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Morphology Engineering of Self-assembled Porous Zinc Manganate Hexagons for Lithium Ion Storage

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Abstract: Porous zinc manganate (ZnMn_2O_4), which is typically fabricated from the decomposition of its carbonates, promises a high-performance anode material for lithium ion batteries (LIBs). Most of porous ZnMn_2O_4 in literature presents in sphere morphology. Herein, a unique type of porous ZnMn_2O_4 hexagons with a side length of about 2 μm and a BET specific surface area of 34.19 $\text{m}^2 \text{g}^{-1}$, assembled by ca. 100 nm nanoparticles, has been successfully fabricated by a solvothermal reaction with subsequent calcination of the self-assembled catenapoly intermediates. The growth mechanism of the solvothermal products has been systematically investigated by adjusting the stoichiometric ratio of oxalic acid, the type of the salt source and acid additive, and the reaction media, resulting in a wide spectrum of morphologies ranging from hexagon, porous sphere, hourglass to belt. The hexagon precursor was calcinated in air to obtain the porous structure, attributed to the space between nanoparticle assemblies. When used for lithium-ion storage, the as-prepared porous ZnMn_2O_4 hexagons-based anode exhibits a reversible capacity of 716 mAh g^{-1} after 200 cycles at 100 mA g^{-1} , outperforming the pure porous Mn_2O_3 hexagons and the non-porous ZnMn_2O_4 hexagons.

Keywords: Zinc manganate; lithium-ion storage; anode materials; solvothermal reaction; hexagons

1. Introduction

Because of the long cycling life, large specific energy, high output voltage and no memory effect, ¹⁻⁴ lithium-ion batteries (LIBs) have been widely adopted in a wide range of applications in electric vehicles and consumable electronics. Although considerable trials have paved the way for pursuing LIBs with high power and energy densities, the present batteries still hardly meet all the requirements of ever-growing energy utilization. The challenges lie in the components of LIBs including the cathode, ⁵ anode, ⁶ and electrolyte, ⁷ which are all key factors determining the electrochemical performance. Recently, cathode materials are developing much faster than that on anode for commercial use, while the anode materials are still limited to graphite family due to the cycling stability issue. ⁸⁻⁹ It is imperative to seek for alternative anode materials with low-cost and high performance. Transition metal oxides (TMOs) are attracting considerable research interests due to their significantly higher theoretical capacities over graphite. Among them, the AB₂O₄ spinel structured oxides are demonstrated to display better electrochemical performance than simple TMOs owing to their higher electrochemical activities. ¹⁰ ZnMn₂O₄ is drawing increasing attention because i) Mn is cheap and has a relatively low oxidation potential, ii) Zn can react with Li ions to form Li-Zn alloy leading to extra capacity. ¹¹⁻¹³

Large volume changes during charge/discharge processes can damage the anode materials, resulting in cycling degradation. One solution is to fabricate novel nanostructures or porous structures. ZnMn₂O₄ (theoretical capacity: 1024 mAh g⁻¹) with various morphologies and structures, such as nanoparticles, ¹⁴⁻¹⁵ nanoplates, ¹⁶ porous spheres, ^{12, 17-18} nano-flowers, ¹⁹ thin films²⁰ and nanorods²¹⁻²² have been reported. The morphology dependent energy storage performance has been widely reported. ²³⁻²⁴ For example, Chen et al. fabricated porous ZnMn₂O₄

nanospheres using a sol-gel method registering a reversible capacity of 810 mAh g⁻¹ at a current density of 100 mA g⁻¹ after 10 cycles' charge/discharge, over those of nanoparticles (680 mAh g⁻¹). Yuan et al. synthesized three-dimensional porous ZnMn₂O₄ thin films on Ni foams through electrostatic spray deposition, displaying a reversible capacity of 982 mAh g⁻¹ at 400 mA g⁻¹ after 100 cycles, in contrast to the capacity of 662 mAh g⁻¹ for the non-porous counterpart. This can be explained by the low charge-transfer impedance of the spinal ZnMn₂O₄ and the porous structure, which not only enhances the contact possibility between electrolyte and active materials, but also buffers the volume change during the lithiation/delithiation process.

Most of the reports on porous ZnMn₂O₄ rely on the thermal decomposition of metal carbonates. For example, Wang et al.²⁵ used a hydrothermal method with urea addition to provide carbonate to form the Zn_xMn_{1-x}CO₃ precipitation for porous ZnMn₂O₄ microspheres. Chen et al.²⁶ fabricated porous ZnMn₂O₄ nanospheres derived from the precursor obtained with a microemulsion method adding (NH₄)HCO₃. Zhong et al.²⁷ used both of (NH₄)HCO₃ and urea to fabricate the precursor for mesoporous ZnMn₂O₄ microspheres through a hydrothermal reaction. The metal carbonates decomposition method leads to limited morphologies of the materials to porous spheres, excepting that a recent research on mesoporous ZnMn₂O₄ submicrocubes whose precursor was obtained through a microemulsion process with adding n-hexane, n-pentanol, CTAB and (NH₄)HCO₃ and extended growth time.²⁸ Furthermore, template method and the annealing of emerging precursors such as Zn-Mn complexes are promising to obtain porous ZnMn₂O₄ in various morphologies. For example, Zhang et al.²⁹ coated ZnMn₂O₄ nanosheets on the surfaces of carbon nanotubes (CNTs). The removal of CNTs by calcination generated porous ZnMn₂O₄ hollow nanotubes. Zhu et al.³⁰ synthesized porous ZnMn₂O₄ micro-belts using a sustainable self-sacrifice biomorphic template. There are several reports on fabricating ZnMn₂O₄ through annealing self-assembled polymer

