Capacitance properties of composite electrodes prepared by electrochemical polymerization of pyrrole on carbon foam in aqueous solution

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Abstract

The polypyrrole/carbon foam composite electrodes for electrochemical capacitors were fabricated by electrochemical polymerization of pyrrole in aqueous solution on the carbon foam, which prepared by carbonization of polyacrylonitrile membranes supported by carbon papers. The carbon foams were characterized with FTIR, SEM and the Brunauer–Emmett–Teller technique. The electrical capacitance of the composite electrodes was investigated with cyclic voltammetry (CV). The prototypes of electrochemical capacitors composed with polypyrrole/carbon foam electrodes were tested with ac impedance spectroscopy and chronopotentiometry technique. The dependence of specific power and specific energy on conditions of electrochemical polymerization of pyrrole was studied. Based on total weight of the electrodes in a prototype electrochemical capacitor, energy density could reach 2.5 Wh/kg. All results showed that polypyrrole/carbon foam composite materials had good potential applications in electrochemical capacitors.
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1. Introduction

Electrochemical capacitors are new kinds of electrical components which have many applications in electrical vehicles, satellites and other electrical devices [1–3]. Research workers in the world have been paid more and more attention on electrochemical capacitors [4,5].

Three types of electrochemical capacitors based on conducting polymers were classified and explained by Rudge et al. [6]. From 1980s, several research groups are engaged in this area [7–13]. Some conducting polymers having rapidly reversible doping/dedoping ability, such as polypyrrole, polythiophene and polyaniline and their derivatives, have potential application in electrochemical capacitors. Among them polypyrrole has good stability in ambient condition. It can be prepared by chemical oxidization and electrochemical oxidization in aqueous solution or non aqueous solution. So lots of researchers did research work on electrochemical capacitors with polypyrrole [14–16]. Their work focused on two aspects: how

to polymerize pyrrole properly by chemical oxidation or electrochemical method, how to use carbon materials for fabricating electrodes of electrochemical capacitors with polypyrrole. Carbon paper having a relatively low specific surface and no electrical capacitance is an ordinary material used as electrodes in electrochemical polymerization of polypyrrole. Carbon nanotubes as a new kind of carbon materials used as electrodes with polypyrrole in electrochemical capacitors cause many researchers' attentions [17,18]. Up to now, fabricating and purifying carbon nanotubes in large amount are still a question in the word.

On the other hand, polyacrylonitrile (PAN) as a raw material for making carbon fibers also can be used for preparing porous membranes, which can be used in purifying water or as solid electrolytes in lithium ion batteries. Several workers [19] prepared carbon foam by carbonizing the porous membranes of PAN and found that foam having relatively high specific capacitance in aqueous solution of H_2SO_4 or KOH. In this paper, the γ-ray irradiation process was added before the carbonization and activation of PAN porous membranes for making better carbon foam. The resulted carbon foams were used as electrodes in polymerization of polypyrrole in aqueous solution of $LiClO_4$. Several prototypes of

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electrochemical capacitors composed of polypyrrole/carbon foam (PPy/carbon foam) electrodes were tested by chronopotentiometry technique.

2. Experimental

Pyrrole, purchased from Acros Organics, was used directly. PAN was kindly provided by Professor Chen Cuixian, Department of Chemical Engineering, Tsinghua University. Carbon paper, $20 \, g/m^2$, was purchased from Kai Feng Tong Ye Fiber Composite Co., Ltd., Kai Feng city, Henan province. Dimethyl sulfoxide (DMSO), analytical purity, was purchased from No. 1 factory of Tianjin Chemical Regent Company. Lithium perchlorate ($LiClO_4$), Beijing Bali Chemical Developing Center. Manila paper was kindly offered by Beijing electronic Components Factory No. 10.

