Electrochimica Acta 117 (2014) 310–321

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Concept of spatial surface heterogeneity in impedance modelling of electrochemically activated glass-like carbon electrode

Katja Magdić[1], Krešimir Kvastek[1], Višnja Horvat-Radošević*,[1]

*Ruđer Bošković Institute, Bijenička c. 54, 10000 Zagreb, Croatia*

ARTICLE INFO

*Article history:*
Received 9 May 2013
Received in revised form
11 November 2013
Accepted 11 November 2013
Available online 4 December 2013

*Keywords:*
Glass-like carbon
Electrochemical activation
Spatial surface heterogeneity
Electrochemical impedance spectroscopy
Impedance modelling.

ABSTRACT

For the first time, the concept of spatial surface heterogeneity has been implemented to the impedance modelling of unmodified, *i.e.* only polished and progressively electrochemically oxidized/reduced, *i.e.* activated glass-like carbon, GC, electrodes. The GC electrode surface is generally treated as spatially heterogeneous in a sense of exhibiting at least two different domains with different electrochemical properties. Consequently, the overall electrode impedance is formally divided into the parallel sum of two global impedances, characteristic for two types of the surface and related by corresponding fractional surface coverage. Assuming the common electrolyte resistance term and indirect influence of surface coverage on impedance parameter values, the impedance/frequency equations are derived for a spatially heterogeneous electrode surface showing: 1) surface roughness due to formation of separate damage sites of surface and subsurface layers with high content of oxygen containing species and 2) partial surface porosity due to formation/reduction of oxide films at damage sites which by progressive oxidation have progressively been spread laterally and towards the bulk of the electrode.

Regression of derived impedance/frequency equations to experimentally measured impedance spectra of GC electrodes in $H_2SO_4$ solution showed predominance of almost smooth, spatially homogeneous surface for unmodified, GC electrode, increased contributions of rough and/or porous parts for weakly to medium activated GC electrodes and domination of completely porous surface for strongly activated GC electrode.

## 1. Introduction

In spite of broadly referred advantages of glass-like (glassy) carbon, GC, electrodes in various areas of their possible applications [1–5], a detailed impedance analysis of either unmodified or chemically/electrochemically modified GC electrode surfaces is scarce in the literature. This is particularly true for the potential region of GC electrode polarisability which is of crucial importance for the background currents in electroanalysis, capacitance values of (super) capacitors and catalytic activity in electrocatalysis. Irrespective to certain complexity of impedance modelling procedure involving ambiguity problems [6], non-ideal capacitive responses inherent to all solid electrodes [7–13] and existence of basically different formulas for estimations of effective capacitance [7,10–13], the electrochemical impedance spectroscopy, EIS, technique provides unique opportunity for analysis of dynamic behaviour of electrodes [14]. As usual with EIS, the problem originates from necessity for the modelling step what would be even more prominent for GC electrode(s) with surface properties determined by sparingly controlled basal/edge carbon planes ratio, inherent porosity and variable surface chemistry [15–21]. Available literature data on impedance of GC electrodes in aqueous electrolytes showed, however, application of less [9,17,21,22] or more [15,23–26] complex models, with choice dependent mainly on GC electrode surface (pre)treatment procedure and/or electrolyte solution used. Thus the simple, constant phase element, CPE, analogue for double-layer capacitive electrode response has been applied for as received, mechanically polished and thermally activated GC electrodes in $H_2SO_4$ solution [17] and also, for mechanically polished GC electrode in KCl solution [9]. Otherwise, the number of impedance elements in modelling of GC electrode has been increased to account for adsorption of impurities [24] or contribution of compact inner and porous outer layers of the GC electrode surface, (pre)anodized in various aqueous electrolytes and measured at various potential values [23]. Similar, “duplex” capacitance model suggesting, however, simultaneous contributions of compact and diffuse parts of interfacial double-layer has also been applied for polished and differently oxidized GC electrodes in KCl solution [15]. For strongly oxidized and then reduced GC electrode in $H_2SO_4$ solution, the so called transmission line-like, TL, element, based

---

* Corresponding author. Tel.: +385 1 4561152.
*E-mail addresses:* kmagdic@irb.hr (K. Magdić), kvastek@irb.hr (K. Kvastek), vhorvat@irb.hr (V. Horvat-Radošević).

