Facile synthesis of interconnected mesoporous ZnMn$_2$O$_4$ nano-peanuts for Li-storage via distinct structure design

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A B S T R A C T

The ZnMn$_2$O$_4$ nano-peanuts with diameters of 16–25 nm have been successfully prepared through a simple one-step surfactant-assisted solvothermal process. The as-synthesized ZnMn$_2$O$_4$ exhibits novel interconnected mesoporous hierarchical architecture, which possesses three advantages: special mesoporous structure, high specific surface and interconnected walls. On one hand, the interconnected structure can provide sufficient surface reaction sites to fully contact Li$^+$ with the electrolyte and improve Li$^+$ diffusion and electron transfer; On the other hand, the mesoporous hierarchical networks can buffer the volume change, accommodate or alleviate the strain during charge-discharge process, thus enhancing the conductivity and stability of the electrodes. Benefiting from the mesoporous design, the interconnected ZnMn$_2$O$_4$ delivers a stable capacity (812 mA h g$^{-1}$ at 100 mA g$^{-1}$ after 200 cycles), and maintains a high capacity of 516 mA h g$^{-1}$ even at 2 A g$^{-1}$ after 200 cycles, which shows that the nanostructured ZnMn$_2$O$_4$ has excellent cycling stability.

1. Introduction

Owing to the fact that traditional energy brings serious environmental pollution, the demand for clean energy is constantly increasing. Lithium-ion batteries (LIBs) have attracted tremendous attention due to their high energy density, high power density and long cycle life [1–3]. At present, graphite-based materials have been utilized as anode materials for commercial LIBs. Unfortunately, the relatively low theoretical capacity of 372 mA h g$^{-1}$ has hindered the further application of LIBs in power vehicles and high-performance requirements [4,5]. As a consequence, it is imperative for researchers to develop novel electrode materials, especially anode materials [2,3,6]. Over the past two decades, transition metal oxides have been identified as potential candidates for high theoretical capacities, environmental friendliness and low cost. Recent studies have found that mixed transition metal oxides (MTMOs) are diverse and complementary compared with single transition metal oxides (STMOs), and thus have enhanced electrochemical performance [6–9]. Spinel-structured ZnMn$_2$O$_4$ with a bivalent Zn$^{2+}$ ion at tetrahedral sites and a trivalent Mn$^{3+}$ ion at octahedral sites stands out among the intriguing mixed manganite oxides, by the virtues of high theoretical capacity, environmental friendliness, low cost and the low oxidation potentials (i.e., delithiation potential) of zinc and manganese at 1.2 and 1.5 V (vs. Li$^+$/Li$^{1+}$) [8–14], which allow large output voltage in batteries, finally resulting in a high specific energy density.

However, similar to most of high capacity materials, ZnMn$_2$O$_4$ suffers particle aggregation and large volume variation during charge-discharge process, which inevitably leads to polarization of electrode and a loss of inter-particle electronic contact and consequently poor stability against cycling [15–17]. ZnMn$_2$O$_4$ nanoparticles of 30–60 nm in size show a reversible capacity up to 569 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$ after 50 cycles, which may suffer particle aggregation after cycles [18]. Yuan et al. reported ZnMn$_2$O$_4$ hollow metal glycolate microspheres with a discharge capacity of 750 mA h g$^{-1}$ at 400 mA g$^{-1}$, which may cause large volume changes and fast drop after 120 cycles [18–22]. The researchers tried their best to maintain the volume and cycling stability of ZnMn$_2$O$_4$, but still have no satisfactory results in the case of large volume variation and rapid drop in capacity. To solve these problems, one of the strategies is to combine with carbon material, but it will decrease the total capacity of the electrode due to the presence of low-capacity carbon. Another strategy is to design the microstructure and regulation of nanomaterials (such as porous structure), that is, to optimize electrode structure considering the stability of the electrodes.

Porous nanostructured materials can not only facilitate the transport kinetics for Li$^+$ and electron, but also increase the active sites of electrochemical reactions, and at the same time, they also could provide enough space to buffer volume change and avoid particle aggregation.

