NaCl-templated synthesis of hierarchical porous carbon with extremely large specific surface area and improved graphitization degree for high energy density lithium ion capacitors†

Ruiying Shi,ac Cuiping Han,ab Hongfei Li, Lei Xu,ac Tengfei Zhang, Junqin Li, Zhiqun Lin,de Ching-Ping Wong,fe Feiyu Kangac and Baohua Liac

Li ion capacitors (LICs) are emerging as a promising device to integrate the high power density of supercapacitors with the high energy density of Li ion batteries. However, the insufficient specific capacity of the conventional capacitive electrode presents a great challenge in achieving high energy density for LICs. Herein, we demonstrate the synthesis of hierarchical porous carbon with an extremely large specific surface area of 3898 m² g⁻¹ and an improved graphitization degree by using egg white biomass as a precursor and NaCl as a template, in which dual functional NaCl served both as a macropore creating template and a graphitic catalyst to enhance the graphitization degree. With rational design, the developed porous carbon exhibits a noticeably enhanced specific capacity of 118.8 mA h g⁻¹ at 0.1 A g⁻¹ with excellent rate capability and improved cycling stability over 4000 cycles in an organic Li ion conducting electrolyte. Furthermore, the obtained porous carbon was employed as a cathode paired with a Fe₃O₄@C anode for LIC applications, which delivers an integrated high energy density of 124.7 W h kg⁻¹ and a power density of 16 984 W kg⁻¹ as well as a superior capacity retention of 88.3% after 2000 cycles at 5 A g⁻¹, demonstrating the promising application as potential electrode candidates for efficient energy storage systems.

1. Introduction

The fast growth of advanced portable electronics and electric vehicles necessitates the development of high-efficiency energy storage devices. Among them, Li ion batteries (LIBs) and supercapacitors (SCs) are currently two of the most promising systems due to their wide success in the past few decades. Their complementary energy storage feature and similar cell configuration have stimulated the development of a hybrid device to inherit their individual advantages. As such, lithium ion capacitors (LICs) are proposed and constructed with a LIB-type anode and a SC-type cathode in conjunction with an organic Li-ion-conducting electrolyte. In the hybrid device, the SC-type cathode provides high power density via physical absorption/desorption of PF₆⁻ anions at the electrode/electrolyte interface, while the LIB-type anode guarantees high energy density by the faradaic lithium ion intercalation/delithiation process. To date, a series of LICs have been proposed with different battery type anodes and porous carbon cathodes. The battery type anodes are currently selected from anode candidates for LIBs which generally demonstrate much higher specific capacities, such as graphite (372 mA h g⁻¹), Sn (990 mA h g⁻¹), Fe₂O₄ (924 mA h g⁻¹), Si (4200 mA h g⁻¹), MnO (742 mA h g⁻¹), etc. In the case of cathodes, commercial activated carbon (AC) is the mostly employed cathode material, which, however, shows relatively low specific capacity (usually <50 mA h g⁻¹) because the tortuous, dead-end or blind micropores of AC are unable to efficiently store solvated ions. Thus, the insufficient cathode capacity will compromise the high specific capacity of LIB-type anodes and trade-off the energy density of LICs. Therefore, the development of high-energy LICs requires further exploration of novel cathodes with enhanced specific capacities.

Recently, biomass derived porous carbons (BDPCs) have shown great promise as alternative substitutes for traditional...
important for minimizing the ionic diffusion distance and as well as provide extra pseudocapacitance from faradic reactions, consequently improving the capacitive performance. Egg white (EW) is a highly nutritious food in our daily diet which is rich in protein. It is also well known for its gelling, foaming and emulsifying characteristics. Most recently, EW has been attempted as a precursor towards N-doped activated carbons with exceptional capacitive performances. Unfortunately, these EW-derived activated carbons are generally free from macropores and mesopores, which are however critically important for minimizing the ionic diffusion distance and promoting the formation of an electrical double layer. Moreover, the graphitization degree of most of the BDCMs is relatively low due to the presence of large amounts of defects, which lead to limited electrical conductivity. Therefore, a proper regulation of the microstructure in EW-derived activated carbon, including pore size distribution, specific surface area (SSA), graphitization degree, etc., is crucial to ensure good performance of the assembled LICs with both high specific capacity and better power density.

