



Glassy carbon electrodes

I. Characterization and electrochemical activation

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Abstract

Electrochemical properties of glassy carbon electrodes of two types were examined, one thermally treated at 1000°C (sample K) and another thermally treated at 2500° (sample G). Mechanically polished or electrochemically polarized electrodes were characterized in NaOH, HClO₄ and H₂SO₄ solutions by cyclic voltammetry (cv) at different sweep rates in the potential range between the hydrogen and oxygen evolution. The activity of the electrodes depended on the properties of the glassy carbon examined, as determined by both the temperature of thermal treatment and the mechanical or electrochemical pretreatment of the sample. It was noticed that both types of electrodes, when polished exhibited an increase in the double layer charge upon increasing the pH value of the solution. The cv charges, for both types of samples, increase upon anodic polarization. The higher the potential of oxidation, the more pronounced is the increase in charge, particularly in acidic solution. The increase in charge amounts from below 1 mC cm^{−2} for polished glassy carbon up to few hundreds of mC cm^{−2} for surfaces anodically polarized in acidic solution. Analysis of the dependence of voltammetric charge, as well as morphological changes of the electrode surface, on the time of oxidation suggests the existence of three stages in the electrochemical activation process. The first one occurs only once at the beginning of the activation, while the other two repeat themselves, reflecting a periodical activation and deactivation process. These stages were discussed and ascribed to a surface layer oxidation, graphite oxide layer growth and mechanical destruction of the surface. Independent surface analysis by AES, XPS and STM confirms the results obtained by electrochemical methods. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Owing to its physical and chemical properties, glassy carbon has become an interesting and widely applied electrode material. It exhibits a rather low oxidation rate and a rather high chemical inertness which, together with very small pore sizes and a small gas and liquid permeability, make glassy carbon a convenient inert electrode [1]. The starting polymer and the temperature of the carbonization have a great influence on physico–chemical properties of glassy carbons [2,3]. Jenkins and Kawamura [3] analyzed carbonization mechanism and structure of

glassy carbon using different techniques and concluded that this material is made up of aromatic ribbon molecules, randomly oriented and tangled in a complicated manner. According to these authors [3] high resolution electron micrographs of glassy carbon thermally treated at 900°C show short-range ordered groups consisting of two or three randomly oriented imperfect parallel layers, while the material heat-treated at 2700°C exhibits a network of stacked graphite-like ribbon molecules with regions of perfect linearity. In addition, the formation of the network is accompanied by a decrease in the density of micropores. Scanning electron micrographs of different samples of glassy carbon, obtained at different temperatures of thermal treatment, show that with increasing temperature the pitting of the surface decreases [4]. These pits are formed

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through the removal of heteroatoms during the thermal treatment of the material. Therefore, the number of the pits formed should be higher if glassy carbon is treated at a higher temperature. However, at higher temperatures the ribbon molecules become flatter and straighter, causing the pores to become smaller and shallower.

Randin and Yeager [5] found out that similar functional groups are present on the surface of glassy carbon and pyrolytic graphite. The existence of some groups which contain oxygen has been confirmed by number of authors [6–12].

Different pretreatments for preparing and activating the glassy carbon electrode surface for electrochemical measurements have been widely discussed [2,4,13–23]. Fresh and well-defined electrode surfaces can be prepared by mechanical treatment, which involves abrasion with emery paper and polishing with alumina. Other methods, such as laser treatment [24], irradiation of glassy carbon with ultrasound [25] or activation of glassy carbon using a carbon arc [26], have been applied to create a reproducible and active glassy carbon surface. However, it seems that the electrochemical treatment of glassy carbon electrodes is most often used for that purpose. Engstrom and Strasser [27] performed such treatment by applying 1.75 V versus SCE for 5 min followed by -1.0 V versus SCE for 1 min. According to these authors, the pre-treated electrode exhibited an enhanced electrochemical activity but no change in its surface area or topography. Kepley and Bard [28] also activated glassy carbon by sweeping the potential to a high anodic value, and assumed that the graphite oxide layer formed was responsible for the activation. This porous and swollen layer grows with uniform composition to a large thickness, of at least one micrometer. The surface is deactivated upon extensive reduction of the layer. On the other hand, if glassy carbon is used as an anode at high voltages/current densities there is a danger of causing erosion through the formation of a non-adherent oxidized layer and exfoliation [29].

Our previous results [30] have shown an increased activity of the electrochemically activated glassy carbon electrodes in comparison with that of mechanically pre-treated ones. However, the activity of the electrode does not increase linearly with the time of the activation, nor does it reach some constant limiting value. On the contrary, the activity increases to a certain degree and then suddenly drops. Such behavior could be explained by the existence of three stages in the electrochemical activation of glassy carbon. These stages are described and discussed in this work.

2. Experimental

The following samples of glassy carbon (GC) (Sigradur–Sigri Elektrographite, GmbH, Germany):

- sample K (thermally treated at 1000°C),
- sample G (thermally treated at 2500°C) were used as working electrodes.

The electrode surfaces were refreshed before each measurement by abrasion with emery paper of decreasing grain size followed by polishing with alumina of 1, 0.3 and $0.05\text{ }\mu\text{m}$ average particle size. The final cleaning of the electrodes was performed in $18\text{ M}\Omega$ water in an ultrasonic bath.

