Characterization of a carbon xerogel-based sensor for detection of acetone, ethanol, and methanol vapors

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ABSTRACT

We report on the sensing properties of carbon xerogel (CX) for detection of acetone, ethanol, and methanol vapors. The sensor was prepared by deposition of a dispersion of CX dispersion onto an FR4 epoxy resin/fiber glass printed circuit board with interdigitated electrodes. The gas sensing performance was monitored by AC impedance spectroscopy. It was found that exposure to acetone, ethanol, and methanol vapors resulted in a change of sensor impedance that was proportional to the gas concentration. The CX sensor showed greater sensitivity to ethanol and acetone vapor, compared to methanol vapor, indicative of selectivity to larger molecules. However, faster response and recovery times were obtained for methanol vapor, indicative of lower binding energy.

1. Introduction

The synthesis of new materials for solid-state devices used to monitor hazardous gases has stimulated research and development in the field of gas sensors. As one of the new trends in nanotechnology, carbon nanomaterials have attracted interest because they can provide highly sensitive gas detection [1–4]. The basic principle of gas detection involves a change in a physical or chemical property of the detecting material upon exposure to the gas [5,6]. In the case of carbon materials, their charge transport and electronic properties have been shown to be extremely sensitive to changes in the local chemical environment. In a theoretical study, Umadevi et al. [7] showed that there was an increase in the polarizability of carbon nanomaterials after binding with gas molecules, with associated changes in electronic behavior.

Carbon nanotubes (CNTs) have been successfully employed for the detection of gases such as H_2, NO, NO_2, CO_2, NH_3, and CH_4 [8–10], and graphene-based sensors have been described for the detection of CO_2, NH_3, CH_4, H_2, and NO_2 [11,12]. Studies have shown that gas sensors based on such materials can provide very low detection limits. However, the preparation of sensors based on

CNT or graphene is complex and involves lengthy procedures. Generally, such devices use composites of CNT or graphene associated with semiconductor metal oxides, or alternatively the deposition of the carbon materials as thin films on metal substrates. Both of these approaches require the use of relatively sophisticated techniques [13–17].

For these reasons, it is important to explore the potential of other nanostructured carbon materials for use in gas sensors, such as carbon xerogels (CXs). These are porous materials with a network structure consisting of interconnected nanosphere-like nodules. This kind of morphology is similar to that observed for nanostructured metal oxides such as SnO_2, WO_3, and ZnO, which have been widely studied as gas sensors [18–22]. This type of pore structure provides a high surface-to-volume ratio, which favors diffusion of the target gas in the sensor material, and CXs have higher electrical conductivity, compared to nanostructured metal oxides [23,24]. CXs are obtained by the polycondensation of hydroxylated benzene and aldehyde in a solvent, followed by drying and pyrolysis of the organic gels formed. The pore texture and the particle size of the carbon nanospheres can be controlled by the synthesis conditions [25]. The morphology and surface properties of these carbon particles are the most important factors influencing their potential for use in applications such as electric double-layer capacitors, thermal and phonic insulators, chromatographic packings, adsorbents, and catalyst supports [26].

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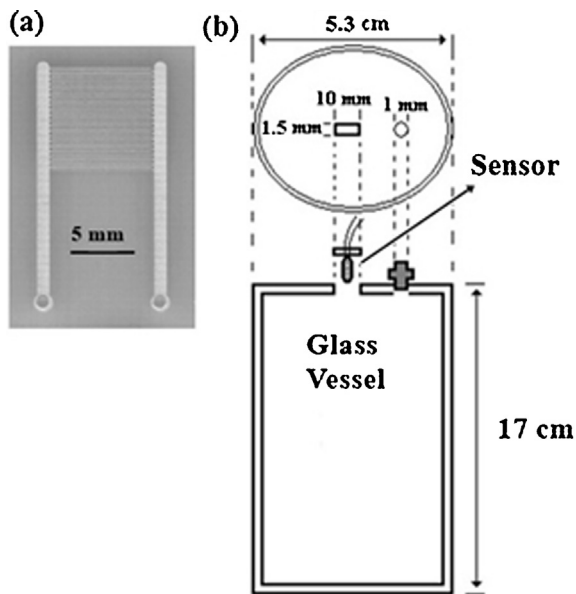E-mail addresses: wagner@ufsj.edu.br, wagner_smachado@yahoo.com.br (W.S. Machado).

Fig. 1. (a) Image of the PCB substrate used. (b) Dimensions of the glass vessel used.

The present work investigates the sensing properties of a CX-based sensor device for the detection of ethanol, methanol, and acetone vapors. This sensor was produced by coating carbon onto interdigitated electrodes by means of direct dispersion on the electrode surface. The electrical behavior of the CX coating when exposed to organic gases was followed by impedance spectroscopy measurements. The effects of AC signal frequency and vapor concentration on the sensitivity of the devices were investigated, together with the times for the sensor to respond to the presence of a specific vapor (t_{res}) and to recover (t_{rec}) after the exposure. The use of an AC signal to investigate the properties of sensing devices reduces unwanted side effects such as the diffusion of electrically active impurities or electrochemical reactions at electrodes [27].