The porous PAN membrane with carbon paper was prepared by a phase inversion method. For example, 1.5 g PAN was dissolved in 30 ml DMSO, and cast the solution on a sheet of carbon paper. The sheet with cast solution layer was placed in a sealed half-filled water box with 50–60 °C for about 2 h, then immersed the composite sheet in ethanol overnight. It followed γ-ray irradiation with certain dose, carbonization at 850 °C for 2 h, and activation by CO_2 at 850 °C for 1 h to form the carbon foam. Details of its fabrication were described in another paper [20]. The carbon foam can be used as an electrode in electrochemical polymerization of pyrrole.

Polypyrrole/carbon foam electrodes were prepared by electrochemical polymerization of pyrrole in a three-electrode cell. A sheet of carbon foam with 10 mm length and 8 mm width was immersed in 0.2 M $LiClO_4$–0.1 M monomer aqueous solution as a work electrode; the counter electrode was a Pt sheet having the same area; the reference was Ag/AgCl. In order to avoid the side effect of oxygen in water, the three-electrode cell was bubbled with nitrogen for about 10 min before every time of electrochemical polymerization or other electrochemical experiments.

All electrochemical experiments were performed using a type of CHI660a electrochemical workstation (Shanghai Chenhua Instruments Company). The voltammetry measurements were performed in 0.2 M $LiClO_4$ aqueous solution without pyrrole monomer.

Two sheets of PPy/carbon foam separated with a sheet of manila paper were encapsulated in a stainless button with a diameter of ~10 mm to form the prototype of electrochemical capacitors. The electrolyte was 1 M $LiClO_4$ aqueous solution.

The morphology of the resulted PPy/carbon foam was observed with SEM of JSM-6301F at acceleration voltage of 5 kV. BET specific surface area was determined using a computer-controlled automatic porosimeter (Micromeritics ASAP2010). The carrier gas was helium and the adsorbed gas was pre-purified nitrogen.

The change of chemical structure of PPy/carbon foam composite was characterized with FTIR spectroscope of Nicolet 560.

3. Results and discussion

The surface morphology of the resulted carbon foam material was shown in Fig. 1. Several cracks were observed in surface of the carbon foam. Blocks of carbon foam are connected together through carbon fibers. It means that the cast solution was penetrated into the carbon paper, and that the resulted carbon foam is a monolithic sheet with a carbon fiber framework but not a sheet with two layers. The carbon fibers framework provides the carbon foam having good electrical conductivity and enough mechanical strength. Fig. 2 is an enlargement of one block in Fig. 1. The pores with micrometer scale are connected each other in the carbon foam. It implies that its specific surface is very large. It is confirmed by measured BET specific surface of $\sim290 \, m^2/g$. This kind of structure is appropriate for migrate of electrolyte and beneficial to store electrical energy according to theory of electrical double layer.
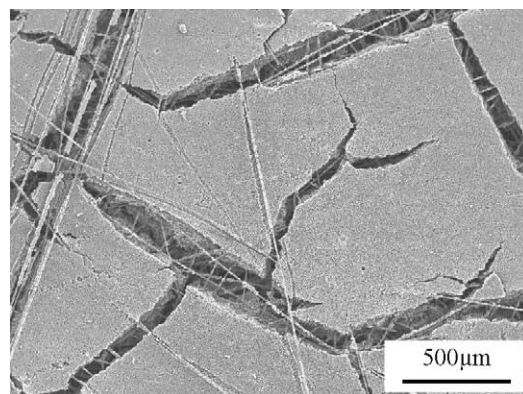

Fig. 1. A SEM micrograph of the resulted carbon foam based on cross-linked PAN supported by carbon paper.
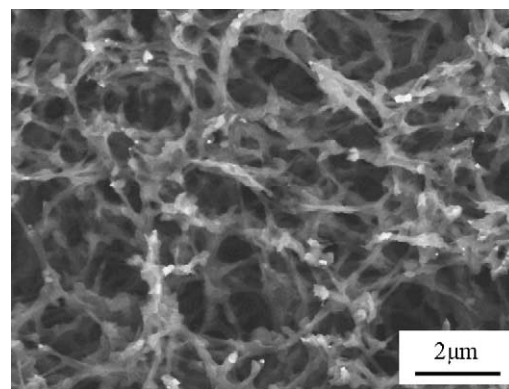

