

Full Paper

Electrochemical Impedance of Oxygen Reduction in Acidic Solution at Silver-Modified Glassy Carbon Electrode

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Abstract- The electro-reduction of oxygen on silver-modified glassy carbon electrode (Ag/GC) in acidic solution at different potentials was studied by ac-impedance spectroscopy. The influence of the electrode potential on impedance of oxygen reduction reaction is studied and a mathematical model was put forward to quantitative account for the impedance behavior of oxygen reduction. At potentials higher than -0.4 V/Ag-AgCl, a pseudo-inductive behavior is observed. The conditions required for this behavior are delineated with the use of the impedance model.

Keywords- Oxygen Reduction Reaction, Impedance, Pseudo-Inductive, Silver

1. INTRODUCTION

Electrochemical Impedance Spectroscopy (EIS) or ac impedance methods have seen tremendous increase in popularity in recent years. Initially applied to the determination of the double-layer capacitance [1-4] and in ac polarography [5-7] they are now applied to the

characterization of electrode processes and complex interfaces. EIS studies the system response to the application of a periodic small amplitude ac signal. These measurements are carried out at different ac frequencies and, thus, the name impedance spectroscopy was later adopted. Analysis of the system response contains information about the interface, its structure and reactions taking place there. EIS is now described in the general books on electrochemistry [8-17] specific books [18,19] on EIS, and there are also numerous articles and reviews. [6,20-23] It became very popular in the research and applied chemistry. The Chemical Abstract database shows ~1,500 citations per year of the term "impedance" since 1993 and ~1,200 in earlier years and ~500 citations per year of "electrochemical impedance". Although the term "impedance" may include also non electrochemical measurements and "electrochemical impedance" may not include all the electrochemical studies, the popularity of this technique cannot be denied.

However, EIS is a very sensitive technique and it must be used with great care. Besides, it is not always well understood. This may be connected with the fact that existing reviews on EIS are very often difficult to understand by non-specialists and, frequently, they do not show the complete mathematical developments of equations connecting the impedance with the physicochemical parameters. It should be stressed that EIS cannot give all the answers. It is a complementary technique and other methods must also be used to elucidate the interfacial processes.

Recently, we conducted the oxygen reduction reaction on a rotating Ag/GC disk electrode in Acidic Solution [24]. The purpose of this work is the analysis of impedance characteristics of electro-reduction of oxygen on Ag/GC in acidic solution over a wide range of potential, aiming at the elucidation of its reaction mechanism. The analysis of the theoretical impedance function provides important information on the kinetic parameters. This information allows the EIS spectrum simulation and therefore predicts the system behavior with regard to the variation of the oxygen reduction reaction over potential.

2. EXPERIMENTAL

Silver plating layers were prepared by chronopotentiometry in AgNO_3 solution that was saturated by silver ions. Glassy carbon (GC) was used as the substrate material [24]. Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat and Solartron model 1255 frequency response analyzer. The system is run by a PC through M270 and M389 commercial software's via a GPIB interface. The frequency range of 100 kHz to 15 MHz and the modulation amplitude of 5 mV were employed for impedance measurements. Fitting of experimental impedance spectroscopy data to the proposed equivalent circuit was done by means of home written least square software based on the Marquardt method for the

optimization of functions and Macdonald weighting for the real and imaginary parts of the impedance [25,26]. A dual Ag/AgCl-Sat'd KCl, a Pt wire and a glassy carbon (GC) disk electrode were used as the reference, counter and working electrodes, respectively. All studies were carried out at 298 ± 2 K.

3. RESULTS AND DISCUSSION

The electrochemical impedance Z of this system is shown in Fig. 1 and 2. In this figures, as same as the current-potential curve, the loci of Z at the following three potentials are presented: a) the potential of charge transfer control (-0.15 to -0.38 V), b) the potential of mixed control of charge transfer and diffusion (-0.4 to -0.47 V). The locus of Z shows two capacitive semicircles under three potential regions that in low frequencies second semicircles with overvoltage increasing, polarization resistance increased up to -0.47 V and then increased anew. Polarization resistance, with increasing potentials, is decreased by negative charge of adsorbed intermediate species such as: O ads and OH ads, according to the Fig. 1. Both the linear trend at middle frequencies in Nyquist plot and the special angle (45°) in Bode-Phase plot are indicator of an OFLD element-Open Finite-Length Diffusion circuit element, which is also resulted from these figures. Appearance of this resistance was caused by either charging of the particle electrical double layers through an ohmic drop resistor network or electronic contact in between various diffusion layers.

