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High performance Li-ion capacitor fabricated with dual graphene-based materials

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Abstract

Lithium-ion capacitors (LICs) are now drawing increasing attention because of their potential to overcome the current energy limitations of supercapacitors and power limitations of lithium-ion batteries. In this work, we designed LICs by combining an electric double-layer capacitor cathode and a lithium-ion battery anode. Both the cathode and anode are derived from graphene-modified phenolic resin with tunable porosity and microstructure. They exhibit high specific capacity, superior rate capability and good cycling stability. Benefiting from the graphene-enhanced electrode materials, the all graphene-based LICs demonstrate a high working voltage (4.2 V), high energy density of 142.9 Wh kg⁻¹, maximum power density of 12.1 kW kg⁻¹ with energy density of 50 Wh kg⁻¹, and long stable cycling performance (with ~88% capacity retention after 5000 cycles). Considering the high performance of the device, the cost-effective and facile preparation process of the active materials, this all graphene-based lithium-ion capacitor could have many promising applications in energy storage systems.

Supplementary material for this article is available online

Keywords: Li-ion capacitor, rate capability, cycling stability, dual graphene-based materials, energy density

(Some figures may appear in colour only in the online journal)

1. Introduction

Lithium-ion batteries (LIBs) and supercapacitors (SCs) are two important energy storage devices which are widely used in portable electronics, smart grid and electric vehicles. LIBs and SCs display different energy storage properties because of their inherently different charge storage mechanisms [1]. LIBs deliver high energy density $(150-250 \text{ Wh kg}^{-1})$ derived from the Faradaic reactions of the electrode materials while they suffer from limited power density (<1 kW kg⁻¹) and poor cycle life (within 4000 times) due to the sluggish Li⁺ diffusion in the bulk electrode and the structural degradation during the

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cycling [2-5]. SCs, especially electrical double-layer capacitors (EDLCs) usually utilize highly porous carbon as activated materials, thus have excellent power capability (~10 kW kg^{-1}) and cycle performance (>100000 times) which is attributed to the non-faradaic reaction with extremely rapid adsorption/desorption of electrolyte ions at the electrode/electrolyte interface [6-8]. However, an inferior energy density (5–10 Wh kg^{-1}) severely limits the applications of SCs. Therefore, it is highly demanded to develop high-performance energy storage devices with the advantages of both LIBs and SCs. Meanwhile, lithium-ion capacitors (LICs), as a hybrid of LIBs and supercapacitors, are receiving intensive attention because of their high energy and power density, large operating voltage, and long-cycle life [9-11]. Typical LICs contain a lithium-ion battery-type electrode as anodes to provide high energy density by lithium insertion/extraction and a supercapacitor-type electrode as cathodes to ensure high power density and stable cycling performance through adsorption/desorption of anions [12–14]. Moreover, since both the energy and power densities are proportional to the square of the operational voltage, an organic electrolyte containing lithium salt is applied to guarantee a wide working voltage window to further improve the electrochemical performance [15]. The combination of two type electrodes with different energy storage mechanisms should bridge the gap between LIBs and SCs and overcome the inherent disadvantages of both.