intermediates with metal ions. For example, Zhang et al.³¹ fabricated hollow microspheres using ethylene glycol additives to form ZnMn-glycolate-2. Zhang et al.³² synthesized ZnMn₂O₄ porous nanowires by the calcination of a one-dimensional long chain polymers of (-Zn_{0.33}-Mn_{0.66}-NTA)_n formed with the assistance of nitrilotriacetic acid (NTA). The morphology of the product obtained by template method depends on the structure of the template, and the fabrication process generally needs one more step to remove the template. However, the template free method by forming Zn-Mn complexes is easy to operate and the versatile metal complexes could enable a wide range of morphologies.

Self-assembled catena-poly³³, as one kind of polymeric complex bridged by anions, has been barely used as precursors for fabrication of metal oxides. This work aims to fabricate porous ZnMn₂O₄ in different morphologies by the calcination of well-controlled catena-poly precursors based on the selection of symmetry molecules and asymmetrical anions. To the best of our knowledge, this is the very first work on reporting porous ZnMn₂O₄ in hexagonal morphologies. The porous hexagons exhibit a high BET surface area of 34.19 m² g⁻¹ (Table S1). Morphology control from porous hexagons, porous spheres, hourglass to belts of the products can be achieved by carefully altering the usage of solvent and additives. When used as the anode of LIBs, the porous ZnMn₂O₄ hexagons exhibit a high capacity of 716 mAh g⁻¹ at 100 mA g⁻¹ after cycling 200 times. Impedance study reveals that porous ZnMn₂O₄ hexagons benefit from the triple transition metal oxide with lower charge transfer resistance than that of Mn₂O₃, and also the porous structure facilitating the diffusion of the electrolyte into the inner part of active materials.

2. Experimental

2.1 Chemicals and Materials.

Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.0%), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$, 99%), manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99.0%), N,N-dimethylformamide (, 99.0%), absolute ethyl alcohol, white polyvinylidene fluoride (PVDF ($\text{C}_2\text{H}_2\text{F}_2$)_n, MW 500 000–700 000) and N-methyl-2-pyrrolidone ($\text{C}_5\text{H}_9\text{NO}$, NMP) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Carbon black, Li foil and Celgard 2300 were obtained from Hefei Kejing Material Technology Co., Ltd, China. LiPF_6 dissolved in ethylene carbonate, dimethyl carbonate, and ethylene methyl carbonate in a volumetric ratio of 1:1:1 was purchased from Shenzhen Biyuan Technology Co., Ltd, China. All the chemicals of analytical grade were used as-received without further purification.

2.2 Synthesis of porous hexagon ZnMn_2O_4 .

In a typical process, 2 mmol $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 1 mmol $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 9 mmol oxalic acid were dispersed in a mixed solution consisting of 20 ml DMF and 30 ml absolute alcohol at room temperature with two-hour stirring. The aged solution was sealed in a Teflon-lined stainless autoclave and heated at 170 °C for 6 h. The resultant precipitate was centrifuged and washed with ethanol for several times, allowed to be dry in an oven at 60 °C for 12 h. The precursor existing in a form of white powders was treated at 600 °C for 2 h in air, and the brown-powder-like final product, porous hexagon ZnMn_2O_4 , was obtained. For comparison study, ZnO and Mn_2O_3 were also prepared following the similar route, while without the addition of either $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, respectively.

2.3 Materials Characterization.

X-ray powder diffraction patterns of the samples were obtained using a Rigaku D/Max-RC X-ray diffractometer with a Ni filtered Cu $\text{K}\alpha$ radiation ($\lambda = 0.1542$ nm, $V = 40$ kV, $I = 50$ mA) in the

range of 10-90 °C at a scanning rate of 4 °C min⁻¹. The microstructure of the final product was examined via a JSM-6700F field emission scanning electron microscope (FE-SEM, accelerating voltage: 20 kV, electric current: 1.0×10^{-10} A) equipped with energy-dispersive X-ray spectroscopy (EDX), and a JEOL JEM-2100 transmission electron microscope (TEM, 200 kV). X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Analytical spectrometer using an Al K α ($h\nu = 1486.6$ eV) radiation as the excitation source under an anode voltage of 12 kV and an emission current of 10 mA. The thermogravimetric analysis (TGA) was carried out via a Mettler-Toledo TGA/SDTA851e Thermo Analyzer in the temperature range from room temperature (R.T.) to 800 °C with an elevating rate of 10 °C min⁻¹ in air. N₂ adsorption/desorption measurement was performed by an ASAP 2020 instrument and Brunauer–Emmet–Teller (BET) methods were used to calculate the surface area.

2.4 Electrochemical measurements.

To fabricate the working electrode, the active material (porous hexagon ZnMn₂O₄), carbon black and PVDF with a weight ratio of 7:2:1 were mixed in NMP to form a homogenous slurry, which was coated on a copper foil substrate and dried in a vacuum oven at 120 °C for 12 h. When the oven was cooled down to room temperature, the copper foil was cut into discs with a diameter of 14 mm. On each disc, the total mass loading, weighed by a microbalance (FA2004, Soptop, China), of the slurry and the active material on the copper foil is 3.3-3.6 mg and 2.3-2.5 mg, respectively. The performance of the cell was evaluated galvanostatically in a voltage range of 0.02-3 V at various current densities using a LAND CT2001A battery test system. Electrochemical impedance spectroscopy (EIS) was tested on an Ivium potentiostat from a frequency range of 0.01 Hz-100 kHz at the open circuit potential. Cyclic voltammetry (CV) measurement was conducted in a potential range of 0.02 to 3 V at a scan rate of 0.3 mV s⁻¹.

