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Combustion synthesized macroporous structure MFe_2O_4 (M= Zn, Co) as anode materials with excellent electrochemical performance for lithium ion batteries



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ABSTRACT

ZnFe₂O₄ and CoFe₂O₄ materials are successfully prepared via solution combustion synthesis with glycine as fuel and complexing agent. The final products are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The average diameter of the prepared particles is in the range of 80-100 nm. Cyclic voltammetry (CV), galvanostatic cycling and electrochemical impedance spectroscopy (EIS) studies are used to investigate the electrochemical properties of the MFe₂O₄ (M = Zn, Co) particles. The reversible capacities of $ZnFe_2O_4$ and $CoFe_2O_4$ are 1037.2 mAh g^{-1} and 994.3 mAh g^{-1} , respectively, after 80 cycles at a current density of 200 mA g^{-1} . The capacity retentions are up to 104.2% and 106.6% compared to the second cycle. The as-synthesized samples also exhibit outstanding rate capability and long cycle life. After 300 cycles at a high current density of 1000 mA g^{-1} , the capacity retention are 109.3% and 87.4% compared to the second cycle with almost no capacity fading but increasing. It could still maintain reversible capacities of 794.7 mAh g^{-1} and 746.5 mAh g^{-1} , respectively. The superior electrochemical performance can be attributed to the macroporous structure in pure phase without any impurities, which can not only ease the volume expansion during the charge/discharge processes but also provide more interstices for lithium ions insertion. What is more, the high crystallinity of two samples is able to stabilize the microstructure no collapse after plenty of lithiation-delithiation processes. The results suggest that this method is a facile, effective and general way to synthesize excellent electrochemical properties of macroporous structure spinel Fe-based binary transition metal oxides as anode material for lithium ion batteries.

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1. Introduction

Lithium ion batteries (LIBs) are widely used in portable electronic devices due to their high energy density, low cost and long cycle life. LIBs also have been looked at attentively as the promising power source of electrical/hybrid vehicles [1–3]. Graphite is the commonly used as anode material in commercial LIBs. However, it is limited to a low theoretical capacity of 372 mAh g⁻¹, which cannot fulfill the increasing demands for LIBs with high power and

high energy density. In addition, Li metal deposition on the graphite anode and concerns about safety of carbon anodes during charging are inherent safety risks [4,5]. Therefore, the demands for next-generation LIBs are developing novel anode materials combining higher theoretical capacity and electrochemical stability.

Nanostructured Fe-based binary and ternary metal oxides with high special capacities and high safety were studied in the past few years [6–9]. Ferrites (MFe₂O₄, M = transition metal) with different morphologies have been synthesized through several methods to improve the performance of LIBs. For example, ZnFe₂O₄ nanofibers synthesized through electrospinning technique gave a specific capacity of about 733 mAh g⁻¹ after 30 cycles [10]; ZnFe₂O₄ hollow microspheres obtained by hydrothermal reaction followed by

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annealing at 600 °C showed a reversible capacity of 900 mAh g^{-1} over 50 cycles [11]. ZnFe₂O₄ octahedrons prepared by one-step hydrothermal method delivered a reversible capacity of 730 mAh g^{-1} after 300 cycles with the current density of 1000 mAh g^{-1} [12]. Other structures such as porous CoFe₂O₄ nanosheets [13], cubic aggregated CoFe₂O₄ nanoparticle [14] and nanostructured MgFe₂O₄ [15] were synthesized and investigated their electrochemical properties. However in most cases, long reaction time, high external temperature or special instrumentation is necessary for obtaining high crystallinity [16]. And in order to control some special structures, a whole host of organic salts, surfactant or templates were added, which will result in the high costs [17,18]. In this work, we have prepared MFe_2O_4 (M = Zn, Co) with macroporous structure, high crystallinity and superior electrochemical performance via using a convenient processing, rapid and low-cost pathway through solution combustion synthesis (SCS).

The most obvious advantage of SCS is its time and energy efficiency. Besides these two advantages, there are other advantages of SCS: (1) simple and inexpensive instrumentation; (2) combustion synthesis in the liquid phase can make sure the excellent product homogeneity; (3) possibility of synthesizing highly pure ternary or quaternary oxides with complex structures; (4) high surface and more sites activity in the case of heterostructured photocatalysts, which is beneficial for the transfer and separation of charge carriers; (5) precise particle property can be controlled (size, crystallinity) by varying temperature and residence time; (6) access to novel materials and performance [6,16]. The as-prepared materials possess macroporous structure and high crystallinity. They show superior rate capability and cycling performance compared with the previous reports (Table S1) [13,14,19–22].