To enhance the performance of LICs, various advanced cathode and anode materials have been developed. Similar to the requirements of EDLC cathodes, ideal LICs cathode candidates usually have high specific surface area, good electrical conductivity, well chemical and electrochemical stability. Considering these requirements, various carbon-based porous materials are investigated, including commonly used activated carbon (AC) [16], pyrolyzed biomass or polymer [17, 18], graphene, and its composites [19, 20]. Among these, graphene-based porous materials are outstanding alternatives to AC which demonstrate strong competition because they have high specific surface area, tunable porosity, inherent high conductivity, and easily modified surface chemistry [21, 22]. Hence, it is reasonable to develop graphene-based cathodes for LICs to pursue excellent power density, energy density, and long cycling life. Unlike the cathodes which are always limited to carbonaceous porous materials, anodes can be made of many kinds of materials, such graphite [23], $Li_4Ti_5O_{12}$ [24], graphene [22], SnO₂ [25], CoS [26], Fe₃O₄ [21], Nb₂O₅ [27], and Si-based composites [28]. Graphite shows a stable voltage plateau of around 0.1 V (vs. Li/Li⁺) through the entire charge/discharge process and can offer a high working potential when paired with AC, making it very attractive for LICs anode. However, the application of graphite is still hindered by unfavorable power density ascribed to the sluggish Li⁺ diffusion. LTO, on the other hand, demonstrates excellent power density and long lifespan due to good structural stability, but the limited specific capacity (175 mAh g^{-1}) and high lithiation/delithiation potential (1.5 V vs. Li/Li⁺) result in a low energy density and decreased output voltage of lower than 3.0 V. In order to obtain high energy density, metal compounds based on mechanism of conversion or alloying have also been considered as anodes for LIC for their high specific capacity, attractive lithiation potential, and high abundance. Nevertheless, these anodes not only need sophisticated fabrication process, but they also suffer from huge volume change during charge/discharge process, large irreversible capacity, low electrical conductivity, and poor Li⁺ diffusion, leading to inferior rate capability and cycle stability. Therefore, it is highly desirable to develop novel anodes which can overcome all the drawbacks.

Carbon-based materials possess the merits of environmental friendliness, low cost, rich reserve, high conductivity, and adjustable microstructure, which make them ideal choices for both cathodes and anodes to fabricate all carbon LICs [29, 30]. Graphene and its various composites have become the focus for energy storage devices due to their extraordinary electrochemical properties [31–35]. Especially in LICs, graphene-based materials have been widely applied because of their high specific surface area, high electrical conductivity, tunable porosity, and rich surface chemistry [20, 21, 36-38]. In this work, we designed and assembled an all carbon LICs with dual graphene-modified cathode and anode prepared via a facile and scalable method. Graphene oxide (GO) was introduced when phenol and formaldehyde were reacted to form phenolic resin through a hydrothermal reaction. With the graphene-modified intermediate product, the cathode of 3D porous structure was obtained under high temperature activation by KOH and the anode was produced by direct thermal annealing. Both the cathode and anode show a high specific capacity, excellent rate capability, and good cycling life. The all-carbon LICs with dual graphene-modified electrodes have a high working voltage of 4.2 V, high energy density of 142.9 Wh kg⁻¹, and a maximum power density of 12.1 kW kg⁻¹ (at energy density of 50 Wh kg⁻¹). Furthermore, the device also shows stable cycle life of up to 5000 cycles with nearly 90% capacity retention. The excellent performance was attributed to the all graphene-based electrodes.

2. Experimental

2.1. Materials synthesis

The cathode and anode materials used in this work were prepared by the same method except that the cathode was activated by KOH to enhance the specific surface area and porosity. Typically, 1.75 g GO powder was homogeneously dispersed in 350 ml water by ultrasonication for 1 h to form a stable solution. Then 11.7 g phenol (P) and 16.8 g formaldehyde (F) (35 wt %) were added into the GO solution and the mixture was stirred for 1 h at room temperature. After that, the homogeneous dispersion was transferred to a sealed Teflon-lined autoclave and heated at 180 °C for 12 h. The obtained black column solid was crushed into powders, washed with water, and finally dried under vacuum at 120 °C for 24 h. Then the intermediate product was mixed with KOH with a mass ratio of 1:4 and was activated in a horizontal tube furnace at 900 °C for 1 h under Ar atmosphere. After cooling down to the room temperature, the KOH treated product was thoroughly washed with 0.1 M HCl and then water until the pH value reached 7 to remove inorganic impurity. The final graphene-based porous carbon (GPC) was acquired after vacuum drying at 120 °C for 24 h. The synthesis of the anode is similar to the cathode except for the activation step. As for the anode material, the intermediate product was directly annealed at 900 °C for 1 h to get graphene-modified carbon (GC).

