Filling and unfilling carbon capsules with transition metal oxide nanoparticles for Li-ion hybrid supercapacitors: towards hundred grade energy density

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ABSTRACT Li-ion hybrid supercapacitors (Li-HECs) facilitate effective combination of the advantages of supercapacitors and Li-ion batteries (LIBs). However, challenges remain in designing and preparing suitable anode and cathode materials, which often require tedious and expensive procedures. Herein, we demonstrated that hollow N-doped carbon capsules (HNC) with and without a Fe₃O₄ nanoparticle core can respectively function as the anode and the cathode in very-high-performance Li-HECs. The Fe₃O₄@NC anode exhibited a high reversible specific capacity exceeding 1530 mA h g⁻¹ at 100 mA g⁻¹ and excellent rate capability (45% capacity retention from 0.1 to 5 A g⁻¹) and cycle stability (>97% retention after 100 cycles). Moreover, high rate performance was achieved in a full-cell using the HNC cathode. By combining the respective structural advantages of the components, the hybrid device with Fe₃O₄@NC//HNC exhibited a remarkable energy density of 185 W h kg⁻¹ at a power density of 39 W kg⁻¹. The hybrid device furnished a battery-inaccessible power density of 28 kW kg⁻¹ with rapid charging/discharging within 9 s at an energy density of 95 W h kg⁻¹.

Keywords: carbon capsules, Fe₃O₄, high energy density, Li-ion hybrid supercapacitor

INTRODUCTION

With the increasing demand for portable electronic devices, researchers have focused on developing low-cost, environment-friendly, and high-performance energy storage devices [1,2]. Supercapacitors are known to possess high power density with excellent duration; however, they often suffer from low energy density or low energy/power

ratio. Li-ion hybrid supercapacitors (Li-HECs), which are expected to combine the respective advantages of supercapacitors and Li-ion batteries (LIBs), have been proposed as an alternative in order to overcome the inherent limitations of supercapacitors [3–6]. Li-HECs comprise a battery-type anode and a capacitor-type cathode in an organic electrolyte containing a Li salt as a solute. Since the cathode and anode work reversibly in distinct voltage regions, Li-HECs can potentially achieve excellent rate capability, long cycle life, and high energy density [7–9]. Properly coupling the high-power cathode and high-energy anode in the same device is the primary challenge in the construction of high-performance Li-HECs.

Amatucci *et al.* [3] first reported a hybrid device, in which activated carbon (AC) was used as the cathode and Li₄Ti₅O₁₂ was used as the anode, and achieved an energy density of 20 W h kg⁻¹, which was nearly three times that of conventional supercapacitors. Since then, insertion-type materials such as Li₄Ti₅O₁₂ [10], Li₃VO₄ [11], MnO [12], Fe₃O₄ [13], and Si-based materials [14–16] have been explored as the electrode materials for Li-HECs. It is worth noting that the discharge voltage plateau of the Li₄Ti₅O₁₂-based anode is ~1.5 V vs. Li/Li⁺. Therefore, Li-HECs might undergo mere charge-discharge below 3.2 V, resulting in a narrow operation voltage. Taking into account that *E* and *P* have a square relationship with the working voltage, enhancing the working voltage is crucial for improving the overall properties of Li-HECs. Metal oxides are perfect candidates for Li-HEC anodes on

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account of their relatively low voltage plateau (~ 0.8 V) and high theoretical capacity. Thus, a low discharge voltage plateau may dramatically improve the operation voltage [17–19]. Among various metal oxides, Fe_3O_4 has earned distinction due to its inherent advantages, including being an abundant natural resource with low cost and high theoretical capacity (924 mA h g^{-1}) [20]. Carbonaceous materials have been extensively explored for the use as capacitor-type cathode, including AC, carbon nanotubes, and more recently, graphene [21–25]. In current approaches, the anode and cathode materials for Li-HECs are often synthesized individually, inevitably involving lengthy preparation, high cost, and capacity and volume mismatch [26–29]. Therefore, new strategies for one-pot synthesis of inherently compatible cathodes and anodes are highly attractive for further development of Li-HECs.

