Porous ZnO/Co₃O₄/N-doped carbon nanocages synthesized *via* pyrolysis of complex metal–organic framework (MOF) hybrids as an advanced lithium-ion battery anode

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Metal oxides have a large storage capacity when employed as anode materials for lithium-ion batteries (LIBs). However, they often suffer from poor capacity retention due to their low electrical conductivity and huge volume variation during the charge–discharge process. To overcome these limitations, fabrication of metal oxides/carbon hybrids with hollow structures can be expected to further improve their electrochemical properties. Herein, ZnO–Co₃O₄ nanocomposites embedded in N-doped carbon (ZnO–Co₃O₄@N-C) nanocages with hollow dodecahedral shapes have been prepared successfully by the simple carbonizing and oxidizing of metal–organic frameworks (MOFs). Benefiting from the advantages of the structural features, *i.e.* the conductive N-doped carbon coating, the porous structure of the nanocages and the synergistic effects of different components, the as-prepared ZnO–Co₃O₄@N-C not only avoids particle aggregation and nanostructure cracking but also facilitates the transport of ions and electrons. As a result, the resultant ZnO–Co₃O₄@N-C shows a discharge capacity of 2373 mAh g^{−1} at the first cycle and exhibits a retention capacity of 1305 mAh g^{−1} even after 300 cycles at 0.1 A g^{−1}. In addition, a reversible capacity of 948 mAh g^{−1} is obtained at a current density of 2 A g^{−1}, which delivers an excellent high-rate cycle ability.

1. Introduction

Lithium-ion batteries (LIBs) have been widely used in the fields of consumer devices, portable electronics, electric vehicles and large-scale stationary energy storage (Zou *et al.*, 2014; Huang *et al.*, 2017). The commonly used anode material in LIBs is graphite. However, graphite no longer satisfies the current market demand due to its low theoretical capacity (372 mAh g^{−1}) (Chen *et al.*, 2013; Lu *et al.*, 2018; Goriparti *et al.*, 2014). Transition-metal oxides (TMOs), such as Co₃O₄ (Reddy *et al.*, 2014), Fe₂O₃ (Chen *et al.*, 2014; Gu *et al.*, 2014), NiO (Wang *et al.*, 2014b), ZnO (Wang *et al.*, 2014c) and MnO (Chen *et al.*, 2016), have been thoroughly investigated as promising anode materials in recent years due to their low cost, natural abundance and especially high theoretical specific capacities (Lv *et al.*, 2015). Among them, Co₃O₄ has been generally acknowledged as one of the most promising electrode materials thanks to its excellent electrochemical activity and stability (Xu *et al.*, 2017). However, the application of Co₃O₄ has encountered obstacles due to the high cost of elemental Co and its low conductivity (Li *et al.*, 2008; Liu *et al.*, 2011). Given that Zn can react reversibly with Li in LIBs

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by alloying/dealloying reactions, replacing Co with Zn in whole or in part to prepare the ZnO/Co₃O₄ hybrid is an economic and ecofriendly way of obtaining excellent anode materials.

Although great success has been achieved for transition-metal oxides when they are employed as anode materials, they still suffer from poor capacity retention due to their intrinsic shortcomings, *i.e.* poor electrical conductivity, low ion diffusion kinetics and huge volume variations (Cheng *et al.*, 2011). In recent years, three general strategies have been employed to further enhance the structural stability, cycling stability and electronic conductivity of TMOs for LIBs (Ge *et al.*, 2015). One strategy is to synthesize the TMO nanostructures with a useful morphology, such as a hollow structure (Han *et al.*, 2017). The second is to fabricate bicomponent-activated TMOs to accommodate volume changes and provide richer redox chemical kinetics during the charge–discharge process (Salunkhe *et al.*, 2017). The last strategy is to wrap the TMOs in a stable carbon layer or impregnate the TMOs into an ordered porous carbon matrix. This carbon layer/matrix acts as a structural buffer frame in easing the interior strain brought about by the significant volume changes of TMOs during the electrochemical cycle (Wang *et al.*, 2014a; Han *et al.*, 2014; Li & Zhou 2012). However, coating bicomponent-activated TMOs with a stable carbon layer by a facile method is still a challenge.