Fig. 2. A SEM micrograph of the resulted carbon foam based on cross-linked PAN with activation by CO_2 at high temperature for 1 h.
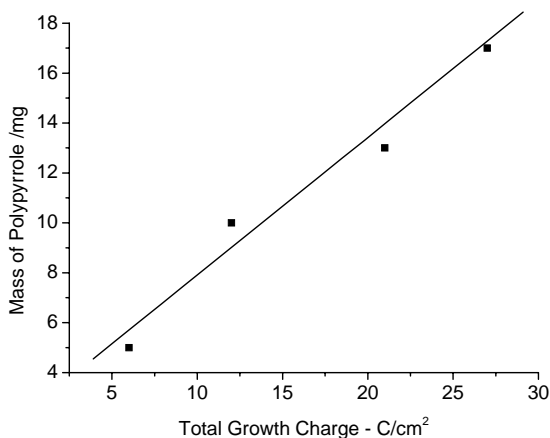
Fig. 3. Dependence of the mass of electrodeposited polymer on total charge passed during galvanostatic growth of polypyrrole from a solution of 0.1 M monomer, 0.2 M LiClO$_4$ in water.
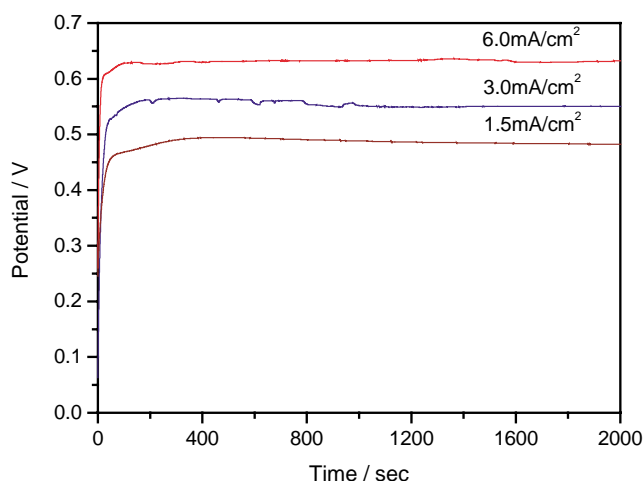

Fig. 4. Dependence of the potential of polymerization on the current density during galvanostatic growth of polypyrrole from a solution of 0.1 M monomer, 0.2 M LiClO$_4$ in water.

We had reported this kind carbon foam material could be used as electrodes of electrochemical capacitors in aqueous solutions [20]. In this paper, we used this carbon foam as working electrodes for electrochemical polymerization of pyrrole in 0.2 M LiClO$_4$ aqueous solution at room temperature. From Fig. 3, we found that the quantity of polypyrrole on the carbon foam electrodes was a linear function of growth charge of polymerization. And the potential of polymerization increases with the current density from 1.5 to 6.0 mA/cm^2, presented in Fig. 4. FTIR spectrum was shown in Fig. 5. Two characteristic absorption bands of 1165 and 1295 cm^{-1} are present in the spectrum for the composite electrode [21,22], and indicate that polypyrrole had deposited on the carbon foam electrodes.

Morphologies of PPy/carbon foam electrodes with different growth charges of polymerization were presented in Figs. 6 and 7. Compared with morphology of carbon foam electrode in Fig. 2, it is obvious that the netting fibrils be-

came thicker and coarser as polypyrrole deposited on. Some granular polypyrrole also appeared in those SEM micrographs. With the growth charge of polymerization accumulated to 27 C/cm^2, some polypyrrole domains deposited on the netting fibrils were connected each other, as shown in Fig. 6. Specific surface area of the PPy/carbon foam composite electrodes would reduce with spacing decrease. It results in decreasing the surface area of polypyrrole domain contacted with electrolyte. That is a disadvantage for store electrical energy. But on the other hand, there is unobvious difference in morphology of PPy/carbon foam composite polymerized from different current densities (Figs. 7–9).

