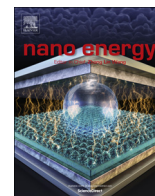




ELSEVIER

Contents lists available at ScienceDirect

Nano Energy

journal homepage: [www.elsevier.com/locate/nanoen](http://www.elsevier.com/locate/nanoen)

# All-manganese-based Li-ion batteries with high rate capability and ultralong cycle life



Jian-Gan Wang<sup>a</sup>, Dandan Jin<sup>a</sup>, Huanyan Liu<sup>a</sup>, Cunbao Zhang<sup>a</sup>, Rui Zhou<sup>a</sup>, Chao Shen<sup>a</sup>, Keyu Xie<sup>a</sup>, Bingqing Wei<sup>a,b,\*</sup>

<sup>a</sup> Center for Nano Energy Materials, State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

<sup>b</sup> Department of Mechanical Engineering, University of Delaware, Newark, DE 19716, USA

## ARTICLE INFO

### Article history:

Received 1 February 2016

Received in revised form

25 February 2016

Accepted 28 February 2016

Available online 3 March 2016

### Keywords:

Li-ion batteries

MnO@C

LiMn<sub>2</sub>O<sub>4</sub>

Full cell

High performance

## ABSTRACT

High-rate and long-cycle life Li-ion batteries constructed with all-manganese-based electrode materials have been successfully realized. The key to the success is the facile green synthesis of the anode: MnO@C core-shell nanowires with internal void spaces and a uniform carbon coating shell. The unique one-dimensional nano-configuration provides reduced solid-state distance for Li-ion/electron transport, enhanced electrical conductivity for charge transfer, and effectively volumetric accommodation for Li-ion insertion/extraction, thus enabling the MnO@C nanostructures to exhibit high-rate Li-ion storage capacity and long cycling stability. When coupled with a nanostructured LiMn<sub>2</sub>O<sub>4</sub> cathode, the all-manganese-based MnO@C||LiMn<sub>2</sub>O<sub>4</sub> full cell characterizes a high energy density of 397 Wh kg<sup>-1</sup>, high rate capability (215 Wh kg<sup>-1</sup> at a power density of 6.2 kW kg<sup>-1</sup>), and an extremely low decay rate of 0.087% per cycle over 1000 cycles. Combining with additional merits of low cost, eco-friendliness, and safe operation, our design will shed light on fabricating high-performance Li-ion batteries from all manganese-based electrode materials.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Li-ion batteries (LIBs) have become one of the most important electrochemical energy storage technologies that show great promise as power sources in a broad application from portable electronics to electric vehicles [1,2]. The current electrode materials used in commercial LIBs typically involve graphite anode and LiCoO<sub>2</sub> cathode. However, both the conventional materials cannot meet the ever-growing demands of higher energy/power densities, lower cost, and safer operation for the next generation LIBs, because (i) the graphite anode suffers from a low theoretical capacity (372 mAh g<sup>-1</sup>), slow reaction kinetics, and safety issues due to its low discharge voltage (<0.2 V) that renders the possible formation of lithium dendrites; and (ii) the cobalt in the LiCoO<sub>2</sub> cathode is expensive, of natural scarcity, and highly toxic [3–5]. Therefore, it is imperative to advance new LIBs with enhanced energy/power densities, low cost, natural abundance, non-toxicity, and improved safety and reliability [6].

Manganese belongs to a transition metal element that can

\* Corresponding author at: Center for Nano Energy Materials, State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China.

E-mail address: [weib@udel.edu](mailto:weib@udel.edu) (B. Wei).

constitute a myriad of promising chemical compounds for advanced LIB electrode materials. In particular, manganese-containing materials offer additional attractive characteristics of low cost, environmental benignity, rich abundance on earth, and high intrinsic mass density [7]. For example, LiMn<sub>2</sub>O<sub>4</sub> is a promising cathode material that has a Li-ion storage capacity of 148 mAh g<sup>-1</sup>, high operating voltage, and high rate capability due to its three-dimensional (3D) spinel structure offering fast Li<sup>+</sup> intercalation and deintercalation paths. It has been demonstrated that the electrochemical performance of LiMn<sub>2</sub>O<sub>4</sub> strongly depends on the phase crystallinity, purity, particle size, and distribution [8–12]. Nanosized LiMn<sub>2</sub>O<sub>4</sub> with high-quality crystallinity is believed to offer high power density and good cyclability due to its fast reaction kinetics and structural stability. With regard to the anode materials, manganese oxides (MnO<sub>x</sub>) possess a 2–4 times higher theoretical capacity than graphite and a lower discharge voltage (0.4–0.5 V vs. Li/Li<sup>+</sup>) compared with other transition metal oxides (e.g., CoO<sub>x</sub>, NiO, FeO<sub>x</sub>, etc.), enabling a higher energy density in full cells [13,14]. However, MnO<sub>x</sub> faces two critical issues of poor electrical conductivity and large volumetric changes during Li<sup>+</sup> insertion/extraction processes, thereby limiting its high power delivery capability and long-term cycling stability [15]. To mitigate these problems, incorporation of nanostructured MnO<sub>x</sub> into a conductive and elastic carbon matrix has