Metal–organic frameworks (MOFs) have recently attracted increasing attention due to their unique structural features, such as adjustable pore size, ultra-high pore volume, specific surface area and a varied internal cage structure (Zheng *et al.*, 2014). These features provide a suitable environment for the lithium ion, which makes MOFs attractive for applications in lithium-ion batteries. Moreover, MOF-derived materials have been exploited extensively in recent years (Furukawa *et al.*, 2013). The abundance of organic ligands in MOFs makes it well suited as a carbon source for the synthesis of porous carbon and also enables the use of metal atoms in the framework to obtain metal-containing carbon hybrids during *in-situ* high-temperature treatment (Wang *et al.*, 2016a; Zhao *et al.*, 2016). For example, Cho and co-authors reported a method using a two-step roasting to get mesoporous α -Fe₂O₃ from MIL-88-Fe. The obtained α -Fe₂O₃ manifested excellent lithium-storage performance (Xu *et al.*, 2012). As a large branch of MOFs, zeolite–imidazole framework (ZIF) materials are effective carbon sources for the preparation of porous carbon (Chaikittisilp *et al.*, 2013). Composite ZIFs with two kinds of metal-ion core-shell structures can be fabricated by the two-step roasting method. Under the condition of retaining the carbon, bimetallic oxides can be prepared with similar morphologies to ZIFs (Chen *et al.*, 2015; Wu *et al.*, 2018). In addition, the unique morphologies of ZIFs derived from metal oxides are conducive to enhancing lithium storage performance due to their great volume and mutual compensations of composites. Based on the above advantages, ZIFs and ZIF-derived materials can be applied to lithium-ion batteries as high-performance anode materials (Zhao *et al.*, 2016).

In this work, we have designed and synthesized a multifunctional binary metal oxide composite by a two-step calcination process. Firstly, ZIF-8@ZIF-67 core-shell nanostructures were prepared through a seed-mediated growth method. The resulting ZIF8@ZIF67 core-shell nanostructures were carbonized in a tube furnace to form ZnO/Co/Co₃O₄@N-C, which was then converted into ZnO/Co₃O₄/N-C nanocomposites by a controlled calcining process. When employed as an anode for LIBs, the porous ZnO-Co₃O₄@N-C dodecahedral nanocages show a discharge capacity of 2373 mAh g^{−1} in the first cycle and exhibit a retention capacity of 1305 mAh g^{−1} even after 300 cycles at 0.1 A g^{−1}. In addition, a reversible capacity of 948 mAh g^{−1} is obtained at a current density of 2 A g^{−1}, delivering an excellent high-rate cycle ability. The enhanced electrochemical storage capacity can be attributed to the conductive N-doped carbon coating, the porous structure of the nanocages and the synergistic effects of the different components, which prevent particle aggregation and nanostructure cracking, as well as providing continuous and flexible conductive carbon frameworks to facilitate ion and electron transport.

2. Experimental

2.1. Synthesis of ZIF-8

For the synthesis of ZIF-8 samples, 3.24 g of Zn(NO₃)₂·6H₂O and 0.80 g of polyvinylpyrrolidone (PVP-K30) were added to methanol (160 ml), followed by magnetic stirring for 5 min to obtain a mixed solution. 2-Methylimidazole (2.104 g) was then added to the above solution. After ultrasonic treatment for 10 min, the obtained solution was stirred magnetically at room temperature for 24 h. The resultant precipitate was collected by centrifugation and washed with methanol several times. Finally, the precipitate was subjected to drying at 60 °C for 12 h.

2.2. Synthesis of core-shell ZIF-8@ZIF-67 nanostructures

The ZIF-8@ZIF-67 core-shell nanostructures were synthesized by a seed-mediated growth technique (Tang *et al.*, 2015). Briefly, ZIF-8 (0.16 g) was added to methanol (20 ml) with ultrasonic treatment for 30 min (solution **A**). Meanwhile, CoCl₂·6H₂O (0.354 g) was dissolved in methanol (6 ml) (solution **B**) and 2-methylimidazole (1.79 g) was added to methanol (6 ml) (solution **C**). Solutions **B** and **C** were added gradually to solution **A**. The mixed solution was stirred for 5 min and then transferred to a 100 ml Teflon-lined stainless steel autoclave and heated to 100 °C for 24 h. After being cooled to room temperature naturally, the resultant precipitate was collected by centrifugation and washed with methanol three times.