The electrochemical treatment of previously polished electrodes was performed by:

- anodic polarization in $0.5\text{ M H}_2\text{SO}_4$ at 2.00; 2.25; 2.50 and 2.75 V versus SCE during 5; 30; 60... i.e. $t_n = t_{n-1} + 30\text{ s}$ up to 1980 s.
- anodic polarization in 1 M NaOH at 1.41 and 1.91 V versus SCE (potentials that should correspond to the values of 2.25 and 2.75 V versus SCE in $0.5\text{ M H}_2\text{SO}_4$ — during 5; 30; 60... i.e.: $t_n = t_{n-1} + 30\text{ s}$ up to 720 s.
- cathodic polarization in $0.5\text{ M H}_2\text{SO}_4$ at -1.45 V versus SCE (potential at which the hydrogen is evaluated at an intensity similar to that of oxygen at 2.25 V) during 5; 30; 60; 90; 120; 150; 180 and 635 s.

The counter electrode was a platinum wire while a saturated calomel electrode (SCE) and a Hg/HgO electrode were used as a reference.

The reagents used were Merck, of p.a. (pro analysi) purity, and the solutions (1 M NaOH , 1 M HClO_4 and $0.5\text{ M H}_2\text{SO}_4$) were prepared with $18\text{ M}\Omega$ water. The electrolytes were purged with purified nitrogen prior to each experiment.

The glassy carbon electrodes were examined by cyclic voltammetry (cv) (at sweep rates of 5, 25, 50 and 100 mV s^{-1}) in the potential range between hydrogen and oxygen evolution.

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) techniques were used for the examination of the surface and near surface composition as well as for the identification of the changes generated during the polarization of the electrodes. The AES spectra were recorded in a RIBER spectrometer with a primary electron beam accelerated voltage of 3 KeV and an absorbed beam current of $3\text{ }\mu\text{A}$. Depth profiling was carried out by argon ion beam sputtering at 4.5 KeV and $4\text{ }\mu\text{A}$, at a rate of $\approx 1\text{ nm min}^{-1}$. The XPS spectra were obtained by using the RIBER OPX 150 X-ray photoelectronic spectrometer with an Al K_{α} X-ray source (350 W).

All spectra presented were obtained by averaging the spectra recorded in three different points on the sample surface (three spectra in each point) followed by fast Fourier transform (FFT) filter smoothing. The deconvolution of the C_{1s} XPS spectra was performed by using a 0.85 Gaussian–0.15 Lorentzian distribution function.

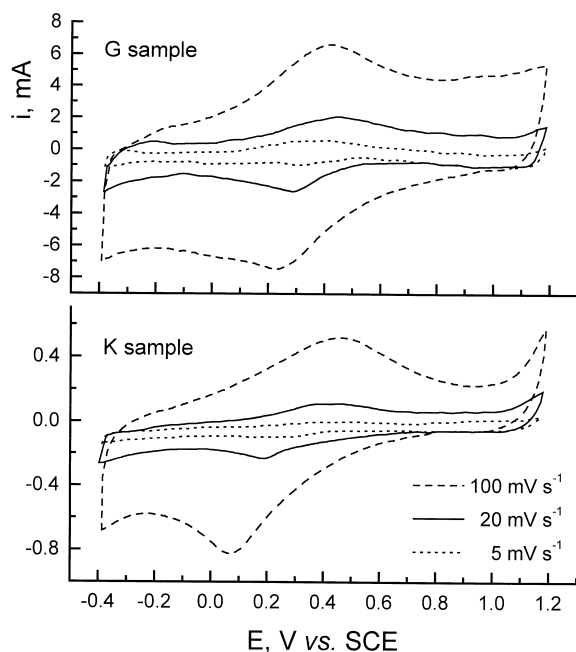


Fig. 1. Cyclic voltammograms of anodically polarized GCEs in 0.5 M H₂SO₄ for 150 s at 3.2 V versus SCE.

The surface morphology of the electrodes was examined by scanning tunneling microscopy (STM) (Nanoscope III, Digital Instruments, USA).

3. Results

Samples of glassy carbon electrodes K and G, thermally treated at different temperatures and mechanically polished or anodically polarized, were electrochemically characterized. The samples were examined before and after polarization by cv in the potential range between those causing hydrogen and oxygen evolution. Typical voltammograms recorded in 0.5 M H₂SO₄ solution for both samples, anodically polarized for 150 s, are presented in Fig. 1. In the potential range examined, sample K is active and sample G is totally inactive for the oxygen evolution reaction. The values of the double layer charge, calculated by the integration of cyclic voltammograms, are presented in Table 1. It may be noted that polished glassy carbon electrodes of K type in 0.5 M H₂SO₄ at slow sweep rates bear three times larger charge, and at fast sweep rates two times larger charge, than the GC electrode of G type. However, after the polarization at 3.2 V in 0.5 M H₂SO₄, the charge for the G type electrode is large in comparison

Table 1
Double layer charge of activated glassy carbon electrodes

Electrolyte	Surface state	Double layer charge, mC cm ⁻²					
		K type electrode (1000°C)			G type electrode (2500°C)		
		100 mV s ⁻¹	25 mV s ⁻¹	5 mV s ⁻¹	100 mV s ⁻¹	25 mV s ⁻¹	5 mV s ⁻¹
0.5 M H ₂ SO ₄	Polished	0.29	0.45	0.76	0.13	0.17	0.23
	Polarized 3.2 V, 5 s	7.63	10.6	15.6	42.5	49.5	59.6
	Polarized 3.2 V, 30 s	11.30	15.60	22.98	49.6	60.4	78.4
	Polarized 3.2 V, 150 s	4.93	7.82	15.03	72.8	86.6	129.1
	Polarized 3.2 V, 450 s	—	—	—	109.3	133.5	181.0
	Polarized 3.2 V, 900 s	—	—	—	89.0	119.0	173.0
1 M NaOH	Polished	0.69	—	1.08	0.53	0.70	1.67
	Polarized 3.2 V, 5 s	0.38	—	1.11	0.43	0.61	1.19
	Polarized 3.2 V, 30 s	0.50	0.75	1.45	0.42	0.59	1.09
	Polarized 3.2 V, 150 s	0.74	1.03	1.22	—	—	—
	Polarized 3.2 V, 450 s	0.79	1.06	1.26	—	—	—
	Polarized 3.2 V, 900 s	0.71	0.98	1.81	—	—	—

with the change for the K type electrode. This effect is more pronounced at longer polarization times. The charge for G electrodes is three to nine times larger than that for K electrodes at slow sweep rates and even 15 times larger at fast sweep rates. It can also be seen that after certain maximum degree of polarization is reached, the activity of both electrodes starts to decrease.

