Dalton Transactions



View Article Online

PAPER

Check for updates

Cite this: *Dalton Trans.*, 2025, **54**, 1948

Received 27th October 2024, Accepted 11th December 2024 DOI: 10.1039/d4dt02999b

rsc.li/dalton

Introduction

Graphite-based lithium-ion batteries (LIBs) are widely used in common energy storage devices due to their safety, reversibility, and economical production.¹ Nevertheless, the disadvantages of LIBs during the charge/discharge process include a low theoretical capacity (372 mA h g^{-1}), unsatisfactory cycling stability, and serious volume expansion.² Recently, anode materials in LIBs have included nickel-based sulfides (NiS, NiS₂, Ni₃S₂, and Ni₃S₄) and iron-based carbides/nitrides (Fe₃C, FeN, Fe₂N, and Fe₃N), which have achieved better electrochemical performance because of their high theoretical capacities (450-880 mA h g⁻¹).³⁻⁸ However, their advantages were hampered by substantial volume fluctuations and nanoparticle pulverization during repeated lithiation/delithiation.9 Therefore, the development of alternative anode materials for LIBs is a key challenge to achieve a high capacity, excellent cycling stability, and superior rate performance.

Phase engineering can greatly improve the adsorption and transportation of Li^+ by an internal electric field. For example,

Fe₃N/Fe₃O₄ hetero-nanocrystals embedded in porous carbon fibers for enhanced lithium storage†

Yuanxiao Ma,^a Chen Hu,^a Miaobing Ruan,^a Yigang Li,^a Xuefan Wang,^a Zepeng Chen,^a Ze-Xing Cai, [®] Yan Han,^b Shenghong Liu*^a and Haibin Sun [®]*^a

Energy storage devices have applications in large-scale portable and smart devices due to their high energy density and long lifespan, but the limited theoretical capacity of the graphite anode in lithium-ion batteries has slowed the development of portable electronic devices. Herein, we prepared porous fibers with heterogeneous Fe_3N/Fe_3O_4 nanocrystals wrapped by a carbon layer. A series of measurements, such as TEM images, Raman spectra, XRD pattern and XPS analysis, were used to unveil the formation of Fe_3N/Fe_3O_4 nanocrystals effect of the large specific surface area originating from the porous structure and the heterogeneous nanocrystals, the porous $Fe_3N/Fe_3O_4@C$ fibers exhibit a good electron/ion transmission route and rich active sites. As anode materials for lithium-ion batteries (LIBs), porous $Fe_3N/Fe_3O_4@C$ fibers delivered a reversible capacity of 964 mA h g⁻¹ after 200 cycles at 2 A g⁻¹ and long-term cycling stability (282 mA h g⁻¹ after 2000 cycles at 5 A g⁻¹). This work provides a method to regulate biphasic anode materials with desirable structures to enhance the reversibility of LIBs.

Liu *et al.* reported a biphasic Ni₃Se₄/NiSe₂ heterostructure with excellent Li storage capacity and a long cycle life.¹⁰ Sun *et al.* synthesized LIBs with a high rate capacity facilitated by Ru doped Ni₃Se₄/NiSe@NC nanotubes.¹¹ Hu *et al.* optimized heterogeneous SnO_{2-x}/Fe_2O_{3-y} nanocrystals for high-power LIBs because of rich oxygen vacancies and the self-catalysis of Fe₂O₃.¹² Their superior electrochemical performance was attributed to the formation of heteroatomic structures that enhanced the conductivity, accelerated the transport of electrons and ions, and boosted the number of active sites.

To avoid the agglomeration/pulverization of the biphasic hetero-nanocrystals during the long-term cycling process, carbon (C) frameworks were frequently used to provide sufficient volume expansion for outstanding electrochemical properties. For example, Jin et al. constructed a MOF-derived N-doped porous carbon to encapsulate Co₃O₄/Fe₂O₃ nanoparticles for superior stability (621 mA h g^{-1} at 1 A g^{-1} after 1000 cycles).¹³ Zhang et al. prepared small Co/Co₃O₄ nanoparticles embedded in N-doped porous carbon to deliver excellent cycling stability and high-rate capability (1313 mA h g⁻¹ after 500 cycles at 2 A g⁻¹).¹⁴ Li et al. designed a hollow Ni/NiO@N-doped porous carbon to improve the cycling stability and rate performance (695.1 mA h g⁻¹ after 200 cycles at 0.1 A g⁻¹).¹⁵ Wang et al. used a pomegranate-like porous carbon to coat Cu_xSn_y/Sn/SnO₂ submicrospheres for use as anode materials for LIBs, exhibiting a capacity of 604 mA h g⁻¹ after 150 cycles at 200 mA g⁻¹.¹⁶ Those excellent electrochemical capacities can be attributed to the synergistic effect that stemmed from the two components, i.e.,