2.3. Synthesis of ZnO-Co₃O₄@N-C dodecahedral nanocages

The ZIF-8@ZIF-67 core-shell nanocrystals were firstly calcined in a tube furnace at 600 °C with a heating rate of 1 °C min^{−1} under an N₂ atmosphere, which gave rise to ZnO/Co/Co₃O₄@N-C samples. The ZnO-Co₃O₄@N-C dodeca-

hedral nanocages were prepared by further calcining ZnO/Co/Co₃O₄@N-C in a muffle furnace at 350 °C for 4 h with a heating rate of 1 °C min⁻¹. The calcined samples are labelled as the final products. As a contrast experiment, ZnO@N-C and Co₃O₄@N-C were prepared by pyrolysis of ZIF-8 and ZIF-67 nanocrystals under the same two-step calcination conditions.

2.4. Materials characterization

X-ray diffraction (XRD) patterns were acquired using Cu K α radiation ($\lambda = 0.1542$ nm) at a scan rate of 8° min⁻¹ (18KW D/MAX2500V/PC, Japan). The detailed morphologies of the products were observed with a field emission scanning electron microscope (FESEM, JSM-6700F, Japan), a transmission electron microscope (TEM, JEM-200CX, Japan) and a high-resolution transmission electron microscope (HR-TEM, JEM-2010F, Japan) with an energy dispersive spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) was carried out using an X-ray photoelectron spectrometer with monochromated Al K α radiation. The specific surface area was obtained from an N₂ adsorption–desorption analysis conducted at 77 K on a Quadrasorb SI.

2.5. Electrode preparation and electrochemical performance

The active material of the anode was thoroughly ground to a powder. The active material, the conductive agent (Super P) and the adhesive PVDF were added in a 1:0.13:5 wt% ratio, followed by *N*-methylpyrrolidone (NMP, 0.3 ml). The mixture was stirred for 10 min with a beater and was then dripped onto a clean piece of copper and dried at 100 °C for 10 h under vacuum. The mass of each pole piece obtained from the above process was subtracted from the mass of the copper piece as the mass of the active material and multiplied by 0.85 as the

mass of the actual active substance. The electrolyte was 1 M LiPF₆, which was dissolved in a mixture of dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethylene carbonate (EC) (1:1:1 wt% ratio). CR 2032 coin-type cells were assembled in an argon-filled glove-box with moisture and an oxygen content below 1 ppm. Charge–discharge tests were performed in a LAND 2001A cell test system at room temperature with a voltage window of 0.05–3.0 V.

3. Results and discussion

The schematic diagram (Fig. 1) clearly shows the synthetic route of the ZnO-Co₃O₄@N-C dodecahedral nanocages. The uniform ZIF-8 seeds were first synthesized by the coordination reaction of Zn²⁺ ions and 2-MeIm. Due to the same topological structure of ZIF-67 with that of ZIF-8 combined with metal cations four-coordinated by 2-MeIm, the ZIF-8@ZIF-67 core-shell nanostructures can be prepared by a facile seed-mediated growth method (Tang *et al.*, 2015). In the subsequent step, the metal atoms were thermally converted to the ZnO/Co/Co₃O₄@N-C nanocomposite by calcining the ZIF-8@ZIF-67 clusters at 600 °C for 2 h under the protection of N₂ at a heating rate of 1 °C min⁻¹. Meanwhile, the organic ligands were converted into N-doped carbon frameworks. Finally, the obtained ZnO/Co/Co₃O₄@N-C was heated to 350 °C for 4 h at a heating rate of 1 °C min⁻¹ under an air atmosphere. Here, the temperature of 350 °C is employed because the N-doped carbon cannot be oxidized at this temperature (Hou *et al.*, 2015). The ZnO-Co₃O₄@N-C dodecahedral nanocages as the final products were successfully synthesized by this circuit process.

In order to investigate the formation and microstructure evolution of ZnO-Co₃O₄@N-C dodecahedral nanocages,

Figure 1
Schematic illustration of the formation of the ZnO-Co₃O₄@N-C dodecahedral nanocages.