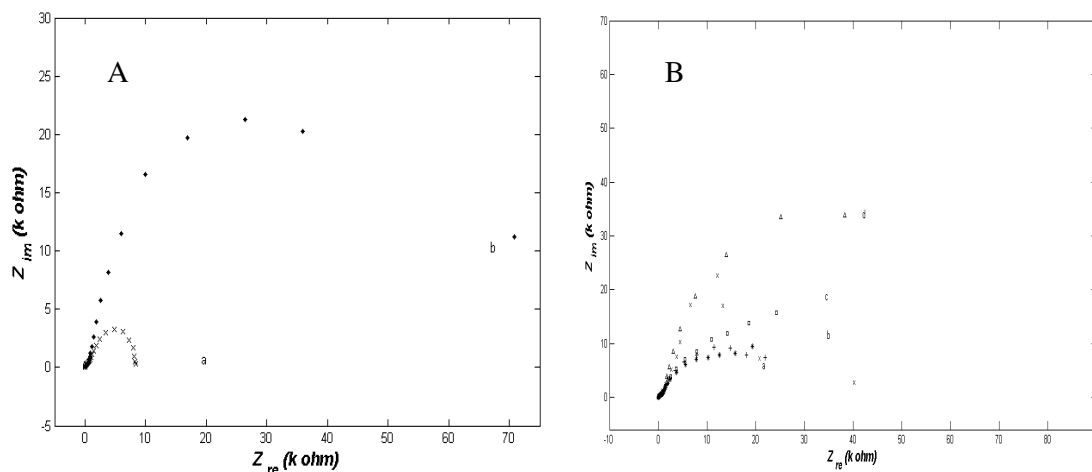


Fig. 1. Experimental Nyquist diagrams as a function of applied potential for oxygen electro-reduction on Ag/GC electrode in acidic solution: (A) in potential (a) 0.515, (b) 0.518 vs. Ag-AgCl; (B) in potential (a) -0.15, (b) -0.24, (c) -0.30 (d) -0.38V vs. Ag-AgCl

In the potential below -0.15 and -0.38 V/Ag-AgCl, two large depressed capacitive semicircles are observed, Fig. 1, revealing a slow reaction rate of oxygen reduction. The semicircles are due to charge transfer resistance in high frequency and intermediates adsorption in low frequency. In the potential between -0.4 and -0.47 V, a typical pseudo-inductive behavior was observed, Fig. 2, where large semicircles at high and medium frequencies are accompanied by a small arc in the forth quadrant at low frequency with all the diameters decreasing sharply with increasing potential. This inductive behavior occurs for relaxation phenomenon characteristics of the generation of further active sites [27-29] and further adsorption of electroactive constituents, oxygen, on active sites [28]. The negative peak also is observed in phase shift plot due to inductive behavior.

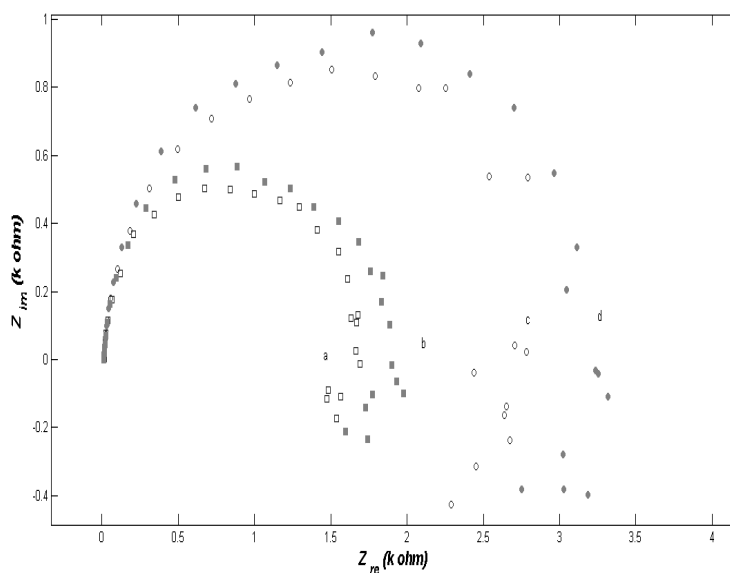


Fig. 2. Experimental Nyquist diagrams as a function of applied potential for oxygen electro-reduction on Ag/GC electrode in acidic solution: in potential (a) -0.4 , (b) -0.42 , (c) -0.44 (d) -0.47 V vs. Ag-AgCl

The phase shift, Fig. 3, of experimental impedance data shows an abrupt jump between the positive and negative values of phase angle, indicating the change of the rate determining step of electro-reduction of oxygen on Ag/GC in potential range -0.15 and -0.38 V.

