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Growth of nano-porous Pt-doped cerium oxide thin films on glassy carbon substrate

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Abstract

Glassy carbon (GC) substrates were treated by the oxygen plasma over several periods of time. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) study showed the dramatic influence of oxygen plasma on the morphology of glassy carbon. The treatment leads to the formation of nanostructured surface, which consists of well separated rod-like nanostructures oriented perpendicularly to the substrate surface. The surface roughness was found to increase with increasing treatment time.

By using magnetron co-sputtering of platinum and cerium oxide we can prepare oxide layers continuously doped with Pt atoms during the growth. This technique combines etching of the carbon substrate and growth of the deposit. This leads to the formation of high surface area catalyst which makes this method promising for production of thin film catalysts.

Keywords: A. Films; B. Electron microscopy; D. Carbon; CeO_2

1. Introduction

Carbon in a variety of forms is widely used as an electrode material in different electrochemical systems [1–6]. In recent years there has been increasing interest in different carbonaceous materials, particularly glassy carbon, as heterogeneous catalyst support in the field of electrocatalysis [7,8]. The physicochemical characteristics and surface chemistry of carbon might influence the properties of catalysts [9–12]. For these applications, carbon materials should have high specific surface area and low resistivity [4,12,13].

It has been shown in the literature that surface morphology of carbon materials can be modified by plasma treatment [14–17] which leads to preparation of high surface area electrode as catalyst support.

Platinum-based catalyst supported on high-surface area carbon is one of the most studied systems. Their electrocatalytic activity, the effects influencing their performance, and their application in fuel cells have been discussed in literature [12,18–24].

In our previous studies [25–29] we showed that Pt-doped cerium oxide films on carbon substrates prepared by magnetron sputtering exhibited porous structure and a high concentration of cationic platinum, which opened the promising way for using such systems as highly active thin film catalysts. We speculated there about mechanisms of formation of porous structures proposing that deposition angle was the parameter influencing the film morphology.

This paper focuses on mapping the morphological changes of GC catalyst support treated by oxygen plasma. We show here that magnetron sputtering of Pt-doped CeO_2 catalyst provides both the deposit growth and oxygen plasma etching of the substrate simultaneously, which allows us to prepare high surface area Pt–CeO_2 catalyst on GC electrode.

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2. Experimental

Glassy carbon plate, 1 mm (0.04 in) thick, was purchased from Alfa Aesar. Oxygen plasma etching of GC was carried out in a MED 020 BalTec Modular High Vacuum Coating System. The etching device consisted of a ring-shaped driven electrode, placed 2 cm above the grounded substrate holder. The etching was carried out in pure oxygen (purity 99.999%) with constant total gas pressure of 20 Pa. The discharge current was set at 10 mA. The discharge voltage automatically adjusted by the MED 020 system was 650 V.

Thin catalyst films were deposited on the un-etched GC by simultaneous magnetron sputtering of CeO_2 and Pt by using two magnetrons: a radio frequency (rf) magnetron (with rf power of 100 W) and dc magnetron (with dc power of 20 W). Deposition was carried out at room temperature of the substrate in an Ar atmosphere by keeping the total pressure in the deposition chamber constant at 2.7 Pa. The growth rate of thin films was approximately 0.5 nm/min.

Morphology was examined by means of scanning electron microscopy (SEM) using the MIRA Tescan microscope at 30 keV electron beam energy, and atomic force microscope (AFM) “Veeco di MultiMode V” in tapping mode. Sharpened silicon probes (RFESP) with nominal tip radius of curvature 8–10 nm were used in the AFM. Lamellas for transmission electron microscopy (TEM) observations were prepared using focused ion beam (FIB) in LYRA Tescan dual beam microscope equipped with gas injection system. TEM observations were carried out with a 200 kV JEOL 2100 (LaB_6) microscope.