2. Experimental

2.1. Sample preparation

All of the chemicals were analytical grade and purchased from Sinopharm Chemcal Reagent Co., Ltd. without further purification. Macroporous structure MFe₂O₄ were prepared by solution combustion synthesis and sintering. The schematic illustration for the synthetic process of the MFe₂O₄ material is shown in Fig. 1. In a typical synthesis process, 5 mmol of metal acetates $(Zn(NO_3)_2 \cdot 6H_2O, Co(NO_3)_2 \cdot 6H_2O)$ and 10 mmol of Fe(NO₃)₃ $\cdot 9H_2O$ were dissolved in 60 mL deionized water. Then, 15 mmol of glycine was added into the solution which acts both as fuel and ligand. The mixture was continuously stirred for 5 min until glycine actually dissolved. The resultant solution was heated at 100 °C with constant stirring for 5 h, to transform the solution into a xerogel. The xerogel underwent self-propagating combustion progress formed a fluffy powder at 200 °C in 1 min. Finally, fluffy precursor was calcined in air at 800 °C for 2 h in the muffle furnace at a heating rate of 4 °C min⁻¹. The single-phase ferrite particles were obtained after being cooled to room temperature.

2.2. Characterization

The crystal structure of as-prepared compounds were identified by X-ray powder diffraction (XRD) using a Rigaku MiniFlex II X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154178$ nm). The morphologies and microstructure of samples were examined by scanning electron microscope (SEM) and transition electron microscope (TEM). SEM micrographs were acquired using a FEI Nova NanoSEM 450 field emission scanning electron microscope (FESEM) at 15 kV. TEM experiments were performed on a JEM 2100 transmission electron microscopy at an accelerating voltage of 200 kV.

2.3. Electrochemical measurements

The electrochemical performances were performed using a standard CR2016 coin cell with lithium metal as counter electrode, a Celgard 2400 microporous polypropylene membrane as the separator, and a solution of 1 mol L⁻¹ LiPF₆ in ethylene carbonate/ dimethyl carbonate(EC/DMC) with a volume ratio of 1:1 as electrolyte. Working electrodes were prepared with the composition of 70 wt% MFe₂O₄, 20 wt% conductive carbon blacks (super P) as a conductive additive, and 10 wt% polyvinylidene fluoride(PVDF). Galvanostatic discharge/charge cycling tested in the range from 0.01 to 3.0 V versus Li/Li⁺ with a Land BTI-40 (Wuhan, China) cell test system at room temperature. The cycling performances were tested at current densities of 200 mA g^{-1} and 1000 mA g^{-1} , respectively. The rate capabilities of samples were tested at current from 100 mA g^{-1} to 1600 mA g^{-1} . The cyclic voltammograms (CVs) properties were carried out using Metrohm Autolab PGSTAT302N (Netherlands) at constant scanning rate of 0.01 mv⁻¹ in the voltage of 0.005-3.0 V (vs. Li/Li⁺) and electrochemical impedance spectroscopy (EIS) measurements were also studied on Autolab PGSTAT302N in the frequency range of 1 MHz to 0.5 Hz with 60 μ A RMS amplitude. Fitting of the impedance spectra to the equivalent circuit was worked out by the code ZSimpWin.

3. Results and discussion

Fig. 2 shows XRD patterns of MFe₂O₄ (M = Zn, Co) and their precursors in the 2 θ range 10–80°, respectively. All of diffraction peaks perfectly match cubic spinel ZnFe₂O₄ (PDF Card, No. 22-1012) and CoFe₂O₄ (PDF Card, No. 22-1086). XRD patterns show very sharp peaks which indicate high crystallinity. There is an obvious peak intensity difference between ZnFe₂O₄ and CoFe₂O₄. The peaks of ZnFe₂O₄ are evidently more intense than that of CoFe₂O₄, while both samples have similar crystallite size, which can demonstrate the crystallinity of ZnFe₂O₄ is higher than that of CoFe₂O₄. Curves of two ferrites as-prepared products are also more intense than precursors implying that the crystallinity is improved after calcination. No peaks of any other phases or impurities were observed, which reveal all the compositions are in pure phase without any impurities. The average crystallite sizes of the two samples are calculated to be 70–100 nm using Scherrer's equation.



