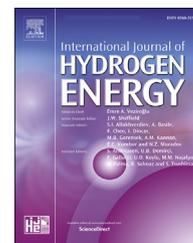




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# Study on electrochemical performances of composite carbon (FeO/C) materials fabricated by coal tar pitch and Fe<sub>3</sub>O<sub>4</sub> particles

Kun Wang<sup>b</sup>, Dongying Ju<sup>b,c,\*\*</sup>, Guiying Xu<sup>a</sup>, Yongfei Wang<sup>a</sup>,  
Shaobei Chen<sup>a</sup>, Jian Zhang<sup>a</sup>, Yuyuan Wu<sup>a</sup>, Weimin Zhou<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Advanced Coal and Coking Technology of Liaoning Province, School of Chemical Engineering, University of Science and Technology Liaoning, Anshan, 114051, PR China

<sup>b</sup> School of Materials and Metallurgy, University of Science and Technology Liaoning, Anshan, 114051, PR China

<sup>c</sup> Advanced Science Research Laboratory, Saitama Institute of Technology, 1690, Fusaiji, Fukaya, Japan

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## ABSTRACT

The new functional FeO/C composite carbon materials are successfully fabricated by controlling the adding amounts of Fe<sub>3</sub>O<sub>4</sub> particles in mixtures of coal tar pitch and Fe<sub>3</sub>O<sub>4</sub> particles. The structures of prepared FeO/C composite carbon materials were verified by XRD measurements. The excellent electrochemical performances of FeO/C composite carbon materials were evaluated in detail. For instance, the prepared materials show the high cycling performances at 679 mAh/g after carrying out charge-discharge 100 cycles. Meanwhile, the high rate performances and long cycle life characteristics of FeO/C composite materials were also observed. As a result, it is palpable that the carbon contents and specific area are the vital factors to improve the electrochemical performances of FeO/C composite materials, which effectively provides the reference to design the transition metal oxide/carbon composite materials as Li<sup>+</sup> ion storage materials.

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## Introduction

With the development of electric vehicle and hybrid electric vehicle, the technologies about energy storage are becoming important than ever before. Therefore, how to increase the storage capacity of batteries is becoming imminent by now. The research subjects of lithium ion batteries (LIBs) as a one of significant new energies mainly show on the aspects which increase the energy densities, charge capacity and cycling effects [1–6].

Graphitized carbon is exceedingly successful commercialization anode materials, for they have remarkable advantages on aspect of cost [7]. However, the relatively low charge efficiency and energy density limit the application of graphitized carbon in fabrications of anode materials. Thus, a great many of research groups pay attention to the transition metal oxides such as Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, NiO, CoO, Co<sub>3</sub>O<sub>4</sub>, Cu<sub>2</sub>O, CuO, RuO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub>, as they have the high theoretical capacity (600–1000 mAh/g). Nevertheless, the intercalation and deintercalation of Li<sup>+</sup> ions easily give rise to the collapsing of lattice structure of transition metal oxides, causing the storage capacity and

\* Corresponding author.

\*\* Corresponding author. School of Materials and Metallurgy, University of Science and Technology Liaoning, Anshan, 114051, PR China.

E-mail address: [aszhou15242870697@163.com](mailto:aszhou15242870697@163.com) (W. Zhou).

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cycling property become worse than before [8–12]. As a consequence, how to maintain the structural integrity and attenuate the volume expansion of transition metal oxides is essential consideration to fabricate anode materials. A lot of groups adopt the way to use the graphene oxide (GO) and carbon nanotube (CNT) to cover the transition metal oxides, in order to maintain the lattice structure of transition metal oxides [13–16]. Although these methods are effective way to solve the defects of transition metal oxides, the high cost of GO and CNT very restrain their actual applications in fabrications of anode materials. In light of mentioned descriptions, choosing the suitable carbon materials to fabricate hybrid transition metal oxides/carbon electrode materials is becoming the urgent subject now.

Based on the concept about coal chemistry, the coal tar pitches containing a lot of polycyclic aromatic hydrocarbons (PAHs) attract us significantly, for they are able to become the carbon materials having network structures, causing that these materials possess the excellent conductivity [17–19]. Meanwhile, the special characteristic such as low softening temperature of coal tar pitch leads it to cover the transition metal oxides easily.

Iron oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{FeO}$ ) are attracted to fabricate anode materials usually, for they have the some advantages, such as low cost, environment-friendly and high theoretical charge capacities. In spite of the fact that the theoretical charge capacity of  $\text{FeO}$  showing at 744 mAh/g is lower than the  $\text{Fe}_2\text{O}_3$  (927 mAh/g) and  $\text{Fe}_3\text{O}_4$  (1007 mAh/g) respectively, the excellent conductivity and small expansion of volume of  $\text{FeO}$  crystals lead it to can achieve the high capacity and cycling stability when they are used as  $\text{Li}^+$  ion storage materials [20–23]. Petnikota et al., prepared the EG/ $\text{FeO}$  complex materials with the relative low specific surface area using the exfoliated GO (EG) and  $\text{Fe}_2\text{O}_3$  as crude materials, and reported their electrochemical performances when these materials were used as electrodes of LIBs. However, the descriptions about electrochemical properties are insufficient. For example, the evaluations about rate performances of prepared EG/ $\text{FeO}$  composite materials are not enough in presented reports [23].

In our studies, the coal tar pitch based C/ $\text{FeO}$  composite carbon materials were firstly fabricated through controlling the adding amounts of  $\text{Fe}_3\text{O}_4$  particles in mixture of coal tar pitches and  $\text{Fe}_3\text{O}_4$  particles, and their excellent electrochemical performances such as high cycling performances, high rate performances and long cycle life were investigated in detail. Moreover, associating with the low cost of coal tar pitches, the excellent electrochemical performances of fabricated C/ $\text{FeO}$  complex materials indicate that they have the high ability in fabrication of LIBs as anode materials.