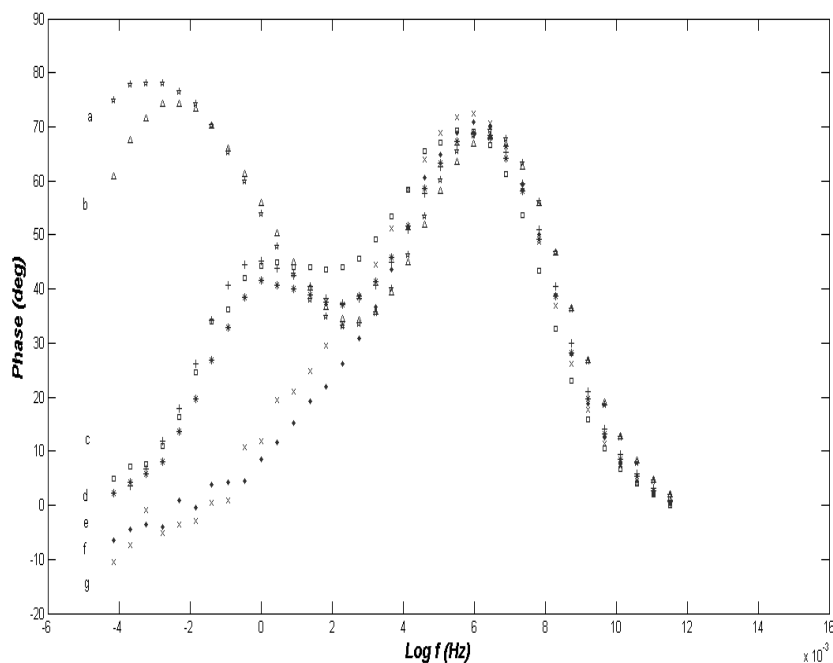


Fig. 3. Experimental phase shift plots as a function of applied potential for oxygen electro-reduction on Ag/GC electrode in acidic solution: in potential (a) -0.15, (b) -0.24, (c) -0.30 (d) -0.38 (e) -0.4, (f) -0.44 (g) -0.47 V vs. Ag-AgCl

The equivalent circuit compatible with the Nyquist diagram recorded in potential range of -0.15 and -0.47 V is depicted in Fig. 4A and B. Table 1 illustrates the equivalent circuit parameters for the impedance spectra of oxygen reduction in different applied potential. As previously mentioned the first depressed semicircle in the entire potential range is due to charge transfer resistance and the inductive behavior in higher potentials is due to the adsorption of oxygen.

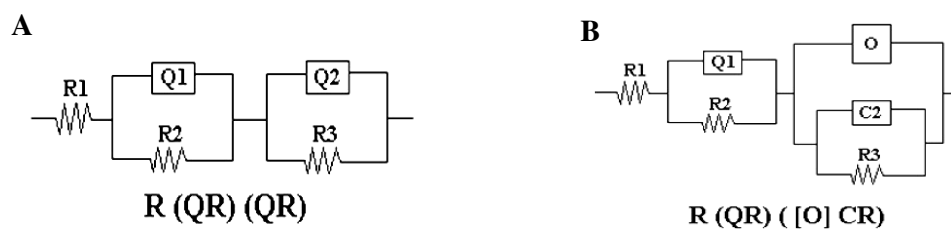
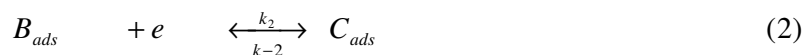


Fig. 4. Equivalent circuits (A and B) compatible with the experimental impedance data in Fig. of 1 and 2 for oxygen electro-reduction on Ag/GC electrode

Table 1. Equivalent circuit parameters of electro-reduction of oxygen on Ag/GC electrode in acidic solution obtained from Fig. 4