Fig. 1. Schematic diagram of the synthesis process for porous MFe₂O₄ materials.



Fig. 2. XRD patterns of MFe_2O_4 (M = Zn, Co) and their precursors.

The morphology and particle sizes of the as-prepared $ZnFe_2O_4$ and $CoFe_2O_4$ were characterized by SEM microscopy (Fig. 3). It can be seen that materials obtained by combustion method present macroporous structure from Fig. 3 (a) and (c). The macropores with different diameters can increase the surface area which offers better contacting between the electrode and electrolyte. The individual nanoparticles are closely united to form micron sized particles as shown in Fig. 3 (b) and (d). Most of the particles are observed to be irregular shape with the size of 200–400 nm.

Fig. 4 reveals the TEM images of $ZnFe_2O_4$ and $CoFe_2O_4$. The grains size is found to be 80–100 nm, which is in good agreement with the crystallite size calculated by Scherrer's equation.

 $ZnFe_2O_4$ and $CoFe_2O_4$ electrodes are characterized by cyclic voltammograms (CVs) in the voltage window of 0.005–3.0 V vs. Li/

 Li^+ at a scan rate of 0.01 mV s⁻¹ using Li metal as the counter and reference electrode. The CV profiles were given in Fig. 5. For two samples, it is obvious that the first cycle is distinct substantially from subsequent ones, indicating a different Li⁺ storage reaction taking place in the first cycle compared with the following cycles. MFe₂O₄ transforms to Li_{0.5}MFe₂O₄ and then to Li₂MFe₂O₄ at the first discharge process, which is electrochemical reversibility (Eqs. (1) and (2)). A sharp peak at 0.74 V around could be ascribed to $Li_2MFe_2O_4$ consuming 6 Li^+ ions formation of M⁰ and Fe⁰ and amorphous Li_2O , which is irreversible (Eq. (3)). After that, there are some differences on the Li storage mechanism between Zn and Co. Zn undergo a alloying process with Li to form Li-Zn alloy in discharged process while Co do not possess the extra reaction (Eq. (4)). In the second cycle, the cathodic peak shifts to a higher voltage of \approx 0.88 V, due to a structure rearrangement and associated with the reversible reduction of Fe^{3+} and $M^{2+}((Eqs. (5) and (6)))$. Guo et al. believe that Fe²⁺ is the intermediate product because the oxidation voltage from FeO to Fe_2O_3 is 1.4057 V closing to the voltage of Fe oxidized to FeO [11]. Meanwhile, an anodic peak in the first cycle centered at 1.68 V, which corresponds to the multistep oxidation of M^0 and Fe^0 to MO and Fe_2O_3 , respectively. The anodic peak shift a bit to about 1.69 V and are well overlapped in the subsequent cycles, indicating that good electrochemical reversibility and capacity retention for MFe₂O₄. A total of 9 Li⁺ ions per ZnFe₂O₄ formula are reacted in the 1st discharge, but 8 Li⁺ ions react with CoFe₂O₄ Therefore, ZnFe₂O₄ possesses superior theoretical capacity compared with CoFe₂O₄. All these 9 or 8 lithium ions can be delivered in the recharge process however MFe₂O₄ cannot be restored [24.25].

$$ZnFe_2O_4 + 0.5Li^+ + 0.5e^- \leftrightarrow Li_{0.5}ZnFe_2O_4$$
 (1)

$$Li_{0.5}ZnFe_2O_4 + 1.5Li^+ + 1.5e^- \leftrightarrow Li_2ZnFe_2O_4$$
 (2)



Fig. 3. SEM images of ZnFe₂O₄ (a and b) and CoFe₂O₄ (c and d) nanoparticles.



Fig. 4. TEM patterns of the ZnFe₂O₄ (a) and CoFe₂O₄ (b), respectively.