Considering the electrochemical characterization results of the mechanically polished G and K glassy carbon electrodes in 1 M NaOH (Table 1), it can be said that there is no pronounced difference in double layer charge between G and K glassy carbon samples, at any of the sweep rates applied. However, when anodically activated, sample K in general exhibits a somewhat larger cv charge in comparison with sample G, and the difference increases with increasing the polarization time. Also, in alkaline solution there appears to be some initial decrease in activity prior to a continuous but very slow increase in activity, within the polarization times considered.

Both (G and K) glassy carbon electrodes were also examined in 1 M HClO₄. The results obtained showed that the charge for sample K was two to three times larger than the charge for sample G regardless of the pre-treatment of the electrodes. One should note that such behavior is opposite to that of polarized samples in 0.5 M H₂SO₄, solution where G type glassy carbon proved to be more active than the K type sample.

Thus, the examinations of the electrodes in different acidic solutions showed that there is difference in electrochemical behavior of the electrodes with respect the anion in the solution. It is known that when sulfate anion is present in the solution in a concentration higher than 90%, during the anodic polarization of carbon materials at potentials more anodic than 1.6 V versus SCE, sulfate anions penetrate through the graphite layers and even a chemical reaction can occur to form intercalate compounds [31]. Similarly to the intercalation process, it can be supposed that sulfate ions can penetrate through glassy carbon, but this penetration is limited by the graphitic structure in the material and can facilitate the oxidation of glassy carbon and the formation of a graphite–oxide layer [31,32]. Sample G of glassy carbon has a more ordered structure and a larger number of graphitic structure domains on the same geometric surface. The consequence is a higher number of active sites and therefore a more pronounced formation of graphite–oxide layers, which leads to a higher charge for the same polarization time in H₂SO₄ solution in comparison with the K glassy carbon sample.

As shown above, the double layer charge (which is a measure of the activity of the electrode) increases upon anodic polarization of glassy carbon electrodes. With respect to this, it could be expected that the activity of these electrodes for an electrochemical redox reaction should be improved as well. Cyclic voltammograms, recorded for the quinone/hydroquinone reaction (Q/H₂Q)

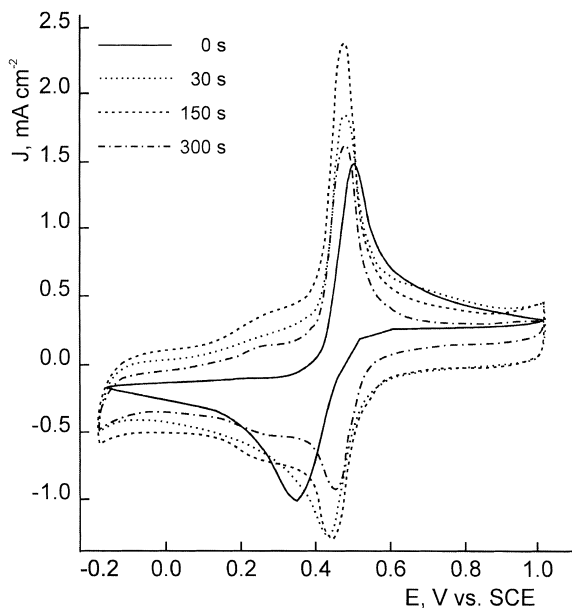


Fig. 2. Cyclic voltammograms of quinone/hydroquinone redox reaction on K type GCE in 0.5 M HClO₄ + 0.005 M quinone after different times of polarization, sweep rate of 100 mV s⁻¹.

on polished and anodically polarized glassy carbon electrodes (0.5 M HClO₄, 0.005 M quinone) are shown in Fig. 2. It can be seen that the currents pertaining to the Q/H₂Q redox reaction at the electrode, which was previously anodically polarized during 300 s, were lower than those obtained for the electrodes polarized during 30 s and 150 s, all charges being higher than that obtained for polished glassy carbon. The decrease of the current for Q/H₂Q redox reaction is obviously a consequence of the decrease in activity of the GC electrodes after reaching their maximum degree of polarization, as shown in Table 1.

In order to further evaluate the electrochemical behavior of the generally more active G type glassy carbon, the electrodes were further examined. The polarized electrodes were examined by cv before and after various electrochemical treatments, which were conducted as follows:

- after anodic polarization in 0.5 M H₂SO₄ at 2.00; 2.25; 2.50 and 2.75 V versus SCE during 5; 30; 60... i.e. $t_n = t_{n-1} + 30$ s up to 1980 s.
- after anodic polarization in 1 M NaOH at 1.41 and 1.91 V versus SCE during 5; 30; 60... i.e. $t_n = t_{n-1} + 30$ s up to 720 s.
- after cathodic polarization in 0.5 M H₂SO₄ at -1.45 V versus SCE during 5; 30; 60; 90; 120; 150; 180 and 635 s.

Also, the surface and morphological characterization of the electrodes was performed by microscopic and spectroscopic techniques.

