Biopolymer-assisted synthesis of 3D interconnected Fe₃O₄@carbon core@shell as anode for asymmetric lithium ion capacitors

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ABSTRACT

Lithium ion capacitor (LIC) has been regarded as a promising device to combine the merits of high-energy lithium ion battery and high-power supercapacitor. The key challenge in developing high performance LIC is to achieve synergy between the high capacity of battery anode and the fast non-Faradaic reaction rate of capacitive cathode without compromising energy density. Here, we report 3D interconnected Fe₃O₄@C core@shell nanocomposites with enhanced lithium storage reaction kinetics as an anode material of LIC. Chitosan, a renewable biopolymer with rich functional groups, has been utilized as both structural directing agent and carbon precursor to assist the synthesis of Fe₃O₄@C composites, which have small particle size and an in-situ formed carbon coating layer. The carbon coating can not only dramatically improve the electronic conductivity, but also buffer the large volume expansion/contraction of Fe₃O₄ during lithiation/delithiation. The Fe₃O₄@C composites show a reversible capacity of 1116.1 mAh g⁻¹ at 0.1 A g⁻¹ and 587.2 mAh g⁻¹ at 2 A g⁻¹, as well as stable capacity retention over cycling. Furthermore, the hybrid device based on Fe₃O₄@C composites achieves a specific energy of 110.1 Wh kg⁻¹ at a specific power of 250 W kg⁻¹, demonstrating promising application of the reported hybrid systems.

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1. Introduction

With the increasing demand for portable electronics (PEs) and hybrid electric vehicles (HEVs) as well as grid storage stations, it is critically important to develop advanced energy storage devices with high energy and power densities, enhanced energy efficiencies, and extended life spans [1–3]. Currently, the most widely studied energy storage devices are lithium-ion batteries (LIBs) and supercapacitors (SCs), which show complementary energy-storage features due to their different charge storage mechanisms [3–5]. For instance, LIBs are able to deliver a high specific energy of 120–200 Wh kg⁻¹ due to the Faradaic reactions associated with electrode materials (e.g., LiCoO₂) [6,7]. However, the sluggish Li ion diffusion in the bulk electrode materials greatly limits the specific power (<1000 W kg⁻¹) and the structural degradation caused by dramatic volume variations during lithiation/delithiation leads to limited cycling life (<1000 cycles) of LIBs [8,9]. In contrast, electrical double-layer capacitors (EDLCs) comprising porous carbon as both electrodes can provide a high specific power (>10,000 W kg⁻¹) and superior cycle life (>100,000 cycles) due to extremely rapid adsorption/desorption processes of electrolyte ions (within seconds) on the surface of porous carbonaceous materials [10,11]. Unfortunately, the limited charge accumulation leads to an insufficient specific energy (<10 Wh kg⁻¹) of EDLCs [12]. In this regard, a capacitor-battery hybrid system called lithium ion capacitor (LIC), has been proposed and demonstrated to combine the merits of both LIBs and EDLCs.
which may satisfy high specific energy and power requirements simultaneously [13,14].

Generally, a LIC composes of an EDLC-type cathode, a LIB-type anode and a Li ion conducting organic electrolyte [15,16]. It stores charge by non-Faradaic adsorption/desorption of electrolyte anions on the capacitor-type cathode and Faradaic lithium ion intercalation/deintercalation from the battery-type anode [17,18]. This combination is expected to offer a high specific energy without sacrificing the specific power due to the large specific capacity of the anode, the fast adsorbing/desorbing rate of the cathode, and the wide working potential window of the organic electrolyte [19,20].

Since two charge-storage mechanisms coexist in one system, one key challenge in developing high performance LIC is to improve the Faradaic reaction kinetic of the anode so that it can match the fast non-Faradaic charging rate of the cathode [21,22].