2.2. Characterization

Scanning electron microscopy (SEM) images were obtained using LEO 1530VP field emission scanning electron microscope with an acceleration voltage of 10 kV. Transmission electron microscopy (TEM) characterization was carried on a JEOL TEM-2100 electron microscope at an acceleration voltage of 200 kV. Powder x-ray diffraction (XRD) patterns were collected on a Rigaku D/Max-2500 diffractometer with Cu KR radiation. The Raman spectra were examined with a LabRAM HR Raman spectrometer using laser excitation at 514.5 nm. The nitrogen adsorption/desorption analysis was conducted at 77 K on a Micromeritics ASAP 2020 apparatus. The specific surface area (SSA) was calculated by the BET (Brunauer-Emmett-Teller) method based on adsorption data in the relative pressure (P/P_0) range of 0.05–0.3. The pore size distribution was analyzed using an NL-DFT (nonlocal density functional theory) method with a slit pore model from the nitrogen adsorption data.

2.3. Cell fabrication and electrochemical analysis

All the devices including LICs, half cells, and EDLCs were measured using coin-type cells. For preparing the electrodes of EDLCs and cathodes of LICs, GPC and polytetrafluoroethylene (PTFE) were directly mixed with a mass ratio of 9:1, rolled into a thin sheet, then punched into 10 mm discs and finally hot-pressed onto carbon-coated Al foil. The typical mass loading of the electrodes was 3.0 ~ 4.0 mg and could be easily adjusted by changing their thickness. Similarly, to fabricate the anodes of LICs, GC, Super P, and PTFE with a mass ratio of 80:5:15 were mixed and uniformly coated onto carboncoated Cu foil. Then the sheet was pressed and punched into 10 mm diameter electrodes with a mass loading of 1.0–1.5 mg. Both the GPC and GC electrodes were heated at 150 °C for 1 h before transferring into an argon-filled glove box to assemble coin cells. GPC and GC were firstly evaluated using half cells with lithium metal foil as the counter/reference electrode to measure the performance of each material. Then the LIC coin cells were fabricated with GPC and pre-activated GC (cycling for several times at a low current density). As a comparison, EDLC coin cells were assembled with GPC. All the devices mentioned above used 1 M LiPF₆ dissolved in 1:1:1 (v/v/v) mixture of ethylene carbonate/diethyl carbonate/dimethyl carbonate (EC/DEC/DMC) as the electrolyte.

All the electrochemical tests were performed at room temperature. The galvanostatic charge/discharge measurements were carried out at various current densities using a battery test system (LAND CT2001Amodel, Wuhan LAND Electronics. Ltd.), and the voltage windows for each device were as follows: 2.0–4.2 V for GPC, 0.01–3.0 V for GC, 0–4.2 V for



Figure 1. Schematic of the fabrication of the GPC and GC.

LICs and 0–2.7 V for EDLC. Cyclic voltammetry (CV) measurements were recorded using an Autolab system (Metrohm).

The energy density values E (Wh kg⁻¹) of LICs and EDLCs were calculated by numerically integrating the Q–V graph (or t–V graph, as the current density *I* is a constant value) area during the discharge process, using the following formula (followed by unit conversion to Wh kg⁻¹):

$$E = \int_{t1}^{t2} IV dt \tag{1}$$

where *I* is the constant current density (A g^{-1}), V (V) is the operational voltage window, and t_1 , t_2 is the start time and end time in the discharge process, respectively.

The power density values P (W kg^{-1}) of LICs and EDLCs were calculated according to

$$P = E/\Delta t \tag{2}$$

where Δt is the discharge time.

3. Results and discussion

To prepare the all graphene-based cathode and anode, we designed a facile approach shown in figure 1, and the details of the synthesis process can be found in the experimental section. Firstly, phenol and formaldehyde were reacted and cross-linked to form phenolic resin on the surface of GO and turned to a carbonaceous composite via a hydrothermal reaction. Keep the requirements of cathode and anode materials of LICs in in mind, the graphene-modified intermediate product was treated by two different ways. The GPC cathode, which is supposed to provide high power, was obtained by activating the intermediate product with KOH at 900 °C. During this process, a hierarchical structure with plenty of interconnected pores was formed and the large pore volume and high SSA help to facilitate ions transportation. On the other side, the GC anode, which was expected to serve as electrode of high energy density, was prepared by direct thermal annealing without KOH activation to remove the residual oxygen-containing functional groups of the hydrothermal product.

