



Effect of impulse high voltage anodic and cathodic electrochemical treatment of a glassy carbon electrode on the oxygen reduction reaction in alkaline media

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ABSTRACT

A glassy carbon (GC) electrode has been modified by 3–6 potential impulses of different polarity with amplitude up to 250 V, duration of 10 ms and pulse rise-time of < 0.5 μs in an aqueous solution of Na₂SO₄. As a result of an anode potential impulses impact, the GC surface is found to show higher electrocatalytic activity toward the oxygen reduction reaction (ORR). Cathodic impulses yet have no considerable effect. The electrocatalytic effect is supposed to be conditioned by carbonyl moieties of functional groups, which are active ORR centres formed on the GC electrode surface as a result of the anodic impulse impact.

1. Introduction

Today, the solution plasma process [1] is widely used in the synthesis of few-layer graphene structures (FLGS) and in modification of the surface of metals and alloys - the number of publications in this area grows constantly. In particular, the work [2] describes a direct synthesis of N-doped FLGS in an electrolyte; in the work [3], solution plasma was used for a graphite exfoliation with further FLGS formation; wear resistance improvement of steel surface is presented in [4]. As to carbon materials modification for the enhancement of their electrocatalytic properties, various kinds of gas plasma are generally used (see reviews [5,6]). Impact of oxygen plasma on a pyrolytic graphite electrode was apparently first studied in the works [7,8], and it was found that there is a growth of the electrode area available for an electrolyte solution and concentration of oxygen functional groups on its surface. The latter, in the authors' opinion, conditions the electrocatalytic effect with respect to some organic depolarizers. In further work [9] these authors showed that there was no considerable impact of GC plasma treatment on cyclic voltammogram shape in a buffer solution. The work [10] studies the effect of GC hydrogen plasma treatment on an electron transfer rate constant (k^0) of some redox systems and shows that the surface modification here results in reduction of concentration of oxygen functional groups on the electrode surface and, therefore, has considerable effect only on the k^0 value for the Fe^{3+/2+} redox reaction. In the present study, a surface of GC electrode was subjected to cathodic and anodic high voltage impulses that resulted in the solution plasma formation. The work is aimed at studying the kinetics of the oxygen reduction reaction (ORR) on the GC

electrodes modified this way.

2. Experimental

Measurements were performed in a three-electrode cell using a VED-06 rotating disk electrode (RDE) setup with an IPC Pro-L potentiostat. A GC disc 3 mm in diameter pressed in teflon was used as a working electrode; platinum foil was taken as an auxiliary electrode; a reference electrode was an Ag/AgCl electrode filled with a saturated KCl solution. All potential values (E) are referred to this electrode. The surface of the pristine GC electrode was polished with a 0.3 μm Al₂O₃ powder. Reference experiments were performed with the GC electrode covered by a commercial platinum catalyst E-TEK C1-40 (40% Pt/Vulcan XC-72). A drop of catalyst suspension was casted on polished GC electrode and dried in ambient environment (platinum loading was ca. 85 μg/cm²). The linear-sweep voltammetry (LSV) was performed in an air-saturated aqueous solution of 0.1 M KOH, with a scan rate $v = 10$ mV/s and electrode rotation rate $\omega = 900$ –6400 rpm. LSV curves were analyzed with the Koutecky-Levich (K-L) equation [11]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d}, \quad j_k = nFkc^0,$$

$$j_d = 0.62nFD^{2/3}\omega^{1/2}v^{-1/6}c^0 \quad (1)$$

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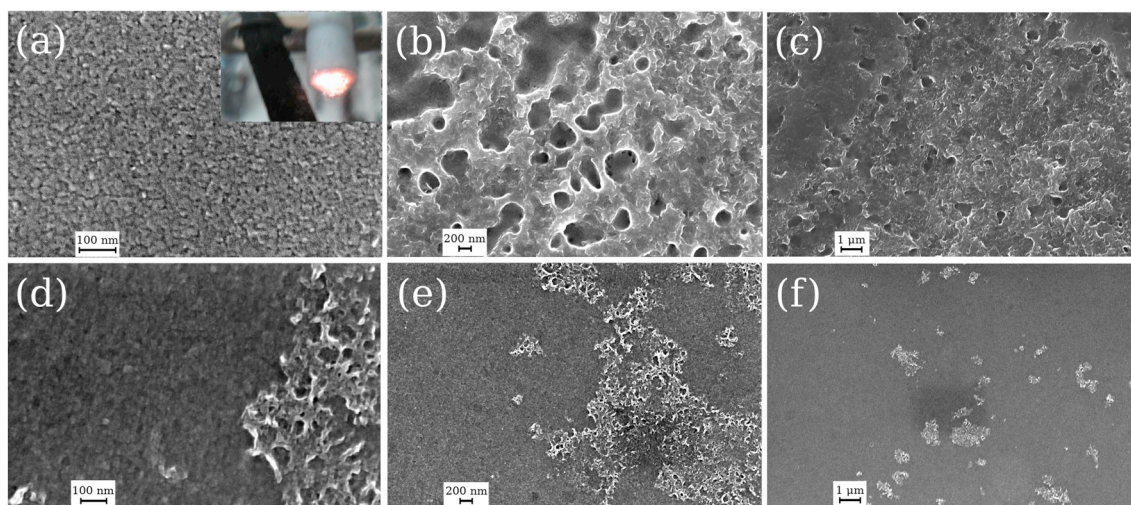


Fig. 1. SEM images of (a) p-GC; (b and c) c-GC; (d, e and f) a-GC. The inset shows plasma formation around a GC electrode.