Among various strategies, one effective approach is to develop novel anode materials with simultaneously large specific capacities, superior rate capabilities, and ultra-stable cycling performances [23,24]. Nanostructured Li4Ti5O12 (LTO) was firstly studied as the anode of LIC due to its excellent rate and cycling performance. By using activated carbon as cathode, the LTO-based LIC delivers a specific energy of 20 Wh kg−1, which is nearly three times that of a conventional EDLC device [25]. However, the limited specific capacity of LTO (175 mA h g−1) along with the high voltage plateau (around 1.5 V vs. Li/Li+) limits to the limited capacity and greatly reduced voltage output of the hybrid device [26,27]. Therefore, a variety of battery-type electrode materials have been explored as anodes of LICs including graphite [28], TiO2 [29], TiC [12], TiNb2O7 [30], Fe2O3 [19], MoS2 [16], VN [31], MnO [32], Si [33], Sn [21], HZTS1013 [34], LiMnBO3 [35], etc. Although the energy densities of most devices are improved significantly at low current densities, the sluggish reaction kinetics of the anode continue to restrict the power performance and cycle stability of LIC. To date, there is still much room for the exploration of novel anode materials with greatly enhanced reaction kinetics, large theoretical capacities, and suitable redox potentials.

Ferriferous oxide (Fe3O4) has long shown great promise as an anode material for LIBs due to its large theoretical specific capacity (924 mAh g−1), relatively low voltage plateau (around 0.8 V), natural abundance, low cost, and environmental benignity [36,37], which render it an appealing anode for LIC with dramatically reduced volume expansion/contraction (~93%) occurred during lithium intercalation/deintercalation, resulting in rapid capacity fading [38,39]. To circumvent these disadvantages, a range of strategies have been explored, such as hybridization with carbonaceous materials [40–43] or morphology control of Fe3O4 [40,44,45]. In particular, surface carbon coating stands out as one of the most simple and efficient approach to achieve high capacity by serving as a conductive network to ensure efficient electron transport and a flexible matrix to buffer the volume expansion/contraction of Fe3O4 during cycling [46,47]. Unfortunately, the control over the thickness, uniformity, continuity and surface chemistry of the carbon layer remains challenging, in which novel carbon precursor plays a critical role.

Herein, we demonstrate the use of 3D interconnected Fe3O4@C core@shell nanocomposites as an anode material for LIC to concurrently achieve high specific energy and high output voltage. Chitosan, an abundant and renewable biomass that contains rich amino and hydroxyl groups, was introduced as a novel carbon coating precursor to prepare Fe3O4@C core@shell nanostructures. A conformal and continuous chitosan coating layer can be spontaneously formed on Fe3O4 particles due to the strong coordination between hydroxyl and amino groups of chitosan and Fe3+ ions, which then converted into N-doped carbon under calcination. The as-prepared Fe3O4@C nanocomposites show dramatically enhanced lithium storage reaction kinetic with high specific capacity and outstanding rate capability. Furthermore, the as-constructed LIC based on the Fe3O4@C anode exhibits extraordinary specific energy and power of 110.1 Wh kg−1 and 250 W kg−1, respectively, together with stable cycling performance, providing a promising solution to solve the kinetic mismatch issue currently plagued in LIC.

2. Results and discussion

2.1. Characterization of 3D interconnected Fe3O4@C anode

The formation process of 3D interconnected Fe3O4@C core@shell structures is illustrated in Fig. 1. Chitosan, a renewable natural resource, is one of the least expensive and most abundant polymers in the biosphere [48]. It is prepared by deacetylation of chitin, which is the structural unit in the exoskeleton of crustaceans such as crabs, crabs and lobsters [49]. There are large amounts of polar groups (hydroxyl and amine) in chitosan, which have strong coordination character with several compounds including metal ions [50,51]. Besides, chitosan has a high percentage of nitrogen (6.89%) and is soluble in weakly acidic solution. These features enable chitosan to act as a promising N-containing precursor for carbonaceous materials with unique nanostructures favorable for energy storage applications [52,53]. In this synthetic process, chitosan was firstly dissolved in 2.5 wt% acetic acid solution to form a white gel-like dispersion. Then the added Fe3+ ions coordinate with functional groups of chitosan to form a uniform chitosan-Fe3+ complex that subsequently goes through a hydrothermal process to form Fe3O4 nanoparticles. The long chains of chitosan biopolymer bridges neighboring Fe3O4 nanoparticles to form 3D interconnected network-like structure. Chitosan itself was then gradually carbonized to form N-containing carbon that was in-situ coated on surface of Fe3O4 nanoparticles under the high temperature and high pressure conditions created by the hydrothermal treatment.