## Experimental section

### Materials

Coal tar pitches were obtained from Ansteel Group Corporation, Anshan, China. Polyvinyl alcohol (PVA), pyridine and  $\text{Fe}_3\text{O}_4$  nano-particles were purchased from Aladdin Industrial Corporation. Ethylene carbonate (EC), Dimethyl carbonate

(DMC), Ethyl methyl carbonate (EMC) and Lithium hexafluorophosphate ( $\text{LiPF}_6$ ) were purchased from Beijing Chemical Reagent Research Institute Co., Ltd.

### Characterization

The FT-IR results were determined by the instrument of Nicolet Company, USA. The measurements of X-ray diffraction (XRD) were carried out by the X'pert Powder instrument from PANalytical, Holland. Electrochemical WorkstationCHI660E, (CHI instruments, China) was used to conduct electrochemical experiments. The evaluations about charge and discharge are performed by the LAND battery test system (LAND CT2001A, China). The scanning electron microscope (SEM) images were detected by the Carl Zeiss AG, Germany. The Brunauer-Emmett-Teller (BET) measurements about specific surface area were evaluated by AutosorbIQ made in Quantachrome instruments, USA.

### Preparation of composite carbon materials

Firstly, the pyridine solvent (100 mL) containing coal tar pitches were obtained by soxhlet extraction method using the pyridine solvent (100 mL) and coal tar pitches (1 g). After adding the obtained pyridine solvent into the solution which was prepared by dissolving the PVA in the water with weight ratio of 1.5 wt%, the  $\text{Fe}_3\text{O}_4$  nano particles (0.2 g, 0.4 g, 0.6 g, 0.8 g, 1.0 g and 1.2 g) were respectively added into the same mixture solution. Then the obtained mixture was carried out ultrasonic dispersion for 5 min, the temperature of mixture was rose to 85 °C and maintained at this temperature for 20 min under stirring. After filtering the mixture, the  $\text{Fe}_3\text{O}_4$  particles covered coal tar pitches were obtained successfully. Thus, for easy description as follows, according to the adding amounts of  $\text{Fe}_3\text{O}_4$  particles, we named the obtained solids as 0.2/C, 0.4/C, 0.6/C, 0.8/C, 1.0/C and 1.2/C, respectively.

### Oxidative stabilization and carbonization of composite carbon materials

Based on the reports about oxidative stabilization and carbonization of coal tar pitches, we firstly performed the oxidative stabilization of iron oxide composite carbon materials (0.2/C~1.2/C) [5,17,24]. The temperature of 0.2/C~1.2/C was rose to the 300 °C with heating rate at 0.15 °C/min under following air and maintained the temperature at 300 °C for 180 min. After oxidative stabilization process, the temperature of 0.2/C~1.2/C was rose to the 700 °C with heating rate at 3 °C/min under following the  $\text{N}_2$  gas and maintained at 700 °C for 180 min. As consequence, the novel composite carbon materials of 0.2/C~1.2/C were prepared successfully via the carbonization process.

### Electrochemical experiment

To prepare the electrodes used for the electrochemical performance measurement, the iron oxide containing carbon materials (0.08 g) were mixed with acetylene black (0.01 g) and polyvinylidene fluoride (PVDF) binder (0.01 g) in a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP) solution. Then

the obtained mixture solutions were stirred to ensure the homogeneity, the obtained slurry was coated on Cu foil and dried in vacuum drying oven at 80 °C for 1 h to remove solution. Subsequently, the Cu foil with the active materials were dried at 120 °C for 12 h in the same vacuum drying oven and cut into round shape strips of  $\phi$  11 mm in size. The two-electrode electrochemical cells were assembled in a glove box filled with high-purity argon, where the lithium metal foil ( $\phi$  15.60 mm  $\times$  0.45 mm) was used as cathode, fiberglass was used as separator, and 12–13 wt% of LiPF<sub>6</sub> in the mixture of EC, DMC, EMC was used as electrolyte. Charge-discharge test was carried out by LAND battery test system. The same electrochemical cells were also used to carry out measurements of cyclic voltammetry (CV).

## Results and discussion

First of all, the conversions about contents of composite materials (0.2/C–1.2/C) were evaluated by measurements of XRD. According to the reports of Petnikota et al. [23], the similar reactions about Fe<sub>3</sub>O<sub>4</sub> with carbon also existed in our studies. As shown in the Fig. 1a and b, according to the JCPDS No.06–0696 and JCPDS No.06–0615, it is verified that the new peaks of Fe and FeO appeared clearly, which indicated the Fe<sub>3</sub>O<sub>4</sub> reacted with the carbon completely when the carbonization was carrying out continuously. Interestingly, with increasing the contents of Fe<sub>3</sub>O<sub>4</sub> in reactive mixture, the intensity of Fe disappeared and intensity of FeO became stronger (Fig. 1c–f), for the Fe subsequently reacted with CO and CO<sub>2</sub> which were produced from reaction of Fe<sub>3</sub>O<sub>4</sub> with carbon [25]. These results clearly indicated the contents of 0.2/C–1.2/C could be controlled by adding amounts of Fe<sub>3</sub>O<sub>4</sub> in reactive mixtures.

The morphologies of 0.2/C–1.2/C were illustrated in the Fig. 2. It is observed that a lot of circular structures appeared in the 0.8/C, 1.0/C and 1.2/C when the FeO formed largely. According to the report of He et al. [16], and associating with the results of Fig. 1c–f, we naturally consider that circular structures are attributed to the formation of FeO covered by carbon.

