



Behavior of activated carbon cloths used as electrode in electrochemical processes



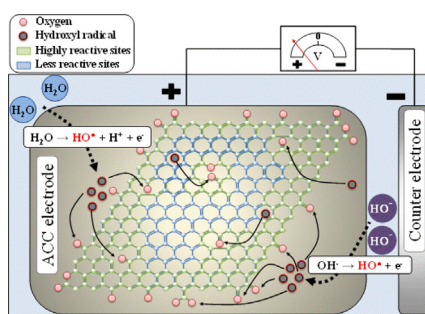
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HIGHLIGHTS

- Electrochemistry is a soft method able to functionalize homogeneously carbon fibers.
- Anodic polarization modulates the hydrophilic character and wettability of carbons.
- Oxygenated groups nature and amount can be monitored using a controlled voltage.
- Below 1.4 V vs Hg/Hg₂SO₄, mainly phenols and lactones are introduced.
- Above 1.4 V vs Hg/Hg₂SO₄, conversion of CO₂-type groups into CO₂-type groups occurs.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of polarization on the nanotexture and the surface chemistry of an activated carbon cloth were investigated. Electrochemical modification was performed in a sodium sulfate electrolyte, by applying negative current or increasing positive potentials. The porous structures of the polarized samples were analyzed by N₂ and CO₂ adsorption. Surface chemistry properties such as the nature and the amount of functional groups were studied through various characterization techniques. Additionally, the electrochemical properties of the modified samples were investigated using cyclic voltammetry. It is shown that anodic polarization leads to a significant oxidation of the pristine carbon material, characterized by the substantial incorporation of a wide variety of oxygenated groups and a significant modification of the porous network. A capacitance increase is highlighted for the anodically polarized samples and can be attributed to the incorporation of CO₂-type surface groups. While cathodic polarization leads to a slight modification in surface chemistry and nanotexture, anodic treatment causes noticeable transformations of the pristine carbon material. Additionally, the oxidation phenomenon which occurs at the carbon electrode appears to be quite different in the two modes. A comparative study with a second carbon material, possessing a different surface chemistry and porous characteristics, was also carried out.

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1. Introduction

Activated carbon cloths (ACC) are composed of fibers that are small in diameter (around 10 μm), extremely porous, and with a high surface area (700–3000 m²/g). Recently, ACCs have been used

in air treatment applications, in particular for the removal of volatile compounds [1], or in biomedical applications because of their good biocompatibility [2]. Due to their microtexture that is directly accessible at the external fiber surface, ACCs show fast intraparticle diffusion, a low resistance to mass transfer and high adsorption rates which makes them ideal candidates for adsorption purposes in waste water treatment [3].

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Electrochemical techniques involving high specific surface area carbon cloths are innovative and environmentally friendly. Thanks to their easy handling, high mechanical integrity and regeneration potential, carbon cloths have numerous advantages compared to powder or granules. As ACCs do not require particular shaping, they can be used directly as electrode material. Consequently, electrochemical polarization has been used to increase their adsorption capacity and kinetics [4–8], but also to accomplish the reversible desorption of ions or organic compounds in order to restore adsorption sites and therefore to increase the lifetime of the adsorbents [9]. Extensive research has been carried out on the reversible electrosorption of inorganic ions [10–12] and more recently on organic ionizable molecules such as phenol, aniline or pesticides [13–16,17,18]. However, only a few studies have investigated the impact of polarization on the intrinsic characteristics of the ACC electrode material [19–24].