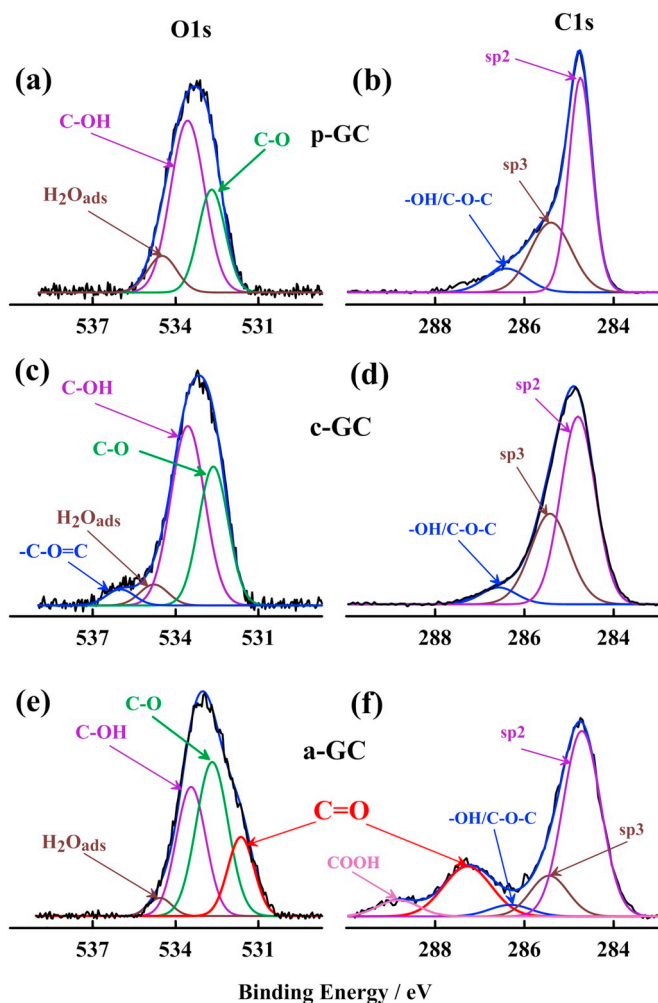


Fig. 2. O1s and C1s XPS spectra of (a and b) p-GC; (c and d) c-GC; (e and f) a-GC.

where j_k and j_d are kinetic and limiting diffusion current densities, respectively, n is the number of electrons involved in ORR, k is the ORR rate constant, F is the Faraday constant, D is the diffusion coefficient of O_2 , ν is the kinematic viscosity of solution, c^0 is the bulk concentration of dissolved oxygen.

The surface morphology of the pristine and modified GC electrodes was characterized with a Carl Zeiss AG SUPRA 40 scanning electron microscope. X-ray photoelectron spectroscopy (XPS) of GC samples was carried out in a Kratos Axis Ultra DLD spectrometer. The probed area for each sample was $300 \times 700 \mu m^2$, and the probing depth was 1–2 nm. The spectra were acquired with monochromatized Al K α radiation (1486.6 eV). Spectra of each sample have been measured in three points on the surface. The error in surface concentration of elements was at most 2%.

The GC electrode was modified in a two-electrode thermostated cell (a counter electrode was a ca. 10 cm^2 GC plate) via applying 3–6 potential impulses with amplitude of 150–250 V, duration of 10 ms and rise-time of ca. $0.5 \mu s$ in the 0.3 M and 1 M Na_2SO_4 solutions for cathodic and anodic polarization, respectively. Under such conditions, current density on the GC electrode was over 20 A/cm^2 . The high rate of the growth of polarization and high current density on the GC electrode led to the flash boiling of solution in the near-electrode region and formation of a steam-gas shell accompanied with an intense light and acoustic generation [3] (inset in Fig. 1). For the cathodic impulses, the conductivity of 0.3 M Na_2SO_4 solution was sufficient for required current density to be achieved. For the anodic impulses, light generation was observed at somewhat higher current density requiring 1 M Na_2SO_4 to be used at the same voltage amplitudes and cell geometry.

3. Results and discussion

Fig. 1 shows scanning electron microscopy (SEM) images of the pristine (p-GC) and the anodic (a-GC) and the cathodic (c-GC) plasma treated electrodes. The p-GC surface is homogenous and relatively smooth, with structural elements not exceeding 10–20 nm. Maximum change in morphology of the surface is observed after cathodic plasma treatment. The c-GC surface is almost entirely covered with dimpled structures with lateral sizes of 200–400 nm. Apparently, this pattern of the surface is explained by a local degradation of GC at the cathodic impact. The topologically similar surface structure was observed in [12] during a long-term polarization of the GC electrode at 1.8 V vs. reversible hydrogen electrode (RHE) in 0.1 M KOH solution. In contrast, a destruction of the a-GC electrode is observed only at 4–6% of its surface, and the morphology of its main part is similar to the structure of the pristine electrode. Typical size of etch pits here is considerably smaller than that of the c-GC and is 20–50 nm.

XPS spectra of the p-GC, c-GC and a-GC electrodes were analyzed and the concentrations of oxygen in the surface layer were obtained as follows: ca. 8.0, 11.0, 26.0 at.%, respectively. Meanwhile, nitrogen content in all

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