It is acknowledged that suitable carbon contents in composite mixture of transition metal oxides and carbon are able

to improve their electrochemical performances, for they can increase the conductivity and restrain the volume expansion of transition metal oxides [26–29]. However, the overmuch carbon generally diminishes the storage capacity of these materials. Therefore, we need to investigate the thermogravimetric analysis, in order to compare the final residue carbon contents and found the relationships between the residue weights and adding amounts of Fe<sub>3</sub>O<sub>4</sub>. As shown in Fig. 3, when rising the temperature from 25 °C to 360 °C, the samples of 0.2/C, 0.4/C, 0.6/C, 0.8/C, 1.0/C and 1.2/C showed the slightly increased weights at 1.4%, 5.0%, 6.0%, 6.5%, 8.0% and 2.7%, respectively, which was attributed to the contents of Fe, and FeO in composite materials were oxidized to the Fe<sub>2</sub>O<sub>3</sub> [23]. On the contrary, samples exhibited the obvious losing weight when the temperature was at range from 450 °C to 600 °C. However, the obvious losing weight was not observed when the temperature was rose to the range from 600 °C to 1000 °C. Consequently, the final carbon contents of 0.2/C, 0.4/C, 0.6/C, 0.8/C, 1.0/C and 1.2/C showed at 76.8%, 44.2%, 33.6%, 23.1%, 17.9% and 7.6%, respectively, which reveals the 1.0/C and 1.2/C possessed the lower carbon contents than other composite materials. These results strongly indicate that increasing the adding amounts of Fe<sub>3</sub>O<sub>4</sub> could decrease the residue carbon contents in composite materials.

Furthermore, based on the measurement results of BET, the 1.0/C possessed the high specific surface area at 113.5 m<sup>2</sup>/g which was higher than the 0.2/C, 0.4/C, 0.6/C, 0.8/C, and 1.2/C respectively showed at 1.7 m<sup>2</sup>/g, 6.0 m<sup>2</sup>/g, 16.7 m<sup>2</sup>/g, 103.6 m<sup>2</sup>/g, and 110.0 m<sup>2</sup>/g, respectively. The reactions of Fe<sub>3</sub>O<sub>4</sub> with carbon caused the formations of substantial holes, for the CO and CO<sub>2</sub> were produced from these reactions, which possibly led to the 1.0/C possessed high specific surface area. Besides, it is possible that the relative low carbon contents reduced the specific surface area of 1.2/C slightly.

Based on the general evaluations about electrochemical properties, the CV measurements were carried out three cycles firstly in our studies [8,27]. As shown in Fig. 4, the characteristic peak attributing to the carbon materials was also clearly observed in Fig. 4a, and peak intensity remarkably decreased from 0.2/C to 1.2/C. Simultaneously, oxidative potentials of 0.2/C, 0.4/C, 0.6/C, 0.8/C, 1.0/C and 1.2/C were observed at 1.62 V, 1.64 V, 1.67 V, 1.66 V, 1.65 V and 1.62 V in first cycle, which led us to consider these differences related to the contents of composite materials. For instance, the existing of Fe elements in 0.2/C and 0.4/C led to the 0.2/C and 0.4/C were oxidized easily [30]. On the other hand, the strong reductive peaks were observed at 0.43 V, 0.33 V, 0.41 V, 0.50 V, 0.55 V and 0.35 V in first cycle, respectively, which was attributed to the formations of solid electrolyte interface (SEI) layers. Similar to the general reports about iron oxide materials, the broad oxidative potential peaks were observed, after first cycle [22,23,33]. Meanwhile, the reductive peaks were observed at 0.95 V, 0.93 V, 0.93 V, 0.93 V, 0.94 V and 0.54 V, respectively. Especially, the remarkably different reductive potential of 1.2/C shown at 0.54 V was possibly attributed to the unusually low carbon contents in 1.2/C comparing with that in the other composite materials, which caused the crystal lattice to be easily broken at process of intercalation and deintercalation of Li<sup>+</sup> ions, leading to low reductive ability of the 1.2/C.

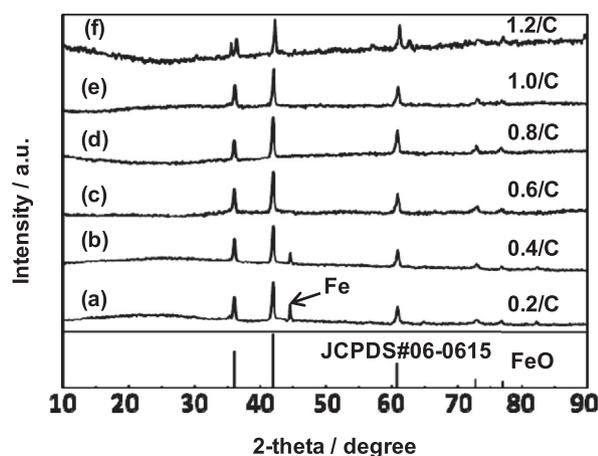


Fig. 1 – XRD results of composite materials (0.2/C–1.2/C) are illustrated.

