



# Activity changes of glassy carbon electrodes caused by their exposure to OH<sup>•</sup> radicals

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## ABSTRACT

GC electrodes were exposed to Fenton solutions. The surface changes produced by the OH<sup>•</sup> radicals of these solution were inspected using SEM, XPS, Raman spectroscopy and electrochemistry. The OH<sup>•</sup> radicals caused erosion and roughening of the surface, selective oxidation and dissolution of sp<sup>2</sup> carbon, and reduction of the number of nucleation sites for silver deposition.

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## 1. Introduction

Carbon-based electrodes are nearly ubiquitous in the laboratory because of their availability in various forms and shapes, and their wide potential window [1,2]. The most common method of activation of glassy carbon (GC) is to polish its surface with micro-sized abrasives. After such treatment a fresh new surface should be obtained, however, the polishing on some types of pads can occasionally deactivate the surface, while the use of too big particles of abrasive can lead to relatively large surface scratches [3]. To remove remains of polishing material the ultrasonication is often needed. The impurities can be also removed by electrochemical oxidative procedures [4]. A number of electrode pretreatments to yield an active and reproducible electrode surface have been proposed [5].

Free radicals can cause substantial changes in the morphology and activity of the conducting surfaces. As it has already been shown for gold, the real surface area of gold electrodes treated with OH<sup>•</sup> radicals can diminish (chemical polishing action) and the voltammetric response of analytes can change due to changes in the electron transfer rate and the reaction path [6,7]. The aim of this paper was to characterize how the action of OH<sup>•</sup> radicals can affect the parameters (including the amount of bound oxygen and the surface roughness) of GC electrodes. The corresponding changes in the chronoamperometric electrodeposition of silver are also shown.

## 2. Experimental section

Cyclic voltammetry was performed with an Autolab, model 12 potentiostat (Eco-Chemie, Utrecht). A GC electrode (3 mm in diameter, BASi, USA) was used as the working electrode; saturated Ag/AgCl and calomel electrodes and a platinum wire were used as the reference and auxiliary electrodes, respectively.

Fenton solutions were always freshly prepared from ammonium iron(II) sulfate hexahydrate (Merck), EDTA (Merck), 0.01 M acetate buffer (pH 4.7) and hydrogen peroxide solution (POCh). Just before each measurement the surface of the working electrode was polished, immersed in the Fenton solution for a defined time interval and washed with purified water. To avoid the change in activity of Fenton solutions the longer exposures consisted of appropriate number of 5-min treatments in freshly prepared solutions.

In the nucleation experiments the following supporting electrolytes were used: 2 mM silver nitrate (POCh, Gliwice, Poland) and 0.25 M potassium nitrate (POCh).

X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCALAB-210 spectrometer from VG Scientific.

Raman spectra were collected in the backscattering configuration with a Labram HR800 (Horiba Jobin Yvon) confocal microscope system equipped with a CCD detector (1024×256 pixel), using a 20 mW HeNe (632.8 nm) laser.

Scanning Electron Microscopy (SEM) images were taken with an Ultra Plus FESEM, Zeiss, Germany, using 1-kV acceleration voltage and a low-energy-loss back-scattered electrons detector which provided a high contrast.

K-type GC plates (cti Chemie + Werkstoff Technik GmbH, Idstein, Germany) used for the XPS, Raman and SEM measurements were produced by pyrolysis of aromatic polymers at circa 1000 °C.

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### 3. Result and discussions

#### 3.1. Surface structure changes

Fig. 1 depicts a SEM image of the GC surface after mechanical polishing and before exposing it to OH<sup>•</sup>. Typical SEM images recorded after immersion of the electrode in Fenton's solution for 30 and 60 min are presented in Fig. 1. A progress in the corrosion of the GC surface with time of the OH<sup>•</sup> action is clearly visible in the micrographs. After 30 min of the radical treatment the surface is still marked with a net of very fine scratches formed during its mechanical polishing before the radical treatment; however, the first effects of the erosion of the material can be already noticed. The net of scratches is almost invisible for the samples treated for 45 min and completely vanishes after 60 min. The disappearing of the scratches on the GC surface indicates the removal of a layer of carbon from the