In order to evaluate performance of PPy/carbon foam composite electrodes used in electrochemical capacitors, cyclic voltammetry test in 0.2 M LiClO$_4$ aqueous solution was carried out. The amount of growth charges of
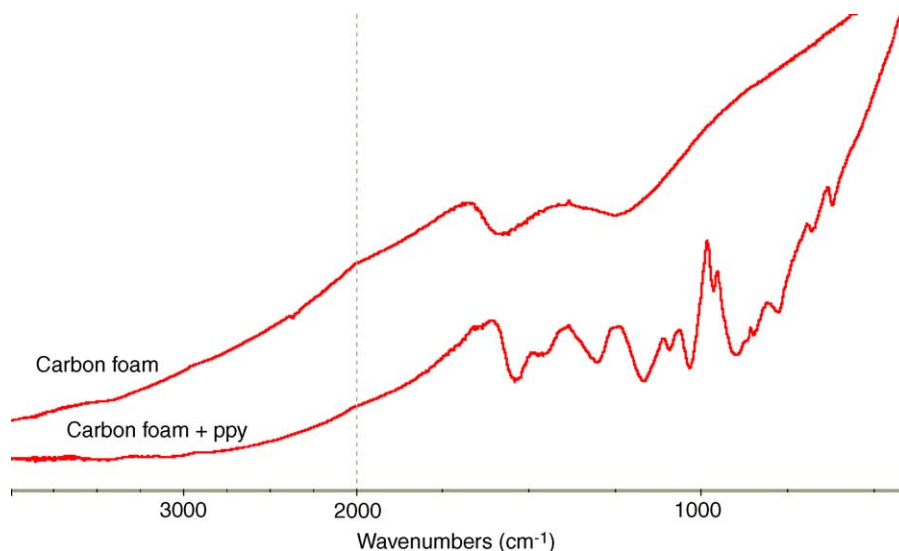

Fig. 5. Infrared spectra of carbon foam/polypyrrole composite sample sintered with KBr.
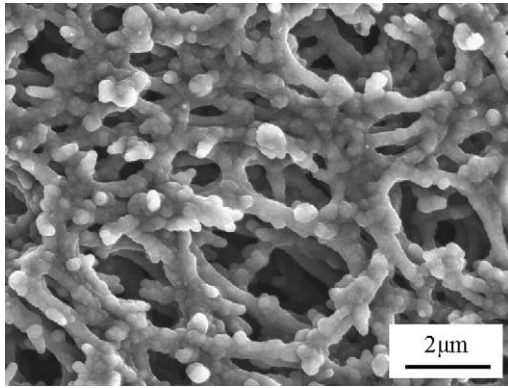
Fig. 6. A SEM micrograph of carbon foam/polypyrrole composite electrodes fabricated by galvanostatic method with total charge of $27\,C/cm^2$ and the current density of $1.5\,mA/cm^2$ for its polymerization in $0.1\,M$ pyrrole–$0.2\,M$ LiClO$_4$ aqueous solution.

Fig. 8. A SEM micrograph of carbon foam/polypyrrole composite electrodes fabricated by galvanostatic method with total charge of $12\,C/cm^2$ and the current density of $3.0\,mA/cm^2$ for its polymerization in $0.1\,M$ pyrrole–$0.2\,M$ LiClO$_4$ aqueous solution.

