Glassy Carbon/KCl-Solution Interface Impedance. Mechanical Surface Treatment Effect

S. V. Mentus
Institute of Physical Chemistry, Faculty of Science, Belgrade, Yugoslavia

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

The dependence of complex impedance behaviour on mechanical surface treatment of glassy carbon electrodes in standard water KCl solutions at room temperature was investigated. A considerable frequency dependence of both the real and the imaginary term of the impedance was observed in the entire 1–50 kHz range of frequencies used for electrodes of different surface roughness. The results are discussed in the light of the Levie theory.

Introduction

Nowadays impedance measurements in a wide range of frequencies are widely applied in conductometry, since under numerous experimental conditions [1–6] it was demonstrated that the resistance dependence on frequency maintains to very high frequencies, in spite of earlier literature [7] where it was reported that the resistance dependence on frequency terminates above 1 kHz.

The results of impedance measurements are mostly presented in the complex plane, as the dependence of the imaginary term of the impedance, $Z'' = -i(\omega C_s)^{-1}$, on the real one, $Z' = R_s$, from which the equivalent circuit of conductometric cells can be constructed [8–10].

The equivalent circuit of the ideal blocking electrode in certain electrolytes consists of a double layer capacitance C_{dl} in series with an electrolyte resistance R_e. The correspondingly complex impedance diagram represents the vertical onto the real axis, crossing the real axis in the point R_e. In this simple case the dependence of R_s on the frequency is absent. The double layer capacitance can be calculated in this ideal case from a certain ordinate point as $C_{dl} = -(\omega Z)^{-1}$ for the corresponding value of the radial frequency ω.

The presence of an electrochemical reaction due to the incomplete blocking character of the electrode is the usual cause for the deviation of the complex impedance diagram from the vertical course. However, de Levie showed earlier [11] that the electrode surface roughness can influence strongly the results of electrochemical measurements. His theoretical considerations can be applied the electrodes in liquid electrolytes, when the electrolyte covers the electrode surface completely. The theory was devised on the basis of a porous electrode model [12] according to which the infinite deep pore shows an impedance corresponding to the circuit presented in Figure 1. The basic result of [11] regarding the conductometry is that the electrode surface roughness causes the frequency dependence of the real term of the impedance even in the case of ideal blocking electrodes.

Since the smooth platinum or carbon electrodes, being most practical, are widely used in conductometry of molten salts, it is important to take into consideration all factors affecting the results of measurements.

The influence of pure mechanical treatment of the glassy carbon electrode surface on its impedance in standard water KCl solutions is investigated in this paper in order to check experimentally the magnitude of the effects predicted by the theory.

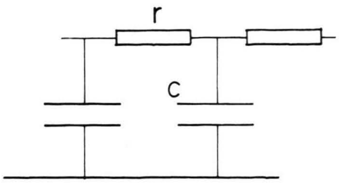

Fig. 1. The equivalent circuit for a pore of a blocking electrode. r represents the resistance of the solution per unit pore length and c the double layer capacitance per unit pore length.

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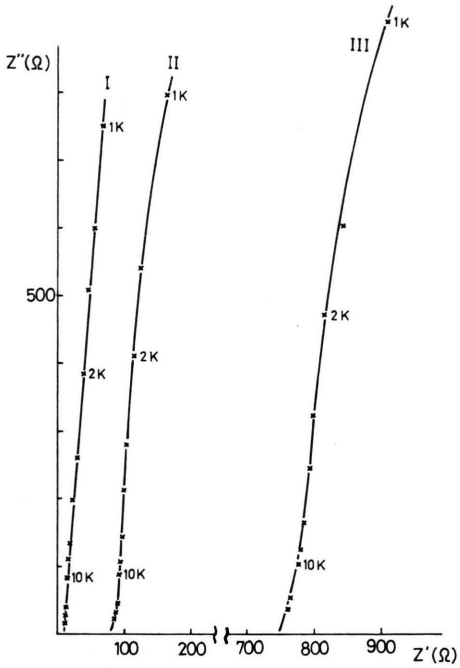

Fig. 2. The complex impedance diagram, $Z'' = -i(\omega C_s)^{-1}$ versus $Z' = R_s$ for polished glassy carbon electrodes in 1 M (I), 0.1 M (II) and 0.01 M (III) aqueous KCl solutions at 25 °C.

