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Electrochemical impedance spectroscopy analysis for oxygen reduction reaction in 3.5% NaCl solution

Fei Kuang · Dun Zhang · Yongjuan Li · Yi Wan · Baorong Hou

Abstract The electrochemical impedance spectroscopy (EIS) at different potentials has been used to study the oxygen reduction reaction (ORR) in 3.5% NaCl solution on glassy carbon (GC) electrode in this work. Results show that ORR consists of three two-electron reaction steps and both superoxide ion (O_2^-) and hydrogen peroxide (H_2O_2), which are produced by ORR, obstruct the diffusion of oxygen to the surface of the electrode and make the EIS results change into a transmissive finite diffusion process with the real part contraction and a reflective finite diffusion process from a semi-infinite diffusion process. The values of electron transfer resistance (R_t) and diffusion resistance (R_d) were calculated from EIS. O_2^- influenced strongly on the R_t values and induced a maximum at −0.45 V.

Keywords Electrochemical impedance spectroscopy · Oxygen reduction reaction · 3.5% NaCl solution · Cyclic voltammetry

Introduction

Oxygen reduction reaction (ORR) plays a key role on the corrosion process [1]. Recently, much attention has been paid on the ORR in the solutions containing sodium chloride (NaCl), which is an important composition in seawater and some industry environments. The influences of materials, pretreatment for materials, different types of passive film, Cl^-, pH and inhibitors on the ORR were studied by polarization, cyclic voltammetry, rotating disk electrode, rotating ring-disk electrode and rotating cylinder electrode voltammetry [2–17].

The electrochemical impedance spectroscopy (EIS), as a sensitive electrochemical method for the state of the surface of electrode, was used to study the gas reaction and the diffusion process. The rate-determining step of the ORR, the concentration of diffusion species, the polarization resistances, the stability of the electrode coated with thin layer of fluoro ionomer, the Warburg and Nernst diffusion coefficient in alkaline medium were studied by EIS in fuel cell [18–24]. A. Bonnel et al. [25] found that ORR on carbon steel in neutral chloride solutions included O_2 electrochemical reduction and chemical oxidation of ferrous to ferric ions by EIS at two potentials.

In this study, EIS at various potentials has been used to study the ORR in 3.5% NaCl solution on GC electrode. The values of electron transfer resistance (R_t) and diffusion resistance (R_d) were calculated from the results of EIS. Cyclic voltammetry were also used to verify the ORR process.

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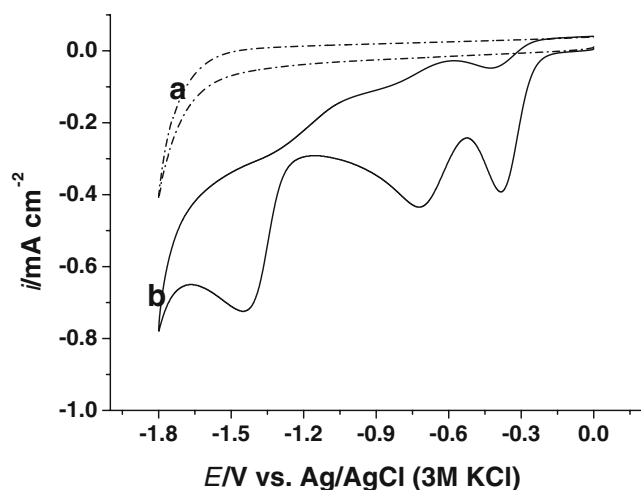19 (Jia) Yuquan Road,
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Experimental

Chemicals

Analytical grade NaCl was obtained from Sinopharm Chemical Reagent Co., Ltd. China. A 3.5%-NaCl solution was prepared with Mill-Q water as supporting electrolyte.

Fig. 1 Cyclic voltammograms obtained on GC electrode in O$_2$-sat. (*curve b*) and N$_2$-sat. (*curve a*) 3.5% NaCl solutions at a scan rate of 100 mV s^{-1}

Ultra-high purity nitrogen (N$_2$) and oxygen (O$_2$) gases (>99.999%, Qingdao Heli Gas Co. China) were fed to the electrochemical cells for 30 min for the deaeration of solution and the preparation of oxygen-saturated solution, respectively.