Herein, based on the comprehensive understanding of the respective energy storage mechanisms in the anode and cathode, we describe a facile route for fabricating such an anode/cathode couple ($\text{Fe}_3\text{O}_4\text{@NC//HNC}$) for full-cell Li-HECs. There are two advantages in this materials design strategy. Firstly, the preparation procedures have been greatly simplified; the hollow N-doped carbon (HNC) cathode is obtained by acid-washing the $\text{Fe}_3\text{O}_4\text{@NC}$ anode, which is fabricated via a simple hydrothermal approach. Secondly, the capacities and volume expansion accommodation abilities of the cathode and anode naturally match, which can be ascribed to their common origin and thus structural similarity. By combining the respective structural advantages of the anode and cathode, the thus-constructed Li-HECs (Fig. 1) can effectively accommodate the kinetic discrepancy and attain an appealing energy density of $185 \text{ W h kg}^{-1}_{\text{electrodes}}$, which remains as approximately hundred-energy density (95 W h kg^{-1}) when the power density reaches 28 kW kg^{-1} at a rapid charging rate.

EXPERIMENTAL SECTION

Material preparation

Mesoporous $\text{Fe}_3\text{O}_4\text{@NC}$ nanocomposites were synthesized via a hydrothermal method and post-calcination treatment. Typically, 6.6 mmol of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 3 mmol of iminodiacetic acid (IDA) were added to 40 mL deionized water under constant agitation. The mixture was then transferred into a teflon-lined autoclave, which was incrementally heated to 160°C and kept for 8 h . The resulting precipitates were harvested by centrifugation and repeatedly washed with water and ethanol, followed by

vacuum drying at 60°C overnight. The sample was finally sintered at 600°C for 2 h under Ar atmosphere.

The HNC was synthesized by etching the synthesized $\text{Fe}_3\text{O}_4\text{@NC}$ nanocomposite in 1 mol L^{-1} HCl solution at 80°C for 12 h .

Material characterization

The crystal structure and surface configuration of the samples were characterized by X-ray diffraction (XRD, Rigaku D/Max-2500, Cu K α radiation), scanning electron microscopy (SEM, FEI Verios 460L), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy-filtered TEM (EFTEM) on a JEOL JEM-2100 TEM. The synthesized materials were also evaluated by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe, ULVAC PHI) and Raman spectroscopy (Renishaw Via, excitation 514.5 nm). The porous nature and specific surface areas of the $\text{Fe}_3\text{O}_4\text{@NC}$ and HNC samples were further analyzed by nitrogen adsorption/desorption measurements (NOVA 2200e, Quantachrome Instruments). The compositions of the sample were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES, ICP-9000).

Fabrication of the half cell

For fabrication of the $\text{Fe}_3\text{O}_4\text{@NC}$ composite electrode, the active material, acetylene black, and poly(vinylidene fluoride) (PVDF) in *N*-methyl-2-pyrrolidone (NMP) were blended in a ratio of 85:10:5 to form a slurry, and subsequently deposited onto copper foil. After heating at 80°C for 12 h in vacuum, the sheet was punched into 12 mm -diameter electrodes. A slightly different process was used for fabrication of the cathode. The HNC powder was mixed directly with 10% PVDF in NMP to form a slurry and was subsequently coated onto Al foil. The electrochemical properties were assessed using CR2032-type coin cells, which were assembled in an argon-filled glove box. Lithium metal acted as the counter and reference electrodes. The electrolyte comprised LiPF_6 (1 mol L^{-1}) dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) in a volume ratio of 1:1:1.