In the following calcination procedure, chitosan-derived carbon will carboxthermally reduce Fe3O4 into Fe3O4. Meanwhile it also functions as a barrier to dramatically reduce the grain sizes of Fe3O4 nanoparticles (around 30–60 nm) during the high temperature calcination process (Fig. 2a). The as-prepared Fe3O4 nanoparticles are spherical in shape and well connected with each other, forming a large number of voids, which are favorable for the contact with electrolyte (Fig. 2c). Higher magnification transmission electron microscope (TEM) image displays the presence of a uniform carbon coating layer with a thickness of around 2 nm over the surface of Fe3O4 nanoparticles (Fig. 2e). The lattice fringes are clearly visible, indicating that the as-prepared Fe3O4 particles are highly crystalline. The lattice spacing between two fringes is 0.37 nm, which is in good agreement with the distance of (111) planes of Fe3O4. In contrast, the control sample prepared without using chitosan are irregular Fe3O4 nanoparticles with sizes around 200–500 nm and exhibits a (012) lattice spacing of 0.37 nm (Fig. 2b, d and f).

When the as-prepared Fe3O4@C is used as an anode material for LIB and LIC, the small size of Fe3O4 greatly shortens the diffusion distance of Li ions while the surface carbon coating layer not only provides sufficient electronic conductivity between Fe3O4 nanoparticles but also functions as a flexible matrix to buffer the significant volume expansion/contraction of Fe3O4 nanoparticles during lithiation/delithiation. More importantly, the Fe3O4 nanoparticles are well connected with each other, forming a unique interconnected 3D framework, which not only favors the diffusion of Li+ ions, but also leaves enough space for the volume variation of
Fe$_3$O$_4$ nanoparticles during cycling, thus contributing to dramatically enhanced lithium storage reaction kinetics of Fe$_3$O$_4$.

The crystallographic structures of as-prepared products with and without chitosan were characterized by X-ray diffraction (XRD) (Fig. 2g). It can be found that the as-prepared products without using chitosan are well indexed to rhombohedral hematite ($\alpha$-Fe$_2$O$_3$). Joint Committee on Powder Diffraction Standards (JCPDS) card 33-0664) while the products obtained using chitosan is indexed to spinel magnetite (Fe$_3$O$_4$. JCPDS card 65-3107), both have good crystallinity. This result indicates the importance of chitosan derived carbon which carbothermally reduces Fe$_2$O$_3$ into Fe$_3$O$_4$ during the high temperature calcination. To verify the amount of carbon in the Fe$_3$O$_4$@C composite, thermogravimetric analysis (TGA) was conducted in an oxygen atmosphere from room temperature to 800 °C (Fig. 2h). The weight increase before 300 °C is caused by the oxidation of Fe$_3$O$_4$ into Fe$_2$O$_3$ and the weight decrease between 300 °C and 500 °C is ascribed to the oxidation of carbon. Therefore, the carbon content is found to be around 15 wt% as determined by the weight loss between 300 °C and 500 °C.

