

HIGH FREQUENCY BEHAVIOUR OF MICROPOROUS CARBONS IN SUPERCAPACITORS

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Abstract

Polyfurfuryl alcohol (PFA) derived carbons can be prepared with controllable microporosity via chemical activation. Activated carbons with apparent BET surface areas ranging from 1070 to 2600 m^2g^{-1} , and corresponding average micropore sizes between 0.6 and 1.6 nm were obtained. High specific capacitance values (150 F g^{-1} at 2.5 V) were obtained using microporous carbons with a L_0 of 1.6 nm and tetraethylammonium tetrafluoroborate as electrolyte. The carbon obtained also displayed an outstanding performance at high current densities delivering up to 100 F g^{-1} at current densities as high as 250 A g^{-1} and 10 Hz.

Introduction

Carbon based electric double layer capacitors, EDLCs, are ideal systems for providing quick bursts of energy. They can be configured in a variety of cell shapes/sizes and assembled into modules to meet the power, energy, and voltage requirements for many specific applications. The major markets where supercapacitors will find their properties better suited to are: industrial power management, consumer electronics and automotive. For the later market, supercapacitors would act as a load-leveling device in combination with batteries in electric and hybrid vehicles (EV's and HEV's, respectively). By developing small high-frequency devices the size of the battery can be significantly reduced. Some studies have revealed a fuel consumption reduction of 15-20 % by adopting a supercapacitor / battery combination [1].

Experimental

The synthesis of Polyfurfuryl alcohol (PFA) has been described elsewhere [2]. Resins derived from furfuryl alcohol (FA) undergo polycondensation under the action of an acidic catalyst which leads to a highly cross-linked black viscous product [3]. The resultant polymer was chemically activated by using KOH as activating agent. PFA was mixed with potassium hydroxide in proportions of: 1:1, 2:1, 2.5:1 or 3:1 parts KOH : PFA-precursor. The mixture was then placed in a crucible and heat treated at 700 °C for 1h, under a N_2 flow (90 ml min^{-1}). The product was neutralized with HCl (reflux, 1h) and thoroughly washed with distilled water until $\text{pH}=7$. The resultant activated carbons were labeled PFA-KX, where X refers to the amount of chemical agent used.

Physical adsorption of nitrogen at 77 K and carbon dioxide at 273 K were performed on a *Micromeritics ASAP 2010* analyser.

Two electrode devices were assembled in laminated pouch-type cells (electrode size: 2.5 cm x 2.5 cm). Carbon coated aluminium collectors (30 μm thick) were utilized as electrodes. The composition of the electrodes carbon coating was: AC, carbon black and carboxymethylcellulose (CMC) binder in a proportion 1 : 0.2 : 0. A 25 μm polypropylene separator was utilised as a separator and a solution of 1M tetraethyl ammonium tetrafluoroborate in acetonitrile was used as electrolyte. Electrochemical testing was performed on a *Solatron 1255B* electrochemical analyser equipped with a 1470 multi channel battery test module. Galvanostatic cycling of the supercapacitors was carried out between 0-2.5 V at current densities ranging from 0.30-225 A g^{-1} . Electrochemical impedance spectroscopy measurements were undertaken in order to study the resistance of the carbon-electrodes in the frequency range of 10 mHz-100 kHz with an AC amplitude of 10 mV.

Results and Discussion

The chemical activation of PFA leads to the formation of highly microporous activated carbons displaying distinctive type I isotherms (Figure 1).

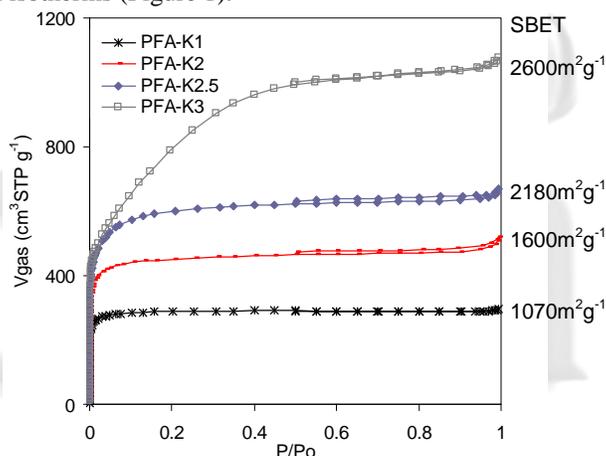


Fig. 1 $\text{N}_2/77$ K adsorption isotherms.

When a KOH to PFA ratio of 1:1 is used, a highly microporous material is obtained with a BET area of 1070 m^2g^{-1} and a very narrow, and uniform, average micropore size; $L_0 \sim 0.6$ nm. An increase in the amount of chemical agent leads to a broadening of the knee in the N_2 -adsorption isotherms at low relative pressures and a corresponding increase in both the surface area and average micropore size. Additional microporosity is formed along with an accompanying increase in fine mesoporosity; which most likely arises from the enlargement of existing smaller pores [4]. The average micropore size (L_0) increases, from 0.6 nm for the PFA-K1 sample to 1.6 nm for the PFA-K3 sample. When the KOH : PFA ratio is 3:1, the proportion of microporosity begins to decline and a large amount of additional fine mesoporosity ($< \sim 5$ nm) develops. Sample PFA-K3 has micropore and mesopore volumes of 0.93 and 0.73 cm^3g^{-1} , respectively. Despite its high proportion of mesoporosity, which often leads to reduced surface areas,

PFA-K3 still has a desirably high surface area ($S_{\text{BET}} \approx 2600 \text{ m}^2 \text{ g}^{-1}$).

