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ORIGINAL PAPER

Supercapacitor based on graphene and ionic liquid electrolyte

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Abstract A new kind of supercapacitor by using chemical reduced graphene (CRG) as electrode material and ionic liquid with addition of acetonitrile as electrolyte is assembled and investigated. CRG materials with high surface area are prepared by chemical reduction of graphene oxide. The capacitive properties of the supercapacitor composed of the CRG and ionic liquid electrolyte are studied by electrical impedance spectroscopy, cyclic voltammetry and galvanostatic charge–discharge. With the combined advantages of graphene and ionic liquid, the supercapacitor shows perfect performance. The supercapacitor possesses wide cell voltage and good stability. The specific capacitance, energy density, and specific power density of the present supercapacitor are 132 Fg^{-1}, 143.7 Wh kg^{-1}, and 2.8 kW kg^{-1}, respectively. The results demonstrate the potential application of electrical energy storage devices with high performance based on this new kind of supercapacitor.

Keywords Graphene · Ionic liquid · Supercapacitor

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Introduction

Supercapacitors (electrochemical capacitors), as excellent electrical energy storage devices, have attracted much attention in many advanced power devices due to the attractive characteristics of high power density, high energy density, and high cyclability [1–3]. Since the practical use of supercapacitors for the storage of electrical charge in 1957 [4, 5], more and more researches focus on improving the properties of supercapacitor for application, which can complement the deficiencies of other power sources such as fuel cells and batteries. Therefore, the search for suitable active materials and electrolytes for supercapacitors to meet the requirements of modern society and emerging ecological is an interesting and promising field of research at all the time. So far, various materials such as carbonaceous material [6, 7], metal oxide [8], conducting polymer [9], and their hybrid materials [10, 11] have been studied as active electrode materials for electrochemical capacitor. Among the different active materials investigated over the years, carbonaceous materials with a variety of forms such as carbon nanotube, carbon fiber and active carbon have been widely used and exhibit nice properties toward supercapacitor. However, the carbon-based supercapacitors have not met the higher expected performance. Recently, graphene has attracted much attention due to its fascinating physicochemical properties and potential applications [12, 13]. Until now, there are many reports that describe graphene, with one-atom thick sheet two-dimensional structure, holds an improved and competitive performance compared with other carbon-based materials [14]. Supercapacitors based on graphene materials and aqueous electrolytes have been fabricated and the remarkable results illustrated the exciting potential for high-performance and environmentally friendly electrical energy storage devices based on this new class of carbon material [5, 15].

Another factor that influences the properties of supercapacitor is the employed electrolyte. Currently, aqueous solutions have been mostly utilized [16]. However, the drawback of the aqueous electrolyte-based supercapacitor is also obvious mainly due to the narrow cell voltage and low energy [17]. Recently, ionic liquids (ILs) have attracted a great deal of attention due to their high thermal stability, good conductivity, non-flammability, suitable polarity, wide electrochemical window and recyclability [18–20]. Furthermore, the physical and chemical properties of ILs can be tuned by altering the cation, anion, and attached substituents. And also, compared to aqueous electrolytes, ILs are both 100% solvents and 100% salts. Recent research demonstrated that the performances of IL-based supercapacitors are enhanced [17].

This paper presents the applications of graphene as active material and IL as electrolyte for electrochemical capacitor, which combines the excellent natures of both graphene and IL. The main purpose of the work is to develop a new kind of supercapacitor which exhibits wide cell voltage and high energy and power densities.

Experimental

Chemicals

Nature graphite flake (99.8%) was purchased from Alfa Aesar. Concentrated H_2SO_4, $KMnO_4$, H_2O_2, hydrazine, acetonitrile and *N*,*N*-dimethylformamide (DMF) were analytical grade and provided by Sinopharm Group Chemical Reagent Co., Ltd. bmimPF_6 (>99%) was synthesized according to the method reported in the literature [21] and dehydrated at 80 °C under vacuum until the weight was constant. Double distilled water was used throughout this study.

