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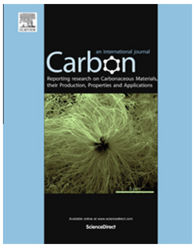

# Improvement of carbon materials performance by nitrogen functional groups in electrochemical capacitors in organic electrolyte at severe conditions

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ABSTRACT

N-doped activated carbon fibers have been synthesized by using chemically polymerized aniline as source of nitrogen. Commercial activated carbon fibers (A20) were chemically modified with a thin film of polyaniline (PANI) inside the microporosity of the carbon fibers. The modified activated carbon fibers were carbonized at 600 and 800 °C, respectively. In this way, activated carbon fibers modified with surface nitrogen species were prepared in order to analyze their influence in the performance of electrochemical capacitors in organic electrolyte. Symmetric capacitors were made of activated carbon fibers and N-doped activated carbon fibers and tested in a two-electrode cell configuration, using triethylmethylammonium tetrafluoroborate/propylene carbonate (TEMA-$BF_4$/PC) as electrolyte. The effect of nitrogen species in the degradation or stabilization of the capacitor has been analyzed through floating durability tests using a high voltage charging (3.2 V). The results show higher stabilizing effect in carbonized samples (N-ACF) than in non-carbonized samples and pristine activated carbon fibers, which is attributed to the presence of aromatic nitrogen group, especially positively charged N-functional groups.

## 1. Introduction

The performance of porous carbons as electrode in electrochemical capacitors such as electric double layer capacitor is strongly dependent on a complex combination of properties which includes carbon material properties, preparation method of the electrode and electrolyte characteristics. The proper selection of these properties will allow to optimize the electrochemical capacitor. Among the carbon material properties, the surface chemistry plays a key role. Since it may have both positive and negative contributions, it is essential to deepen into the mechanisms through which it participates when the carbon material is used as electrode. The surface chemistry of the porous carbons can be modified through different methods in which the amount and the nature of surface functionalities can be tailored to adapt it to the specific application. In the case of using porous carbons as electrodes in electrochemical capacitors, it is known that oxygen, nitrogen, phosphorous and sulfur functionalities have a strong influence in the performance of the material [1,2].

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They can affect the wettability of the electrolyte and contribute to the capacitance through redox processes, being both of them positive contributions [1–5]. However, they can also have a strong influence in the stability of the capacitor upon cycling, either promoting the degradation of the material and the electrolyte [6], or reducing the degradation rate [7].

Regarding N-functional groups, some studies have shown that the modification of the carbon materials with nitrogen species causes the improvement in the electrochemical behavior. This change in the electrochemical performance can be related with the improvement in the wettability [4,8], electron transfer rate [9,10], stability [7], decrease of ESR [4], contribution of space-charge-layer capacitance or the pseudocapacitance [4,5].

Pseudocapacitance in N-doped carbons has been attributed to negatively charged groups located at the edges of the graphene sheets, like pyridine [5,11,12], while the positively charged groups, such as quaternary N and oxidized N, do not have any effect on the pseudocapacitance. However, due to the variety of N-functional groups generated by using the conventional methods, it is very difficult to unravel the role of the different N-functional groups. This is the reason why numerous studies have been carried out in order to synthesize N-functional groups which fulfil the requirements to be used in specific applications [13].

Different methods lead to the formation of nitrogen-containing porous carbons [9,13–22] that can be summarized as:

(a) Reaction between a nitrogen-containing compound ($NH_3$, NO, urea, [N,N]-dimethylformamide or dicyandiamide) and a porous carbon material.
(b) Carbonization process, followed or not by chemical activation (with alkaline hydroxides, phosphoric acid,...) or physical activation (with $CO_2$ or steam), of N-containing precursors, such as melamine, pyridine, quinoline, acetonitrile, and so on.
(c) Hydrothermal carbonization using glucosamine or cyanuric acid.
(d) Templating method consists of filling the nanosized pores of a template (zeolite, mica,...) with N-precursor (polyacrylonitrile, melamine,...). Subsequently, the infiltrated template is subjected to a thermal treatment.

One possibility related to the second method indicated above is the carbonization of nitrogen-containing conjugated polymers. One of the most used polymers is polyaniline because of its easy synthesis and its low cost. Moreover, it presents the advantage of having a defined chemical structure which can be generated by using various chemical and electrochemical processes [23,24]. This well-defined structure in the N-containing precursor may facilitate the formation of N-doped carbon with a particular kind of nitrogen functionality, which may play an important role in the final properties of these materials for the energy storage application [25,26].

Recently, we have succeeded in the preparation of PANI-containing porous carbons by chemical and electrochemical polymerization of aniline where the PANI is distributed as a thin film with an average thickness of about 0.5 nm (approximate value), which covers the porosity of the material [24,27]. It is expected that the carbonization of the PANI-containing porous carbons will produce N-doped porous carbons very suited to analyze the effect of these functional groups in the electrochemical performance of the materials.

Then, the main objective of this work is to deepen into the role of the N-functional groups on the electrochemical performance of N-containing porous carbons as electrodes for electrochemical capacitors in aprotic organic electrolyte. For this purpose, symmetric electrochemical capacitors based on N-doped activated carbons fibers were subjected to galvanostatic charge–discharge experiments under severe conditions of temperature and applied voltage in a typical organic electrolyte (TEMA-$BF_4$/PC) for EDLC and the results have been related to the nature of the N-functionalities.

## 2. Experimental

### 2.1. Materials

Activated carbon fibers used are A20 from Osaka Gas Co. Ltd. Ammonium persulfate, hydrochloric acid, ammonium hydroxide were from Merck p.a., 1 M triethylmethylammonium tetrafluoroborate (TEMA-$BF_4$) in propylene carbonate was provided by Toyo Gosei Co. Ltd. (Japan); polytetrafluoroethylene (PTFE) 6J from Du Pont-Mitsui Fluorochemicals Co. Ltd.; Denka black (acetylene black) supplied by Denki Kagaku Kogyo. Aniline monomer (Sigma–Aldrich) was distilled by refluxing under reduced pressure before use. Aniline solutions were prepared with purified water obtained from an Elga Labwater Purelab system (18 MΩ cm).

### 2.2. PANI/ACF and N-doped/ACF preparation

PANI/ACF samples were synthesized by a chemical polymerization method described elsewhere [24]. Previously, the adsorption isotherm of aniline in water solution on the A20 sample was measured. Then, different molar concentrations (10, 30 and 70 mM) were selected in order to achieve different loadings of aniline in the A20 sample according to the aniline isotherm. After aniline adsorption during 24 h at 30 °C, the sample was filtered and introduced in a reactor at 0 °C, which contained an ammonium persulfate solution in 1 M HCl, for one hour. The aniline monomer: ammonium persulfate molar ratio was equal to 1:1. A thin polyaniline film (of about 0.5 nm thickness) is deposited inside the porosity of the ACF [24]. The composite was washed with 1 M HCl, 1 M ammonia aqueous solution and distilled water. Finally, the material was dried in dynamic vacuum for 24 h.

N-doped/ACF samples were prepared from the PANI/ACF samples, using a tubular oven and by carbonization in $N_2$ at a heating rate of 5 °C $min^{-1}$ up to 600 and 800 °C and these maximum temperatures were kept for 1 h. The samples are referred to as A20_xmM_y, being “x” the monomer concentration and “y” the carbonization temperature.

### 2.3. Physicochemical characterization

Porous texture of all the samples was characterized by physical adsorption of $N_2$ at −196 °C and $CO_2$ at 0 °C, using an automatic adsorption system (Autosorb-6, Quantachrome). The samples