The electrical conductivity of the PFA derived carbons was also measured and the results show significantly high conductivity values; $130 \text{ S}\cdot\text{cm}^{-1}$ for sample PFA-K1 reducing to $20 \text{ S}\cdot\text{cm}^{-1}$ for PFA-K3. When the ratio of chemical agent increases, the oxygen content of the resultant activated carbons tends to increase. When a ratio 1:1 PFA to KOH is used an oxygen content of around 3.11 wt. % is obtained, which increases to 7.62 wt. % when the ratio is 3:1. The increase in oxygen content which is inevitably introduced in the carbon when increasing the degree of activation also influences the decrease of electrical conductivity previously mentioned.

Galvanostatic cycling of the electrochemical devices at several current densities was utilized to calculate the specific capacitance values displayed in Table 1.

Table 1. Capacitance values (F g^{-1}) from galvanostatic cycling at various current densities. Voltage window 2.5 V.

sample	$C_{i(\text{Ag}^{-1})} (\text{F g}^{-1})$				
	$C_{0.3}$	C_{15}	C_{90}	C_{180}	C_{225}
PFA-K1	65	16	-	-	-
PFA-K2	97	81	68	53	-
PFA-K2.5	124	112	99	90	87
PFA-K3	147	134	120	109	103

Current densities varied from 0.3 to 225 A g^{-1} . At a very low current density, the devices present the highest capacitance values and they tend to decrease, quite drastically for some samples, when the current density increases. Sample PFA-K1 show the most drastic reduction of capacitance values when increasing the current density used. This can be explained by the small pore size of this material. With only an average pore size of 0.6 nm, accessibility issues of electrolyte ions into pores can be expected. This was experimentally confirmed by performing cyclic voltametry experiments in a three electrode configuration where sieving-effect issues were visible [5]. Samples PFA-K2.5 and PFA-K3 could be cycled at a quite high current density (225 A g^{-1}), showing capacitance values of around 90 and 100 F g^{-1} , respectively.

Impedance spectroscopy is a powerful method for investigating the penetration of the alternating current into the pore system of the electrode materials and reflects the ion access into the pores at a specific frequency. The specific capacitance values for the carbons investigated were calculated within the frequency range from 0.01 to 100,000 Hz. A capacitance vs. frequency plot for carbons investigated is shown in Figure 2. The capacitance is maximum, for all samples, at low frequency because the ions have sufficient time to access the electrode surface. When the frequency increases, the ions have difficulty reaching the depth of the less accessible pores. However, PFA-derived carbons still provide high capacitance values at 10 Hz (33, 68 and 100 F g^{-1}

, respectively). The results shown by sample PFA-K3 are quite remarkable as specific capacitance values of 30 F g^{-1} can still be supplied at a frequency of 100 Hz, where most of the other materials used in supercapacitors would provide negligible capacitance. Therefore it is demonstrated that the chemical activation of PFA creates improved porous materials where the ion dynamics are optimized to facilitate ion accessibility. Finally, it is worth mentioning that the samples could be cycled up to 5,000 cycles showing a decay of only 5-10 % of the initial capacitance values.

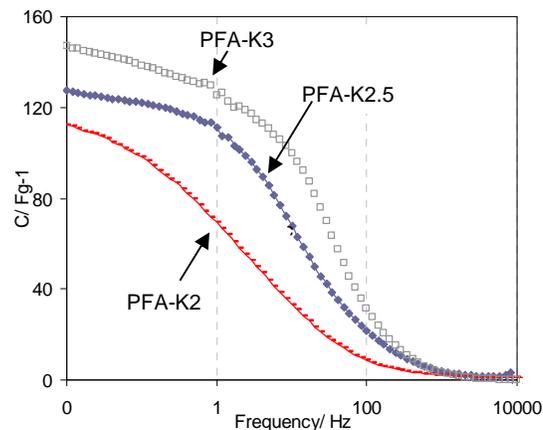


Fig. 2 Specific capacitance values as a function of the frequency. Frequency range 10 mHz- 100kHz. Completely discharged state.

Conclusions

In this paper we investigated electric double layer capacitance of polufurfuryl-KOH activated carbons in an organic electrolyte (1M tetraethylammonium tetrafluoroborate in acetonitrile). The porous carbons exhibited large capacitance values (up to 150 F g^{-1} for sample PFA-K3) at a voltage window of 0-2.5 V. Due to both a high surface area and outstanding rate capability, capacitance values of up to 100 F g^{-1} were obtained at a current density of 225 A g^{-1} and a frequency of 10 Hz.

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