Synthesis and characterization of CRG

Graphene oxide was prepared from graphite according to the modified Hummers' method [22] and was then dispersed in water by ultrasonication for 2 h. Hydrazine was used to reduce graphene oxide for 24 h and finally graphene was obtained by filtration and drying under vacuum. The microstructure of the synthesized CRG material was characterized by scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, TECNAI F20) and X-ray diffraction (XRD, Bruker D8 Advance Diffractometer, Cu Kα1). The N_2 adsorption analysis was measured on a Micromeritics ASAP 2020 apparatus.

Electrochemical

The graphene electrode was prepared as follows: 20 mg graphene was dispersed in 10 mL DMF and then subjected to ultrasonication for about 6 h, 5 μL of the resultant solution was placed onto the glassy carbon electrode surface (S=0.0314 cm^2) and dried. Prior to modification, the glassy carbon electrode was polished to a mirror finish using alumina powder and then was ultrasonicated in ethanol and double distilled water for 3 min respectively.

All electrochemical measurements were carried out with a CHI model 760C electrochemical workstation (Shanghai Chenhua Instrument Factory, China) in a three-electrode cell, which consisted of a CRG working electrode, a platinum counter electrode, and an Ag wire quasi-reference electrode. All potentials were measured versus the reference electrode. The electrolyte, bmimPF_6 and acetonitrile solution was purged with pure N_2 for 15 min prior to the measurements. All the electrochemical experiments were conducted at 25±1 °C which was controlled by a thermostatic bath (HH-S, Yuhua Instrument Co. China).

Results and discussion

Characterization of CRG

Graphene possesses excellent properties due to its unique structure and morphology. It is reported that graphene exhibits one-atom thick sheet two-dimensional structure with high chemical stability and electrical conductivity. Figure 1a, b shows the SEM and TEM images of the prepared CRG. These images show that the prepared CRG presents almost entirely individual or very thin sheets with a low degree of agglomeration, which is consistent with other reports [14]. To further confirm the CRG materials, Fig. 2 shows the XRD patterns of graphite, graphene oxide and CRG. It can be observed that after oxidation, the sharp diffraction peak of graphite (2θ=26.5°, corresponding to the interlayer distance d=0.336 nm) disappeared, and a new diffraction peak (2θ=11.3°) of graphene oxide appeared, indicating the entire oxidation of graphite. After the chemical reduction, the diffraction peak at 2θ=26.5°, did not reappear, and displayed an amorphous structure, which are consistent with other reports [23]. The surface area of the CRG material measured by the N_2 absorption Brunauer–Emmett–Teller method is 617 m^{2}g^{-1}. The high surface area facilitates electrolyte accessing to the CRG. Here we also have observed that the experimental value for surface area of the prepared CRG is lower than the theoretical value (about 2,600 m^2/g), which suggests that the CRG are mixture of single- or few-layered sheets. Graphene material with single- or few-layered sheets and high surface area can be

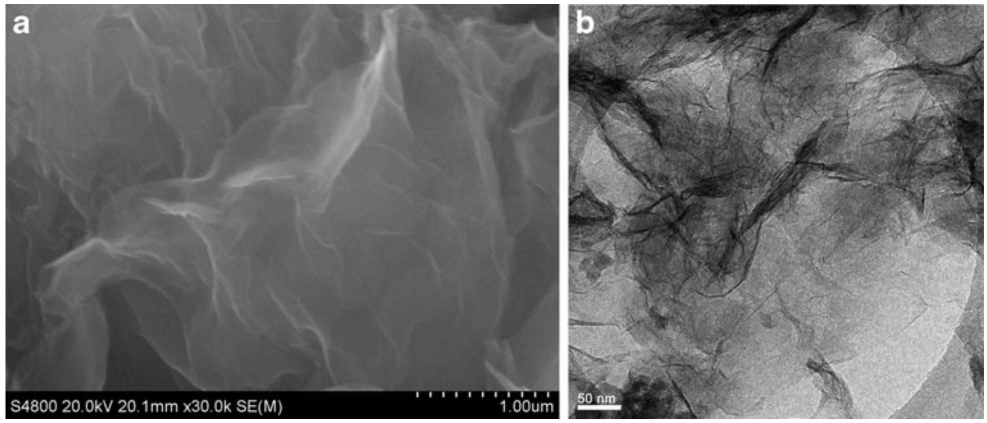

Fig. 1 SEM and TEM images of the prepared graphene

considered to offer an ideal structure and store much more charges, and thus the supercapacitor based on graphene results in excellent capacitive performance.