The Raman spectrum of the Fe$_3$O$_4$@C composites was examined to characterize the properties of the surface carbon (Figure S1). It presents two characteristic bands at around 1335 cm$^{-1}$ (D band, corresponding to graphite in-plane vibrations with $E_{2g}$ symmetry), which confirm the presence of a carbon layer over the particles [26]. The $I_D/I_G$ ratio can be used to evaluate the degree of disorder for pyrolytic carbon. The $I_D/I_G$ ratio of the Fe$_3$O$_4$@C composite is 3.7, implying that the carbon is mainly in amorphous state [54]. X-ray photoelectron spectroscopy (XPS) was used to investigate the surface and bulk chemical compositions of the Fe$_3$O$_4$@C composite. As expected, the XPS spectrum of Fe$_3$O$_4$@C reveals the presence of Fe, O, and C elements in the composites (Figure S2a). A small peak at around 401.0 eV appears, which can be assigned to the N1s peak. The N content is 3 atomic % as determined by XPS, indicating the existence of a high level of nitrogen in the Fe$_3$O$_4$@C sample. High resolution N1s XPS spectrum exhibits that the N1s band mainly consists of three peaks, corresponding to different chemical configurations of nitrogen (Figure S2b). The peaks at 398.6, 400.7, and 401.9 eV can be assigned to pyridinic (N1), pyrrolic (N2), and graphitic (N3) nitrogen atoms, respectively, suggesting three different types of nitrogen doping in the carbon layer [27]. The doped nitrogen atoms may break the symmetrical arrangement of C–C hexagonal rings and introduce defects into the carbon layer. These defects will be beneficial for fast Li ions transportation through the carbon layer. Therefore, chitosan, which has rich amino groups, is an appealing precursor for nitrogen-doped carbon coating layer.

The Li ion storage properties of Fe$_2$O$_3$ and Fe$_3$O$_4$@C was systematically investigated in a half-cell configuration by using lithium foil as both the counter and reference electrode before constructing the LIC. Cyclic voltammetry (CV) measurements were firstly conducted to examine the redox processes occurring in the as-prepared Fe$_3$O$_4$@C electrode. As shown in Fig. 3a, a very strong reduction peak at about 0.5 V vs. Li/Li$^+$ is observed in the first cathodic scan, corresponding to the reduction of Fe$^{3+}$ to Fe$^{2+}$ and the irreversible decomposition reaction of electrolyte due to SEI formation [37]. A well-defined anodic peak at around 1.7 V vs. Li/Li$^+$ is observed in the first anodic scan, which corresponds to the reversible oxidation of Fe$^{0}$ to Fe$^{2+}$/Fe$^{3+}$ [37]. In the subsequent cycles, the CV curves overlap with each other, suggesting that the redox reactions of lithium insertion/extraction in Fe$_3$O$_4$@C composite are highly reversible. The distinct peaks appear at 0.92 V vs. Li/Li$^+$ during cathodic scan and at around 1.77 V vs. Li/Li$^+$ during anodic scan can be ascribed to the electrochemical reduction and oxidation (Fe$_3$O$_4$$\rightarrow$$\rightarrow$Fe) reactions, respectively, which have been well elaborated in previous studies [36].

The galvanostatic charge-discharge voltage profiles of Fe$_3$O$_4$@C anode in half-Li cell at multiple cycles are then compared. As shown in Figure S3, the initial discharge profile of Fe$_3$O$_4$@C anode shows an extended voltage plateau at around 0.72 V, which corresponds to the reduction of Fe$_3$O$_4$ to Fe and is similar to literature results of Fe$_3$O$_4$ anode [36,47]. From the second cycle onward, the charge/discharge profiles of Fe$_3$O$_4$@C overlapped with each other with...
unchanged specific capacities, suggesting the stable and superior reversibility of the Fe$_3$O$_4$@C sample under extended cycles. Fig. 3b and c illustrates the stabilized charge/discharge curves of Fe$_3$O$_4$ and Fe$_3$O$_4$@C at various current densities (i.e., the second charge/discharge curve under each current density). The discharge/charge curves of Fe$_3$O$_4$@C present a discharge voltage plateau at about 0.8 V vs. Li/Li$^+$ and a sloped charging voltage profile above 1.5 V vs. Li/Li$^+$ under 0.1 A g$^{-1}$, which are characteristic voltage profiles for the Fe$_3$O$_4$ electrode. It can be found that the bare Fe$_3$O$_4$ sample can only deliver specific discharge capacities of 660.8, 390.4, 266.1, 198.0, and 135.0 mA h g$^{-1}$ at 0.1, 0.2, 0.5, 1 and 2 A g$^{-1}$, respectively (Fig. 3b). In contrast, the Fe$_3$O$_4$@C composite exhibits remarkably higher capacities of 1116.1, 1054.1, 906.7, 762.4 and 587.2 mA h g$^{-1}$ at all current densities than those of the bare Fe$_3$O$_4$ electrode (Fig. 3c), respectively. Notably, even at a high current density of 5 A g$^{-1}$, the Fe$_3$O$_4$@C sample still keeps a high capacity of 323.1 mA h g$^{-1}$. Moreover, the charge/discharge capacities are extremely stable at all current densities with a high Coulombic efficiency of nearly 100% (except when current densities are changed) (Fig. 3d). Besides, when the current density is reduced back to 0.1 A g$^{-1}$ after various high rate cycles, the capacity of the Fe$_3$O$_4$@C electrode could be fully recovered, demonstrating a superior rate capability and a strong capacity recovery ability (Fig. 3d). This result is attributed to the surface carbon coating layer over
Fe₃O₄ nanoparticles, which not only facilitates fast electron transport between nanoparticles, but also serves as a flexible matrix to well buffer the volume variations of Fe₃O₄ during lithiation/delithiation reactions.