Fig. 5. Cyclic voltammograms curves of ZnFe₂O₄ (a) and CoFe₂O₄ (b) electrodes at a rate of 0.1 mv⁻¹ in the voltage of 0.005–3.0 V vs. Li/Li⁺.

$$Li_2ZnFe_2O_4 + 6Li^+ + 6e^- \rightarrow 4Li_2O + Zn + 2Fe$$
 (3)

$$Zn + Li^{+} + e^{-} \leftrightarrow Zn - Li$$
(4)

 $3Li_2O + 2Fe \leftrightarrow Fe_2O_3 + 6Li^+ + 6e^-$ (5)

$$Li_2O + Zn \leftrightarrow ZnO + 2Li^+ + 2e^-$$
 (6)

Fig. 6 illustrates that the typical charge-discharge profiles and the cycle performances of ZnFe₂O₄ and CoFe₂O₄ in the potential range of 0.01–3.0 V at a current density of 200 mA g^{-1} (vs. Li⁺/Li). Initial discharge and charge capacities of ZnFe₂O₄ and CoFe₂O₄ are 1404.6/985.2 mAh g^{-1} and 1258.6/936.2 mAh g^{-1} , respectively. For the two samples, it can be observed a voltage plateau at 0.8 V in the first cycle. Fig. 6(a) shows the second discharge capacity decreased to 990.7 mAh g⁻¹ with a voltage plateau at 1.5 V and the second discharge capacity of CoFe₂O₄ is 932.4 mAh g^{-1} with a voltage plateau at 1.6 V by Fig. 6(b). A large irreversible capacity loss between the first and second cycles can be observed which may be due to the formation of a solid electrolyte interphase layer (SEI) and the decomposition of electrolyte [20]. After 10 cycles, irreversible capacities increased compared with the second one. But after 30 cycles, discharge capacities of ZnFe₂O₄ and CoFe₂O₄ are 1055.6 mAh g^{-1} and 980.1 mAh g^{-1} , which is higher than that in the second cycle. Fig. 6(c) and (b) show the cycling performance and coulombic efficiencies of the ZnFe₂O₄/Li and CoFe₂O₄/Li cells at 200 mA g⁻¹. The capacities of both samples decrease at first and then increase and decrease again remaining in a tight range. The capacity fading during the first few tens of cycles may be attributed to structural degradation and rearrangement with the formation of a polymeric gel-like film on the active materials [26]. The polymeric gel-like film is due to kinetically activated electrolyte decomposition, which can store excess Li⁺ ions through a so-called "pseudo-capacitance-type behavior" [27]. As a result, the capacity gradually increased in subsequent cycles. The discharge capacity of $ZnFe_2O_4$ and $CoFe_2O_4$ remained 1037.2 mAh g⁻¹ and 994.3 mAh g⁻¹ after 80 cycles, the capacity retentions are up to 104.2% and 106.6% compared to the second cycle, respectively, indicating superior capacity retention to those reported previously [19–21].

At a current density of 1000 mA g^{-1} , the change rule of capac-ities is as same as them at 200 mA g^{-1} as shown in Fig. 7 (a) and (b). The capacities of two products are first decrease then increase and decrease at last, and coulombic efficiency is always higher than 95% except the first cycle. After 300 cycles, the specific capacity of $ZnFe_2O_4$ could maintain to 794.7 mAh g⁻¹ and $CoFe_2O_4$ is 746.5 mAh g^{-1} . Additionally, the capacities of two samples are higher than most of the previous works [28,29]. It may be attributed to the macroporous structure with plenty of interspaces not only can ease the volume expansion during the charge/discharge processes but also provide more interstices for lithium ions insertion and consequently improve the cycle performance [30,31]. What is more, the high crystallinity of two samples is able to stabilize the microstructure no collapse after plenty of charge/ discharge processes, which is also beneficial to improve the cycle performance. Galvanostatic cycling tests reveal that both the first discharge capacities and the remaining capacities after hundreds cycles of ZnFe₂O₄ are higher than that of CoFe₂O₄.

Besides the high capacity and excellent cycling stability, the good rate capability is another important property for highperformance anodes. The rate capability of the ZnFe₂O₄ and CoFe₂O₄ electrode were evaluated under different current densities



Fig. 6. The discharge/charge profiles of ZnFe₂O₄ (a) and CoFe₂O₄ (b) and cycling performance of ZnFe₂O₄ (c) and CoFe₂O₄ (d) in a voltage range of 0.01–3.0 V vs. Li/Li⁺ at current density of 200 mA g⁻¹.