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during the discharge-charge process [15,23]. Therefore, the combination of nanocrystallization and porosity is one of the practical methods to improve the relevant electrochemical performance of electrode materials. Herein, we report the uniform mesoporous ZnMn$_2$O$_4$ nano-peanuts with diameters of 16–25 nm. The ZnMn$_2$O$_4$ nano-peanuts are not only non-toxic and environment-friendly, but also have three advantages: special mesoporous structure, high specific surface area and interconnected walls. When evaluated for LIBs, ZnMn$_2$O$_4$ nano-peanuts deliver a stable capacity of 812 mA h g$^{-1}$ at 100 mA g$^{-1}$ after 200 cycles, showing higher reversible capacity and superior cycle performance compared with bulk ZnO and bulk Mn$_2$O$_3$.

2. Experimental

All chemicals were of analytical grade and used directly without further purification. Distilled water was used throughout the whole experiments.

2.1. Synthesis of mesoporous ZnMn$_2$O$_4$ nano-peanuts

ZnMn$_2$O$_4$ nano-peanuts were synthesized by a simple solvothermal method. Firstly, 2.0 g of hexadecyl trimethyl ammonium bromide (CTAB) was dissolved in 50 mL ethylene glycol to form a homogeneous solution under vigorous stirring at room temperature. Secondly, 1.0 mmol of zinc acetylacetonate Zn(acac)$_2$ was added to the above solution. Thirdly, 1.0 mmol of manganese acetylacetonate Mn(acac)$_2$ was added to the former solution and then kept ultrasonically for 30 min. After that, the mixed solution was under vigorous stirring for 15 min. The obtained mixed solution was transferred into a 100 mL Teflon-sealed autoclave and maintained at 180 °C for 13 h to obtain the precursor. After the reaction system dropped to room temperature, the resultant precipitates were collected by centrifugation, washed several times with distilled water and ethanol, and then dried at 60 °C for 6 h. To obtain the uniform nano-peanuts, the precursor was annealed in air at 600 °C for 3 h at the ramp rate of 4 °C min$^{-1}$.

2.2. Synthesis of bulk ZnO and bulk Mn$_2$O$_3$

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XRD with Cu-K$_\alpha$ radiation ($\lambda$ = 1.5406 Å). Thermogravimetric analysis (TGA) was conducted on a Netzsch TG 209 apparatus with a heating rate of 10 °C min$^{-1}$. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi instrument with monochromatic Al K$\alpha$ radiation ($h\nu$ = 1486.6 eV) at ultrahigh vacuum (below 10$^{-8}$ Pa). The binding energies were calibrated using C 1 s peak (284.8 eV) as a reference.

2.3. Material characterization

Crystallographic phases of the samples were analyzed by SmartLab XRD with Cu-K$_\alpha$ radiation ($\lambda$ = 1.5406 Å). Thermogravimetric analysis (TGA) was conducted on a Netzsch TG 209 apparatus with a heating rate of 10 °C min$^{-1}$. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi instrument with monochromatic Al K$\alpha$ radiation ($h\nu$ = 1486.6 eV) at ultrahigh vacuum (below 10$^{-8}$ Pa). The binding energies were calibrated using C 1 s peak (284.8 eV) as a reference.

2.4. Electrochemical measurements

Working electrodes were prepared by mixing the as-prepared active materials (ZnMn$_2$O$_4$ nano-peanuts, bulk ZnO and bulk Mn$_2$O$_3$) with water-soluble sodium alginate (SA) and carbon black in a weight ratio of 70:15:15 (wt.%) on a clean copper foil. The copper was dried at 85 °C for 12 h in a vacuum oven and the CR2025-type coin cells (20 mm in diameter and 2.5 mm in thickness) were assembled in a glove box filled with argon with a moisture and oxygen concentration of less than 1 ppm. The mass loadings of ZnMn$_2$O$_4$, ZnO and Mn$_2$O$_3$ composites for cell testing were 1.2 mg, 1.1 mg and 1.0 mg, respectively. The electrolyte consisted of 1 M LiPF$_6$ solution of ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 in volume). The electrochemical performances were tested on a LAND CT2001 battery test system in a voltage range of 0.01 V–3.00 V at room temperature. Cyclic voltammetry (CV) measurements (over the potential range of 0.01 V–3.00 V at a scan rate of 0.1 mV s$^{-1}$) and electrochemical impedance spectroscopy (EIS) tests were carried out on a Metrohm Autolab electrochemical workstation (PGSTAT 302 N) with a frequency range from 100 kHz to 0.01 Hz.

