Carbon 115 (2017) 95–104

Contents lists available at ScienceDirect

Carbon

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

Smart reconstruction of dual-carbon decorated MnO for anode with high-capacity and ultralong-life lithium storage properties

Jie Zhang, Wei Zhang, Ting He, Ibrahim Saana Amiinu, Zongkui Kou, Jiannian Li, Shichun Mu*

State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China

ARTICLE INFO

Article history:
Received 11 September 2016
Received in revised form
28 December 2016
Accepted 30 December 2016
Available online 2 January 2017

Keywords:
Graphene
Amorphous carbon
Manganese oxide
Nanorods
Lithium ion battery

ABSTRACT

To tackle the issues of inferior cycling stability and low intrinsic conductivity for MnO as anode material for lithium ion batteries (LIBs), we design and rationally confine MnO@C core-shell nanorods homogeneously in the flexible graphene matrix via a facile process. The obtained composite exhibits a high reversible capacity (1165.3 mAh g^{-1} at 0.1 A g^{-1}), excellent rate capability (618.5 mAh g^{-1} at 2 A g^{-1}), and superior cyclability (almost no capacity fading even after 4000 cycles), which has been rarely reported for LIBs. The lithiation and delithiation behavior suggests that the further oxidation of Mn^{2+} to Mn^{4+} and the surface pseudocapacitance contribute to the distinctive capacity enhancement. Additionally, the structure reconstruction from MnO nanorods to nanoworm-like and subsequently to nanoparticles achieves faster kinetics of conversion reactions. The excellent rate capability benefits from the presence of 2D dual conductive graphene and amorphous carbon, as well as the synergistic effect between them for elevating the transportation of both lithium ions and electrons. Moreover, the superb cyclic stability can be attributed to the well-defined dual-carbon decoration that alleviates the volume variation as well as the agglomeration and dissolution of MnO, and yields a long-life anode material.

1. Introduction

With the ever-growing demand for hybrid electric vehicles and the desire for portable electronics, the development of efficient electrode materials which may greatly outperform the state-of-the-art lithium-ion batteries (LIBs) still remains a great challenge [1–3]. Thus, seeking high-performance anode materials with the high energy density, power density and long-term life is much urgently required [4]. Recently, novel anode materials and the related mechanism including alloying or conversion reaction with silicon, tin-based alloys, metal oxides, metal hydrides, metal sulfides, and metal phosphides, have been extensively explored to improve the capacity performance and cyclic stability [5,6]. In terms of the unique properties of low cost, availability, non-toxicity and safety, transition metal oxides (TMOs) are considered as one of the most promising electrode materials for rechargeable energy-storage devices [7].

Among the various TMOs investigated for LIBs, MnO emerges as one of the most promising candidates, mainly due to its suitable voltage hysteresis (<0.8 V), relatively lower thermodynamic equilibrium potential (~1.0 V vs. Li^+/Li), high density (5.43 g cm^{-3}), high theoretical capacity (756 mAh g^{-1}), relatively low cost, and environmental benignity compared to other TMOs [8,9]. However, like other TMOs, on account of the inferior rate capacity and cycle life induced by the low intrinsic electrical transport, and the drastic volumetric expansion that can result in structural pulverization during the repeated lithium insertion/extraction process, MnO is limited to niche application in LIBs. Especially, the biggest issue of MnO materials towards LIBs is that they can react with lithium to form metal Mn (dispersed in the Li_2O matrix), resulting in severe agglomeration and repeated volume change during cycling. This could also give rise to drastic pulverization of the entire MnO electrodes and leads to shedding and dissolution of Mn into the electrolyte and to rapid capacity fading upon cycling [10].

In previous studies, tremendous efforts have been made to address the above-mentioned issues with the expectancy to increase the electrochemical properties of MnO-based materials when used as anode material for LIBs. On the one hand, coating general carbonaceous materials on such MnO-based materials provides an advanced avenue for stabilizing the interfaces and

---

* Corresponding author.
E-mail address: msc@whut.edu.cn (S. Mu).

http://dx.doi.org/10.1016/j.carbon.2016.12.090
0008-6223/

enhancing the power and energy densities [11]. These hybrid strategies have been demonstrated on the synthesis of MnO/C core-shell nanorods [12,13], MnO nanoparticles embedded in a carbon matrix [14–16], carbon anchored MnO nanocrystals [17–19], and coaxial MnO/C nanowires [20–22]. However, above improvement measurements have also hindered their commercial applications because of limited elasticity and structural stability of carbon. With the rising of advanced 2D carbon materials, masses of graphene/metal monoxide composites have also been developed owing to their superior conductivity, large surface area, structural flexibility, and chemical stability [23–25]. For instance, graphene supported MnO nanoparticles [26–28], MnO nanowire/graphene composites [29], and MnO nanorods hybrids with graphene [30] have been reported. These hybrids have been extensively probed for energy-storage applications, which exhibit enhanced electrochemical performance with high reversible capacity and good rate capability. However, the integrity maintenance of such materials during continuous charge/discharge cycling is still unsatisfactory, rendering the conventional core/shell morphology ineffective in keeping the integrity of MnO for long-life LIBs, and resulting in their limited cycle life for practical implementation.