Electrochemical properties for supercapacitor

The electrolyte for the present supercapacitor is composed of IL. Compared with aqueous solutions, ILs have high viscosity, which is disadvantage for ions transfer. In the present paper, 25% volume ratio of acetonitrile was added into bmimPF_6 in order to decrease the viscosity and increase the ionic conductivity. Our result reveals that the specific capacitance of the graphene electrode in bmimPF_6 containing 25% acetonitrile is much higher than that in pure bmimPF_6. And also the electrochemical window of the electrolyte composed of bmimPF_6 and 25% acetonitrile still keeps relative wide about 2.8 V. Therefore, all the IL electrolytes mentioned in the present research are composed of 75% bmimPF_6 and 25% acetonitrile. The electrochemical measurements of cyclic voltammetry (CV), electrical impedance spectroscopy (EIS), and galvanostatic charge–discharge were conducted to study the performance of supercapacitor with graphene electrode in bmimPF_6 ionic liquid electrolyte.

CV is an effective method to determine the nonfaradaic behavior and evaluate the capacitance. Figure 3 shows CV curves of the CRG electrode in IL electrolyte at different scan rates varying from 10 to 60 mV s^{-1} in the potential range from −1.4 to 1.4 V. As can be seen, the CV curves at all scan rates are nearly rectangular shape which is typical for the pure capacitive characteristic, indicating the excellent capacitive behavior of the CRG electrode [3, 9]. The specific capacitance can be determined appropriately by integrating the full CV curves. Table 1 shows the specific capacitance at different scan rates, and the results reveal that the specific capacitance nearly keeps constant at all scan rates. This suggests that the graphene electrode holds high charge storage and high rate capability in IL electrolyte [17]. Furthermore, it is also necessary to