Fig. 9. A SEM micrograph of carbon foam/polypyrrole composite electrodes fabricated by galvanostatic method with total charge of $12\,C/cm^2$ and the current density of $6.0\,mA/cm^2$ for its polymerization in $0.1\,M$ pyrrole–$0.2\,M$ LiClO$_4$ aqueous solution.

polypyrrole polymerization has great effect on the shape of cyclic voltammetry curves, as presented in Fig. 10. The shape of cyclic voltammetry curves shows a prolate rectangle when bare carbon foam electrode was used. That indicates the bare carbon foam has some electrical double layer capacitance in $0.2\,M$ LiClO$_4$ aqueous solution due to its relatively high specific surface area. With polypyrrole increasing in the composite electrodes, the area encased by cyclic voltammetry curves augments rapidly. That is because pseudofaradaic capacitance of polypyrrole increases with the amount of polypyrrole. On the other hand, the shape of the cyclic voltammetry curves changes remarkably with the growth charge increasing. That is because the resistance of this system increased. As shown in Fig. 6, with the amount of growth charge increasing, thickness of polypyrrole on the surface of the netting fibrils increases. The ac impedance spectrum of prototype capacitor composed of the PPy/carbon foam composite electrodes with 12 and $27\,C/cm^2$ total growth charges (Fig. 11) provides another data to prove the above explanation. The prototype capacitor, which composite electrodes with $27\,C/cm^2$
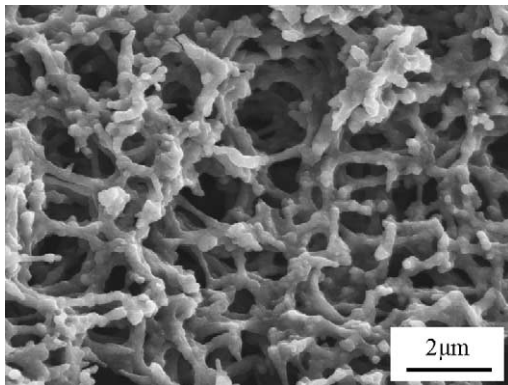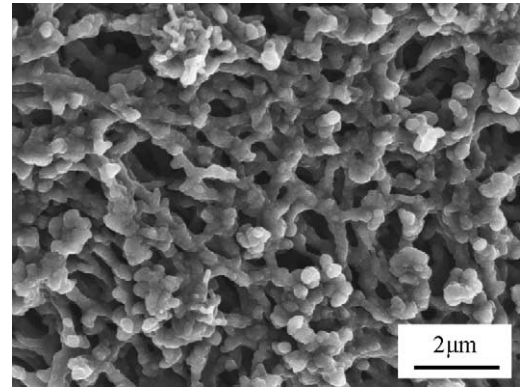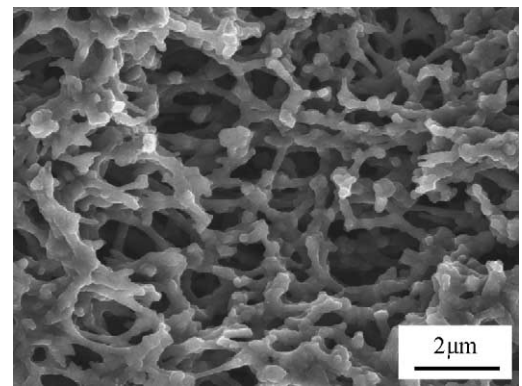

Fig. 7. A SEM micrograph of carbon foam/polypyrrole composite electrodes fabricated by galvanostatic method with total charge of $12\,C/cm^2$ and the current density of $1.5\,mA/cm^2$ for its polymerization in $0.1\,M$ pyrrole–$0.2\,M$ LiClO$_4$ aqueous solution.