2. Materials and methods

2.1. Carbon xerogel preparation and characterization

Resorcinol (Vetec, 99%), formaldehyde (Aldrich, 37 wt% in water, stabilized with 10–15 wt% methanol), and sodium carbonate (anhydrous, ACS, Fisher) were used as received. The preparation of the CX was based on previous work describing the polycondensation reaction of resorcinol and formaldehyde [25,26,28], using a resorcinol/formaldehyde molar ratio of 0.5 (the stoichiometric ratio). Sodium carbonate (Synth, 99.5%) was used as the catalyst, at a resorcinol/catalyst molar ratio of 350. The reagents were mixed in distilled water at room temperature (20 °C), maintaining a total solution volume of 500 mL. The solution was heated to 358 K, with stirring, and then transferred to an Erlenmeyer flask, which was sealed and kept at 358 K in a water bath (Tecnal) for 3 days. After the incubation period, the gels obtained were dried in an oven at 373 K for three days, and then pyrolyzed in a tubular oven under a flow of nitrogen. The oven heating program was as follows: (1) ramp at 2 K min^{-1} to 423 K and hold for 120 min; (2) ramp at 2 K min^{-1} to 573 K and hold for 60 min; (3) ramp at 2 K min^{-1} to 873 K and hold for 60 min; and (4) ramp at 2 K min^{-1} to 1073 K and hold for 120 min. The xerogel obtained was denoted CX500.

The CX500 specific surface area (A_{BET}) was determined by the BET nitrogen adsorption method, using an Autosorb-2 Analyzer (Quantachrome). The total pore volume (V_p) was determined at a relative pressure of 0.98. The samples were degassed for 180 min
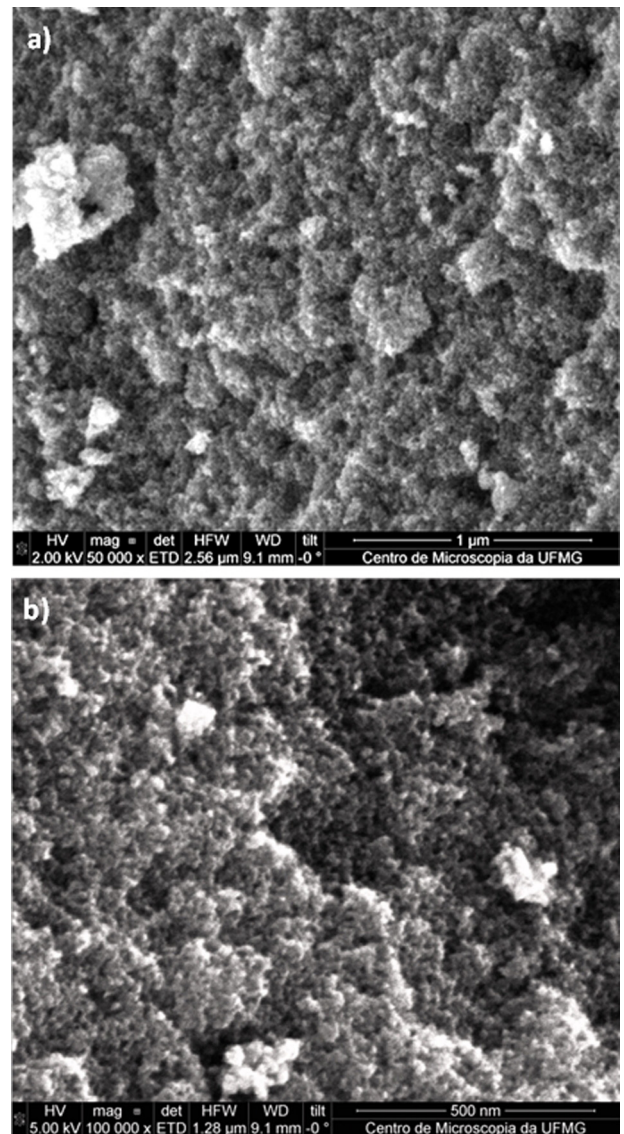

Fig. 2. SEM images of CX500 at magnifications of (a) ×50,000 and (b) ×100,000.

at 300 °C before analysis. All data analyses were performed using ASiQwin v. 1.11 software (Quantachrome). Surface morphological observations were performed with a Quanta 200 FEG scanning electron microscope (FEI). The samples were attached to the metal sample holders with adhesive carbon tape.

The concentrations of acidic/basic surface groups on the CX500 were determined by potentiometric titration (PT), using a Titrando 905 microburette system (Metrohm) interfaced to a microcomputer with Tiamo v. 2.2 software. The general procedure consisted of adding 20.0 mg of CX500 and 1.0 mL of HCl (0.1 mol L^{-1}) to an electrochemical cell, under a nitrogen atmosphere. The ionic strength was adjusted to 0.1 mol L^{-1} (the optimal value determined previously) with KCl (0.1 mol L^{-1}), in a total volume of 10.0 mL. Titrations were conducted with 0.01 mL injections of 0.05 mol L^{-1} NaOH at intervals of 100 s. All solutions were prepared with degassed water prepared by boiling and cooling Milli-Q water (resistivity >18 MΩ cm) under a flow of nitrogen. The potentiometric titration data were fitted using nonlinear regression, as described elsewhere [29].

X-ray diffraction analysis of the CX500 was performed using a Shimadzu XRD-6000 diffractometer operated under the following conditions: λ = 1.5418 Å, 30 kV, 30 mA, scanning rate of 0.02°.