various technical characterizations have been applied in detail. Fig. 2 shows the SEM images of ZIF-8 (Fig. 2*a*) and ZIF-8@ZIF-67 (Fig. 2*b*), a TEM image of ZIF-8@ZIF-67 (Fig. 2*c*), XRD patterns of ZIF-8, ZIF-67 and ZIF-8@ZIF-67 (Fig. 2*d*), and digital photographs of ZIF-8, ZIF-67 and ZIF-8@ZIF-67 samples. The SEM image in Fig. 2(*a*) reveals that the ZIF-8 nanocrystals exhibit a regular rhombic dodecahedral morphology composed of well-defined rhombus faces and straight edges. For the preparation of ZIF-8@ZIF-67 core-shell nanostructures, uniform ZIF-8 nanocrystals, with an average size of 0.96 μm , were selected as seeds. After the addition of a methanolic solution of CoCl_2 , the Co^{2+} ions were immobilized on the surface of the ZIF-8 seeds through coordinative interaction with the 2-MeIm units exposed on the surface, followed by the growth of the ZIF-67 shell *via* interaction with the additive 2-MeIm linkers (Hu *et al.*, 2017). As shown in Fig. 2(*b*), the obtained ZIF-8@ZIF-67 powders have a similar morphology to ZIF-8 due to their similar topological structure and unit-cell parameters. The TEM image in Fig. 2(*c*) further demonstrates that the ZIF-8@ZIF-67 core-shell nanocrystals are also made up of dispersed rhombic dodecahedral crystals of uniform size ($\sim 1 \mu\text{m}$). Fig. 2(*d*) shows the XRD patterns of the as-obtained ZIF-8, ZIF-67 and ZIF-8@ZIF-67. It is found that the pattern of ZIF-8@ZIF-67 matches well with the simulated patterns of ZIF-8 and ZIF-67. The strong and sharp profiles further confirm the high crystallinity of the three samples. Figs. 2(*e*–*g*) show the digital photographs of ZIF-8, ZIF-67 and ZIF-8@ZIF-67. It can be intuitively seen that the colour of the obtained ZIF-8@ZIF-67 is between those of ZIF-8 and ZIF-67, suggesting that the ZIF-67 shell may homogeneously grow on the surface of the ZIF-8 nanocrystals.

$\text{ZnO/Co/Co}_3\text{O}_4\text{@N-C}$ was obtained by calcining the ZIF-8@ZIF-67 core-shell nanostructures in a tube furnace at 600 $^\circ\text{C}$ under an N_2 atmosphere. The SEM images indicate that $\text{ZnO/Co/Co}_3\text{O}_4\text{@N-C}$ retains the morphology of the original ZIF-8@ZIF-67 core-shell nanostructures (Fig. S1 in

the supporting information). Nevertheless, the surface became rough and concave, and the structure also shows remarkable shrinkage. This could be attributed to the massive loss of the organic components during the annealing process. The TEM images shown in Fig. S2 (see supporting information) suggest that $\text{ZnO/Co/Co}_3\text{O}_4\text{@N-C}$ shows an apparent hollow structure in the hexagonal carbon nanocage exterior, and the concavity of the hexagonal edge is clearly observed. These results indicate that the organic ligands are transformed into a porous carbon network with nitrogen doping, while the metal cations are converted *in situ* to metallic ZnO, Co and Co_3O_4 , which were retained in the carbon matrix. When $\text{ZnO/Co/Co}_3\text{O}_4\text{@N-C}$ was further calcined in air at 350 $^\circ\text{C}$ for 4 h, the product was characterized by SEM and TEM imaging techniques. A typical SEM image of the final product is shown in Fig. 3(*a*). The surface of the dodecahedron is very rough and composed of dense small nanoparticles. It is found that the skeleton of the $\text{ZnO-Co}_3\text{O}_4\text{@N-C}$ dodecahedron is very similar to $\text{ZnO/Co/Co}_3\text{O}_4\text{@N-C}$ and the morphology is maintained. The hollow interior of the $\text{ZnO-Co}_3\text{O}_4\text{@N-C}$ dodecahedron is further confirmed by TEM analysis, as shown in Figs. 3(*b*) and 3(*c*). The $\text{ZnO-Co}_3\text{O}_4\text{@N-C}$ dodecahedron exhibits a sharp contrast between the shells (dark) and the interior cavities (gray). Meanwhile, the carbon frame can be clearly observed. It can be seen clearly that the highly symmetric dodecahedral shell frameworks are composed of small subunits and the inter-particle mesopores are distributed in the shell. It is worth noting that the porous hollow $\text{ZnO-Co}_3\text{O}_4\text{@N-C}$ dodecahedron can keep its structural integrity even after the second-step oxidation. In the clear crystal lattices observed in the HRTEM image (Fig. 3*d*) can be identified two sets of *d*-spacings at 0.467 and 0.247 nm, which correspond with the (111) crystal plane of Co_3O_4 and the (101) crystal plane of ZnO, respectively. The selected area electron diffraction pattern is shown in Fig. 3(*e*), indicating that the $\text{ZnO-Co}_3\text{O}_4\text{@N-C}$ dodecahedron is polycrystalline. The diffraction rings are in good agreement with the (111), (220) and (400)

Figure 2

SEM images of (*a*) the as-synthesized ZIF-8 nanocrystals and (*b*) the ZIF-8@ZIF-67 core-shell nanostructure. (*c*) TEM image of ZIF-8@ZIF-67 and (*d*) XRD patterns of ZIF-8, ZIF-67 and ZIF-8@ZIF-67. Digital photographs of (*e*) ZIF-8, (*f*) ZIF-8@ZIF-67 and (*g*) ZIF-67 samples.

