



Effects of thermal treatments on the supercapacitive performances of PAN-based carbon fiber electrodes

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ABSTRACT

Thermal treatments including oxidative stabilization, carbonization, and activation were performed on poly (acrylonitrile)-based carbon fibers (PAN-CFs) to enhance their supercapacitive performances. In the oxidative stabilization and carbonization process, only the thermal treatment duration was controlled while in the activation process, both thermal treatment duration and pressure of carrier gas were varied to investigate their effects on the morphology and electrochemical performances of PAN-CFs. The activation process is found to favor the formation and dispersion of pores on the surface of the activated PAN-CFs, which increases the specific surface areas and subsequently improves the specific capacitances from 0.25 mF/cm² for the pristine PAN-CFs to 34.7 mF/cm² for the activated PAN-CFs, operated at 100 mV/s scan rate.

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1. Introduction

Among energy storage devices, supercapacitors have attracted considerable attentions due to their excellent performances such as long cycle life, high power density, and high energy density compared to secondary batteries and conventional dielectric capacitors [1] for applications in backup power storage systems, electric vehicles, and communication systems [2–4]. Supercapacitors can be classified into two major categories in terms of the energy storage mechanisms, namely, electrochemical double-layer capacitors (EDLCs) and faradic pseudo-capacitors [5]. EDLCs are based on the separation of charges at the interface of electrode and electrolyte, i.e., electrons in electrode materials and ionic charges in electrolyte. On the contrary, pseudo-capacitors store energy via redox reactions between electrode materials and electrolyte happened on the electrode surface. Three main types of supercapacitor materials have been extensively investigated: (1) carbon materials with high specific surface areas such as activated carbon [6,7], carbon nanotubes [8–10], and carbon fibers [11,12]; (2) transition metal oxides such as MnO₂ and RuO₂ [13,14]; (3) electronically conducting polymers [15] such as polyaniline.

Poly(acrylonitrile)-based carbon fibers (PAN-CFs), the most extensively used carbon fibers, have been recognized as a promising material for EDLCs due to the high specific surface area, good chemical stability, and fabrication simplicity. Earlier reports have shown that the structural and electrical properties of PAN-CFs could be improved by oxidative stabilization [16] and carbonization [17] treatments. The

oxidative stabilization treatment aims to increase the carbon yield and make the structure more stable via the formation of intermolecular net by cross-linking of oxygen molecules. The carbonization treatment is adopted to remove non-carbon elements and promote the growth and linking of crystallization zone of carbon, which could improve the electric conductivity of PAN-CFs significantly. On the other hand, a further activation treatment is found to be essential for PAN-CFs to have better capacitive performances [11,18,19]. During the activation process, numerous pores were formed on the surface of PAN-CFs uniformly, resulting in a further increase in the specific surface area of PAN-CFs.

In general, there are many factors that can influence the structural, electrical and capacitive properties of PAN-CFs during the various thermal treatments. The previous reports [11,16–19] have investigated the effects of treatment temperature, heating rate, and/or feeding gas. However, less experimentation has been conducted on the treatment duration and pressure of feeding gas. In this work, the treatment duration and/or the pressure of carrier gas in the various thermal treatment processes were varied to investigate their effects on the morphology and electrochemical performances of PAN-CFs.

2. Experimental

2.1. Thermal treatments of PAN-CFs

In this work, PAN-based carbon paper composed of carbon nano-fibers was produced via solution blown with polyacrylonitrile precursor. All thermal treatments were carried out in an Al₂O₃ tubular furnace. The oxidative stabilization process was performed at 280 °C in air at a heating rate of 2 °C/min with different treatment durations of 1, 2, and 4 h. In order to increase the strength of PAN-CFs, tension

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was applied by placing the material between two graphite plates before inserted into the Al_2O_3 tubular furnace. The stabilized carbon fibers were then used as starting materials for carbonization process. The carbonization treatment was carried out in a protected environment of 1 atm N_2 flowing (1000 sccm) at consecutive heating rates of $8^\circ\text{C}/\text{min}$ to 800°C then $4^\circ\text{C}/\text{min}$ to 1200°C , and held at 1200°C for 1 h to obtain carbonized fibers. In the activation process, a small quantity of water vapor, created by passing N_2 carrier gas (15 and 30 psi) through a water bubbler, was introduced into the tubular furnace while the temperature was raised to 1000°C . At the same time, the stabilized carbon fibers with 1 h treatment duration were inserted into the central heating zone of the tubular furnace and kept it in there for 1 and 2 min. Then, the activated carbon fibers were taken out of the tubular furnace and cooled down to room temperature.

2.2. Microstructure characterizations

After thermal treatments, the surface morphology and microcrystalline structure of the stabilized PAN-CFs, carbonized PAN-CFs, and activated PAN-CFs were characterized by field-emission scanning electron microscopy (FESEM) and Raman spectroscopy with 632.8 nm He-Ne laser excitation.

2.3. Electrochemical measurements

The stabilized PAN-CFs, carbonized PAN-CFs and activated PAN-CFs with exposed size of $1\text{ cm} \times 1\text{ cm}$ were used as working electrode materials. Before electrochemical measurements, the thermal treated PAN-CFs samples were immersed in 6 M H_2SO_4 aqueous solution maintained at 50°C for 1 h to remove impurities and make the surface of PAN-CFs more hydrophilic. After acidic treatments, the PAN-CFs were attached to a current collector (Ti plate) and used as a working electrode. Electrochemical behavior and specific capacitance of the PAN-CFs were examined in a three-electrode cyclic voltammetry (CV) with platinum wire and saturated calomel electrode (SCE) used as counter and reference electrodes, respectively. And a 1 M H_2SO_4 aqueous solution was used as electrolyte.