Electrochemical cell and electrodes

The electrochemical measurements were performed in a three-electrode one-compartment cell. A GC electrode (3 mm diameter), an Ag/AgCl electrode (3 M KCl) and a platinum wire electrode were purchased from CH Instruments, Inc. and used as a working electrode, a reference electrode and a counter electrode, respectively. The reason GC electrode was chosen as a working electrode owes to its better stability than metal electrodes, especially steel in NaCl solutions, and the influence of electrode self-reaction on the EIS can be ignored.

Prior to each experiment, the working electrode was firstly polished with silicon carbide paper and two kinds of alumina powder with particle sizes of 1 and 0.05 μm on a polishing cloth. Electrodes were then ultrasonically cleaned with Milli-Q water for 10 min.

Electrochemical measurements

Electrochemical experiments of EIS and cyclic voltammetry were measured using a computer-controlled system (CHI 760C).

Potential vs. time curve at different potentials were measured and the current density achieved stability after 20 s. Therefore, the EIS was performed at different potentials after it was stabilized for 20 s.

EIS measurements were performed at different potentials in O$_2$-sat. and N$_2$-sat. 3.5% NaCl solutions at frequencies of 0.05–100,000 Hz with an amplitude of 5 mV. The EIS results were analyzed with Zview software.

Cyclic voltammetry were run in N$_2$-sat. and O$_2$-sat. 3.5% NaCl solutions at the potential range of 0 to −1.8 V at a scan rate of 100 mV s^{-1}. All experiments were conducted at room temperature 25±2 °C.

Results

Cyclic voltammetry

Figure 1 curves a and b are the cyclic voltammograms in N$_2$-sat. and O$_2$-sat. 3.5% NaCl solutions, respectively. No reaction happens in N$_2$-sat. solution except hydrogen evolution appearing at the potentials below −1.20 V. Therefore, the three peaks in O$_2$-sat. solution at potentials of −0.39, −0.72 and −1.44 V can be characterized as three steps for ORR. At the first step (−0.39 V), O$_2$ is reduced to H$_2$O$_2$ via O$_2^-$-produced catalyzing by quinone-like functional groups on the surface of the GC electrode [26]. Although O$_2$ is a strong oxidant at pH 7 when utilized as a four-electron transfer agent, it is an extremely weak one-
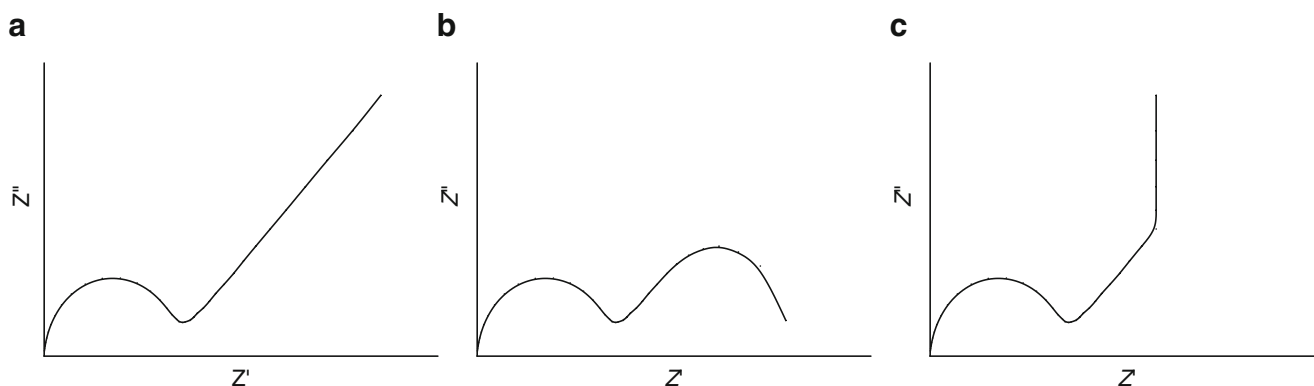

