



# Dealloying to porous hybrid manganese oxides microspheres for high performance anodes in lithium ion batteries



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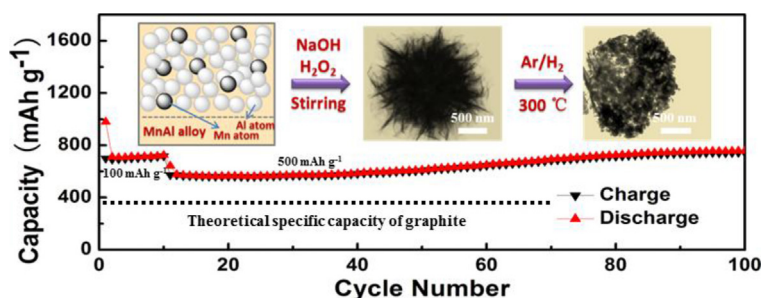
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## HIGHLIGHTS

- Hierarchical Mn-contained nano-flowers are synthesized by simple dealloying.
- Porous MnO<sub>x</sub> microspheres are obtained via mediate temperature annealing.
- MnO<sub>x</sub> exhibits a reversible capacity of 757 mAh g<sup>-1</sup> after 100 cycles at 500 mA g<sup>-1</sup>.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Mn-contained nano-flowers can be fabricated by dealloying Mn/Al alloys in aqueous NaOH solution in the presence of H<sub>2</sub>O<sub>2</sub>, and upon annealing the resulted samples exhibit a hierarchically porous MnO<sub>x</sub> microsphere morphology composed of nanoparticles of MnO and Mn<sub>3</sub>O<sub>4</sub>. When tested as anode materials for lithium ion batteries, those MnO<sub>x</sub> microspheres exhibit a high specific capacity of 1018, 901 and 757 mAh g<sup>-1</sup> with nearly 100% retention capacity after 100 cycles at 100, 200 and 500 mA g<sup>-1</sup>, respectively. The enhanced storage capacity, impressive cycling performance, and good rate capability for the electrodes are ascribed to the porous structures for buffering the volume change during the discharge/charge processes, and the nano-hybrids for enhancing electronic and ionic transport in the electrode materials.

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## 1. Introduction

Rechargeable lithium ion batteries (LIBs) with high storage capacity and cycling stability are considered to be the versatile, clean, and promising power sources to accommodate the rapid

development of portable electronic devices and hybrid electric vehicles [1–3]. Compared with the commercial graphite-based anode materials that typically show a theoretical specific capacity of 372 mAh g<sup>-1</sup> (for LiC<sub>6</sub>), transition metal oxides (M<sub>x</sub>O<sub>y</sub>, M = Fe [4], Co [5], Mn [6,7], Zn [8], etc.) could exhibit higher theoretical specific capacity (>600 mAh g<sup>-1</sup>) due to a special lithium oxidation-reduction storage mechanism (M<sub>x</sub>O<sub>y</sub> + 2y Li<sup>+</sup> + 2y e<sup>-</sup> ↔ y Li<sub>2</sub>O + x M), which are highly desired for the development of new generation high energy high power density LIBs [9]. Among various transition metal oxides, manganese oxides (MnO, Mn<sub>3</sub>O<sub>4</sub>, etc.) are

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characterized by low cost, high abundance, low voltage hysteresis, high theoretical specific capacity, and environment-friendliness [10,11]. However, during the discharge/charge cycling, manganese oxides have to confront substantial volume changes and structure deformation due to the redox conversion reaction, resulting in comparatively poor apparent electrochemical performance [12]. Therefore, new strategies have been explored for synthesizing various nano-structures (nanorod [13], sponge-like [14], porous microspheres [15,16] and nano-sheet [17]) to improve the capacity and cycling stability of manganese oxides. Especially, these porous micro/nano-structures with enough space can enhance the capacity retention by reversibly accommodating large volume changes [18–20]. Among reported approaches, manganese oxides (especially MnO) were often fabricated by hydrothermal [21], template [22], wet-impregnation [23] and chemical sputtering [24], which are more or less associated with the use of surfactants, organic agents, templates, sophisticated equipment, thus restricting the application of manganese oxides as green anode materials for LIBs.

Compared with approaches mentioned above, dealloying, usually adopted to manipulate nanoporous metals [25–27], is in recent years under intensive development due to its ease in room temperature aqueous solution processing to various functional transition metal oxides [28–30]. Taking aluminum-based alloys as an example, this method only requires the immersion of the M/Al ( $M = \text{Fe, Co, Mn, Ti, etc.}$ ) alloys into NaOH solution under ambient atmospheric conditions and can readily scale up for mass production. More recently, Hao et al. reported that the capacity of  $\text{Mn}_3\text{O}_4$  octahedra [31] for LIBs anodes dropped to  $335 \text{ mA h g}^{-1}$  after 50 cycles at  $100 \text{ mA g}^{-1}$ . As discussed above, porous structures may reduce the intrinsic strain-stress caused by the severe volume change of  $\text{M}_x\text{O}_y$  electrode materials, and nanoscale particles could shorten the electronic and ionic transport pathway. In present work, we provide a modified dealloying process to the fabrication of hierarchically porous  $\text{MnO}_x$  microspheres. By optimizing the interfacial structures of different components, these nanocomposites exhibit impressive electrochemical performance as LIBs anodes.