3. Results and discussion

3.1 Morphology and structures of mesoporous ZnMn_2O_4 hexagons.

Mesoporous ZnMn_2O_4 hexagons are prepared by a self-assembly process and subsequent thermal decomposition, as shown in Fig. 1. When Mn^{2+} , Zn^{2+} and oxalic acid are added into a N,N-dimethylformamide (DMF)/ethanol solution, metal ions interact with the aldehyde (-CHO) groups from DMF and carboxyl groups (-COOH) of oxalic acid, resulting in plate-like catena-poly precipitate (step I). The catena-poly undergoes reorganization under hydrothermal conditions to form layered hexagons (step II). The mesoporous structure is finally obtained by an annealing treatment (step III) to remove the DMF and oxalic molecules.

The morphology and phase property of the product obtained in each step are investigated. As shown in Fig. 1(a), the morphology of the sedimentation before solvothermal process is bulky with uniform dispersion. It clearly shows that the bulky sedimentation is constructed with nanoflakes with a length of ca. 2 μm . XRD patterns of the sedimentation fit well with that of catena-poly (COD: 96-221-1889 for Mn and 96-223-1719 for Zn) (Fig. 1 (b)).³⁴⁻³⁵ DMF and oxalic acid are believed to serve as the surfactants to make the sedimentation uniformly dispersed, in a way that two DMF molecules and one oxalic acid molecule coordinate to one divalent metal ion. FTIR is also used to confirm the structure of catena-poly (Fig. 1(c)). The strong bands at 1616.30 and 1652.95 cm^{-1} can be assigned to the symmetric and antisymmetric C=O stretching modes of oxalic acid and DMF molecules.³⁶⁻³⁷ Double bands at 1313.48 and 1386.78 cm^{-1} are attributed to the O-C stretching modes from oxalic acid, with the O-C-O bending mode located at 796.58 cm^{-1} . The typical CH_3 symmetric stretching and C-H stretching mode for DMF are at around 2937.50 cm^{-1} ,³⁸ as well as the CH_3 asymmetric deformation mode at 1431 cm^{-1} and CH_3 rocking mode at 1093 and 1063 cm^{-1} .³⁹ The typical N-C-H bending mode from DMF is located at 1386.78 cm^{-1} , with

O=C-N stretching at 659 cm^{-1} .⁴⁰ The peaks at the wavenumber range between 3200 and 3500 cm^{-1} belong to the O-H stretching vibration due to traces of water.⁴¹

Fig. 1 . Schematic illustration of the synthesis process of porous ZnMn_2O_4 hexagons and the corresponding SEM images and XRD patterns of the product obtained from each step ((a) and (b): the first step; (d) and (e): the second step; (g) and (h): the third step). FTIR spectra of the precursors in the first step (c), and the second step (f); N_2 adsorption-desorption isotherm and pore size distribution (PSD) (i) of the as-obtained porous ZnMn_2O_4 sample.

During the hydrothermal treatment (high pressure and high temperature), the sedimentations transform their structure to hexagons, as shown in Fig. 1(d). In low magnification, the products are all hexagons with an edge size of 1-3 μm confirmed by SEM (Fig. S1(a)). The side-view SEM image (inset of Fig. S1(a)) indicates that hexagons are assembled by nanoflakes. The surface of a single hexagon shows that the precursor is solid without porous structure. The crystalline phase and component of the precursor are examined by XRD. As shown in Fig. 1(e), the diffraction peaks of the sample match well with the catena-poly. After the solvothermal treatment, the peak intensities at around 10° becomes stronger, which is likely due to either the larger lattice space caused by forming sheet structure, or the anisotropy favored orientation.⁴² It means the solvothermal process is crucial for the formation of hexagons. FTIR is also used to confirm the above statements. As displayed in Fig. 1(f), the typical peaks for oxalic acid and DMF can be observed in the FTIR curve after solvothermal process. It means the products exist as catena-poly, corresponding well with the XRD results. FESEM EDS (Fig. S1) shows that the elemental oxygen (white), zinc (red), manganese (green) in a selected area are homogeneously distributed all over the hexagons, and the percentage ratio of Zn and Mn is about 1:2. There are no clear boundaries between Zn and Mn catena-poly.