Recent studies, focusing on the anodic oxidation of granular activated carbon (GAC) [19,23,24] and commercial activated carbon cloth [23,24] have been performed in a NaCl and HNO₃ medium. The influence of electrochemical parameters such as the anode material, the applied current and the treatment time, on the textural and chemical properties of these activated carbon materials was studied. Advanced oxidation characterized by the introduction of numerous oxygenated groups was observed in particular when the carbon electrode was submitted to a high potential or current density [19–24]. In most cases, electrochemical treatments do not increase the porous volume of activated carbons [19]. However, in the case of an oxygen saturated electrolyte in the cathodic mode, the porous volume increases significantly. This increase can be attributed to carbon gasification due to peroxide species coming from oxygen electroreduction [20]. The amount of incorporated oxygen functionalities strongly depends on the electrolyte nature. In NaOH or H₂SO₄, only a slight oxidation is observed whatever the polarization mode (cathodic or anodic) whereas in the presence of chloride ions (NaCl containing electrolyte) in the anodic mode, a strong oxidation occurs due to electrochemical reactions implying the generation of chlorine species [19]. The amount of oxygen functionalities increases gradually with the current density and polarization time and depends also on the nature of the anode material and its ability to generate chlorine species [20]. In such conditions, electrochemical oxidation becomes very oxidative and comparable to general chemical oxidation using strong oxidants such as ammonium sulfate [20]. More precisely, Tabti et al. demonstrated that using a NaCl electrolyte the formation of carboxylic acids and phenolic groups was favored at low and medium currents, whereas the carbonyl/quinone content decreased. At higher currents, if the carboxylic acid and anhydride content increased further, the carbonyl content still decreased and the lactone content remained stable [23]. Furthermore, the low CO/CO₂ ratio measured by temperature programmed desorption (TPD) experiments on the anodic polarized samples was attributed to the reoxidation of freshly generated CO-groups into CO₂-groups such as carboxylic acid and anhydride groups. Incorporation of the oxygenated surface groups at the pore entrance of the carbon material led to a progressive obstruction and destruction of the porosity after anodic treatment. For example, Tabti et al. reported both a significant decrease in the apparent specific area (11–20%) and in the total volume of the ACC micropores. While applying a current ranging from 0.2 to 1 A, a significant decrease in the microporous volume from 5 to 15% was measured by N₂ adsorption and nearly 15% by CO₂ adsorption [23]. In the case of a NaCl electrolyte, the oxidation of the carbon material came from direct oxidation by the electrode polarization due to the potential rise and/or from indirect oxidation induced by the electro-generation of chlorine species. The electro-oxidation of chloride ions led to the formation of high amounts of chlorine spe-

cies such as free chlorine, hypochlorous acid and hypochlorite ions. However, the oxidation mechanism appeared to be quite different depending on the nature of the electrolyte employed [21–23]. Even in the case of an inert electrolyte such as sodium sulfate, secondary reactions with *in-situ* produced hydroxyl radical species at the working electrode were responsible for oxidation of the carbon material [21,22]. These side reactions are due to the presence of dissolved oxygen traces. Furthermore, direct oxidation of the carbon surface appears to be the prevailing mechanism in an oxidative electrolyte such as HNO₃ [23]. The carbon oxidation was not connected to the anode employed but on the contrary was related to the electrolysis conditions. A NaCl medium is a more oxidizing electrolyte compared to other electrolytes tested in the literature such as Na₂SO₄ or HNO₃ for example. Furthermore, Bayram et al. demonstrated a capacitance loss of the carbon material with the degree of oxidation and attributed it to pore blockage during polarization [21]. However, numerous studies found a different electrochemical behavior with an increase in capacitance upon oxidation [25,26]. Bleda-Martinez et al. [25,26] and Tabti et al. [23] reported that not only the quinone groups but also all CO-groups are responsible for the improvement in the carbon material capacitance. A direct correlation between the capacitance and the total amount of CO-groups has been indeed highlighted [23,25]. Under prolonged negative polarization, it appears that neither the chemical functionality nor the porous nanotexture of the carbon cloth is modified to a large extent [25,27–29]. The slight oxidation is due to a direct reduction by the electrode potential and/or indirect oxidation induced by the electro-generation of hydrogen peroxide species. Furthermore, it has been demonstrated that the presence in the carbon material surface of Brønsted basic sites such as quinone/carbonyl, pyrone or chromene groups and/or Lewis basic sites, catalyzed the decomposition of hydrogen peroxide into highly free hydroxyl radical species, thus favoring the oxidation of the carbon material under cathodic polarization, particularly for carbons having a basic character [30,31].

When using electrochemical techniques to regenerate carbon material loaded with pollutants after adsorption [32], it is crucial to understand the carbon material properties and the evolution of its characteristics in order to define the working conditions and the limitations imposed by the carbon material itself. The main objective of the present work was therefore to study the behavior and the stability towards oxidation of carbon materials in electrochemical processes performed in a non-reactive electrolyte such as sodium sulfate. We focused especially on the analysis and the quantification of the carbon material functionalization through electrochemical oxidation which takes place mainly during anodic polarization and to a lesser extent during cathodic polarization. We first investigated the behavior of a microporous activated carbon cloth possessing a hydrophobic character (low oxygen content) under anodic and cathodic polarization in a sodium sulfate electrolyte. Furthermore, in order to investigate the stability under polarization of ACCs having different nanotexture and surface chemical characteristics, a comparative study was conducted on two activated carbon cloths. The stability of the two materials towards an electrochemical polarization (negative or positive) during several hours was determined through a complete characterization of the oxygen functionalities introduced in the polarized samples, in correlation with the reactive species and electrochemical mechanisms involved.

2. Experimental

2.1. Material and reagents

The activated carbon cloth referenced KIP 1200, prepared from a phenolic resin precursor and physically activated (water steam),

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