Herein, we demonstrate the preparation of EW-derived activated carbon (a-EW-NaCl) with an exceptionally high SSA of 3898 m² g⁻¹, combined micro-, meso-, and micro-porosities as well as improved graphitization degree by employing NaCl as a template combined with KOH activation. Dual functional NaCl served both as a macropore creating template and a graphitic catalyst to enhance the graphitization degree. Inorganic impurities such as the ramiﬁcation of Ca, K, Zn, and Fe substances that initially exist in the EW protein serve as the scaffold for mesopores. Moreover, N atoms and O atoms in the peptide bond of EW proteins can be in situ doped into the final a-EW-NaCl, which is widely reported to enhance the overall performance of the materials. Owing to the synergistic effect of extremely high SSA, hierarchical porous structure, enhanced graphitization degree and N heteroatom doping, a-EW-NaCl achieves a high speciﬁc capacity of 118.8 mA h g⁻¹ at 0.1 A g⁻¹ with excellent rate capability and improved cycling stability in a half cell with Li. Furthermore, the obtained EW-NaCl was employed as a cathode paired with a Fe₃O₄@C anode for LIC applications, which demonstrates a superior energy density of 124.7 W h kg⁻¹ (based on both cathode and anode active materials) at a high power density of 2547 W kg⁻¹ and outstanding cycling life.

2. Experimental section

2.1 Synthesis of the a-EW-NaCl cathode

EW (40 mL) was firstly diluted with 10 mL of deionized water to obtain a uniform protein solution. Then, 1.0 g of sodium chloride (NaCl, 99%, Aladdin) was added to the above solution and was stirred for 2 h to obtain a transparent solution. The mixed solution was heated at 110 °C for another 1.5 h to form a jelly-like protein gel, which was then freeze-dried to obtain a protein xerogel. Subsequently, the xerogel was pyrolyzed in a tubular furnace at 700 °C for 2 h under an Ar atmosphere with a ramp rate of 5 °C min⁻¹ to acquire the carbonized protein (c-EW-NaCl). After carbonization, the as-prepared c-EW-NaCl was washed with 30 mL of 1 M HCl at 40 °C for 24 h followed by deionized water to remove the NaCl template and some other impurities to obtain the washed carbon powder (w-EW-NaCl). Finally, the w-EW-NaCl, mixed with KOH in a mass ratio of 1 : 3, was further activated at 700 °C for 1 h under an Ar atmosphere and thoroughly washed with deionized water until pH = 7 was reached to obtain the activated carbon powder (a-EW-NaCl). For comparison, pure EW derived carbon was prepared without a NaCl template following the same carbonization (c-EW), HCl washing (w-EW) and activation (a-EW) procedure and served as the control sample. Commercial AC was also purchased from XFNANO Corp. China for comparison.

2.2 Synthesis of the Fe₃O₄@C anode

In detail, 0.6 g of iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, Macklin, 99.99% purity) and 0.3 g of gelatin (Macklin, 99% purity) were dissolved in 30 mL of deionized water with magnetic stirring at ambient temperature until the gelatin was fully dissolved. Then, the mixed solution was transferred into a 50 mL Teflon-lined autoclave and heated at 180 °C for 12 h. The autoclave was cooled to obtain the precursor precipitate, which was filtered and washed with deionized water and then dried at 80 °C for 12 h. Finally, the dried precipitate was annealed at 600 °C for 2 h under an Ar atmosphere with a ramp rate of 5 °C min⁻¹ to acquire Fe₃O₄@C particles.

2.3 Materials characterization

A field emission scanning electron microscope (FE-SEM, HITACH S4800) and a high resolution transmission electron microscopy (HRTEM, TECNAIG2 F30) were employed for the morphological characterization. X-Ray Diffraction (XRD, Bruker D8 Advance) was used to analyse the structure of the as-prepared samples with Cu Kα radiation. The Raman spectra were collected with a 532 nm laser on HORIBA LabRAM HR800. X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II) with Al Kα radiation was used to study the surface chemistry and elemental composition. The porous texture of carbon materials was characterized using nitrogen adsorption/desorption isotherms on ASAP2020M+C at 77 K and the SSA was calculated by the Brunauer–Emmett–Teller method (BET). The Horváth–Kawazoe (HK) method was used to calculate the micropore size distribution and the Barrett–Joyner–Halenda (BJH) method was developed for mesopore size distribution.