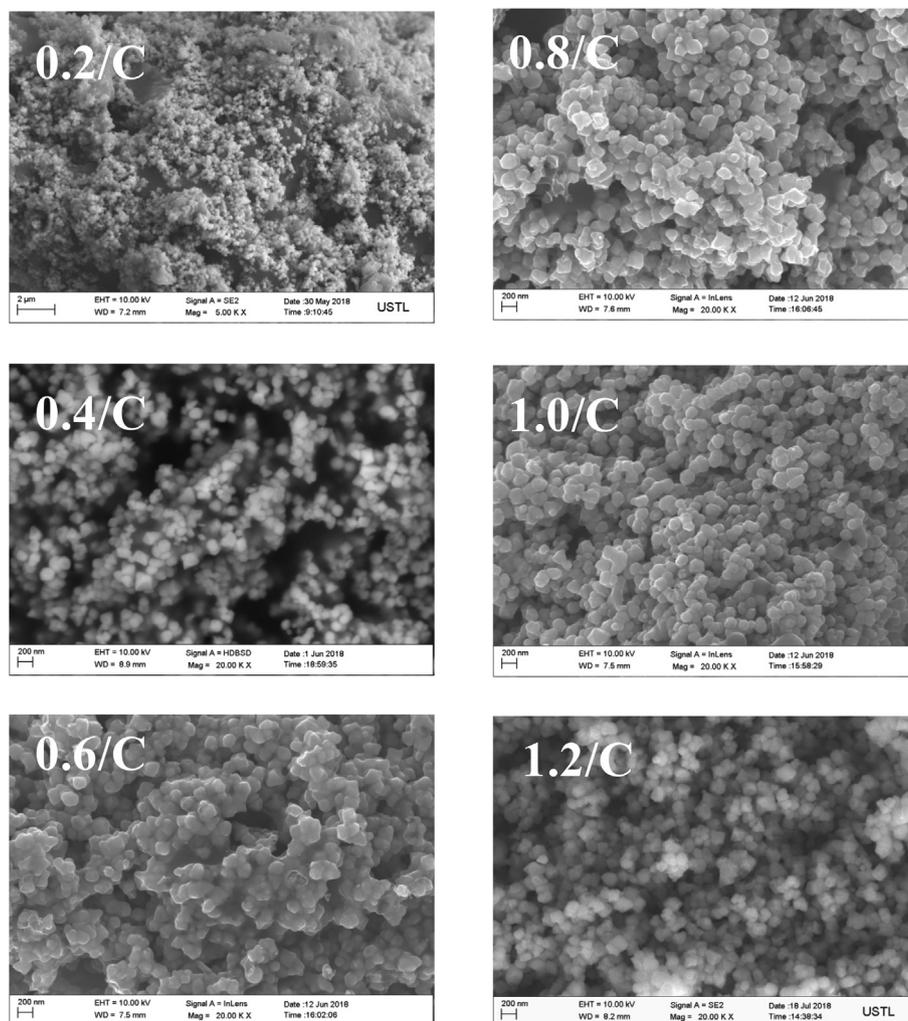


Fig. 2 – SEM images of composite materials (0.2/C~1.2/C).

Fig. 5 illustrated the charge-discharge measurements of iron oxide/carbon materials under voltage range of (0.05–3.00 V) and current density of 100 mA/g. All composite materials (0.2/C~1.2/C) showed the distinct plateaus around 0.75 V in the first cycle, which was ascribed to the

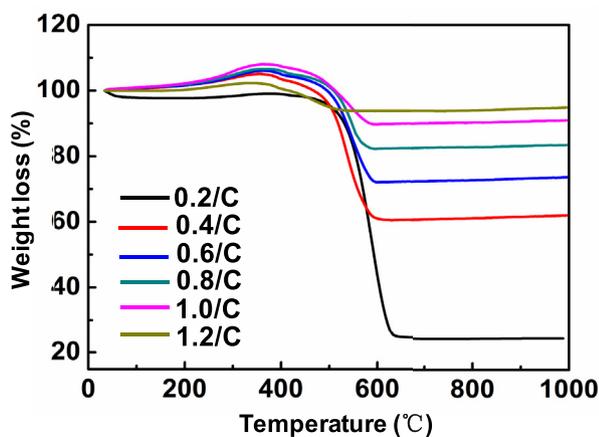


Fig. 3 – Thermogravimetric results of composite materials (0.2/C~1.2/C).

transformation from  $\text{Fe}^{2+}$  to  $\text{Fe}^0$  and formation of  $\text{Li}_2\text{O}$ . After first cycle, another distinct plateaus were observed at 1.0 V, which responded to the reductive potentials around 1.0 V in CV [22,23]. The slightly high plateaus of 1.0 V also show the advantage, which is able to diminish the risk about  $\text{Li}^+$  plating at end of recharge [30].

The cycling performances of 0.2/C~1.2/C were illustrated in the Fig. 6a. Firstly, the carbon materials obtained by carbonization of coal tar pitches showed the exceedingly poor  $\text{Li}^+$  ion storage capacity at 122 mAh/g, after cycling the  $\text{Li}^+$  ions charge-discharge 100 times. Additionally, it is observed that 0.2/C~1.2/C showed the similar tendency that first cycle showed high capacity around 505 mAh/g, 675 mAh/g, 821 mAh/g, 921 mAh/g, 1010 mAh/g, 1080 mAh/g, whereas since the second cycle the capacity rapidly decreased to the 305 mAh/g, 452 mAh/g, 553 mAh/g, 600 mAh/g, 692 mAh/g and 630 mAh/g respectively. These phenomena are also naturally attributed to the general explanation that SEI layers formed during the first cycle [31–33]. At the same time, the similar tendency was also reflected on the measurement results of coulombic efficiency. Namely, the coulombic efficiencies of 0.2/C~1.2/C were at 63%, 69%, 68%, 66%, 69% and 59%, respectively, at first cycle. However, from the second cycle,