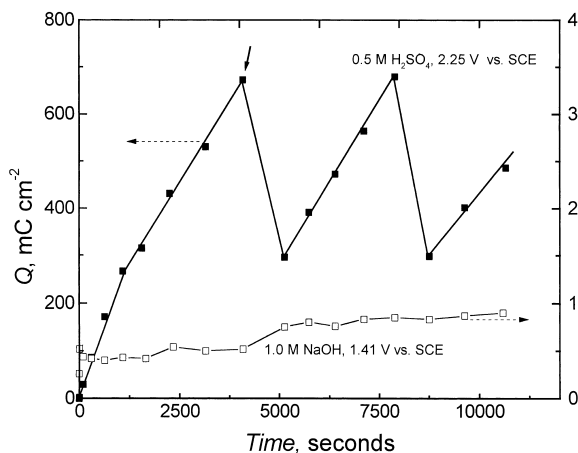


Fig. 3. Charge versus time of polarization dependence for the G type GCE. The arrow shows the point of most extensive exfoliation during the polarization in H_2SO_4 , sweep rate of 100 mV s^{-1} .

3.1. Electrochemical characterization

3.1.1. Anodic polarization

Fig. 3 shows the changes of the double layer charge with time of activation for the G type glassy carbon electrode polarized in 1 M NaOH and 0.5 M H_2SO_4 . It is clear from the diagram that the increase of the charge upon the polarization in acidic solution is much more pronounced than the increase upon the polarization in alkaline solution. When type G glassy carbon electrode is polarized in the alkaline solution (1 M NaOH), the increase of the polarization potential from 1.41 V to 1.97 V leads to a moderate increase of the double layer charge (i.e., the electrode activity). The charge after 5 s of polarization increases to approximately twice the charge of the polished electrode, regardless of the polarization potential. Further polarization at the same potential (Fig. 3) at first leads to a small decrease of the charge, but after that the charge increases slowly and continuously to reach a value three times higher than that of the polished electrode after about 10 500 s.

Activation of type G glassy carbon in acidic solution, as shown in Fig. 3 by the dependence of the cv charge on the time of polarization, is characterized by three stages:

- a first stage of linear dependence of charge on the polarization time [$Q = f(t)$] with a relatively high slope,
- a second stage where the $Q = f(t)$ function is linear with a somewhat lower slope and
- a third stage that corresponds to an abrupt decrease of the charge.

After this sudden decrease of the charge, further polari-

zation of the electrode leads to another linear increase of the charge with polarization time, with a slope virtually identical to that of the second stage. This increase of the charge ends up with another sudden drop of the double layer charge. In this way the second and third stages are repeated periodically. If the electrode is polarized for the same time at a more positive potential, the charge attains a higher value and the sudden drop of the charge occurs sooner, i.e. the third stage is reached earlier (Fig. 4). Further analysis shows that, regardless of the polarization potential, the transition from the first to the second stage occurs when the charge attains a value of $250 \pm 50 \text{ mC cm}^{-2}$. The sudden decrease of the charge after the second

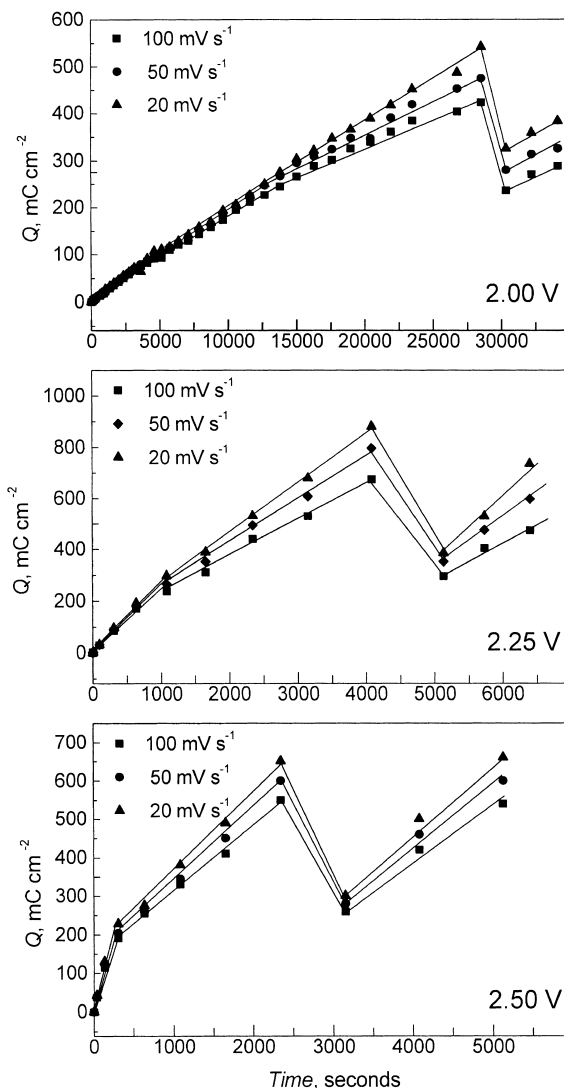


Fig. 4. Charge versus time of polarization dependence for the G type GCE at different polarization potentials (versus SCE) and at different sweep rates in 0.5 M H_2SO_4 .

stage is again up to this characteristic value of $250 \pm 50 \text{ mC cm}^{-2}$ for type G glassy carbon electrodes.

The fact that the charge increases with decreasing sweep rate points out to the porosity of the electrode surface [33]. The larger increase of the charge at slower sweep rates and higher polarization potentials is a consequence of the more intensive oxidation of active sites in the subsurface layer. When the time of anodic polarization increases, the increase in charge with decreasing sweep rate is more pronounced. Subsurface active centers are formed to a limited extent due to the limited penetration of the electrolyte into the graphitic electrodes' close porous structure.