The outstanding Li storage performance of the Fe₃O₄@C composite is further verified by the stable cycling performance tests (Fig. 3e). After activation at small current densities (2 cycles at 0.1 A g⁻¹ followed by 2 cycles at 0.2 A g⁻¹), the Fe₃O₄@C composites were cycled at 0.5 A g⁻¹ with a starting discharge capacity of 913.7 mA h g⁻¹, corresponding to a high capacity retention of 91.2%. In addition, the Coulombic efficiency of the Fe₃O₄@C composites electrode is nearly 100% during the whole cycling measurements except for the first few cycles (right axis in Fig. 3e). As a comparison, the Fe₂O₃ electrode shows a poor cycling performance (Fig. S5), where the specific capacity quickly fades from 259.3 to 133.1 mA h g⁻¹ after 200 cycles at 0.5 A g⁻¹. The large Li-ion storage capacity, excellent rate capability, extremely stable cycling behavior as well as a suitable voltage range of Fe₃O₄@C make it an appealing candidate of anode for LIC.

2.2. Characterization of the activated carbon (AC) cathode

Before constructing the LIC, the electrochemical performances of AC cathode were systematically evaluated in a Li half-cell system with Li foil as both the counter and reference electrode over a potential range of 2.0–4.5 V vs. Li/Li⁺. The selected AC shows an irregular bulk-like morphology with a porous structure (Figure S5). Moreover, the AC has a large specific surface area of 1928.4 m² g⁻¹ and total pore volume of 0.84 cm³ g⁻¹ with well-controlled pore size distribution of 0.4–4 nm (Figure S5). All the CV curves recorded at various scan rates reveal quasi-rectangular shapes with slight humps, suggesting dominating EDLC-type capacitance of AC cathode (Figure S7a) [12]. Galvanostatic charge-discharge profiles
exhibit a linear variation of voltage with respect to capacity, demonstrating the capacitive adsorption/desorption behavior of electrolyte anions on the surface of AC (Figure S7b) [20]. The AC electrode shows a stable discharge capacity of 98.8 mA h g$^{-1}$ at 0.1 A g$^{-1}$ (Figure S7b, c), which is much higher than those reported [12,55,56]. At high current densities of 5 and 8 A g$^{-1}$, the AC cathode still provides a high capacity of 40.5 and 31.9 mA h g$^{-1}$, respectively. Moreover, the discharge and charge capacity are extremely stable during repeated cycles with high Coulombic efficiency (Figure S7c, d). A high capacity retention rate of 81.8% is achieved for 1000 cycles at 1 A g$^{-1}$. The extraordinary capacitive performance of AC is promising for applications in LIC.

