

石墨烯改性聚丙烯腈基多孔炭用于高倍率性能超级电容器

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摘 要:作为一种富氮碳源, 聚丙烯腈历来被作为生产炭材料的重要原料。但是聚丙烯腈直接炭化会导致其烧结不利于后续深度活化。通过干法球磨石墨烯和聚丙烯腈复合原料, 结合稳定化和 KOH 活化, 制备了杂化多孔炭, 并系统研究了石墨烯和聚丙烯腈配比及后活化处理对杂化多孔炭性能的影响。结果表明: 石墨烯的存在有利于高能球磨过程中热量地快速扩散, 有效避免了聚丙烯腈的烧结; 而聚丙烯腈进一步抑制了石墨烯片层的团聚, 使石墨烯/聚丙烯腈复合前驱体呈现蓬松的粉体结构, 利于碱的深度活化。同时, 石墨烯在多孔炭结构中形成的三维柔性导电网络便于电荷地快速转移。由于其发达的孔、大的比表面积、优异的导电性以及氮/氧杂原子诱导的赝电容, 所制备的杂化多孔炭用作超级电容器电极材料时, 在水系和有机系电解液中均表现出了优异的电化学性能。尤其是, 优化的 HPC-4 复合炭材料用作超级电容器的电极时, 在 1 mol/L 四乙基四氟硼酸铵有机电解液中, 当功率密度为 337.5 W/kg 时, 能量密度可达 30.38 W·h/kg。该工作为面向高功率兼高能量超级电容器电极材料的开发提供了一种简易且高效的制备策略。

关键词: 石墨烯; 聚丙烯腈; 球磨; 杂化多孔炭; 超级电容器

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Graphene Modified Polyacrylonitrile-Based Porous Carbon for High Rate Supercapacitor

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Abstract: As a carbon resource with abundant nitrogen, polyacrylonitrile (PAN) has been used for the key raw materials to produce carbon materials. However, the direct carbonization will lead to the cementation of PAN particles, which is adverse to the subsequent activation. In this work, a hybrid porous carbon (HPC) was synthesized via dry ball-milling of thermal-reduced graphene and polyacrylonitrile, and subsequent stabilization and KOH activation. The effect of the ratio of graphene and polyacrylonitrile, along with activation treatment on the properties of hybrid porous carbon are systematically studied. The results demonstrate that the existence of graphene nanosheets enable the fast dissipation of heat produced in ball-milling process and avoid the cementation of PAN particles, while PAN particles act as spacers to prevent graphene restacking. The as-obtained polyacrylonitrile/graphene precursor is a loose powder, which favors the dispersion of activation agents within the precursor and results in a more homogeneous and effective activation. Meanwhile, graphene works as a 3D micro-current collector, thus providing a conductive network for convenient charge transfer in HPC. Based on the electrochemical characterization in either

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water or a non-aqueous electrolyte, HPC exhibits a superior capacitive behavior because of its well-developed porosity, large specific surface area, excellent electrical conductivity as well as nitrogen/oxygen heteroatom induced pseudo-capacitance. Particularly, HPC-4 offers a high energy density of 30.38 W·h/kg at a power density of 337.5 W/kg in TEABF₄/EC-DMC electrolyte. This work provides an easy-to-operate and efficient synthesis strategy for developing porous carbon electrode towards supercapacitors with high power and energy density.

Keywords: graphene; polyacrylonitrile; ball milling; hybrid porous carbon; supercapacitor

1 Introduction

The rapid development of electrical vehicles and renewable energy has triggered more research efforts on fabricating devices for high-performance energy storage^[1–4]. Supercapacitor as an electrochemical capacitor has attracted recent attention due to the fast charge/discharge processes, high specific power density, long-term cycle performance and superior reliability. Exploring advanced electrode materials is one of the most straightforward approaches to further improve the efficiency of electrochemical energy storage systems^[4–6].

The existing active electrode materials in commercialized supercapacitors are activated carbons due to the high specific surface area, low costs, rich resources, and good chemical stability. However, the potential application of activated carbon as an electrode material is greatly restricted because the massive pores are usually inaccessible for electrolyte ions^[7–8]. To satisfy the ever-increasing demand for higher energy density/power density of energy storage, considerable efforts have been made to search for novel carbon materials, such as carbon nanotubes, mesoporous carbon, and graphene nanosheets^[9–12]. Among those electrode materials, graphene with a high electrical conductivity and a superior chemical stability is considered as a promising candidate for application in energy conversion and storage. Graphene has a larger specific surface area (SSA) of 2 630 m²/g, and its capacitance can reach up to 550 F/g^[13–15]. However, the re-stacking and agglomeration of graphene nanosheets occur due to the van der Waals attraction and strong π - π interactions, severely affecting the performance of single graphene layer and thereby resulting in a deteriorated supercapacitor performance^[16–17].

To address the problems, the nano-structured electroactive polymer or metal oxide/hydroxide as a spacer were introduced into graphene materials to fabricate graphene-based hybrid composites as high-performance electrode materials to improve the electrochemical behavior of supercapacitors^[1,6,18–19]. Although the specific capacity is significantly improved by developing graphene-based hybrid composites, and the rate capability and/or the cycle performance are still insufficient for their practical application. The poor rate capability of graphene-based hybrid composites is probably due to their dependence on the surface Faradaic redox reactions that are limited at a fast charge/discharge rate. By contrast, the porous carbon material is one of options because it can keep graphene from aggregation

and enhance the cyclability and rate performance^[1,20–21].

Polyacrylonitrile is a well-known porous carbon precursor due to its simple processing, low manufacture cost, a high carbon yield and abundant nitrogen atoms^[22–25]. A combination of polyacrylonitrile and graphene to prepare hybrid porous carbon could afford an effective route for developing next-generation porous carbon electrode towards high power supercapacitors. Besides, ball milling is an effective tool resulting in the chemical reactions, which reduces the amount of solvent and operates at ambient temperature *via* the application of mechanical energy. Also, this method is relatively simple and easy-to large-scale.

In this paper, graphene/polyacrylonitrile-based hierarchical porous carbon (HPC) was synthesized *via* dry ball-milling and subsequent thermal stabilization and chemical activation as an effective method. In addition, the electrochemical performances in either water or a non-aqueous electrolyte (*i.e.*, TEABF₄/EC-DMC) of the resultant hybrid porous carbon were also investigated.