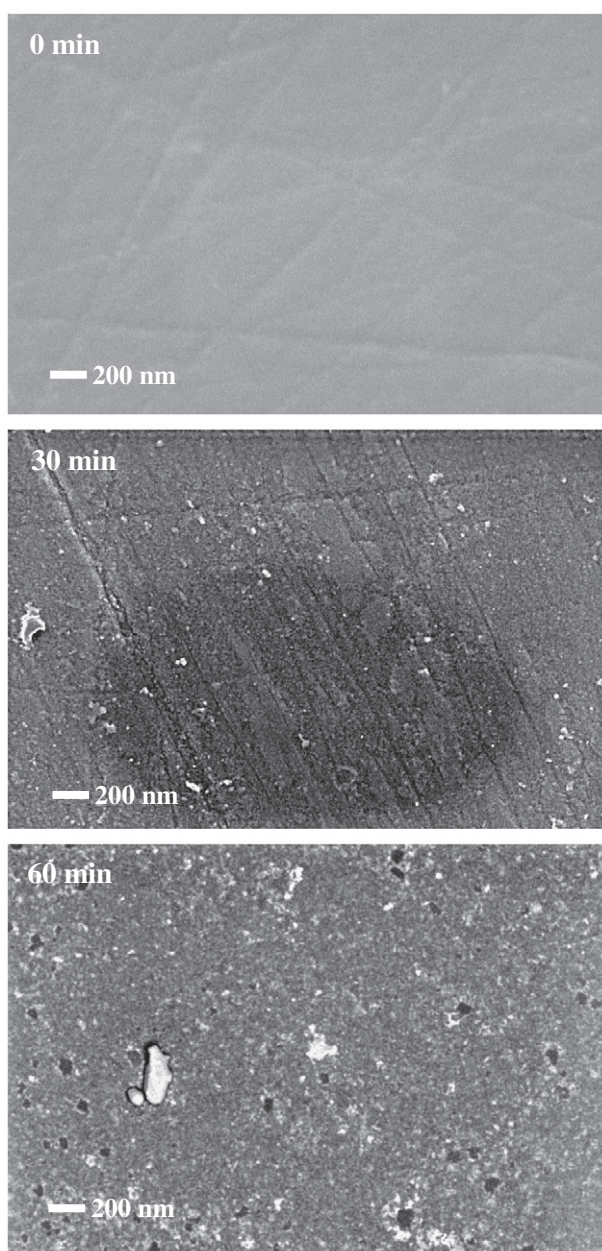


Fig. 1. Micrographs of GC surface obtained after: 0, 30 and 60 min of OH<sup>•</sup> radicals' treatment. Concentrations of Fe<sup>2+</sup>, EDTA and H<sub>2</sub>O<sub>2</sub> are 1, 1 and 10 mM, respectively.

GC surface treated. It can be a combined process of mechanical crumbling and chemical oxidation.

According to the model proposed by Jenkins and Kawamura [8], glassy carbon consists of long sheets (microfibrils) of hexagonally oriented, sp<sup>2</sup>-hybridized carbon atoms. However, unlike graphite, there is no precise orientation of the carbon atoms from layer to layer [9], also, some sp<sup>3</sup> carbon atoms can be expected. XPS experiments showed that the amount of oxygen at the surface layer increased (from 8 to 35%) with time of electrode treatment by OH<sup>•</sup> radicals up to 45 min, and then surprisingly dropped below 30%. Apparently, OH<sup>•</sup> radicals first oxidized the sp<sup>2</sup> carbon atoms to alcohol, carbonyl or carboxyl groups and finally detached those carbon atoms as CO<sub>2</sub>. At the same time the amount of the sp<sup>3</sup> bonds (diamond-like) significantly increased (from 11 to 16%) while the percentage of carbon sp<sup>2</sup> (graphite type) decreased (from 60 to 31%), which is a significant change in sp<sup>3</sup>/sp<sup>2</sup> molar ratio.

The above XPS results are in good agreement with the Raman data. In the range 600–1800 cm<sup>-1</sup> the bare GC exhibits two characteristic intense Raman bands at ~1360 cm<sup>-1</sup> (diamond band) and ~1600 cm<sup>-1</sup> (graphite band) [10]. Both the graphite and the diamond bands undergo significant changes upon interactions with OH<sup>•</sup> radicals. Intensities of both bands increase (up to 30 min), but only the graphite-type band changes its position: it shifts towards higher frequencies. This shift towards higher energies is characteristic for the oxidation state of carbon [11].

#### 3.2. Electroactivity changes

We have examined the electrodeposition and nucleation of silver on pure GC and GC treated with OH<sup>•</sup>. Typical experimental current transients for 0.12 V vs. SCE (overpotential of 0.44 V) obtained with a pure GC electrode and the GC electrodes treated with OH<sup>•</sup> are presented in Fig. 2A. The first parts of the chronoamperometric curves reflect an increase in the current related to the nucleation (increase in number of active sites) and growth of silver particles on the surface of GC electrode. The current reaches a maximum and then starts to decrease due to the overlap of diffusion fields around the nuclei. The current maximum of silver deposition decreases and occurs at longer times as the time of dipping of GC electrode in Fenton solution is prolonged. These results suggest that the number of active sites and silver nuclei decrease with an extension of time of OH<sup>•</sup> interaction with GC substrate.

A comparison between the experimental curves and the theoretical data allows determining the nucleation type. According to the model of diffusion-controlled growth of hemispherical particles proposed by Scharifker and Hills [12], two limiting nucleation mechanisms can be considered: the progressive and the so-called instantaneous. The progressive nucleation is related to the growth of number of nucleation sites activated during the course of the electrodeposition process. The so-called instantaneous nucleation corresponds to the growth of the nuclei on a smaller number of active sites, all activated at the same time during the initial phase of the electroreduction.

The theoretical current–time transients for the two considered cases: instantaneous and progressive nucleation can be described by the equations:

$$\left(\frac{i^2}{i_m^2}\right) = \frac{1.9542}{t/t_m} \left\{ 1 - \exp \left[ -1.2564 \left( \frac{t}{t_m} \right) \right] \right\}^2 \quad (1)$$

$$\left(\frac{i^2}{i_m^2}\right) = \frac{1.2254}{t/t_m} \left\{ 1 - \exp \left[ -2.3367 \left( \frac{t}{t_m} \right)^2 \right] \right\}^2 \quad (2)$$

where  $i$  is current density and  $t$  is time;  $i_m$  and  $t_m$  are the coordinates of the peak.

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