Arabian Journal of Chemistry (2015) 8, 518–526

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Effect of carbon microfiber materials on sensitivity of adenosine and hydroxyadenine at carbon microfiber sensors

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Received 20 July 2013; accepted 29 August 2013
Available online 7 September 2013

KEYWORDS

Carbon microfiber electrode;
Nanostructured ultramicroelectrode;
Adenosine;
2,8-Dihydroxyadenine;
Carbon fiber sensor;
Fast scan voltammetry

Abstract The relationship between the sensitivity measurements and microfiber electrodes made from different carbon microfiber materials, such as polyacrylonitrile (PAN T650 and PAN HCB) and Pitch P25 was established in this work. The different microfiber electrodes were nanostructured by an electrochemical pretreatment method. Sensitivity of adenosine (ADO) and 2,8-dihydroxyadenine (2,8-DHA) was measured at different carbon microfiber sensors made from different carbon microfiber materials. Sensitivity of PAN microfiber electrodes for ADO and 2,8-DHA determinations measured at 500 V s^{-1} vs. SCE is higher than that measured at Pitch P25 microfiber electrodes due to more defects in PAN microfiber electrodes. Adsorption of ADO and 2,8-DHA is greater at PAN HCB electrodes. High conductivity of PAN fibers correlates with sensitivity determinations of the investigated analytes.

1. Introduction

Microelectrodes exhibit several attractive possibilities, including the exploration of microscopic domains, detection in microflow systems, time-resolved probing of processes in single cells, the *in vivo* monitoring of biological events and analyses of very small sample volumes (Kennedy et al., 1993).

Electrodes of different materials have been miniaturized in many geometrical shapes, with the common characteristic that the electrode dimension is significantly smaller than the diffusion layer at their surface. Due to the greatly reduced double-layer capacitance of microelectrodes, associated with their small area, and radial diffusion to the edges of microelectrodes, the signal-to background characteristics are much better than with conventional electrodes. Because of their geometries and low current intensities, it is possible to work in highly resistive situations, including low dielectric solvents, at low temperatures, in the gas phase, with ionically conductive polymers, and with solutions without the addition of a supporting electrolyte (Stradiotto et al., 2003).

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.arabjc.2013.08.025

For amperometry, a wide range of electrode materials are currently available, including noble metals, boron-doped diamond and a broad spectrum of carbon-based working electrodes. Among carbon-based materials, cylindrical carbon fiber microelectrodes (CFMEs) are widespread tools for monitoring biological events *in vivo* using amperometry and/or voltammetry (Huffman and Venton, 2009). They have also been applied to trace and ultratrace determination of both organic and inorganic electroactive species (Malinski and Taha, 1992; Guzmán et al., 2002).

Carbon fibers are materials made by pyrolysis of suitable precursors with polyacrylonitrile (PAN), pitch, and rayon being the most important. The common feature of the carbon fibers prepared in such a way is their composition from graphitic sheets which can be packed in the following three configurations: (i) radiating out from the center of the fiber (radial type), (ii) aligned in concentric arrangement (onion type), and (iii) distributed randomly (random type) throughout the fiber. The basal plane forms the backbone of the graphitic lattice, and the edge plane contains a significant population of oxygen-containing functional groups. Importantly, the final orientation of the graphitic structure largely determines the electrochemical performance. Because the edge plane of the graphitic sheet is more reactive than the basal plane, the application of a given carbon fiber electrode is dictated by its microstructure.

The sensitivity of carbon fiber electrode (CFE) can be substantially increased by suitable modifications of carbon fiber surface, which include electrochemical conditioning. The electrochemical conditioning (pretreatment) is the preferred carbon fiber modification method due to its good reproducibility, high efficiency, and speed. The essence of the pretreatment is electrooxidation/electroreduction of the fiber's surface, yielding increased amount of surficial oxygen containing functional groups (carbonyl, carboxyl, quinone, ether, ester, and hydroxyl), often denoted as carbon or graphitic oxide (Kepley and Bard, 1988). XPS and Raman studies (Proctor and Sherwood, 1983; Ray and McCreery, 1997) have shown that carbonyl and hydroxyl groups are the predominated surface oxide functionalities on carbon. These moieties can modulate electron transfer rates for many electroactive species and can be specifically blocked using special derivatives (Roberts et al., 2010). This way, the electrode surface properties can be adjusted for an optimum sensitivity toward the desired group of analytes. Besides specific modification of carbon fiber surface by the formation of surficial oxygen-containing groups, nonspecific effects also occur, such as physical removal (etching) of the outer part of carbon fiber, resulting in fiber thinning. Accompanying the process is the increase in electrochemical surface area, typically about five-fold (Kovach et al., 1986), which is also beneficial for higher current densities achieved on "pretreated" fibers.