Fig. 7. Discharge/charge capacity of ZnFe₂O₄ (a) and CoFe₂O₄ (b) at 1000 mA g⁻¹, and rate capability of ZnFe₂O₄ (c) and CoFe₂O₄ (d) at current from 100 mA g⁻¹ to 1600 mA g⁻¹.

in the 100 mA g⁻¹ to 1600 mA g⁻¹ range. As shown in Fig. 7 (c) $ZnFe_2O_4$ nanoparticles exhibits the average discharge capacity of 979.4, 903.7, 873.5, 847.2, 803.0 mAh g⁻¹ at the current densities of 100, 200, 400, 800, 1600 mA g⁻¹, respectively. In terms of CoFe₂O₄ nanoparticles the discharge capacities of CoFe₂O₄ nanoparticles are

1174.0, 1154.2, 1140.6, 1113.5, 1036.4 mAh g^{-1} at the current densities of 100, 200, 400, 800, 1600 mA g^{-1} , respectively. Lines of capacities change gently especially the one of CoFe₂O₄. The restoration of two samples after high rate cycling is significant, when the current density returns to 100 mA g^{-1} after 10 cycles at



Fig. 8. Nyquist plots of ZnFe₂O₄ (a) and CoFe₂O₄ (b) electrodes before 1st discharge cycle, impedance spectrum of ZnFe₂O₄ (c) and CoFe₂O₄ (d) in the charge state to 1.7 V after 10 cycle. (e) Equivalent circuit used for observed the impedance spectra.

1600 mA g^{-1} , the ZnFe₂O₄ electrode resumes capacity of 1011.6 mAh g^{-1} and the cell of CoFe₂O₄ recovers full charge capacity of 1309.7 mAh g^{-1} . The result indicate that the as prepared materials have good retention capability and good rate performance in a wide range of current densities.

To further demonstrate the transport kinetics for the electrochemical properties of $ZnFe_2O_4$ and $CoFe_2O_4$ electrodes, electrochemical impedance spectroscopy (EIS) measurements were carried out for two samples before 1st discharge cycle and after 10 cycles at the current density of 200 mA g⁻¹. As shown in Fig. 8, all impedance spectrum consist of a depressed semicircle in high to medium frequency range and a tail in the low frequency range and the equivalent circuit for the observed Nyquist plots is shown in Fig. 8 (e) [32]. In this equivalent circuit, R_s indicates the ohmic resistance of electrolyte, R_b represents the electronic resistance of the active material and ionic conductivity in the electrode, R_{ct} corresponds to the charge transfer resistance; CPE represents the double-layer capacitance and W is the Warburg impedance. The impedance parameters of R_b and R_{ct} are listed in Table 1. The resistance of two fresh cells is very similar, but R_b of the ZnFe₂O₄ cell is much lower than CoFe₂O₄ one after 10 cycles. It might be because the surface film of CoFe₂O₄ cells is thicker than ZnFe₂O₄ cells after charge/discharge, which also can prove that the electrochemical performance of ZnFe₂O₄ is better than that of CoFe₂O₄.

4. Conclusion

In conclusion, we have presented a facile and effective route for

Table 1

Resistance values obtained from equivalent circuit fitting of experimental data for all samples.

	ZnFe ₂ O ₄ (fresh cell)	ZnFe ₂ O ₄ (after 10 cycles)	CoFe ₂ O ₄ (fresh cell)	CoFe ₂ O ₄ (after 10 cycles)
$R_{b}(\Omega)$	20.65	34.79	29.29	229.20
$R_{ct}(\Omega)$	58.70	8.72	80.41	9.99

synthesizing MFe₂O₄ (M = Zn, Co) materials using SCS. The synthesized materials characterized by XRD, SEM and TEM studies are found to contain particles 80–100 nm in size with a great quantity of macropores. After 80 cycles, the reversible capacity of 1021.7 mAh g⁻¹ and 1041.8 mAh g⁻¹ for ZnFe₂O₄ and CoFe₂O₄ at 200 mA g⁻¹ in the voltage range of 0.01–3.0 V, respectively. At the high current density of 1000 mA g⁻¹ even after 300 cycles, 794.7 mAh g⁻¹ could be maintained for ZnFe₂O₄ and 746.5 mAh g⁻¹ could be maintained for CoFe₂O₄. The merits of high lithium storage capacity, excellent reversible capacity and rate capability, in combination with the simple and rapid method, make MFe₂O₄ (M = Zn, Co) materials very prospective candidates as anode materials for high energy LIBs in next generation. We believe that this method also can be used to synthesize another Fe-based binary transition metal compounds, such as CuFe₂O₄, MgFe₂O₄ and NiFe₂O₄ and so on.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2016.12.225.

