DEVELOPMENT OF ACTIVATED CARBON NANOFIBER ELECTRODE MATERIALS FOR SUPERCAPACITORS

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Introduction

Supercapacitors are electrochemical energy storage devices. They have higher power density than batteries and higher energy density than dielectric capacitors [1]. The energy in supercapacitors is stored in the form of charge separation at the interface of a high surface area electrode material and electrolyte [2]. The unique positions of supercapacitors in terms of power and energy density make them useful in conjunction with batteries in hybrid electric vehicles apart from the back-up memory application. High surface area carbon based electrode materials have a pivotal role in increasing the energy storage capacity for the upcoming applications in hybrid electric vehicles. High energy storage activated carbon electrodes can be produced via thermal processing of electrospun polymer nanofibers. Nanofibers offer considerable design flexibility in terms of accessibility of pores for electrochemical reaction at the surface. The advantage of electrospun activated carbon nanofibers is that they can be produced in a sheet form directly thereby eliminating the use of binder that is commonly used in carbon powder based electrode manufacturing technology. From commercial point of view, high surface to mass ratio of nanofibers reduces the amount of material required leading to the lower production cost of supercapacitors.

Experimental

Activated carbon nanofibers (ACnF) were produced from three different polymer nanofiber webs via thermal processing. The precursor polymer nanofibers were producing by electrospinning technique. The electrospun polymer nanofibers were characterized for fiber diameter and subjected to stabilization, carbonization and activation to prepare ACnF. The stabilization process was carried out in an oxygen-rich environment with temperature range of 150 – 300^{o}C. Once the polymer nanofiber webs were stabilized, they were subjected to carbonization at 800^{o}C in N_2 environment and activated in CO_2 or steam environment.

Porosity of ACnF material was characterized using gas sorption analysis using nitrogen gas. Specifically, surface area, average pore size, pores size distribution and total pore volumes were obtained using BET method. Electrochemical characteristics of ACnFs were derived by constructing them in a CR2032 coin cell. The coin cell consists of two identical ACnF electrodes separated by a separator. CR2032 coin cell supercapacitors were fabricated in a N_2 filled mBraun® glove box using a crimper (Hohsen Corp., Japan). Activated carbon mats were punched and used as electrodes with an area of 1 cm^2 each. The electrolyte consisted of tetraethylammonium tetrafluoroborate salt dissolved in a high purity acetonitrile solvent up to 1.4 M concentration.

The specific capacitance (F/g) and equivalent series resistance (ESR) of CR2032 coin cell supercapacitors were measured using constant current charge - discharge method. The capacitor was charged to 2.5 V and given rest time of 15 sec and discharged to 1 V. Data from the third cycle was used to calculate specific capacitance (discharge cycle), and ESR was calculated from voltage drop during the 15 sec rest time after the charging cycle. Charge-discharge experiments were performed using Arbin Electrochemical workstation. The coin cells were also characterized for shelf life, cycle life (sp. capacitance vs. no. of cycles) and constant power discharge (Ragone plot).

Results and Discussion

The surface areas along with activation time of three ACnFs processed from three different polymer precursor nanofibers are presented in Table 1. It can be seen from the table, the development of pore structure is strongly dependent on the precursor source. In case of ACnF derived from polymer nanofiber B, just 30 minutes of activation time was enough to get a surface area of 1058 m^2/g. The specific capacitance (F/g), ESR and energy density of ACnFs is also presented in the table. As can be observed from the table, ACnF derived from polymer precursor 'C' (ACnF-C) has showed highest specific capacitance, energy density and lowest ESR among other ACnFs. The data from the table also indicates that the specific capacitance is not directly proportional to the surface area but it is strongly depends on the nature of the precursor for the ACnF.

Table 1. Surface areas and activation times (activating agent – CO_2) of three ACnFs, Specific capacitance, ESR and Energy density of ACnFs in CR2032 cell. (* measured based on both electrodes weight). [Acetonitrile was the solvent]

ACnF precursor polymer nF	Activation Time	Surface area (m^2/g)	C * (F/g)	ESR (ohm)	E * (Wh/kg)
A	8 hrs	1528	22	52	16.16
B	30 min	1058	21	172	15.43
C	12 hrs	1410	31.5	14	27.34

Figure 1 shows the constant current charge discharge curve of CR2032 cell comprised of ACnF-C material. As can be observed from the charge-discharge curve, it depicts the ideal capacitor characteristics (inverted triangle) of the electrode material. The activated carbon nanofibers yielded a specific capacitance of 31.5 F/g, calculated from the slope of the discharge curve. One more important feature of this material is that the charge/discharge time efficiency was 0.99, a characteristic of ideality of the ACnF-C electrode. The energy density of the cell was calculated based on the weight of the both activated carbon electrodes and it is 27 Wh/kg.