Analytical response of carbon fiber electrodes has been related to tensile modulus of the fibers (De Carvalho et al., 2001). A direct relationship between carbon fiber tensile modulus and electrical conductivity has been reported (Minus and Kumar, 2005), but not with the precursor material of the fiber (Huffman and Venton, 2008). However, the method of carbon fiber electrode surface fabrication may have contributed to the observed behaviors (Huffman and Venton, 2008). Since electrochemistry is based fundamentally on interfacial phenomena, the structure and chemistry of the electrode surface are of obvious importance (McCreery, 2008).

Adenosine is a purine nucleotide that performs many important functions in the human body and biological processes (Cummings et al., 1994). It modulates physiological functions in the heart and brain, regulates oxygen supply during cell stress and plays an important role in the regulation of renal functions (Zhang et al., 1997; Kloor et al., 2000).

Adenine is one of the purine nucleobases and is therefore an essential molecule of life and evolution. Adenine is a component of adenosine, according to the previous studies of adenine oxidation it was concluded that the first $2e^-$, $2H^+$ oxidation of adenine leads to 2-hydroxyadenine which on further $2e^-$, $2H^+$ oxidations form 2,8 dihydroxyadenine as is reported for adenine in the literature (Kathiwala et al., 2010; Goyal and Sangal, 2002).

In this work, a direct measurement of the effect of material structure on electrochemical performance of carbon fiber microdisk electrodes was done. The electrodes were made by a method, which produces stable and renewable electrodes (Brajter-Toth et al., 2000; Kathiwala et al., 2008, 2010); stability of the electrodes is due to the limited overoxidation of the electrode surface. The surface nanostructures of the electrodes have been characterized (Brajter-Toth et al., 2000; Kathiwala et al., 2008). Fast scan measurements were successfully done at such electrodes. In addition, fast scan methods facilitate the acquisition of a large number of signals that can be averaged in a short period of time, and allow for kinetic filtering, which reduces interference effects (Bravo et al., 1998).

Both adenosine (ADO) and 2,8-dihydroxyadenine (2,8-DHA) adsorb weakly at carbon fiber electrodes and undergo fast electron transfer kinetics (Abou El-Nour and Brajter-Toth, 2000; Kathiwala et al., 2010), they produce highly reproducible signals at carbon fiber electrodes These characteristics make them suitable as electrochemical probes for characterizing the nanostructured surfaces by FSV at 500 V s^{-1}. The results confirm contributions of material properties to electroanalytical performance of carbon fiber electrodes. The observed correlations between material properties and electrochemical parameters are discussed.

2. Experimental

2.1. Reagents and methods

All chemicals were of the analytical reagent grade and were used as received. 6-amino-1H-purine-2,8-dione i.e., (2,8-dihydroxyadenine) and adenosine were obtained from Sigma-Aldrich, St. Louis, MO. All other chemicals were obtained from Fisher Scientific (Pittsburgh, PA). Solutions were prepared in doubly deionized water daily before experiments. Phosphate buffer, pH 7.4, contained sodium phosphate monobasic monohydrate ($NaH_2PO_4.H_2O$) and dibasic anhydrous (Na_2HPO_4) at a total concentration of 31 mM was used. The pH of solutions was adjusted with NaOH or HCl before experiments.

Adenosine (ADO) and 2,8-dihydroxyadenine (2,8-DHA) were prepared before the experiments in 31 mM phosphate buffer (pH 7.4). Potassium ferricyanide was prepared in 0.5 M KCl (pH 6.0). All determinations were performed at room temperature. The percentage of CO_2 in air of 0.03%