References

- C. Cheng, L. Tan, A. Hu, H. Liu, X. Huang, Synthesis of LiNi_{0.65}Co_{0.25}Mn_{0.1}O₂ as cathode material for lithium-ion batteries by rheological phase method, J. Alloys Compd. 506 (2010) 888–891.
- [2] H. Luo, L. Shen, K. Rui, H. Li, X. Zhang, Carbon coated Li₄Ti₅O₁₂ nanorods as superior anode material for high rate lithium ion batteries, J. Alloys Compd. 572 (2013) 37–42.
- [3] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, Nature 414 (2001) 359–367.
- [4] L. Yao, X. Hou, S. Hu, X. Tang, X. Liu, Q. . Ru, An excellent performance anode of ZnFe₂O₄/flake graphite composite for lithium ion battery, J. Alloys Compd. 585 (2014) 398–403.
- [5] S.K. Das, M. Gnanavel, M.U.M. Patel, C. Shivakumara, A.J. Bhattacharyya, Anamolously high lithium storage in mesoporous nanoparticulate aggregation of Fe³⁺ doped anatase titania, J. Electrochem. Soc. 158 (2011) A1290–A1297.
- [6] Y. Wu, L. Zhan, K. Huang, H. Wang, H. Yu, S. Wang, F. Peng, C. Lai, Iron based dual-metal oxides on graphene for lithium-ion batteries anode: effects of composition and morphology, J. Alloys Compd. 684 (2016) 47–54.
- [7] Y.Q. Chu, Z.W. Fu, Q.Z. Qin, Cobalt ferrite thin films as anode material for lithium ion batteries, Electrochim. Acta 49 (2004) 4915–4921.
- [8] J. Mao, X. Hou, F. Huang, K. Shen, K.H. Lam, Q. Lu, S. Hu, Zn substitution NiFe₂O₄ nanoparticles with enhanced conductivity as high-performances electrodes for lithium ion batteries, J. Alloys Compd. 676 (2016) 265–274.
- [9] H.M. Fan, J.B. Yi, Y. Yang, K.W. Kho, H.R. Tan, Z.X. Shen, J. Ding, X.W. Sun, M.C. Olivo, Y.P. Feng, Single-crystalline MFe₂O₄ nanotubes/nanorings synthesized by thermal transformation process for biological applications, ACS Nano 3 (2009) 2798–2808.