E(V)	R ₁ (Ω)	Q ₁ (×10 ⁴ F)	R ₂ (×10 ⁻² Ω)	Q ₂ (×10 ⁴ F)	O	R ₃ (×10 ⁻² Ω)	n ₁	n ₂
-0.15	2.88	10.45	4.64	2.04	-	29.22	0.91	0.92
-0.24	2.21	10.01	5.19	16.7	-	37.98	0.93	0.93
-0.30	2.01	9.45	9.81	13.22	-	51.06	0.90	0.93
-0.38	1.76	9.17	11.5	15.43	-	94.41	0.89	0.90
-0.40	1.31	4.62	15.9	17.10	5.2	105.11	0.94	0.89
-0.42	1.22	4.54	19.42	20.90	9.3	121.83	0.87	0.89
-0.44	1.02	4.51	21.02	23.33	14	129.09	0.95	0.91
-0.47	0.81	3.86	23.08	27.13	18	134.38	0.95	0.96

Typical examples of processes involving two or more adsorbed species are reactions of corrosion or anodic dissolution of metals, oxygen evolution, etc. In the case of two adsorbed species O ads and OH ads the electrochemical reactions written as [24]:



Where A, B, C are O₂ (sol), O ads and OH ads respectively. The rates of eqns. (1-3) may be expressed with respect to the equilibrium potential:

$$v_1 = \bar{k}_1(1 - \Theta_1 - \Theta_2) - k_{-1}\Theta_1 \quad (4)$$

$$v_2 = \bar{k}_2\Theta_1 - k_{-2}\Theta_2 \quad (5)$$

$$v_3 = k_3\Theta_2 - k_{-3}(1 - \Theta_1 - \Theta_2) \quad (6)$$

Where Θ_1 and Θ_2 are the surface coverage's by B and C, respectively, and rate constants k_3 and k_{-3} are potential independent. From the condition at the equilibrium potential: $v_1 = v_2 = v = 0$ the following condition for the rate constants is obtained:

$$\frac{k_1 k_2 k_3}{k_{-1} k_{-2} k_{-3}} = 1 \quad (7)$$

The charge is exchanged in reactions (1) and (2) only, therefore the total current is given as:

$$i = f(v_1 + v_2) = Fr_0 \quad (8)$$

Mass balance for Θ_1 and Θ_2 gives:

$$\frac{\sigma_1}{F} \frac{d\Theta_1}{dt} = v_1 - v_2 = r_1 \quad (9)$$

$$\frac{\sigma_2}{F} \frac{d\Theta_2}{dt} = v_2 - v_3 = r_2 \quad (10)$$

Taking into account that r_0 , r_1 and r_2 are the functions of η , Θ_1 and Θ_2 , linearization of eqns. (8-10) and introduction of phases gives:

$$\tilde{i} = F \left[\left(\frac{\partial r_0}{\partial \eta} \right)_{\Theta_1, \Theta_2} \tilde{\eta} + \left(\frac{\partial r_0}{\partial \Theta_1} \right)_{\eta, \Theta_2} \tilde{\Theta}_1 + \left(\frac{\partial r_0}{\partial \Theta_2} \right)_{\eta, \Theta_1} \tilde{\Theta}_2 \right] \quad (11)$$

$$jw \frac{\sigma_1}{F} \tilde{\Theta}_1 = \left(\frac{\partial r_1}{\partial \eta} \right)_{\Theta_1, \Theta_2} \tilde{\eta} + \left(\frac{\partial r_1}{\partial \Theta_1} \right)_{\eta, \Theta_2} \tilde{\Theta}_1 + \left(\frac{\partial r_1}{\partial \Theta_2} \right)_{\eta, \Theta_1} \tilde{\Theta}_2 \quad (12)$$

$$jw \frac{\sigma_2}{F} \tilde{\Theta}_2 = \left(\frac{\partial r_2}{\partial \eta} \right)_{\Theta_1, \Theta_2} \tilde{\eta} + \left(\frac{\partial r_2}{\partial \Theta_1} \right)_{\eta, \Theta_2} \tilde{\Theta}_1 + \left(\frac{\partial r_2}{\partial \Theta_2} \right)_{\eta, \Theta_1} \tilde{\Theta}_2 \quad (13)$$