Fabrication and characterization of the hybrid device

Li-HECs were assembled in coin cells with pre-lithiated $\text{Fe}_3\text{O}_4\text{@NC}$ as the anode, HNC as the cathode, and Celgard 2400 membrane as the separator. The electrolyte was the same as that in the half cells.

Galvanostatic charge-discharge measurements of the half

cells and Li-HECs were performed by using a LAND battery test instrument (CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted by using a Zahner IM6e electrochemical workstation.

RESULTS AND DISCUSSION

Morphological and structural analysis

Fig. 1 presents a schematic illustration of the structure of Li-HECs employing the proposed electrode materials. Firstly, an Fe-based complex with nanorod morphology (Fig. S1) was prepared by using IDA as the chelating agent in a hydrothermal approach. After a short annealing procedure, the $\text{Fe}_3\text{O}_4@\text{NC}$ composites were synthesized. Upon further acid etching, the HNC materials, which function as the cathode materials, were prepared.

Fig. 2a highlights the overall morphology of the as-synthesized $\text{Fe}_3\text{O}_4@\text{NC}$ composites, in which the parent Fe-IDA nanorod morphology was well-preserved without collapse of the structure. From the zoom-in images in Fig. 2b and c, the $\text{Fe}_3\text{O}_4@\text{NC}$ nanorods comprise an assembly of numerous spherical particles, which is different from the structure of the precursor Fe-IDA nanorods. TEM characterization (Fig. 2d and e) further clarifies that the

$\text{Fe}_3\text{O}_4@\text{NC}$ nanorods with porous structure are made up of connected nanoscale sub-units. The HRTEM image in Fig. 2f demonstrates that the Fe_3O_4 particles are crystalline and the interplanar crystal spacing of 0.293 nm can be ascribed to the 220 plane of Fe_3O_4 . The sub-units possess a core-shell structure with an ultra-small and homogeneous size (~ 15 nm), as demonstrated by the EFTEM images (Fig. 2g and h). Moreover, the mapping results demonstrate that the three elements C, Fe, and O, are homogeneously and uniformly distributed throughout the product (Fig. 2i).

The HNC retains the overall rod-like configuration with a diameter of about 200 nm (Fig. 3). A high percentage of holes were found after etching the Fe_3O_4 core (Fig. 3a). The SEM images further indicate the well-retained HNC nanorods (Fig. 3a). Many three dimensional (3D) interconnected mesopores are uniformly distributed to form the integral rod-like structure (Fig. 3b). The diameter of the big pores between the nanoparticles is ~ 7 nm (Fig. 3c), which is suitable for promoting the infiltration of the electrolyte molecules. The HRTEM image (Fig. 3d) illustrates that the big pores are linked to small mesopores (about 4 nm) and the walls of the small pores are composed of amorphous carbon. The novel nanostructure offers an opportunity to minimize the inner-pore resistance, resulting in improvement of the ion-accessible surface area. As shown in

Figure 1 Illustration of the fabricated Li-HECs. The cathode employs HNC materials and the anode utilizes pre-lithiated $\text{Fe}_3\text{O}_4@\text{NC}$ hybrids.

Figure 2 SEM (a–c), TEM (d–f), EFTEM (g–h) images, and the corresponding element mapping (i) of the $\text{Fe}_3\text{O}_4@\text{NC}$ electrode material.

Fig. 3e and f, the mapping results demonstrate the homogeneous distribution of C.