2 Experimental

2.1 Materials

Graphene with a high conductivity, which was prepared by a modified Hummers method and subsequent vacuum thermal reduction at 1 000 °C, was provided from Sinocarbon-CAS Co., China. Polyacrylonitrile (average molecular mass: 80 000) was provided by Makepolo Co., China.

2.2 Sample preparation

Fig. 1 shows the preparation process of hybrid porous carbon (HPC-*x*). For the preparation of HPC-*x*, 1.92 g polyacrylonitrile (PAN) and 0.08 g graphene (GN) were firstly mixed and ground in an agate jar at 300 r/min for 1 h to obtain a uniform polyacrylonitrile/graphene precursor. The resulting polyacrylonitrile/graphene precursor was further stabilized at 250 °C under air flow (80 mL/min) at a heating rate of 2 °C/min for 2 h. Afterwards, the intermediate product was ground and fully mixed with KOH. The mass ratio of KOH and the intermediate product was 2:1. The mixture composed of the intermediate product and KOH was placed in a nickel crucible and thermally treated at 800 °C under Ar flow (60 mL/min) at a ramp rate of 3 °C/min for 1 h.

The resultant graphene/polyacrylonitrile-based sample was washed with 5% (in mass fraction) HCl and deionized water. The final sample was obtained by drying in a vacuum oven at 100 °C for 10 h. The mass contents of dry graphene powder added into polyacrylonitrile/graphene precursor were 2%, 4%, and 6% (in mass

fraction), and thus the final products were named as HPC-2, HPC-4, and HPC-6, respectively. For comparison, 0.5 g graphene and 2.0 g polyacrylonitrile were treated by

the same procedure, and the resulting samples with KOH activated graphene and polyacrylonitrile (PAN) were denoted as AG and APAN, respectively.

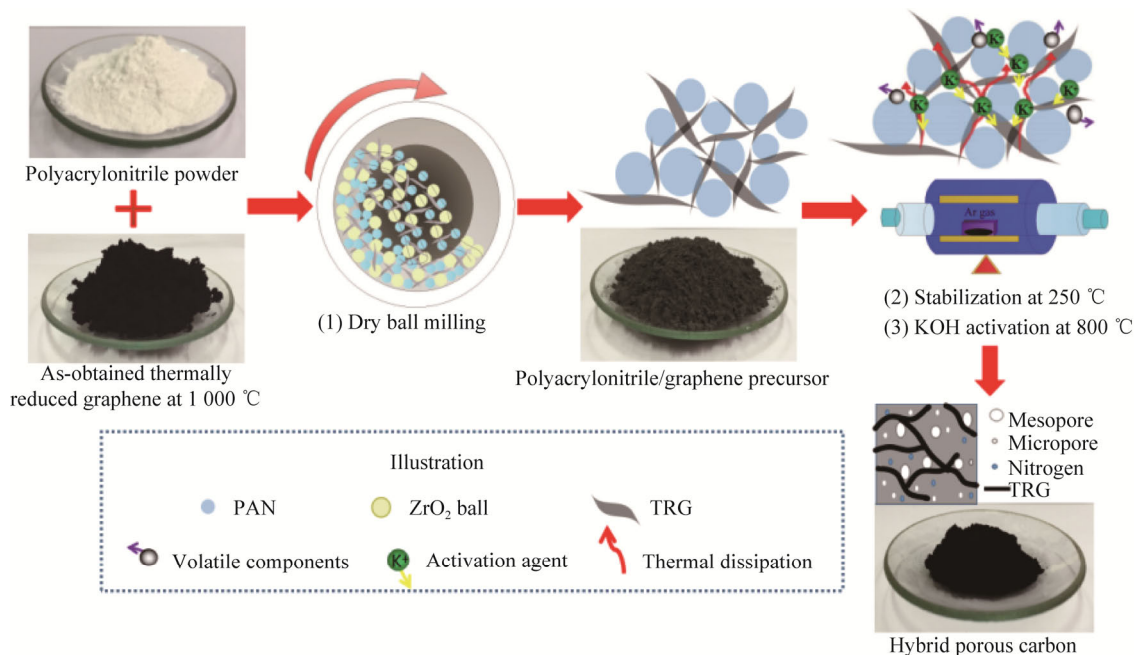


Fig. 1 Preparation process of hybrid porous carbon

2.3 Characterizations

The morphology and porous structure of the samples were observed by a model JSM-700 scanning electron microscope (SEM, JEOL Co., Japan) at an accelerating voltage of 10.0 kV, and a model 2100F transmission electron microscope (TEM, JEOL Co., Japan) operating at 200 kV. The phase composition was measured on a model D/Max-2400 X-ray diffractometer (XRD, Rigaku Co., Ltd., Japan). The specific gravimetric surface areas (S_{BET}) were determined based on the Brunauer-Emmett-Teller (BET) principle. The total pore volume (V_{total}) was estimated from the adsorbed amount at a relative pressure p/p_0 of 0.99. The micropore volume (V_{micro}) was estimated using the t-Plot method. The pore size distribution (PSD) curves were derived according to the density functional theory (DFT) assuming a slit-like pore geometry. The surface element distribution was determined by a model AXIS Ultra DLD X-ray photoelectron spectroscope (XPS, Thermo ESCALAB 250XI, USA with an excitation source of Mg K_{α} (1 486.6 eV). The electrical conductivity of the samples was carried out on a powder resistance instrument (Institute of Coal Chemistry, China)

2.4 Electrochemical measurement

The mixture of containing 85% (in mass fraction, the same below) active material, 10% acetylene black, and 5% the polytetrafluoroethylene dispersed in the ethanol solution was first fully stirred to pre-prepare a well-distributed slurry. The resultant slurry was coated to form a uniform membrane and punched into 8 mm in-diameter circular pieces. The resulting circular

electrodes were put in a drier at 100 °C for overnight, and the dried electrodes were used to fabricate a supercapacitor. Each as-fabricated electrode contained 2 mg active materials. To fully evaluate the capacitive behavior of the as-obtained active materials, a symmetrical two-electrode configuration was constructed, in which one electrode was served as a work electrode, and another electrode with the same size and mass was served as the part of both the counter and the reference electrodes. Meanwhile, a polypropylene membrane filled with 6 mol/L KOH electrolyte was used as a separator. The maximum voltage window is limited by 0.9 V in an aqueous system, which greatly restricts the improvement of the energy density. To increase the energy density, the electrochemical behavior of active material was also analyzed in an organic electrolyte TEABF₄/EC-DMC. The used solvent and the loading number of active materials were N-methyl pyrrolidone (NMP) and 1.5 mg, respectively. The two electrodes with the same mass and a piece of polypropylene separator were sandwiched together to form a complete symmetrical supercapacitor. 1 mol/L TEABF₄/EC-DMC as an organic electrolyte was used for the electrochemical evaluation. The cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were carried out on an electrochemical workstation named Autolab302N (PGSTSAT 302N, Metrohm, Switzerland) and a model LAND CT2001A instrument (LAND, Wuhan, China) at room temperature.

