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A systematic study on the changes in properties of an activated carbon cloth upon polarization

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ABSTRACT

The effects of polarization on properties of activated carbon cloth (ACC) have been investigated systematically. The polarization-treated ACC samples were prepared by polarizing them in Na_2SO_4 or KH_2PO_4/KOH buffer solutions at potentials from −1.5 to 5.0 V. The properties, such as surface area, pore size distribution (PSD), total pore volume, amount and nature of the surface functional groups and surface acidity, of pristine and polarization-treated ACC samples were determined. The samples were also characterized electrochemically by determining the properties such as specific capacitance and potential at point of zero charge (E_{PZC}). Anodic polarization in different electrolytes was found to cause oxidation on ACC. Although the surface textural properties did not change considerably, the changes took place in chemical and electrochemical properties upon anodic polarization were found to be important. The increase in surface acidity shifted the pH_{PZC} from 7.40 to 3.21 and E_{PZC} from 164 to 355 mV. The optimum potential range, considered to be safe for polarization of ACC, was determined as −1.5 to +0.8 V.

1. Introduction

Activated carbons are widely used in electrochemistry as an electrode material due to their high specific surface area, developed pore structure and electrical properties such as low electrical resistance and high conductivity. Among the activated carbons, activated carbon cloth (ACC) or fibers have the advantages of mechanical integrity and easy handling [1]. These advantages make ACC more favorable than the other forms of activated carbons such as granular or powder for electrochemical processes.

Electrochemical treatment technologies, using activated carbons as an electrode material, include electro-oxidation/reduction [2–4] and electrosorption [5–7]. Electro-oxidation/reduction reactions are Faradaic processes containing charge transfer through the phase boundary. However, electrosorption, which is generally defined as potential-induced adsorption on the surface of electrodes, is a non-Faradaic process. In electrosorption processes such as waste water treatment [8], desalination [9] and electrical double layer applications [10], the performance of the electrode depends on the surface chemistry and pore structure of electrode. However surface chemistry, surface area and pore size distribution of activated carbons may also be affected from electrochemical polarization applied during electrosorption and thus weakly acidic surface functional groups such as carboxylic, phenolic and lactonic may be formed [11].

Oxidation of carbon materials by nitric acid has been extensively studied by some authors [12,13]. The effect of surface oxygen groups on capacitance of samples was examined and it was found that such groups cause an increase in the capacitance of carbon material in strongly acidic medium. On the other hand, electrochemical oxidation of granular activated carbon by catholic and anodic treatment in different electrolytic media, were studied by several groups [14–16], but few studies focus on activated carbon cloth or fibers [7,17–19]. The effect of polarization on the surface morphologies of activated carbon fibers before and after polarization at the potential range between 0.2 and 0.8 V were characterized and it was found that surface area and average pore size of fibers increase with increasing anodic potential [11]. In another study [17], electrochemical regeneration of activated carbon fiber previously exhausted with acid orange-7 was carried out by polarizing the activated carbon fiber in a potential range from −10 to 10 V and the changes in the amount of surface functional groups upon polarization were determined. Gulyas et al. [18] investigated the changes in surface chemistry of activated carbon fiber upon polarization in different electrolytes by FTIR spectroscopy and they found that the surface chemistry is determined by the type of electrolyte, as well as by the other conditions of the process. Recently, Harry et al. [19] oxidized the activated carbon cloth galvanostatically in KCl solution for different periods of time and examined the changes in the surface properties.

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The potential at point of zero charge, E_{PZC}, which is believed to be an important parameter in determining the surface properties of an electrode, has not received much attention in the limited number of works reported on electrochemical oxidation of ACC or activated carbon fiber. It is also believed that there is a lack of information on the effects of variables such as the nature of electrolyte and both the anodic and cathodic potential on the surface chemistry of ACC. A systematic study is necessary not only for electrochemical oxidation as an alternative to the traditional chemical methods, but also for the development of new electrochemical technologies. Besides it would be helpful to solve the problems, which may be encountered during the electrochemical processes.

The aim of this study is to investigate systematically the changes in surface properties, chemical composition and electrochemical properties of ACC upon polarization at different anodic and cathodic potentials in different electrolytes.

2. Experimental

2.1. Materials

The high specific surface area ACC was obtained from Spectra Corp., coded as Spectracarb 2225. Although the full details of its mode of preparation are regarded as proprietary, it originates from pyrolysis of phenolic polymer fibers followed by heat treatment in O_2-free N_2 between 800 °C and 900 °C for some hours [20].

Reagents used in this study were Merck grade. High purity water used in all experiments was from an 18.2 MΩ Milli-Q UV (Millipore) water treatment system.

