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Grain Boundaries Enriched Hierarchically Mesoporous MnO/Carbon Microspheres for Superior Lithium Ion Battery Anode

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ABSTRACT

To develop high-performance anode materials of lithium ion batteries (LIBs) for practical high energy application, a grain boundaries enriched hierarchically mesoporous MnO/C microsphere composite has been fabricated by an *in-situ* carbonization process. The mesoporous MnO/C microsphere is constructed by abundant grains and grain boundaries that are uniformly embedded in a carbon matrix. Such unique nanoarchitecture exhibits high tap density and structural stability, and provides 3D continuous transport pathways for electrons and Li-ions, enabling high electrochemical stability and improved lithium storage kinetics. As a consequence, the mesoporous MnO/C electrode delivers ever-increasing specific capacity (1200 $mAh\,g^{-1}$ after 100 cycles at 100 $mA\,g^{-1}$) and excellent rate capability (588 $mAh\,g^{-1}$ at 2 $A\,g^{-1}$). Such superior lithium storage performance suggests that the hierarchically mesoporous MnO/C microsphere electrode should be one of the most promising anode materials for electric vehicle and grid energy storage application.

1. Introduction

Lithium ion batteries (LIBs) are one of the most efficient energy storage systems due to their high energy density, environmental benignity and long lifetime. However, conventional LIBs using graphite as the anode material generally exhibit limited performance in terms of low specific capacity, poor rate capability and serious safety problems. Currently, intensive efforts have been dedicated to discovering practical alternatives for conventional LIB anode that can continuously deliver high power and energy densities with high safety assurance [1–4]. Conversion reaction electrodes such as transition metal oxides (TMOs) are attractive anode substitutes owing to their high theoretical specific capacity and safety [5–8]. Among them, manganese monoxide (MnO) should be the most promising one because it has high specific capacity (756 $mAh\,g^{-1}$), lower voltage hysteresis (<0.8 V) compared to other TMOs, suitable working potential (1.032 V *versus* Li/Li^+), low cost and low toxicity [9–12]. Nevertheless, similar to other conversion-based metal oxides, the practical implementation of MnO is hampered by the poor cyclability and rate capability originating from the low electrical conductivity and drastic volume variation [13,14].

Generally, designing hollow/porous nanostructured materials can shorten the Li^+ diffusion pathway and accommodate the volume change upon cycling, thus improve the rate capability and electrode stability [9,15,16]. Further studies reveal that compositing or coating conductive carbonaceous matrix can largely improve the electrical conductivity and further buffer the volume expansion/contraction [17–19]. Therefore, designing hollow/porous nanoarchitecture with carbon compositing/coating is appealing in this regard and has been widely adopted to design the MnO electrode materials [20,21]. For example, Tang *et al.* [21] have designed and synthesized a porous MnO/C composite material

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through a promoted template method combined with post carbon coating process. The porous MnO/C composite anode material exhibited superior electrochemical performance due to its multimodal pore structure and conductive carbon layers. Guo et al. [22] have prepared a carbon-coated MnO microparticulate porous nanocomposite *via* a thermal decomposition followed by carbon coating. Owing to its porous structure and carbon coating, the cycling performance is highly improved. However, most of the reports on porous MnO/C composites employ complex fabrication process or expensive additives, which hinder their practical application for LIBs [21,23]. Moreover, the post carbon coating process in most works cannot assure that every MnO nanograin and grain boundaries are effectively embedded in the carbon matrix. Such poor electrical contact between the grains and incontinuous electron pathway result in limited cycling performance [17,21–23]. In this context, direct *in-situ* carbonization of the inorganic-organic hybrid material is a very facile and effective strategy to fabricate the carbon coated porous composite with extremely uniform crystal distribution in carbon matrix [24]. This strategy can make sure that all the crystalline grains and grain boundaries are homogeneously embedded in the carbon matrix, which not only provides abundant channels to allow Li^+ intercalation and stabilizes the electrode surface, but also creates an interconnected 3D network for continuous electron transport [25–27]. Therefore, it is very much expected that if the designed materials have rich grains and grain boundaries embedded in carbon matrix, they will show much improved lithium storage properties. However, this approach is rarely reported for MnO/C-based materials.

Herein, we develop a facile and effective *in-situ* carbonization strategy to synthesize the mesoporous MnO/C microspheres with abundant grains (average grain size: 8–13 nm) and grain boundaries embedded in carbon matrix. Unlike most MnO/C composites using post carbon coating process, the grain boundaries enriched MnO/C (GBMOC) is obtained via directly carbonizing an inorganic-organic hybrid material (manganese alkoxide), which results in the MnO nanocrystals uniformly dispersed in carbon matrix. Moreover, the grains and grain boundaries perfectly embedded in the carbon material creates an interconnected 3D network for fast and efficient Li-ion and electron transport. A synergy of the design routes and superior nanostructure endows the mesoporous GBMOC electrode with highly enhanced reaction kinetics, namely, fast Li^+ diffusion and highly efficient electron transport, resulting in the excellent lithium storage performance.