The surface roughness was calculated from AFM images using the Veeco AFM software. The roughness parameters should not be considered absolute values of roughness, they merely permit to compare roughness parameters for different samples measured in the same instrument configuration. For each sample we used the same AFM tip and the same fitting procedure. Surface roughness was expressed by the mean roughness (R_a) parameter, which averages the height relative to the centre plane and it is calculated as:

$$R_a = \frac{1}{L_x L_y}\int_0^{Lx}\int_0^{Ly} |f(x,y)|\,dxdy$$

where $f(x,y)$ is the surface height relative to the centre plane and L_x and L_y are the dimensions of the surface scan area.

3. Results and discussion

In order to investigate the oxygen plasma interaction with GC we exposed the GC substrates to oxygen plasma for several different periods of time. High resolution SEM was used for investigation of surface morphology of plasma modified GC surface. In Fig. 1 we show the SEM images of GC substrate: untreated and treated by oxygen plasma for 20 and 40 min respectively. From these images it is evident that the morphology of glassy carbon strongly depends on the oxygen plasma exposure time. The 40-min of treatment led to the formation of nanostructured surface consisting of well separated vertical nanostructures oriented perpendicularly to the substrate surface whilst the 20-min treatment resulted in a finer dispersion of the surface nanostructures.

In addition to the SEM characterization we carried out an AFM study in order to obtain more information about the surface roughness. Morphology evolution during the plasma modification of GC substrates studied by AFM is plotted on Fig. 2. The R_a values determined from 1×1 μm AFM scan area for each sample are shown in Table 1. It clearly shows that the increase of the plasma treatment time is accompanied by an increase in the surface roughness.

For further investigation of the oxygen plasma etching of GC we partially masked a part of fresh GC surfaces by a droplet of varnish and placed the substrates into oxygen plasma for the same time as described above. After removing the varnish we observed formation of a step between non-etched (masked by varnish) and etched GC surface. In Fig. 3, a SEM image and an AFM profile of the step obtained for the 20-min treated sample are shown. We can clearly distinguish the treated and untreated parts of the substrate and determine the amount of material etched away by simply measuring the step height from the AFM profile across the edge. The step height values obtained from AFM profiles of all samples are shown in Table 1.

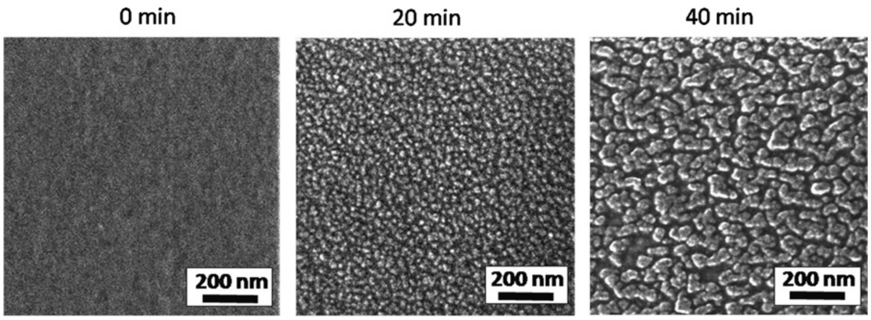

Fig. 1. SEM images of untreated and treated for 20 and 40 min GC surface.

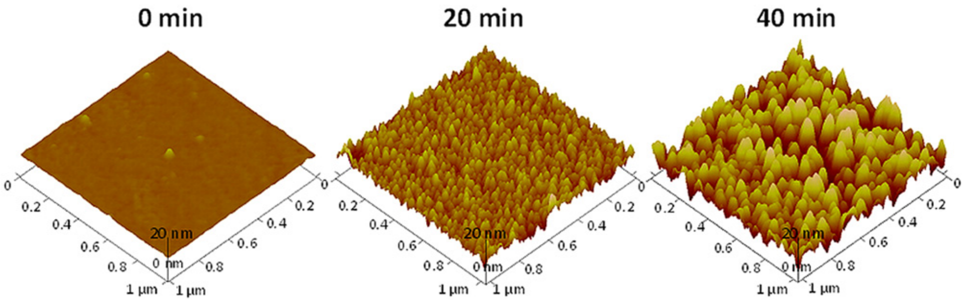

Fig. 2. AFM 3D images of 1 × 1 µm GC surface untreated and treated for 20 and 40 min.