3. Results and discussion

The Zn-Mn oxides were prepared by a simple solvothermal method and carbonization process. Fig. 1a shows the XRD patterns of the products before and after annealing at 600 °C for 3 h in air. The diffraction peaks at around 33°, 36° and 38° are the characteristics of metal glycolates [24]. For the products after annealing, these peaks can be indexed to tetragonal ZnMn$_2$O$_4$ (JCPDS no.: 77-0470, $a = b = 5.720\, \text{Å}$, $c = 9.240\, \text{Å}$). The sharp diffraction peaks at 20 of 18.22°, 29.32°, 31.24°, 33.00°, 36.41° and 60.82° can be assigned to (101), (112), (200), (103), (211) and (224) crystal planes, respectively, indicating the high purity of synthesized sample. For the ZnO and Mn$_2$O$_3$ (Fig. 1b), all the diffraction peaks correspond to hexagonal ZnO (JCPDS no.: 76-0704) and cubic Mn$_2$O$_3$ (JCPDS no.: 71-0636), respectively. Fig. 1c shows the TG-DTA analysis of the products before annealing. The TG-DTA analysis was performed in air at a ramp rate of 10 °C min$^{-1}$ from 30 °C to 800 °C. It can be seen that there is a significant weight loss at 85–550 °C, indicating a total weight loss of 13%. The weight loss may be ascribed to the evaporation of water and the decomposition of CTAB. Subsequently, the TG curve has no significant weight loss above 550 °C, indicating that the ZnMn$_2$O$_4$ has excellent thermal stability at even higher temperatures. Therefore, we determine that the heat treatment temperature of the products is 600 °C, and we believe that under this condition, the precursor can be completely converted to the final ZnMn$_2$O$_4$.

To determine the chemical composition and chemical valence state of the as-synthesized products, XPS analysis was performed, and the results are shown in Fig. 2. Fig. 2a demonstrates the photoelectron spectra of the Zn, Mn, O and C elements, where C is inferred from the carbonate species of the XPS instrument. As shown in Fig. 2b, the peaks at 1044.4 eV and 1021.1 eV can be assigned to Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$. The splitting gap between these two peaks is 23.3 eV, which is consistent with that of ZnMn$_2$O$_4$ [25]. Additionally, in Fig. 2c, the peaks at 653.9 eV and 642.1 eV can be assigned to Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$ [26]. The energy difference between Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$ is approximately 11.9 eV. As reported previously, it can be demonstrated that the manganese ion in the ZnMn$_2$O$_4$ is trivalent [27]. The O 1 s spectrum can be
and severely agglomerated, as shown in Fig. S2. Mesoporous and macroporous structure can overcome the major kinetic limitations of electrochemical processes and act as ion buffering reservoirs during the de-intercalation of lithium [29–31]. The ultra-small particles can not only provide active sites for the insertion and extraction of Li⁺, but also reduce the diffusion distance of Li⁺, which can overcome the diffusion limitations of LIBs [32,34]. Meanwhile, the mesoporous features have great benefits for the transport and diffusion of electrolyte during the charge-discharge process. Fig. 3d shows the elemental mapping and the EDS spectrum of the samples, indicating that the Zn, Mn, and O are uniformly distributed in ZnMn₂O₄. The EDS spectrum indicates that the mesoporous ZnMn₂O₄ nano-peanuts mainly consist of Zn, Mn, and O. In addition, the atomic ratio of Zn/Mn is determined to be about 1:2, which is consistent with the stoichiometry ratio of ZnMn₂O₄. The same solution was established using CTAB to obtain bulk ZnO and bulk Mn₂O₃, but the products were heterogeneous, as shown in Figs. 3e and f. Under the same preparation conditions, ZnMn₂O₄ is much more homogeneous compared to ZnO and Mn₂O₃, which could be caused by the synergistic features of the combination of Zn ion and Mn ion.

To further investigate the microstructure of the ZnMn₂O₄, we also carried out extensive TEM examination of the ZnMn₂O₄ nano-peanuts. Figs. 4a, c show BF TEM images of ZnMn₂O₄. Fig. 4b presents that the as-prepared ZnMn₂O₄ nano-peanuts are uniform, with an average diameter of 18 nm. It can be clearly seen from Fig. 4c that the nano-peanut consists of two or three interconnected nanoparticles with a diameter of 16–25 nm, which is consistent with the SEM results. Fig. 4d shows the HRTEM image of the ZnMn₂O₄, which is taken along (102) zone-axis. A clear lattice fringe can be clearly seen, which corresponds to the crystal planes of ZnMn₂O₄ nano-peanuts. The crystal lattice spacings measured from HRTEM images are 2.86, 2.47 and 2.47 Å, respectively, which correspond to the interplanar spacings of (020), (211) and (211) planes of the tetragonal ZnMn₂O₄.