[1] ISE member

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.11.065

on De Levie's treatment of well-ordered porous electrode [27], has already been found appropriate in impedance modelling and explained by completely porous surface film formed at the cost of bulk electrode material [25,26]. Almost all these results pointed towards a predominant influence of surface morphology on measured impedance spectra of GC electrodes, what has already been approved by rather different images of polished and oxidized GC samples observed using high resolution scanning electron [19,21], scanning tunnelling [15,28,29], scanning force [18] and atomic force microscopy techniques [2,17,20,30]. Although being stressed as the necessary prerequisite for activation (electrochemical, at least) of carbon surfaces [31], creation of spatial surface heterogeneity has only indirectly been included in impedance analysis, through differentiation between contributions of edge *vs.* basal planes capacitive impedances in the overall GC electrode response [15]. In the present paper, however, GC electrode surfaces will generally be treated as spatially heterogeneous in a sense of exhibiting at least two different domains with rather different electrochemical properties sharing total electrode surface [10,32,33]. The model will be tested by analysis of experimental impedance spectra of only polished and progressively oxidized/reduced, *i.e.* electrochemically activated GC electrodes.

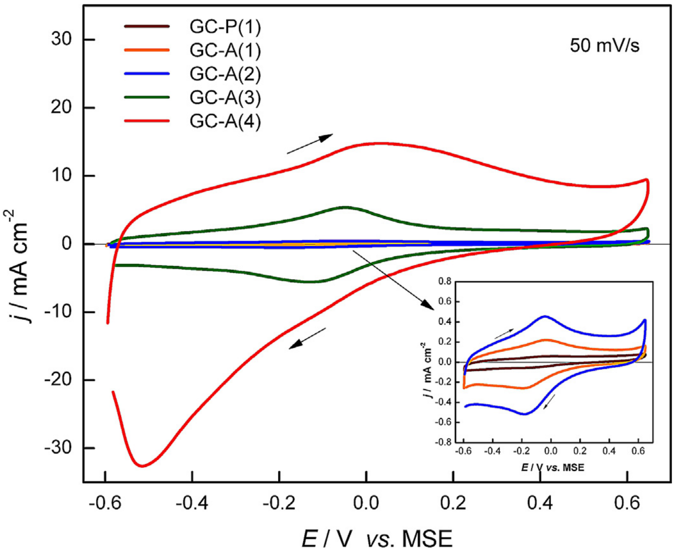

**Fig. 1.** CVs (4th cycle) of GC electrodes (*cf.* Table 1) in 0.5 mol $dm^{-3}$ $H_2SO_4$.

## 2. Experimental

### 2.1. Electrode surface preparation and testing

Newly purchased GC electrode disks (EG&G, USA) of 0.028 $cm^2$ geometric surface area were hand polished forming GC-P electrodes. Grid papers of successively smaller grades were used, after which the electrodes were washed and ultrasonicated for 15 minutes using ultrapure water. Gradual activations of GC-P electrode surfaces were made by electrochemical oxidation/reduction procedure, forming gradually activated GC-A(1 – 4) electrodes. Voltammetric cycling at the scan rate of 10 mV $s^{-1}$ in three-electrode cell filled with 0.5 mol $dm^{-3}$ $H_2SO_4$ (high purity BDH, Aristar), and room temperature has been applied. The extent of surface oxidation was controlled by number of voltammetric cycles applied between –0.70 V *vs.* $Hg/Hg_2SO_4$ (sat. $K_2SO_4$), MSE, electrode (MSE is 0.40 V *vs.* saturated calomel electrode, SCE) and potential of the anodic limit, $E_a$. Reduction steps have always been performed by holding the electrodes at –0.60 V *vs.* MSE for at least 30 minutes [2,19,20,25,26,30]. More details of GC electrode surface preparations are summarized in Table 1. All prepared GC electrodes were tested for their double-layer responses in fresh, 0.5 mol $dm^{-3}$ $H_2SO_4$, electrolyte by applying four cycles of CV experiments at 50 mV $s^{-1}$. Solartron 1287 ECI under $Z_{corr}$ software control was used. In the set of parallel experiments, some of GC electrodes, denoted by asterisks in Table 1, are taken from the cell, dried and held in vacuum conditions prior being scanned by scanning electron microscope (JSM-700F, JEOL, Japan).