Table 1
R_a and the step height values obtained by AFM for untreated and treated for 20 and 40 min GC in oxygen plasma.

Treatment time	0 min	20 min	40 min
R_a	0.2 nm	2 nm	4.8 nm
Step height	–	200 nm	320 nm

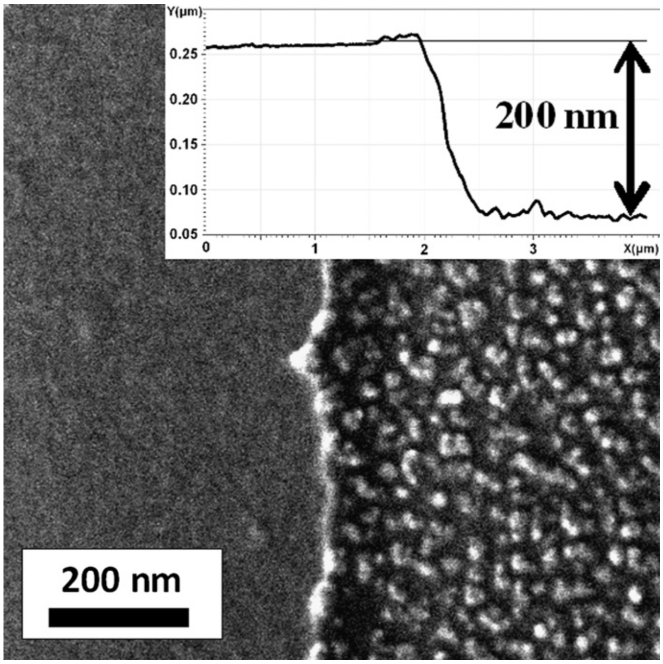

Fig. 3. SEM image and AFM profile of the edge obtained for the 20 min treated sample.

This means that during the oxygen plasma etching of the GC surface two processes take part simultaneously: a removal of a part of the GC material and a surface nanostructuring. This technique allows us to prepare high surface area glassy carbon substrate and to tune the surface roughness and porosity by varying the oxygen plasma treatment time. Such modified glassy carbon makes this material interesting as a catalyst support in the field of electrochemistry, particularly for cyclic voltammetry study of morphology-dependent thin film catalyst activity.

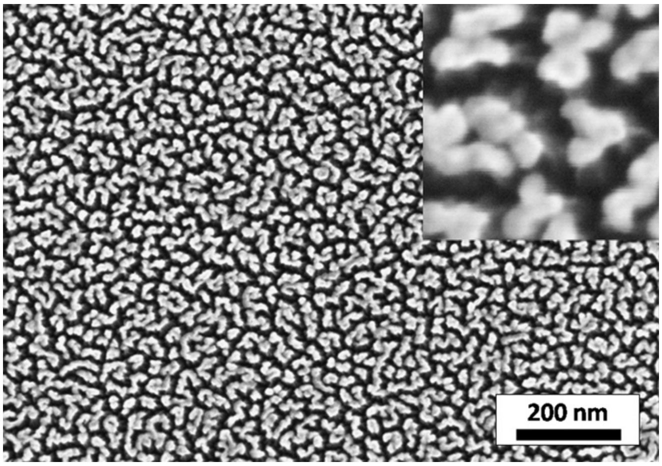

Fig. 4. SEM image of Pt–CeO_2 films deposited on GC substrate for 20 min.

In the second part of the experiment we prepared Pt-doped CeO_2 catalyst films by simultaneous magnetron sputtering of cerium oxide and platinum onto the GC substrate. Although the deposition takes place in Ar atmosphere, the working atmosphere contains oxygen sputtered off from the cerium oxide target which makes possible formation of oxide films as we have shown in Refs. [25–29]. Therefore, one can expect that growth of oxide thin films on carbon substrate is accompanied by a simultaneous etching of the carbon substrate surface. Indeed, in the case of 20 min deposition we observed a formation of a rough structure (Fig. 4) similar to the case of 20 min GC oxygen plasma etching (see Fig. 1).