In general, both the high specific surface area and suitable pore size play important roles in the electrochemical properties of the electrode materials. Thus, an N₂ adsorption/desorption test was conducted on the activated ZnMn₂O₄ to evaluate the permanent porosity. As shown in Fig. 5a, the curve illustrates the reversible type-III isotherm with hysteresis loops at the relative pressure P/P₀ of 0.55–1.0, which is one of the main characteristics of mesoporous materials. The specific surface area of ZnMn₂O₄ is 104.16 m² g⁻¹ and the total pore volume is 0.290 cm³ g⁻¹. The pore size distribution curve was calculated by the BJH desorption branches and the pores are in the range of 8–20 nm (Fig. 5b). The presence of a high surface area and mesoporous structure with a suitable pore size keeps the electrolyte and materials in effective contact and facilitates the diffusion of lithium ions in the electrode [35–37]. Such a mesoporous hierarchical architecture will effectively promote lithium storage, because it can enhance the diffusion of electrolyte into the active materials and buffer against the volume change during the charge-discharge process.

To study the ion diffusion process and phase transition of the electrode materials during charge-discharge process, the CV curve of ZnMn₂O₄ nano-peanuts was tested. Fig. 6a shows the cyclic voltammetric (CV) curves for the first six cycles of ZnMn₂O₄ at the potential range of 0.01–3.00 V (vs. Li/Li⁺) with a scan rate of 0.1 mV s⁻¹. In the first cycle, there is a slight reduction peak at 1.12 V, which could be ascribed to the reduction of Mn³⁺ to Mn²⁺ [37]. Another strong reduction peak at 0.14 V is considered to be the reduction from Mn²⁺ and Zn²⁺ to metallic Mn and Zn in Li₂O matrix. In the meantime, it also can be connected to the formation of solid electrolyte interface (SEI) due to the electrolyte degradation, resulting in a large initial irreversible capacity [38,39]. Moreover, there is a broad and weak peak below 0.14 V, which is the formation of ZnLi alloy. The oxidation peaks at approximately 1.2 V and 1.5 V correspond to the oxidation of Mn⁺ and Zn⁺ to Mn²⁺ and Zn²⁺, respectively, along with the decomposition of Li₂O matrix. In the following cycles, the oxidation peaks are similar to the first cycle, which show the analogous electrochemical process for
Fig. 2. XPS core level spectra of as-fabricated nanocrystalline ZnMn$_2$O$_4$. (a) full scan, (b) Zn 2p, (c) Mn 2p, (d) O 1s of ZnMn$_2$O$_4$.

Fig. 3. (a,b) SEM images of the final ZnMn$_2$O$_4$; (c) A low magnification FESEM image and Zn, Mn, O elemental mapping of ZnMn$_2$O$_4$; (d) Typical EDS spectrum of ZnMn$_2$O$_4$; (e) SEM image of bulk ZnO; (f) SEM image of bulk Mn$_2$O$_3$. 
the anodic scan. While the reduction peaks shift from 0.14 V to 0.45 V, which may be related to the rearrangement of structure [35]. And the peaks at around 0.45/1.25 V corresponds to the redox reaction between Mn and MnO, while 0.8/1.5 V corresponds to the reduction/oxidation of ZnO [24]. The CV curves of the second and sixth cycles almost overlap, indicating high electrochemical reversibility and good structural durability of the electrode fabricated during the insertion and extraction of Li⁺ from the ZnMn₂O₄ nano-peanuts [27].