Fig. 2 Scheme of impedance for diffusive systems: **a** semi-infinite diffusion; **b** transmissive finite diffusion; **c** reflective finite diffusion
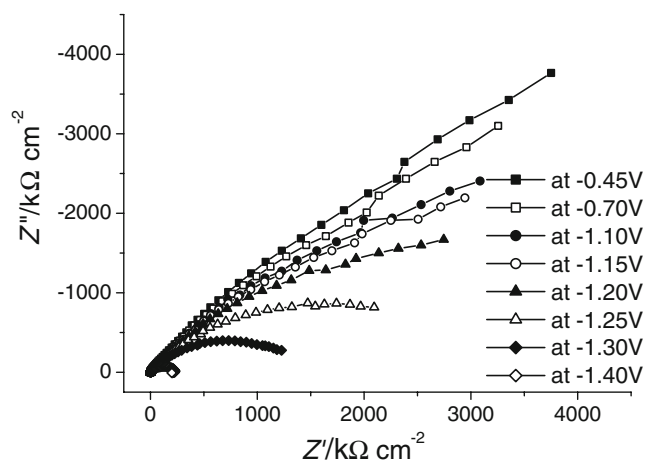
Fig. 3 Nyquist plots obtained at GC electrode in N_2-sat. 3.5% NaCl solution at −0.45, −0.70, −1.10, −1.15, −1.20, −1.25, −1.30 and −1.40 V, respectively

electron oxidant [27]. Electrochemical reactions have been proposed as Eqs. (1) and (2) [28].

$$O_2 + e \rightarrow O_2^- \qquad (1)$$

$$O_2^- + 2H^+ + e \rightarrow H_2O_2 \qquad (2)$$

At the second and the third steps, the pathway of O_2 reduction follows the usual two two-electron reactions shown as Eqs. (3) and (4) [29].

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2 \qquad (3)$$

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \qquad (4)$$

Therefore, O_2 is reduced into H_2O via the intermediates O_2^- produced by one-electron O_2 reduction and H_2O_2
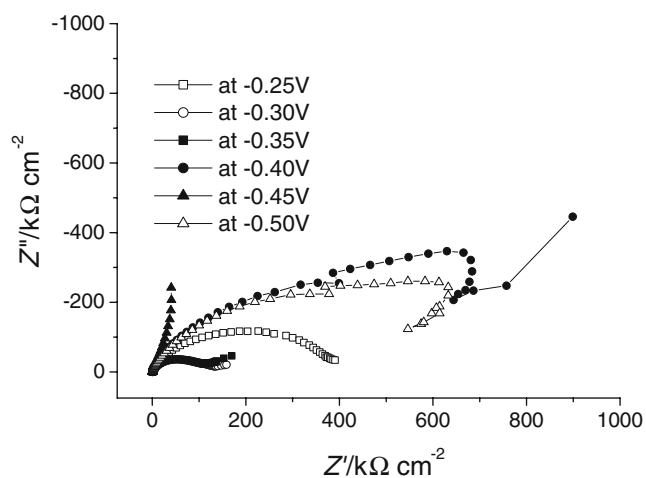

Fig. 4 Nyquist plots obtained at GC electrode in O_2-sat. 3.5% NaCl solution at −0.25, −0.30, −0.35, −0.40, −0.45 and −0.50 V, respectively
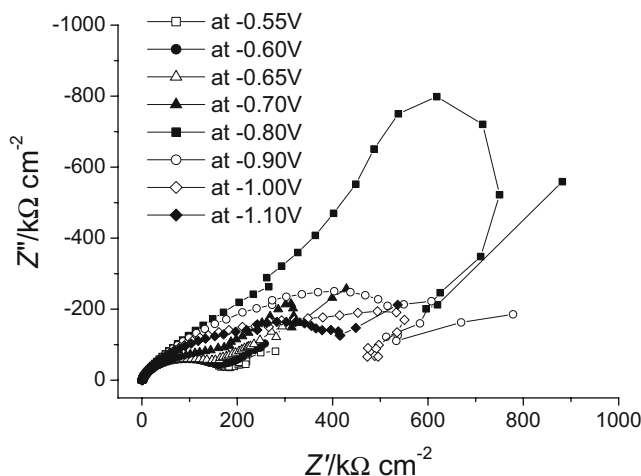

Fig. 5 Nyquist plots obtained at GC electrode in O_2-sat. 3.5% NaCl solution at −0.55, −0.60, −0.65, −0.70, −0.80, −0.90, −1.00 and −1.10 V, respectively

produced by two-electron O_2 reduction and one-electron O_2^- reduction in this study.