The morphology and microstructure of GPC and GC were characterized by SEM and TEM. As shown in figure 2, the KOH activated GPC exhibits sponge-like morphology with



Figure 2. SEM images of GPC (a), (b) and GC (c), (d); TEM images of GPC (e), (f) and GC (g), (h).

rougher surface (figures 2(a) and (b)), significantly different from the solid and sheet-like structure of GC derived from direct thermal annealing of the intermediate (figures 2(c) and (d)). The microstructure difference between GPC and GC can also be reflected by the TEM images clearly, indicating that the as-prepared GPC has a highly porous structure with abundant mesopores due to the activation treatment (figures 2(e) and (f)) while GC shows a relatively smooth surface without obvious pores (figures 2(g) and (h)). From the SEM and TEM, GPC with porous structure and defects created by KOH activation are expected to have a high BET surface area and large pore volume, which enables a fast ion transport channel and makes it a promising electrode material for high power energy storage devices. The carbonized GC under high temperature possesses thin layered structure, like the phenolic resin derived carbon reported by elsewhere [39], which can provide high Li⁺ capacity in a high energy electrode.

The nitrogen adsorption-desorption isothermal analysis strongly supports the previous SEM and TEM investigations. As shown in figure 3(a), GPC exhibits typical type IV adsorption-desorption isotherms with a hysteresis loop associated with capillary condensation of mesopores while



Figure 3. (a) Nitrogen adsorption/desorption isotherms, (b) pore-size distribution plot, (c) XRD profiles and (d) Raman spectra of GPC and GC.

GC shows a type I isotherms indicating its micropores characteristic [40]. Based on the BET method, the specific

surface area of GPC is as high as 2958.5 m^2 g⁻¹ with a large pore volume of 1.75 m³ g⁻¹, much higher than that of GC (409.7 m² g⁻¹ and 0.47 m³ g⁻¹). Figure 3(b) shows the pore size distribution calculated by the NL-DFT method, revealing that GPC contains primarily mesopores with a size range of 2-10 nm and some micropores around 1 nm created by the violent KOH activation. As for GC, it mainly consists of micropores formed by removing oxygen-containing groups during the high-temperature pyrolysis. It should be noted that the micropores-predominant structure with moderate SSA and micropores of GC can enhance the ion transport, thus vital for high rate capability of GC. Moreover, from the XRD profile in figure 3(c), GPC displays an extremely broad and weak peak (002) from 15° to 25°, demonstrating a much more disordered and amorphous structure without long-range graphene domains [41]. In contrast, GC shows a relatively strong peak around 25°, which indicates that more sp² carbonbased aromatic structure with long-range order are formed. Raman spectra of GPC and GC (figure 3(d)) show two main peaks at ~1350 cm⁻¹ (D band) and ~1580 cm⁻¹ (G band), which can be ascribed to the sp³ and sp² carbon networks, respectively [42]. The I_D/I_G ratio of GPC is 0.96 while only 0.89 for GC, suggesting that graphene structure of GPC is severely destroyed after KOH activation, which is consistent with the above characterizations [19].

The above analysis shows that GPC has an amorphous structure with large SSA and plenty of pores, which is beneficial for easy electrolyte access, high capacity, and high rate performance, thus can be an ideal cathode material for LICs. On the other hand, GC shows relatively lower SSA and contains smaller pores, which can work as the anode in LICs. And before we investigate the all graphene-based LICs with GPC as the cathode and GC as the anode materials, we should first evaluate the electrochemical performance of GPC and GC, respectively.