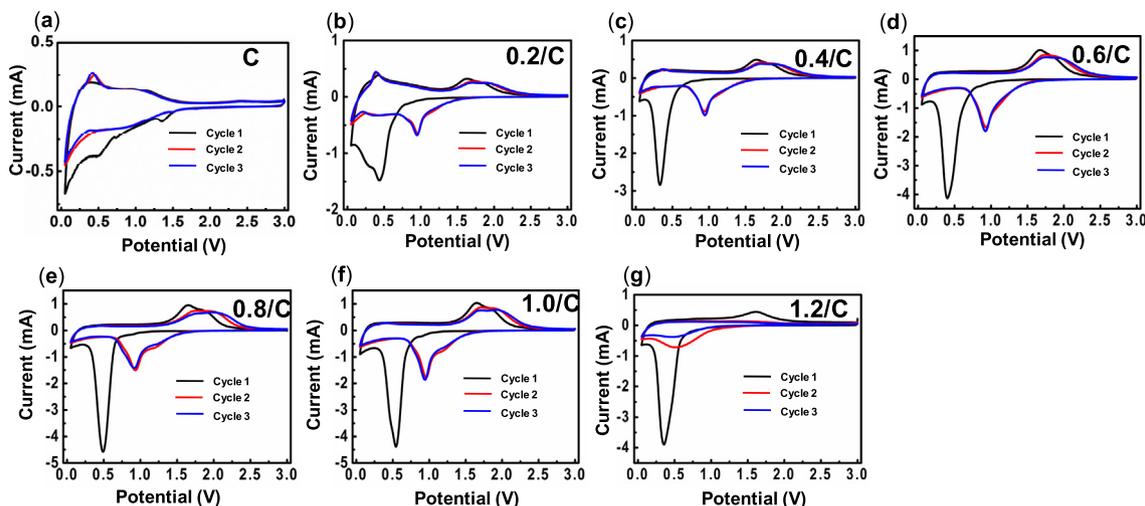


Fig. 4 – CV results of carbon materials (a) obtained after carbonization of coal tar pitches and composite materials (b-d).

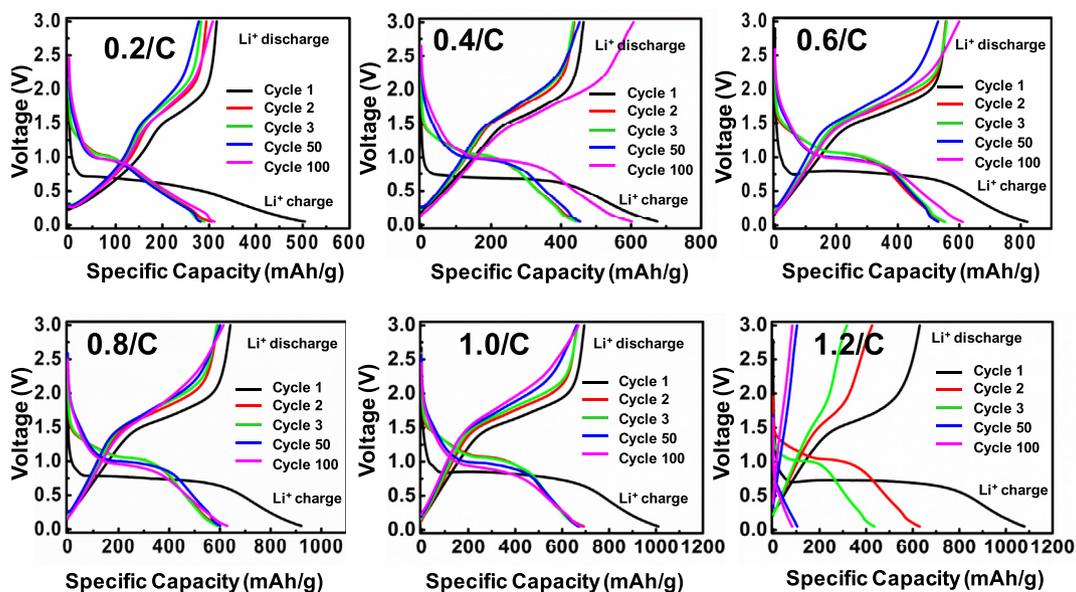


Fig. 5 – Illustrations of charge-discharge results about  $\text{Li}^+$  ion of composite materials (0.2/C~1.2/C).

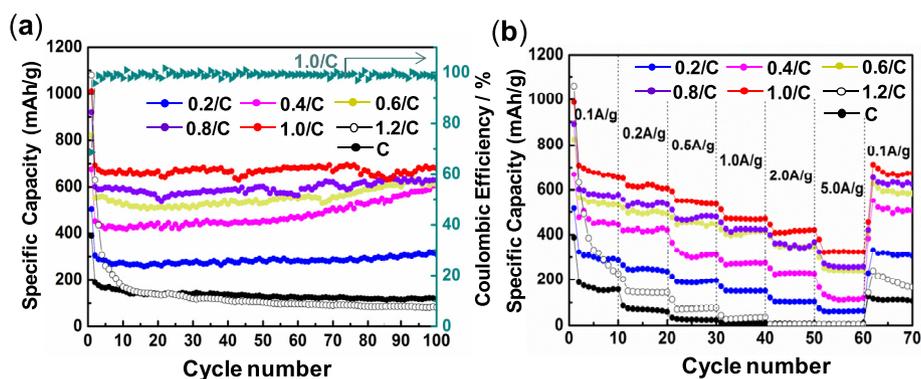


Fig. 6 – (a) Illustrates the cycling performances of carbon materials obtained after carbonization of coal tar pitches and composite materials (0.2/C~1.2/C). (b) Illustrates the rate performances of carbon materials obtained after carbonization of coal tar pitches and composite materials (0.2/C~1.2/C).

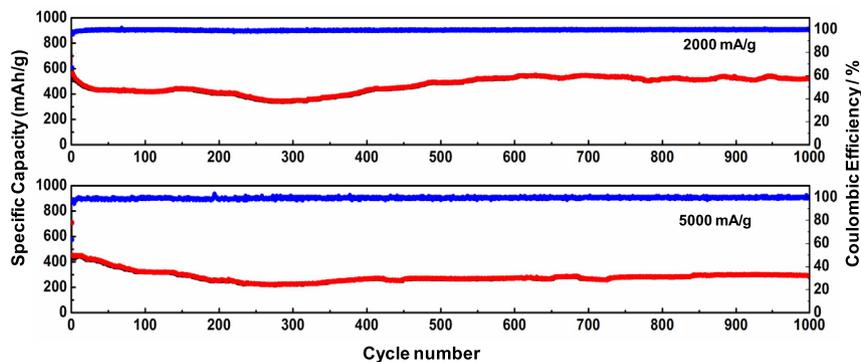


Fig. 7 – Cycling performances of 1.0/C at high current density of 2000 mA/g and 5000 mA/g.