As illustrated in Fig. 4a, the XRD profiles of the synthesized $\text{Fe}_3\text{O}_4@\text{NC}$ sample correspond to the crystal plane of Fe_3O_4 (JCPDS No. 75-1609) and amorphous carbon, as evidenced by the broad peak centered around 25° . No other peaks were detected. Hence, it can be deduced that the Fe-IDA complex is completely converted to $\text{Fe}_3\text{O}_4@\text{NC}$ composites. Furthermore, elemental analysis (EA) reveals that the content of carbon and nitrogen are approximately 14.7 and 5.1 wt.%, respectively. The $\text{Fe}_3\text{O}_4@\text{NC}$ Raman spectrum (Fig. 4b) shows the characteristic peaks of Fe_3O_4 (302, 540, and 670 cm^{-1} , corresponding to the E_g , T_{2g} , and A_{1g} vibration modes, respectively) [30], and typical peaks of amorphous carbon (D and G bands at about 1345 and 1586 cm^{-1} , corresponding to sp^3 -type disordered carbon

and sp^2 -type graphitized carbon, respectively). The I_D/I_G value of the $\text{Fe}_3\text{O}_4@\text{NC}$ composites is 0.88, demonstrating a higher content of sp^2 -type carbon relative to sp^3 -type, which is beneficial for achieving high electronic conductivity [31].

The HNC could be obtained after leaching the Fe_3O_4 nanocrystals. The XRD pattern (Fig. 4a) exhibits a characteristic peak of amorphous carbon at 25° , indicating the complete leaching of Fe_3O_4 from the $\text{Fe}_3\text{O}_4@\text{NC}$ composite. The Raman spectrum of the HNC is shown in Fig. 4b. The peaks representing the D- and G-band of amorphous carbon are located at 1337 and 1584 cm^{-1} , respectively. The calculated I_D/I_G value is 0.89, indicating the high degree of graphitization and the ordered structure of the as-prepared HNC, which is consistent with the HRTEM data (marked by the red circles in Fig. 3d) [9,13].

Figure 3 (a, b) SEM, (c, d) TEM images, and the corresponding element mapping (e, f) of the HNC electrode material.

Figure 4 The XRD patterns (a) and Raman spectra (b) of the corresponding electrodes.

The carbon-layer coating on the Fe_3O_4 nanoparticles forms a new order of structural hierarchy, as evidenced by the conductive network formed throughout the composites, preventing agglomeration of the Fe_3O_4 nanoparticles and accommodating the volume expansion/shrinkage in the process of charging and discharging, which are regarded as key issues for alleviating the poor cycling performance of conventional Fe_3O_4 -based devices [32,33]. Further evidence of the porous structure was derived from analysis of the nitrogen sorption isotherms of the $\text{Fe}_3\text{O}_4@\text{NC}$ composite (Fig. S2). The specific surface area of $\text{Fe}_3\text{O}_4@\text{NC}$ is $144.9 \text{ m}^2 \text{ g}^{-1}$, which is favorable for ef-

fective electrolyte permeation. Therefore, the small Fe_3O_4 particles coated by thin carbon capsules, in conjunction with the enhanced conductivity and electrolyte accessibility, should lead to improved electrochemical properties.

The XPS analyses of the $\text{Fe}_3\text{O}_4@\text{NC}$ composites are summarized in Fig. S3. The Fe 2p spectra (Fig. S3a) present two obvious peaks centered at binding energies (BE) of 710.2 and 723.9 eV. The deconvoluted Fe 2p_{3/2} peaks at 709.7, 710.8, and 713.2 eV are attributed to the Fe^{2+} octahedral site, Fe^{3+} octahedral site, and Fe^{3+} tetrahedral site in Fe_3O_4 , in agreement with the literature [34–36]. O 1s XPS analysis was carried out to verify the surface oxygen states of

the $\text{Fe}_3\text{O}_4@\text{NC}$ composites (Fig. S3b). The O 1s peak of the $\text{Fe}_3\text{O}_4@\text{NC}$ composites at 530 eV could be deconvoluted to two components at 529.5 and 531.6 eV, which correspond to the lattice O^{2-} of metallic oxides or the physically sorbed H_2O [37–38]. The C 1s XPS spectra (Fig. S3c) could be deconvoluted into three peaks: $\text{sp}^2\text{-sp}^2\text{C}$ (284.0 eV), -C-N (284.9 eV), and C=O (288.0 eV) [12,15]. The N 1s core level (Fig. S3d) could be deconvoluted into two distinct peaks: pyridinic N (398.0 eV) and pyrrolic N (399.5 eV) [22,23].

