Controllable interior structure of ZnCo₂O₄ microspheres for high-performance lithium-ion batteries

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Abstract In this work, different interior structures of ZnCo_2O_4 microspheres have been fabricated by a hydrothermal method followed by thermal decomposition via a calcination process at various furnace ramp rates. When evaluated as anode materials in lithium-ion half cells, the core-shell microspheres showed high electrochemical performance with a first discharge specific capacity of 1280 mAh/g at 200 mA/g and demonstrated excellent cycling stability with only 3.9% capacity loss between the second and fiftieth cycles at 400 mA/g.

Keywords: ZnCo_2O_4 microspheres, core-shell structure, lithium ion batteries, long cycling stability

Introduction

Rechargeable Li-ion batteries (LIBs) are the dominate power source for portable electronic devices and are being actively pursued for energy storage in electric vehicles.^[1-5] However, challenges still remain for LIB applications which require increased energy and power densities beyond current benchmarks. Most efforts have been focused on exploring prospective anode materials to replace graphite in LIBs. Transition metal oxides e.g. MO and M_3O_4 (where $\text{M} = \text{Mn}, \text{Co}, \text{Zn}, \text{Fe}$) which incorporate Li^+ through conversion reactions and exhibit large reversible capacity compared to insertion type electrodes such as graphite or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ have been drawing great attention.^[6-10] The specific capacities of these kinds of materials could achieve as high as 1000 mAh/g, which is about three times that of commonly used graphitic carbons. Comparative studies of the several binary and ternary transition metal oxides revealed that cobalt oxide exhibited the best anodic performance, however the high cost and toxic nature of cobalt hindered their application.^[11-14] One approach to mitigate this concern is to partially replace the Co in spinel structured Co_3O_4 by cheaper and environmentally friendly metals, such as Ni, Zn and Cu, which are also cable of reversible electrochemical reactions with Li^+ .^[15, 16] ZnCo_2O_4 is an attractive material for evaluation as anode for LIBs because it is low-cost, environmentally

benign relative to the pure cobalt oxide compound, and has a high theoretical capacity.^[17-19] ZnCo_2O_4 crystallizes in a normal spinel structure with bivalent Zn-ions occupying one eighth of the tetrahedral sites and trivalent Co-ions occupying one half of the octahedral sites in the face centred cubic oxygen lattice. Recently, various ZnCo_2O_4 nanostructures have been reported as anode materials for LIB, including nanoparticles, nanowires, nanoflakes and microspheres showing encouraging reversible capacities.^[20-22] Nevertheless, there are still several shortcomings which prevent their potential application such as poor rate capability and capacity fade during extended cycling.

Recently, mesoporous hollow micro-structures with large surface area and short ion diffusion path have been attracting considerable attention for building up well-suited architectures for high performance rechargeable batteries.^[23, 24] Metal-organic frameworks (MOFs) have been proven to be an effective precursor or sacrificial template to construct the corresponding morphology-inherited hollow metal oxides.^[25] Several hollow or multi-shell structured oxides such as CuO , Co_3O_4 , CoMn_2O_4 and Fe_2O_3 have been successfully synthesized through their MOFs and have a great reversible capacity in LIBs application, which also demonstrate the advantage of this kind of hollow structure for rechargeable batteries.^[26-30] Despite the great progress that has been made, further refinement of these hollow structures for complex metal oxides is needed to optimize these materials.

Herein, we report a facile and convenient non-equilibrium heat-treatment process to control the interior micro-structure of ZnCo_2O_4 ranging from porous solid, hollow and core-shell microspheres by regulating heat treatment ramp rates. When evaluated electrochemically in lithium ion half cells, the hollow and core-shell microspheres of ZnCo_2O_4 exhibited high specific capacity and good cycling stability.

Experimental

All the reagents used in the experiment were of analytical grade and used without further purification.

Synthesis of ZnCo_2O_4 microspheres. In a typical synthesis process, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.164 g), $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.072 g) and 0.2 g polyethylene glycol 1000 were dissolved in 40 ml ethylene glycol to form a clear solution. After being stirred vigorously for 120 min, the mixture was put into a Teflon-lined stainless steel autoclave. The autoclave was heated to 200 °C and maintained for 8 h before furnace cooled to room temperature. The resulting precipitates were filtered and washed several times with absolute ethanol and finally dried under oven at 80°C in air. These precipitates were calcined at 600°C for 3 h at various ramp rates as describe in the main text to obtain different interior structure of ZnCo_2O_4 microspheres.