Cyclic voltammetry shows that the state of the electrode surface just after the third stage is similar to the surface state just at the beginning of the second stage in the process of oxidation.

These results lead to the conclusion that the number of active sites on type G GC that can be induced and oxidized by polarization is limited. After all sites are oxidized (first stage), the oxide layers formed grow until the moment when the space between the ribbon molecules of GC becomes insufficient to accommodate them (second stage). The result is the peeling off of the top layers, and the charge drops due to a decrease of the total number of active sites of the electrode (third stage).

All the glassy carbon electrodes examined exhibited peeling of the surface layers and the change in the color of the electrolyte towards a yellow–brown color, upon increasing the polarization potential more anodically and/or prolonging the polarization time. The coloring of the electrolyte is related to the graphite oxide particles peeled off from the electrode surface. The particles, peeled off from the surface during the polarization in alkaline solution, are very fine, and the surface of the electrode at the end of the process is shiny, gray–black in color and less rough. When anodic polarization is performed in acidic solution, the peeled off particles are small, the color of the electrode surface changes from the beginning of the process, and finally at the end the surface is dim, black and rough. The most intensive exfoliation of the electrode surface layers is followed by the sudden decrease of double layer charge after which, by further polarization of the electrode, the charge of the double layer increases again. This second increase of the charge is followed by the less intensive peeling of the glassy carbon layers, and when the most intensive peeling is attained then again the sudden decrease of the cv charge occurs, followed by less intensive peeling. The behavior just described periodically repeats itself upon further polarization. Microphotographs presented in Fig. 5A show that the electrode surface has a grainy structure covered with cracks. In the second stage (Fig. 5B) the color of the surface of the electrode does not change anymore, but the appearance becomes 'swollen' and the peeling of the surface layers starts. When the most intensive peeling occurs and the double layer charge drops

(third stage) the electrode surface becomes dark, dim and intensely cracked, as shown on microphotographs in Fig. 5 (C_1 , C_2 and C_3). As can be seen, the higher the polarization potential, the more cracked the surface becomes.

3.1.2. Cathodic polarization

Type G glassy carbon electrodes were also exposed to cathodic polarization in order to examine the influence of such a treatment on the electrode behavior. The electrodes were cathodically polarized in 0.5 M H_2SO_4 solution at -1.45 V versus SCE. The time of polarization was chosen to correspond to the first stage of $Q = f(t)$ dependence in anodic polarization.

The results obtained showed minor changes in the double layer charge with polarization time, in comparison with the changes noted upon anodic polarization. Also, no sign of the peeling off of the electrode surface was noticed during the cathodic treatment.

Hence, cathodic polarization, i.e. reduction of glassy carbon in acidic solution, does not lead to the activation of the surface.

Cathodic polarization in alkaline solutions, although only briefly examined, leads to the conclusion that the electrode activity is also unchanged by this treatment.

3.2. Surface characterization of glassy carbon by nonelectrochemical methods

3.2.1. Auger-electron spectroscopy (AES)

The approximate composition (in atomic percentage) of surface and subsurface layers of glassy carbon electrodes, being polished and polarized during 635 s at: 1.41 V versus SCE in 1 M NaOH, 2.25 V versus SCE in 0.5 M H_2SO_4 and -1.45 V versus SCE in 0.5 M H_2SO_4 has been determined by qualitative and quantitative analysis of AES spectra. The results obtained are listed in Table 2.

The content of oxygen, which can be regarded as a measure of the degree of surface oxidation, is higher for the anodically polarized samples and practically unchanged for the cathodically polarized ones, in comparison with the polished electrodes (Table 2). Also, after anodic polarization in acidic media the oxidation of the surface is more intensive than in basic media, particularly towards the external surfaces (low scattering times).

3.2.2. X-ray photoelectron spectroscopy (XPS)

The samples, examined by AES analysis, were also analyzed by an XPS technique. XPS C1s spectra recorded were deconvoluted using a five peaks model [34,35] (Fig. 6). Four peaks were identified as graphitic carbon– C_{gr} and carbon bonded to different functional groups (primarily phenolic, carboxyl, carbonyl)– C_{ox} . The smallest fifth peak reflecting the presence of impurities adsorbed from air was subtracted from the overall spectra. The percentage of C_{gr} and carbon bonded to different functional groups– C_{ox} , as well as the ratio $\text{C}_{\text{ox}}/\text{C}_{\text{gr}}$, were calculated from the