2.3. LIC performance based on Fe$_3$O$_4$@C anode and AC cathode

The LIC, denoted Fe$_3$O$_4$@C/AC, is constructed by utilizing the as-prepared Fe$_3$O$_4$@C composite as anode and AC as cathode with a 1 M lithium hexafluorophosphate (LiPF$_6$) in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 vol. vol) electrolyte solution. Before fabricating the hybrid device, the Fe$_3$O$_4$@C anode was pre-activated for 10 cycles at 0.2 A g$^{-1}$ in a Li half-cell and then lithiated at 1.0 V vs. Li/Li$^+$ to achieve high efficiency. A proper mass balance between AC and Fe$_3$O$_4$@C is important to achieve charge balance between the cathode and anode and attain high efficiency of the LIC. The mass ratio of the AC cathode to Fe$_3$O$_4$@C anode was optimized to be 3:1 (Figure S8a). The voltage window of 0–4.0 V vs. Li/Li$^+$ was chosen to achieve high energy density (Figure S8b-d). During the charge process, Li$^+$ ions from the electrolyte are intercalated into the Fe$_3$O$_4$@C nanoparticles. Meanwhile, to maintain the charge neutrality in the electrolyte, the PF$_6^-$ anions are absorbed on the surface of highly porous AC cathode and form an electric double layer (Fig. 4a). Reverse reactions occur during the discharge process.

The CV profiles of the Fe$_3$O$_4$@C/AC LIC at various scan rates are shown in Fig. 4b. Different from the symmetric supercapacitor comprising AC as both cathode and anode (i.e., AC/AC, Figure S9a), the CV profiles of Fe$_3$O$_4$@C/AC LIC show a deviation from the ideal rectangular shape due to the synergistic effect of two charge storage mechanisms (i.e., Faradaic lithiation/delithiation on the anode and non-Faradaic surface adsorption/desorption on the cathode). As the scan rate increases, the nearly symmetric shape of the CV curves could be well-retained, suggesting that the intercalation/deintercalation of Li$^+$ cations and adsorption/desorption of PF$_6^-$ anions are highly reversible.

The electrochemical properties of the constructed LIC were further investigated by galvanostatic charge/discharge tests at different current densities ranging from 0.5 to 5 A g$^{-1}$ (based on the mass of Fe$_3$O$_4$@C anode). Three electrode cell was fabricated with AC as cathode, Fe$_3$O$_4$@C as anode and Li metal as the reference electrode. The relative potentials of the LIC, Fe$_3$O$_4$@C anode and AC cathode were measured simultaneously. As shown in Fig. S10, the sloping curve of AC cathode indicates the absorption and desorption of PF$_6^-$ anions over the surface of the AC cathode. The potential profile of Fe$_3$O$_4$@C anode corresponds to the intercalation and deintercalation of Li$^+$ ions into Fe$_3$O$_4$. There is no obvious charge/discharge plateau of the Fe$_3$O$_4$@C anode, which may due to the relatively short charge/discharge time. Furthermore, the potential profile of the LIC resembles that of the AC cathode, which signify that the behavior of this hybrid device is much more similar to EDLCs than to batteries. Fig. 4c displays the charge/discharge curves of the LIC measured using two electrode coin cell. As expected, these charge/discharge curves are very similar to the sloping curves of an ideal EDLC supercapacitor (Figure S9b).