Electrochemical impedance spectroscopy

The EIS of the ORR on GC electrode has three different diffusion characters [30]. The first one happens when the thickness of stagnant layer is infinite. The ideal character of this kind of process in a Nyquist graph is shown in Fig. 2a, which is called semi-infinite diffusion process. The transmissive finite diffusion process happens when the thickness of the stagnant layer is finite. This kind of process in Nyquist graph is shown in Fig. 2b. The third one is a reflective finite diffusion process, which happens when only the transmission takes place in a limited distance and the ideal character is shown in Fig. 2c.

Figure 3 shows the Nyquist plots obtained in N_2-sat. 3.5% NaCl solution at the potential range of −0.45 to −1.40 V. It is obvious that the semicircle diameter, which is in proportional to the electron transfer resistance (R_t) at −0.45 to −1.20 V, is larger than those obtained at −1.25 to −1.40 V. The hydrogen evolution reaction induces the decrease of R_t values at −1.25 to −1.40 V in N_2-sat. 3.5% NaCl solution. This result can also be proved by the CV results that the hydrogen evolution reaction occurred at the potentials from −1.20 V to the negative direction as curve a shown in Fig. 1.

The Nyquist plots obtained in O_2-sat. 3.5% NaCl solution at the potential range corresponding to the three reaction steps for ORR obtained from CV results are shown in Figs. 4, 5, and 6. The EIS for the first step of ORR showed semi-infinite diffusion process [30] at the potential range of −0.25 to −0.35 V. Then, it showed a transmissive finite diffusion process [30] with a real part contraction phenomenon at −0.40 V and a reflective finite diffusion
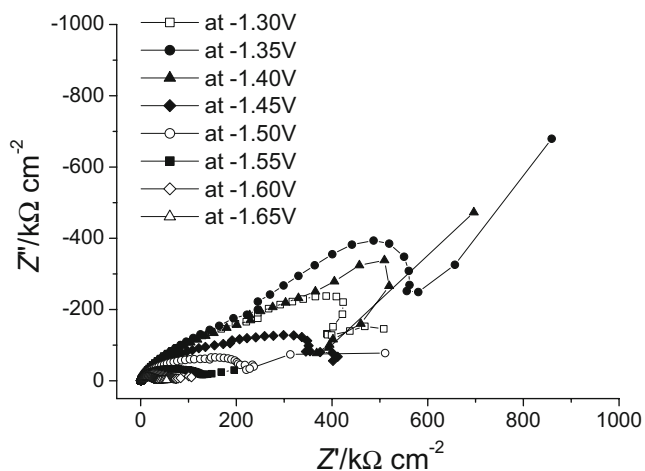
Fig. 6 Nyquist plots obtained at GC electrode in O_2-sat. 3.5% NaCl solution at −1.30, −1.35, −1.40, −1.45, −1.50, −1.55, −1.60 and −1.65 V, respectively

process [30] at −0.45 V, respectively, and it changed into transmissive finite diffusion process again at −0.50 V. At the second step of ORR, EIS appeared firstly as semi-infinite diffusion process at the potentials of −0.55 to −0.70 V, and then indicated transmissive finite diffusion process with real part contraction at the potential range of −0.80 to −1.45 V, at which ORR went through the second and the third reaction steps. EIS results expressed semi-infinite process at the potential range of −1.50 to −1.60 V, and the diffusion process disappeared at −1.65 V as shown in Fig. 6.

