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Electrochemical, morphological and microstructural characterization of carbon film resistor electrodes for application in electrochemical sensors

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ABSTRACT

The electrochemical and microstructural properties of carbon film electrodes made from carbon film electrical resistors of 1.5, 15, 140 Ω and 2.0 kΩ nominal resistance have been investigated before and after electrochemical pre-treatment at +0.9 V vs SCE, in order to assess the potential use of these carbon film electrodes as electrochemical sensors and as substrates for sensors and biosensors. The results obtained are compared with those at electrodes made from previously investigated 2 Ω carbon film resistors. Cyclic voltammetry was performed in acetate buffer and phosphate buffer saline electrolytes and the kinetic parameters of the model redox system $Fe(CN)_6^{3-/4-}$ obtained. The 1.5 Ω resistor electrodes show the best properties for sensor development with wide potential windows, similar electrochemical behaviour to those of 2 Ω and close-to-reversible kinetic parameters after electrochemical pre-treatment. The 15 and 140 Ω resistor electrodes show wide potential windows although with slower kinetics, whereas the 2.0 kΩ resistor electrodes show poor cyclic voltammetric profiles even after pre-treatment. Electrochemical impedance spectroscopy related these findings to the interfacial properties of the electrodes. Microstructural and morphological studies were carried out using contact mode Atomic Force Microscopy (AFM), Confocal Raman spectroscopy and X-ray diffraction. AFM showed more homogeneity of the films with lower nominal resistances, related to better electrochemical characteristics. X-ray diffraction and Confocal Raman spectroscopy indicate the existence of a graphitic structure in the carbon films.

1. Introduction

New electrode materials have recently been studied for environmental and health applications, particularly to avoid the traditionally used mercury. For application as electrochemical sensors, such materials must have a large potential window and low background current, as well as simple surface regeneration and inertness [1].

Carbon is a commonly used solid electrode material, particularly in the form of glassy carbon, due to its wide positive potential window, mechanical stability, and low porosity. Carbon film electrodes made from carbon film resistors, obtained by coating a substrate with a thin pyrolytic carbon layer, have recently been introduced as a promising alternative form of carbon electrode. Carbon film resistor electrodes have a large potential window after electrochemical surface pre-treatment [2] and have been characterized [2–4] and successfully applied to the development of sensors, e.g. [4–9] and biosensors, e.g. [10–13].

Atomic Force Microscopy (AFM) is a well-established technique which has been used in many applications and in the study of the surface morphology of materials, including thin and thick coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers, and semiconductors [14].

Raman spectroscopy allows the characterization of the molecular or chemical composition of many types of samples without any specific preparation, and is a rapid and non-destructive technique and is a very effective way to investigate the detailed bonding structure of carbon films [14]. Confocal Raman spectroscopy is a specific form of Raman spectroscopy that can be used where a high spatial resolution is required. It has been widely applied in several fields, imaging microscopy being one of the most extensive applications, because it provides 3D spatial resolution. The major advantage of confocal Raman spectroscopy is the ability to collect Raman scatter from a small point within the interior of a larger sample. Typical applications are in structure determination, multicomponent qualitative and quantitative

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analysis. In materials science it has been used for sample composition and crystallinity studies [15].

The purpose of this work was to evaluate the electrochemical and microstructural characteristics of carbon film electrical resistors of different resistances, from 1.5 Ω to 2.0 kΩ, as electrodes for sensor and biosensor applications with and without pre-treatment. Comparison is made with results obtained at previously investigated carbon film electrodes of 2 Ω nominal resistance [2–4].

2. Experimental

2.1. Electrode preparation

Electrodes were made from carbon film electrical resistors of different nominal values: 1.5, 2.0, 15, 140 Ω and 2.0 kΩ; the preparation protocol is described in detail elsewhere [3]. The preparation of the carbon film resistors by pyrolysis of hydrocarbons on ceramic cylinder substrates inside a quartz bottle held in a furnace at 1100 °C in a continuous flow of nitrogen containing a fraction of hydrocarbons (usually methane) is described in greater detail in [2]. The cylindrical resistors used have length 0.6 cm and external diameter 0.15 cm, with two tight-fitting metal caps and connecting wires as external contact. Briefly, to prepare the electrodes one of these metal caps is removed and after sheathing the connecting wire, the other is protected by normal epoxy resin. The final exposed carbon film electrode geometric area is ~0.20 cm^2.

Nafion coatings, when required, were made by placing 5 μL of a solution of 0.25 wt% Nafion in alcohols, followed by 3 μL of *N*,*N*′-dimethylformamide, directly on top of the surface of the carbon film electrode. After evaporation of the solvents, the film was cured with a jet of warm air for about 1 min. The film is of ca. 1 μm thickness. This procedure was the same as used in [16].