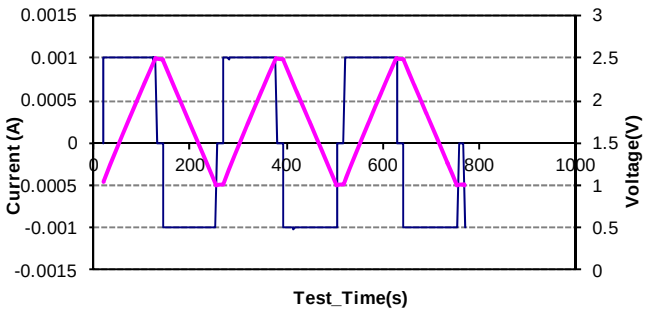

Fig. 1 Constant current (1mA) charge/discharge curves of CR2032 cell comprising of ACnF-C electrode material

Since the ideal capacitance characteristics were observed in ACnF-C electrode material, it was further tested for shelf discharge, cycle life and constant power discharge studies.

Shelf life is important in real world applications where capacitor will be charged and left alone before it is reused. In hybrid electric vehicles, supercapacitors are used for acceleration and absorbing breaking energy. Breaking energy is stored in the capacitor as capacitive energy. This energy is stored until it is reutilized for acceleration of the vehicle. During storage, capacitors should have a very low leakage current. If the leakage current is very high, the stored energy cannot be used effectively. The ability of a capacitor to store energy is measured by shelf discharge. To test for shelf life, the capacitor is charged to maximum voltage and then the voltage of the capacitor is monitored under zero current. The lower the voltage drop, the better the energy-storing capacity of the capacitor. The shelf discharge studies were conducted on CR2032 cells by charging to 2.5 V at 1 mA current and the floating voltage was measured for 16 hours. ACnF-C electrode material displayed remarkable voltage retention, voltage dropped by just 0.45 V (18% of the maximum voltage) after 16 hours.

Long term cycle life studies were performed on CR2032 coin cells fabricated from ACnF-C electrode material by subjected them to many charge/discharge cycles to determine the stability of capacitance as a function of cycling. The capacitance was remarkably stable over several hundred cycles (just 3% loss of specific capacitance over 1200 cycles). This means that ACnF-C based capacitor can deliver constant power and energy for the long term. This is particularly very important for hybrid electric vehicle applications where a capacitor will be expected to undergo many charge-discharge cycles.

ACnF-C electrode material in CR2032 cell was subjected to constant power discharge tests and the results were plotted as Ragone plot. As noted earlier, the energy stored by ACnF-C material was calculated to be 27 Wh/kg, however, the energy delivered will be a little less due to the resistance of the capacitor and also practical devices do not work at low capacitor voltage. Hence CR2032 capacitor cells were discharged at constant power until the voltage falls to 1V (i.e. from 2.5V to 1.0 V). Constant power tests were performed at different power levels (1 – 75 mW) and Ragone plot is generated energy density as a function of power density. The plot gives the available energy at a certain power density. ACnF-C electrode material provides energy density of 22.8 Wh/kg at a power density of 421 W/kg and provides energy density of 18.4 Wh/kg at a power density of 31.6 kW/kg.

Conclusions

Activated carbon nanofiber mats were prepared by thermally processing of three different electrospun polymer precursor nanofiber mats. The activated carbon nanofiber characteristics such as fiber diameter, surface area, total pore volume and average pore size were determined. The specific capacitance, ESR, and energy density of ACnF mats were determined in a CR2032 coin cell configuration. ACnF derived from polymer precursor 'C' showed highest capacitance (31.5 F/g) and lowest ESR (14 Ω). The ACnF-C was further tested for shelf life, cycle life and constant power discharge (Ragone plot). The ACnF-C electrode material showed energy density of 18.4 Wh/kg at power density of 31.6 kW/kg. It also showed remarkable capacity retention over several hundred cycles, good shelf life and charge/discharge efficiency.

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References

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