Fig. 6b shows the representative galvanostatic discharge-charge curves of the ZnMn₂O₄ nano-peanuts electrode from the first to third cycles, which was tested at a current density of 100 mA g⁻¹ (vs. Li/Li⁺). Obviously, the initial discharge process can be divided into three stages. In the first stage, the voltage drops very quickly. In the second stage, the curve exhibits a short platform at about 1.25 V, which is assigned to the Mn-III/II reduction, and also shows a long platform at about 0.45 V, which corresponds to the formation of Zn°, Mn° and Li-Zn alloy, consistent with the CV results. In the third stage, the voltage slowly drops and this process stores most of the lithium ions and contributes to the most of discharge capacity. The initial discharge and charge capacities of the ZnMn₂O₄ nano-peanuts are 1289 and 863 mA h g⁻¹, respectively, and the initial charge-discharge coulombic efficiency is 64.5%. This may be ascribed to the formation of the SEI layer and electrolyte decomposition, which is common to most anode materials [32]. In the second cycle, the discharge profile exhibits a specific capacity of approximately 870 mAhg⁻¹, which is similar to the first charge curve, but with a lower capacity and a higher plateau voltage. Moreover, the subsequent discharge-charge curves demonstrate a qualitative resemblance to the second cycle curve, except for a slight decreasing capacity and a stable capacity. All of these phase transitions after the reduction and oxidation processes are in good agreement with the CV results.

As presented in Fig. 6d, the rate performance of ZnMn₂O₄ nano-
peanuts was measured at various current densities from 0.1 to 2 A g\(^{-1}\). Obviously, the capacities of ZnMn\(_2\)O\(_4\) decrease as the currents increase. When the current rises to 2 A g\(^{-1}\), the capacity is 550 mA g\(^{-1}\). More importantly, when the current density is restored to 0.1 A g\(^{-1}\), the capacity is higher than the initial capacity at 0.1 A g\(^{-1}\). The cycling performance of the ZnMn\(_2\)O\(_4\) was tested via the galvanostatic charge-discharge cycling at a current density of 100 mA g\(^{-1}\) (Fig. 6e). The capacity curve for 100 mA g\(^{-1}\) showed a reduction in the first few cycles, which may be due to the irreversible reactions and rapid structure changes. Afterwards, the capacity curves decreased slightly and then stabilized at 812 mA h g\(^{-1}\) after 200 cycles. Such a phenomenon was generally observed for the transition metal oxide-based anodes and was commonly ascribed to the reversible formation of a polymeric gel-like film that originates from kinetic activation in the electrode [11,26]. To further evaluate the electrochemical properties of the ZnMn\(_2\)O\(_4\) peanuts, the battery was charged and discharged at a high current density of 2 A g\(^{-1}\). To our surprise, 516 mA h g\(^{-1}\) discharge capacity remained after 200 cycles. As shown in Fig. 6c, we make the comparative cycling performance of ZnMn\(_2\)O\(_4\) nano-peanuts, bulk ZnO and bulk Mn\(_2\)O\(_3\) at a current density of 500 mA g\(^{-1}\). It can be seen that the ZnMn\(_2\)O\(_4\) nano-peanuts can maintain a reversible capacity value of 586 mA h g\(^{-1}\) after 30th cycles. Subsequently, the reversible capacity increased slightly and then stabilized. The bulk Mn\(_2\)O\(_3\) begins to rise at about the 40th cycle, but starts to decline after the 150th cycle. The reversible capacity of the bulk ZnO is the worst among the three materials. The above results indicate that the nano-peanuts-like ZnMn\(_2\)O\(_4\) possesses excellent electrochemical properties. As an anode material, the electrochemical performance of ZnMn\(_2\)O\(_4\) nanostructures could be comparable to outstanding performance of magnesium molybdate in the battery system [33]. All in all, the excellent stability of ZnMn\(_2\)O\(_4\) peanuts, the battery was charged and discharged at a high current density of 2 A g\(^{-1}\). To our surprise, 516 mA h g\(^{-1}\) discharge capacity remained after 200 cycles. As shown in Fig. 6c, we make the comparative cycling performance of ZnMn\(_2\)O\(_4\) nano-peanuts, bulk ZnO and bulk Mn\(_2\)O\(_3\) at a current density of 500 mA g\(^{-1}\). It can be seen that the ZnMn\(_2\)O\(_4\) nano-peanuts can maintain a reversible capacity value of 586 mA h g\(^{-1}\) after 30th cycles. Subsequently, the reversible capacity increased slightly and then stabilized. The bulk Mn\(_2\)O\(_3\) begins to rise at about the 40th cycle, but starts to decline after the 150th cycle. The reversible capacity of the bulk ZnO is the worst among the three materials. The above results indicate that the nano-peanuts-like ZnMn\(_2\)O\(_4\) possesses excellent electrochemical properties. As an anode material, the electrochemical performance of ZnMn\(_2\)O\(_4\) nanostructures could be comparable to outstanding performance of magnesium molybdate in the battery system [33]. All in all, the excellent stability of ZnMn\(_2\)O\(_4\)
can be attributed to the homogeneous nanoparticles and the heterogeneous pores distributed among the particles [6,7,28].