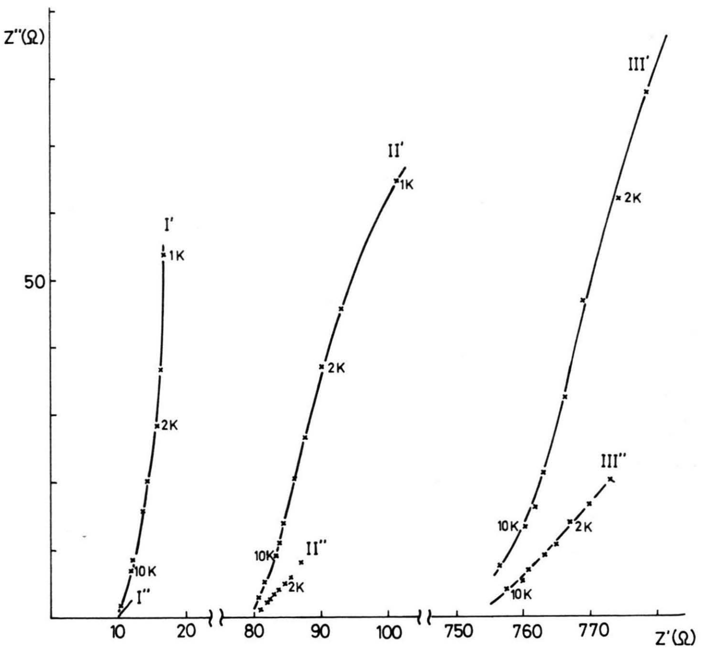

Fig. 3. The complex impedance diagrams, $Z'' = -i(\omega C_s)^{-1}$ versus $Z' = R_s$ for partially (10% of surface area) roughened glassy carbon electrodes in 1 M (I′), 0.1 M (II′) and 0.01 M (III′) and for completely roughened ones in 1 M (I″), 0.1 M (II″) and 0.01 M (III″) aqueous KCl solutions at 25 °C.

Experimental

The glassy carbon electrodes made in prismatic form of base dimensions 1.8 × 3 mm^2 were polished by cotton textile carefully to obtain a mirror reflectance. By teflon band coating only the lower part of the electrode, 5.5 mm high, was in contact with the electrolyte. The electrodes were fixed in a holder to obtain an unchangeable cell constant.

The progressive roughing of electrode surfaces was carried out by extra fine carborundum BDH (about 300 Grit Powder).

The RLC bridge Wayne Kerr B224 with external function generator Iskra MA 3731 was used for impedance measurements. The sinusoidal alternating voltage amplitude used was 60 mV pk-pk.

Results

Three series of impedance measurements in standard 1 M, 0.1 M and 0.01 M water KCl solutions were carried out with polished electrodes, with electrodes partially (10% of surface area) roughened and with electrose completely roughened. Figures 2, 3 represent the obtained complex impedance diagrams. The values of the series capacitances for 2 kHz and 20 kHz were calculate as $C_s = (\omega Z'')^{-1}$ and presented in Table 1.

Discussion

By the above treatment the electrode surface gets numerous long wedge-like grooves (Fig. 4), the form

Notation	C_s (2 kHz)	C_s (10 kHz)
I	0.71	0.67
II	0.67	0.63
III	0.58	0.54
I′	9.6	7.8
II′	7.4	5.9
III′	4.4	3.0
I″	154.2	81.9
II″	54.9	27.0
III″	19.5	12.9

Table 1. C_s in (μF · cm^{-2}) at 2 and 10 kHz for glassy carbon electrodes polished, partially (10% of surface area) roughened (′-notation) and completely roughened (″-notation), in 1 M (I), 0.1 M (II) and 0.01 M (III) aqueous KCl solutions at 25 °C.

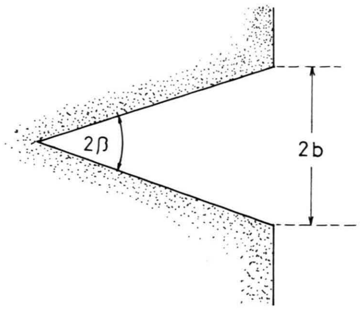

Fig. 4. The profile of a wedge-shaped groove at the electrode surface.

of which corresponds well to the ones considered theoretically by de Levie [11]. Thus it is reasonable to exspect that this theory can be well applied to experimental results in this paper.

According to theory [11] the impedance of an ideal blocking rough electrode per unit apparent surface area can be described by the following equation:

$$Z^* = \varrho \cot\beta \cdot \varphi(\omega) - i\,(4 b \omega C_{\mathrm{dl}} \operatorname{cosec}\beta \cdot \psi(\omega))^{-1}. \tag{1}$$

The functions $\varphi(\omega)$ and $\psi(\omega)$ are defined in [11]. They are constants for:

$$\omega \leqq \frac{\sin\beta \tan\beta}{4 \varrho b C_{\mathrm{dl}}} \tag{2}$$

and tend to zero with further increase of frequency. The meaning of the parameters b and β is shown in Figure 2. ϱ and C_{dl} are the electrolyte resistance and the double layer capacitance per true surface area unit, respectively.

The real term of Eq. (1) presents the resistance of the electrolyte inside the grooves, which can be very high at small frequencies, and tends to zero when the frequency increases. The term C_s in the imaginary term of impedance, $i(\omega C_s)^{-1}$, presents the double layer capacity of the true electrode/electrolyte interface per unit of apparent (geometric) surface area, for frequencies which satisfy (2). For higher frequencies the penetration depth of the current into grooves decreases, and therefore the measuring instrument "feels" decreased reactive resistance. For frequencies that satisfy the condition:

$$\omega > \frac{3 \sin\beta \tan\beta}{\varrho b C_{\mathrm{dl}}} \tag{3}$$

the impedance diagram has theoretically a 45° slope against the real axis (Warburg-like behaviour).

