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AC impedance tracking of glassy carbon activation

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Owing to its physico-chemical properties, carbon is extensively used in a variety of forms as an electrode material in different electrochemical systems. Different carbon materials are often used as substrates for supercapacitors and different catalysts. For these applications, carbon materials should have high specific surface area, low resistivity, high porosity and surface hydrophilicity [1]. To achieve these properties, carbon should be chemically or electrochemically activated. Glassy carbon can be successfully used as a model for studying the process of activation.

In this work, the activation of glassy carbon, carried out by electrochemical oxidation in sulfuric acid, was investigated by cyclic voltammetry, electrochemical impedance spectroscopy and atomic force microscopy. Glassy carbon was oxidized for fixed time at 5 different potentials.

The GC (Sigradur – Sigri, Elektrographite, GmbH, Germany) electrode surfaces were either mechanically and/or electrochemically treated. The mechanical treatment was performed before each experiment by abrasion with emery papers of decreasing grain size followed by polishing with alumina of 1, 0.3 and 0.05 μm particle size. The final cleaning of the electrodes was performed in high purity water (Millipore 18 M Ω) in an ultrasonic bath. The electrochemical treatment of polished electrodes was performed by anodic polarization for 95 s in 0.5 M H₂SO₄ at chosen potentials. In such way, 7 electrodes were prepared:

- GC – I (polished and cycled in the potential range -0.4 to 0.8 V vs SCE);
- GC – II (polished and cycled in the potential range -0.4 to 1.2 V vs SCE)
- GC_{ox} – III (polished and oxidized at 1.2 V vs. SCE)
- GC_{ox} – IV (polished and oxidized at 1.5 V vs. SCE)
- GC_{ox} – V (polished and oxidized 1.7 V vs. SCE)
- GC_{ox} – VI (polished and oxidized at 2.0 V vs. SCE)
- GC_{ox} – VII (polished and oxidized at 2.2 V vs. SCE)

GC and GC_{ox} electrodes were investigated by electrochemical impedance spectroscopy (EIS) in 0.5 M H₂SO₄ at the potentials of 0.3 and 0.6 V vs. SCE. The EIS responses to the input sinusoidal potential of 5 mV amplitude were registered in the frequency range between 50 kHz and 5 mHz.

The glassy carbon electrodes were examined also by cyclic voltammetry (cv) in 0.5 M H₂SO₄ at the sweep rates of 5, 25, 50 and 100 mV s⁻¹ in the potential range between hydrogen and oxygen evolution, except GC-I when the potential was cycled up to 0.8 V..

All experiments were done at room temperature with Pt wire as counter electrode and bridged saturated calomel electrode (SCE) as the reference electrode. All the potentials are given *versus* SCE. The electrolytes were purged with purified nitrogen prior to each experiment.

All GC electrodes were examined by AFM in air at room temperature as well. The structural characterization was performed with a NanoScope E (VEECO Digital Instruments, USA) microscope. AFM observations were carried out in the height mode using NanoProbes silicon nitride cantilevers with a force constant of 0.06 N/m. Analysis of the surface AFM images were done observing a few different parts of the samples in order to find out typical appearance.

Electrochemical oxidation of glassy carbon leads to an increase in voltammetric charge. This increase depended on the conditions, *i.e.*, potential applied for the electrochemical activation. As shown in Fig. 1, the more positive the potential is, the more pronounced is the increase in charge. The voltammetric charge decreases with the increase in sweep rate. This kind of the dependence of voltammetric charge on the sweep rate is commonly explained by the existence of the less accessible surface (active sites) in the porous electrodes. Since glassy carbon is porous material this increase in charge with slowing of sweep rate is expected. Also, this increase is more pronounced for the electrodes oxidized at more positive potentials. Thus, electrochemical oxidation of glassy carbon results in an increase in porosity of the material, which leads to the higher surface area and roughness.

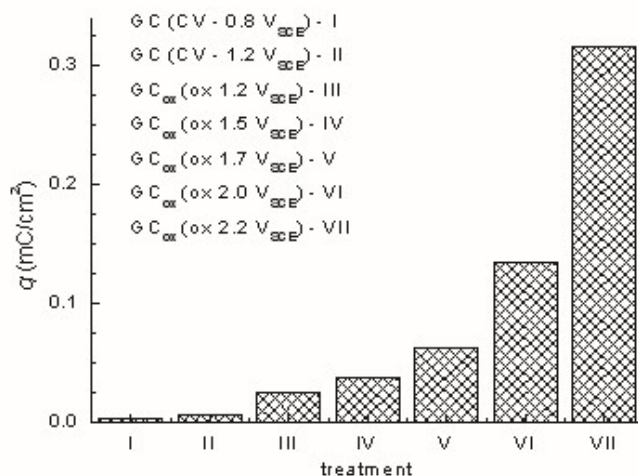


Fig. 1. Voltammetric charge for differently treated GC in 0.5 M H₂SO₄.

