Highly mesoporous and chemically bonded Fe$_3$O$_4$/N-doped carbon nanocomposite with an outstanding cycling life as lithium-ion-battery anode

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Abstract. Owing to high theoretical capacity (926 mAh g$^{-1}$), Fe$_3$O$_4$ has achieved much focus as a prospective anode material for lithium-ion batteries (LIBs). A one-step vapor-pressured induced approach considering the synthesis of chemically bonded Fe$_3$O$_4$/N-doped carbon nanocomposites (Fe$_3$O$_4$/NC) via Fe-O-C and Fe-N-C, together with the encapsulation of Fe$_3$O$_4$ nanoparticles (~80 nm) into highly mesoporous N-doped carbon matrix via pyrolyzing the mixture of iron oxalate and dimethylformamide in a sealed vessel, does not exist at present. As LIB anode, the Fe$_3$O$_4$/NC presents a high capacity of 1250.2 mAh g$^{-1}$ at 0.1 A g$^{-1}$, an outstanding cyclability with a capacity of 600.1 mAh g$^{-1}$ after 4000 cycles at 5 A g$^{-1}$, and a high rate capability (244.8 mAh g$^{-1}$ at 20 A g$^{-1}$). Such excellent performances can be ascribed to its unique structure that Fe$_3$O$_4$ nanoparticles tightly encapsulated into highly mesoporous N-doped carbon matrix can increase active sites, electrical conductivity, and cyclability.

1. Introduction
Over the past decade improved techniques have revealed many advantages involving good cyclability, high specific energy, as well as high safe of lithium-ion batteries (LIBs) to allow them widely used in various electronics and vehicles [1,2]. Up to now graphite is still utilized as main LIB anode materials. Nevertheless, its relatively low theoretical capacity (372 mAh g$^{-1}$) severely limits further development of higher-energy-density LIBs. At present, transition metal oxides (Fe$_3$O$_4$, Fe$_2$O$_3$, and GeO$_2$, etc) have been invoked in many studies as important alternatives to graphite due to high capacity [3]. Among them, Fe$_3$O$_4$ has focused public’s attention [4]. However, challenges such as terrible volume change and bad electrical conductivity (EC), resulting in rapid capacity decay and poor ion transport rate, limit the commercial application. In order to address these problems, a series of carbon involving disorder carbon [5], carbon nanotubes [6], and graphene [7] as a buffer materials have been added into Fe$_3$O$_4$-based composite to suppress volume variation of Fe$_3$O$_4$ nanoparticles, to inhibit Fe$_3$O$_4$ particles from agglomeration on cycling, and to serve as a conductive network for boosting ion/electron transport.
movement. Consequently, vast Fe₃O₄/C nanocomposites involving nanoparticles [8], nanospheres [9], nanotubes [10], nanoflakes [11], and nanobelts [12] have been designed by sol-gel route [13], electrostatic spinning [14], and solvothermal process [15], etc, to ameliorate volume expansion and EC of Fe₃O₄-based electrode. For instance, Fe₃O₄/C nanospheres exhibited a significantly enhanced discharge capacity of 930 mAh g⁻¹ after 50 cycles at 0.1 A g⁻¹, in comparison with 316 mAh g⁻¹ for bare Fe₃O₄ nanospheres [16]. Additionally, a foam-like Fe₃O₄/C nanocomposite delivered a higher capacity of 1008 mAh g⁻¹ than 540.8 mAh g⁻¹ of bare Fe₃O₄ nanoparticles after 400 deep cycles at 0.2 A g⁻¹ [17]. A hierarchical Fe₃O₄/C hollow nanosphere fabricated via an aerosol-pyrolysis route achieved a high capacity of 383 mAh g⁻¹ after 1000 cycles with no obvious capacity loss at 10 A g⁻¹ [18]. The above results demonstrate that Fe₃O₄/C nanocomposites possess remarkable superiority as high-level LIBs anode materials. However, for practical application, a longer lifetime with thousands of cycles should be obtained, particularly at high current density. In addition, their preparation ways are extremely fussy and complicated to signal the great importance of a simple method for preparing Fe₃O₄/C nanocomposites.