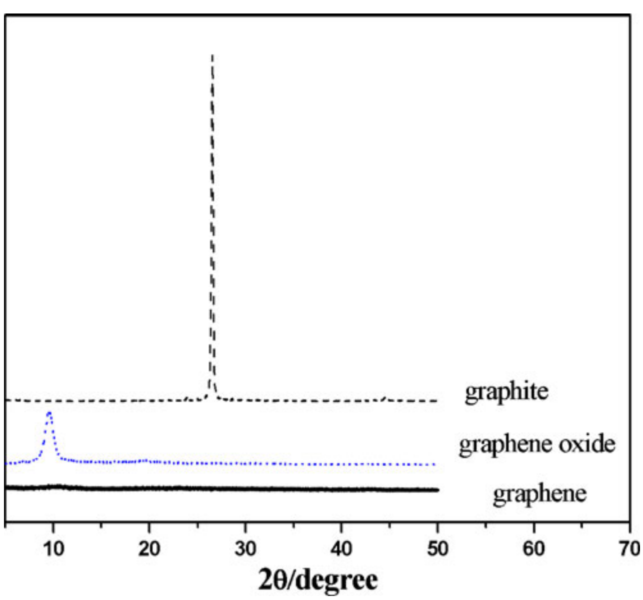

Fig. 2 XRD patterns of graphite, graphene oxide, and graphene

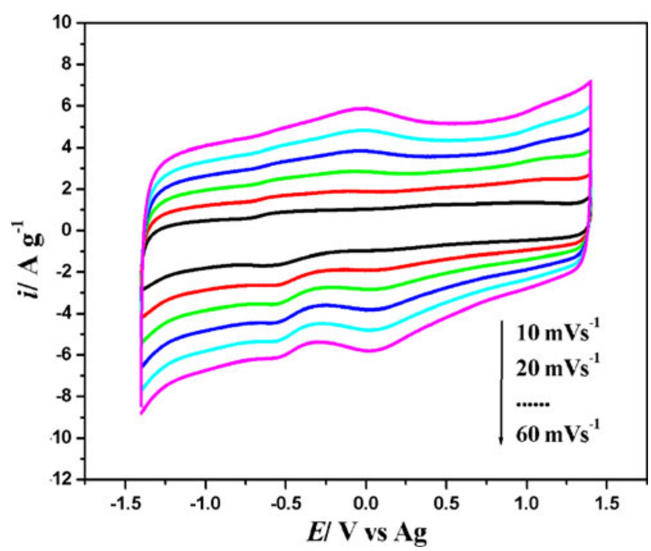

Fig. 3 CV curves of the CRG electrode in bmimPF_6 containing 25% acetonitrile at different scan rates (10, 20, 30, 40, 50, 60 mVs^{-1})

Table 1 Specific capacitance of the CRG electrode

Scan rate (mV s^{-1})	CV specific capacitance (F g^{-1})
10	118
20	115
30	112
40	111
50	110
60	108

mention that the electrochemical window is 2.8 V, which is much wider than that for aqueous electrolyte (about 1.0 V). Obviously, the wide electrochemical window can enable the capacitor possess wide cell voltage and high energy density, which is benefit to the practical application.

EIS measurement was conducted at 0.6 V with sinusoidal signal of 5 mV over the frequency range from 0.05 Hz to 100 kHz. Figure 4 shows the Nyquist plot of the CRG electrode in IL electrolyte. The Nyquist plot contains a semicircle in high frequency region and two linear sections in middle and low frequency regions. The semicircle represents the charge transfer resistance at the electrode/electrolyte interface. The linear section with the slope of 45° in the middle frequency region is related to the ion diffusion to the electrode interface [5, 11]. The third section in the low frequency region exhibits a vertical line, which demonstrates a pure capacitive behavior and represents an ideal supercapacitor [5, 24]. The result of EIS measurement indicates that the fabricated supercapacitor has good capacitive performance.

Galvanostatic charge–discharge method was also used to evaluate the capacitance behavior of the graphene electrode. Figure 5a describes the galvanostatic cycling of the CRG electrode in IL electrolyte with a potential range from −1.4 V to 1.4 V at a constant current density of 1 A g^{-1}. The curve behaves as triangular during the charge–discharge process within all the potential range, which proves that the supercapacitor has good charge–discharge reversibility and perfect capacitive behavior. The specific capacitance can be deduced from the slope of the charge–discharge curve according to the equation $C = I\Delta t/(m\Delta E)$, where I is the applied current and m is the mass of graphene [2, 8, 11]. The specific capacitance was calculated to be 132 Fg^{-1}. Long-term stability is a significant consideration for the practical application of supercapacitor. The stability of the graphene capacitor was evaluated over 1,000 consecutive charge–discharge cycles. The result in Fig. 5b shows that the specific capacitance still keeps 86% of the initial value, which

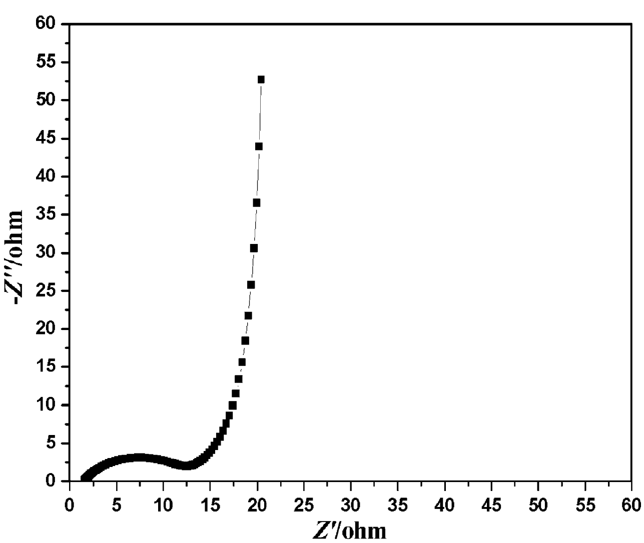

Fig. 4 Nyquist plot of the CRG electrode in bmimPF_6 containing 25% acetonitrile at 0.6 V with sinusoidal signal of 5 mV over the frequency range from 0.05 Hz to 100 kHz