^aKey Laboratory of Microelectronics and Energy of Henan Province, Department of Physics and Electronic Engineering, Xinyang Normal University, Xinyang, 464000, P. R. China. E-mail: liush@xynu.edu.cn, sunhaibin@xynu.edu.cn

^bSchool of Physics and Electronic Information, Nanchang Normal University, Nanchang, 330032, P. R. China

[†]Electronic supplementary information (ESI) available. See DOI: https://doi.org/ 10.1039/d4dt02999b

heterogeneously structured biphasic materials and the *in situ* formed porous carbon support, can lead to excellent lithium storage performance.

In this work, we designed and prepared highly dispersed Fe_3N/Fe_3O_4 heterogeneous nanocrystals embedded in porous electrospinning carbon fibers by consecutive carbonization and nitridation treatment. Observations by SEM, TEM, Raman spectroscopy, XRD, and XPS demonstrate the formation of heteroatomic Fe–O and Fe–N bonds. Consequently, the porous Fe_3N/Fe_3O_4 @C fibers delivered excellent lithium storage capacity due to the enhanced electrochemical reaction kinetics and the greater number of active sites.

Experimental section

Synthesis of Fe₃N/Fe₃O₄@C

Preparation of an Fe-based mixture. First, 0.64 g of polyacrylonitrile (PAN) and 0.15 g of polystyrene (PS) were dispersed in 10 mL of *N*,*N*-dimethylformamide (DMF) to obtain a milky suspension. Then, 0.3 g of iron acetylacetonate ($Fe(C_5H_7O_2)_3$) was added to the above suspension to form a red solution, which was vigorously stirred at room temperature for 12 h.

Preparation of Fe-based fibers. The electrospinning experiment was carried out using an applied voltage of 15 kV, a solution flow rate of 0.94 ml h^{-1} , a distance between the nozzle and drum of 25 cm, and a drum speed of 50 r min⁻¹.

Preparation of Fe₃N/Fe₃O₄@C fibers. The collected membrane was dried in an oven at 60 °C for 2 h and then transferred into a muffle furnace to undergo peroxidation at 200 °C for 6 h. For carbonization, the product was heated to 900 °C for 2 h at a heating rate of 5 °C min⁻¹ under an Ar atmosphere. Next, the product was placed in a tube furnace for nitridation treatment at 500 °C for 2 h at a heating rate of 5 °C min⁻¹ under an NH₃/Ar (10/90, v/v) atmosphere. The obtained porous Fe₃N/Fe₃O₄@C fibers were allowed to naturally cool to room temperature. In contrast, the nonporous Fe₃N/Fe₃O₄@C fibers were obtained using the same synthetic procedure, except a flowing Ar atmosphere was not used during the carbonization step.

Material characterization

The crystalline structures of as-prepared samples were identified by X-ray diffraction (XRD) using a Cu K α radiation source and Raman spectroscopy (Renishaw inVia confocal Raman spectrometer). The morphologies were characterized by coldfield-emission scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, JEOL 2100F at 200 kV), and energy-dispersive X-ray spectrometry (EDX). Thermogravimetric analysis (TGA, TA Q600, Waters) was employed to characterize the carbon content in the temperature range of 40–800 °C with a heating rate of 10 °C min⁻¹. The nitrogen sorption isotherms were measured at 77 K using an ASAP 2460 system (Micromeritics Instrument Corp.). The specific surface area and the pore size distribution were analyzed using the Brunauer–Emmett–Teller (BET) method. X-ray photoelectron spectroscopy (XPS) was performed with monochromatic Mg K α (1253.6 eV) radiation. The magnetic properties were measured using a comprehensive physical property testing system (DyaCool-9T, Quantum Design) in the magnetic field range of -3-3 kOe at 300 K.