The gravimetric specific capacitance for a single electrode was calculated from the GCD curve in a

two-electrode system^[26]:

$$C_{\text{single}} = \frac{4I\Delta t}{m\Delta V} \quad (1)$$

Where C_{single} is the specific capacitance for a single electrode in F/g; I is the discharge current in A; Δt is the discharge time in s; m (g) is the total mass of the active materials in the two electrodes, and ΔV is the voltage window for aqueous solution (0–0.9 V) and for organic electrolyte (0–2.7 V).

3 Results and discussion

3.1 Structural characterization of hybrid porous carbon

Fig. 2 shows the SEM images of PAN-derived porous carbon, KOH activated graphene (AG) and hybrid porous carbon, PAN-derived porous carbon, KOH activated graphene (AG) and hybrid porous carbon HPC-4 has a 3D interconnected framework with a

carbons, respectively. In Fig. 2(a), PAN-derived porous carbon shows an aggregated structure with many cavities, while AG exhibits closely packed graphene agglomerates, in which graphene sheets with high-density ripples and wrinkles are randomly crumpled (see Fig. 2 (b)). In contrast, the introduction of graphene sheets in PAN effectively suppressed their agglomeration (see Fig. 2(c)–Fig. 2(e)). This can be since graphene nanosheets with a high thermal conductivity enable a fast dissipation of heat produced by dry ball-milling and further avoid the cementation of PAN particles, and the existence of PAN particles among graphene sheets effectively mitigate the re-stacking and self-aggregation of graphene. When an optimum TRG mass ratio is 4%, the final hybrid porous carbon HPC-4 has a 3D interconnected framework with a