The electrochemical performance of GPC was studied by assembling half-cell with Li as the counter electrode in LiPF₆containing organic electrolyte. As shown in figures 4(a) and (b), GPC exhibits almost rectangular voltammetry characteristics at different scan rates in CV without obvious redox reaction and all nearly straight lines in galvanostatic chargedischarge curves in the potential window of 2-4.2 V vs. Li/Li⁺. These results are well in accord with the symmetric supercapacitor using two identical GPC electrodes, which shows a standard capacitive behavior of EDLC type supercapacitor with fast ions absorption/desorption process (figure S1 (available online at stacks.iop.org/NANO/32/015403/ mmedia)) [41]. As expected, GPC exhibits both high specific capacity and rate capability. As shown in figure 4(c), the specific capacities of GPC were in the range of 40–95 mAh g^{-1} obtained from the half-cell device at current densities of 0.1-5.0 A g⁻¹. More importantly, GPC shows super cycling stability of 65 mAh g^{-1} at the current density of 1.0 A g^{-1} without obvious degradation over the whole 5500 cycles. The GPC material has a typical capacitive behavior with an outstanding rate and cycling performance, thus it can be used as an excellent cathode for LICs.



Figure 4. Electrochemical performance of GPC: (a) CV curves at different scan rates; (b) galvanostatic charge–discharge profiles and (c) rate performance at different current densities; (d) cycling performance at 1 A g^{-1} .

The electrochemical performances of GC were also investigated using half-cells in the potential range of 0.01-3 V vs. Li/Li⁺. The rate performance of GC samples prepared at different temperature is shown in figure S1. The anode annealing at 900 °C demonstrates the highest specific capacity and was chosen for further investigation. Figure 5(a) presents the CV curves of the first three cycles at a scan rate of 0.1 mV s^{-1} . There is a distinct cathodic peak at around 0.62 V, which disappeared in the following two cycles. It can be ascribed to the formation of solid electrolyte interphase (SEI). From the galvanostatic charge–discharge profiles at 0.1 A g^{-1} (figure 5(b)), GC shows a reversible specific capacity as high as 535 mAh g^{-1} . The initial Coulombic efficiency is 40% and dramatically increases to 95% in the third cycle. A high irreversibility is also reflected in CV and relates to the enormous SEI consumption of Li⁺. It should be noted that both the CV and galvanostatic charge-discharge curves of the second and third cycles almost overlap, indicating an excellent reversibility. Benefiting from the unique structure of moderate SSA with micropores, GC shows excellent rate capability. As demonstrated in figure 5(c), a reversible capacity of 530 mAh g^{-1} at 0.1 A g^{-1} is obtained and, even at high current density of 5.0 A g^{-1} (~10 C), it still delivers over 210 mAh g^{-1} , illustrating fast Li⁺ intercalation and de-intercalation process. Furthermore, GC also exhibits excellent cycle stability. As shown in figure 5(d), after cycling for 1500 times at a high current density of 5.0 A g^{-1} , the specific capacity still keeps more than 210 mAh g^{-1} with a retention of near 90%. Such extraordinary electrochemical properties of high reversible capacity, super rate, and cycle performances make GC an ideal anode for LICs.

Based on the above results, the as-prepared GPC and GC are expected to be promising electrode materials for highenergy and high-power LICs. Hence, LICs (GPC//GC) in LiPF₆-containing organic electrolyte using the EDLC-type GPC as the cathode and the pre-lithiated battery-type GC as the anode with a high operational voltage of 0-4.2 V were designed and assembled. During the charge process, PF_6^- ions in the electrolyte are absorbed in the pores of GPC, while Li⁺ ions are intercalated into GC, so that the voltage increases from the open circuit potential (~ 0 V) to the cut-off voltage of 4.2 V. For the discharge process, the PF_6^- and Li⁺ leave the cathode and anode, respectively, and return to the electrolyte. From the electrochemical analysis above, it can be seen that the specific capacity of GPC is much less than that of GC, so the capacity balance between cathode and anode was studied. The performance of LICs with mass ratios of GPC:GC from 2.0 to 3.5 was measured, which is shown in figure 6(a) of the Ragone plots (energy density vs. power density). Obviously, the LIC with a mass ratio of 3.0 has the highest energy density of 142.9 Wh kg⁻¹ (at 98 W kg⁻¹) based on the total mass of active materials of cathode and anode, which is not only more than four times higher than that of symmetric supercapacitor (see figure S2) but also superior to the other ratios. The tendency remains almost the same with increasing the rate and it still shows an energy density of





Figure 5. Electrochemical performance of GC: (a) CV curves of the first three cycles at 0.1 mV s⁻¹; (b) first three charge/discharge profiles at a current density of 0.1 A g⁻¹; (c) charge/discharge curves at different current densities of 0.1–5.0 A g⁻¹; (d) cycling performance at 5 A g⁻¹.