Here, a one-step vapor-pressured induced synthesis route was proposed to prepare Fe₃O₄/N-doped carbon (Fe₃O₄/NC) nanocomposites by heating a mixture of ferric oxalate and dimethylformamide in a sealed vessel. In the nanocomposites, Fe₃O₄ nanoparticles with an average size of 80 nm are uniformly and tightly dispersed in a highly mesoporous N-doped carbon matrix via chemical bonds of Fe-O-C and Fe-N-C. The small size of Fe₃O₄, the highly mesoporous N-doped carbon matrix, and the homogeneously distributed structure not only contribute to Li⁺ diffusion and improve EC, but also inhibit aggregation and volume expansion of nanoparticles upon cycling. As LIB anode, Fe₃O₄/NC shows a high capacity, an outstanding cyclability, and an ascendant rate capability.

2. **Experimental**

2.1. **Preparation of Fe₃O₄/NC**

Typically, ferric oxalate (0.5 g, Macklin) and dimethylformamide (0.5 g, Macklin) were placed in a vessel with a volume of 5 ml, and then sealed in a Ar-filled glove box. Subsequently, the vessel was heated at 500°C in a tube furnace for 0.5 h at 10°C min⁻¹ under Ar atmosphere. After that, the tube furnace was cooled to room temperature, and the Fe₃O₄/NC sample was obtained.

2.2. **Characterizations**

X-ray diffraction (XRD) pattern was used to determine crystalline structures. Thermogravimetric analysis (TGA) was tested in air with a heating rate of 10 °C min⁻¹. Scanning electron microscopy (SEM, Hitachi 4800) was used to observe morphology. Transmission electron microscopy (TEM, TECNAI G2 F20) with energy dispersive spectroscopy (EDS) was used to test the microstructures. Raman spectroscopy was performed to test carbon material. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was operated to investigate the valence structure of elements and surface composite. The EC of sample was tested by a Powder Electrical Resistivity Tester (ST-2722, Suzhou Jingge Electronic Co., Ltd., China). Specific surface area and pore size distribution were tested using an Accelerated Surface Area and Porosimetry System (Micromeritics ASAP 2010).

2.3. **Electrochemical measurements**

CR2032 type coin half cells composing of working electrode, Celgard 2400 as separator, electrolyte (1 M LiPF₆ in a mixture of 1:1:1 volume ratio of ethylene carbonate, ethylene methyl carbonate, and dimethyl carbonate), and lithium foil as a counter electrode were assembled to test lithium ion storage performance of samples in Ar-filled glove box (amount of O₂ and H₂O < 0.01 ppm). Coating a slurry containing 80 wt% samples, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride on copper foil was performed to make working electrodes, which were dried at 120 °C under vacuum overnight. The active mass loading of the electrodes was ~1.1 mg cm⁻². An electrochemical workstation (Land CT 2001A, Wuhan, China) was used to test the cycling and rate performances in a voltage range from
0.01 to 3.0 V (vs. Li⁺/Li) at room temperature. An electrochemical workstation (Chenhua CHI660, Shanghai, China) was used to measure electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CV) curves.

3. Results and discussion

Figures 1a-c represent the SEM images of the Fe₃O₄/NC, which shows a porous bulk structure integrating enormous nanoparticles. The TEM (Figures 1d,e) and high-resolution TEM (HRTEM) images (Figure 1f) show that the carbon layers coat on the surface of Fe₃O₄ nanocrystals with an average size of ~80 nm and a lattice fringe of 0.49 nm contributes from interplanar spacing of (111) crystal plane of Fe₃O₄. Fe, O, C, and N elements are dispersed uniformly in Fe₃O₄/NC nanocomposites, confirmed by high angle annular dark field image (HAADF) and corresponding EDS mapping images (Figures 1g-k), indicating that Fe₃O₄ nanocrystals are evenly embedded into N-doped carbon matrix.