2.2. Treatment of ACC

Before it was used in the experiments, the ACC was first washed with warm deionized water by a procedure described in our previous works [8,21]. The washed and dried ACC was then cut into desired dimensions, weighed accurately and then kept in a desiccator for further use. For the purpose of polarization treatments, the ACC piece was dipped into a 0.01 M Na_2SO_4 or 0.01 M KH_2PO_4/KOH (pH 6.7) solution to act as a working electrode (WE), a Pt plate was used as a counter electrode (CE) and a Ag/AgCl electrode (BAS, MF-2030, Bioanalytical systems Inc. USA) as a reference electrode (RE). N_2 was bubbled through the solution to remove the dissolved gasses. ACC pieces polarized, either in 0.01 M Na_2SO_4 or in 0.01 M KH_2PO_4/KOH solution, at constant applied potentials of +0.5 V, +0.8 V, +1.5 V, +5.0 V or −1.5 V with the use of a potentiostat/galvanostat (Gamry Instruments Inc.) for a period of 90 min, were washed with water at 60 °C and then dried at room temperature. Those polarized in 0.01 M Na_2SO_4 were labeled as ACC + 0.5, ACC + 0.8, ACC + 1.5, ACC + 5.0 or ACC – 1.5 and those polarized in 0.01 M KH_2PO_4/KOH were labeled as ACC + 1.5T or ACC – 1.5T. The sign and figures in these labels indicate the sign and magnitude of the potential applied during polarization.

2.3. Surface properties and textural characterization of ACC samples

Prior to nitrogen adsorption experiments to determine surface properties, ACC samples were degassed at 130 °C under vacuum (up to 10^{-6} torr) for 12 h. The N_2 adsorption data were obtained with a Quantachrome Autosorb-1-C/MS apparatus over a relative pressure ranging from 10^{-6} to 1. The specific surface area was calculated from the linear part of the adsorption isotherm using the BET method (S_{BET}). The total pore volume (V_{tot}) was estimated from the amount adsorbed at a relative pressure of 0.99. The Dubinin–Radushkevich (DR) theory was employed for estimating the micropore volume (V_{micro}). Mesopore volume (V_{meso}) was obtained from ($V_{tot} - V_{micro}$). Pore size distribution (PSD) was calculated using density functional theory (DFT) method. All the calculations were done by using the software of the instrument which assumes slit shapes for pores. A LECO 932 elemental analyzer was used to determine the percentages of carbon, oxygen, nitrogen, hydrogen and sulfur contents of ACC samples.

The pH_{PZC} value of ACC, defined as the pH of the solution when the net charge on ACC piece dipped into it is zero, was determined with a procedure described in our previous work [22] using batch equilibrium method reported earlier [23].

The contents of acidic and basic surface groups on ACC samples were determined according to the Boehm method [22,24].

2.4. Electrochemical characterization of ACC samples

All the electrochemical experiments were performed using a standard three electrode system connected to the potentiostat/galvanostat interfaced to a computer with its own software. In cyclic voltammetric studies, WE was an ACC piece of about 12 mg attached to a Pt wire, CE was a Pt plate, and RE was a Ag/AgCl electrode. It is known that $SO_4{}^{2-}$ ions do not specifically adsorb onto ACC [8]. Thus 0.01 M Na_2SO_4 (pH ∼ 6.8) solution was used as inert supporting electrolyte.

Potential of zero charge (E_{PZC}) is the potential at the surface when the net charge on it is zero. Immersion potential of a material in the absence of any Faradaic process should be equal to E_{PZC} [25]. Thus the immersion potential of ACC to be measured in Na_2SO_4 solution will be its E_{PZC}. For the measurement of E_{PZC}, ACC sample of about 12 mg dipped into 0.01 M Na_2SO_4 solution was degassed first by applying vacuum for a short period of time and then by bubbling N_2 through the solution. Then the potential was measured against a Ag/AgCl reference electrode. The subsequent open circuit potentials (E_{OC}) of ACC samples were determined in the same manner.

3. Results and discussion

3.1. Surface textural characteristics of ACC samples

Physical characteristics of porous materials such as surface area and pore structure are important in sorption processes. The surface area is the reactive zone where chemisorption and/or physisorption occur. Alternatively, pore size and shape will define the process performance, since kinetics of adsorption is directly related to adsorbate intraparticle diffusion. The S_{BET} obtained from N_2 adsorption isotherm data and the calculated V_{tot}, V_{micro} and V_{meso} data of pristine and polarization-treated ACC samples are given in Table 1.

All ACC samples analyzed in this study have high specific BET surface area which decreases with electrochemical polarization. Maximum decrease observed in S_{BET} relative to pristine ACC was about 18% with ACC + 5.0 sample. The decrease in anodically polarized ACC samples could be a consequence of a combination of the direct oxidation by the anodically polarized electrode according to Eqs. (1) and (2) [8] and the indirect oxidation by electrogenerated

Table 1
Surface textural properties of pristine and polarization treated ACC samples.

Sample	S_{BET} ($m^2\,g^{-1}$)	V_{tot} ($cm^3\,g^{-1}$)	V_{micro} ($cm^3\,g^{-1}$)	V_{meso} ($cm^3\,g^{-1}$)
ACC	1596	0.697	0.695	0.17×10^{-2}
ACC + 0.5	1549	0.671	0.660	1.01×10^{-2}
ACC + 0.8	1541	0.655	0.654	0.17×10^{-2}
ACC + 1.5	1488	0.652	0.643	0.91×10^{-2}
ACC + 5.0	1300	0.559	0.540	2.00×10^{-2}
ACC – 11.5	1518	0.662	0.659	0.22×10^{-2}
ACC + 1.5T	1422	0.619	0.603	1.60×10^{-2}
ACC – 11.5T	1565	0.686	0.673	1.31×10^{-2}