To find out the proper calcination temperature, thermogravimetric analysis (TGA) is used to investigate the thermal degradation behaviors of hexagonal catena-poly precursors obtained by the solvothermal process. As shown in Fig. S2, the initial weight has decreased by 49.9% at 270 $^\circ\text{C}$ due to the evaporation of water and DMF molecules²⁵, followed by the removal of oxalic acid and oxidation of Mn species by ca. 23.9% when heated up to 300 $^\circ\text{C}$. The total weight loss by 72.6% corresponds to the transition from catena-poly to porous ZnMn_2O_4 . When the hexagonal precursor is annealed at a temperature of 300 $^\circ\text{C}$, the product shows non-porous structure and low

crystallinity, which is examined by XRD and SEM, as shown in Fig. S3. In the XRD patterns in Fig. S3(a), the product tends to be amorphous, and the weak peaks can be indexed to ZnMn_2O_4 (JCPDS No. 24-1133). It indicates that the product has been transformed into ZnMn_2O_4 at 300 °C. As for the data from TGA, when the temperature exceeds 300 °C, no more weight loss occurs, indicating the precursors are all transferred into ZnMn_2O_4 . The SEM image in Fig. S3(b) shows the surface of the hexagon is rough and solid, in the same size as the structure in the precursors. The final product is treated under 600 °C to obtain the porous structure shown in Fig. 1(g). It can be found the porous hexagon is an assembly of nanoparticles in ca. 100 nm. The XRD patterns (Fig. 1(h)) of the porous material show the typical crystalline feature of tetragonal ZnMn_2O_4 (JCPDS No. 24-1133, $a = b = 5.7204 \text{ \AA}$, $c = 9.245 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$) with a space group of $I4_1/amd$. The lattice parameters of the product are calculated to be $a = b = 5.7624 \text{ \AA}$, $c = 9.2686 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, respectively. No peaks of any other phases can be detected, indicative of the high purity of ZnMn_2O_4 . The formation of the porous structure is mainly due to the decomposition of the catenapoly by evaporating of DMF and release CO_2 from oxalic acid, resulting in a high specific surface area.⁴³ Nitrogen adsorption-desorption isotherms are recorded to characterize the specific surface area and the pore structure of the porous hexagonal ZnMn_2O_4 , as displayed in Fig. 1(i). It indicates the specific BET surface area is about $34.19 \text{ m}^2 \text{ g}^{-1}$, with a wide pore size distribution from 60 to 160 nm caused by the space of nanoparticles. Small pores (2-6 nm) are likely attributed to the pores on the nanoparticles. The BET surface area in some published articles using ZnMn_2O_4 as lithium ion batteries are collected in Table S1. For example, Wang et al. synthesized porous ZnMn_2O_4 microspheres with a surface area of $17.7 \text{ m}^2 \text{ g}^{-1}$ and the pore size in a range of 45-90 nm, which can enhance the diffusion of electrolyte to active materials.²⁵ Chen et al. synthesized mesoporous ZnMn_2O_4 submicrobucses with a surface area of $22.92 \text{ m}^2 \text{ g}^{-1}$ and a pore size in range

of 2 to 8 nm, which was shown to buffer the large volume change during the Li^+ insertion/extraction.⁴² Comparing with the published articles, this porous hexagonal ZnMn_2O_4 has both large and small pores.

The TEM images further confirm that the obtained sample displays hexagon structure with a size of ca. 3 μm (Fig. 2(a)). In the HRTEM image (Fig. 2(b)), the porous structure can be clearly observed. The size of the nanoparticle assembled hexagon is confirmed again to be about 100 nm (Fig. 2(c)). The corresponding selected area electron diffraction pattern (Fig. 1(g)) shows multi-crystal diffraction rings, implying that the porous ZnMn_2O_4 hexagons are multi-crystal materials,⁴⁴ which is caused by the nanoparticles assembling. The pores between nanoparticles can be clearly observed with radius in the range 50-80 nm. The porous structure in size of 2 to 10 nm on the single particles could also be observed clearly in Fig. 2(d), in good agreement with the observation from the pore size distribution (Fig. 1(i)). In addition, the typical lattice fringe spacing on one nanoparticle is well-defined and measured to be 0.48 nm, corresponding to the (101) crystal plane of ZnMn_2O_4 (Fig. 2(d)).

To ascertain the chemical composition and electronic state of porous ZnMn_2O_4 hexagons product, XPS measurement was conducted. From the survey scan spectrum (Fig. 2(e)), four kinds of elements (Zn, Mn, O and C) are present in the products. The existence of the C 1s peak is likely due to carbon contamination. The peaks at 654.5 and 642.7 eV (in Fig. 2(f)) are attributed to Mn 2p_{1/2} and Mn 2p_{3/2}, respectively, which are assigned to Mn^{3+} .⁴⁵ In Fig. 2(g), the two peaks located at 1021.6 and 1044.5 eV are assigned to Zn 2p_{1/2} and Zn 2p_{3/2} from Zn^{2+} ,⁴⁶ respectively. Using Gaussian fitting method, O 1s spectrum (Fig. 2(h)) can be divided into three peaks. The peak at 530.1 eV is the typical lattice oxygen in AB_2O_4 spinel structured oxides,⁴⁷ and the other two weak

peaks at 532.3 and 531.3 eV can be attributed to the C-O bonds form surface adsorbed carbon dioxide and the hydroxyl groups from absorbing water, respectively.⁴⁸

Fig. 2 TEM images (a)-(d) of porous hexagon ZnMn_2O_4 at different magnifications. XPS survey spectrum (e), Mn 2p (f), Zn 2p (g) and O 1s (h) spectrum of the porous hexagon ZnMn_2O_4 . The inset of (c) is the selected area electron diffraction (SAED) pattern.

3.2 Evaluation of governing parameters during the formation of ZnMn_2O_4 .

A series of experiments, such as varying the amount and type of acid, the solution and salt types, are carried out to investigate their effects on the formation of the hexagons.

