



Optimal hydrothermal synthesis of hierarchical porous ZnMn₂O₄ microspheres with more porous core for improved lithium storage performance



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ABSTRACT

ZnMn₂O₄ spinel is a promising anode material for lithium-ion batteries (LIBs) which can utilize both conversion reaction and alloying reaction to provide its lithium storage capacity. In this study, we developed hierarchical porous ZnMn₂O₄ microspheres with more porous interior as high-performance anode for LIBs by adjusting the parameters of hydrothermal synthesis (e.g., temperature and time). With increasing hydrothermal temperature, the morphology of the microspheres progressively changed from a hollow interior to a porous interior, while the thickness of the more dense shell was reduced. The crystallinity of the spinel phase increased with hydrothermal temperature and time. The resultant morphologies of the samples indicate the dominant formation of hollow microspheres at 140 and 160 °C and porous microspheres with more dense shell at 180 °C. N₂ adsorption-desorption isotherms reveal the dominant presence of mesopores and increased porosity with increasing temperature and time durations. Tested in a coin-type half-cell with Li counter electrode, a sample with optimized hydrothermal condition at 180 °C for 9 hours provides the optimal anode performance, retained 726 mAh g⁻¹ capacity after 90 cycles at 500 mA g⁻¹ current discharge rate.

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1. Introduction

Rechargeable lithium ion batteries (LIBs) have become the energy storage device of choice given their high voltage (and thus high energy density), long life and light weight [1–3]. For applications in hybrid or all-electric vehicle and in large-scale energy grid systems, however, a significant improvement of the energy density from that offered by the state-of-the-art LIBs technologies with graphite-based anode and LiCoO₂ cathode (of 150 Wh kg⁻¹) is required [4,5]. The increase in energy densities of LIBs can be attained by developing high voltage cathodes and/or high capacity cathodes and/or high capacity anodes [6,7]. Towards high capacity anodes development, various transition metal single oxides and mixed metal oxide frameworks have been assessed as potential candidates from the perspective of their potential high reversible capacity as compared to graphite in addition to abundant availability [8–10]. In particular, ZnMn₂O₄ spinel has

been widely studied due to abundant resources of Zinc and Manganese, low price, non-toxicity and high electrochemical activity. Furthermore, the suitable allocation of bivalent Zn²⁺ in the tetrahedral site and trivalent Mn³⁺ in the octahedral sites within the spinel structure ensures the stable cycle performance [11,12]. The theoretical specific capacity of ZnMn₂O₄ reaches 784 mAh g⁻¹, which is made available through conversion reactions (i.e., ZnMn₂O₄ + 8Li⁺ + 8e⁻ → Zn + 2Mn + 4Li₂O; Zn + Li₂O → ZnO + 2Li⁺ + 2e⁻ and Mn + Li₂O → MnO + 2Li⁺ + 2e⁻) and alloying reaction (i.e., Zn + Li⁺ + e⁻ → LiZn) [13]. Accordingly, in addition to the dual lithium storage capacity enabled by Zn and Mn conversions within the framework, additional storage capacity comes from the Zn capability to form alloy with Li.

Still, challenges remain for practical application of ZnMn₂O₄ spinel material due to its poor electrical conductivity and large volume change during charge/discharge which leads to poor rate capability and quick capacity degradation [14,15]. To address these drawbacks, developing novel nano-structure to enhance its capacity and rate capability is required [16–19]. Within this context, the particle size reduction to nanometer scale is envisioned to enhance the electrons and lithium ions transport

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by reducing diffusion distance for charged species, which also translates to increased effective surface area (on electrode) for charge transfer. Yang and co-workers prepared ~30–60 nm particles by a polymer-pyrolysis method, which demonstrated a relatively high capacity of 569 mAh g^{-1} at 100 mA g^{-1} discharge rate on its 50th cycle [20]. Courtel et al. employed a co-precipitation process to synthesize nanoparticles with ~75–150 nm size which attained a capacity of 690 mAh g^{-1} at 0.1 C discharge rate (Note: 1 C is the current rate at which the battery can be completely discharged in 1 hour) after 70 cycles [21].

