10.1016/j.jpowsour.2018.05.064
Received 21 January 2018; Received in revised form 17 April 2018; Accepted 17 May 2018
0378-7753/

anode materials with significantly larger reversible specific capacity [4,5]. Transition metal oxides (MO_x, where M is Mn, Co, Ni, Cu or Fe etc.) are promising anode candidate materials, owing to their high theoretical capacity and low cost [6,7]. Among those materials, Mn_3O_4 has been intensively investigated as one of the most promising anode materials due to its abundance, low oxidation potential and competitive electrochemical performance [7,8]. However, several issues hamper the utilization of transition metal oxides as anode materials in LIBs: First, the poor intrinsic electrical conductivity of metal oxides limits the electron transfer throughout the electrode, leading to poor active materials utilization and low ratability [9]. Second, the large volume expansion and shrinkage of the metal oxides during the lithiation and delithiation can result in electrode pulverization that promotes capacity fading during cycling [10]. It has been well recognized that nano-engineering and carbon hybridization are effective ways to overcome or limit these issues [11–16]. One such approach is through use of metal organic complex (MOC) derived carbon coated metal oxide, which exhibited improved electrical conductivity and good accommodation of the strain during the lithiation and delithiation process. Those MOC derived materials are an emergent class of novel anode materials in LIBs [17–19]. For instance, mesoporous Fe_2O_3 that was derived from an iron-based metal organic frameworks (MOFs) [20] exhibited specific capacity of 911 mAh/g after 50 charge/discharge cycles. Similarly, MOFs are effective precursors for ZnO@ZnO quantum dots/C nanorods that were reported to deliver a reversible specific capacity of 699 mAh/g after 100 cycles [21]. NiO-CoO-C microspheres with a yolk-shell structure [22] exhibited a high specific capacity of 1194 mAh/g and good ratability (821 mAh/g at 2 A/g). Many additional MOC derived carbon coated metal oxide materials, including Co_3O_4, Co_3O_4/Co, CuO/Cu_2O and ZnO/$ZnFe_2O_4$ etc., have been explored and exhibited good lithium storage capability [23–27]. Despite these successes, due to the intrinsic volume change of the metal oxide anode during the cycling that can lead to pulverization of the anode, the extended cycle life (over 1000 cycles) of metal oxide anodes has rarely been demonstrated and represents a challenge for the further development of this class of anode materials.

In this work, a facile method to synthesize highly porous Mn_3O_4/C nanospheres with hierarchical structure was achieved by self-assembly to form spherical Mn based MOC, followed by a thermal annealing process. The Mn_3O_4/C nanospheres consisted of homogeneously distributed Mn_3O_4 nanocrystals with a conformal carbon coating. Such a hierarchical, porous structure provided both good electrical conductivity and volume changes accommodation capability, which were desired for transition metal oxide based conversion reaction type electrode [28,29]. These characteristics led to high specific capacity, excellent ratability and ultra-long cycle life in a lithium-ion half-cell for the Mn_3O_4/C nanosphere electrode.

2. Experimental

2.1. Materials and characterization

Manganese nitrate (50-52% aqueous solution, TREM CHEMICALS), trimesic acid (95% Sigma-Aldrich), ethanol (200 proof, Decon Laboratories, Inc.), N,N-dimethylformamide (DMF, ACS grade, EMD), N-methyl-2-pyrrolidone (NMP, 99.5% EMD), fluoroethylene carbonate (FEC, 98% Alfa Aesar), Super P carbon (MTI Corporation), and lithium foil (15.6 mm in diameter and 0.25 mm in thickness, MTI Corporation) were used as received. Poly(acrylic acid) (PAA, $M_w = 450\,kg\,mol^{-1}$) was purchased from Scientific Polymer Products, Inc.