Electrochemical measurements

Coin-type (CR2032) cells were assembled inside an Ar-filled glovebox. Fe₃N/Fe₃O₄@C served as the working electrode, which was mixed with 80 wt% active material, 10 wt% Kochen black, 10 wt% polyvinylidene difluoride (PVDF), and N-methyl-2-pyrrolidone (NMP) to form a slurry. Then, the slurry was coated onto a copper sheet and dried under vacuum at 80 °C for 12 h. The mass loading of active materials was about ~0.5 mg cm⁻². Lithium metal was used as the counter electrode and a glass fiber membrane as the separator. The electrolyte solution was 1 M LiPF₆ dissolved in a mixed solvent of ethylene carbonate, dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (1:1:1). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a CHI 660D workstation. The galvanostatic charge-discharge (GCD) tests were performed and rate performances were measured using a NEWARE battery testing system (BTS-610) with cut-off voltages of 0.01 V and 3.0 V (vs. Li/Li⁺).

Results and discussion

As shown in Fig. 1a, Fe₃N/Fe₃O₄@C fibers were synthesised by the electrospinning method with consecutive carbonization and nitridation treatment. The biphasic heterostructure of Fe₃N/Fe₃O₄ is depicted in Fig. 1b. Fe and N atoms constitute a structure, while Fe atoms are bonded to O atoms, reflecting the top and side views of Fe₃N/Fe₃O₄ hetero-nanocrystal structures. The morphology and microstructures of Fe₃N/Fe₃O₄@C samples were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images in Fig. 2a and b show that the carbon fibers were cross-connected to form a freestanding membrane. Abundant pores were formed on the carbon fibers, as shown in the zoomed-in SEM image in Fig. 2c. As a comparison, Fig. S1[†] shows that many carbon fibers did not have pores due to the absence of carbonization treatment under an Ar atmosphere. The TEM image in Fig. 2d shows that Fe₃N/Fe₃O₄@C particles were uniformly embedded in the carbon nanofibers. The high-resolution TEM image in Fig. 2e exhibits clear lattice fringes related to the (100) plane of Fe_3N , the (400) plane of Fe_3O_4 , and the (101) plane of C. The corresponding elemental maps in Fig. 2f confirm the existence of Fe, N, O, and C elements, revealing the successful construction of Fe₃N/Fe₃O₄ hetero-nanocrystals.

The Raman spectrum in Fig. 3a exhibits two characteristic peaks at 1342 and 1588 cm⁻¹, which were attributed to the D band for defect-induced disordered carbon and the G band for sp² hybridized graphitic carbon.¹⁷ The intensity ratio of the two peaks ($I_{\rm D}/I_{\rm G} \approx 1.17$) illustrates the presence of a large amount of defective carbon and active sites in porous Fe₃N/



Fig. 1 (a) Illustration of the synthesis route of porous Fe₃N/Fe₃O₄@C fibers. (b) Top and side views of Fe₃N/Fe₃O₄ hetero-nanocrystal structures.



Fig. 2 Morphologies of porous Fe₃N/Fe₃O₄@C fibers. (a-c) SEM images, (d-f) TEM images, and the corresponding elemental maps.

 $Fe_3O_4@C$ fibers.¹⁸ Additionally, the three main peaks at 214, 272, and 381 cm⁻¹ confirmed the existence of Fe_3N .⁷ The XRD patterns in Fig. 3b show the presence of characteristic peaks of

Fe₃N, which closely match its crystal phases (PDF# 49-1662). The other diffraction peaks were indexed to Fe₃O₄ (PDF#19-0629), which is in good agreement with the TEM results.

Paper



Fig. 3 Crystal structure of porous Fe₃N/Fe₃O₄@C fibers. (a) Raman spectrum, (b) XRD patterns, (c) TGA curve, (d) and pore size distribution.