By comparing the Pt–CeO_2 growth on the silicon substrate [25,30], where only non-porous films were formed, and on the GC substrate in this work, we clearly see that carbon plays an active part in porosity promotion.

In our recent study we showed by using the Photoelectron spectroscopy (PES) that the porous Pt–CeO_2 films on graphite foil are partially reduced. The dependence of Pt^{2+}/Pt^{4+} and Ce^{3+}/Ce^{4+} ratios on the film thickness pointed out that the films are more reduced in deeper parts, i.e. closer to the interface [31].

In order to compare carbon modification by pure oxygen plasma etching and by the oxide material sputtering on carbon substrate, we investigated the roughness of

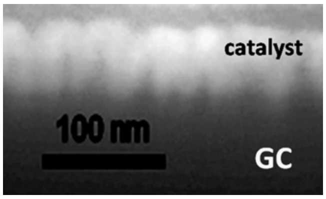

Fig. 5. TEM image of Pt–CeO_2/GC interface prepared by means of FIB.

the catalyst film/substrate interface by TEM of a lamella cut out perpendicularly to the interface using a FIB technique. Fig. 5 shows the formation of rough interface with 35 nm deep cavities etched in the GC surface coated by the 20 min deposition catalyst film. Therefore, we can conclude that the GC substrate is modified by oxygen plasma etching during magnetron sputtering process in a way similar to the case of oxygen plasma etching.

Thus, the observed behaviour of porous growth can be explained by a simultaneous growth of the catalysts film and etching of the GC substrate. We expect hypothesize that randomly distributed Pt–Ce–O islands are formed in the early stages of the growth and, simultaneously, the oxygen plasma is etching the GC substrate in the space between the islands. These islands serve as an etching mask and define the film morphology. The sputtering rate in that case should be small enough to ensure sputtered particles migration at the surface and nucleus formation, which is necessary in the same time for keeping the CG surface partially uncovered for oxygen interaction with carbon. We suppose that during the growth the incoming particles will preferentially deposit on top of the nuclei due to higher accessibility of the upper parts of the 3D structures [32] and Pt-doped cerium oxide, thus, form three dimensional catalyst structures (see Fig. 4 inset). The proposed mechanism also well explains the dependence of pore size on the deposition rate (not shown). We observed that at high deposition rates (generally above 3 nm/min) porosity of deposits disappears, apparently due to rapid covering of the substrate by the sputtered overlayer.

According to the literature [33,34], oxygen atoms seem to be the main active species in the etching process in oxygen plasma. In our case the etching process is assigned to the chemical oxygen plasma etching, which provides the oxygen interaction with carbon substrate and the removal of carbon in the form of CO and CO_2 gases. This process has already been proven by monitoring CO_2 production by mass spectrometer during the etching process [35]. It explains the fast removal of carbon from the sample, see Fig. 3.

In this work we showed the Pt-doped cerium oxide catalyst as an example because of its application in fuel cell technology [25,28]. We should note, however, that the same morphological effects were obtained by using pure cerium oxide film deposition on carbon substrates, which means that the addition of Pt does not influence the eventual film porosity. Magnetron sputtering growth of porous ceria based thin films was observed on different carbon substrates (CNTs, HOPG, sputtered carbon films). It suggests that carbon substrate modification by oxygen plasma is a universal effect.

4. Conclusions

It was shown that oxygen plasma etching leads to dramatic changes of GC substrate morphology. By changing plasma exposure time we are able to tune the morphology of GC surface. Such modified large-surface glassy carbon is an interesting material for catalyst support in the field of electrochemistry, particularly for cyclic voltammetry studies of morphology-dependent thin film catalyst activity, because it can be coated, in principle, with a large variety of thin films.

Magnetron sputtering of Pt doped CeO_2 catalyst was found to provide both deposit growth and oxygen plasma etching of the substrate simultaneously. Thus, a high surface area Pt–CeO_2 catalyst was formed on GC electrode. However, this technique depends on many factors such as RF voltage, pressure, deposition rate etc. and needs further investigation.

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