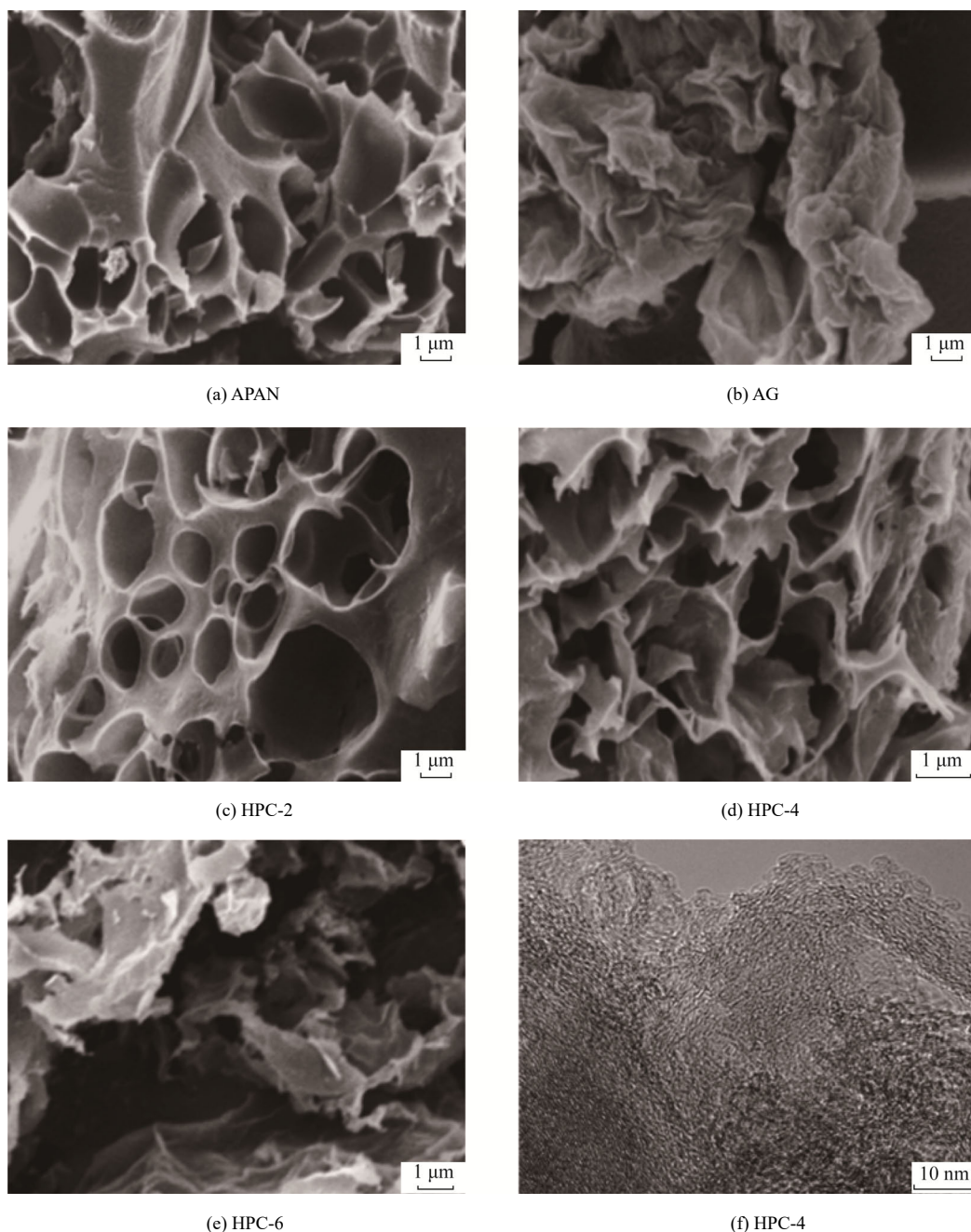


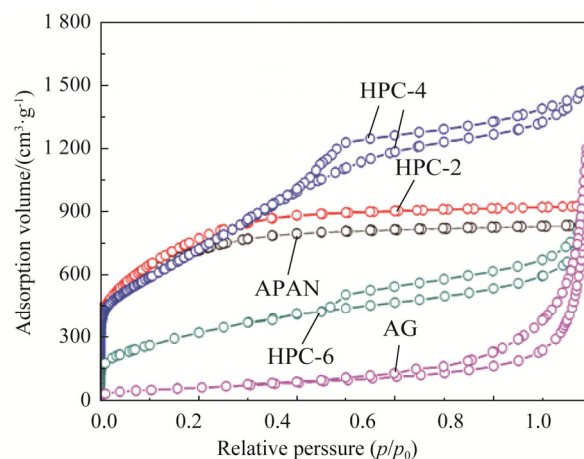
Fig. 2 SEM and TEM images of samples

randomly opened macroporous structure, thereby providing effective diffusion pathways for the electrolyte ion diffusion within HPC-4. Besides, Fig. 2(f) shows the high-resolution TEM images of hybrid porous carbon HPC-4. Clearly, abundant interconnected mesopores and micropores resulting from the KOH activation are homogeneously distributed through the structure of hybrid porous carbon HPC-4.

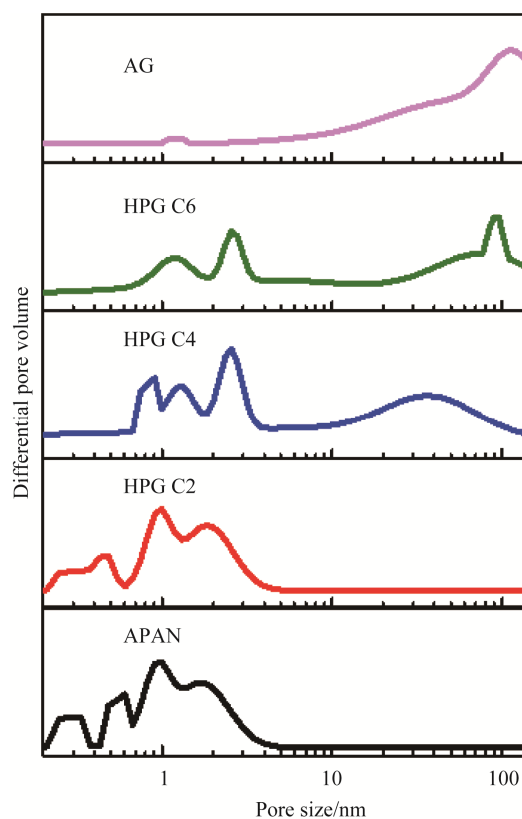
Fig. 3 shows the N_2 sorption isotherms and pore size distributions of pure PAN-derived porous carbon (APAN), KOH activated graphene (AG), and hybrid porous carbons (*i.e.*, HPC-2, HPC-4 and HPC-6). In Fig. 3(a) pure APAN presents a type I sorption isotherm with both adsorption and desorption profiles completely overlapping, indicating a high microporosity, and AG shows a type III/H3 sorption isotherm and an obvious hysteresis loop developed from a unique sorption behavior of the slit-shaped mesopores. It is interested to see that the introduction of graphene into the PAN-derived carbon matrix to construct a 3D interconnected framework affects the adsorption/desorption behavior of the as-obtained HPC-*x*. For the HPC-4, a combination of I/IV type adsorption/desorption isotherm with a hysteresis loop appears. In detail, a sharp adsorbed amount at a relative pressure of below 0.1 reveals the presence of massive micropores, which can be attributed to the introduction of micropores due to the KOH activation. The wide knee in a relative low-pressure range from 0.1 to 0.4 indicates the development of small mesopores. Meanwhile, the appearance of a hysteresis loop in a relative high-pressure range from 0.4 to 0.9 demonstrates the existence of abundant mesopores. This illustrates that the as-obtained polyacrylonitrile/graphene precursor is a loose powder, which ensures the more homogeneous and effective activation. Furthermore, the obvious tails at a relative pressure of above 0.9 indicates the formation of macropores in the HPC-4 composite, resulting from the construction of 3D interconnected framework with a randomly opened macroporous structure^[27–29].

Fig. 3(b) and Table 1 show the pore size distribution and the porous properties, respectively. Except AG mainly consisted of mesopores and macropores, all the other samples including APAN and HPC-*x* are composed of massive micropores with the pore diameters of 0.4–2.0 nm, and some mesopores with the pore diameters of 2.0–5.8 nm. As a result of the TGR incorporation, the average pore size and the mesopores volume increase from 1.57–4.34 nm and 28.46% to 83.95%, respectively. The final structural changes of the as-obtained HPC-*x* may be associated with the nanoscale modulation triggered by the intercalation of TGR sheets into the carbon matrix, which regulate the specific surface area and pore size distribution of HPC-*x*. A greater content of TGR in the HPC-*x* may cause the aggregation and layer-to-layer stacking of graphene sheets and pore blockage by graphene, which is unfavorable for KOH

activation and results in a low microporosity and a small specific surface area for HPC-6 composite. The abundant mesopores and high specific surface area of HPC-4 composite afford a larger contact area for electrolyte, which is extremely beneficial for an efficient transfer of small molecules or ions in the composite, especially at a high charge/discharge rate^[30]. Another criterion that should be considered is carbon yield. The carbon yield of HPC-*x* increases with increasing the amount of graphene, indicating graphene in the composite can promote the fast dissipation of heat produced by the activation process and slow down the ablation of PAN particles.



(a) N_2 sorption isotherms of all the samples



(b) Pore size distributions of all the samples

Fig. 3 N_2 sorption isotherms and pore size distributions of APAN, AG, HPC-2, HPC-4 and HPC-6

Table 1 Textural properties of of APAN, AG, HPC-2, HPC-4 and HPC-6

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$V_{\text{total}}/(\text{cm}^3 \cdot \text{g}^{-1})$	D/nm	$V_{\text{micro}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$V_{\text{meso}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$V_{\text{meso}}/V_{\text{total}}$	$w(\text{yield})/\%$
APAN	2 597	1.30	1.57	0.930	0.370	0.284 6	31.3
HPC-2	2 734	1.58	1.66	1.120	0.460	0.291 1	32.1
HPC-4	2 522	1.98	2.63	0.780	1.200	0.606 1	43.6
HPC-6	1 326	1.62	4.34	0.260	1.360	0.839 5	48.5
AG	238	1.90	30.94	0.003	1.897	0.998 4	77.2

S_{BET} is BET specific surface area; V_{total} is total pore volume; D is average pore diameter; V_{micro} is micro-pore volume; V_{meso} is mesopore volume; w is mass fraction.