Figure 2a confirms the crystal structure of Fe₃O₄/NC, apparently, all the diffraction peaks can be completely attributed to Fe₃O₄ (JCPDS card no. 19-0629). The Raman spectrum in Figure 2b depicts characteristic peaks of Fe₃O₄ at 214.4, 276.7, and 379.5 cm⁻¹ [15,18], and two characteristic peaks of D and G band of carbon materials at 1345.4 and 1593.7 cm⁻¹, respectively [19]. The I_D/I_G value of 0.92 proves partial graphitization of the carbon in the composite, which suggests that the carbon matrix are beneficial for the improvement of EC and Li⁺ storage capacity [19]. As tested, the value of EC is 1.2x10⁴ S/m. Such a high value can boost Li⁺ transport to obtain superior rate performances. XPS clearly presents that the dominating elements of the Fe₃O₄/NC composites are Fe, N, C and O (Figure 2c). The Fe 2p spectrum (Figure 2d) presents two peaks fitted into four peaks at 709.3 eV (Fe²⁺, 2p₃/2), 710.8 eV (Fe³⁺, 2p₃/2), 723.2 eV (Fe²⁺, 2p½), and 724.1 eV (Fe³⁺, 2p½). The O 1s spectrum (Figure 2e) involves three peaks at 529.7 (Fe-O), 532.5 (O deficiency), and 531.2 eV (Fe-O-C) [15,18]. The C 1s spectrum (Figure 2f) involves three peaks at 284.6 eV (C-C), 285.9 eV (C-N), and 288.7 eV (C=O). Additionally, the formation of C-N bond proves that N is doped into the carbon. The N 1s spectrum (Figure 2g) displays four peaks at 398.5, 399.3, 400.4 and 401.3 eV, assigned to pyridic N, Fe-N,
The appearance of Fe-N bond proves the presence of Fe-N-C bonds. The presence of Fe-O-C and Fe-N-C bonds signals that the Fe$_3$O$_4$ nanoparticles are firmly dispersed into the carbon matrix, benefiting for inhibiting aggregation and adapting to enormous volume expansion of Fe$_3$O$_4$ during lithiation. The pyridic N and Fe-O/N-C bonds were highly chemically active sites and can make vast defects and accommodate more Li$^+$ to the improvement of the capacity [19,20]. Besides, the Fe$_3$O$_4$/NC nanocomposite has a mesoporous structure with a surface area of 128.4 m$^2$ g$^{-1}$, a pore volume of 0.78 cm$^3$ g$^{-1}$, and a well-defined mesopore centered at 2.4 nm (Figure 2h), which can obtain a high contact area with electrolyte, boost ion transport, store Li$^+$, and alleviate volume expansion of Fe$_3$O$_4$ during cycling, thus comprehensively enhancing lithium storage performances of the Fe$_3$O$_4$/NC nanocomposite.

Figure 2 (a) XRD pattern, (b) Raman spectrum, (c) XPS survey peak, (d) Fe 2p, (e) O 1s, (f) C 1s, (g) N 1s, and (h) Nitrogen adsorption-desorption isotherms of Fe$_3$O$_4$/NC.