Figure 6. (a) Ragone plots of LICs with different mass ratios $(m^+/m^- \text{ of } 2.0, 2.5, 3.0 \text{ and } 3.5)$; (b) galvanostatic charge–discharge curves at different current densities of 0.1–5 A g^{-1} ; (c) rate performance at various current densities of 0.05–5 A g^{-1} ; (d) cycle stability of LIC at 2.0 A g^{-1} .

around 50 Wh kg⁻¹ even at a high power density of 12.1 kW kg⁻¹. Thus, the LIC with a GPC:GC ratio of 3.0 has the best performance and is selected for further investigation in this work.

Figure 6(b) shows galvanostatic charge–discharge curves of LICs at different current densities. It should be noted that the slopes of the curves are not strictly linear especially at low current densities, illustrating that the as-prepared LICs exhibit a charge-discharge performance with the combination of a supercapacitor and a battery [21]. The result is in consistence with the CV curves in various scan rates (see figure S3), which is different from the typical symmetric supercapacitor and demonstrates a gradual deviation from the ideal rectangular shape. This phenomenon can be attributed to the synergistic effect of two different energy-storage mechanisms of cathode and anode. The LICs of dual graphene electrodes shows excellent rate capability, as shown in figure 6(c). Based on the mass of both GPC and GC, the LIC delivers a reversible capacity of 66.3 mAh g^{-1} at 0.1 A g^{-1} . Even when the current density increases to 5.0 A g⁻¹, over 65% of the capacity (43.1 mAh g⁻¹) can be obtained. Furthermore, the as assembled LIC also displays good cycling stability and high Coulombic efficiency of ~100% during the whole cycles at a high current density of 2.0 A g^{-1} . As demonstrated in figures 6(d) and S4, the all graphene-based LIC has an initial energy density of over 82 Wh kg⁻¹, and still affords a retention of ~88% after 5000 cycles (corresponding to ~0.0024% fading per cycle), which is much better than other reported LICs and demonstrates the outstanding structural stability of GPC and GC [22, 43, 44].

At last, keeping in mind the excellent energy density ranging from 142.9 to 50 Wh kg⁻¹ at the power density of 0.098–12.1 kW kg⁻¹ of the as-prepared LIC, we compared it with other reported LICs. As shown in figure 7, it could be easily concluded that the LIC GPC//GC exhibits superior electrochemical properties over various materials, including G-SU//G-LTO [24], CoS//FCS [26], CTAB – Sn(IV)@Ti₃C₂//AC [45], N-DGA//DGA/AC [46], SFAC//MCMB [47], cZIF-8//Ni/NiO/C [48], AC//graphdiyne [49], Li₃VO₄//AC [50], and NPCM-A//NPCM [51].

4. Conclusion

In summary, graphene-based materials of GPC cathode and GC anode were prepared from GO and phenolic resin via a facile hydrothermal method followed by KOH activation or direct thermal annealing, respectively. The microstructure and electrochemical performances of GPC and GC were fully investigated. Both the GPC and GC demonstrate high specific capacity, excellent rate capability and good cycling stability. LICs assembled with GPC and GC deliver a high energy density of 142.9 Wh kg⁻¹ at 95 W kg⁻¹. Even at a power density of over 12.1 kW kg⁻¹, a high energy density of 50 Wh kg⁻¹ can still be kept. In addition, the as-prepared LICs have a high cycling performance of over 88% retention after 5000 cycles. These encouraging results can be attributed to the well tunable microstructure of GPC and GC and the synergistic effect of their energy storage mechanisms.



Figure 7. Ragone plots of LIC of GPC//GC compared with other reports.

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