From the thermogravimetric analysis (TGA) curve seen in Fig. 3c, a slight weight loss below 400 °C can be observed by the continuous evaporation of the adsorbed water. A sharp weight loss appeared between 400 °C and 500 °C, which can be ascribed to the oxidation of carbon $(C + O_2 \rightarrow CO_2)$, the subsequent oxidation of $Fe_3N(Fe_3N + O_2 \rightarrow Fe_2O_3 + NO_x)$, and the further oxidation of Fe_3O_4 ($Fe_3O_4 + O_2 \rightarrow 2Fe_2O_3$). The weight loss after 500 °C was estimated to account for about 73.1% of Fe₃N/Fe₃O₄@C fibers. This might be used to verify the importance of carbonization treatment in achieving porous fibers. The porous microstructure was analyzed using the Brunauer-Emmett-Teller (BET) method. As shown in Fig. 3d and Fig. S2,† the specific surface area of porous Fe₃N/Fe₃O₄@C fibers was estimated to be 328.9 m² g⁻¹ larger than that of the nonporous structure (18.8 m² g⁻¹, as shown in Fig. S3†). The corresponding pore size distribution revealed the presence of microporous structures, in accordance with a type-IV adsorption/desorption isotherm.¹⁹ Thus, the highly porous structure provided abundant space and active sites that could accommodate the transmission of ions, which should accelerate the reaction kinetics to enhance lithium-ion storage.²⁰

X-ray photoelectron spectroscopy (XPS) was used to investigate the elemental valence states and chemical bonds, as

shown in Fig. S4.† The high-resolution Fe 2p spectrum in Fig. 4a shows two major peaks at 712.3 eV and 724.8 eV, respectively, which corresponded to the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ spin–orbit doublets of Fe in Fe₃O₄.⁶ They could be divided into several peaks at 711.0 eV and 719.2 eV for Fe²⁺, and at 713.3 eV and 724.8 eV for Fe³⁺.²¹ The satellite peak at 707.4 eV indicates the presence of Fe–N bonds. The high-resolution N 1s spectrum in Fig. 4b was split into five peaks at 398.2, 399.7, 401.0, 401.6, and 402.7 eV, which belonged to pyridinic N, Fe–N, pyrrolic N, graphitic N, and oxidized N.²² The high-resolution O 1s spectrum is shown in Fig. 4c, which demonstrates the presence of Fe–O bonds in Fe₃N/Fe₃O₄@C fibers. Additionally, the presence of C–N bonds in the high-resolution C 1s spectrum (Fig. 4d) may improve the conductivity and provide additional active sites for lithium storage.²³

The electrochemical performance of the porous Fe_3N/Fe_3O_4 @C fibers was examined in half-cells using metal lithium as counter electrodes. Fig. 5a shows the first three cyclic voltammograms (CVs) achieved at a scan rate of 0.2 m V s⁻¹ within 0.01–3.0 V. During the first discharge process, reduction peaks were observed at 1.54 and 0.67 V, indicating the gradual conversion of Fe₃N and Fe₃O₄ into Li₃N and Li₂O, as well as the generation of a solid electrolyte interface (SEI)



Fig. 4 High-resolution XPS (a) Fe 2p, (b) N 1s, (c) O 1s, and (d) C 1s spectra of porous Fe₃N/Fe₃O₄@C fibers.

layer, respectively.^{7,12} Subsequently, the reduction peak at 0.67 V disappeared from the CV profiles in the second and third discharge processes, indicating the formation of a stable SEI layer on the electrode surface. During the subsequent charge process, the corresponding oxidation peaks appeared at 1.04 V and 1.60 V, indicating that the transformation of Fe₃N and Fe₃O₄ was reversible. The subsequent CV profiles nearly overlapped, indicating excellent electrochemical reversibility due to the synergistic effects between the porous structure and biphasic heterostructure. Fig. 5b shows the first three galvanostatic charge/discharge (GCD) profiles at a current density of 0.1 Ag^{-1} . The potential plateaus closely matched the peaks in CV curves. The subsequent cycles nearly overlapped, indicating that the GCD profiles remained stable, with a close to 100% coulombic efficiency. Compared with the nonporous Fe₃N/ Fe₃O₄@C fibers shown in Fig. 5c, the porous Fe₃N/Fe₃O₄@C fibers showed a large specific capacity (1984 mA h g^{-1} at 0.1 A g^{-1}) and coulombic efficiency (62.7%) in the initial GCD profiles.