2.4 Electrochemical characterization

All electrochemical measurements were carried out in a two-electrode system using a CR2032-type coin cell. For half cell testing, a-EW-NaCl, a-EW, commercial AC and Fe₃O₄@C electrodes were used as working electrodes and pieces of pure lithium foil served as both counter and reference electrodes. The working electrodes were prepared by mixing 60 wt% of...
active material (i.e., a-EW-NaCl, a-EW, commercial AC or Fe₃O₄@C), 20 wt% of Super-P, and 20 wt% of sodium alginate in deionized water to form a homogeneous slurry. Then a-EW-NaCl and a-EW based slurries were coated on aluminum foil and the Fe₃O₄@C based slurry was coated on copper foil. After vacuum drying at 110 °C for 12 h, the aluminum and copper foils loaded with active materials were punched into disk-shaped electrodes with diameters of 12 mm. The mass loadings of the as-developed a-EW-NaCl cathode and Fe₃O₄@C anode materials are around 3.2 mg cm⁻² and 1.0–2.3 mg cm⁻², respectively. Half cells were then assembled in an Ar-filled glove box (Mbraum). Celgard 2400 served as the separator and 1 M LiPF₆ in a mixture of ethylene carbonate and diethyl carbonate (EC/DEC, 1 : 1 in vol/vol) (Dongguan Shanshan Tech., China) was used as the electrolyte. The voltage range of a-EW-NaCl, a-EW and a commercial AC half cell was 2–4.5 V while the voltage range of the Fe₃O₄@C half cell was 0.005–3 V. Cyclic voltammetry (CV) curves were recorded on a VMP3 (bio-logic) multichannel electrochemical station while the galvanostatic charge/discharge (GCD) curves were recorded using a Land battery testing system.

Before assembling LICs, Fe₃O₄@C based half cells were activated at 100 mA g⁻¹ for 5 cycles within 0.005–3 V and ended with lithiating to 1.0 V to attain high efficiency and offer extra Li⁺ ions. LICs were then assembled with a-EW-NaCl as the cathode and pre-lithiated Fe₃O₄@C as the anode in a mass ratio of 2 : 1 and 3 : 1 (cathode/anode), respectively. The CV curves of the as-constructed LICs were recorded on a VMP3 (bio-logic) multichannel electrochemical station while the GCD curves were recorded using a Land battery testing system.

The specific capacity (C, mA h g⁻¹) of both half cells and full cells was calculated from the GCD curves using the following equations:

\[ C = I \times \frac{t}{m} \]

where, \( I \) is the discharge current and \( t \) is the discharge time. For half cells, \( m \) is the mass loading of active materials on the working electrode. For LICs, \( m \) is the mass loading of a-EW-NaCl.

The energy density (\( E \), W h kg⁻¹) and power density (\( P \), W kg⁻¹) of the LIC were calculated from the GCD curves using the following equations:\n
\[ E = \frac{\int V(t) \, d(t)}{m} \]

\[ P = \frac{E}{t} \]

where \( I \) is the constant current density, \( V(t) \) is the voltage of the device, \( t \) is the corresponding discharge time, and \( m \) is the total mass of the a-EW-NaCl cathode and Fe₃O₄@C anode.

3. Results and discussion

3.1 Morphological and physical characterization of the a-EW-NaCl cathode

The detailed preparation of the a-EW-NaCl cathode is illustrated in Fig. 1. Here, EW is explored as a novel biomass precursor due to its high protein content and good solubility in water. Compared with a plant-based precursor, these EW proteins are naturally rich in nitrogen, containing an average 15% by weight. An organic solvent-based precipitation method is generally used to precipitate the EW protein from the solution, which will cause aggregation. Here, the NaCl salt is introduced as a macropore-creating template and is firstly dissolved in the diluted EW solution followed by heating and freeze drying to