Eqns. (11-13) present a system of three equations with three unknowns: Θ_1 , Θ_2 and $i \sim \tilde{i} / \tilde{\eta}$. The faradic admittance is determined as:

$$\hat{Y}_f = \frac{1}{\hat{Z}_f} = \frac{\tilde{i}}{\tilde{\eta}} = A + \frac{B + jwc}{jwD - w^2 + E} \quad (14)$$

Where

$$A = \frac{1}{R_{ct}} = -F \left(\frac{\partial r_0}{\partial \eta} \right)_{\Theta_1, \Theta_2} \quad (15)$$

$$B = -\frac{F^3}{\sigma / \sigma_2} \left\{ \begin{array}{l} -\left(\frac{\partial r_0}{\partial \Theta_1} \right) \left(\frac{\partial r_1}{\partial \eta} \right) \left(\frac{\partial r_1}{\partial \Theta_2} \right) + \left(\frac{\partial r_0}{\partial \Theta_1} \right) \left(\frac{\partial r_1}{\partial \Theta_2} \right) \left(\frac{\partial r_2}{\partial \eta} \right) \\ -\left(\frac{\partial r_0}{\partial \Theta_1} \right) \left(\frac{\partial r_1}{\partial \Theta_1} \right) \left(\frac{\partial r_2}{\partial \eta} \right) + \left(\frac{\partial r_0}{\partial \Theta_2} \right) \left(\frac{\partial r_1}{\partial \eta} \right) \left(\frac{\partial r_2}{\partial \Theta_1} \right) \end{array} \right\} \quad (16)$$

$$C = -F^2 \left[\frac{1}{\sigma_1} \left(\frac{\partial r_0}{\partial \Theta_1} \right) \left(\frac{\partial r_1}{\partial \eta} \right) + \frac{1}{\sigma_2} \left(\frac{\partial r_0}{\partial \Theta_2} \right) \left(\frac{\partial r_2}{\partial \eta} \right) \right] \quad (17)$$

$$D = -F \left[\frac{1}{\sigma_1} \left(\frac{\partial r_1}{\partial \Theta_1} \right) + \frac{1}{\sigma_2} \left(\frac{\partial r_2}{\partial \Theta_2} \right) \right] \quad (18)$$

$$E = \frac{F^2}{\sigma / \sigma_2} \left[\left(\frac{\partial r_1}{\partial \Theta_1} \right) \left(\frac{\partial r_2}{\partial \Theta_2} \right) - \left(\frac{\partial r_1}{\partial \Theta_2} \right) \left(\frac{\partial r_2}{\partial \Theta_1} \right) \right] \quad (19)$$

Where the negative sign before the parameters A, B and C originates from the current definition (positive current for reduction). If the reactions (1-3) are written as reductions this sign should be omitted. Calculation of the derivatives show that parameters A, D and E are always positive and parameters B and C may be positive or negative. On the whole the impedance behaviors of oxygen electro-reduction in different potential ranges can be categorized as:

(1) At low potential region (-0.15 and -0.38 V), assuming reaction (2), is rate determining step. So, these analyses from EIS indicate that, at low potential region, reaction (2) might be rate-determining step, and means the reduction of intermediates in comparison with generation of intermediates is fast.

(2) At high potential range (-0.4 and -0.47 V), reaction (3) can be assumed. The EIS data can also be simulated using the equivalent circuit of Fig. 4b. In this circuit R_1 , R_2 , Q_1 and Q_2 are R_{ct} , R_{ads} , Q_{dl} and Q_{ads} while R_3 is actually the time constant of the process of the regeneration of active sites for the adsorption and reduction of oxygen.

4. CONCLUSION

Ag film was formed electrochemically by chronopotentiometry on a glassy carbon electrode and tested for electro-reduction of oxygen in acidic media. Electrochemical

impedance studies of oxygen reduction on Ag/GC electrode demonstrate the potentialities of this method as a tool for investigating the mechanism of oxygen reduction. A theoretical impedance model based on kinetics is proposed which captures and explains all of the features of potential dependence of experimental impedance. The impedance behaviors in different potential regions reveal that the mechanism and rate-determining step in oxygen electro-reduction vary with potential. At low potential range, oxygen reduction is rate-determining step, while at high potential range, the reduction and removal of adsorbed intermediates became rate-determining step. In EIS investigates, polarization resistance is decreased by negative charge of adsorbed intermediate species such as: O ads and OH ads. Both the linear trend at middle frequencies in Nyquist plot and the 45° angle in Bode-Phase plot are indicator of an OFLD element.

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