The spin polarization of Fe atoms was explored by performing magnetic measurements after the first discharge process. The magnetic hysteresis (MH) profiles in Fig. 5d show S-like loops, suggesting the ferromagnetic properties of the samples.²⁴ The porous Fe₃N/Fe₃O₄@C fibers exhibited a much larger saturation magnetization (M_s) of 11.6225 emu g⁻¹ than nonporous Fe₃N/Fe₃O₄@C fibers (9.0075 emu g⁻¹). The remanent magnetization (M_R) and coercive force (H_C) of the former were lower than those of the latter, indicating the presence of many more reduced Fe atoms in porous Fe₃N/Fe₃O₄@C fibers than in nonporous Fe₃N/Fe₃O₄@C fibers.²⁵ The magnetization of porous Fe₃N/Fe₃O₄@C fibers was measured with zero-fieldcooled (ZFC) and field-cooled (FC) temperature at 10 Oe and shown in Fig. S5.† The electrode showed a ferromagnetic signature with a blocking temperature of around 297 K, in good agreement with the MH measurement. The resultant high spin polarization of porous Fe₃N/Fe₃O₄@C fibers enhanced the bonding of N atoms with Li atoms to provide superior lithiumion storage.

Fig. 5e shows their GCD profiles at current densities in the range of 0.1–10 A g⁻¹. The sample delivered the highest reversible capacity of 1194.9 mA h g⁻¹ at 0.1 A g⁻¹, while it was only 492.4 mA h g⁻¹ at 5 A g⁻¹. When the current density returned to 0.1 A g⁻¹, the capacity reached 905.8 mA h g⁻¹. The rate capacity of porous Fe₃N/Fe₃O₄@C fibers, as shown in Fig. 5f, surpassed that of the nonporous samples and many previous results^{7,26–29} due to the enhanced active sites and increased Li⁺ adsorption. The cycling test results in Fig. 5g show that porous Fe₃N/Fe₃O₄@C fibers delivered a specific capacity of 964 mA h g⁻¹ after 200 cycles at 2 A g⁻¹, while this was only 318 mA h g⁻¹ for nonporous Fe₃N/Fe₃O₄@C fibers. Additionally, a notable increase was observed in porous Fe₃N/Fe₃O₄@C fibers, suggesting the high activation of active



Fig. 5 (a) First three CV profiles at 0.2 mV s⁻¹, (b) GCD curves of porous $Fe_3N/Fe_3O_4@C$ fibers at 0.1 A g⁻¹. Comparison with the nonporous $Fe_3N/Fe_3O_4@C$ fibers: (c) first GCD profiles at 0.1 A g⁻¹, (d) magnetic hysteresis profiles at 300 K, (e) rate capabilities, (f) comparison with previous reports, and (g) cycling performance at 2 A g⁻¹. (h) Long-term cycling performance of porous $Fe_3N/Fe_3O_4@C$ fibers at 5 A g⁻¹.

materials during the first charge/discharge cycle. The coulombic efficiency was nearly 100%. As shown in Fig. 5h, the specific capacity of porous Fe₃N/Fe₃O₄@C fibers exhibited an increasing trend during the high current density of 5 A g^{-1} , reaching up to the maximum specific capacity of 640 mA h g^{-1} after 844 cycles. This case can be ascribed to the rich microporous/mesoporous structure to promote quick electron/ion transport and the additional electrochemical activation sites. In the subsequent cycles, the specific capacity faded to 282 mA h g⁻¹ after 2000 cycles. The capacity loss was due to the irreversible formation of a SEI film to suppress the electron/ion transport between the electrode materials and the electrolyte. Additionally, the capacity retention was about 69% over 2000 cycles at 5 A g^{-1} . This excellent cycling stability indicated synergistic effects between the porous architecture and the hetero-nanocrystals of Fe₃N/Fe₃O₄ to promote charge transport and structural durability.