---

**Fig. 1** Schematic diagram for the detailed preparation process of a-EW-NaCl.
form a uniform protein xerogel (Fig. S1†). Then, the subsequent high temperature carbonization and washing process converts the protein xerogel into porous carbon (denoted as w-EW-NaCl), during which the molten salt NaCl not only promotes the graphitization degree of as-derived carbon,27–29 but also functions as a template to produce macropores (>50 nm).30,31 Meanwhile, inorganic impurities such as the ramification of Ca, K, Zn, and Fe substances that initially exist in the EW serve as the scaffold for mesopores. Furthermore, to enlarge the surface area for charge storage, KOH activation was employed to generate rich micropores (<2 nm). Thus, the as-prepared a-EW-NaCl shows a hierarchical porous structure, in which micropores account for maximizing effective surface area for charge storage and mesopores can promote the formation of an electrical double layer and decrease the ion transfer impedance from the electrolyte to micropores while the macropores function as ion-buffering reservoirs to minimize the diffusion distances of electrolyte ions to the interior surfaces.23,24,31 Moreover, it should be noted that N atoms and O atoms in the peptide bond of EW protein can’t be completely removed during the carbonization and activation process, and will in situ dope into the final a-EW-NaCl, which is widely reported to benefit the surface wettability and provide additional pseudocapacitance.22,23 Therefore, through this template approach, we could obtain a hierarchical porous a-EW-NaCl with a large SSA and rich N-heteroatoms, which is expected to have better capacitive performance for LIC applications.

Fig. 2 and S2† show the TEM and SEM images of a-EW-NaCl and a-EW. With the assistance of a NaCl template, a-EW-NaCl displays the fluffy 3D interconnected macroporous architecture with most of its pores having a size of around 150 nm to several micrometers (Fig. 2a). Different from the irregular circular pores originating from the releasing gases during pyrolysis, such macropores of a-EW-NaCl have distinct edges and corners because of the cubic crystal of NaCl salt (Fig. 2b),30 which can benefit the infiltration of the electrolyte into almost the entire active materials and minimize the diffusion distances of electrolyte ions to the electrode.23 In sharp contrast, pure a-EW mainly demonstrates huge bulk lumps with bits of independent macropores (around 50–700 nm) (Fig. S2a and b†), which are generated by the released gases during the pyrolysis process. With careful observation in high magnification TEM, a-EW-NaCl also exhibits mesopores with diameters of several nanometers (Fig. 2c), which may arise from the removal of inorganic impurities such as the ramification of Ca, K, Zn, and Fe substances, etc., as proved by the XRD profile of c-EW (Fig. S2c and d†). Similar mesoporosity has also been observed in the control sample c-EW and other biomass derived amorphous carbons.20,34 Furthermore, clear graphitic layers with an approximate interplanar spacing of 0.34 nm are observed in the HRTEM images of a-EW-NaCl while not in the a-EW sample (Fig. 2d and S3d†), which suggests that the introduced molten salt NaCl facilitates the graphitic degree of the a-EW-NaCl sample.27–29

To gain further insights into the crystalline structure and phase composition of the a-EW-NaCl and a-EW samples, XRD tests have been carried out. As Fig. 3a shows, the XRD profile of c-EW-NaCl displays six sharp peaks located at 27.3°, 31.6°, 45.3°, 56.3°, 65.9° and 75.1°, respectively, corresponding to the (111), (200), (220), (222), (400) and (420) planes of crystal NaCl (PDF 70-2509). After HCl washing, the diffraction peaks of NaCl disappear while two broad peaks at around 23.8° and 43.8° are observed from the XRD patterns of w-EW-NaCl, which are well-indexed to the (002) and (101) reflection peaks of amorphous carbon. The (002) peak of a-EW-NaCl slightly shifts to a lower diffraction angle with decreased intensity due to KOH activation. As for the control sample, it is worth noting that the c-EW also demonstrates sharp diffraction peaks of carbonate species,
which are speculated to be inorganic impurities of EW and are most possibly responsible for the presence of mesoporosity in both a-EW and a-EW-NaCl (Fig. 2c and S2c†).