Fig. 4 shows the XRD patterns of PAN-derived porous carbon (APAN), KOH activated graphene (AG), and hybrid porous carbons (HPC-2, HPC-4 and HPC-6). For KOH activated graphene (AG), a distinct reflection peak occurs at 43° , which corresponds to the periodically arranged (100) plane of graphitic domain^[31–32]. Comparison with APAN, the intensity of a peak (100) of HPC- x gradually increases with increasing the TRG content. Moreover, an additional reflex at 36.7° clearly appears in the XRD patterns of all the samples, which can be attributed to potassium residue. This illustrates that the introduction of graphene in HPC- x is not making the chemical activation more effectively but promoting the graphenization process, which can provide a stable structure for a high-rate capability and a long-term stability for energy storage.

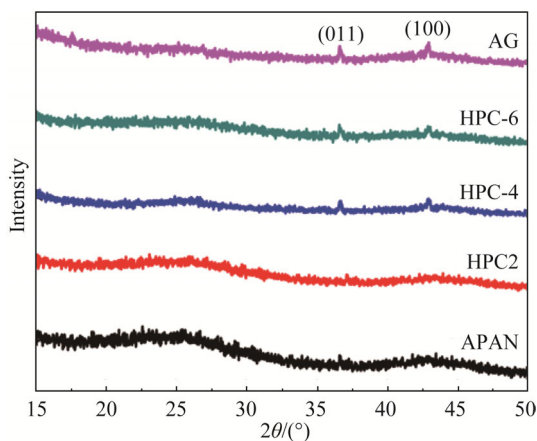


Fig. 4 XRD patterns of APAN, AG, HPC-2, HPC-4 and HPC-6

Fig. 5 shows the X-ray photoelectron spectra of hybrid porous carbon HPC-4. In Figs. 5(b)–Fig. 5(d), the high-resolution spectra of C 1s, O 1s and N 1s indicate the chemical states of carbon, nitrogen and oxygen species in HPC-4 composite. In Fig. 5(b), a sharp peak centered at 284.65 eV appears, which corresponds to C—C. Other three peaks at 286.1, 287.8 eV, and 290.7 eV are associated with different C—X bonding configurations, such as the corresponding forms of C—N (286.1 eV), C=O (287.8 eV), and O—C=O (290.7 eV)^[33].

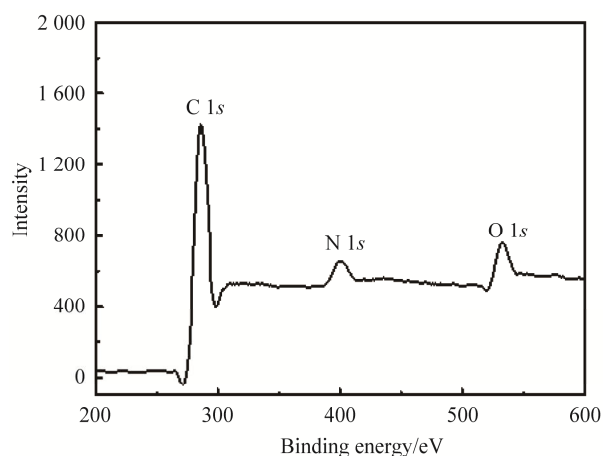
The O 1s signal can be resolved into three peaks at 538, 533 eV and 530.7 eV, which are assigned to three oxygen functional groups such as carboxyl (O-III), phenolic hydroxyl or ether (O-II) and quinone (O-I), respectively^[28]. In Fig. 5(d), the N 1s signal can be de-convoluted into pyridinic nitrogen (N-6) at 398.5 eV, pyrrolic or pyridonic nitrogen (N-5) at 399.9 eV and quaternary nitrogen (N-Q) at 401 eV, respectively. Xie *et al.*^[28] reported that pyridinic-N and pyrrolic/pyridone-N functional groups both could produce the pseudo-capacitance to enhance the total capacitance of nitrogen-doped carbon materials due to the electrochemically active in an alkaline aqueous electrolyte. In addition, the proper quaternary-N functional groups are beneficial for improving the electrical conductivity of hybrid porous carbon HPC-4. This phenomenon can be interpreted by the fact that the quaternary-N functional group embedded into the carbon matrix and bonded to three carbon atoms can significantly facilitate electron transfer and consequently contribute to the enhanced electrical conductivity of nitrogen-doped carbon materials^[26]. Meanwhile, the presence of nitrogen/oxygen functional groups is also able to increase the wettability of the HPC-4 surface, which favors the enhancement of electrochemical performance.

3.2 Electrochemical measurement in 6 mol/L KOH

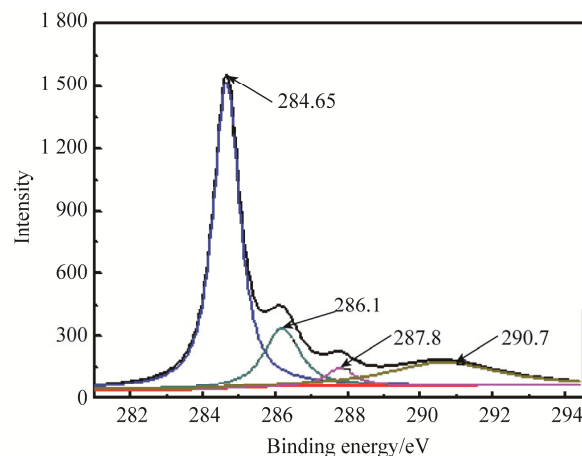
Fig. 6 shows the electrochemical properties of PAN-derived porous carbon (APAN), KOH activated graphene (AG), and hybrid porous carbons (*i.e.*, HPC-2, HPC-4 and HPC-6) measured in a two-electrode symmetric cell. Clearly, the slightly distorted rectangular CV curves with broadened pseudo-peaks of APAN, HPC-2, HPC-4, HPC-6 and AG electrodes indicate a complex capacitance from electrochemical double-layer capacitor (EDLC) and pseudo-capacitance in the presence of active nitrogen and oxygen functional groups^[26,34]. An intriguing finding is that the degree of deviation from the ideal rectangular shape is alleviated as the graphene content is increased, thus manifesting an increased contribution from EDLC and an improved rate capability related to a lower electrical resistance. Among the as-obtained samples, the hybrid porous carbon HPC-4 offers the maximum capacitance with the maximum CV area. In Fig. 6(b), the corresponding CV