Equivalent circuits

The equivalent circuit for the EIS at the potential range of −0.25 to −1.65 V is expressed and shown as Fig. 7 following Ref. [24], where R_s represents the solution resistance, R_t is the charge transfer resistance, C_{dl} is the capacitance of double layer with a Cole–Cole coefficient n_{dl} [31, 32] and Z_W is the impedance of the diffusion component. It represents resistance, diffusion impedance and capacitance as the n_{dl} value is 0, 0.5 and 1, respectively. n_{dl} calculated in this study is ca. 0.9; thus, the double layer
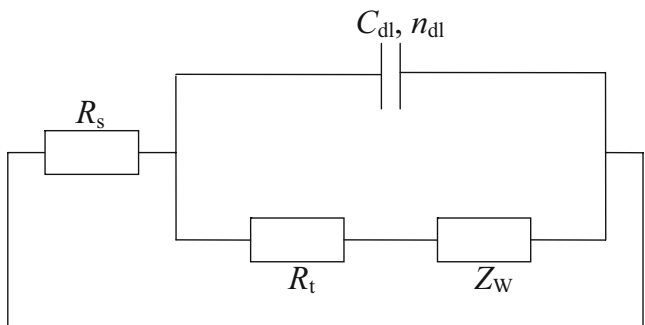

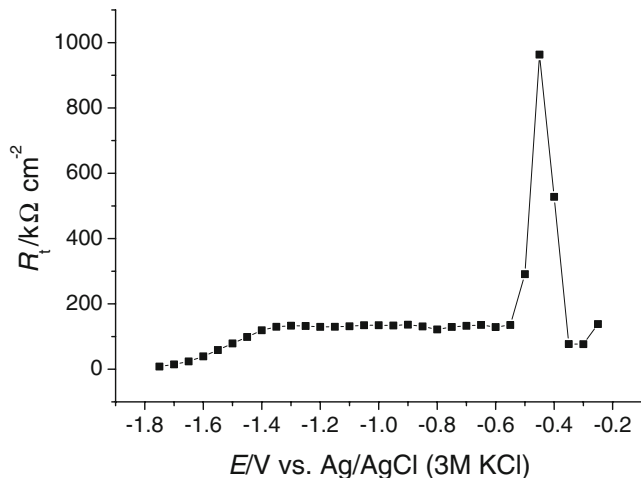Fig. 7 The equivalent circuit for the EIS as shown in Figs. 4, 5, and 6

Fig. 8 Plot of R_t values vs. the potential (E) of working electrode calculated from Figs. 4, 5, and 6

in this study shows an ideal capacitance with a little deviation caused by the diffusion impedance [18, 32].

The equivalent circuit can be expressed as [31, 32]:

$$Z(f) = R_s + \frac{R_t + Z_w(f)}{1 + \{[R_t + Z_w(f)]i2\pi f C_{dl}\}^{n_{dl}}} \tag{5}$$

$$Z_w(f) = R_d \frac{\tanh \sqrt{i2\pi fT}}{\sqrt{i2\pi fT}} \tag{6}$$

where R_d is the diffusion resistance, T is a constant, and f is the frequency.

For low frequency, Eq. (5) can be expressed as:

$$\lim_{f \to 0} Z(f) = R_s + R_t + R_d \tag{7}$$

The plots of R_t vs. E calculated from Zview software are shown in Fig. 8 and R_d vs. E calculated from Eq. (7) shown in Fig. 9. There is a maximum value of R_t at the potential of
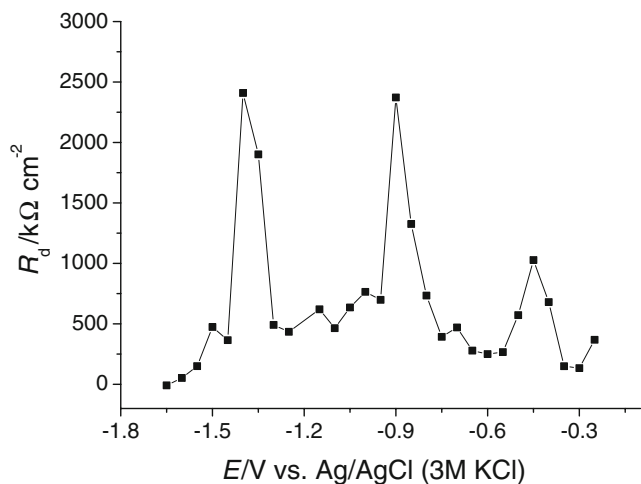

Fig. 9 Plot of R_d values vs. the potential (E) of working electrode calculated from Figs. 4, 5, and 6

-0.45 V. With the potential shifts to negative direction from -1.50 V, the R_t values decrease greatly. The R_d values show three peaks at the three potential ranges corresponding to the three steps of ORR.