The nitrogen sorption isotherms of the HNC (Fig. S4a) are type-I/IV, and the BET surface area is $804.8\text{ m}^2\text{ g}^{-1}$. The high contact area between the Fe_3O_4 nanoparticles and the interconnected carbon capsules is favorable for accelerating charge transfer and furnishing excellent rate capability. The

pore size distribution of the HNC (Fig. S4b) was measured to be 9.7 nm.

The XPS spectra in Fig. S5 were used to elucidate the electronic structure of the core levels, with peaks of sp^2C at 284.5 eV, -C-N at 285.2 eV, and C=O at 288.0 eV in the C 1s region, along with pyridinic N (398.5 eV) and pyrrolic N (400.2 eV) in the N 1s region, demonstrating the successful combination of these elements [15,22].

Li-ion battery performance

The lithium storage performance of the $\text{Fe}_3\text{O}_4@\text{NC}$ composite as an anode material was assessed by using coin-type cells. Fig. 5a shows the first three cycles in the CV curves of the $\text{Fe}_3\text{O}_4@\text{NC}$ electrode. Two distinct peaks are located

Figure 5 (a) CV curves at 0.5 mV s^{-1} , (b) charge-discharge curves, (c) rate performance, (d) cycle stability of the $\text{Fe}_3\text{O}_4@\text{NC}$ electrode. (e) Galvanostatic charge-discharge curves, (f) discharge capacities of HNC-based Li-ion battery at different current densities.

at 0.64 and 0.49 V (vs. Li^+/Li) in the first cycle of the cathodic scan, which may correspond to the reaction: $\text{Fe}_3\text{O}_4 + 8\text{Li}^+ \rightarrow 3\text{Fe}^0 + 4\text{Li}_2\text{O}$ [39]. The oxidation peak around 1.87 V in the anodic scan can be ascribed to the oxidation of Fe^0 to Fe_3O_4 [13,20]. In the successive scans, the anodic and cathodic peaks are both shifted and the peak intensity drops significantly, corresponding to polarization of the electrode [40]. In addition, the CV curves of the post two cycles approximately overlap, implying good invertibility.

As shown in Fig. 5b, the cell exhibits a specific capacity of 1530 mA h g^{-1} during the first discharge procedure. During the corresponding charge process, the obtained reversible capacity is 992 mA h g^{-1} , corresponding to an initial Coulombic efficiency of about 65%. The formation of a solid electrolyte interface (SEI) film causes irreversible capacity loss in the first cycle [41,42]. In the subsequent cycles, there are no obvious changes in the charge-discharge profiles, demonstrating outstanding capacity retention. In addition, the specific capacity of the $\text{Fe}_3\text{O}_4@\text{NC}$ electrode decreases slowly with increasing discharge current density, demonstrating excellent rate performance (Fig. 5c). When the current density increases to 5 A g^{-1} , the specific capacity of the $\text{Fe}_3\text{O}_4@\text{NC}$ electrode still remains at 690 mA h g^{-1} , which corresponds to retention of 45% of the initial capacity. In addition, the $\text{Fe}_3\text{O}_4@\text{NC}$ electrode exhibits good cycle stability, as depicted in Fig. 5d. At 0.8 A g^{-1} current density, after 100 cycles, a specific capacity retention of >97% was achieved, with nearly perfect Coulombic efficiency in each cycle. TEM observation (Fig. S6) reveals that the structural integrity is well maintained even after 100 charge-discharge cycles, indicative of the stable operation of the $\text{Fe}_3\text{O}_4@\text{NC}$ hybrids.