Figure 3
(a) SEM image, (b)/(c)/(f) TEM images, (d) HRTEM image, (e) electron diffraction pattern and (g–k) element mapping analysis of the ZnO-Co₃O₄@N-C nanocages.

planes of Co₃O₄, and with the (101), (110) and (103) planes of ZnO. These crystal planes can also be supported by the XRD measurement shown in Fig. 4. In addition, the distribution of the carbon element can be inferred in the black-framed area by the TEM bright-field image in Fig. 3(c) and in the white-framed area by the TEM dark-field image in Fig. 3(f). The element mapping clearly indicates that all of these elements are distributed homogeneously in the product, including Zn, Co and O, as shown in Figs. 3(g–k). Nevertheless, the content of the C and N elements is less than the other elements, as shown in Figs. 3(j) and 3(k), respectively, probably because of the combustion of carbon with oxygen and the lesser amount of nitrogen in the precursor.

X-ray diffraction (XRD) patterns can provide more crystallinity and phase information on the composite materials. As shown in Fig. S3 (see supporting information), the characteristic peaks of ZIF-8 and ZIF-67 disappear completely after being calcined at 600 °C under an N₂ atmosphere, indicating that the ZIF-8@ZIF-67 nanocrystals were successfully converted into ZnO, and Co and Co₃O₄. Interestingly, the Co metal can be thoroughly transformed into Co₃O₄ after further heat treatment at 350 °C in air, which gives rise to ZnO-Co₃O₄@N-C nanocages. According to the XRD patterns, as shown in Fig. 4, the calcination of ZIF-8, ZIF-67 and ZIF-8@ZIF-67 leads to the formation of ZnO@N-C, Co₃O₄@N-C and ZnO-Co₃O₄@N-C, respectively. The diffraction peaks

located at 31.8, 34.4, 36.3, 47.5, 56.6, 62.9, 68.0, 69.1 and 77.0° can be indexed to the (100), (002), (101), (102), (110), (103), (112), (201) and (202) planes, respectively, of ZnO [JCPDS:36-1451, space group *P63mc* (No. 186), lattice constant $a = b = 3.249$ Å]. The diffraction peaks located at 19.0, 31.3, 36.9, 38.5, 44.8, 55.7 and 59.4° can be indexed to the (111), (220), (311), (222), (400), (422), (511) and (440) planes, respectively, of Co₃O₄ (JCPDS:42-1467, space group: *Fd3m*, lattice constant $a = b = c = 8.084$ Å). No other impurity peaks are observed, indicating the high purity of the sample. No diffraction peaks for the N-doped carbon can be observed, which might be due to its low amount and relatively low diffraction intensity.

X-ray photoelectron spectroscopy (XPS) was carried out to identify the surface composition and oxidation state of the sample. The survey shown in Fig. 5(a) confirms the presence of the Zn, Co, O, C and N elements, which is in complete agreement with the results of the element mapping analysis (Figs. 3g–k). The high-resolution XPS spectrum of Zn 2p, as shown in Fig. 5(b), exhibits two prominent bands at 1022.0 and 1045.2 eV, which can be readily assigned to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively. This result suggests that the Zn in the components has been converted to ZnO (Zhang *et al.*, 2017a). For the Co 2p, two distinct peaks appearing at 780 eV for Co 2p_{3/2} and at 795 eV for Co 2p_{1/2} are decomposed into four peaks with binding energies equivalent to 779.4, 780.0, 794.3 and 795.5 eV, respectively (Fig. 5c), demonstrating a high-resolution spectrum of the +2 and +3 valences for Co ions (Sun *et al.*, 2015). The C 1s (Fig. 5d) can be deconvoluted into two bands corresponding to C–C at 284.5 eV, C–O at 286.2 eV and C=O at 288.5 eV. The N 1s spectrum can be deconvoluted into two peaks at 398.8 and 400.5 eV corresponding to the pyridinic and pyrrolic N atom, respectively (Fig. 5e) (Zhang *et al.*, 2014). This result confirms that the successful N-doping in the carbon frameworks of the ZnO-Co₃O₄@N-C nanocages is achieved, which is expected to improve the performance of LIBs. The O 1s spectrum (Fig. 5f) exhibits two oxygen bonding features. The peak at 529.1 eV is typical of a metal–oxygen bond, while the peak at 531.4 eV is