been proven to be an effective and promising approach [16]. There are a considerable number of studies reporting  $\text{MnO}_x/\text{C}$  nanostructures with improved performance in half cells [17–26], but very few work paid their attention to the electrochemical properties when coupled with cathodes in full cell configurations [27,28]. Surprisingly, these limited reports on full cells demonstrated a poor rate capability and short cycling endurance (250 cycles) which were attributed to the  $\text{MnO}_x$  side in the full cells [27]. Therefore, it is of great interest yet challenge to develop all manganese-based LIBs that feature high capacity, high rate capability, long cycle life, as well as low cost, environmental friendliness, and safety.

In this work, we report a high-rate and long-cycle-life all-manganese-based Li-ion full cell using  $\text{MnO}@C$  core-shell nanowires as the anode and  $\text{LiMn}_2\text{O}_4$  nanoparticles as the cathode. A rational and green approach has been developed to synthesize  $\text{MnO}@C$  core-shell nanowires with uniform carbon nanoshells and internal void spaces along the one-dimensional configuration, which permit the hybrid nanostructures to show a high specific capacity ( $\sim 900 \text{ mAh g}^{-1}$ ), excellent rate capability, and great cycle stability. The  $\text{MnO}@C$  anode is coupled to the high crystalline  $\text{LiMn}_2\text{O}_4$  nanoparticle cathode to constitute a full LIB cell. Impressively, the  $\text{MnO}@C||\text{LiMn}_2\text{O}_4$  full cells can deliver a high energy density of  $397 \text{ Wh kg}^{-1}$ , a high-rate performance at 13.5 C, and an exceptional low capacity decay rate of 0.087% per cycle over an extended cycling operation (1000 cycles).

## 2. Experimental

### 2.1. Material synthesis

**$\text{MnO}_2$  nanowire:** In a typical procedure, 2 mmol of  $\text{KMnO}_4$  and 2 mmol of  $\text{NH}_4\text{F}$  were dissolved in 75 ml of deionized water to form a dark pink solution under magnetic stirring. Then the solution was transferred into a Teflon-lined stainless steel autoclave with 100 ml capacity. The autoclave was sealed and heated at  $160^\circ\text{C}$  for 24 h. Black powders were collected after naturally cooling down to room temperature.

**$\text{MnO}@C$  nanowire:** 100 mg of the as-prepared  $\text{MnO}_2$  powders were dispersed in 30 ml of deionized water. And 15  $\mu\text{L}$  of aniline monomers was dissolved into a diluted  $\text{H}_2\text{SO}_4$  solution (0.05 M). Then the aniline-contained solution was added to the  $\text{MnO}_2$  suspension for polymerization. Two hours later, the dark green precipitates were obtained and washed using ethanol and deionized water. Finally, the as-prepared  $\text{MnO}_2@PANI$  products were carbonized at  $600^\circ\text{C}$  for 4 h under the protection of inert Ar gas flow, and black  $\text{MnO}@C$  powders were obtained. For comparison, pure  $\text{MnO}$  nanowires were yielded by annealing  $\text{MnO}_2$  under the same conditions. As for the synthesis of pure carbon nanotubes, pure PANI was first prepared using an excess amount of aniline monomers, followed by the same carbonization process.

**$\text{LiMn}_2\text{O}_4$  nanoparticle:** Manganese acetate ( $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ ) and lithium acetate ( $\text{LiAc} \cdot 2\text{H}_2\text{O}$ ) with a molar ratio of 2:1.1 were dissolved in a purity ethanol. The ethanol was then evaporated under magnetic stirring at  $100^\circ\text{C}$  to obtain a dried powder mixture. The mixture was then calcined at  $750^\circ\text{C}$  in air for 12 h.