On the other hand, delicate engineering and processing of the intrinsic materials for the rational design of MnO-based materials have also been considered principally to keep the structural integrity of the electrode materials for enhanced cyclability [31]. For example, three-dimensional (3D) yolk-shell MnO@CF composites [32], peanut-like MnO@C core-shell composites [33], Chinese lantern-like MnO@N-C materials [34], 3D porous MnO thin films [35], and MnO/C nanopeapods [10], have been investigated to determine effective buffering effects as well as shortening of the path for Li^+/electron transport, improving the cycle life and rate performance of electrode materials [29]. Although the above methods have positive influence in prolonging the cycling life of MnO materials, the level of improvement is still very limited. Hence, developing a strategy to further elevate the electrochemical properties will be significantly meaningful to construct advanced MnO-based anode materials which meet the ever-increasing demands of high energy/power densities and long cycle life for LIBs.

Herein, we report on a high-efficiency citric acid adhesive-assisted composite procedure combined with a subsequent heat reduction treatment to rationally design a MnO-based nanohybrid (G/MnO@C/G) composite, in which carbon-coated MnO nanorods (MnO@C NRs) are embedded into a 3D conductive framework, constructed by flexible 2D reduced graphene oxide (RGO). As expected, the G/MnO@C/G hybrid electrode will provide a high electrochemically active surface area, faster electron transport and ions diffusion, leading to substantially improved capacity, high rate and superior cycle performances. Owing to the conductive frameworks composed of dual interconnected carbon materials, the present nanocomposites become much highly efficient MnO-based materials compared with previous reports. Remarkably, this kind of integrated electrode structure exhibits a long-term cycle life (471.3 mAh g^{-1} after 4000 discharge/charge cycles at a high current density of 4 A g^{-1} with ~93.5% capacity retention). Undoubtedly, our work paves a new comprehension for advancing the design of double carbon layer decorated composite materials to further improve the EES performance with the potentiality to greatly outperform the state-of-the-art energy storage devices.

2. Experimental section

2.1. Preparation of G/MnO@C/G

In a typical process, 30 mg of GO nanosheets [36] were dispersed in 20 mL deionized water with 1 h of sonication, which was called solution A. Meanwhile, 200 mg of MnO_2 powders were added into 20 mL deionized water followed by 10 min of sonification. Then, the MnO_2 solution was dissolved in a mixture of citric acid (200 mg), H_2O (10 mL) and PVP (150 mg) with continuous stirring at room temperature for 0.5 h, which was called solution B. Solution A was then added to solution B under continuous stirring at room temperature for 2 h. After that, the solvents were removed from the obtained solution by dialysis and freeze drying with a lyophilizer (SCIENTZ-10 N), resulting in the formation of raw materials for the preparation of G/MnO@C/G nanohybrids. Finally, the expected MnO-based materials were obtained by annealing the corresponding raw materials at 650 °C (heating rate: 5 °C min^{-1}) in a H_2 atmosphere for 3 h. For comparison, the bare MnO, MnO@C nanorods and MnO@RGO composites were also prepared under the same conditions.

2.2. Material characterization

Field emission scanning electron microscopy (FESEM, Hitachi S-4800, 10 kV) and High-resolution transmission electron microscopy (HRTEM, JEM-2100F, 200 kV) were used to investigate the micro-structure of the sample. The phase and crystalline structure of the samples were determined by X-ray diffraction (XRD, D/MAX-IIIA, Japan, Cu Kα radiation, $\lambda = 0.15406$ nm). The valence state of the key elements in the samples was studied by X-ray photoelectron spectroscopy (XPS, PHI Quantera, U-P). The Raman spectra were obtained using a RM-1000 Renishaw confocal Raman micro-spectroscope with 514.5 nm laser radiation. Thermogravimetric analysis (TGA) was performed with STA 449C Jupiter (Netzsch) at a heating rate of 10 °C min^{-1} from room temperature to 800 °C in flowing oxygen. The specific surface area and pore size distribution were analyzed via Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption measurements (Japan, BELSORP-Mini).

2.3. Electrochemical measurements

Electrodes were prepared by dispersing the as-prepared G/MnO@C/G (70 wt%), acetylene carbon black (20 wt%) and polyvinylidene fluoride binder (PVDF, 10 wt%) in *N*-methyl-2-pyrrolidone (NMP) to form a slurry. The resultant slurry was coated onto a copper foil substrate and dried in a vacuum oven for 24 h. The electrochemical measurements were carried out using the two-electrode coin cells (CR2016-type). The lithium foil was used as reference and counter electrode, 1 M solution of $LiPF_6$ in 1:1 solvent mixture of EC and DEC as electrolyte with a Celgard membrane as separator. The coin cells were assembled in an argon-filled glove box. The discharge-charge tests were performed on the Land battery measurement system (Wuhan, China) with galvanostatic in the voltage range of 0.01–3.0 V vs. Li^+/Li at room temperature. Cyclic voltammetry (CV) tests and electrochemical impedance spectroscopy (EIS) measurements were measured by a CHI660E electrochemical workstation (Chenhua, Shanghai, China).

3. Results and discussion

The typical preparation process of the G/MnO@C/G composite is illustrated in Scheme. 1. First, dispersed MnO_2 nanorods (NRs) obtained by a conventional hydrothermal approach are coated with a citric acid (CA) layer to produce core-shell MnO_2@CA NRs and subsequently react with polyvinylpyrrolidone (PVP) in a fully dispersed GO solution, giving rise to the GO/MnO_2@CA/GO composites(Details are given in Supporting Information). The G/MnO@C/G nanohybrid is finally obtained by annealing the corresponding intermediate materials in a H_2 atmosphere.

To identify the composition, the crystalline structure and phase