Figure 4
XRD patterns of the ZnO@N-C, Co₃O₄@N-C and ZnO-Co₃O₄@N-C nanocages.

commonly associated with defects, chemisorbed oxygen or under-coordinated lattice oxygen. The calculation results show that the normalized peak areas of Zn and Co are 0.24 and 0.08, respectively. Thus, the molar ratio of Zn and Co is determined to be 3, which is equal to the ratio of the normalized peak area. Based on the above results, the molar ratio of ZnO to Co₃O₄ is 9. In addition, the result shows that the molar contents of C and N are 26.5 and 2.47%, respectively.

The nitrogen adsorption and desorption measurements were conducted to evaluate the Brunauer–Emmett–Teller (BET) surface area and the pore-size distribution of the as-prepared ZnO-Co₃O₄@N-C nanocages. As illustrated in Fig. S4(a) (see supporting information), the sample exhibits a typical type IV characteristic with a distinct H3-type hysteresis loop at 0.4–1.0 P/P_0 , indicating that the as-prepared ZnO-Co₃O₄@N-C nanocages have a typical mesoporous nature. Moreover, the pores are in the range 2–42 nm, with an average pore size of 10.9 nm, as depicted in the pore-size distribution curve (Fig. S4b in the supporting information). The BET-specific surface area is calculated to be 65.9 m² g⁻¹ and the pore volume is determined to be 0.217 cm³ g⁻¹. The mesoporous structure with higher specific surface area is propitious in accommodating the volumetric change during the Li⁺ extraction/insertion process, favouring an improved lithium-storage performance of the ZnO-Co₃O₄@N-C nanocages.

In order to investigate the electrochemical performances of the as-prepared samples, *i.e.* ZnO@N-C, Co₃O₄@N-C and ZnO-Co₃O₄@N-C, the cyclic voltammetry (CV) measurements were conducted separately at a scan rate of 0.1 mV s⁻¹

in the voltage range 0.01–3.0 V. Fig. 6(a) shows the first three consecutive CV curves of the ZnO@N-C electrodes. There is a broad anodic peak around 1.0 V during the first charge, which could be ascribed to the oxidation of metallic Zn to ZnO. As can be seen in Fig. 6(c) of the first three consecutive CV curves of the Co₃O₄@N-C electrodes, the broad cathodic peak around 0.72 V on the first cathodic sweep is attributed to the conversion reactions and the formation of a solid electrolyte interface (SEI), while a broad anodic peak around 2.19 V on the first anodic sweep is ascribed to the oxidation reactions of metallic Co (Wu *et al.*, 2014). Fig. 6(e) shows the first three consecutive CV curves of the ZnO-Co₃O₄@N-C sample. It can be seen clearly that a weak cathodic peak observed at 0.9 V is associated with the reduction of Co³⁺ to Co²⁺, while another peak below 0.3 V is concerned with the reduction of Co²⁺ to Co⁰ coupled with the formation of Li₂O during the first cycle, which indicates the irreversible reduction of electrolytes and the generation of a solid electrolyte interphase (SEI) film. In addition, the redox peak at around 1.3 V during the first cathodic sweep derives from the reduction of ZnO to Zn (Zhang *et al.*, 2017b). The subsequent oxidation peaks can be observed at 1.73 and 2.16 V for metallic Co and Zn, respectively. This shows that the oxidation peaks maintain their original positions and shapes, almost overlapping the first cycle, especially compared with the ZnO@N-C and Co₃O₄@N-C samples, implying the stability and reversibility of ZnO-Co₃O₄@N-C after the first cycle. Figs. 6(b), 6(d) and 6(f) show the discharge–charge profiles for the 1st, 2nd, 10th and 100th cycles of the ZnO@N-C, Co₃O₄@N-C and ZnO-Co₃O₄@N-C

Figure 5
XPS spectra of the as-obtained ZnO-Co₃O₄@N-C nanocages, showing (a) the survey and the high-resolution spectra of (b) Zn 2p, (c) Co 2p, (d) C 1s, (e) N 1s and (f) O 1s.