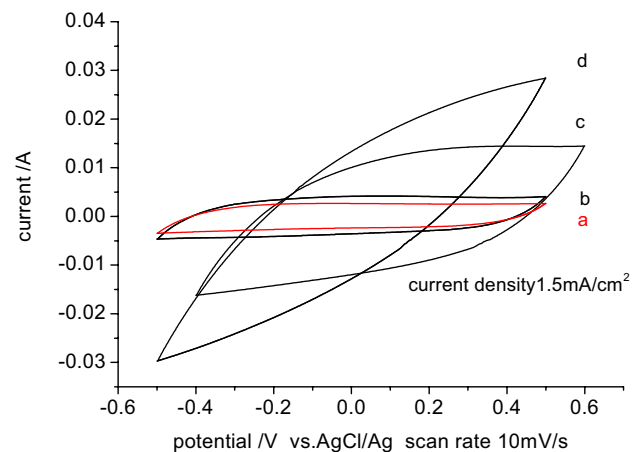

Fig. 10. Cyclic voltammograms of carbon foam/polypyrrole composite electrodes in a three-electrode cell configuration in $0.2\,M$ LiClO$_4$ aqueous solution with scan rate of $10\,mV/s$: (a) a bare carbon foam electrode; (b) a carbon foam electrode with total charge of $6\,C/cm^2$; (c) a carbon foam electrode with total charge of $12\,C/cm^2$; (d) a carbon foam electrode with total charge of $27\,C/cm^2$.
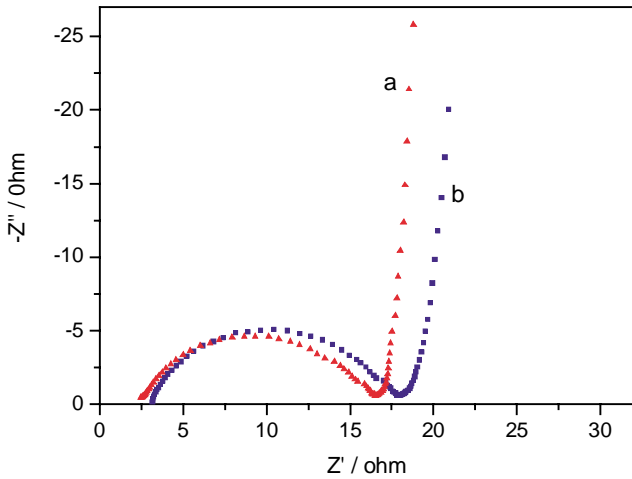
Fig. 11. The ac impedance spectra of the prototype capacitors composed of carbon foam/polypyrrole composite electrodes separated by a sheet manila paper. (a) Total charge for each carbon foam/polypyrrole composite electrodes is $12\,C/cm^2$; (b) total charge for each carbon foam/polypyrrole composite electrodes is $27\,C/cm^2$ current density: $1.5\,mA/cm^2$.

growth charge, shows relatively high resistivity in its spectrum.

Chronopotentiometry technique is an important method for determining capacitance of a prototype electrochemical capacitor. A typical curve of charge/discharge at $1.25\,mA/cm^2$ for the capacitor constructed with polypyrrole/carbon foam composite electrodes was presented in Fig. 12. It is a typical discharge curve of Type I electrochemical capacitor defined by Rudge et al. [6]. For the prototype capacitor composed of carbon foam coated by polypyrrole at $27\,C/cm^2$, a series of discharge curves at different discharge rates in the range of $1–8\,mA/cm^2$ is shown in Fig. 13. From these discharge curves, the relationship between power density and energy density was obtained.
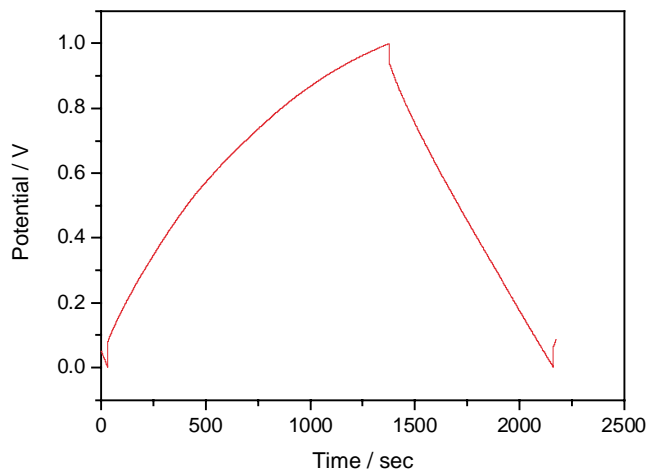