Raman spectroscopy was carried out to further elucidate the structural features and graphitization degree of the as-prepared sample. Fig. 3b shows the deconvolution results of the Raman spectra of a-EW-NaCl and a-EW, which demonstrates two relatively wide peaks at 1176 and 1493 cm⁻¹, corresponding to the short-range vibrations of sp³-structured carbon atoms.³⁵ Another two main characteristic bands centered at 1330 and 1591 cm⁻¹ are also observed, which are denoted as the D band and the G band and are caused by the sp³ defects and disorders in the graphitic structure and the E₂g in-plane vibration of sp³-bonded graphitic carbon atoms, respectively.¹⁹,³⁶ It’s reported that the intensity ratio of I_D and I_G can be used to analyze the graphitization degree of carbon materials including amorphous carbon.³⁷ The I_D/I_G values of a-EW-NaCl and a-EW are 2.25 and 2.46, respectively, suggesting a higher graphitization degree of a-EW-NaCl than that of a-EW. The enhanced graphitization degree of a-EW-NaCl can be attributed to the promoting effect of graphitization using NaCl molten salt at high heat-treatment temperature,²⁷–²⁹ which coincides well with the HRTEM characterization in Fig. 2d.

XPS analysis was employed to investigate the chemical composition of the a-EW-NaCl. The survey XPS spectrum of a-EW-NaCl shows three obvious peaks assigned to C1s, O1s and N1s (Fig. S4†) whose contents are 91.8 at%, 7.0 at% and 1.2 at%, respectively (Table 1). The detailed C1s spectrum is dominated by carbon atoms in the C–C bond (diamond and graphite types) at 284.8 eV with a small amount of C–N at 286.3 eV, C–O at 287.9 eV and CO–O at 289.9 eV (Fig. 3c).³⁸,³⁹ The detailed O1s spectra can be deconvoluted into oxygen atoms in C–O at
Table 1: Physical properties of a-EW-NaCl and a-EW

<table>
<thead>
<tr>
<th>Sample</th>
<th>S BET (m² g⁻¹)</th>
<th>V total (cm³ g⁻¹)</th>
<th>C%</th>
<th>N%</th>
<th>O%</th>
<th>I D/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-EW-NaCl</td>
<td>3898.0</td>
<td>1.81</td>
<td>91.8</td>
<td>1.2</td>
<td>7.0</td>
<td>2.25</td>
</tr>
<tr>
<td>a-EW</td>
<td>2714.4</td>
<td>1.26</td>
<td>91.4</td>
<td>1.3</td>
<td>7.3</td>
<td>2.46</td>
</tr>
</tbody>
</table>

531.3 eV, C–OH and/or C–O–C at 532.9 eV and COOR at 535.2 eV, which is in line with the XPS patterns of C1s. These types of oxygen-containing surface functional groups are well known to influence the capacity of the engineered carbon due to their high reactivity. Also, the detailed N1s peaks could be deconvoluted into three peaks at 398.5, 400.4 and 402.3 eV, ascribing to pyridinic N, pyrrolic N and graphitic N, respectively (Fig. 3e). It’s widely reported that the pyridinic- and pyrrolic-N atoms can offer electron lone pairs into carbon conjugated systems and consequently induce electron donor effects while the graphitic-N could improve the electron transfer. Therefore, on one hand, a certain amount of electron-donor N dopants along with induced structural defects/voids offer excellent electrical conductivity and transport paths, laying solid foundation for highly efficient electron and ion transfer. On the other hand, introduction of N species endows the electron donor characteristics of carbon layers and provides abundant electrochemically active sites for pseudocapacitive reactions.