The role of oxalic acid is examined. Without addition of oxalic acid, the metal ions would be homogenously surrounded by DMF molecules. As shown in Fig. 3(a) and (e), the products after calcination are only in one morphology of porous microspheres with size ranging from 1 to 5 μm . It indicates that the DMF helps to form porous structures. Increasing the oxalic acid concentration, the products tend to form hexagons. Due to the metal ions can form catena-poly with the presence of both oxalic acid and DMF, the addition of 3 mmol oxalic acid leads to flake products (Fig. 3(b, f)), however with a widely distributed size range. When using 6 mmol oxalic acid (Fig. 3(c)), the resulting hexagons are in a relative narrow size range from 1 to 10 μm . However, some of the flakes are still layered (Fig. 3(g)). 9 mmol oxalic acid is chosen as the optimal concentration,

leading to most of the flakes are hexagons (Fig. 3(d)). The size of porous hexagons is in a range of 1-3 μm , with a thickness of about 500 nm (Fig. 3(h)). It can be concluded that oxalic acid helps to form more edges. In order to evaluate the role of carboxyl group of oxalic acid, citric acid is used during the formation process, considering that each citric acid molecule has three carboxyl groups. The resulting products present flake structure (Fig. S4(a)). However, the nanoparticles on the surface of the flakes (Fig. S4(b)) are randomly distributed.

Fig. 3 SEM images of the ZnMn_2O_4 prepared with 0 (a, e), 3 (b, f), 6 (c, g) and 9 mmol (d, h) oxalic acid.

The role of the solvent for the solvothermal process is also studied. As above mentioned, the existence of DMF is one of the governing factors to form catena-poly. When using pure ethanol as the solvent, the metal ions coordinate with both oxygen atoms of the carboxyl group. The morphology of the precursor obtained with pure DMF is mainly belt with a width of 100 nm (Fig. 4(a)). The hexagon structure can also be found but with non-uniform edge size. According to XRD in Fig. S5(a), the precursor is not pure catena-poly (COD: 96-221-1889 for Mn and 96-223-1719 for Zn), indicating the catena-poly formation requires the existence of ethanol. After calcination in air, the organic solvent is assembled by nanoparticles with the same size as found in the precursor. The hexagons turn to be porous structure with the same size of hexagons obtained by

mixed solvent, but the length of each edge is not uniform. When the solvent is changed into pure ethanol, the precursor presents hourglass-shape like structure (Fig. 4(b)), with lengths ranging from 5 to 10 μm . The hourglass has nanowire-like ends. XRD (Fig. S5(b)) is used to investigate the component of the precursor. The precipitation is attributed to manganese oxalate (COD: 00-001-0160) and zinc oxalate (COD: 00-037-0718). After annealed in air, the oxalates transform into metal oxides by removing carbon dioxide, resulting in ZnMn_2O_4 composed of nanoparticles, as displayed in Fig. 4(d). It's likely that ethanol helps to form homogenous hexagons with edges in the same size.

The oxalic acid is the bridge for forming the polymeric complex, which leads to the microscale edges during the reaction, and the DMF provides the branches on the catena-poly, contributing to the sheet structure formation. Zinc and manganese ion both can form the pure Zn catena-poly or Mn catena-poly, with the similar structure to Zn-Mn catena-poly. The knowledge is transferrable as a general strategy to fabricate different metal oxide hexagons, such as ZnO and Mn_2O_3 hexagons. As shown in Fig. 5(a) and (c), the products fabricated using pure Zn salts show a hexagon flake structure with the size from 1 to 5 μm . In higher magnification of SEM (Fig. 5(c)), the surfaces of the hexagons can be clearly observed. They are all nanoparticles with a particle size much larger than that of the product synthesized via the mixed salts. The phase of the products is hexagonal ZnO (COD No. 96-230-0113, $a=b=3.2490\text{ \AA}$, $c=5.2050\text{ \AA}$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$) (Fig. S6(a)), which has a space group of P63mc. No peaks of any other phases can be detected, illustrating the high purity of ZnO. The morphology of the product fabricated by pure Mn salt (Fig. 5(b) and (d)) is also hexagonal structure with much smaller nanoparticles than porous ZnMn_2O_4 . In the XRD patterns image (Fig. S6(b)), all diffraction peaks can be well indexed to orthorhombic Mn_2O_3 (ICDD No. 01-073-1826, $a=9.4118$, $b=9.4177\text{ \AA}$, $c=9.4233\text{ \AA}$, $\alpha=\beta=\gamma=90^\circ$), which

has a space group of $Pbca$. No peaks of any other phases can be detected, illustrating the high purity of Mn_2O_3 . Therefore, the fabrication process of porous hexagons could be used for synthesizing porous pure ZnO and pure Mn_2O_3 hexagons.

Fig. 4 SEM images of the precursors (a, b) obtained by adding pure DMF solvent, precursors (c) obtained by adding pure ethanol. The corresponding $ZnMn_2O_4$ prepared by calcination of precursors obtained by (d, e) adding pure DMF and (f) pure ethanol.

Fig. 5 SEM images of porous ZnO (a, c) and Mn_2O_3 (b, d).

These results prove that the acid is one of the key factors for the formation of the flake structure, and the presence of oxalic acid and DMF can facilitate the formation of hexagons.⁴⁹⁻⁵¹ Even changing the salt to the pure one, the hexagons can also be obtained. The summarized mechanisms for synthesizing different morphologies are displayed in Fig. 6. It's likely that the symmetric structure of oxalic acid helps to form micro-structured catenaploids with edges, rather than

spheres. The usage of the mixed-solvent of DMF and ethanol is also essential to form uniform hexagons with a high yield.