samples at a scan rate of 100 mA g^{-1} in the voltage range 0.01–3.0 V. It is found that the stability of the capacity of ZnO@N-C and Co_3O_4 @N-C with voltage change is inferior, which only keeps capacities of 610 and 746 mAh g^{-1} , respectively. Interestingly, the ZnO- Co_3O_4 @N-C sample keeps a capacity of 1102 mAh g^{-1} after 100 cycles. In addition, the first three consecutive CV curves and discharge–charge profiles for the 1st, 2nd, 10th and 100th cycles of ZnO/Co/ Co_3O_4 @N-C are shown in Figs. S5(a) and S5(b) (see supporting information). The broad anodic peaks around 2.14 V in the first charge are ascribed to the oxidation reactions of metallic cobalt. It also shows the best stability, and maintains a capacity of 807 mAh g^{-1} after 100 cycles. Given the circumstances mentioned above, the conclusion can be drawn that the ZnO- Co_3O_4 @N-C sample is more reversible and maintains a much higher capacity than ZnO@N-C, Co_3O_4 @N-C and ZnO/Co/ Co_3O_4 @N-C.

The cycling performance along with the Coulombic efficiency (CE) of porous ZnO- Co_3O_4 @N-C polyhedral nanocages was investigated at a constant current density of 100 mA g^{-1} between 0.01 and 3.0 V, as shown in Fig. 7(a). The reversible discharge capacity of the ZnO- Co_3O_4 @N-C anode is $\sim 1305 \text{ mAh g}^{-1}$ after 300 cycles, together with a high Coulombic efficiency of $\sim 98\%$ after the first several cycles. The initial charge and discharge capacities are found to be about 1495 and 2373 mAh g^{-1} , with an initial Coulombic efficiency of $\sim 62.9\%$. The initial irreversible capacity loss usually accounts for the inevitable formation of the SEI and the decomposition of the electrolyte (Vetter *et al.*, 2005). The

specific capacity gradually decreased during the first 60 cycles, which may be due to the presence of irreversible substances produced during cyclic process. However, the capacity gradually increased in subsequent cycles. Gradually increasing reversible capacities during cycling is a common phenomenon for metal oxide/carbon anode materials. This phenomenon can be attributed to the following reasons: firstly, the gradual formation of a stable SEI layer on the surface of the active material is helpful in reducing the loose electric contact during cycles, and the extra lithium could be stored in polypolymeric gel-like films to increase the specific capacity (Wang *et al.*, 2016a,b,c). Secondly, parts of the N-doped carbon are heavily cracked during multiple cycles, which leads to an increase of the interfacial area contact with the electrolyte (creating more SEI films) (Liang *et al.*, 2015). Thus, the interfacial storage of additional charge between the primary nanoparticles contributes to the increase of capacity (Peng *et al.*, 2012). Thirdly, during the charge–discharge process, the newly generated transition-metal nanoparticles might also work as electrochemical catalysts for the reversible conversion of some SEI components and hence present a certain electrochemical capacity. Therefore, the capacity of the ZnO- Co_3O_4 @N-C nanocages has an increasing trend in the long-term cycle. Fig. 7(b) demonstrates the remarkable rate capability of the ZnO- Co_3O_4 @N-C anode, with steady discharge capacities of 1458, 1398, 1165, 1056, 880 and 716 mAh g^{-1} at 0.1, 0.2, 0.5, 1, 2 and 5 A g^{-1} , respectively. When the current density was turned back to 0.1 A g^{-1} , ZnO- Co_3O_4 @N-C still regained a reversible capacity of 1460 mAh g^{-1} . More importantly, when

Figure 6

Consecutive CV curves of (a) ZnO@N-C, (c) Co_3O_4 @N-C and (e) ZnO- Co_3O_4 @N-C at a scan rate of 0.5 mV s^{-1} in the voltage range 0.01–3.0 V. Discharge and charge profiles for the 1st, 2nd, 10th and 100th cycles of (b) ZnO@N-C, (d) Co_3O_4 @N-C and (f) ZnO- Co_3O_4 @N-C.