The above results clearly demonstrate that the mesoporous core-shell structure of the $\text{Fe}_3\text{O}_4@\text{NC}$ composite plays a crucial role in enhancing the electrochemical properties. The promising performance is due to the following four critical aspects. Firstly, the uniform building sub-units are beneficial for fast transport of lithium ions and electrons and provide a high surface area, leading to the excellent rate capability. Secondly, the carbon shells can prevent direct contact between Fe_3O_4 and the electrolyte, consequently lessening the interfacial reactions, which is crucial for structural stabilization of the electrode. Thirdly, the mesoporous structure can tolerate the volume expansion/contraction during the charge-discharge process, resulting in remarkable structural stability. Finally, the carbon capsules are strongly interconnected with the sub-units to form a continuous network, leading to good electrical conductivity and enhanced electrochemical per-

formance. Such extraordinary properties of the $\text{Fe}_3\text{O}_4@\text{NC}$ make it a good candidate for Li-HECs and provide enhanced electrochemical performance.

The linear galvanostatic charge-discharge curve of the HNC electrode (Fig. 5e) indicates capacitive behavior, corresponding to the adsorption-desorption of ions on the electrode surface. The HNC has a high discharge capacity of 87 mA h g^{-1} at 0.1 A g^{-1} current density. With increasing discharge current density, the discharge capacity of the HNC electrode decreases slowly, demonstrating excellent rate capacity (Fig. 5f). Even when the current density was increased to 5 A g^{-1} , the specific capacity of the HNC electrode still remained at 69.4 mA h g^{-1} (79% of the initial capacity). Thus, it can be concluded that the 3D micro-structure effectively improves the diffusion kinetics and enhances the lithium storage ability.

Li-HEC performance

Asymmetrically assembled Li-HECs can achieve high-voltage, giving rise to high energy and power density of the devices. Therefore, Li-HECs were assembled using $\text{Fe}_3\text{O}_4@\text{NC}$ as the anode and HNC as the cathode. In the charging process, the porous capsules of the HNC can adsorb PF_6^- ions from the electrolyte, while Li^+ ions are intercalated into the $\text{Fe}_3\text{O}_4@\text{NC}$ electrode. The electrode discharge process involves the reverse sequence of events. To achieve high energy density of the Li-HECs, the mass ratio of the electrodes and the voltage window must be optimized to achieve the best state of both the anode and cathode. As illustrated in Fig. 5b, the plateau region of the $\text{Fe}_3\text{O}_4@\text{NC}$ anode is located at about 0.9 V (vs. Li/Li^+). Thus, the plot for the HNC cathode has a linear region from 2.5 to 4.0 V (vs. Li/Li^+) (Fig. 5e), indicating that the maximum charge voltage can reach 4.0 V (vs. Li/Li^+). Hence, the performance of the Li-HEC device was evaluated in the range of 1.0 to 4.0 V (vs. Li/Li^+). Based on the equation: $Q_+ = Q_-$, the mass ratio of the electrode active materials is optimized to 4:1.

The CV curves of the Li-HECs adopt a quasi-rectangular shape irrespective of the scan rate due to the superimposed effects of the two different energy-storage mechanisms (Fig. 6a). The representative charge-discharge profiles (Fig. 6b) illustrate a similar linear relationship, which is in accordance with the ideal capacitor performance. Furthermore, at a current density of 0.5 A g^{-1} , the $\text{Fe}_3\text{O}_4@\text{NC}/\text{HNC}$ Li-HEC exhibits an ultrahigh capacitance of 245 F g^{-1} (Fig. S7). Even when the current density reaches 40 A g^{-1} (rapid charging/discharging within 9 s, Fig. S8), the capacitance retention is maintained at 65.3%, indicating the excellent