## 2. Experimental section

### 2.1. Synthesis method

#### 2.1.1. Synthesis of Mn-based precursor

Mn/Al alloys were prepared by melting high purity Mn (99.9 wt.%) and Al (99.9 wt.%) in 5:95 atomic ratio in a quartz crucible in atmosphere. The alloys were cut into appropriate size and re-melted in a quartz tube, which upon a subsequent melt-spinning, generated thin foils with thickness of  $\sim 50 \mu\text{m}$  [30]. Mn/Al alloy foils were placed into 72 mL  $\text{H}_2\text{O}$  and 28 mL  $\text{H}_2\text{O}_2$  (30 wt.%) in a 500 mL flask under magnetic stirring. Then, 100 mL NaOH ( $2 \text{ mol L}^{-1}$ ) was added into the flask at a rate of about  $10 \text{ mL min}^{-1}$  under vigorously stirring, and maintained for 8 h. The products were collected by centrifugation, and then washed several times with ultra-pure water and dried in vacuum oven.

#### 2.1.2. Synthesis of porous $\text{MnO}_x$ microspheres

Porous  $\text{MnO}_x$  microspheres were synthesized by calcining the Mn-based precursors at  $300 \text{ }^\circ\text{C}$  for 5 h in Ar/ $\text{H}_2$  atmosphere, at an increasing rate of  $5 \text{ }^\circ\text{C min}^{-1}$ . The final product was washed several times with ultra-pure water and dried in vacuum oven.

### 2.2. Characterizations

The X-ray powder diffraction (XRD) patterns were obtained on a Bruker D8 advanced X-Ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The microstructures of the as-prepared materials were characterized by scanning emission microscope (SEM, Hitachi X650), transmission electron microscope (TEM, JEOL JEM-1011) and HRTEM (JEOL JEM-2100). Element was analyzed on X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The  $\text{N}_2$  adsorption/desorption isotherms were obtained from a Quadrasorb SI analyzer at 77 K.

### 2.3. Electrochemical measurements

The electrodes were prepared by making slurry of 70 wt.% active materials, 20 wt.% Super-P carbon black and 10 wt.% carboxymethylcellulose sodium (CMC) in ultrapure water. The slurry with a wet film thickness of about  $300 \mu\text{m}$  was coated on Cu foil and dried in vacuum at  $60 \text{ }^\circ\text{C}$  for 12 h. The resultant films were pressed and punched into the discs with a diameter of 12 mm and used as the electrodes. The cells were assembled in an argon-filled glove box using metallic lithium as the counter electrode, Celgard 2300 membrane as a separator and  $1 \text{ mol L}^{-1}$   $\text{LiPF}_6$  in a mixture of ethylene carbonate and dimethyl carbonate (1:1 volume) as the electrolyte. Cyclic voltammetry (CV) was operated between 0.05 and 3.0 V at a scanning rate of  $0.1 \text{ mV s}^{-1}$  from an electrochemical workstation (CHI 760C, Shanghai, China). Galvanostatic discharge/charge cycles were performed between 0.05 and 3.0 V on a lithium battery cycler (LAND CT-2001A, Wuhan, China) at  $30 \text{ }^\circ\text{C}$  in the incubator. In comparison, Mn-based precursors of nano-flowers, MnO (purchased from Aladdin Industrial Co., Ltd) and  $\text{Mn}_3\text{O}_4$  (purchased from Sinopharm Chemical Reagent Co., Ltd) electrodes were prepared in the same way. Electrochemical impedance spectroscopy (EIS) was performed on a Zahner IM6 electrochemical workstation (Zahner-Elektrik GmbH & Co.KG, Germany) in a frequency range of 100 kHz to 0.01 Hz.

## 3. Results and discussion

The approach to hierarchically porous  $\text{MnO}_x$  microspheres is illustrated in Fig. 1. In alkaline solution, Al atoms in the Mn/Al alloys are preferentially dissolved, left behind Mn species, which react with other chemicals in the solution to form nano-sheets which in turn assemble into a nano-flower structure in the presence of  $\text{H}_2\text{O}_2$ . Upon thermal annealing, these nano-flowers decompose into microspheres with porous structures which can be deemed as controlled aggregates of nanoparticles.

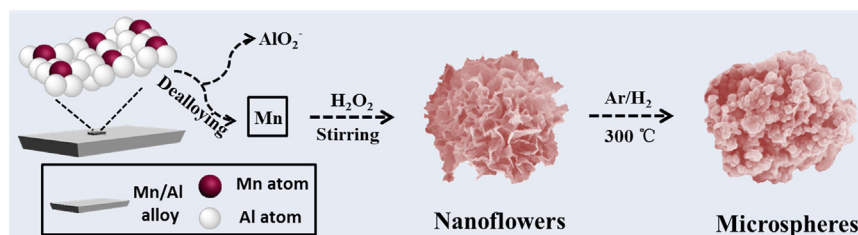


Fig. 1. Schematic illustration of the formation process of porous  $\text{MnO}_x$  microspheres.

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