Considering the low current collection efficiency on nanoparticles, agglomerating nanoparticles to porous micrometer-sized particles is highly attractive, since it combines the advantages of the facile current collection for microparticles and the short diffusion distance and the large surface area for nanoparticles to obtain increased capacity and rate capability [22–24]. In addition, the porous space inside the microparticles may further provide buffer space for the volume change of the electrode material during the charge-discharge process, thus improving the cycling stability [25–27]. Spherical morphology structure is highly desirable for LIB electrode in view of higher packing density. Different types of ZnMn_2O_4 microspheres have been synthesized and investigated for LIBs anode. Recently, flower-like microspheres comprising numerous randomly oriented tapering nanorods was synthesized by Xiao and co-workers and showed a capacity of 626 mAh g^{-1} after 50 cycles at a current rate of 100 mA g^{-1} [28]. Lou et al. synthesized hollow microspheres with ~2–4 μm diameter via a co-precipitation and annealing method which exhibited a capacity of 607 mAh g^{-1} at 400 mA g^{-1} after 100 cycles [29]. They also developed a polyol method combined with post-annealing process to obtain ball-in-ball hollow microspheres which provided a capacity of 750 mAh g^{-1} at 400 mA g^{-1} after 120 cycles [30]. Wang et al. reported one step hydrothermal route to prepare ZnMn_2O_4 hollow microspheres with 0.5–3 μm diameter; the Li half-cell of which attained a capacity of 737 mAh g^{-1} at 50 mA g^{-1} current rate after 100 cycles in addition to a capacity of 283 mAh g^{-1} at 400 mA g^{-1} current rate [31].

From a practical use point of view, the ideal ZnMn_2O_4 microspheres for LIBs should have sufficiently high mechanical strength to prevent the collapse of the structure during cycling, abundant void space to buffer the expansion of the electrode material during the charge/discharge processes, short diffusion distances for electrons and lithium ions, and minimized movement distance for the electrode material while accommodating the volume change from conversion/alloying reaction. For these considerations, the distribution of void space within the whole microspheres is more preferable than a hollow microsphere particularly since hollow microsphere may allow larger contraction and expansion. To achieve better mechanical strength and higher current collection efficiency, denser surface is preferable for ZnMn_2O_4 electrode since the pulverization of the surface layer can deteriorate the overall contact between the electrode particles and conducting additives. Core-shell structured microspheres with denser surface is considered a better choice than flower-like microspheres with low surface area.

Herein, we developed a core-shell structured microsphere ZnMn_2O_4 as the anode for LIBs. The highly mesoporous structure of the microsphere ensures penetration of liquid electrolyte and effectively accommodates the volume expansion of the electrode material. In addition, denser surface provides better mechanical strength and more efficient current collection. Furthermore, the fine crystals of ZnMn_2O_4 microspheres enable shorter Li^+ and electron diffusion length. More significantly, such morphology structure of ZnMn_2O_4 can be easily obtained by adjusting the temperature and the duration of the one-pot hydrothermal synthesis. The as-obtained hierarchical mesoporous ZnMn_2O_4

microspheres showed improved capacity, rate capacity and cycling stability as compared with the hollow microsphere counterpart.

2. Experimental

2.1. Materials synthesis

In a typical synthesis of hierarchical ZnMn_2O_4 microspheres: de-ionized water and absolute ethyl alcohol (1:3 in volume) were mixed under magnetic stirring to form a 60 mL transparent solution as the hydrothermal solvent. After that, 1.2 mmol citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), 0.5 mmol of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 1.0 mmol of manganese (II) nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) were dissolved into the solvent under continuous magnetic stirring for 30 min. The resultant mixture was then transferred into a 100 mL-Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at different temperatures and times in an oven. Upon cooling to ambient temperature, the final yellowish-brown solid products were collected using filtration and washed with de-ionized water and ethanol several times followed by drying at 60°C in an oven overnight.

2.2. Characterizations

The crystal structures of the products were characterized by powder X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with filtered $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) over a 2θ range of $10\text{--}90^\circ$. The morphologies of the resultant samples were probed using field-emission scanning electron microscope (FESEM, Hitachi S-4800) and transmission electron microscope (TEM, JEOL JEM-2100). The specific surface area and porosity of the products were quantified by N_2 adsorption-desorption isotherms at 77 K using a BELSORP II instrument.

2.3. Electrochemical measurements

The working electrode was prepared by mixing 80 wt.% of active material, 10 wt.% of Super P (as conductive additive) and 10 wt.% of polyvinylidene fluoride (PVDF) (as binder) with N-methyl-2-pyrrolidone (NMP) (as solvent); to form slurry. The slurry was subsequently coated onto the surface of a copper foil and dried at 100°C for 12 hours under vacuum. Electrochemical measurements were performed using coin cells (CR2016) assembled in a glove box filled with argon. Lithium foil was used as both the counter electrode and the reference electrode. The electrolyte was 1 M LiPF_6 in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 in volume). The charge and discharge profile of the cells were recorded over the potential range between 0.01 and 3.0 V using a NEWARE BTS computer-controlled galvanostat. The cyclic voltammetry (CV) was obtained using a Princeton Applied Research potentiostat/galvanostat model 273A at 0.1 mV s^{-1} scan rate between 0.01 and 3.0 V. Electrochemical impedance spectroscopy (EIS) was carried out under open circuit potential using a PARSTAT 2273 potentiostat in the frequency range of 100 kHz to 10 mHz.

3. Results and discussion

3.1. Structure and morphology evolution

Temperature and time duration during the hydrothermal synthesis were found to affect significantly the particulate morphology and crystallite size of the hydrothermal products while the crystalline structure was less affected. To investigate the

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