Discussions

EIS for ORR

At the first step of ORR, O_2 diffuses to the surface of the electrode and is reduced to O_2^-. EIS showed the semi-infinite diffusion process at the potentials of -0.25 to -0.35 V. With the increasing amount of O_2^- adsorbed on the surface of the electrode, the transmissive finite diffusion process with a real part contraction appeared at -0.40 V. When the ORR current reached the peak current, the amount of adsorbed O_2^- arrived at the maximum value and the EIS suggested a reflective finite diffusion process at -0.45 V. Then, O_2^- is reduced into H_2O_2 (Eq. 2) at -0.50 V and the H_2O_2 adsorbed on the electrode surface caused the transmissive finite diffusion with the real part contraction.

At the second step of ORR, O_2 diffuses to the electrode surface and is reduced to the H_2O_2 (Eq. 3) that adsorbed on the surface of the electrode. The H_2O_2 adsorbed on the surface of the electrode resulted in the EIS appearing at the semi-infinite diffusion process at the potentials of -0.55 to -0.70 V and transmissive finite diffusion with the real part contraction at the potentials from -0.80 V until the third step of ORR occurred. The reflective finite diffusion process did not appear at the second step. These results indicated that the effect of adsorbed H_2O_2 on the EIS was different from that of adsorbed O_2^-.

At the third step of ORR, H_2O_2, which is produced by ORR at the second step and adsorbed on the surface of the electrode, is reduced to H_2O (Eq. 4) and the EIS shown in Fig. 5 illustrated the transmissive finite diffusion process at -1.30 to -1.45 V. EIS showed a semi-infinite diffusion process at more negative potentials from -1.55 V, at which hydrogen evolution reaction was the main reaction.

The values of R_t and R_d in the ORR process

The R_t values showed different character in the three steps of ORR: R_t values were almost the same in the second and the third steps, and appeared at a maximum in the first step that was much larger than those in the second and the third steps. The maximum value of R_t occurred at -0.45 V, at the potential that reflective finite diffusion process happened. This suggested that O_2^- produced by O_2 reduction obstructed both the diffusion process of O_2 to the surface of electrode and the electron transfer process on the surface of electrode.

The values of R_d showed three peak values at -0.45, -0.90 and -1.40 V, respectively, and corresponded to the three steps of ORR. At the potential of -0.45 V, the amount of O_2^- reduced by O_2 in the first step reached the maximum value on the surface of the GC electrode and O_2^- obstructed O_2 diffused to the surface of the electrode from the bulk solution, leading to a maximum value of R_d. At the potentials of -0.90 and -1.40 V, the H_2O_2 adsorbed on the electrode surface caused the R_d peak value. The results could also be verified by the EIS results, which transmissive finite diffusion process with the real part contraction appeared at the potential range of -0.80 to -1.45 V. According to Figs. 8 and 9, the effect of O_2^- on the R_t value was larger than that of H_2O_2, and the effect of O_2^- on the R_d value was smaller than that of H_2O_2.

Conclusions

The present results indicate that ORR on the GC electrode in a 3.5%-NaCl solution is a three two-electron reaction process. The EIS results show that O_2^- and H_2O_2 produced by ORR are adsorbed on the surface of the electrode and obstruct the diffusion of O_2 to the surface of the electrode from bulk solution and make the EIS results change into a transmissive finite diffusion process with the real part contraction and a reflective finite diffusion process from a semi-infinite diffusion process. O_2^- influenced strongly on R_t value. The values of R_d calculated from EIS suggested three peaks in the ORR process.

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