The SEM and TEM images were collected using JEOL JSM-7401F and JEOL 1203 microscopes, respectively. HRTEM images, and corresponding EDX maps were obtained using FEI Tecnai G2 F20 equipped with an EDAX SUTW (super ultrathin window) energy-dispersive X-ray spectrometer (EDAX). Powder XRD speactra were obtained by using a Rigaku Ultima IV X-ray diffractometer with a Cu Kα radiation ($\lambda = 1.5604$ Å). TGA were performed on a Q500 station (TA Instruments) under Ar or air with a ramp rate of 5 °C/min. The surface area was measured with a Micromeritics TriStar II instrument (Micromeritics VacPrep 061). The sample was degassed at 80 °C for 12 h, prior to determining specific surface area, Nitrogen adsorption/desorption isotherms were obtained at 77 K using a TriStar II (Micromeritics). The Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area in the relative vapor pressure range of 0.04–0.27. The nitrogen adsorption isotherm was used to determine the pore size distribution using the Barrett-Joyner-Halenda (BJH) model. Cyclic voltammetry profiles were obtained by using a CHI608E electrochemical workstation with a scan rate of 0.2 mV/s. Galvanostatic charge and discharge tests were carried out by using a Battery Analyzer BST-8A (MTI) within the voltage range of 0.005–3 V (*vs.* Li/Li^+).

2.2. Synthesis of Mn-MOC

The Mn-MOC was synthesized via a solvothermal reaction. 0.1 g (50-52% wt) $Mn(NO_3)_2$ aqueous solution, and 0.03 g trimesic acid were dissolved in a solution mixture of 10 ml DMF and 10 ml ethanol under vigorous stir and then transferred into a Teflon-lined autoclave. The autoclave was heated to 150 °C and held at 150 °C for 6 h for the reaction. The solids were washed with ethanol four times. The as-prepared Mn-MOC was collected by centrifuging (4000 rpm) and drying (80 °C).

2.3. Synthesis of Mn_3O_4/C nanosphere

The as-prepared Mn-MOC was placed in a combustion boat and inserted into a tube furnace under argon atmosphere. Then the sample was heated up to 500 °C using a temperature ramp of 4 °C/min and held for 1 h. After the furnace was naturally cooled down to room temperature, the powder of Mn_3O_4/C nanosphere was collected.

2.4. Battery fabrication

The electrode slurry was prepared by mixing 70% active material, 15% Super P carbon, and 15% PAA with NMP. The slurry was cast on copper foil using a doctor blade and dried at 80 °C overnight. The electrode was punched into disks with a diameter of 5/16 inch. The mass loading of the active materials is 0.6 mg/cm^2. Lithium metal foil was used as the counter electrode. 1 M lithium hexafluorophosphate in EC/DEC (1:1 v/v) with 10% fluoroethylene carbonate was used as the electrolyte. The coin cell was assembled in an argon filled glovebox with oxygen and water content below 0.5 ppm.

3. Results and discussion

The procedure to fabricate the highly porous hierarchical Mn_3O_4/C nanosphere is illustrated in Fig. 1. The porous spherical manganese metal organic complex (Mn-MOC) was first prepared via a hydrothermal reaction with manganese nitrate as the metal source and trimesic acid as the organic ligand. The Mn-MOC was then annealed in Ar to transform the manganese ion into manganese oxide and decomposing the organic ligand to form carbon layers. The resulting Mn_3O_4/C nanospheres exhibit a highly porous hierarchical structure.

As shown in Fig. 2a, the as prepared Mn-MOC exhibited a uniform spherical structure with a diameter of ~400 nm (inset picture in Fig. 2a). It is worthwhile to note that no surfactant or other templating materials were used to generate this uniform nanosphere structure, which renders this method highly scalable. After annealing under argon (Ar), the spherical structure was well-maintained (Fig. 2b). The carbonization temperature was determined to be 500 °C by TGA analysis (Fig. 2c). The weight loss below 150 °C could be attributed to the evaporation of solvent trapped in the pores of Mn-MOC nanospheres