Fig. 6 Schematic illustration of the formation process of microspheres (a), hourglass-shaped structures (b), belts (c) and hexagons (d), and corresponding SEM images.

3.3 Electrochemical performance of porous hexagon ZnMn₂O₄.

The electrochemical behavior of the as-prepared porous ZnMn₂O₄ hexagons serving as anodes in LIBs, has been compared to those of solid ZnMn₂O₄ hexagons and porous Mn₂O₃ hexagons. As shown in Fig. 7(a), in the first cathodic scan, three peaks are observed at approximately 1.1, 0.75 and 0.2 V, which can be assigned to the reduction of Mn³⁺ to Mn²⁺, formation of SEI film and the reduction of Mn²⁺ and Zn²⁺ to Mn⁰ and Zn⁰, respectively, companied by the formation of LiZn.⁵² The initial anodic scan shows an intensive peak at 1.1 V and a broad one at 1.5 V, ascribed to the

oxidation of Mn^0 to Mn^{2+} and Zn^0 to Zn^{2+} , respectively. In the following cycles, the cathodic peaks at 1.1 and 0.7 V disappear, implying that the transformation of Mn^{3+} to Mn^{2+} and the SEI film formation are irreversible.^{14, 53} The porous $ZnMn_2O_4$ hexagons are charged and discharged at a current density of 100 mA g^{-1} between 0.01-3 V (Fig. 7(b)). In the first discharge profile of the porous $ZnMn_2O_4$ hexagons exhibits two obvious platforms at about 1.1, 0.7 and 0.2 V. The platform at 1.1 V corresponds to the reduction of Mn^{3+} to Mn^{2+} ,⁵⁴ and the 0.7 and 0.2 V ones are from the reversible reaction of the electrolyte and the formation of SEI layer, and the formation of Zn^0 , $LiZn$ and Mn^0 , respectively. The first discharge specific capacity of the porous $ZnMn_2O_4$ is estimated to be 1039 mAh g^{-1} , slightly higher than the theoretical capacity of $ZnMn_2O_4$ (1024 mAh g^{-1}),⁵⁴ which can be attributed to the decomposition of electrolyte and the formation of SEI films.⁵⁵ While in the charge curve, there are two plateaus at ca. 1.1 and 1.5 V corresponding to the oxidation of Mn to Mn^{2+} and Zn to Zn^{2+} , respectively.⁵⁴ The overall charging capacity is about 582.4 mAh g^{-1} , and the initial coulombic efficiency (CE) is ca. 56%, The initial CE of ca. 56% can be explained by the irreversible formation of solid electrolyte interphase (SEI), a process that the electrolyte is reduced to form a film on the surface of the active material.⁵⁶⁻⁵⁷ The second discharge/charge cycle shows good capacity retention due to the stabilized reaction between the electrolyte and the porous structure of the electrode. The galvanostatic discharge/charge process is in good agreement to the CV curves, and the reactions can be written as below:⁵⁸

Initial discharge:

Following reversible reactions:

In comparison, the charge and discharge curves of porous Mn₂O₃ and solid ZnMn₂O₄ are shown in Fig. 7(c) and 7(d), respectively. The platforms of porous Mn₂O₃ during discharge curve are located at ca. 1.1, 0.7 and 0.2 V, corresponding the reduction of Mn³⁺ to Mn²⁺, SEI film formation and reduction of Mn²⁺ to Mn⁰, respectively. While there is only one platform during charge process associated to the oxidation of Mn⁰ to Mn²⁺. As for solid ZnMn₂O₄, the platform during discharge could be observed at the same potential with porous ZnMn₂O₄. Two platforms are expected during charging, but only one is observed because the solid material cannot be fully used during charge and discharge process. The initial CEs of porous Mn₂O₃ and solid ZnMn₂O₄ are 50.2% and 44.8%, respectively, lower than that of porous ZnMn₂O₄ (56%).

The electron transfer resistance on the electrolyte/active material interfaces is investigated by electrochemical impedance spectroscopy (EIS) measurements for half cells, which is conducted at an open circuit voltage. The Nyquist plots of porous Mn₂O₃, and solid and porous ZnMn₂O₄ hexagons before and after cycling for 200 cycles are presented in Fig. 7(e) and (f). The plots display a small semicircle at the high-frequency region and a straight line at the low frequency region. The diameter of the semicircle reveals the value of the charge-transfer impedance (R_{ct}).⁵⁹ As shown in Fig. 7(e), the porous ZnMn₂O₄ anode owns a lower R_{ct} (80 Ω) than those of the Mn₂O₃ (230 Ω) and solid ZnMn₂O₄ anode (120 Ω) before cycling, indicating the electronic conductivity of the porous ZnMn₂O₄ is better than the other two anode. In addition, the straight line is attributed to the Warburg impedance, which could reflect rate of intercalation/deintercalation of Li⁺ by diffusion coefficient (D_{Li^+}). The linear fitting of the Warburg impedance with the real part Z' is

shown in Fig.7g, allowing the estimation of the Warburg coefficient (A_w), which is the diffusion coefficient of ions in solution, and D_{Li^+} based on the following equations:^{46, 60}

$$Z' = R_s + R_{ct} + A_w \omega^{-\frac{1}{2}} \quad (5)$$

$$D_{Li^+} = \left[\frac{V_m}{FAA_w} \left(-\frac{dE}{dx} \right) \right]^2 \quad (6)$$