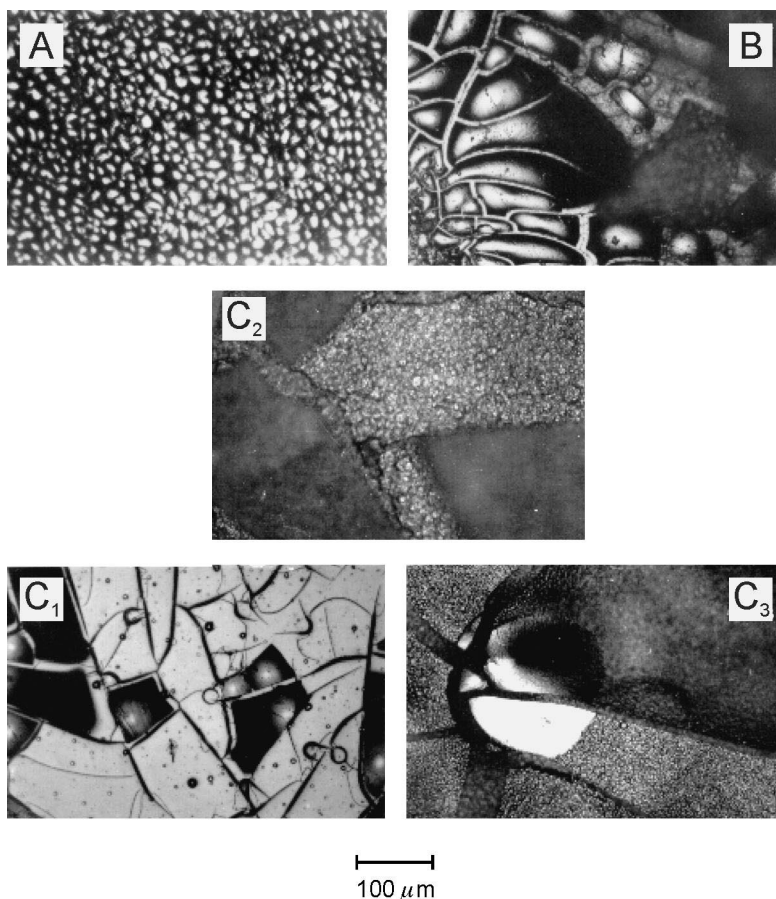


Fig. 5. Microphotographs of GCE surface after polarization in acid solution at 2.25 V versus SCE in the middle of: (A) First and (B) second stage of $Q = f(t)$ dependence, and at different polarization potentials: (C₁) 2.00 V; (C₂) 2.25 V and (C₃) 2.50 V versus SCE at the end of third stage of $Q = f(t)$ dependence.

deconvoluted spectra. The values determined are listed in Table 3. These results give further evidence that the surface layer of glassy carbon is oxidized during anodic polarization, and are consistent with the results from the electrochemical measurements discussed above. The portion of graphitic carbon in XPS C1s spectra provides the best evidence in this regard. This portion is highest for the polished electrodes and lowest for the electrodes polarized in acidic solution. Thus, the C_{ox}/C_{gr} ratio is lowest for the polished electrode and highest for the electrode polarized in acid. The results also indicate that cathodic polarization does not result in any significant changes of the GC surface in comparison with the polished i.e. mechanically treated electrode.

Accepting the model proposed by Nakayama and co-workers [34] and Sundberg and coworkers [35] for the deconvolution of carbon XPS C1s spectra, the presence of three functional groups (phenolic, carboxyl and carbonyl), was assumed.

If the glassy carbon electrode is polarized in alkaline

media, the percentage of phenolic groups present is highest, and it follows that carbonyl and carboxyl groups are present in the lowest percentage. The percentage of phenolic group is highest also when glassy carbon is anodically polarized in acidic media, but in this case the percentage of carbonyl and carboxyl groups is practically equal.

In addition, the percentage of phenolic groups present is significantly higher in the case of the electrode polarized in acidic media in comparison with the value for the sample polarized in alkaline media.

When the polished electrode and the one polarized in alkaline solution are compared, the results show that the percentage of phenolic groups is lower for the polarized sample. At the same time, the polarization in alkaline media leads to an increase of carbonyl and carboxyl percentage to an equal extent. Analysis of type G glassy carbon polarized in acidic solution shows that the percentage of phenolic groups is significantly increased in comparison with the value for the polished electrode, while

Table 2

Approximate composition of surface and subsurface layers of polished and anodically polarized (during 635 s) G type GCEs, determined by AES

Sample	Time of scattering, min ^a	Approximate composition at. %		
		C	N	O
Polished	0	96.3	1.8	1.9
	1	96.0	2.1	1.9
	5	96.6	2.1	1.3
	10	96.6	2.1	1.3
	30	96.6	2.1	1.3
Anodically polarized in 0.5 M H ₂ SO ₄ at 2.25 V versus SCE	0	92.5	2.8	4.7
	1	93.9	3.1	3.0
	5	95.2	2.0	2.8
	10	95.3	2.0	2.7
	20	95.8	1.7	2.5
Anodically polarized in 1.0 M NaOH at 1.41 V versus SCE	0	94.1	2.7	3.2
	1	94.5	2.7	2.8
	5	94.9	2.6	2.5
	10	95.4	2.5	2.1
	20	96.3	1.7	2.0
Cathodically polarized in 0.5 MH ₂ SO ₄ at –1.45 V versus SCE	0	95.9	2.0	2.1
	1	96.0	2.1	1.9
	5	96.4	2.1	1.5
	10	96.5	2.1	1.4
	30	96.7	2.1	1.2

^a Time of scattering by high energy argon ions, rate ~1 nm min^{–1}.

the increase of the percentage of carbonyl and carboxyl groups occurs to a lower extent than for the electrode polarized in alkaline media.

3.2.3. Scanning tunneling microscopy (STM)

Typical STM images of glassy carbon surfaces after polishing, polarization in acid solution and polarization in alkaline media are presented in Fig. 7. As can be seen in Fig. 7A, the STM image of polished glassy carbon surface shows that the surface roughness is low and confirms that the polishing procedure leads to a mirror-like appearance of the electrode surface. On the other hand, anodic polarization has a main part in getting a rough surface as a consequence of the oxidation process. Therefore, the roughness is more pronounced on the electrode polarized in acid (Fig. 7C) and less pronounced if the electrode is polarized in alkaline solution (Fig. 7B).

Attempts to obtain images of the surfaces on the atomic level were of no success due to the porosity and the high portion of oxide on the electrode surface (roughness).

4. Discussion

On the basis of the results presented above, the following mechanism for glassy carbon oxidation by anodic polarization in acidic media can be proposed:

Anodic polarization of GC starts with the oxidation of surface active sites, which are presumably defects of graphitic structure (discontinuities in basal plane) and functional groups formed. That results in the increase of the charge — first stage of $Q = f(t)$ dependence, as seen in Fig. 3. When all of surface active sites are oxidized, electrolyte penetration through the domains of graphitic structure of GC become more intensive and growth of a *graphite–oxide layer* starts. This is followed by an increase in the distance between graphitic layers and, finally, by the appearance of cracks on the surface. Macroscopically, this can be observed as the swelling or bubbling of the GCE surface.