Taking into consideration the blocking character of the glassy carbon electrode, the equivalent circuit of the electrode/electrolyte system can be predicted as shown in Figure 5a.

Strictly speaking, the exact equivalent circuit for observed system should be drawn as in Fig. 5b, in which R_t represents the resistance of the teflon coated part of the electrode in contact with the electrolyte, while C_t represents the sum of the electrode/teflon/electrolyte system capacity and the geometric capacity in normal parallel connection on to the electrolyte resistance R_e. However, by one additional experiment with totally teflon coated electrodes it was shown that R_t is of the order of $10^8\,\Omega$, and C_t is of the order of 10^{-12} F. Thus in the corresponding expression for the impedance:

$$Z = \frac{1}{\dfrac{1}{R_e} + \dfrac{1}{R_t} + i\omega C_t} + Z^* = \frac{\dfrac{R_e + R_t}{R_e R_t} - i\omega C_t}{\dfrac{R_e + R_t^2}{R_e R_t} + \omega^2 C_t^2} + Z^*; \tag{4}$$

the term $(R_e + R_t)/R_e R_t$ can be replaced by $1/R_e$ with accuracy better than 10^{-4}% while the measurable influence of (ωC_t) could be expected at frequencies higher than 10^9 Hz. Consequently the exact equivalent circuit reduces to the simplified form (Fig. 5a) for the observed frequency range.

There is no possibility for the electrolyte to penetrate between electrodes and teflon coating by capillary forces, since both glassy carbon and teflon can not be wetted by a KCl solution, and teflon band adheres tightly to the carbon electrode. Thus the occurrence of capillary response [13] (i.e. corre-

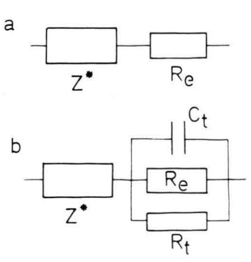

Fig. 5. a) The equivalent circuit for the glassy carbon electrode in aqueous KCl solutions valid in the frequency range 1–50 kHz. b) Exact equivalent circuit. Z^* means groove impedance according to Eq. (1), R_e bulk electrolyte resistance, R_t resistance of the teflon isolated part of the electrode, and C_t total value of the glassy carbon/teflon/electrolyte capacitance and the geometric capacitance

sponding elements of impedance in the equivalent circuit) is not to be expected.

According to (1) and (4), true double layer capacitance of the rough blocking electrode/electrolyte interface is observable at low frequencies, and bulk electrolyte resistance is observable at high frequencies with respect to condition (2). These discrepancies do not exist with ideally smooth electrodes. Namely, in such a case $\beta = 90°$ and $b = 0$, so that no frequency dependence of any term of the impedance exists, and all frequencies are equally well suited for the determination of both R_e and C_{dl}.

It is very difficult to control the polishing and roughing of the electrode surface quantitatively, i.e. it is practically impossible to cover the electrode surface with uniform grooves in order to check the theory of surface roughness. However, some semiquantitative relations can be obtained, by covering the electrode surface with grooves where the dimensions are allowed to vary within certain limits.

Figure 3 represents the impedance diagrams obtained by the use of well polished electrodes. The impedance diagram for the concentrated 1 M KCl solution has a high slope of 86° against the real axis. This diagram is very near to the impedance diagram of an ideally smooth blocking electrode. The series capacity change with frequency is below 6% for the range 2 – 10 kHz (Table 1). This indicates that the series capacity represents the double layer capacity per true surface area unit, in this case equal to the geometric one. However, a considerable frequency dependence of the series resistance indicates that nevertheless the electrode surface contains certain amounts of small grooves, inside of which the electrolyte shows considerable resistance.

For decreased concentrations the nonlinearity of the impedance diagrams becomes readily observable, indicating the nonuniform distribution of groove dimensions. Therefore a decrease of series capacitance occurs. This decrease indicates the capacitance of the diffusion part of the double layer present. This part of the capacitance decreases considerably with decreasing concentration and is connected serialy to the capacitance of the inner part of the double layer [14]:

$$\frac{1}{C_{dl}} = \frac{1}{C_i} + \frac{1}{C_d}.$$

The progressive roughening of the electrode surface causes a change of impedance diagrams according to theory [11]. With an increase of the surface roughness (increase of b in (1)) the limiting value of ω becomes smaller according to (2), which means that region of Warburg-like behaviour expands towards lower frequencies. With a 10% surface coverage by grooves the impedance behaviour goes from a smooth electrode-like to rough electrode-like one (Figure 3). With 100% surface coverage by grooves, the rough electrode-like (Warburg-like) behaviour prevails over the entire frequency range 1 – 50 kHz. The frequency dependence of the series capacitance in this region is considerable, since the penetration depth of the current into grooves depends on the frequency.

The agreement of the behaviour of the glassy carbon electrode in an aqueous KCl solution with theory [11] is important for the determination of the real graphite surface area. Namely, if the measurements could be extended into a frequency independent region, the ratio of true rough electrode surface area to its apparent one (roughness factor) could be determined by the ratio of rough to smooth electrode series capacitance. This problem is present in the carbon fibre research [15].

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