Where V_m is the molar volume ($\text{cm}^3 \text{mol}^{-1}$), F is the Faraday constant ($96485 \text{ s A mol}^{-1}$), A is the surface area of the electrode (cm^2), and $(dE)/(dx)$ is the slope of the open circuit potential and the Li ion concentration.⁶¹ Eq. 6 indicates that D_{Li^+} is mainly determined by $(1/A_w)^2$ and a small A_w represents a large D_{Li^+} . As shown in table 1. The fresh solid ZnMn_2O_4 has the lowest A_w ($48 \Omega \text{ s}^{-1/2}$) than those of porous ZnMn_2O_4 ($61 \Omega \text{ s}^{-1/2}$) and porous Mn_2O_3 ($84 \Omega \text{ s}^{-1/2}$), implying the best ion conductivity and highest Li^+ diffusion coefficient. However, after cycling test, porous ZnMn_2O_4 has the lower A_w (Fig. 7h, $29 \Omega \text{ s}^{-1/2}$) than those of solid ZnMn_2O_4 ($981 \Omega \text{ s}^{-1/2}$) and porous Mn_2O_3 ($1182 \Omega \text{ s}^{-1/2}$). Additionally, the R_{ct} of ZnMn_2O_4 slightly increases to 93Ω , while considerably increases to 800Ω and 1000Ω for the porous Mn_2O_3 and the solid ZnMn_2O_4 , respectively. It reveals that the as-prepared solid and porous ZnMn_2O_4 hexagons have better conductivity than that of the porous Mn_2O_3 due to the spinel structure. In total, the electronic conductivity and ion conductivity of the porous ZnMn_2O_4 are all the best after 200 cycles testing, mainly due to the porous structure could buffer the volume change during the repetitive charge and discharge process and the hexagon structure could be maintained.

Table 1 EIS parameters of the anode electrode before and after cycling test.

Electrode	Fresh electrode			After cycling		
	Rs (Ω)	Rct (Ω)	Aw (Ω s ^{-1/2})	Rs (Ω)	Rct (Ω)	Aw (Ω s ^{-1/2})
Porous ZnMn ₂ O ₄	2.6	80	61	21	93	29
Solid ZnMn ₂ O ₄	2.9	120	48	7	800	981
Porous Mn ₂ O ₃	2.8	230	84	13	1000	1182

The cycling stability of as-prepared products is also studied. Fig. 7(i) presents the cycling performances and coulombic efficiency (CE) of the ZnMn₂O₄ and Mn₂O₃ materials at 100 mA g⁻¹. The porous ZnMn₂O₄ delivers a stable reversible capacity of 716 mAh g⁻¹ after 200 cycles (corresponding to an energy density of ca. 1064 Wh kg⁻¹, normalized to the weight of active materials). The CE of ZnMn₂O₄ quickly reaches 91% in the third cycle, which remains more than 95% in the subsequent cycles. The morphology of porous ZnMn₂O₄ hexagons after 200 cycles was investigated by SEM. Although it's difficult to recognize the detailed morphology of the active materials that are mixed with PVDF binder and carbon black (Fig. S7), there are visible integrate hexagons (indicated by arrows) with an edge size of ca. 2 μ m. It means that the integrity of the morphology during the charge and discharge is likely maintained even after 200 cycles. It means that the integrity of the morphology during the charge and discharge is likely maintained even after 200 cycles. For Mn₂O₃ samples, the first discharge capacity reaches 1196.6 mAh g⁻¹, much higher than that of the ZnMn₂O₄, but the charge capacity is only about 639.2 mAh g⁻¹. After 10 cycles' charge/discharge, the CE just stays at ca. 95%. In addition, the reversible capacity of the as-prepared ZnMn₂O₄ (716 mAh g⁻¹) is much higher than that of the pure Mn₂O₃ (183 mAh g⁻¹) after 200 cycles at the same current density of 100 mA g⁻¹. Moreover, the solid ZnMn₂O₄ prepared by calcination at 300 °C in air maintains a reversible capacity of 336 mAh g⁻¹ after 200 cycles at 100 mA g⁻¹. Its initial discharge capacity is 1278 mAh g⁻¹, much higher than that of porous ZnMn₂O₄, but the initial charge capacity quickly drops to 642 mAh g⁻¹. Moreover, after 80 cycles, the CE of

the solid ZnMn_2O_4 stabilized at 99.2%. Interestingly, there is an obvious increase in the cycling curve of ZnMn_2O_4 and Mn_2O_3 , a common phenomenon for the TMO electrodes,⁶²⁻⁶³ which is due to the activation process of the electrode materials. The electrochemical performance in terms of capacity and cycling performance of the proposed porous ZnMn_2O_4 hexagons is better than most of reported ZnMn_2O_4 materials and some of single metal oxides, such as MnO and FeO (Table S1). For example, the pure ZnMn_2O_4 microspheres fabricated via a mixed solvothermal method exhibits 602 mAh g^{-1} after 100 cycles at the 100 mA g^{-1} .⁶⁴ The reversible capacity of flowerlike ZnMn_2O_4 microspheres assembled with porous nanosheets fabricated by solvothermal process reaches 662 mAh g^{-1} after 120 cycles at the same current density.⁶⁵ And the porous ZnMn_2O_4 hexagons is also better than particle materials. Particle materials tend to aggregate, which may result in poor long-term stability issue.⁶⁶ While the porous hexagons own high porosity, which not only help to increase the contact between the electrode and electrolyte, but also shorten the diffusion length of electrons and Li ions. In addition, the pores on hexagons can accommodate the volume expansion to maintain the integration of the active materials. This is confirmed by the comparison of the lithium ion storage performance of porous hexagon ZnMn_2O_4 with the ones in literature (Table S1). In summary, the porous hexagon structure can effectively improve the electrochemical performance of the materials by buffering the volume expansion during the reactions. The high specific surface area improves the connection between the electrolyte and the electrode, and the thin flake built by nanoparticles can effectively avoid aggregation during the reaction process. Furthermore, the spinel ZnMn_2O_4 has better performance than the pure transition metal oxides as observed in the lower R_{ct} in the ZnMn_2O_4 than that for Mn_2O_3 .