Fig. 12. A typical galvanic charge/discharge cycle of a prototype capacitor between 0 and $1.0\,V$ at current density of $1.25\,mA/cm^2$ carbon foam/polypyrrole composite electrodes each with $27\,C/cm^2$ growth charge at current density of $1.5\,mA/cm^2$ for its polymerization.
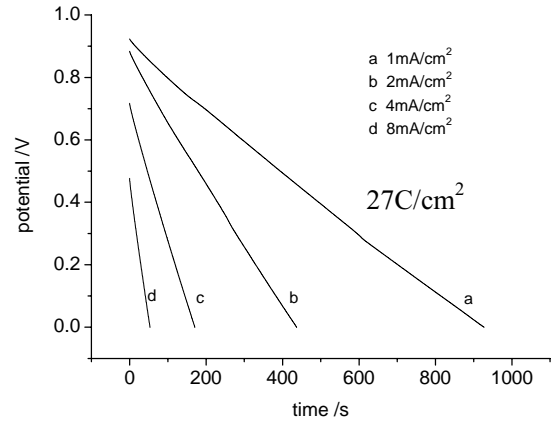

Fig. 13. Potential vs. discharge curves obtained for a prototype capacitor based on carbon foam/polypyrrole composite electrodes each with growth charge of $27\,C/cm^2$.

The power density and energy density of the prototype capacitors were calculated as the value per unit mass of polypyrrole. Deposited charge on carbon foam electrodes has great influence on the relation of power density and energy density. When deposited charge is about $27\,C/cm^2$, a capacitor has a highest energy density of about $5.3\,Wh/kg$, while the power density is the lowest among them as shown in Fig. 14. Current density used for pyrrole polymerization in $0.2\,M$ $LiClO_4$ aqueous solution has some effect on the relationship of power density versus energy density. Higher current density used in polymerization of pyrrole could be favorable to get high energy density. The carbon foam electrodes as presented in this paper have certain double layer capacitance because of their high specific surface. PPy/carbon foam composite electrodes fabricated by electrochemical polymerization of pyrrole also have a relatively high specific surface presented from Figs. 6–9. So the capacitance of the prototype capacitor is including two parts:
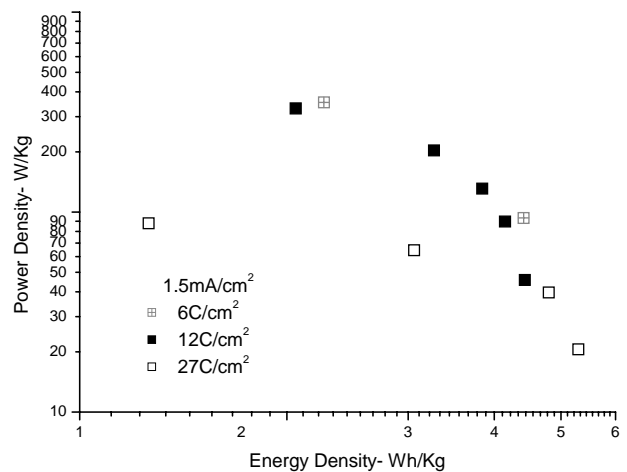

Fig. 14. Plots of power density vs. energy density for different growth charge. Calculation based on the weight of polypyrrole. Current density of polymerization: $1.5\,mA/cm^2$.
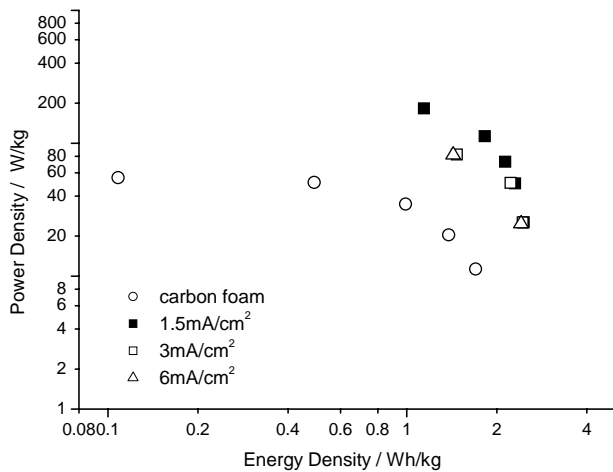
Fig. 15. Plots of power density vs. energy density for different current density in polymerization. Calculation based on the all weight of carbon foam/polypyrrole composite electrodes. Total growth charge of polymerization: $12\,C/cm^2$.