The porous structure of a-EW-NaCl and a-EW was further analyzed by N₂-adsorption/desorption isotherms at 77 K (Fig. 3f). The N₂-adsorption isotherms of a-EW-NaCl and a-EW show typical features of I and IV type isotherms with well-defined plateaus between P/P₀ of 0.1–0.9 and an obvious hysteresis loop at P/P₀ > 0.5 (IUPAC classification), suggesting the presence of both micropores and mesopores. The BET specific surface area of a-EW-NaCl is as high as 3898.0 m² g⁻¹ with a total pore volume of 1.81 cm³ g⁻¹, which outperforms the control sample (2714.4 m² g⁻¹ and 1.26 cm³ g⁻¹ for a-EW) and a number of state-of-the-art carbon materials. The corresponding pore-size distribution is calculated from the isotherms based on HK and BJH models. As shown in Fig. 3g, the micropores of a-EW-NaCl and a-EW produced by KOH activation are concentrated below 2 nm based on the HK model. Studies found that micropores between 0.8 and 1.4 nm are fully accessible to PF₆⁻ anions of the electrolyte, suggesting that both a-EW-NaCl and a-EW are suitable for LIC applications. However, compared with a-EW, there is an obvious broad peak at pore diameter values of 2–6 nm in the pore size distribution curve of a-EW-NaCl. These mesopores are beneficial to the specific capacity via promoting the formation of the electrical double layer as well as decreasing the ion transfer impedance from the electrolyte to micropores. Furthermore, the interconnected macropores of a-EW-NaCl could function as ion-buffering reservoirs to minimize the diffusion distances of electrolyte ions to the interior surfaces. Benefiting from the hierarchical porous structure with suitable pore size distribution, large SSA and N-heteroatom doping, a-EW-NaCl is expected to have better capacitive performance in LIC applications.

3.2 Electrochemical characterization of the a-EW-NaCl cathode

The electrochemical performance of a-EW-NaCl and a-EW as the capacitive electrode for LIC was evaluated by half-cell configuration with metallic Li as a counter and a reference electrode using cyclic voltammetry and galvanostatic charge/discharge tests. Fig. 4a shows the CV profiles of a-EW-NaCl under various sweep rates from 5 mV s⁻¹ to 100 mV s⁻¹ in the potential range of 2.0–4.5 V vs. Li⁺/Li, which shows a quasi-rectangular shape at a small scan rate, representing the dominant EDLC contribution to the capacity. When increasing the scan rate, the largely expanded current density indicates its excellent capacitive rate performance and good reversibility due to its optimized hierarchical porous structures and ultra-large SSA. In addition, the CV of a-EW-NaCl displays a very small and broad anodic peak between 3.5 and 4.0 V at relatively large scan rate, which is most probably due to the pseudocapacitive contribution of O- and/or N-containing surface functional groups. This is supported by the XPS analysis results. Compared with a-EW-NaCl, the CV curves of a-EW and commercial AC show much pronounced derivation from the quasi-rectangular shape with sharply reduced area, which is due to the limited specific surface area and the lack of macroporosity (Fig. S5a and S6a†).

Furthermore, GCD measurements of a-EW-NaCl, a-EW and commercial AC were performed under different current densities. As shown in Fig. 4b, the GCD curves of a-EW-NaCl are almost equal to an isosceles triangle and there is no discernible platform at any current density, which is in line with the CV curves. In the case of a-EW and commercial AC, the GCD curves demonstrate greatly reduced charge and discharge time (Fig. S5b and S6b†). The specific capacities of the three samples are calculated from the GCD curves and are compared in Fig. 4c. At a low current density of 0.1 A g⁻¹, a-EW-NaCl and a-EW samples show similar specific capacities of 118.8 mA h g⁻¹ and 110.0 mA h g⁻¹, respectively, while the specific capacity of commercial AC is significantly lower than those of a-EW and a-EW-NaCl (only 80 mA h g⁻¹). When the current density increases to 0.2, 0.5, 0.8, 1, 1.5, 2, 3, 5, 8, and 10 A g⁻¹, the specific capacity of a-EW-NaCl remains at 103.7, 99.1, 89.4, 83.6, 80.5, 75.2, 71.1, 65.0, 56.3, 47.1 and 43.3 mA h g⁻¹, respectively, which are much higher than those of the control sample a-EW and commercial AC, as well as those of previously reported AC, e.g., 113 mA h g⁻¹ of B and N dual-doped carbon nanofibers (BNC) at 0.1 A g⁻¹,¹¹ 109 mA h g⁻¹ of high defect mesoporous dominant porous carbon (HDMPC) at 0.1 A g⁻¹,¹⁹ 90 mA h g⁻¹ of sisal fiber activated carbon (SFAC-3) at 0.05 A g⁻¹,⁴⁵ 81.5 mA h g⁻¹ of pyridine-derived hierarchical porous nitrogen-doped carbon (PHPNC) at 0.1 A g⁻¹,¹⁹ etc. It’s observed from Fig. 4c that the coulombic efficiency of the a-EW-NaCl cathode is slightly lower than that of the other two cathodes at a low current density of 0.2 A g⁻¹ even after 100 cycles. This is because charged EDLCs are in their high energy state and there is a self-discharge process, which may lead to higher charge capacity and reduced discharge capacity than that of a normal value, especially at low current density.⁴⁶-⁴⁸ Since the a-EW-NaCl cathode has the largest specific...
surface area, this may cause more self-discharge and a comparatively low coulombic efficiency at low current density.