To further explore excellent electrochemical performance of the interconnected mesoporous ZnMn2O4 nano-peanuts, the EIS measurements were performed. As shown in Fig. 7, typical EIS data of the bare charged electrodes during the first and the 200th cycle are represented in Nyquist plots ($Z'$ vs. $-Z''$). In the medium frequency range, the diameter of the semicircle indicates the Li$^+$ transport resistance of the SEI layer ($R_{sf}$) and the charge-transfer resistance ($R_{ct}$) [20]. According to the fitting values of the equivalent circuit, the $R_{sf + ct}$ of the first cycle is 565 $\Omega$, and it drops to 99.4 $\Omega$ after 200 cycles. Obviously, the semicircle diameter of the electrodes ($\Omega$) after cycling is much smaller than the electrode ($\Omega$) before cycling in the high-medium frequency regions, which implies that the electrodes after cycling possess a more efficient charge transfer than those before cycling, thus suggesting that the ZnMn2O4 nano-peanuts with interconnected mesoporous structure can reduce the resistance and facilitate the electron transport during charge and discharging processes.

The XPS measurement was carried out to examine the elemental oxidation state and composition of the ZnMn2O4 samples after 200 cycles. Fig. 8a shows the XPS spectrum of Zn 2p, in which two typical peaks located at 1022.1 and 1045.1 eV proved to be Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$. The energy difference between Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ is approximately 23 eV, which is well in the accordance with Zn$^{2+}$ according to previous reports. It can be confirmed that ZnO exists after cycling [6,11,20]. As shown in Fig. 8b, the peaks at 642.1 eV and 653.6 eV are Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ with a satellite peak at 647.8 eV, which is the characteristic peak of Mn$^{2+}$, thus MnO is also present in the compounds after the cycling [6,11]. Because of the existence of ZnO and MnO after cycling, the discharge capacity increases slightly and is higher than the theoretical capacity of ZnMn2O$_4$.

To elucidate the structural stability of ZnMn$_2$O$_4$ nano-peanuts, a detailed microstructure analysis of the electrode materials (after the 200th cycle at a current rate of 100 mA g$^{-1}$) was performed. The additional features in the TEM image (Fig. 9a) could be sodium alginate (SA) and carbon black, which were introduced during the preparation process of the working electrode. The electrode materials might have slight volume expansion after cycling, but will not coalesce or rupture after cycling. Thus, the morphology is basically consistent with that before cycling. It suggests that the mesoporous interconnected 3D framework can prevent the structure from crushing and keep the ZnMn$_2$O$_4$ stable, thus improving the cycling performance of LIBs. Figs. 9b, c indicate the reversibility of the conversion reaction of ZnMn$_2$O$_4$. Both XPS and TEM results all demonstrate the presence of ZnO and MnO in the compounds after cycling, which corresponds to the CV plot in Fig. 6a.

4. Conclusions

In summary, the ZnMn$_2$O$_4$ nano-peanuts with interconnected mesoporous structure were successfully synthesized by a facile one-step solvothermal method. The method is simple, no-toxic and environment-friendly. The interconnected mesoporous structure integrates three advantages: special mesoporous structure, a high specific surface and interconnected walls, which shorten the Li ion pathway, reduce the resistance, buffer the volume change and accommodate or alleviate strain alleviate during the charge-discharge process. As anode materials for LIBs, the interconnected mesoporous ZnMn$_2$O$_4$ nano-peanuts have excellent cycling performance, high reversible capacity and good rate capability. The XPS and TEM results of the electrode materials after cycling show that the original appearance can be preserved and that ZnO and MnO are generated, thereby, the discharge capacity increases slightly and is stable, also is higher than the theoretical capacity of ZnMn$_2$O$_4$. The interconnected mesoporous ZnMn$_2$O$_4$ nano-peanuts are expected to extend for synthesis of other MTMOs with enhanced energy storage applications.
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