3. Results and discussion

Fig. 1(A) and (B) shows the Raman spectra of PAN-CFs subjected to the stabilization and carbonization treatments, respectively, with curves (a) to (c) corresponding to 1 h, 2 h, and 4 h of treatment durations in sequence. The crystalline nature of PAN-CFs can be evaluated from the intensity ratio of G-band to D-band peak (i.e. I_G/I_D) [20,21]. In both figures, we could observe I_G/I_D ratios increase with increasing treatment durations. When the stabilization treatment duration was varied from 1 h, 2 h, to 4 h, the I_G/I_D ratios increased from 0.62, 0.66, to 0.77, Fig. 1(A). After the carbonization process, the corresponding I_G/I_D ratios further increased to 0.82, 0.90, and 0.93, Fig. 1(B). From these results, we could conclude that the structural quality of the samples was improved due to the improvement in crystallization via stabilization treatment. And the higher increments in I_G/I_D ratios after carbonization treatment as shown in Fig. 1(B) indicate that carbonization indeed further improved the structural quality of PAN-CFs.

Fig. 2 illustrates the effects of the stabilization and carbonization treatments on the surface morphology of PAN-CFs. The stabilization process was carried out at 280°C for duration of 4 h, and a similar sample under the same stabilized condition was subsequently subjected to the carbonization process. The average diameters of pristine PAN-CFs, stabilized PAN-CFs, and carbonized PAN-CFs were estimated from the low-magnification SEM images, Fig. 2(A)–(C), to be approximately 800 nm, 500 nm, and 400 nm, respectively. As it is indicated, the average diameter of PAN-CFs decreases after thermal treatments, while the size distribution of PAN-CFs became more

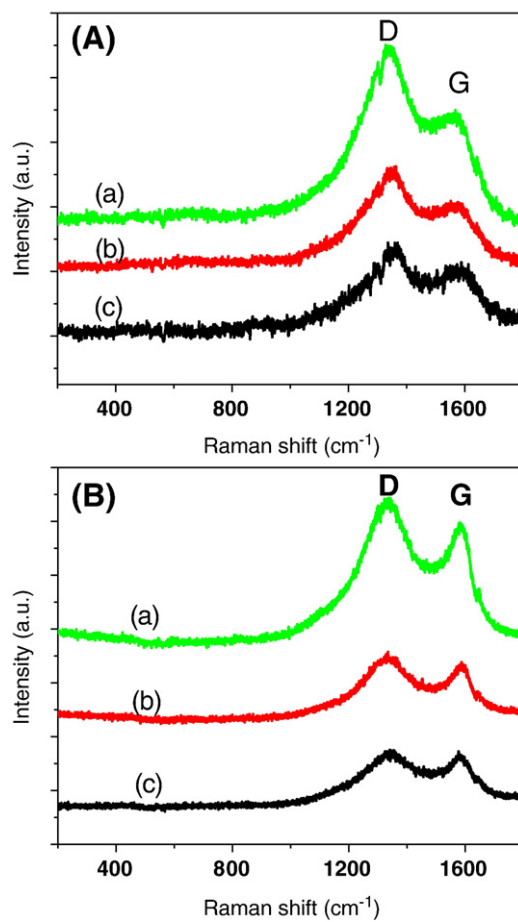


Fig. 1. Raman spectra of PAN-CFs subjected to (A) stabilization and (B) carbonization treatments, with curves (a) to (c) corresponding to 1, 2, and 4 h of treatment durations.

uniform. Moreover, it could be seen from the high-magnification SEM images, Fig. 2(D)–(F), the surface roughness of carbon fibers decreased with thermal treatments. This phenomenon resulted in electric conductivity enhancement due to the improvement of electron transportation over a smoother surface of carbon fibers.

The surface morphology of PAN-CFs subjected to four different activation conditions is presented in Fig. 3. When the activation duration increased, the surface of activated PAN-CFs got rougher, attributed possibly by the removal of amorphous carbon from the surface of carbon fibers by water vapor. We have observed that if PAN-CFs were placed in a moisture environment for a long period of time, the fiber surface became rough and the pores dispersed on the surface would increase. Fig. 3 also indicates that the pressure of carrier gas affected the surface morphology of PAN-CFs. In general, as the pressure of carrier gas N_2 is created, the surface roughness of PAN-CFs became more uniformly distributed and more pores are formed. We postulate that when the pressure of carrier gas is higher, a greater amount of water molecules are introduced into the processing environment, causing a more effective etching to the surface of PAN-CFs. Hence, the locally etched situation was effectively decreased and the distribution of pores created via the reaction between the carbon fibers and water vapor was more uniform.

Fig. 4(A)–(C) displays the CV curves of pristine PAN-CFs, stabilized PAN-CFs, and carbonized PAN-CFs, respectively. The stabilization treatment was carried out at 280°C for duration of 4 h, and samples with the same stabilization process parameters were used as the starting material of carbonization treatment. The CV measurements were carried out in a potential window of 0 to 1 V with different scan rates ranging from 100 to 1000 mV/s. The observed rectangular-

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