- [10] F.T. Pei, Y. Sharma, S.S. Pramana, M. Srinivasan, Nanoweb anodes composed of one- dimensional, high aspect ratio, size tunable electrospun ZnFe₂O₄ nanofibers for lithium ion batteries, J. Mater. Chem. 21 (2011) 14999–15008.
- [11] X.W. Guo, X. Lu, X.P. Fang, Y. Mao, Z.X. Wang, L.Q. Chen, X.X. Xu, H. . Yang, Y.N. Liu, Lithium storage in hollow spherical ZnFe₂O₄ as anode materials for lithium ion batteries, Electrochem. Commun. 12 (2010) 847–850.
- [12] Z. Xing, Z.C. Ju, J. Yang, H.Y. Xu, Y.T. Qian, One-step hydrothermal synthesis of ZnFe₂O₄ nano-octahedrons as a high capacity anode material for Li-ion batteries, Nano Res. 5 (2012) 477–485.
- [13] X. Yao, J. Kong, X. Tang, D. Zhou, C. Zhao, R. Zhou, X. Lu, Facile synthesis of porous CoFe₂O₄ nanosheets for lithium-ion battery anodes with enhanced rate capability and cycling stability, RSC Adv. 4 (2014) 27488–27492.
- [14] J. Mao, X. Hou, X. Wang, S. Hu, L. Xiang, The cubic aggregated CoFe₂O₄ nanoparticle anode material for lithium ion battery with good performance, Mater. Lett. 161 (2015) 652–655.
- [15] N. Sivakumar, S.R.P. Gnanakan, K. Karthikeyan, S. Amaresh, W.S. Yoon, G.J. Park, Y.S. Lee, Nanostructured MgFe₂O₄ as anode materials for lithium-ion batteries, J. Alloys Compd. 509 (2011) 7038–7041.
- [16] F.T. Li, J. Ra, M. Jaroniec, S.Z. Qiao, Solution combustion synthesis of metal oxide nanomaterials for energy storage and conversion, Nanoscale 7 (2015) 17590–17610.
- [17] S. Sun, X. Yang, Y. Zhang, F. Zhang, J. Ding, J. Bao, C. Gao, Enhanced photocatalytic activity of sponge-like ZnFe₂O₄ synthesized by solution combustion method, Prog. Nat. Sci Mater. 22 (2012) 639–643.
- [18] X. Zhang, W. Jiang, D. Song, H. Sun, Z. Sun, F. Li, Salt-assisted combustion synthesis of highly dispersed superparamagnetic CoFe₂O₄ nanoparticles, J. Alloys Compd. 475 (2009) L34–L37.
- [19] X. Fu, D. Chen, M. Wang, Y. Yang, Q. Wu, J. Ma, X. Zhao, Synthesis of porous CoFe₂O₄ octahedral structures and studies on electrochemical Li storage behavior, Electrochim. Acta 116 (2014) 164–169.
- [20] H. Xia, Y. Qian, Y. Fu, X. Wang, Graphene anchored with ZnFe₂O₄ nanoparticles as a high-capacity anode material for lithium-ion batteries, Solid State Sci. 17 (2013) 67–71.
- [21] A.S. Hameed, H. Bahirae, M.V. Reddy, M.Z. Shoushtari, J.J. Vittal, C.K. Ong, B.V.R. Chowdari, Lithium storage properties of pristine and (Mg, Cu) codoped ZnFe₂O₄ Nanoparticles, ACS Appl. Mater. Interfaces 6 (2014) 10744–10753.
- [22] N. Wang, H. Xu, L. Chen, X. Gu, J. Yang, Y. Qian, A general approach for MFe₂O₄ (M= Zn, Co, Ni) nanorods and their high performance as anode materials for lithium ion batteries, J. Power Sources 247 (2014) 163–169.
- [24] X. Zhang, Y.P. Xie, Y.F. Sun, Q. Zhang, Q.Y. Zhu, D. Hou, J.X. Guo, Self-template synthesis of CoFe₂O₄ nanotubes for high-performance lithium storage, RSC Adv. 5 (2015) 29837–29841.
- [25] L. Yao, X. Hou, S. Hu, Q. Ru, X. Tang, L. Zhao, D. Sun, A facile bubble-assisted synthesis of porous Zn ferrite hollow microsphere and their excellent performance as an anode in lithium ion battery, J. Solid State Electrochem 17 (2013) 2055–2060.
- [26] Z.S. Wu, W. Ren, L. Wen, L. Gao, J. Zhao, Z. Chen, G. Zhou, F. Li, H.M. Cheng, Graphene anchored with co(3)o(4) nanoparticles as anode of lithium ion batteries with enhanced reversible capacity and cyclic performance, ACS Nano 4 (2010) 3187–3194.
- [27] J. Wang, Q. Zhang, X. Li, B. Zhang, L. Mai, K. Zhang, Smart construction of three-dimensional hierarchical tubular transition metal oxide core/shell heterostructures with high-capacity and long-cycle-life lithium storage, Nano Energy 12 (2015) 437–446.
- [28] J. Xiao, G. Xu, S.G. Sun, S. Yang, MFe₂O₄ and MFe@Oxide core-shell nanoparticles anchored on N-doped graphene sheets for synergistically enhancing lithium storage performance and electrocatalytic activity for oxygen reduction reactions, Part. Part. Syst. Char. 30 (2013) 893–904.
- [29] Z.H. Li, T.P. Zhao, X.Y. Zhan, D.S. Gao, Q.Z. Xiao, G.T. Lei, High capacity threedimensional ordered macroporous CoFe₂O₄ as anode material for lithium ion batteries, Electrochim. Acta 55 (2010) 4594–4598.
- [30] J. Mao, X. Hou, X. Wang, G. He, Z. Shao, S. Hu, Corncob-shaped ZnFe₂O₄/C nanostructures for improved anode rate and cycle performance in lithium-ion batteries, RSC Adv. 5 (2015) 31807–31814.
- [31] S. Liu, J. Xie, C. Fang, G. Cao, T. Zhu, X. Zhao, Self-assembly of a ZnFe₂O₄/graphene sandwich by a controllable and general route: towards a highperformance anode for Li-ion batteries, J. Mater. Chem. 22 (2012) 19738–19743.
- [32] S.H. Yeon, W. Ahn, S.N. Lim, K.H. Shin, C.S. Jin, J.D. Jeon, K.B. Kim, S.B. Park, Unique cyclic performance of post-treated carbide-derived carbon as an anode electrode, Carbon 78 (2014) 91–101.