Figure 6 Electrochemical performance of the $\text{Fe}_3\text{O}_4@NC//\text{HNC}$ Li-HECs. (a) CV curves, b) galvanostatic charge-discharge curves, c) cycle stability of the $\text{Fe}_3\text{O}_4@NC//\text{HNC}$ Li-HECs over 3000 cycles at a current density of 5 A g^{-1} . (d) Ragone plots of the $\text{Fe}_3\text{O}_4@NC//\text{HNC}$ Li-HECs and $\text{Fe}_3\text{O}_4@NC//\text{AC}$ Li-HECs at various charge-discharge rates. (e) Ragone plots (energy density vs. power density) of the $\text{Fe}_3\text{O}_4@NC//\text{HNC}$ Li-HECs compared with other reported hybrid supercapacitors (all based on total mass of both electrodes).

rate capability. The $\text{Fe}_3\text{O}_4@NC//\text{AC}$ device was also constructed for comparison. The $\text{Fe}_3\text{O}_4@NC//\text{HNC}$ system exhibits a certain extent of enhancement relative to the $\text{Fe}_3\text{O}_4@NC//\text{AC}$ configuration, confirming the complementarity of the as-synthesized anode and cathode materials in the former (Fig. S9). At a high current density of 5 A g^{-1} , the Li-HECs also presents favorable cyclic stability (Fig. 6c) with a capacity retention of 91.2% after 1500 cycles that could be maintained up to 3000 cycles (with

86.9% retention), as well as good Coulombic efficiency.

The interfacial electron and ion transfer process was evaluated by EIS (Fig. S10). The EIS data could be fitted to an equivalent circuit consisting of the bulk solution resistance R_s , charge-transfer resistance R_{ct} , pseudocapacitive element C_p of the redox process, and the constant phase element (CPE) to account for the double-layer capacitance. R_s and R_{ct} can be obtained from the Nyquist plots, where the high-frequency semicircle intercepts the real axis at R_s

and ($R_s + R_{ct}$), respectively. The charge-transfer resistance is deduced by fitting the EIS data. From the results shown in Fig. S10, the deduced solution resistance, R_s , is 28 Ω , and the charge-transfer resistance, R_{ct} , is 82 Ω for the $\text{Fe}_3\text{O}_4@\text{NC}/\text{HNC}$ Li-HEC device. The more vertical line leaning towards the imaginary axis in the low-frequency region of the $\text{Fe}_3\text{O}_4@\text{NC}/\text{HNC}$ Li-HECs device indicates the lower CPE value. This suggests more facile electrolyte diffusion to the composite surface and more ideal capacitor behavior. The above results demonstrate that the combination of fast ion diffusion and low charge-transfer resistance results in high utilization of the active materials, thereby enhancing the electrochemical properties of the $\text{Fe}_3\text{O}_4@\text{NC}/\text{HNC}$ Li-HECs device.