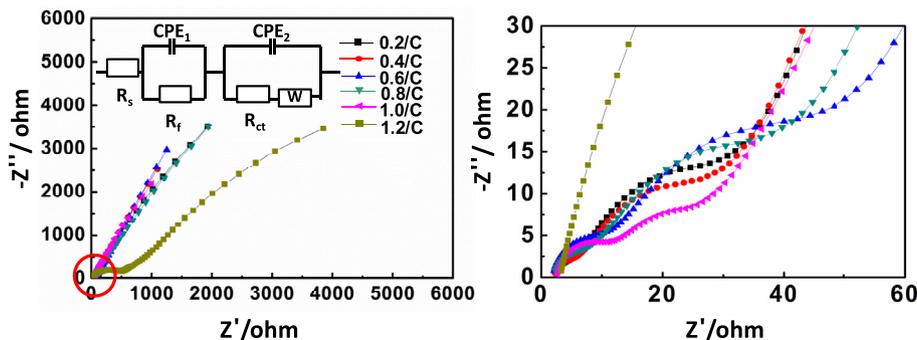


Fig. 8 – Nyquist plot results of composite materials (0.2/C~1.2/C).

they were able to be recovery quickly. As a result, the coulombic efficiencies maintain the high level at 97%–100%, even though the cycling numbers were changed. In particular, the 1.0/C possessed the relative high first coulombic efficiency than other materials and EG/FeO composite materials which were reported by Petnikota et al. [23].

On the other side, after being carried out the charge-discharge 100 cycles, the  $\text{Li}^+$  ion storage capacity of 1.0/C showed the relative high capacity at 679 mAh/g, which was higher than the 0.2/C (311 mAh/g), 0.4/C (605 mAh/g), 0.6/C (610 mAh/g), 0.8/C (628 mAh/g) and 1.2/C (82 mAh/g), respectively (Fig. 6a). Associating with the measurement results of thermogravimetric experiments (Fig. 3), we consider that the suitable carbon contents in 1.0/C remarkably influenced the electrochemical properties about cycling performances.

Similar to the report of Yu et al., the  $\text{Li}^+$  ion charge capacity of 0.4/C and 0.6/C showed the tendency that  $\text{Li}^+$  ion charge capacity slowly increased after cycling of 20 times, which was possibly attributed to the carbon contents existing in the 0.4/C and 0.6/C were more than that in 0.8/C, 1.0/C and 1.2/C remarkably [26]. Moreover, the 1.2/C showed the really low  $\text{Li}^+$  ion storage capacity at 82 mAh/g, for the FeO lattice of 1.2/C was easily collapsed in charge-discharge process, which was attributed to 1.2/C has the lower carbon contents than other composite materials (Fig. 3). Consequently, the aforementioned analyses firmly supported that 1.0/C possessed the relatively excellent cycling performances.

Fig. 6b illustrates the rate performances when the current density was changed from 100 mA/g to 5000 mA/g. Namely,

we carried out the charge-discharge cycles 10 times at different current densities, such as 100 mA/g, 200 mA/g, 500 mA/g, 1000 mA/g, 2000 mA/g, 5000 mA/g, respectively. As a result, the all cells showed the similar tendency that charge and discharge capacity decreased with increasing the current density, which was ascribed to the general reasons that polarization increases when increasing the current density. Nevertheless, the 1.0/C showed the relatively stronger capability against the polarization. For example, the  $\text{Li}^+$  ion storage capacities of 1.0/C showed at 653 mAh/g, 606 mAh/g, 536 mAh/g, 471 mAh/g, 420 mAh/g and 324 mAh/g, when the current densities were adjusted to 100 mA/g, 200 mA/g, 500 mA/g, 1000 mA/g, 2000 mA/g, 5000 mA/g, respectively, which are higher than other composite materials remarkably in the same investigations, which is connected to the 1.0/C owned the relative high specific surface area and suitable carbon contents than other composite materials [16,37].

In addition,  $\text{Li}^+$  ion storage capacity of cell fabricated by the 1.0/C stayed at 673 mAh/g when adjusted the current density to the 100 mA/g again, after being carried out the charge-discharge cycles 10 times at different current densities, such as 100 mA/g, 200 mA/g, 500 mA/g, 1000 mA/g, 2000 mA/g, 5000 mA/g, respectively (Fig. 6b). This storage capacity of 673 mAh/g was also higher than the other composite materials which were detected in the same investigations with the 1.0/C. As a consequence, we consider the 1.0/C shows that remarkable improvement capability against the polarization and excellent electrochemical stability.

Furthermore, it is really interest that 1.0/C has the excellent long cycle life at high current density (Fig. 7). For example, the 1.0/C still showed the  $\text{Li}^+$  ion storage capacity at 524 mAh/g and 292 mAh/g, when the charge-discharge measurements were performed 1000 times at the current densities adjusted to the 2000 mA/g and 5000 mA/g, respectively. In view of the report of Zhang, the uneven curves were also observed in our studies (Fig. 7) [34,35]. The reasons about this analogous phenomenon were reported and explained in other systems [6,27,36–37].

Finally, Fig. 8 exhibits the electrochemical research-impedance results of 0.2/C–1.2/C. As a result, the diameter of the semicircle in medium frequency of anode electrodes using 1.0/C was much smaller than that of anode electrodes fabricated using other composite materials, which has been considerable that 1.0/C electrode possesses lower charge-transfer impedances. Additionally, according to the reports of Guo et al. [38,39], the equivalent circuit fitting to the plots was also described. For example, the  $R_{ct}$  values of 0.2/C–1.2/C were calculated to the 31  $\Omega$ , 32  $\Omega$ , 54  $\Omega$ , 43  $\Omega$ , 26  $\Omega$  and 474  $\Omega$ , respectively, indicating the 1.0/C has the relatively lower  $R_{ct}$  than other composite materials [38].