Fig. 17. Plots of power density vs. energy density for different current density in polymerization. Calculation based on the weight of polypyrrole. Total growth charge of polymerization: $12\,C/cm^2$.

double layer capacitance based on the carbon foam and pseudocapacitance based on deposited polypyrrole.

General speaking, the power density and energy density are calculated with the total weight of electrodes. In $12\,C/cm^2$ growth charge case, the calculated energy density of the capacitor could reach 2.5 Wh/kg. The plots of power density versus energy density of the prototype capacitors presented in Figs. 15 and 16 were calculated based on the total weight of electrodes. The trends of power density and energy density are not the same as that in Figs. 14 and 17. In order to get a good performance of a capacitor, the deposited charge should be adjusted to a certain range. If the amount of deposited charge were too small, power density and energy density of the composite electrodes would be at a low level because weight of carbon foam possessed a great percent in that of the total electrode. On the other hand, when the amount of deposited charge was too large, they

would be decreased due to the collapse of pores. The prototype capacitor consisting of the PPy/carbon foam composite electrodes had higher power density and energy density compared with that of the bare carbon foam electrodes.

4. Conclusions

A new kind of carbon foam materials can be prepared by carbonization and activation of PAN membrane supported by carbon paper. The carbon foams have certain electrical double layer capacitance and can be used as electrodes for electrochemical polymerization. Polypyrrole/carbon foam composite can be directly used as electrodes of prototype capacitors, and shows good potential application in electrochemical capacitors.
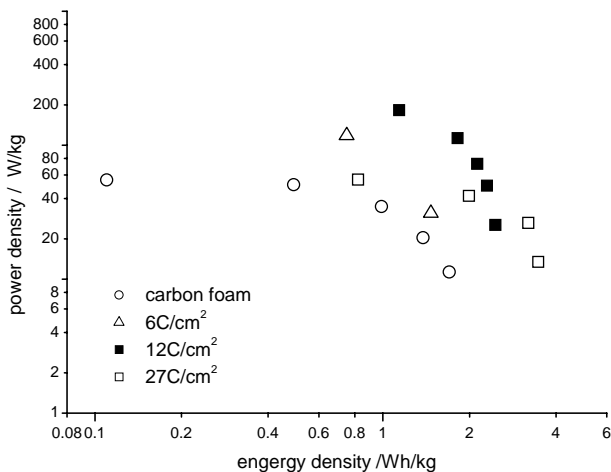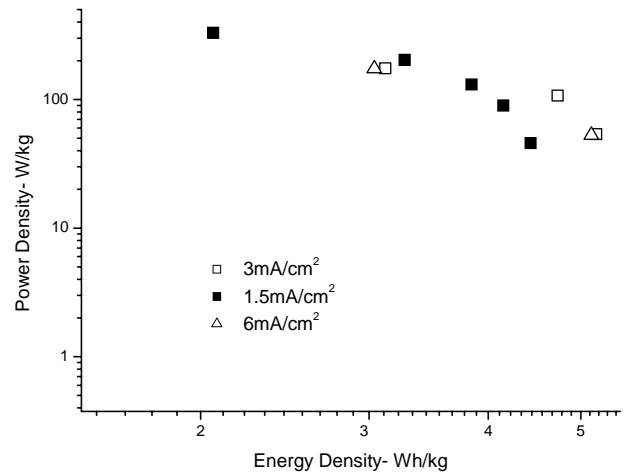
Fig. 16. Plots of power density vs. energy density for different growth charge. Calculation based on the all weight of carbon foam/polypyrrole composite electrodes. Current density of polymerization: $1.5\,mA/cm^2$.

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