The specific capacities (calculated based on the total mass of cathodic and anodic active material) of the as-constructed LIC at different current densities are shown in Fig. 4d. The LIC delivers an extraordinary initial discharge capacity of 60.1 mA h g$^{-1}$ within only 29 min at a current density of 0.5 A g$^{-1}$. With the increase of cycle numbers and current densities, the charge and discharge capacities of the Fe$_3$O$_4$@C/AC LIC gradually become stabilized and the Coulombic efficiencies gradually increases to around 96% (Fig. 4d). Stable and high discharge capacities of 39.6, 30.1, and 19.5 mA h g$^{-1}$ can be attained at current densities of 1, 2, and 5 A g$^{-1}$, respectively. When the current densities were reduced back to 2, 1 and 0.5 A g$^{-1}$, the original specific capacities could be well-retained, demonstrating excellent rate capability of the LIC (Fig. 4d). It is noted that the LIC shows a relatively low coulombic efficiency at current densities of 0.5 A g$^{-1}$. This is because in this hybrid device, the EDLC-type cathode stores charge via physical absorption/desorption of PF$_6^-$ anions at the electrode/electrolyte interface, while LIB-type anode stores energy by the faradaic lithium ion intercalation/ delithiation process. The kinetic mismatch of these two charge storage mechanisms may cause the low initial coulombic efficiency at relatively small current density. In addition, the as-constructed Fe$_3$O$_4$@C/AC LIC device may need an activation process to guarantee that the electrolyte thoroughly infiltrates the electrode surface. Subsequently, the cycling performance of the LIC was also characterized. The as-constructed LIC shows an exceptional capacity retention rate of 95.7% over 1000 cycles at a current density of 1 A g$^{-1}$ with a high Coulombic efficiency of over 90% (Fig. 4e).

In order to further evaluate the practical applicability of the Fe$_3$O$_4$@C/AC LIC system, Ragone plot (energy density vs. power density based on the total mass of both electrode materials) is constructed from the galvanostatic discharge curves (Fig. 5a). As expected, the Fe$_3$O$_4$@C/AC system delivers an impressive energy density of 110.1 Wh kg$^{-1}$ at a power density of 250 W kg$^{-1}$, which is much higher than the symmetric AC/AC supercapacitor (28.7 Wh kg$^{-1}$) and is comparable with other hybrid systems listed in Table 1. Even at high power densities of 1000 and 2500 W kg$^{-1}$, the Fe$_3$O$_4$@C/AC system can still deliver high energy densities of 60.0 and 36.8 Wh kg$^{-1}$, respectively.

A digital clock and a blue light-emitting diode (LED) were used to further test the performance of our hybrid device in practical applications. After fast charging, a single 4 V hybrid device can easily power the digital clock for over 5 h without failure (Fig. 5b, Supplementary Video 1). Moreover, the same cell is able to drive a blue LED for over 5 min (Fig. 5c, Supplementary Video 2), suggesting the high-output voltage and high energy density of our hybrid device.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.carbon.2018.09.010.

To reveal the mechanism behind this excellent performance, the electrochemical impedance spectra (EIS) of the Fe$_3$O$_4$@C/AC LIC hybrid cell before and after 1000 cycles were measured and compared (Fig. 5d). The EIS profiles comprise a semicircle in the high frequency range and a slope line in the low frequency range [54]. The intersection of the EIS profile with the real axis refers to the solution resistance (R$_s$), which mainly reflects the resistance of electrode and electrolyte. The depressed semicircle at the high frequency region is attributed to the charge transfer resistance (R$_ct$), while the straight line at low frequency range corresponds to the Warburg impedance ($Z_w$), which is related to the lithium ion diffusion in the active anode material [26,35]. The EIS curves were fitted using equivalent circuit model in Figure S11 to quantify the resistance values and the fitting results are listed in Table S1. After cycling, the charge transfer resistance ($R_{ct}$) shows obvious decrease (decrease from 235.6 to 64.30) due to the gradual activation of electrode materials during cycling [57]. The solution resistance ($R_s$) slightly changed from 1.6 Ω to 1.7 Ω and slope of the EIS in the low
Fig. 4. (a) Schematic illustration of the structure of Fe₃O₄@C/AC LIC. (b) CV profiles of the Fe₃O₄@C/AC LIC at different scan rates between a voltage window of 0–4.0 V vs. Li/Li⁺. (c) Galvanostatic charge/discharge curves and (d) rate capability of the Fe₃O₄@C/AC LIC at different current densities. (e) Cycling performance of the Fe₃O₄@C/AC LIC at a current density of 1 A g⁻¹. Right column is the corresponding Coulombic efficiency. (A colour version of this figure can be viewed online.)
frequency remain almost the same after cycling, demonstrating efficient electron transportation and fast lithium ion diffusion in the hybrid system. This result clearly verifies the outstanding synergistic effect between the battery type-anode and capacitor-type cathode, which translates into superior electrochemical performance of the hybrid device.