### 2.2. Materials characterization

The crystallographic phase of the as-prepared samples was examined using X-ray powder diffraction (XRD, X'Pert Pro MPD, Philips). The morphology and the structure were observed using field emission scanning electron microscopy (FESEM, Zeiss Supra 55) and transmission electron microscopy (TEM, FEI Tecnai F30G<sup>2</sup>). Raman spectrum was recorded with a Renishaw Invia RM200

(England). The carbon content of the  $\text{MnO}@C$  nanocomposites was determined by thermogravimetric analysis (TGA–DSC 2, Switzerland) in an air atmosphere. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific) was employed to investigate the surface chemistry of the nanocomposites.

### 2.3. Electrochemical measurements

The electrochemical performance was evaluated using CR2032 coin-type cells. The working electrodes were fabricated by mixing active materials, carbon black and polyvinylidene fluoride (PVDF) binder in N-methylpyrrolidone (NMP) solvent with a weight ratio of 8:1:1. Then the resulting  $\text{MnO}@C$  and  $\text{LiMn}_2\text{O}_4$  slurries were pasted onto Cu and Al foils, respectively, followed by a vacuum drying at  $100^\circ\text{C}$  overnight. The mass loading of active materials was about 1.2 and  $3.5 \text{ mg cm}^{-2}$  in the anode and cathode, respectively. Coin half cells were assembled by using Li foil as the counter electrode, Celgard 2400 as the separator, and a solution of 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC) (1:1:1 by volume) in an argon-filled glovebox. For the full cell assembly, the  $\text{MnO}@C$  anode was first prelithiated by discharging the half cell to 0.005 V, because the large irreversible capacity loss of the  $\text{MnO}@C$  anode in the first cycle would lead to a severe capacity loss and degradation in a full cell (see Fig. S1 in the Supporting information) [27,29]. Then the lithiated anode was reassembled with a  $\text{LiMn}_2\text{O}_4$  cathode to constitute a full cell using the same assembling process. The galvanostatic charge/discharge measurements were performed on a Land battery system (LAND, BT2013A) at different current densities at a constant temperature ( $25^\circ\text{C}$ ). Solartron electrochemical workstation (1260+1287) was employed for obtaining cyclic voltammetry (CV) curves at a scan rate of  $0.2 \text{ mV s}^{-1}$  and electrochemical impedance spectra (EIS) in the frequency range from 100 kHz to 50 mHz.

## 3. Results and discussion

### 3.1. $\text{MnO}@C$ anode materials

As discussed earlier, the electrochemical performance of a full cell is closely associated with the  $\text{MnO}_x$  anode materials. Although carbon coating strategy has been proven to be effective to address the critical issues of  $\text{MnO}_x$  (i.e., a low electric conductivity and large volumetric variation), it is still a significant challenge to create a uniform carbon coating layer onto a  $\text{MnO}_x$  matrix. Fig. 1(a) shows the schematic illustration of our unique synthesis protocol of  $\text{MnO}@C$  nanocomposites. Herein, polyaniline (PANI) is employed as the carbon precursor. The PANI formation mechanism is on the basis of the reactive template of  $\text{MnO}_2$ , which does not require additional oxidative agents and organic surfactants. It is previously reported that  $\text{MnO}_2$  could be used as oxidants to synthesize polyaniline nanostructures, because the chemical oxidation potential of  $\text{MnO}_2$  in acidic condition ( $\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$ ,  $\varphi(\text{MnO}_2/\text{Mn}^{2+}) = 1.23 \text{ V}$ ) is much higher than that of aniline monomers (0.5 V) [30]. When the monomers are adsorbed on the  $\text{MnO}_2$  surfaces, an in situ polymerization occurs at the solid–liquid interfaces, thereby generating homogenous and conformal PANI nanocoating shells. The shell thickness can be easily modulated by changing aniline/ $\text{MnO}_2$  molar ratio. Finally, core-shell  $\text{MnO}@C$  nanowire composites with well-defined carbon shell and internal void spaces were obtained via a simple carbonization process.

Fig. 1(b) shows the XRD patterns of the as-prepared samples. The diffraction peaks of the pristine  $\text{MnO}_2$  can be readily indexed to the pure tetragonal phase of  $\alpha\text{-MnO}_2$  (JPCDS no. 44-0141) [31]. After a carbonization treatment, the annealed products derived

Download English Version:

<https://daneshyari.com/en/article/7953697>

Download Persian Version:

<https://daneshyari.com/article/7953697>

[Daneshyari.com](https://daneshyari.com)