The rate properties tested by the various current densities (from 100 to 800 mA g^{-1}) of porous ZnMn_2O_4 hexagons, solid ZnMn_2O_4 hexagons and porous Mn_2O_3 are shown in Fig. S8. The porous

ZnMn₂O₄ delivers a reversible capacity of 480 mAh g⁻¹ at 100 mA g⁻¹, 365 mAh g⁻¹ at 200 mA g⁻¹, 283 mAh g⁻¹ at 400 mA g⁻¹, 213 mAh g⁻¹ at 800 mA g⁻¹, and finally back to 430 mAh g⁻¹ at 100 mA g⁻¹, subsequently. At a high current density, the porous Mn₂O₃ delivers nearly the same capacity with porous ZnMn₂O₄. For example, the porous Mn₂O₃ has a reversible capacity of 210 mAh g⁻¹ at current density of 800 mA g⁻¹. However, when the current density increases to 100 mA g⁻¹, porous Mn₂O₃ would deliver a lower capacity than porous ZnMn₂O₄. It is mainly because that zinc oxide could contribute to the overall capacity during charge and discharge due to the sluggish formation of LiZn alloy, which doesn't contribute greatly when charged/discharged at high current densities. For example, Jing et al.⁶⁷ fabricated ZnO nanorods which deliver 47 mAh g⁻¹ at current density of 800 mA g⁻¹. Park et al.⁶⁸ synthesized ZnO sphere which deliver 75 mAh g⁻¹ at current density of 500 mA g⁻¹. Therefore, there will be less difference for porous ZnMn₂O₄ and porous Mn₂O₃ at high current densities. However, the solid ZnMn₂O₄ delivers much lower capacities, which is only 43 mAh g⁻¹ at 800 mA g⁻¹. It indicates that the porous structure could effectively increase the reaction rate of the active materials. When reset to 100 mA g⁻¹, the porous ZnMn₂O₄, porous Mn₃O₄ and solid ZnMn₂O₄ reserve their initial capacities, which are 420 (40.4%), 360 (29.8%) and 270 (21.1%) mAh g⁻¹, respectively. The porous ZnMn₂O₄ shows the best retention ratio after the high current charge/discharge process.

Fig. 7 CV curves of ZnMn₂O₄ hexagons at a scan rate of 0.3 mV s⁻¹ (a); Galvanostatic discharge/charge curves of the 1st, 2nd, and 200th cycles of porous ZnMn₂O₄ hexagons (b), porous Mn₂O₃ (c) and solid ZnMn₂O₄ (d) at 100 mA g⁻¹; Nyquist plots of porous Mn₂O₃ and solid and porous ZnMn₂O₄ hexagons before (e) and after (f) 200 testing cycles. Linear fitting of the square root of Warburg impedance with real part Z' obtained for the Nyquist plot of ZnMn₂O₄ hexagons before (g) and after (h) cycling. Comparison of charge-discharge cycling performances and coulombic efficiency of the battery anodes based on porous ZnMn₂O₄, solid ZnMn₂O₄ and porous Mn₂O₃ hexagons (i) at 100 mA g⁻¹. Inset of (g) and (h) are the equivalent circuits.

4. Conclusions

In summary, the porous ZnMn₂O₄ hexagons consisting of porous nanoparticles have been fabricated by solvothermal synthesis followed with calcination. The formation of hexagon structure is significantly affected by the type of acid and the solvent used during solvothermal process. The knowledge on rational control the morphology of the porous ZnMn₂O₄ gained herein can be transferred to other TMOs for functional material design. When used as the electrode active materials of lithium ion batteries, the porous ZnMn₂O₄ hexagons exhibited better capacitance retention capability and long cycling performance, compared to the pure Mn₂O₃ and the solid

ZnMn₂O₄. This is mainly attributed to the porous structure, which facilitates the diffusion of the Li⁺ ions and the reaction with the materials, and the lower charge-transfer impedance.

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Associated Content

Supporting Information

Additional information and figures including SEM images, EDX mapping and TGA curve of the ZnMn₂O₄ hexagons precursors, SEM images and XRD patterns of the solid ZnMn₂O₄ hexagons; XRD patterns of the ZnMn₂O₄ obtained by using pure solvent and pure salt source; SEM image of the porous ZnMn₂O₄ after cycling, and the rate capability curves of the porous ZnMn₂O₄, Mn₂O₃ and solid ZnMn₂O₄; The comparison table of the proposed ZnMn₂O₄ materials with those in literature displaying different morphologies.

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