2.2. Instrumentation and methods

Voltammetric experiments and Electrochemical Impedance Spectroscopy (EIS) were carried out using a standard three-electrode configuration in a glass cell of capacity 15 cm^3. Besides the carbon film working electrode, the cell contained a platinum wire counter electrode and a saturated calomel electrode (SCE) as reference. Electrochemical pre-treatment of the electrodes, was done by applying a potential of +0.9 V vs SCE during periods of 1–6 min in the buffer electrolyte solution in which experiments were conducted.

Voltammetric experiments were conducted using a μAutolab II potentiostat (Eco Chemie, Utrecht, Netherlands) controlled by GPES 4.9 software.

Electrochemical impedance spectra were recorded using a Solartron 1250 Frequency Response Analyzer coupled to a Solartron 1286 Electrochemical Interface using ZPlot 2.4 software (Solartron Analytical, UK). The frequency range from 65.5 kHz to 0.1 Hz was scanned logarithmically with an applied sinusoidal voltage perturbation of amplitude 10 mV, 10 points per frequency decade, superimposed on the chosen applied potential. An auto-integration time of 60 s was employed.

AFM was performed with a Multimode™ Atomic Force Microscope controlled by a Digital Instruments Nanoscope E controller (Veeco Instruments, USA). Silicon nitride NanoProbes™ V-shaped cantilevers, 100 μm length, 0.58 N m^{-1} spring constant were used. All images were recorded in contact mode AFM in air at room temperature. Image contrast and brightness were adjusted.

Confocal Raman spectroscopy was performed using a Scanning Near-field Optical Microscope, AlphaSNOM (WiTec, Germany).

The microstructure was evaluated by X-ray diffraction (XRD). The diffraction patterns were acquired from a Philips X'Pert apparatus (PANalytical, Netherlands) with a Co anode ($\lambda_{k\alpha 1}$ = 1.788 96 Å, $\lambda_{k\alpha 2}$ = 1.792 85 Å) and a collimated detector in Bragg–Brentano mode.

2.3. Reagents and solutions

All solutions were made from analytical grade reagents and Milli-Q ultrapure water (resistivity ≥ 18 MΩ cm). Solutions used as supporting electrolytes were 0.1 M phosphate buffer saline solution (PBS), pH 7.0, prepared from sodium dihydrogenphosphate, disodium hydrogenphosphate and 0.05 M NaCl; 0.1 M sodium acetate/acetic acid buffer, pH 4.2, and 0.4 M potassium sulphate. All experiments were carried out at room temperature (25 ± 1 °C).

3. Results and discussion

The electrochemical characterization of the carbon film electrodes was done by cyclic voltammetry and electrochemical impedance spectroscopy. Morphological and microstructural studies were carried out by Atomic Force Microscopy, Confocal Raman spectroscopy and X-ray diffraction. The principal results will be discussed below.

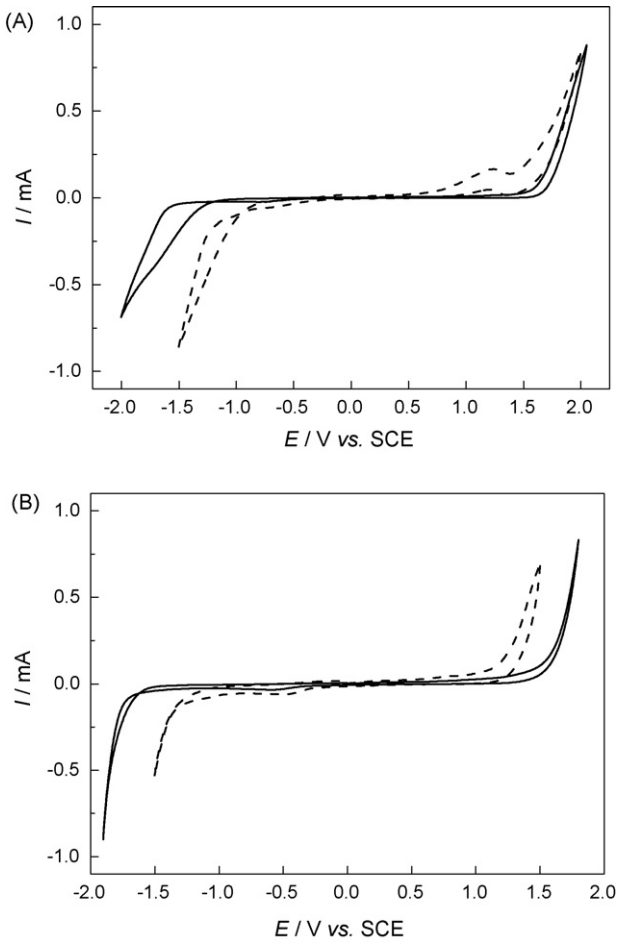

Fig. 1. Cyclic voltammograms in (A) pH 4.2 acetate buffer solution and (B) phosphate buffer saline solution at carbon film electrodes of 1.5 Ω nominal resistance, area 0.2 cm^2 (- -) before and (–) after pre-treatment. Pre-treatment: +0.9 V vs SCE during 4 min in the same buffer solution.