curves at different scan rates from 5 mV/s to 300 mV/s appear and the hybrid porous carbon HPC-4 electrode still exhibits a little distorted rectangular shape even at a high scan rate. Fig. 6(c) and Fig. 6(d) show the galvanostatic charge/discharge curves of APAN, HPC-2, HPC-4, HPC-6 and AG electrodes at a current density of 1 A/g and the galvanostatic charge/discharge curves of the hybrid porous carbon HPC-4 at current densities from 0.5 A/g to 20.0 A/g, respectively. In Fig. 6(c), all these profiles of the as-obtained samples display a symmetric triangle with little distortion, indicating a superior supercapacitive characteristic. In contrast, the internal resistance (IR) drop of the hybrid porous carbon HPC-4 (0.004 V) is lower than that of PAN-derived porous carbon (0.024 V) and KOH activated graphene (0.017 V), illustrating a low internal series resistance, which can be ascribed to the stability of 3D continuous porous microstructure, the proper surface N-/O-containing groups and the enhanced conductivity. As is expected, the charge/discharge curve of hybrid porous carbon HPC-4 electrode even at a high current density still exhibits a quasi-triangular shape,

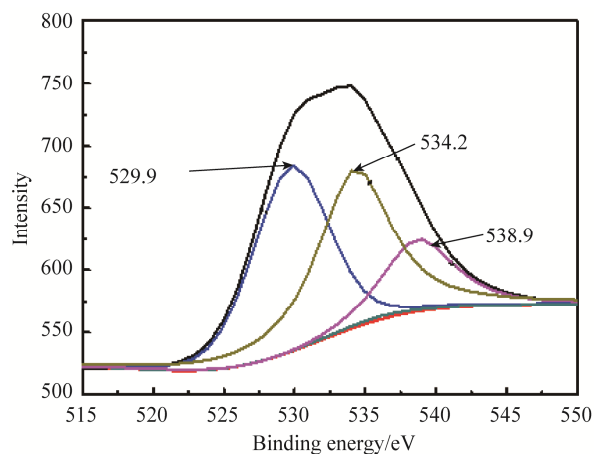
indicating an enhanced capacitive behavior. These results are consistent with the cyclic voltammetric results (see Fig. 6(a) and Fig. 6(b)). Fig. 6(e) shows the specific capacitance of the as-obtained samples as a function of the current density ranging from 0.5 A/g to 20.0 A/g. The specific capacitances of electrode HPC-4 are 270, 266, 255, 244, 230 F/g and 222 F/g, which are calculated based on the galvanostatic charge/discharge rates in the whole range of current densities from 0.5 A/g to 20.0 A/g. Also, the maximum capacitance retention of HPC-4 is up to 82.2% when the current density increases from 1 A/g to 20 A/g. In addition, a high specific capacitance of 247.5 F/g (or 95.7% of the initial value) is still retained after 10 000 cycles of consecutive charge/discharge at 1 A/g (see Fig. 7(f)). The inset in Fig. 7(f) shows the charge/discharge curves before and after cycling. There is little change in the charge/discharge curve after cycling, demonstrating its excellent electrochemical stability. Based on the thickness of 11.6 μm and the density of 0.24 g/cm^3 of an electrode, the gravimetric capacitance is converted to the volumetric capacitance *via*:



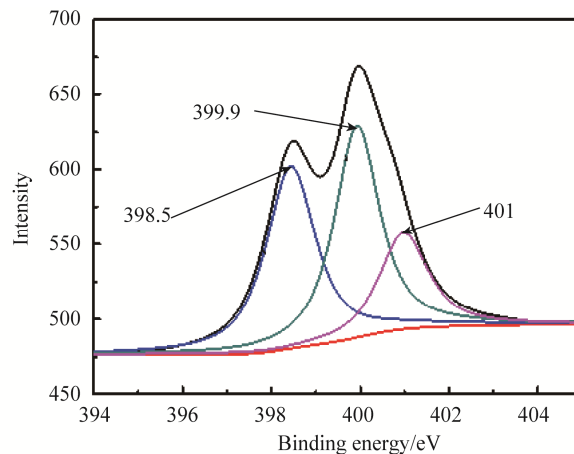
(a) General spectra of HPC-4



(b) High-resolution spectra of C 1s



(c) High-resolution spectra of O 1s



(d) High-resolution spectra of N 1s

Fig. 5 X-ray photoelectron spectra of HPC-4

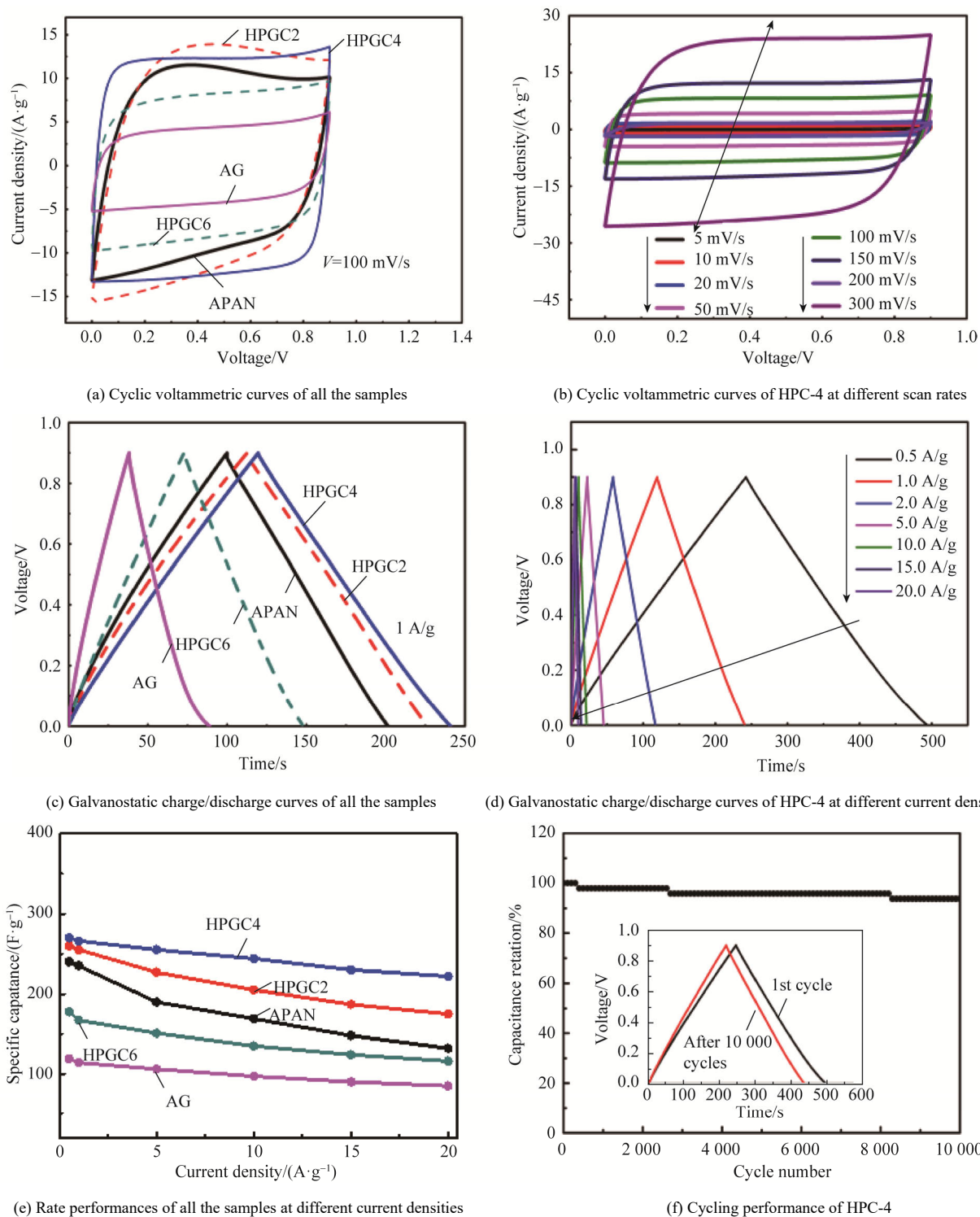


Fig. 6 Electrochemical properties of APAN, AG, HPC-2, HPC-4 and HPC-6

$$C_v = C_g \cdot \rho \quad (2)$$

Where C_v is the volumetric capacitance in F/cm³; C_g is gravimetric capacitance in F/g; ρ is the compacted density in g/cm³. This electrode has a volumetric capacitance of 63.84 F/cm³ at 2 mA/cm² and retains 53.28 F/cm³ at 60 mA/cm². The following reasons for the enhanced performance of the hybrid porous carbon HPC-4 can be given: 1) the abundant mesopores and high specific surface area of HPC-4 composite give a large

contact area with electrolyte for an efficient transfer of small molecules or ions in composite, especially at a high charge/discharge rate; 2) the electrical conductivity of HPC-4 electrode measured is 8.24 S/m, which is much greater than that of APAN material (*i.e.*, 0.26 S/m). The improved electronic conductivity is attributed to the formation of a well-defined 3D continuous porous network; and 3) the presence of nitrogen/oxygen functional groups improves the wettability of the HPC-4 surface, which

favors the enhancement in electrochemical performance.

3.3 Electrochemical measurements in 1 mol/L TEABF₄/EC-DMC electrolyte

To satisfy the requirements for practical applications, advanced energy storage device such as supercapacitor must have both a high power density and a high energy density. In general, increasing the specific capacitance or widening the operation voltage was widely studied to improve the energy density^[1]. Fig. 7 shows the electrochemical properties of the symmetric cell based hybrid porous carbons HPC-4 electrode with 1 mol/L TEABF₄/EC-DMC as an organic electrolyte. In Fig. 8(a), the cyclic voltammetric curve of the as-fabricated cell at a lower scan rate exhibits a quasi-rectangular shape and little changes occur with the increase of the scan rate, indicating a fast and efficient charge transfer at high

current densities. In Fig. 7(b), all the galvanostatic charge/discharge curves of the as-fabricated cell at different current densities present nearly symmetric linear curves without an obvious IR drop, further revealing its superior electrochemical performance. These results are in reasonable agreement with the results of cyclic voltammetric curve. Also, the capacitance still can retain 71.6% as the current density increases from 0.5 A/g to 10 A/g. The superior electrochemical performance mainly benefits from its high accessible specific surface area, well-established 3D continuous porous network as well as high conductivity, resulting in a more efficient and rapid charge transfer within the HPC-4 carbon material even at a high current density. Besides, a long-term cycle life with 88.9% of the initial capacitance is obtained after 5 000 cycles of consecutive charge/discharge at 5 A/g.