As mentioned above, the existing Fe element in 0.2/C and 0.4/C plays the main role to increase the conductive properties remarkably. In contrast, the FeO composite carbon materials as 1.0/C also showed the excellent conductivities, which led us easily to consider this effect is attributed to 1.0/C possessed the relatively high specific surface area and suitable carbon contents.

## Conclusions

The FeO/C composite carbon materials were fabricated using the coal tar pitches and  $\text{Fe}_3\text{O}_4$  particles. The carbon contents and specific surface area can be controlled by controlling the adding amounts of  $\text{Fe}_3\text{O}_4$  particles which were verified by measurements of thermogravimetric and BET. As a result, the suitable carbon contents and relative high specific surface area contribute the remarkable improvement effects of electrochemical performances of FeO/C composite carbon materials, which was determined by electrochemical measurements. For example, the 1.0/C exhibits the high cycling performances at 679 mAh/g after carrying out the charge-discharge 100 times, high long cycle life under heavy current such as 2000 mA/g and 5000 mA/g, respectively. Considering the coal tar pitches are the general industrial products, these FeO/C composite carbon materials show the significant prospects in fabrications of anode of LIBs.

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## REFERENCES

- [1] Liu C, Li F, Ma LP, Cheng HM. Advanced materials for energy storage. *Adv Mater* 2010;22:E28–62.
- [2] Dunn B, Kamath H, Tarascon JM. Electrical energy storage for the grid: a battery of choices. *Science* 2011;334:928–35.
- [3] Zhao MW, Lu Y, Chang LM, Wang LM, Cheng Y. Facile synthesis of nitrogen-doped Sn@NC composites as high-performance anodes for lithium-ion batteries. *Int J Hydrogen Energy* 2018;43:22401–8.
- [4] Gu ZQ, Liu C, Fan RY, Zhou Z, Chen YX, He YD, Xia XH, Wang ZY, Liu HB. Double core-shell of Si@PANI@TiO<sub>2</sub> nanocomposite as anode for lithium-ion batteries with enhanced electrochemical performance. *Int J Hydrogen Energy* 2018;43:20843–52.
- [5] Li L, Wu Z, Yuan S, Zhang XB. Advances and challenges for flexible energy storage and conversion devices and systems. *Energy Environ Sci* 2014;7:2101–22.
- [6] Sun T, Li ZJ, Wang HG, Bao D, Meng FL, Zhang XB. A biodegradable polydopamine-derived electrode material for high-capacity and long-life lithium-ion and sodium-ion batteries. *Angew Chem Int Ed* 2016;55:1–6.
- [7] Guo ZH, Wang CY, Chen MM, Li MW. Hard carbon derived from coal tar pitch for use as the anode material in lithium ion batteries. *Int J Electrochem Sci* 2013;8(2):2702–9.
- [8] Guo J, Zhu H, Sun Y, Zhang X. Construction of sandwiched graphene paper@Fe<sub>3</sub>O<sub>4</sub> nanorod array@graphene for large and fast lithium storage with an extended lifespan. *J Mater Chem* 2015;3:19384–92.
- [9] Zhang LS, Jiang LY, Yan HJ, Wang WD, Wang W, Song WG, et al. Mono dispersed SnO<sub>2</sub> nanoparticles on both sides of single layer graphene sheets as anode materials in Li-ion batteries. *J Mater Chem* 2010;20:5462–7.
- [10] Jin R, Wang Q, Cui Y, Zhang S. MFe<sub>2</sub>O<sub>4</sub> (M = Ni, Co) nanoparticles anchored on amorphous carbon coated multiwalled carbon nanotubes as anode materials for lithium-ion batteries. *Carbon* 2017;123:448–59.
- [11] Do JS, Weng CH. Preparation and characterization of CoO used as anodic material of lithium battery. *J Power Sources* 2005;146:482–6.
- [12] Han C, Xu L, Li H, Shi R, Zhang T, Li J, et al. Biopolymer-assisted synthesis of 3D interconnected Fe<sub>3</sub>O<sub>4</sub>@carbon core@shell as anode for asymmetric lithium ion capacitors. *Carbon* 2018;140:296–305.
- [13] Hu S, Yin F, Uchaker E, Chen W, Zhang M, Zhou J, et al. Facile and green preparation for the formation of MoO<sub>2</sub>-GO composites as anode material for lithium-ion batteries. *J Phys Chem C* 2014;118:24890–7.
- [14] Wang L, Wang D, Dong Z, Zhang F, Jin J. Interface chemistry engineering for stable cycling of reduced GO/SnO<sub>2</sub> nanocomposites for lithium ion battery. *Nano Lett* 2013;13:1711–6.
- [15] Atchudan R, Jebakumar Immanuel Edison TN, Perumal S, Ranjithkumar D, Lee YR. Direct growth of iron oxide nanoparticles filled multi-walled carbon nanotube via chemical vapour deposition method as high-performance supercapacitors. *Int J Hydrogen Energy* 2019;44:2349–60.
- [16] Zhao N, Wu S, He C, Wang Z, Shi C, Liu E, et al. One-pot synthesis of uniform Fe<sub>3</sub>O<sub>4</sub> nanocrystals encapsulated in interconnected carbon nanospheres for superior lithium storage capability. *Carbon* 2013;57:130–8.
- [17] Lee JS, Kim YK, Hwang JY, Joh HI, Park CR, Lee S. Carbon nanosheets by the graphenization of ungraphitizable isotropic pitch molecules. *Carbon* 2017;121:479–89.
- [18] Yuan G, Li X, Xiong X, Dong Z, Westwood A, Li B, et al. A comprehensive study on the oxidative stabilization of