The Li⁺ storage process of porous Fe₃N/Fe₃O₄@C fibers was investigated using CV measurements at scan rates from 0.2 to 1.2 mV s⁻¹ (Fig. 6a). The CV profiles produced similar redox peaks during the discharge–charge process, indicating superior reversibility. The electrochemical kinetics were explored using the relationship between the peak current (*i*) and scan rate (ν), which was expressed using the following formulas:³⁰

1

$$i = a v^b \tag{1}$$

$$og(i) = b \log(v) + \log(a)$$
(2)

where *a* is the proportionality coefficient and *b* is evaluated by the slope of log (*i*) and log (*v*), while *i* and *v* are variables. When *b* is similar to 0.5, it indicates a capacitive-controlled process, while when *b* reaches 1, the domination of capacity storage is the diffusion-controlled process.³¹ As shown in Fig. 6b, the values of *b* were close to 1, indicating the dominant charge storage process for the capacitive-controlled pseudocapacitive behavior. At a scan rate of 0.8 mV s⁻¹ in Fig. 6c, the CV curve was enclosed by capacitive- and diffusion-controlled contributions. Here, the capacitive contribution ratio of the porous Fe₃N/Fe₃O₄@C fibers was 59%, as calculated using the following formula:³²

$$i = k_1 \nu + k_2 \nu^{1/2} \tag{3}$$

where *i* is composed of capacitive-dominant contribution $(k_1\nu)$ and diffusion-dominant contribution $(k_2\nu^{1/2})$. As shown in Fig. 6d, the capacitive contribution gradually increased as the



Fig. 6 (a) CV curves at scan rates from 0.2 to 1.2 mV s⁻¹, (b) Log (*i*) versus log (v) at different scan rates, (c) capacitive (reseda) and diffusion (white) contributions at 0.8 mV s⁻¹, and (d) contribution ratio of the capacitive behavior of Ni₃Se₄/NiSe@NC at different scan rates. Comparison with the nonporous Fe₃N/Fe₃O₄@C fibers: (e) EIS spectra before cycling, and (f) the relationship between Z_{re} and $\omega^{-1/2}$ at a low frequency before cycling.

scan rate increased from 0.2 to 1.2 mV s⁻¹, indicating superior reaction kinetics.³³

Fig. 6e shows the electrochemical impedance spectroscopy (EIS) spectra of the initial two electrodes. The Nyquist plots were composed of a semicircle in the high-frequency region and a straight line in the low-frequency region. The charge transfer resistance (R_{ct}) value of porous Fe₃N/Fe₃O₄@C fibers (110.8 Ω) was smaller than that of nonporous Fe₃N/Fe₃O₄@C fibers (221.7 Ω). The Li⁺ diffusion coefficient (D_{Li^+}) was explored using the following formulas:³⁴

$$\omega = 2\pi f \tag{4}$$

$$Z_{\rm re} = R + \sigma \omega^{-1/2} \tag{5}$$

$$D_{\rm Li^+} = \frac{R^2 T^2}{2A^2 n^2 F^4 C^2 \sigma^2} \tag{6}$$

where *f*, *n*, *R*, *T*, *A*, and *C* are the frequency, the number of electron transfers per molecule (mol cm⁻³), the ideal gas constant (8.314 JK⁻¹ mol⁻¹), the absolute temperature (298 K), the electrode surface area, and the Faraday constant (96 500 C mol⁻¹), respectively. Thus, the slope (σ) can be estimated by the function relation of the Warburg diffusion process (Z_{re}) and $\omega^{-1/2}$, as shown in Fig. 6f. The porous Fe₃N/Fe₃O₄@C fibers exhibited a lower σ value (82.4) than the nonporous Fe₃N/Fe₃O₄@C fibers (131.1), once again confirming the superior Li⁺ diffusion coefficient and stronger electrochemical dynamics.³⁵

Conclusions

 $Fe_3N/Fe_3O_4@C$ porous fibers were prepared by electrospinning, and consecutive carbonization and nitridation. XPS analysis

unveiled the formation of Fe–N and Fe–O bonds, which further confirmed the formation of heterogeneous nanocrystals by TEM and XRD. The porous Fe_3N/Fe_3O_4 @C fibers delivered a capacity of 1984 mA h g⁻¹ at 0.1 A g⁻¹, a rate capacity of 407.8 mA h g⁻¹ at 10 A g⁻¹, and a specific capacity of 282 mA h g⁻¹ after 2000 cycles at 5 A g⁻¹. Overall, this biphasic porous heterostructure with a high specific surface area and wrapped by a carbon layer greatly improved the electrochemical performance and structural stability of LIBs.