Cycling stabilities of the as-prepared a-EW-NaCl, a-EW and commercial AC electrodes were also examined by repeated charging and discharging. After 4000 cycles at a high current density of 5 A g\(^{-1}\), the specific capacity of a-EW-NaCl could still remain at 40.2 mA h g\(^{-1}\), corresponding to a stable capacity retention rate of 80.0%, while a-EW only delivers a specific capacity of 21.2 mA h g\(^{-1}\) after 4000 cycles with a capacity retention rate of 68.4%. Commercial AC delivers the lowest capacity of 11.2 mA h g\(^{-1}\) after 4000 cycles (Fig. 4d). Therefore, a-EW-NaCl shows both enhanced rate capability and cycling stability compared to a-EW and commercial AC due to the synergistic effect of an ultra-high specific surface area of 3898.0 m\(^2\) g\(^{-1}\) and an optimized hierarchical porous structure.

3.3 Hybrid device performance

LICs were fabricated with the as-prepared a-EW-NaCl cathode and Fe\(_3\)O\(_4@C\) anode with 1 M LiPF\(_6\) in a mixture of EC and DEC (1 : 1, vol/vol) solution. Before fabricating the LIC, the morphology and structural characterization, as well as the electrochemical performance of the Fe\(_3\)O\(_4@C\) anode were performed (Fig. S7\(^\dagger\)). The device configuration and charge storage mechanism of the a-EW-NaCl cathode and the Fe\(_3\)O\(_4@C\) anode based LIC are shown in Fig. 5a. Briefly, Li ions intercalate into the pre-activated Fe\(_3\)O\(_4@C\) anode during the charge process (faradaic reaction) along with the PF\(_6\)\(^{-}\) anions simultaneously absorbed into the hierarchical porous structure of the a-EW-NaCl cathode via the EDLC effect (non-faradaic reaction). The reactions are reverse during the discharge process. Therefore, the pore size distribution and accessible surface area of the a-EW-NaCl cathode are mostly important for the energy density of the as-constructed LICs.

The CV curves of the a-EW-NaCl/Fe\(_3\)O\(_4@C\) based LICs were slightly different from the ideal rectangular shape of traditional EDLCs due to the integration of two different charge storage mechanisms (Fig. 5b). As the scan rate increases, the initial shape of the CV curves was well-retained without severe distortion, indicating high reversibility and stability of the hybrid device. Correspondingly, the shape of the GCD curves of a-EW-NaCl/Fe\(_3\)O\(_4@C\) was slope lines with slight difference from the highly linear slope of ideal EDLCs (Fig. 5c). The specific capacities of the as-assembled LICs with different mass ratios are then calculated according to the GCD curves and are shown in Fig. 5d and S8.\(^\dagger\) It is seen that the a-EW-NaCl/Fe\(_3\)O\(_4@C\) with a mass ratio of 2 : 1 demonstrates much higher specific capacity and coulombic efficiencies than that of 3 : 1.