Besenhard and Fritz [36] and Kepley and Bard [28] find that intensive oxidation of graphite, or electrochemical oxidation of GC in concentrated sulfuric acid, can increase the distance between graphite layers from 0.35 nm up to 0.62 nm. This occurs through the formation of functional groups, not only at the edges of the layers, but in the interlayer spaces as well. In the case of graphite, functional groups can be formed up to 1 μm deep in the structure [31], depending on the electrolyte used, as well as on the potential of polarization. Their formation is more intensive in acidic than in neutral electrolytes, while in alkaline electrolytes the formation of a *graphite–oxide layer* is not recorded.

Keeping in mind the closed pore structure of glassy carbon, the *graphite–oxide layer* may be formed only to a limited extent. Thus, the bubbling of the electrode surface can reach only the outermost undersurface regions. This process leads to an increase of the real electrode surface and provoke a further, but slower, increase in double layer charge — second stage of $Q = f(t)$ dependence. Microphotographs of glassy carbon electrodes confirm this by showing the dependence of the surface state on the electrode potential (Fig. 5). This observation is in agreement with the results of Yang and Lin [32].

When formed, the *graphite–oxide layer* fills up all the space between the graphitic molecules. Further oxidation leads to the destruction of the surface, i.e. bubbling of the surface and sudden exfoliation of the electrode. In that way both the real electrode surface and the number of the active sites on the surface decrease, resulting in the sudden decay of the charge — third stage of $Q = f(t)$ dependence (Fig. 4).

After the third stage, a ‘new’ surface, e.g. freshly exposed graphitic structure domains, is in contact with the electrolyte. The *graphite–oxide layer* starts to thicken again (second stage), up to the moment when a new exfoliation of the surface occurs (third stage). These two processes, e.g. these two stages, are then repeated successively.

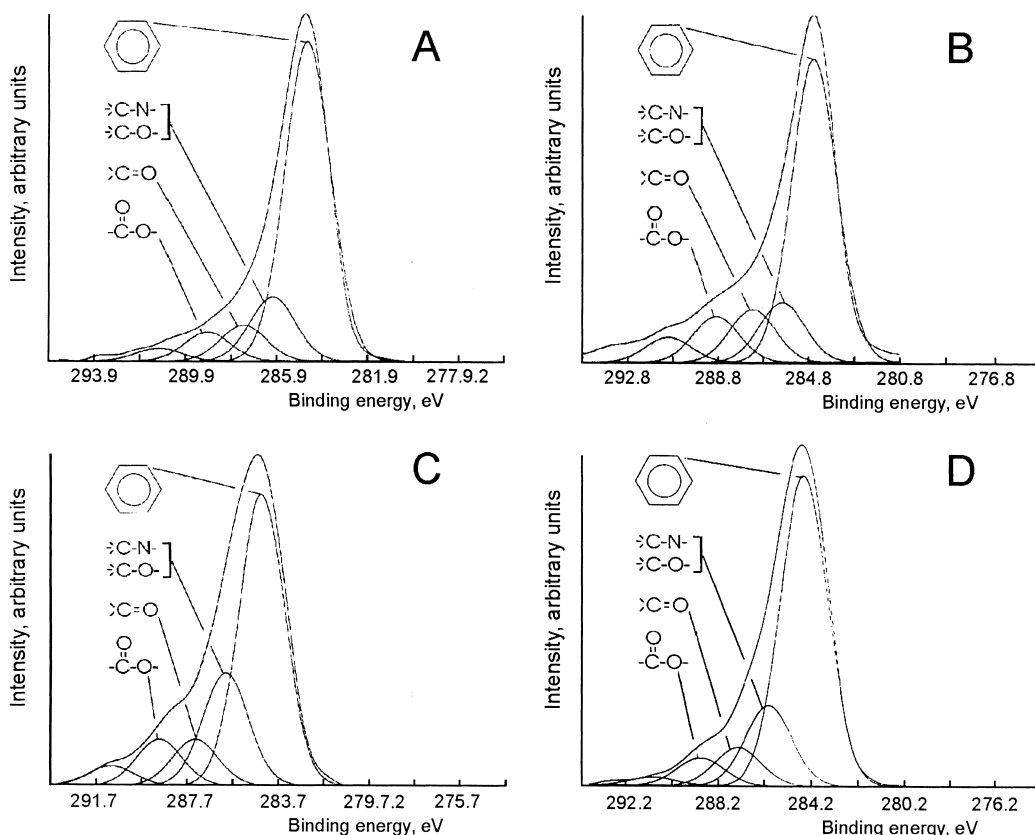


Fig. 6. Deconvoluted XPS C1s spectra of the surface of G type GCE: (A) Polished; (B) anodically polarized in alkaline solution; (C) anodically polarized in acid solution and (D) cathodically polarized in acid solution (for the details see text).