Author contributions

Yuanxiao Ma: data curation and writing – original draft. Chen Hu: investigation. Miaobing Ruan: methodology and formal analysis. Yigang Li: magnetization measurement. Xuefan Wang: XPS measurement and analysis. Zepeng Chen: sample preparation. Ze-Xing Cai: visualization. Yan Han: review & editing. Shenghong Liu: review & editing. Haibin Sun: conceptualization, supervision, and funding acquisition.

Data availability

All data on the measured ecosystem variables indicating ecosystem functions that support the findings of this study are included within this paper and its ESI.[†]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (11874317 and 22305207), the Key Scientific Research Projects of Colleges and Universities in Henan Province (22A140009), and the Program for Young Scholars of Xinyang Normal University. This work was supported by the Analysis and Testing Center of XYNU.

References

- X. Yu, J. Xiang, Q. Shi, L. Li, J. Wang, X. Liu, C. Zhang, Z. Wang, J. Zhang, H. Hu, A. Bachmatiuk, B. Trzebicka, J. Chen, T. Guo, Y. Shen, J. Choi, C. Huang and M. H. Rümmel, *Small*, 2024, **12**, 2406309.
- 2 Q. Liu, X. Su, D. Lei, Y. Qin, J. Wen, F. Guo, Y. A. Wu, Y. Rong, R. Kou and X. Xiao, *Nat. Energy*, 2018, 3, 936.
- 3 V. Mullaivananathan, N. K. Shakkeel and N. Kalaiselv, *Energy Fuels*, 2021, **35**, 8991–9000.
- 4 D. Zhou, X. Guo, Q. Zhang, Y. Shi, H. Zhang, C. Yu and H. Pang, *Adv. Funct. Mater.*, 2022, **32**, 2107928.
- 5 X. Qian, J. Cheng, Y. Wang, L. Jin, J. Chen, Q. Hao and K. Zhang, *Phys. Chem. Chem. Phys.*, 2023, **25**, 5559–5568.
- 6 J. He, A. Bhargav, H. Sul and A. Manthiram, *Angew. Chem.*, *Int. Ed.*, 2023, **62**, e202216267.
- 7 S. Liu, W. Zheng, W. Xie, H. Cui, Y. Li, C. Zhang, Z. Ji, F. Liu, R. Chen, H. Sun and J. Xu, *Carbon*, 2022, **192**, 162–169.
- 8 M. Idrees, A. S. Haidyrah, A. Rehman, Q. Zhang, X. Li and S. M. Abbas, *J. Alloys Compd.*, 2021, 883, 160824.
- 9 H. Cheng, J. G. Shapter, Y. Li and G. Gao, *J. Energy Chem.*, 2021, 57, 451–468.
- 10 Z. Liu, D. Wang, Z. Liu, W. Li, R. Zhang, L. Wu, H. Mu, Y. Hou, Q. Gao, L. Feng and G. Wen, *J. Colloid Interface Sci.*, 2022, **627**, 716–729.
- 11 H. Sun, C. Liu, Y. Liang, S. Liu, Y. Qiao, C. Li, W. Xie, G. Ge and Z.-X. Cai, *ACS Appl. Nano Mater.*, 2024, 7, 13017–13026.
- 12 C. Hu, L. Chen, Y. Hu, A. Chen, L. Chen, H. Jiang and C. Li, *Small*, 2021, 17, 2103532.
- 13 M. Jin, G. Sun, J. Yuan, Y. Wang, J. Zhou, J. Li, X. Ni, X. Pan and E. Xie, *J. Alloys Compd.*, 2022, 922, 166231.
- 14 C. Zhang, Y. Song, L. Xu and F. Yin, *Chem. Eng. J.*, 2020, **380**, 122545.
- 15 Y. Li, H. Yu, L. Miao, L. Wang and Y. Song, J. Alloys Compd., 2024, 1005, 176080.
- 16 H. Wang, X. Du, X. Jiang, Y. Chai, X. Yang and R. Yuan, *Chem. Eng. J.*, 2017, **313**, 535–543.