Here, the electrochemical properties of Fe$_3$O$_4$/NC are measured in detail. Figure 3a displays the typical CV curves of Fe$_3$O$_4$/NC, in which a peak appears at 0.59 V mainly attributed to the formation of solid electrolyte interface (SEI) film/Li$_2$O in the first cathodic scanning. Besides, three peaks appear at 1.26, 0.99, and 0.81 V, which are mainly attributed to the reaction of active materials with electrolyte and the formation of Li$_2$Fe$_3$O$_4$ [11,13]. In the anodic scanning, two peaks at 1.64 and 1.83 V are ascribed to gradual oxidation of Fe$^0$ to Fe$^{2+}$ and then to Fe$^{3+}$ [15,18]. Moreover, all peaks overlap after the first scanning to prove high-level reversibility of Fe$_3$O$_4$/NC. The charge/discharge curves (Figure 3b) display homologous voltage plateaus with CV curves. Besides, Fe$_3$O$_4$/NC reveals first lithiation and delithiation capacities of 1736.4 and 1250.2 mAh g$^{-1}$, respectively, to produce a coulombic efficiency (CE) of 72.0%. Such a low CE mostly originates from the formation of SEI and Li$_2$O [21,22]. The Nyquist plots at various cycling number are represented (Figure 3c), in which the value of charge transfer resistance ($R_{ct}$, the diameter of depressed semicircle) originally rises after the 1st cycle owing to the construction of SEI film, and then gradually diminishes, presumably arising from activation of electrode material. The decrease of $R_{ct}$ is profitable for strengthening capacity and stability [21,22]. Subsequently, the cycling life at 1 A g$^{-1}$ of Fe$_3$O$_4$/NC is assessed, which delivers a first reversible capacity of 985.2 mAh g$^{-1}$ with a CE of 71.3%, and 896.1 mAh g$^{-1}$ after 800 cycles with a CE of 99.82% (Figure 3d). So high capacity retention of 91.1% is gained to fully testify a good cyclability of the Fe$_3$O$_4$/NC. An ultralong cycling lifetime is acquired at 5 A g$^{-1}$ (Figure 3e), before which the cell is activated at 0.1 A g$^{-1}$ for three cycles, in which a high capacity of 600.1 mAh g$^{-1}$ after 4000 cycles with a high CE of 98.9% and 89.6% capacity retention is revealed. Such a low capacity loss per cycle of 0.0026% sufficiently demonstrates a distinguished stability of electrode materials during large-current cycle. The rate capability of Fe$_3$O$_4$/NC is tested at 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 A g$^{-1}$ (Figure 3f), and corresponding capacities are 1260.2, 1165.6, 1160.8, 988.9, 814.1, 627.8, 399.4, and 244.8 mAh g$^{-1}$. When the current density returns to initial value, the capacity can be back to 1196.2 mAh g$^{-1}$, confirming splendid rate capability. The outstanding Li$^+$ storage performances
primarily are contributed from its unique structure, such as smaller particle size of Fe₃O₄, highly mesoporous N-doped carbon matrix, and the formation of interfacial chemical bonds of Fe-O-C and Fe-N-C.

Figure 3 (a) CV curves at a scanning rate of 0.1 mV s⁻¹, (b) Charge/discharge curves at 0.1 A g⁻¹, (c) EIS spectra, (d) cycling curve at 1 A g⁻¹, (e) cycling curve at 5 A g⁻¹, and (f) rate curves of Fe₃O₄/NC.

To expounds ion storage mechanism and concrete capacity contribution of the Fe₃O₄/NC, the electrochemical kinetics and pseudocapacitive behaviors are surveyed by CV curves at various scanning rates (ν). The CV (Figure 4a) curves display homologous Li⁺ storage behavior at ν of 0.1 to 2 mV s⁻¹ to corroborate a stable pseudocapacitive behavior. In general, peak current (i) and ν is directly related to the Eq. log i=blog ν⁺log a. It can be observed that the b is the slope of log i-log ν plots, where 1.0 suggests a capacitive-controlled process and 0.5 indicates a diffusion-dominated process. Based on the calculation results, b values of all the peaks range from 0.86 to 0.92 (Figure 4b), exhibiting that both diffusion-controlled and pseudocapacitive-controlled process contribute the total capacity [23,24]. To survey their particular contribution, Eq. i=kiν+kν 0.5 is presented, where i composes of pseudocapacitive process (k₁ν) and diffusion-controlled behaviors (k₂ν 0.5). Obviously, the percentage of pseudocapacitive contribution raising gradually from 43.1 to 78.5% with a rise of ν from 0.1 to 2 mV s⁻¹ (Figure 4c), demonstrating high influence of pseudocapacitive ion storage on the enhancement of the capacity and rate performances. So high pseudocapacitive contribution primarily originates from extra Li⁺ storage sites, such as interfaces, defects, and mesoporous structure [23,24].

Figure 4 (a) CV curves at different ν, (b) The line relationship of Log(i) vs Log(ν) at peaks 1 and 2 marked in (a); (c) The percentages of pseudocapacitive contribution at different ν of Fe₃O₄/NC.

4. Conclusions
To conclude, a one-step vapor-pressured induced synthesis route is developed for synthesizing Fe₃O₄/NC nanocomposite for the first time by pyrolysis of mixture of ferric oxalate and dimethylformamide in a sealed vessel. The structural advantages, involving small size of 80 nm, highly mesoporous N-doped carbon matrix, and Fe-N-C/Fe-O-C bonds, of the hybrid nanocomposites induce a high pseudocapacitive contribution, a rapid ion transport route, and a highly stable structure,
thus bringing about excellent electrochemical performances. As LIB anode, Fe₃O₄/NC shows a high reversible capacity (1250.2 mAh g⁻¹ at 0.1 A g⁻¹), an outstanding cyclability (up to 4000 cycles at 5 A g⁻¹), and rate capability (244.8 mAh g⁻¹).