the current density was increased to multiples of the original ($0.1\text{--}1\text{ A g}^{-1}$), the discharge capacity still stabilizes at $\sim 72\%$ of the original value. Furthermore, when the current density returned to the original value, the cycle remains stable and the capacity appears to increase slightly after several cycles, probably due to the reduced impedance of the anode materials after high current density discharge (Fig. 7*b*). As we know, ZnO possesses a theoretical capacity of 978 mAh g^{-1} , but it has rarely been used as an anode material in lithium-ion batteries because ZnO exhibits poor cyclability compared with other transition-metal oxides (Huang *et al.*, 2011). The capacities of ZnO- Co_3O_4 @N-C are much larger than the theoretical capacity of bulk Co_3O_4 (892 mAh g^{-1}) (Tian *et al.*, 2010). The lithium-storage properties of ZnO- Co_3O_4 @N-C are better than those of porous ZnO/ Co_3O_4 nanocomposites, which has a reversible discharge capacity of 957 mAh g^{-1} after 100 cycles in a previous report (Zhu *et al.*, 2015). The excellent electrochemical performance can be attributed to the unique structure of the ZnO- Co_3O_4 @N-C nanocages and the mesoporous carbon-containing systems. We also tested the cycling behaviour of the ZnO@N-C, Co_3O_4 @N-C and ZnO- Co_3O_4 @N-C anodes, and compared their performances as shown in Fig. 7(*c*). It is found that the ZnO- Co_3O_4 @N-C sample maintains a higher capacity ($\sim 1179\text{ mAh g}^{-1}$) and a stable performance over 200 cycles in contrast to the ZnO@N-C and Co_3O_4 @N-C samples, with values of 610 and 746 mAh g^{-1}

after 100 cycles, respectively. As shown in Fig. S6 (see supporting information), ZnO/Co/ Co_3O_4 @N-C exhibits better stability and capacity, which maintains at 807 mAh g^{-1} after 100 cycles. Interestingly, the ZnO- Co_3O_4 @N-C sample shows significant advantages in the long-term cycle of capacity retention and stability. Meanwhile, the superior lithium-storage performance of the ZnO- Co_3O_4 @N-C sample can be attributed to the predominant designed structure advantages involving well-dispersed ZnO in dodecahedron nanocages, as well as embedded Co_3O_4 nanocrystals and mutual compensation. In order to identify lithium-storage properties, an AC impedance measurement was employed (Fig. 7*d*). It can be seen that each Nyquist plot can be divided roughly into three parts. The high-frequency intercept on the real axis represents the electrolyte resistance. The depressed semicircle occurring at middle frequencies is generally concerned with charge-transfer resistance, and a slope at low frequencies represents the Warburg impedance in relation to the diffusion of the lithium-ion process (Hong *et al.*, 2016). Compared with the EIS spectra of the ZnO@N-C and Co_3O_4 @N-C samples, it is found that the EIS spectra of the ZnO- Co_3O_4 @N-C electrodes display a smaller diameter, verifying that the ZnO- Co_3O_4 @N-C electrode possesses lower contact and a faster reaction rate during the charge-discharge process. These results indicate that the introduction of N-doped carbon not only improves the conductivity of the electrodes, but also enhances the fast

Figure 7

(a) Cycle-life performance at 100 mA g^{-1} and Coulombic efficiency, and (b) rate capability of ZnO- Co_3O_4 @N-C nanocages; (c) cycle-life performance at 100 mA g^{-1} for ZnO@N-C, Co_3O_4 @N-C and ZnO- Co_3O_4 @N-C nanocages; and (d) AC impedance plots for ZnO@N-C, Co_3O_4 @N-C and ZnO- Co_3O_4 @N-C.

transfer of Li^+ ions and electrons, both of which are responsible for the enhanced reaction kinetics (Li & Yin, 2015).

4. Conclusion

In summary, $\text{ZnO-Co}_3\text{O}_4$ nanocomposites embedded in N-doped carbon nanocages with hollow dodecahedral shapes have been prepared successfully by simply carbonizing and oxidizing ZIF-8@ZIF-67 core-shell nanocrystals. Evaluated as an anode material for LIBs, the $\text{ZnO-Co}_3\text{O}_4\text{@N-C}$ nanocages exhibited an enhanced reversible capacity and cyclic stability (1305 mAh g^{-1} after 300 cycles) compared with the ZnO@N-C and $\text{Co}_3\text{O}_4\text{@N-C}$ samples. The outstanding lithium-storage performance of the porous $\text{ZnO-Co}_3\text{O}_4\text{@N-C}$ polyhedral nanocages could be ascribed to structural features and a synergistic effect between the bimetallic oxides and N-doped carbon, which facilitates the transport of ions and electrons. This outstanding performance makes the $\text{ZnO-Co}_3\text{O}_4\text{@N-C}$ nanocages promising anode material candidates for the high performance of LIBs. The synthesis approach presented here can be extended to other carbon-based functional MOF materials with rationally designed morphologies and architectures.

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