### 2.2. Electrochemical impedance spectroscopy

Impedance measurements were carried out at room temperature in three-electrode cell filled with 0.5 mol $dm^{-3}$ $H_2SO_4$ electrolyte deoxygenated by purging high purity $N_2$. High surface Pt-spiral in a separate compartment and Luggin capillary ended MSE electrodes were used as the counter and reference electrodes, respectively. The Solartron equipment with 1255B FRA and 1287 ECI under $Z_{plot}$ software control was used with sine wave *ac* signal of 10 mV amplitude, frequency, *f*, between 100 kHz and 0.02 Hz and 10 impedance points measured per decade. A delay of 10 – 30 minutes has always been performed before the start of impedance measurements. Impedance data fittings were performed using experimental impedance spectra strained from the wild-points, $Z_{View}$ software and complex non-linear least square, CNLS, routine with presumed electrical equivalent circuits, EECs. Corrections for the capacitive/inductive artefact impedances, $Z_L$ and $Z_C$, induced by three-electrode cell [34] were performed according to the already described procedure [35]. The models were regressed to experimental data with impedance modulus proportional weighting. Regressions always started from a simpler towards more complicated EEC until reasonable fits were obtained with all parameters stated free in calculations. Statistical criteria for defining reasonable fits were low frequency distribution and small, ≤ 0.05, values of real, $\Delta'$, and imaginary, $\Delta''$, fitting residual errors defined by eqn. (1a) and standard deviation of the overall fit defined by eqn. (1b), $\chi^2 \leq 5 \times 10^{-4}$.

$$\Delta''_k = \frac{Z''_{k(\exp)} - Z''_{k(cal)}}{\left|Z_{k(\exp)}\right|} \qquad \Delta'_k = \frac{Z'_{k(\exp)} - Z'_{k(cal)}}{\left|Z_{k(\exp)}\right|}; \tag{1a}$$

$$\chi^2 = \sum_{k=1}^{N} \left[ \frac{(Z'_{k(\exp)} - Z'_{k(cal)})^2 + (Z''_{k(\exp)} - Z''_{k(cal)})^2}{\left|Z_{k(cal)}\right|^2} \right] \tag{1b}$$

In eqn. (1), $Z'$, $Z''$, $k$ and $N$ are real and imaginary impedances, particular frequency of measurements and total number of measured frequencies (data points), respectively. $|Z|$ is impedance modulus, while "*exp*" and "*cal*" referred to the experimentally measured and calculated quantities.

## 3. Experimental results

### 3.1. 3.1 CV testing

CVs of different GC electrodes (*cf.* Table 1) measured over potentials of double-layer region are presented in Figure 1.

The shapes of CVs in Fig. 1, including formation of peaks at about –0.10 V *vs.* MSE, are similar to pseudo-capacitive "double-layer responses" not only of GC [2,16,19–21,25,29,30], but also of other types of carbon electrodes in acidic electrolyte solutions [36–38]. For all carbon electrodes, contribution of pseudo-capacity to double-layer charging/discharging currents originated from fast faradaic reaction of redox active surface carbon oxygen containing species identified as hydroquinione/quinone, $H_2Q/Q$, couple, formed at the exposed edge plane sites of carbon [2,16,21,25,29,36–38]. Except on pseudo-capacity, the measured