Therefore, the optimized mass ratio of the a-EW-NaCl cathode to the Fe\(_3\)O\(_4@C\) anode was set to be 2 : 1. The corresponding specific capacitance values (based on the mass of a-EW-NaCl) are 73.4, 56.3, 49.2, 45.4, 42.4, 36.8, and 34.0 mA h g\(^{-1}\) at current densities of 1.5, 2, 3, 4, 5, 8, and 10 A g\(^{-1}\), respectively (Fig. 5d). It is noted in Fig. 5d that the a-EW-NaCl/Fe\(_3\)O\(_4@C\) LIC shows a low initial coulombic efficiency. This may be attributed to the kinetic mismatch of the capacitive cathode and the battery type anode at relatively small current density. In addition, the as-constructed a-EW-NaCl/Fe\(_3\)O\(_4@C\) LIC device may need an activation process to guarantee that the electrolyte thoroughly infiltrates the electrode surface. Therefore, during the activation process, the coulombic efficiency gradually increases and remains at around 100% for the subsequent current densities.
Furthermore, the cycling performance of LICs is an important parameter in practical applications. An outstanding cycling stability was obtained for the as-assembled device with a capacity retention of 88.3% after 2000 GCD cycles at a high current density of 5 A g\(^{-1}\), as well as good coulombic efficiency of nearly 100% (Fig. 5e). The cycling performance of our a-EW-NaCl//Fe\(_3\)O\(_4@C\) LIC device is compared with previously reported LICs based on other anodes (such as Li\(_4\)Ti\(_5\)O\(_12\), SnO\(_2\), MnO, carbon-based anode materials, etc). As shown in Table S1, the cycling performance of such a-EW-NaCl//Fe\(_3\)O\(_4@C\) LIC device is comparable with reported values.

The Ragone plot (energy density vs. power density) of the a-EW-NaCl//Fe\(_3\)O\(_4@C\) LICs is shown in Fig. 5f in comparison with previously reported LICs, which were calculated based on the total mass of a-EW-NaCl and Fe\(_3\)O\(_4@C\). A maximum energy density of 124.7 W h kg\(^{-1}\) can be achieved at a power density of 2547 W kg\(^{-1}\), while the energy density could still remain at 57.8 W h kg\(^{-1}\) at a battery-inaccessible power density of 16 984 W kg\(^{-1}\). The integrated high energy and power performance of the a-EW-NaCl//Fe\(_3\)O\(_4@C\) LIC was better than the previously reported studies as shown in Table S2, such as commercial AC based LICs including AC//hard carbon (AC//HC), AC//microspherical Li\(_4\)Ti\(_5\)O\(_12\) (AC//M-LTO), AC//Li\(_4\)Ti\(_5\)O\(_12\) (AC//LTO), AC//MnN\(_\text{CN}\), and other types of carbonaceous material based LICs, e.g., 3D graphene//Fe\(_3\)O\(_4@graphene\), tubular mesoporous carbon//SnO\(_2@C\), HDMP\(_\text{C}^\text{MC}\)//HDMP\(_\text{C}\), etc., demonstrating the promising application of a-EW-NaCl in high performance energy storage devices.

**4. Conclusions**

In summary, EW derived activated carbon with an exceptionally high SSA of 3898 m\(^2\) g\(^{-1}\), a hierarchical porous structure and an improved graphitization degree was prepared by employing NaCl as a template, which serves both as a macropore creating template and a graphitic catalyst to enhance the graphitization degree. Inorganic impurities such as the ramification of Ca, K, Zn, and Fe substances that initially exist in the EW protein serve as the scaffold for mesopores. Furthermore, chemical activation enlarges the specific surface area by producing rich micropores. The as-prepared EW-NaCl demonstrates excellent electrochemical performance with a high specific capacity of...
118.8 mA h g⁻¹ and a stable capacity retention of 80.1% after 4000 cycles. Furthermore, a LIC is fabricated by coupling with a Fe₃O₄@C anode, which can deliver maximum energy and power densities of 124.7 W h kg⁻¹ and 16 984 W kg⁻¹, respectively, with a capacity retention of 88.3% after 2000 cycles at 5 A g⁻¹, demonstrating a promising approach to develop advanced activated carbon electrodes for high performance lithium ion capacitors.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
This work was supported by the Research Grants Council of Hong Kong (Grant No. T23-407/13-N), National Key Basic Research Program of China (No. 2014CB932400), Joint Fund of the National Natural Science Foundation of China (No. U1401243), National Nature Science Foundation of China (No. 51220105), Shenzhen Technical Plan Project (No. JCYJ20150529164918735, QJSCX20160226191136), and Guangdong Technical Plan Project (No. 2015TX01N011).

References