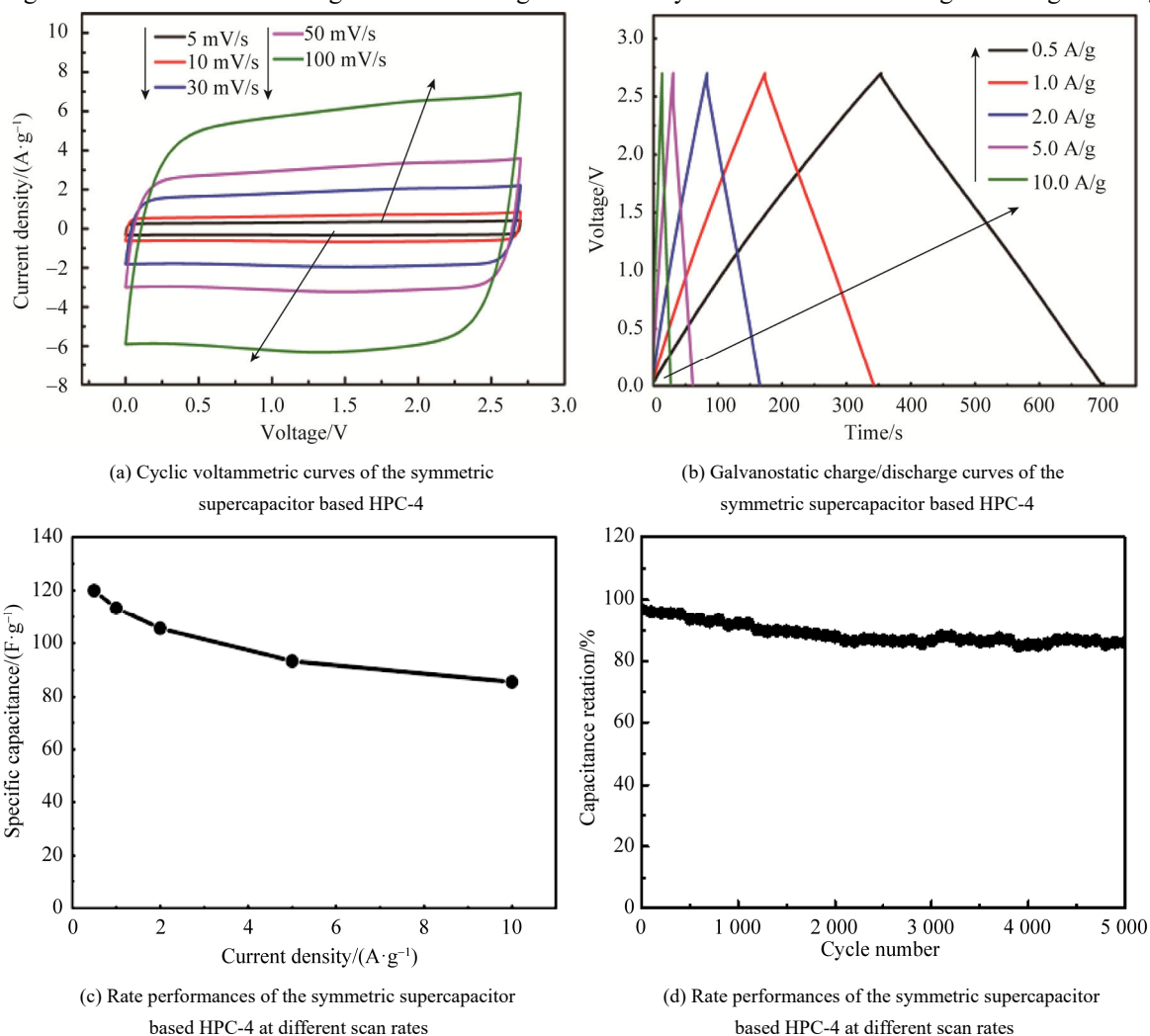


Fig. 7 Electrochemical properties of the symmetric cell based hybrid porous carbons HPC-4 electrode with 1 mol/L TEABF₄/EC-DMC as an organic electrolyte

Fig. 8 shows the Ragone plots of the symmetric cell based hybrid porous carbons HPC-4 electrodes with KOH and TEABF₄ as electrolytes, respectively. The energy and power densities can be calculated by^[34]:

$$E_s = \frac{C_g \Delta V^2}{4 \times 3600} \quad (3)$$

$$P_s = \frac{E_s}{t} \quad (4)$$

Where E_s is the specific energy density in W·h/kg; V is the operating voltage in aqueous (0–0.9 V) and in organic electrolyte (0–2.7 V); P_s is the power density in W/kg and t is the total discharge time in h. The symmetric cell

based hybrid porous carbons HPC-4 electrodes exhibits a specific energy of 7.65 W·h/kg at a power density of 225 W/kg in aqueous electrolyte. Also, a specific energy of 6.27 W·h/kg can be achieved even at a high power density of 4 500 W/kg. The high power capability values are matched well with its rate performance (Fig. 8(d) and Fig.8(e)). Furthermore, in the widening operation voltage range of 0–2.7 V in TEABF₄/EC-DMC organic electrolyte, the higher specific energy densities of 30.38 W·h/kg and 21.66 W·h/kg can be obtained at power densities of 337.5 W/kg and 6 750.7 W/kg, respectively. Such high energy densities are superior to those of the existing commercial devices with activated carbon (*i.e.*, <3 W·h/kg). Therefore, an as-fabricated R2032 coin-type symmetric supercapacitor based on TEABF₄/EC-DMC electrolyte can drive a LED bulb brightly.

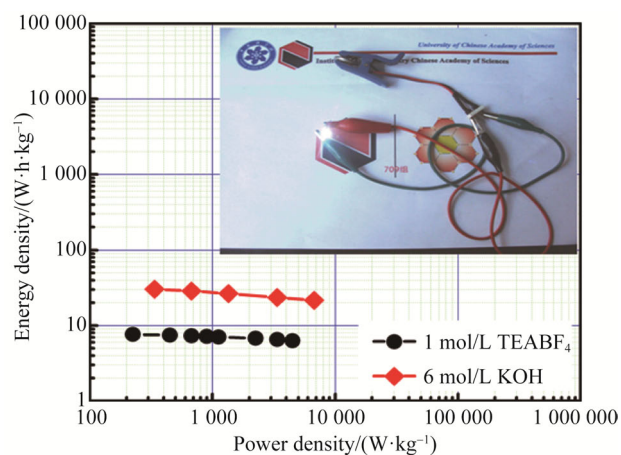


Fig. 8 Ragone plot of the supercapacitors with hybrid porous carbons HPC-4 as an electrode material in both aqueous and organic system and its application demonstration (insert)

4 Conclusions

A series of graphene/polyacrylonitrile-based hybrid porous carbons were prepared *via* ball-milling and subsequent stabilization and KOH chemical activation with polyacrylonitrile and thermally reduced graphene as precursors. The introduction of graphene had an effect on the textural property, surface chemistry as well as the electrical conductivity of the hybrid porous carbons, resulting in an improvement of the electrochemical performance. The typical hybrid porous carbon HPC-4 possessed a high surface area of 2 426 m²/g, a large pore volume of 2.42 cm³/g, a proper nitrogen of 5.64% (in mass fraction) and oxygen content of 4.36% (in mass fraction). The electrochemical performance of the as-obtained samples was carried out both in 6 mol/L KOH and 1 mol/L TEABF₄/EC-DMC electrolytes. The optimum hybrid porous carbon HPC-4 electrode had the maximum specific capacitance of 270 F/g at 0.5 A/g in 6 mol/L KOH electrolyte and the better rate capability with a capacitance retention rate of 71.6% when the current density increased from 0.5–10.0 A/g. A high

specific capacitance of 247.5 F/g (or 95.7% of the initial value) was retained after 10 000 cycles of consecutive charge/discharge at 1 A/g. Moreover, in the widening operation voltage range of 0–2.7 V in TEABF₄/EC-DMC electrolyte, the higher specific energy densities of 30.38 W·h/kg and 21.66 W·h/kg could be obtained at the power densities of 337.5 W/kg and 6 750.7 W/kg, respectively, indicating a promising application of hybrid porous carbons HPC-4 electrode for advanced supercapacitor.

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