Characterization. The phases of the samples were identified by X-ray diffraction (XRD) analysis (PANalytical X'Pert PRO Alpha-1). The microstructure and morphology were examined using a scanning electron microscope (LEO 1530 field emission SEM) and a high resolution transmission electron microscope (JEOL 4000 EX).

Preparation and testing of electrode. The electrochemical behavior of the ZnCo_2O_4 microspheres was examined using “Swagelok” cells vs. Li with 1 M LiPF_6 in 1:1ethylene carbonate/dimethyl carbonate electrolyte (Novolyte). A piece of Li metal with an area of 1.26 cm² was used as both the counter and pseudo-reference electrode. All electrochemical measurements were made using an Arbin BT-2000 battery tester. For cycling measurements, specific current density (mA/g) was fixed to a desired C rate using the mass of the active material and the cell was charged or discharged until the cell potential reached the desired cutoff. The working electrode was fabricated by compressing a mixture of the active materials, conductive material (acetylene black, ATB), and binder (polyvinylidene fluoride (PVDF)) in a weight ratio of ZnCo_2O_4 /carbon/PVDF= 70:15:15 onto a copper foil current collector. The cells were assembled in an argon filled glove box.

Results and Discussion

The micro-structures of ZnCo_2O_4 were fabricated through a facile hydrothermal method to produce a ZnCo-glycolate precursor followed by a thermal decomposition

process. The ZnCo-glycolate precursor was prepared by the reaction of ethylene glycol with divalent Zn and Co ions under hydrothermal conditions.

The SEM and TEM images of the precursor demonstrate a solid microstructure of ZnCo-glycolate (Figure S1). Further, Fourier transform infrared spectroscopy (FTIR) was used to characterize the composition of the precursor, detail description was shown in Figure S2.

The as-synthesized product is first characterized by X-ray diffraction (XRD) to identify its crystallographic structure. As can be seen from Figure S3, all of the diffraction peaks can be assigned to cubic ZnCo_2O_4 (JCPDS card no. 23-1390, space group: $Fd-3m$, $a = b = c = 8.0946 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$). No residues or contaminants have been detected, indicating the high purity of the sample.

The detailed morphology and structural features of ZnCo_2O_4 were further characterized by SEM and TEM. The typical SEM images of all the ZnCo_2O_4 products are shown in Figure. 1, suggesting that they consist of porous microspheres with irregular diameters from 300 nm to 1 μm . The interior structures of ZnCo_2O_4 produced at different ramp rates were observed by TEM. At a ramp rate of $1^\circ\text{C}/\text{min}$, the TEM images show solid porous spheres consisting of discrete nanoparticles with sizes around 20 nm (Figure 1a, 1d, 1g). For samples produced at a ramp rate of $2^\circ\text{C}/\text{min}$, hollow spheres of ZnCo_2O_4 are clearly observed with a shell thickness around 50 nm (Figure S4). At the highest ramp rate of $3^\circ\text{C}/\text{min}$, the structures of ZnCo_2O_4 are found to be core-shell spheres, which are composed of an outside thin shell around 30 nm and a porous solid core inside (Figure 1b-i). The selected area electron diffraction (SAED) pattern and HRTEM image show that the porous ZnCo_2O_4 spheres are polycrystalline (Figure 1k). An interplaner spacing of 0.22 nm was obtained from the HRTEM resolved lattice fringes and corresponded to the (311) plane of cubic spinel ZnCo_2O_4 (Figure 1j). The spatial distributions of the elements in the core-shell structures were characterized using energy-dispersive x-ray spectroscopy (EDS) in the form of line scan profiles of individual elements (Co, Zn, and O) (Figure 1l). With the unique properties contain high surface area, large pore

volume, and regular large pore size from porous hollow or core-shell structure, samples of ZnCo_2O_4 microspheres have great potential as high performance LIBs anode material.