- 17 H. Sun, J. Xu, C. Wang, G. Ge, Y. Jia, J. Liu, F. Song and J. Wan, *Carbon*, 2016, **108**, 356–362.
- 18 H. Sun, X. Kong, H. Park, F. Liu, Z. H. Lee and F. Ding, Adv. Mater., 2022, 9, 2107587.
- 19 W. Xie, Q. Wang, J. Xu, Y. Yu, R. Zhao, N. Li, M. Li, Y. Du, S. Peng and G. Cao, *J. Mater. Chem. A*, 2019, 7, 10523– 10533.
- 20 S. Liu, W. Zheng, C. Hu, Y. Li, H. Cui, X. Chu, X. Li, Y. Xue, W. Xie, F. Liu, H. Sun and J. Xu, *J. Power Sources*, 2024, **605**, 234536.
- 21 J. Zhao, Y. Weng, S. Xu, A. Sheb, X. Wen and G. Yang, J. Power Sources, 2020, **464**, 228246.
- 22 X. Zhang, F. Ma, K. Srinivas, B. Yu, X. Chen, B. Wang, X. Wang, D. Liu, Z. Zhang, J. He and Y. Chen, *Energy Storage Mater.*, 2022, **45**, 656–666.
- 23 H. Huang, S. Gao, A.-M. Wu, K. Cheng, X.-N. Li, X.-X. Gao, J.-J. Zhao, X.-L. Dong and G.-Z. Cao, *Nano Energy*, 2017, 31, 74–83.
- 24 S. Liang, C. Liu, H. Sun, C. Li, M. Feng, S. Gao, S. Liu, H. Pan and G. Ge, *J. Energy Storage*, 2023, **59**, 106540.
- 25 Z. Li, Y. Zhang, X. Li, F. Gu, L. Zhang, H. Liu, Q. Xia, Q. Li, W. Ye, C. Ge, H. Li, H. Hu, S. Li, Y.-Z. Long, S. Yan, G.-X. Miao and Q. Li, *J. Am. Chem. Soc.*, 2021, **143**, 12800– 12808.
- 26 Y. Zhang, H. Xu, P. Li, W. Li, H. Yue, H. Li, L. Wu, W. Fa, Q. Yu and Q. Guo, *Ionics*, 2024, **30**, 1329–1337.
- 27 L. Tian, Y. Xie, J. Lu, T. Liu, Q. Hu, Y. Xiao, X. Zhu and X. Su, *J. Alloys Compd.*, 2022, **922**, 166208.
- 28 S. Liu, W. Zheng, M. Huang, Y. Xu, W. Xie, H. Sun and Y. Zhao, *Nanotechnology*, 2022, 33, 135401.
- 29 D. Zhang, C. Zhang, X. Shi, H. Xu, S. Shi, Y. Li, B. Luo, G. Liu, X. Liu, C. Yu and X. Li, *J. Power Sources*, 2023, 579, 233288.
- 30 W. Xie, W. Wang, L. Duan, W. Zheng, S. Liang, S. Liu, F. Liu, X. Wang, H. Sun and X. Sun, *J. Alloys Compd.*, 2022, 918, 165687.
- 31 D. Wang, Y. Chao, K. Guo, Z. Wang, M. Yang, J. Zhu, X. Cui and Q. Xu, *Adv. Funct. Mater.*, 2024, 2405642.
- 32 Q. Wei, X. Chang, D. Butts, R. DeBlock, K. Lan, J. Li, D. Chao, D.-L. Peng and B. Dunn, *Nat. Commun.*, 2023, 14, 7.
- 33 H. Sun, W. Wang, L. Zeng, C. Liu, S. Liang, W. Xie, S. Gao,
 S. Liu and X. Wang, *Dalton Trans.*, 2022, 51, 12071.
- 34 J. Liu, X. Xu, R. Hu, L. Yang and M. Zhu, *Adv. Energy Mater.*, 2016, **6**, 1600256.
- 35 T.-F. Yi, T.-T. Wei, Y. Li, Y.-B. He and Z.-B. Wang, *Energy Storage Mater.*, 2020, **26**, 165–197.