The Ragone plots of the $\text{Fe}_3\text{O}_4@\text{NC}/\text{HNC}$ and $\text{Fe}_3\text{O}_4@\text{NC}/\text{AC}$ Li-HECs are shown in Fig. 6d. The energy and power density were determined based on the total mass of both electrodes. The energy density and power density of the $\text{Fe}_3\text{O}_4@\text{NC}/\text{HNC}$ system are much higher than that of the $\text{Fe}_3\text{O}_4@\text{NC}/\text{AC}$ system. For instance, the $\text{Fe}_3\text{O}_4@\text{NC}/\text{HNC}$ Li-HEC system delivers a high-level energy density of 151 $\text{W h kg}^{-1}_{\text{electrodes}}$ at 180 W kg^{-1} and 185 $\text{W h kg}^{-1}_{\text{electrodes}}$ at 39 W kg^{-1} , while the $\text{Fe}_3\text{O}_4@\text{NC}/\text{AC}$ device affords only 80 $\text{W h kg}^{-1}_{\text{electrodes}}$ at 180 W kg^{-1} . Even when the power density reaches 28 kW kg^{-1} , which is well above the suggested target (15 kW kg^{-1}) for electric vehicles, the $\text{Fe}_3\text{O}_4@\text{NC}/\text{HNC}$ device maintains an energy density of 95 $\text{W h kg}^{-1}_{\text{electrodes}}$, demonstrating its exceptional rate performance. From comparison of the performance of the Li-HECs with the best Li-ion capacitor systems reported to date (Table S1), such as B-Si/SiO₂/C//PSC [14], 3D-MnO/CNS//3D-CNS [21], m-Nb₂O₅-C//AC [33], CNT-threaded TiO₂//CNT-AC [41], etc., it can be concluded that the developed Li-HEC exhibits one of the most promising energy-power combinations (Fig. 6e). Since the mass of both electrodes accounts for 30%–40% of the entire system, the overall Li-HEC system presents hope for achieving hundred- W h kg^{-1} energy density as well as retaining capacitor-level power density (Fig. S11), and represents a superb energy-power combination for bridging the gap between LIBs and capacitors. An energy density of 54 $\text{W h kg}^{-1}_{\text{package}}$ could be achieved at a power density of 4000 $\text{W kg}^{-1}_{\text{package}}$. Likewise, an energy density of 49 $\text{W h kg}^{-1}_{\text{package}}$ could be maintained even at the ultrahigh package power of 9000 $\text{W kg}^{-1}_{\text{package}}$. As shown in Fig. 6d (inset) and Fig. S12, a single 3 V Li-HEC can readily drive light-emitting diodes (LEDs) where the signal "TJUT" could be observed, which implies the potential for practical application of the Li-HECs.

CONCLUSIONS

In summary, an anode and cathode ($\text{Fe}_3\text{O}_4@\text{NC}/\text{HNC}$) couple was fabricated by a facile process and subsequently applied in Li-HECs. The core-shell structure of the $\text{Fe}_3\text{O}_4@\text{NC}$ anode provides a large specific surface area and restricts diffusion-controlled lithiation/delithiation processes, while the HNC cathode with tailored micro/meso-porosity exhibits enhanced super-capacitive performance. Based on the design of the electrode materials, energy densities of 185–95 W h kg^{-1} were achieved with the Li-HECs, along with power densities ranging from 39 to 28,000 W kg^{-1} , which are almost the highest values reported for hybrid-type systems. These Li-HECs, which combine high energy and power performance, narrow the gap between supercapacitors and batteries, and represent a forward step in this field.

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Supplementary information Supporting data are available in the online version of the paper.

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面向百瓦时/千克级能量密度锂离子混合超级电容器电极材料的研究

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摘要 锂离子混合电容器是一种集合了超级电容器和锂离子电池双重优点的储能器件。然而,正负极电极材料的选择和设计仍存在着巨大的挑战。本文采用水热反应与热处理相结合的方法,合成了四氧化三铁纳米颗粒填充的氮掺杂碳胶囊负极材料($\text{Fe}_3\text{O}_4@\text{NC}$),用稀酸洗去 Fe_3O_4 核,得到中空氮掺杂碳胶囊正极材料(HNC),并测定了其作为锂离子混合电容器电极材料的性能。结果表明, $\text{Fe}_3\text{O}_4@\text{NC}$ 负极材料在 100 mA g^{-1} 电流密度下具有 1530 mA h g^{-1} 的容量,且具有优异的倍率性能和循环稳定性。同时HNC正极材料确保锂离子混合电容器具有大倍率性能。结合上述正负极材料的优点, $\text{Fe}_3\text{O}_4@\text{NC}/\text{HNC}$ 锂离子混合电容器在 39 W kg^{-1} 的功率密度下表现出 185 W h kg^{-1} 的能量密度,并且当该锂离子混合电容器的能量密度为 95 W h kg^{-1} 时,其功率密度可高达 28 kW kg^{-1} 。本文采用的制备电极材料的方法操作简便,廉价易得,组装成的锂离子混合电容器具有优异的能量密度和功率密度,为新型锂离子混合电容器电极材料的设计提供了新思路。