Sintering the as-obtained solid microspheres of ZnCo-glycolate at 600°C for 3h with different furnace ramp rates produced ZnCo_2O_4 porous microspheres with different interior structures ranging from solid to core-shell structure. As depicted schematically in Figure 2, the porous solid microsphere of ZnCo_2O_4 (ZCO-s) was achieved when the ramp rate was $1^\circ\text{C}/\text{min}$. By increasing the ramp rate to 2 and $3^\circ\text{C}/\text{min}$, the porous hollow (ZCO-h) and core-shell (ZCO-cs) microspheres could be obtained, respectively. The formation of these kinds of porous spheres during the thermal decomposition of ZnCo-glycolate is reportedly due to the heterogeneous contraction caused by a non-equilibrium heat treatment.^[31] For a low ramp rate like $1^\circ\text{C}/\text{min}$, the precursor spheres are almost homogeneously heated from the surface to centre and shrink into a solid structure. Carbon dioxide evolution from the decomposition of the organic precursor component establishes the porous structure. For a high ramp rate, a large temperature gradient (ΔT) could be generated along the radial direction during the initial decomposition process, which may cause a formation of ZnCo_2O_4 shell on the surface of ZnCo-glycolate spheres. Two forces of opposite direction act on the interface between the ZnCo_2O_4 shell and the ZnCo-glycolate core, namely the cohesive force (F_{co}) and the adhesive force (F_{ad}). The F_{co} comes from the inner core which may promote an inward shrinkage accompanying mass loss of organic components, while the F_{ad} resists shrinkage in the outer shell. The differential magnitudes of F_{co} and F_{ad} could contribute to the formation of the observed interior micro-structures, through heterogeneous contraction. As F_{ad} surpasses F_{co} , the inner core prefers to resist shrinking to the ZnCo_2O_4 shell, and cause a hollow structure at $2^\circ\text{C}/\text{min}$. Increasing the ramp rate to $3^\circ\text{C}/\text{min}$ forms a large ΔT at the beginning stage such that F_{co} exceeds F_{ad} and the inner core will contract. This results in a separation from the pre-formed shell. As calcination continues, the reduction of ΔT will cause a homogeneous heating which may form a

solid core inside and produce the observed core-shell structure.

The lithium-storage properties of the porous ZnCo_2O_4 microspheres were evaluated with the standard $\text{ZnCo}_2\text{O}_4/\text{Li}$ metal half-cell configuration. Typical cyclic voltammograms (CVs) of the electrode made from the ZnCo_2O_4 core-shell structures are shown in Figure 3a. On the basis of the CVs and the results of a previous report,^[22] the lithium insertion and extraction reactions for ZCO-cs electrode are believed to proceed as follows:

The first discharge cycle shows a large and broad irreversible reduction peak at 0.82 V vs Li/Li^+ , corresponding to the decomposition of the ZnCo_2O_4 to metallic Zn and Co as described in eqn(1). Compared to the first cycle, the cathodic polarization peak of second and third discharge cycle shifts towards 1.0 V vs Li/Li^+ , indicating a different lithium reaction pathway is followed after the first complete cycle. In addition, these three cathodic sweeps are followed by two current peaks at around 1.7 V vs Li/Li^+ and 2.2 V vs Li/Li^+ during the anodic sweep, which consistent with the electrochemical lithium extraction reactions of to produce ZnO and Co_3O_4 shown in equations 3-5.^[32, 33]

Figure 3b shows the first-cycle voltage-capacity profiles of ZnCo_2O_4 microspheres at a current density of 200 mA/ g in the potential range from 0.005 V vs Li/Li^+ to 3 V vs Li/Li^+ . In the first discharge curve, the potential drops quickly to a 1.1V plateau and then gradually declines to the cut-off potential of 0.005 V vs Li/Li^+ . This observation is analogous to previous reports.^[20] The initial specific capacity of ZCO-s, ZCO-h and ZCO-cs based on the first discharge and normalized by the mass of active material is 1090, 1110 and 1280 mAh/g, respectively, which is higher than the theoretical value obtained from reaction 1 (867 mAh/g based on the molar mass of

ZnCo₂O₄). This phenomenon is usually ascribed to irreversible reactions, such as decomposition of the electrolyte or the formation of a solid electrolyte interphase (SEI) layer and possibly interfacial lithium storage. [34, 35]

The cycling performance of porous ZnCo₂O₄ microspheres at current density of 200 mA/g is shown in the Figure S5. The ZCO-cs exhibits a best cycling stability and highest specific capacity after the first charge and discharge process. The capacity of ZCO-s, ZCO-h and ZCO-cs maintains as high as 345, 831 and 985 mAh/g after 50 cycles, respectively, corresponding to capacity retention of 42.1%, 93.0% and 107.5% compare to the second discharge capacity. It should be noted that the cycling performance of hollow and core-shell structure in our work is substantially improved compared to previously report about 3D porous microspheres of ZnCo₂O₄. [20] This cycling performance enhancement is reasonable based on the porous shell and the void space within the hollow and core-shell structure could efficiently endure the volume expansion / contraction during the Li⁺ insertion/extraction. To further characterize the cycling stability of the porous ZnCo₂O₄ microstructures, 50 charge and discharge cycles under a high current density of 400 mA/g were carried out in the potential window of 0.005 V vs Li/Li⁺- 3 V vs Li/Li⁺. The ZCO-cs still shows the best cycling performance with a second cycle capacity of 869 mAh/g remain to 835 mAh/g after 50 cycling testing (Figure 4). It should be mentioned that the coulombic efficiency for all samples can reach around 95% after the second cycle (Figure S6).