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**References**

[1] J. Liu, Z. Bao, Y. Cui, E. J. Dufek, J. Goodenough, P. Khalifah, Q. Li, B. Liaw, P. Liu, A. Manthiram, Y. Meng, V. R. Subramanian, M. Toney, V. Viswanathan, M. Whittingham, J. Xiao, W. Xu, J. Yang, X. Yang, J. Zhang, Nat. Energy, 2019, 4, 180-186.

[2] Y. Liu, Y. Zhu, Y. Cui, Nat. Energy, 2019, 4, 540-550.

[3] C. Liu, Q. Li, Q. Zhang, B. He, P. Man, Z. Zhou, C. Li, L. Xie, Y. Yao, Electrochim. Acta 2020, 330, 135247.

[4] J. Liu, X. Xu, R. Hu, L. Yang, M. Zhu, Adv. Energy Mater. 2016, 6, 1600256.

[5] Q. Qu, J. Chen, X. Li, T. Gao, J. Shao and H. Zheng, J. Mater. Chem. A, 2015, 3, 18289-18295.

[6] Y. He, L. Huang, J. S. Cai, X. M. Zheng, S. G. Sun, Electrochim. Acta, 2010, 55, 1140-1144.

[7] J. Guo, H. Zhu, Y. Sun, X. Zhang, J. Mater. Chem. A, 2015, 3, 19384-19392.

[8] C. Lei, F. Han, Q. Sun, W. C. Li, A. H. Lu, Chem. Eur. J., 2014, 20, 139-145.

[9] F. X. Ma, H. Hu, H. B. Wu, C. Y. Xu, Z. Xu, L. Zhen, Adv. Mater., 2015, 27, 4097-4101.

[10] F. Han, L. Ma, Q. Sun, C. Lei, A. Lu, Nano Res., 2014, 7, 1706-1717.

[11] Z. Zhang, F. Wang, Q. An, W. Li, P. Wu, J. Mater. Chem. A., 2015, 3, 7036-7043.

[12] L. Lang, Z. Xu, ACS Appl. Mater. Interfaces, 2013, 5, 1698-1703.

[13] C. He, S. Wu, N. Zhao, C. Shi, E. Liu, J. Li, ACS nano, 2013, 7, 4459-4469.

[14] M. H. Ryu, K. N. Jung, K. H. Shin, K. S. Han, S. Yoon, J. Phys. Chem. C, 2013, 117, 8092-8098.

[15] X. Meng, Y. Xu, X. Sun, J. Wang, L. Xiong, X. Du, S. Mao, J. Mater. Chem. A, 2015, 3, 12938-12946.

[16] Y. Gan, H. Gu, H. Xiao, Y. Xia, X. Tao, H. Huang, J. Du, L. Xu, W. Zhang, New J. Chem., 2014, 38, 2428-2434.

[17] W. Zhang, X. Hou, J. Shen, S. Hu, Q. Ru, K. Lam, Electrochim. Acta, 2016, 118, 734-743.

[18] J. Huang, S. Cheng, Y. Chen, Z. Chen, H. Luo, X. Xia, H. Liu, J. Mater. Chem. A, 2019, 7, 16720.

[19] M. Han, Z. Lin, J. Yu, J. Mater. Chem. A, 2019, 7, 4804-4812.

[20] M. Han, Y. Mu, F. Yuan, J. Liang, T. Jiang, X. Bai, J. Yu, J. Mater. Chem. A, 2020, 8, 3822-3833.

[21] M. Han, J. Yu, J. Power Sources, 2019, 414, 435-443.

[22] M. Han, Y. Mu, F. Yuan, X. Bai, J. Yu, J. Power Sources, 2020, 465, 228206.

[23] M. Han, Z. Lin, X. Ji, Y. Mu, J. Li, J. Yu, Mater. Today Energy, 2020, 17, 100445.

[24] Y. Mu, M. Han, J. Li, J. Liang, J. Yu, Carbon, 2021, 173, 477-484.