- mesophase pitch-based tape-shaped thick fibers with oxygen. *Carbon* 2017;115:59–76.
- [19] Taberna PL, Mitra S, Poizot P, Simon P, Tarascon JM. High rate capabilities  $\text{Fe}_3\text{O}_4$ -based Cu nano-architected electrodes for lithium-ion battery applications. *Nat Mater* 2006;5:567–73.
- [20] Ji L, Toprakci O, Alcoulabi M, Yao Y, Li Y, Zhang S, et al. Alpha- $\text{Fe}_2\text{O}_3$  nanoparticle-loaded carbon nanofibers as stable and high-capacity anodes for rechargeable lithium-ion batteries. *ACS Appl Mater Interfaces* 2012;4:2672–9.
- [21] Poizot P, Laruelle S, Grugeon S, Dupont L, Tarascon JM. Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries. *Nature* 2000;407:496–9.
- [22] Gao M, Zhou P, Wang P, Wang J, Liang C, Zhang J, et al.  $\text{FeO/C}$  anode materials of high capacity and cycle stability for lithium-ion batteries synthesized by carbothermal reduction. *J Alloy Comp* 2013;565:97–103.
- [23] Petnikota S, Marka SK, Banerjee A, Reddy MV, Srikanth VVSS, Chowdari BVR. Graphothermal reduction synthesis of 'exfoliated graphene oxide/iron (II) oxide' composite for anode application in lithium ion batteries. *J Power Sources* 2015;293:253–63.
- [24] Fujimoto H, Tokumitsu K, Mabuchi A, Chinnasamy N, Kasuh T. The anode performance of the hard carbon for the lithium ion battery derived from the oxygen-containing aromatic precursors. *J Power Sources* 2010;195:7452–6.
- [25] Pettit FS, Wagner JB. Transition the linear to the parabolic rate low during the oxidation of iron to wustite in  $\text{CO-CO}_2$  mixture. *Acta Metall* 1964;12:35–40.
- [26] Hao SM, Li QJ, Qu J, An F, Zhang YJ, Yu ZZ. Neuron-inspired  $\text{Fe}_3\text{O}_4$ /conductive carbon filament network for high-speed and stable lithium storage. *ACS Appl Mater Interfaces* 2018;10:17923–32.
- [27] Zhang YJ, Qu J, Hao SM, Chang W, Ji QY, Yu ZZ. High lithium storage capacity and long cycling life  $\text{Fe}_3\text{S}_4$  anodes with reversible solid electrolyte interface films and sandwiched reduced graphene oxide shells. *ACS Appl Mater Interfaces* 2017;9:41878–86.
- [28] Pan L, Zhu XD, Xie XM, Liu YT. Smart hybridization of  $\text{TiO}_2$  nanorods and  $\text{Fe}_3\text{O}_4$  nanoparticles with pristine graphene nanosheets: hierarchically nanoengineered ternary heterostructures for high-rate lithium storage. *Adv Funct Mater* 2015;25:3341–50.
- [29] Huang Y, Xu Z, Mai J, Lau TK, Lu X, Hsu YJ, et al. Revisiting the origin of cycling enhanced capacity of  $\text{Fe}_3\text{O}_4$  based nanostructured electrode for lithium ion batteries. *Nano Energy* 2017;41:426–33.
- [30] Zhao X, Xia D, Zheng K.  $\text{Fe}_3\text{O}_4/\text{Fe}$ /carbon composite and its application as anode material for lithium-ion batteries. *ACS Appl Mater Interfaces* 2012;4:1350–6.
- [31] Lian P, Zhu X, Xiang H, Li Z, Yang W, Wang H. Enhanced cycling performance of  $\text{Fe}_3\text{O}_4$ -graphene nanocomposite as an anode material for lithium-ion batteries. *Electrochim Acta* 2010;56:834–40.
- [32] Palmieri A, Spinner N, Zhao S, Mustain WE. Explaining the role and mechanism of carbon matrices in enhancing reaction reversibility of metal oxide anodes for high performance lithium ion batteries. *Carbon* 2018;130:515–24.
- [33] He CN, Wu S, Zhao NQ, Shi CS, Liu EZ, Li JJ. Carbon-encapsulated  $\text{Fe}_3\text{O}_4$  nanoparticles as a high-rate lithium ion battery anode material. *ACS Nano* 2013;7:4459–69.
- [34] Choi SH, Kang YC.  $\text{Fe}_3\text{O}_4$ -decorated hollow graphene balls prepared by spray pyrolysis process for ultrafast and long cycle-life lithium ion batteries. *Carbon* 2014;79:58–66.
- [35] Zhang W, Li X, Liang J, Tang K, Zhu Y, Qian Y. One-step thermolysis synthesis of two-dimensional ultrafine  $\text{Fe}_3\text{O}_4$  particles/carbon nanonetworks for high-performance lithium-ion batteries. *Nanoscale* 2016;8:4733–41.
- [36] Fan L, Li B, Rooney DW, Zhang N, Sun K. In situ preparation of 3D graphene aerogels@hierarchical  $\text{Fe}_3\text{O}_4$  nanoclusters as high rate and long cycle anode materials for lithium ion batteries. *Chem Commun (Camb)* 2015;51:1597–600.
- [37] Dong Y, Yung KC, Ma R, Yang X, Chui YS, Lee JM, et al. Graphene/acid assisted facile synthesis of structure-tuned  $\text{Fe}_3\text{O}_4$  and graphene composites as anode materials for lithium ion batteries. *Carbon* 2015;86:310–7.
- [38] Lin C, Hu L, Cheng C, Sun K, Guo X, Shao Q, et al. Nano- $\text{TiNb}_2\text{O}_7$ /carbon nanotubes composite anode for enhanced lithium-ion storage. *Electrochim Acta* 2018;260:65–72.
- [39] Lou XM, Lin CF, Luo Q, Zhao JB, Wang B, Li JB, et al. Crystal structure modification enhanced  $\text{FeNb}_{11}\text{O}_{29}$  anodes for lithium-ion batteries. *Chem ElectroChem* 2017;4:3171–80.