Table 3

Percentage of different functional groups in XPS C1s spectra of polished and anodically polarized G type GCEs

Sample	Fraction of different functional groups in C _{1s} spectra of GCEs, %				C_{ox}/C_{gr}
	Graphitic C 284.6 eV	Phenolic 286.0 eV	Carbonyl 287.3 eV	Carboxyl 288.9 eV	
Polished	71.9	14.1	7.8	6.2	0.39
Anodically polarized in 1.0 M NaOH at 1.41 V versus SCE	65.9	12.8	11.4	9.9	0.52
Anodically polarized in 0.5 M H ₂ SO ₄ at 2.25 V versus SCE	58.5	22.7	9.4	9.4	0.71
Cathodically polarized in 0.5 M H ₂ SO ₄ – 1.45 V versus SCE	69.4	16.3	8.2	6.1	0.44

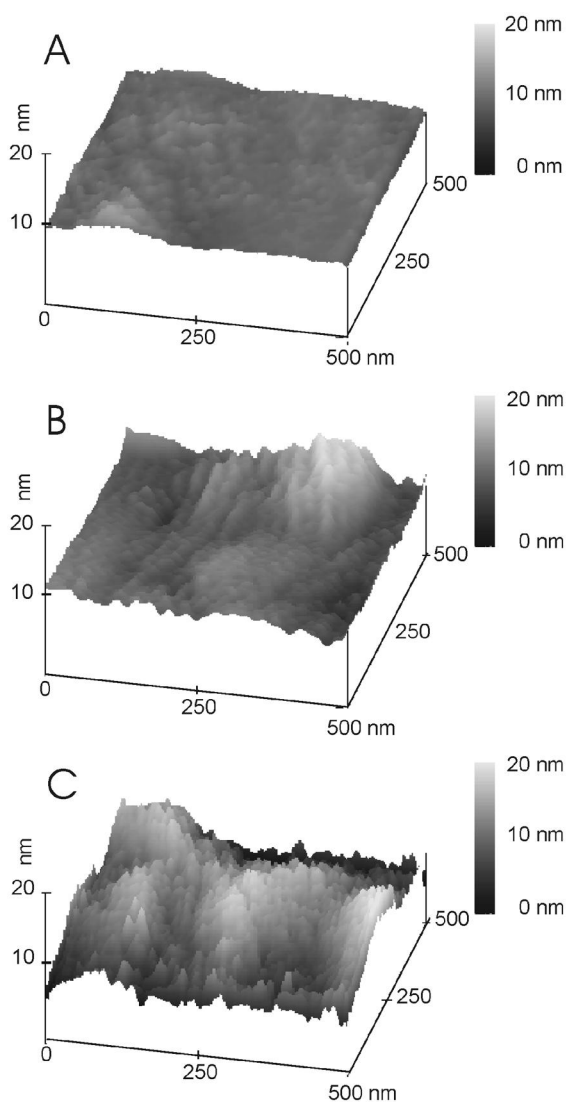


Fig. 7. STM images of the surface of: (A) Polished, and anodically polarized GCEs during 635 s in (B) NaOH at 1.41 V versus SCE and (C) in H_2SO_4 at 2.25 V versus SCE.

The rate of the oxidation obviously depends on the degree of order in the structure of glassy carbon. The rate of the growth of the graphite–oxide layers is higher for the K type of glassy carbon. This type of carbon is less stable, more porous, and has less ordered structure, so that electrolytes can penetrate through the sample deeper and more easily leading to its faster oxidation. Due to this, but also because of the weaker bonds between the ribbon molecules (as a consequence of the less ordered structure), intensive peeling occurs even before all available free space is filled with graphite–oxide. Therefore, the third stage of $Q = f(t)$ dependence during the anodic polarization of K type glassy carbon is reached earlier, although

the increase in charge is slower in comparison with that of G type glassy carbon, as the number of the active centers formed is lower.

It should be noted that in acid, at such high positive potentials, oxidation of carbon to CO and/or CO_2 may occur [31]. This can in addition lead to the destruction of the surface and an increase in the electrochemical activity of the glassy carbon.

The XPS results indicate that when GC is polarized in alkaline solution, the products of the oxidation of the surface are similar to those formed in acidic media. However, the cyclic voltammograms and the charge show that there is no drastic increase in the charge during polarization, and no change in the $Q = f(t)$ dependence, as observed in acidic media. As already mentioned, peeling of the surface in the case of polarization in alkaline media is much less intense, and the resulting particles are very fine, most probably because in alkaline solutions the electrolyte does not penetrate through the graphite structure. Hence, oxidation is taking place only on the external surface of the glassy carbon, thereby leading to the peeling of fine particles and to a relatively small increase in charge during the oxidation process.

The AES results, which show an increase in the content of oxygen only in surface and near surface layers of glassy carbon polarized in alkaline media, confirm the above discussed assumption that only external surface oxidation of glassy carbon occurs in this medium. The microphotographs of the glassy carbon after polarization in alkali, showing a less cracked surface and no indication of bubbling of the glassy carbon, also support the above assumption.

STM images of the glassy carbon samples give additional support to the proposed mechanism of glassy carbon oxidation. The very smooth and flat surface of polished G-type glassy carbon, without any deformations registered, shows the highly ordered structure of this sample. Roughness of the surface increases with polarization in alkaline solution, but this increase is much smaller in comparison with that arising in acidic solution. This is because in alkaline solution only the external surface of glassy carbon is oxidized, while in acid both surface and subsurface layers undergo oxidation with an intensive destruction of the graphite structure, as already described.

5. Conclusion

On the basis of electrochemical and surface characterization tests, it can be concluded that the oxidation of glassy carbon by anodic polarization is more intense in acidic than in alkaline media, and that in acidic media oxidation proceeds also more deeply through the glassy carbon. As the oxidation of glassy carbon occurs at the same time as the electrochemical activation, it can be concluded that glassy carbon oxidized in acidic solution is

more active in comparison with the one oxidized in alkali. Also, the degree of the activation depends on the type of glassy carbon employed. The less ordered structure (K-type) is more readily activated, but the degree of activation (measured by the gain in double layer charge) is lower than in the case of glassy carbon of the highly ordered structure (G-type).

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