3. Conclusions

In summary, we have successfully constructed a battery-capacitor hybrid system (i.e., LIC) using interconnected Fe3O4@C core@shell composite as the anode and high specific surface area AC as the cathode, which bridges the gap between lithium ion batteries and EDLC-type supercapacitors. The interconnected Fe3O4@C composites with greatly reduced particle sizes and an in-situ formed surface carbon coating layer were prepared by utilizing the correlation of Fe3+ ions with chitosan biomass to achieve high lithium ion storage capacity and excellent rate capability. This assembled hybrid system (Fe3O4@C//AC) delivers an energy density of 110.1 Wh kg⁻¹ at a power density of 250 W kg⁻¹, along with extraordinary cyclic stability (95.7% capacitance retention after 1000 cycles at 1 A g⁻¹) over a wide voltage window of 0–4.0 V vs. Li/Li⁺, which are among the highest values reported for this hybrid systems so far. These results offer an insight into developing high-performance LIC through tailoring the nanostructures of electrode materials. With further research and optimization, this hybrid device could become a promising energy storage device for a myriad of applications.

Table 1
Comparisons of energy density, power density, and cycle stability of various LIC systems Note: G: graphene; PHPNC: pyridine-derived hierarchical porous nitrogen-doped carbon; CFs: carbon fibers; PJ-AC: Prosopis juliflora-derived activated carbon; PGM: porous graphene macroform; 3D MnO@GNS: 3D MnO-graphene composite; HNC: hierarchical porous N-doped carbon; NB: nanobelt; ACHH: human hair-derived activated carbon.

<table>
<thead>
<tr>
<th>System (anode//cathode)</th>
<th>Energy density (Wh kg⁻¹)</th>
<th>Power density (W kg⁻¹)</th>
<th>Capacity retention (%)/cycle number/current density (A g⁻¹)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Fe3O4@C//AC (This work)</td>
<td>110.1</td>
<td>250</td>
<td>95.7/1000/1.0</td>
<td></td>
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<tr>
<td>TiC//PHPNC</td>
<td>101.5</td>
<td>450.0</td>
<td>82.0/5000/2.0</td>
<td>12</td>
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<tr>
<td>Fe3O4@C//3D graphene</td>
<td>204.0</td>
<td>55.0</td>
<td>70.0/1000/2.0</td>
<td>19</td>
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<tr>
<td>TiNbO4@C//CFs</td>
<td>110.4</td>
<td>99.6</td>
<td>77.0/1500/0.2</td>
<td>30</td>
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<tr>
<td>Pr-lithiated graphite//PJ-AC</td>
<td>162.3</td>
<td>150.0</td>
<td>79.0/7000/0.5</td>
<td>57</td>
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<tr>
<td>Li4Ti3O12//PGM</td>
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<td>650.0</td>
<td>65.0/1000/10.0</td>
<td>58</td>
</tr>
<tr>
<td>3D MnO@GNS//HNC</td>
<td>127.0</td>
<td>125.0</td>
<td>76.0/3000/5.0</td>
<td>59</td>
</tr>
<tr>
<td>TiO2@NB/G</td>
<td>82.0</td>
<td>570.0</td>
<td>73.0/600/1.0</td>
<td>60</td>
</tr>
<tr>
<td>Li4V2O7//AC</td>
<td>49.1</td>
<td>72.5</td>
<td>88.0/1000/0.2</td>
<td>61</td>
</tr>
<tr>
<td>Li4Ti3O12//ACHH</td>
<td>22.5</td>
<td>100.0</td>
<td>80.0/1000/0.1</td>
<td>62</td>
</tr>
<tr>
<td>Li3V2(PO4)3//AC</td>
<td>27.0</td>
<td>255.0</td>
<td>/</td>
<td>63</td>
</tr>
</tbody>
</table>
Acknowledgements

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Appendix A. Supplementary data

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References