AFM analysis of the polished and oxidized GC electrodes confirmed distinct expansion of surface area and porosity of the electrodes oxidized at more positive potentials. Fig. 2 presents the images of some of those electrodes.

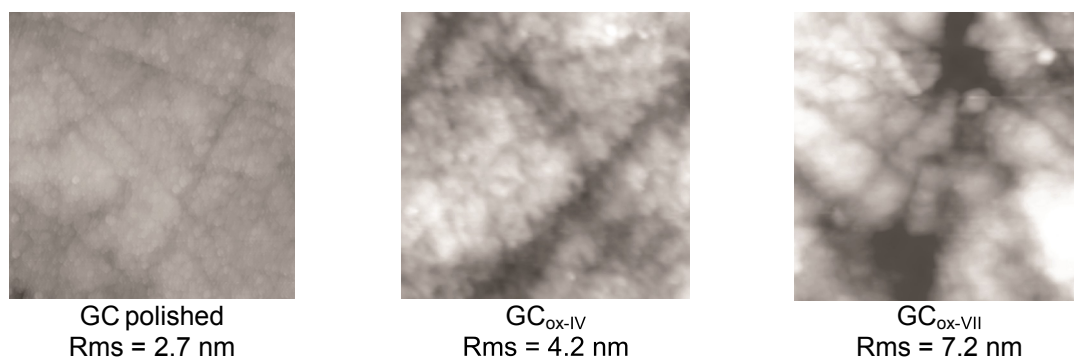


Fig. 2: AFM images (2x2 μm) of differently treated GC electrodes.

The capacitance complex plane plots for polished and activated GC electrodes, obtained in H₂SO₄ solution at the potentials of 0.3 V_{SCE} and 0.6 V_{SCE} are given in Fig. 3a. Registered capacitive loops indicate capacitor-like behavior of the electrodes. The loop for activated GC is of much larger diameter, meaning the capacitance is considerably increased by GC anodic activation.

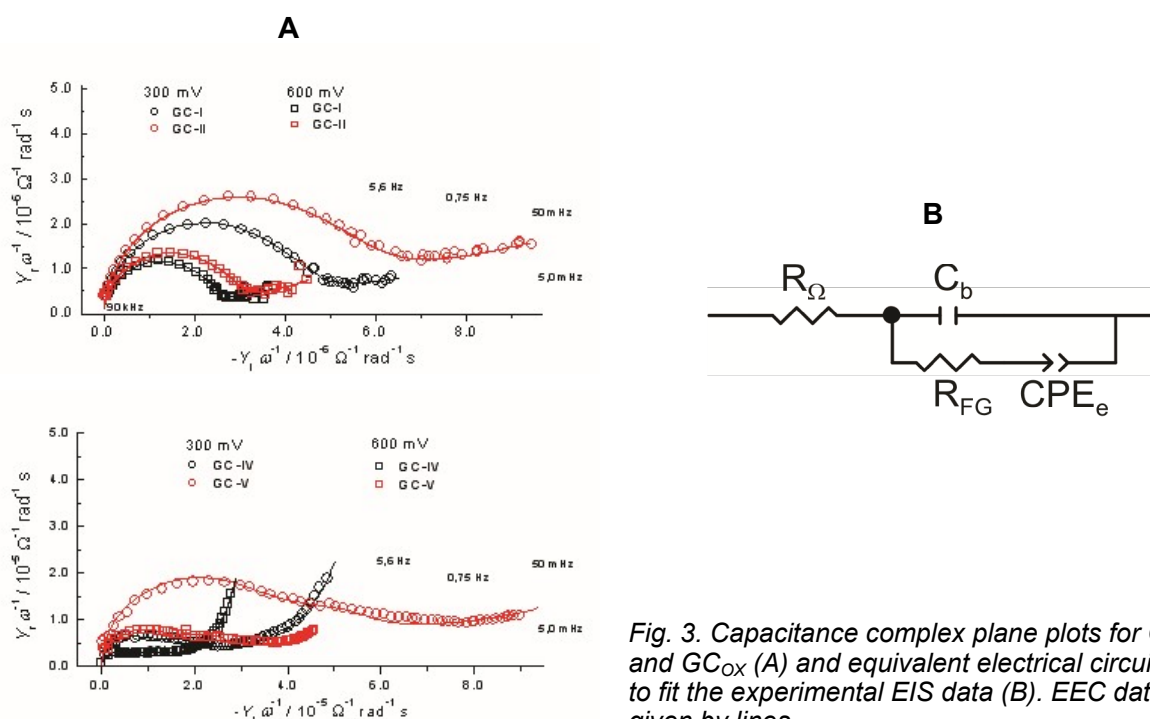


Fig. 3. Capacitance complex plane plots for GC and GC_{ox} (A) and equivalent electrical circuit used to fit the experimental EIS data (B). EEC data are given by lines.