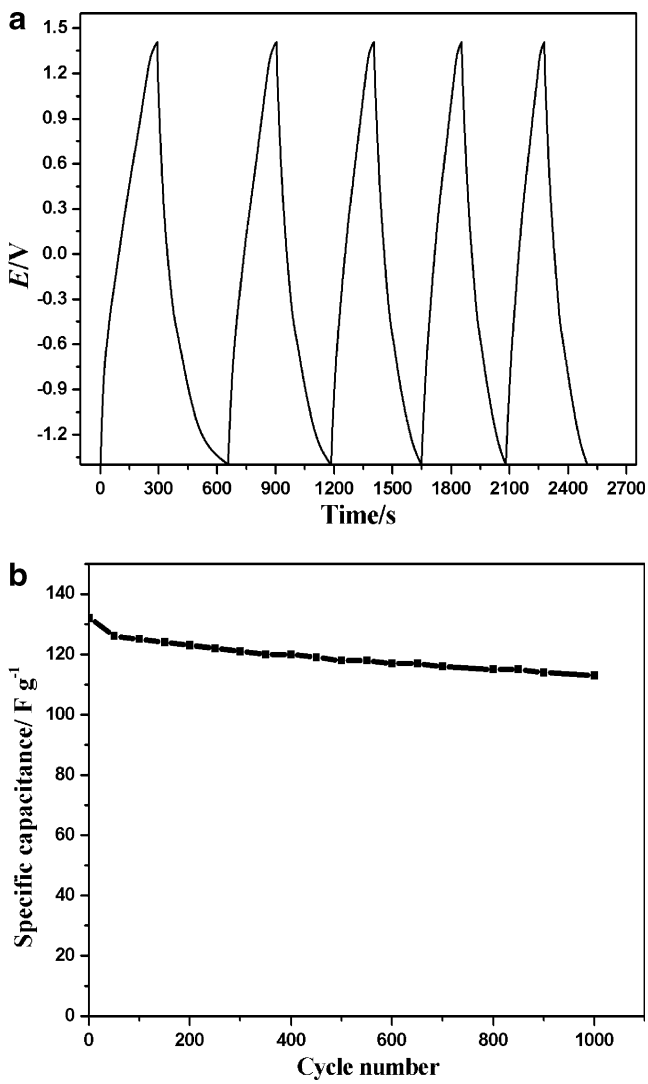

Fig. 5 **a** Galvanostatic charge–discharge curve of the CRG electrode in bmimPF_6 containing 25% acetonitrile at a constant current density of 1 A g^{-1}, **b** The specific capacitance change at a constant current density of 1 A g^{-1} as a function of cycle number

indicates that the supercapacitor has high stability for practical application.

The energy density (E) and specific power density (P) of the present supercapacitor can be calculated by employing the equation: $E = (CU^2)/2$ and $P = IU/m$ respectively, where C is capacitance, U is cell voltage [8, 17]. One advantage of IL as electrolyte is the wide electrochemical window, which enables the supercapacitor possess high cell voltage. Given the ideas that the energy density of an electrochemical capacitor is directly proportional to the square of its cell voltage and the specific power density is proportional to its cell voltage, the use of IL electrolyte would greatly improve the performance of the graphene supercapacitor. The energy density and specific power density of the present supercapacitor were calculated to be 143.7 and 2.8 kW kg^{-1}, respectively.

Conclusions

The supercapacitor using the CRG material and ionic liquid with addition of 25% (*v*/*v*) acetonitrile as electrolyte was fabricated and investigated in the present research. The results show that graphene is one of the most suitable carbon materials for supercapacitor and IL electrolyte with wide electrochemical window can greatly enhance energy density and specific power density. The specific capacitance, energy density and specific power density of the present supercapacitor is 132 Fg^{-1}, 143.7 Wh kg^{-1}, and 2.8 kW kg^{-1} respectively. Furthermore, the supercapacitor has wide cell voltage and good stability. It's believed that graphene-based material and ionic liquid with addition of acetonitrile electrolyte will lead to the development of high-performance supercapacitors.

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