The rate capability was evaluated by a multiple-step galvanostatic strategy at various current densities ranging from 200 to 1600 mA/ g. (Figure 5) The hollow and core-shell structures reveal a good rate performance. The average discharge capacity of ZCO-cs at current densities of 200, 400, 800, 1600 mA/g is 965, 886, 808 and 727 mAh/g. For the hollow structure, an average capacity of 902, 830, 725 and 608 mAh/g is observed under the same current density as ZCO-cs. Moreover, after returning to a lower current density of 200 mA/g, the specific capacity of ZCO-h and ZCO-cs recovers to 950 and 840 mAh/g, respectively, indicating the great reversibility of the electrode materials.

From our results, it is clear that the core-shell structured ZnCo_2O_4 microspheres produces the best electrochemical performance among the structures studied. The improved capacity retention and enhanced rate capability of ZCO-cs is most likely due to an increased surface area compared to the ZCO-s and ZCO-h (Figure S7). Higher surface areas would create decreased path length for lithium diffusion and lead to higher utilization of electrode materials. Moreover, much thinner shell of ZCO-cs than the shell thickness of ZCO-h may provide fast de/lithiation reaction kinetics and demonstrate high rate capability. Consistent with previous studies, the porous shell and the void space between the porous cores of the core-shell structure provides space for volume expansion, avoiding structural damage due to electrochemical pulverization during cycling.

Conclusions

In this work, microspheres of ZnCo_2O_4 with controlled interior structures have been successfully fabricated using a facile hydrothermal method followed by a calcination process. Varied microstructures from a porous solid, hollow sphere to core-shell microspheres were produced by controlling ramp rate and accompanying heterogeneous contraction of a metal organic precursor. When evaluated as the anode materials for LIBs, the core-shell microspheres show superior cycling stability and rate capability compare to the other two microspheres. This remarkable performance could be explained from the unique structure properties of core-shell architecture, which may endure the volume expansion/contraction during the lithium ions insertion/extraction and provide improved path access for electrochemical lithiation and delithiation. Thus, the porous core-shell microspheres are a promising future anode material for rechargeable lithium-ion batteries.

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References

- [1] Q. Zhang, E. Uchaker, S.L. Candelaria, G. Cao, Chemical Society Reviews 42 (2013) 3127.
- [2] B. Kang, G. Ceder, Nature 458 (2009) 190.
- [3] M.R. Palacin, Chemical Society Reviews 38 (2009) 2565.
- [4] D.C.S. Souza, V. Pralong, A.J. Jacobson, L.F. Nazar, Science 296 (2002) 2012.
- [5] K.T. Lee, J. Cho, Nano Today 6 (2011) 28.
- [6] M.V. Reddy, G.V. Subba Rao, B.V. Chowdari, Chemical Reviews 113 (2013) 5364.
- [7] R. Wu, X. Qian, K. Zhou, J. Wei, J. Lou, P.M. Ajayan, ACS Nano 8 (2014) 6297.
- [8] P. Meduri, E. Clark, J.H. Kim, E. Dayalan, G.U. Sumanasekera, M.K. Sunkara, Nano Letters 12 (2012) 1784.
- [9] Y. Xu, G. Jian, Y. Liu, Y. Zhu, M.R. Zachariah, C. Wang, Nano Energy 3 (2014) 26.
- [10] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, Nature 407 (2000) 496.
- [11] J. Liu, H. Xia, L. Lu, D. Xue, Journal Of Materials Chemistry 20 (2010) 1506.
- [12] X. Wang, X.-L. Wu, Y.-G. Guo, Y. Zhong, X. Cao, Y. Ma, J. Yao, Advanced Functional Materials 20 (2010) 1680.