2. Experimental section

2.1. Material synthesis

All the reactants and solvents are analytical grade and used as received. The preparation of the precursor manganese alkoxide (Mn-DEG) is depicted as follows: 0.002 mol of $KMnO_4$ is dispersed in 40 mL diethylene glycol (DEG) and stirred for 30 min; subsequently, the brown-black solution is heated to 150 °C in a thermostatic oil bath with vigorous stirring and then 2 mL ethylenediamine (EN) is rapidly injected into the above solution. The solution is further heated to 200 °C with vigorous stirring for 5 h. The obtained brown precipitate (referred to as Mn-DEG) is washed with ethanol repeatedly until the organic reagents are washed out. Then the Mn-DEG powder is obtained by drying at 60 °C for 4 h. To obtain the hierarchically mesoporous GBMOC, the Mn-DEG powder is carbonized in Ar/H_2 (95/5, Vol%) at 550 °C for 8 h. As for the synthesis of bare MnO microsphere (BMO), the Mn-DEG precursor is first annealed in air at 450 °C for 4 h, and then annealed in Ar/H_2 (95/5, Vol%) at 550 °C for 8 h

2.2. Material characterization

X-ray diffraction (XRD) patterns are obtained by a Bruker diffractometer at 40 kV, 40 mA, with Cu Kα radiation ($\lambda = 1.54056$ Å). Crystallite size is inferred using the Scherrer formula. The morphology of all the products is performed on scanning electron microscopy (SEM, Hitachi S-4800) equipped with a field-emission gun with an accelerated voltage at 5 kV. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) are performed on a JEOL JEM-2100F with an acceleration voltage of 200 kV. The Brunauer-Emmett-Teller (BET) specific surface area of the powders is analyzed in a Micrometrics Tri Star II 3020 nitrogen adsorption-desorption apparatus. The thermogravimetric/differential scanning calorimetry (TG/DSC) analysis of the as-fabricated materials is performed using a Labsys Evo S60/58458 thermal analysis instrument at a temperature ramping rate of 5 °C min^{-1} in air. Energy-dispersive X-ray spectroscopy (EDS) is performed using an EDAX Genesis instrument with an acceleration voltage of 30 kV. Fourier transform infrared (FT-IR) spectra are recorded on a Bruker Vertex 80 V FT-IR spectrometer using KBr pellet technique in the range of 400–4000 cm^{-1}. Tap density of the GBMOC microspheres are measured by a BT-301 tap denser. Powder samples are poured into 25 mL glass cylinder and this cylinder is tapped for 10 min with 300 taps min^{-1} frequency.

2.3. Electrochemical characterization

The working electrodes are fabricated by mixing the MnO microspheres, conductive carbon blacks (Super-P) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 80:10:10. The slurry is coated on a copper foil and dried in a vacuum oven at 120 °C for 12 h. The average mass loading of active material is 1.4 mg cm^{-2}. Electrochemical measurements are carried out *via* CR2025 coin type cell using lithium pellets as the counter electrode and reference electrode, a 1 M solution of $LiPF_6$ in ethylene carbon (EC)/dimethyl carbonate (DMC) (1:1 w/w) as electrolyte. The cells are assembled in an argon-filled glove-box. Cyclic Voltammetry (CV) measurements are carried out using a CHI 660D electrochemical workstation at a scanning rate of 0.2 mV s^{-1}. Galvanostatic discharge/charge cycling is studied in a potential range of 0.01 V – 3 V *versus* Li/Li^+ with a multichannel battery testing system (LAND CT2001A), respectively. Electrochemical impedance spectra (EIS) are measured with an electrochemical workstation (Autolab PGSTAT 302N) in the frequency range from 100 KHz to 10 mHz.

3. Results and discussion

The grain boundaries enriched MnO/C microspheres (GBMOC) are prepared by an *in-situ* carbonization of an inorganic-organic hybrid precursor (manganese alkoxide, Mn-DEG) in H_2/Ar atmosphere (Fig. 1a), where the organic species are converted to carbon skeleton along with the formation of MnO nanocrystals. The structure of the Mn-DEG precursor is first characterized by XRD (Fig. 2a). The strong low-angle reflection located at 10° corresponds to the lamellar structure [28]. The lamellar structure of Mn-DEG can be described as manganese oxide layers seperated by bonded DEG anions (Fig. 1b) [24]. According to the Bragg equation [29], the interlayer spacing of the lamellar structure is calculated to be 0.89 nm. The weak peaks at 16.8, 32.5 and 34.5° may be from the crystal reflection of the manganese oxide layers. Fourier transform infrared (FT-IR) spectroscopy can further identify the inorganic-organic hybrid structure of Mn-DEG (Fig. 2b). The strong absorption bands lying in 2831 cm^{-1}, 1460 cm^{-1} and 1051–1103 cm^{-1} correspond to the C—H symmetric stretching