It is known that the GC surface consists of basal and edge planes, which can behave electrically different [2]. Also, the edge plane is considerably more active and different kinds of functional groups (FGs) are present mostly at this highly active plane. The ratio between basal and edge planes as well as the content of FGs strongly depends on the degree of oxidation, *i.e.*, activation of GC surface. Having in mind these properties of GC and EIS characteristics (Fig. 3a), the impedance behavior of investigated GC electrodes can be fitted by equivalent electrical circuit (EEC) shown in Fig. 3b. The circuit proposes capacitive response of basal (capacitor C_b) and edge plane (constant phase element CPE_e) in parallel similar to the approach by Heidushka *et al.* [2]. The resistance related to the presence of FGs at reactive edge planes is represented by resistor R_{FG} . The impedance characteristics of EECs are given by lines in Fig. 3a.

The values of the EEC parameters as obtained by fitting the experimental EIS data are given in Fig. 4 as the functions of voltammetric charge (Fig. 1). As the electrode is more activated, the capacitance values increase for almost three orders of magnitude. The relative increase is similar for the capacitances of basal and edge planes. This indicates that activation by anodization of GC lead to the surface functionalization (mainly involving edge planes) and roughening (related to the basal planes). While being roughened, the basal planes become more active due to the formation of surface defects, and hence also subjected to the formation of FGs

Once the basal planes are roughened by oxidation, they are opened for the formation of FGs. Hence, the value of R_{FG} increases with activation. This indicates that the oxidation provokes the formation of FGs and could induce pronounced pseudocapacitive behavior. This is also seen in cyclic voltammograms of investigated electrodes, as much more pronounced redox pair at around 0.40 V and higher voltammetric currents in the case of activated electrodes [3].

However, at highest applied activation potentials (2.0 and 2.2 V *i.e.* 0.12 and 0.3 mC cm^{-2} , Fig. 4), R_{FG} is considerably lower than at lower activation potentials. The R_{FG} value for GC of 0.3 mC cm^{-2} is similar to the value obtained for polished electrode of $3 \times 10^{-3} \text{ mC cm}^{-2}$. These findings indicate that activation potentials above 1.7 V can result in a removal of FGs, since R_{FG} decreases with the activation potential in that range. The removal could be caused by mechanical depletion of functionalized surface layer or possibly even by further electrochemical oxidation of FGs to CO_2 or both.

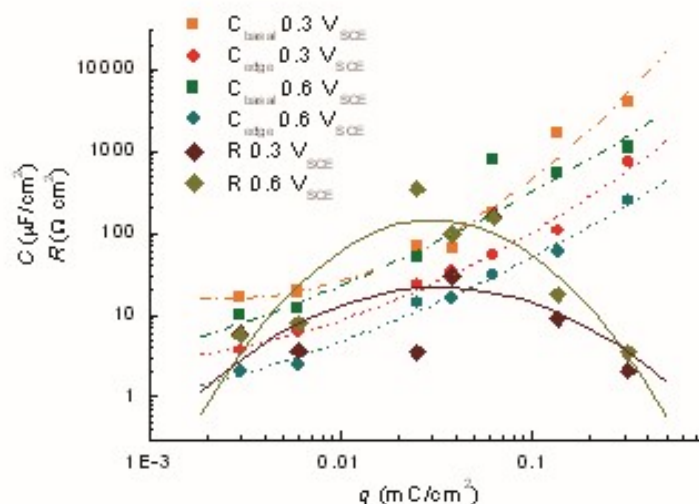


Fig. 4. Capacitance and resistance (EIS data) of differently treated GC vs. double layer charge

All of these results are in very good agreement with our previous work on electrochemical oxidation of glassy carbon [3]. Thus, anodic polarization of GC, based on the analysis of CV and EIS data, as well as morphological changes of the electrode surface, proceeds through the three stages in the electrochemical activation process. It starts with oxidation of surface active sites which are presumably defects of graphite structure (discontinuities in basal plane) and functional groups formed. When all of surface active sites are oxidized, electrolyte penetration through the domains of graphitic structure of GC becomes more intensive and leads to the growth of graphite-oxide layer what is followed by the destruction of the surface and eventually when graphite-oxide layer fills up the space between the graphitic molecules to exfoliation of the material.

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