- [13] J. Wang, N. Yang, H. Tang, Z. Dong, Q. Jin, M. Yang, D. Kisailus, H. Zhao, Z. Tang, D. Wang, *Angewandte Chemie International Edition* 52 (2013) 6417.
- [14] H. Guan, X. Wang, H. Li, C. Zhi, T. Zhai, Y. Bando, D. Golberg, *Chemical Communications* 48 (2012) 4878.
- [15] F.M. Courtel, H. Duncan, Y. Abu-Lebdeh, I.J. Davidson, *Journal Of Materials Chemistry* 21 (2011) 10206.
- [16] Y. Sharma, N. Sharma, G.V.S. Rao, B.V.R. Chowdari, *Journal Of Power Sources* 173 (2007) 495.
- [17] Y. Sharma, N. Sharma, G.V. Subba Rao, B.V.R. Chowdari, *Advanced Functional Materials* 17 (2007) 2855.
- [18] W. Luo, X. Hu, Y. Sun, Y. Huang, *Journal Of Materials Chemistry* 22 (2012) 8916.
- [19] B. Liu, J. Zhang, X. Wang, G. Chen, D. Chen, C. Zhou, G. Shen, *Nano Letters* 12 (2012) 3005.
- [20] L. Hu, B. Qu, C. Li, Y. Chen, L. Mei, D. Lei, L. Chen, Q. Li, T. Wang, *Journal of Materials Chemistry A* 1 (2013) 5596.
- [21] N. Du, Y. Xu, H. Zhang, J. Yu, C. Zhai, D. Yang, *Inorganic Chemistry* 50 (2011) 3320.
- [22] Y. Qiu, S. Yang, H. Deng, L. Jin, W. Li, *Journal Of Materials Chemistry* 20 (2010) 4439.
- [23] Z. Wang, L. Zhou, X.W. David Lou, *Advanced Materials* 24 (2012) 1903.
- [24] M. Hu, A.A. Belik, M. Imura, K. Mibu, Y. Tsujimoto, Y. Yamauchi, *Chemistry Of Materials* 24 (2012) 2698.
- [25] H.-L. Jiang, Q. Xu, *Chemical Communications* 47 (2011) 3351.
- [26] L. Zhang, H.B. Wu, S. Madhavi, H.H. Hng, X.W. Lou, *Journal Of The American Chemical Society* 134 (2012) 17388.
- [27] L. Zhou, D. Zhao, X.W. Lou, *Advanced Materials* 24 (2012) 745.
- [28] L. Hu, Y. Huang, F. Zhang, Q. Chen, *Nanoscale* 5 (2013) 4186.
- [29] R. Wu, X. Qian, X. Rui, H. Liu, B. Yadian, K. Zhou, J. Wei, Q. Yan, X.-Q. Feng, Y. Long, L. Wang, Y. Huang, *Small* 10 (2014) 1932.

- [30] N. Yan, L. Hu, Y. Li, Y. Wang, H. Zhong, X. Hu, X. Kong, Q. Chen, *The Journal of Physical Chemistry C* 116 (2012) 7227.
- [31] J. Guan, F. Mou, Z. Sun, W. Shi, *Chemical Communications* 46 (2010) 6605.
- [32] Y. Li, B. Tan, Y. Wu, *Nano Letters*, 8 (2007) 265.
- [33] C.Q. Zhang, J.P. Tu, Y.F. Yuan, X.H. Huang, X.T. Chen, F. Mao, *Journal Of The Electrochemical Society* 154 (2007) A65.
- [34] S. Laruelle, S. Grugeon, P. Poizot, M. Dollé, L. Dupont, J.-M. Tarascon, *Journal Of The Electrochemical Society* 149 (2002) A627.
- [35] G. Binotto, D. Larcher, A.S. Prakash, R. Herrera Urbina, M.S. Hegde, J.M. Tarascon, *Chemistry Of Materials* 19 (2007) 3032.

Figures

Figure 1. SEM images of different interior structures of ZnCo_2O_4 ; (a) ZCO-s, (b) ZCO-h and (c) ZCO-cs. TEM and scan TEM (STEM) images of these three microspheres; (d) (g) ZCO-s, (e) (h) ZCO-h and (f) (i) ZCO-cs. High resolution TEM image (j) and SAED pattern (k) display the crystalline phase of ZCO-sc. EDS spectrum of ZCO-cs (l).

Figure 2. Mechanism for the formation of the different interior structure of ZnCo_2O_4 microspheres under different ramping rate.

Figure 3. (a) The first three CVs of the ZCO-sc at a scan rate of 0.1 mV/ s in the voltage range of 0.05–3 V. (b) First discharge–charge curve of ZnCo_2O_4 microspheres at current density of 200 mA/g.

Figure 4. Capacity versus cycle number plot for core-shell, hollow and solid ZnCo₂O₄ microspheres at current rate of 400 mA/g.

Figure 5. Rate capability of different interior structure of ZnCo_2O_4 micro-spheres at different current density.

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Graphical abstract