

A study of oxygen reduction on platinum-dispersed porous carbon electrodes at room and elevated temperatures by using a.c. impedance spectroscopy

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Received 14 November 1995; accepted 24 November 1995

Abstract

Oxygen reduction on unwetted and pre-wetted platinum-dispersed porous carbon electrodes (Pt/C) is investigated in 1 M H₂SO₄ solution at room temperature by using a.c. impedance spectroscopy in combination with a current-decay transient technique (chronoamperometry). From the appearance of an inductive arc in Nyquist plots from the unwetted Pt/C electrode specimen, it is suggested that oxygen reduction proceeds via formation of an intermediate state. The a.c. impedance spectra are also obtained from the Pt/C electrode in 85% H₃PO₄ solution at 140 °C, with and without oxygen and air blowings. In both cases, an inductive arc in the low-frequency range of the Nyquist plots is observed. The change in impedance spectra with pre-wetting treatment of the Pt/C electrode specimen in 1 M H₂SO₄ solution and the alteration of spectra without oxygen and air blowings in 85% H₃PO₄ solution are discussed in terms of the Epeleboin model. From the analysis, it is concluded that as depletion of the dissolved oxygen occurs markedly within the narrow pores of the Pt/C electrode, the inductive arc moves towards the capacitive arc in the low-frequency range. The results of current-decay transients strongly suggest the occurrence of depletion of the dissolved oxygen within the narrow pores.

Keywords: Impedance spectroscopy; Platinum; Electrode; Oxygen reduction; Current transient; Carbon

1. Introduction

Platinum-dispersed carbon (Pt/C) has been used as electrode materials for phosphoric acid fuel cells (PAFCs). Many studies have been performed [1-3] in order to increase the operation efficiency and life-time of PAFC electrodes.

Oxygen reduction on a PAFC cathode at elevated temperature is a kinetically slow reaction. It is generally known that sluggishness of oxygen reduction determines the operation efficiency of the PAFC [1]. Platinum is commonly used as a catalyst for oxygen reduction in PAFC. Hence, many researches concerning the mechanism and kinetics of oxygen reduction on platinum and other noble metals have been conducted, mainly by using the rotating ring disc electrode (RRDE) technique at room temperature [4-6], or by using cyclic voltammetry and polarization methods at 140-180 °C [1,7]. It has been reported that oxygen reduction proceeds via formation of an intermediate state, viz., H₂O₂ or D₂O₂. The former [4-6] and latter [1,7] researchers used geomet-

rically well-defined smooth noble-metal electrodes, respectively as the working electrode.

The RRDE technique cannot be applied to porous electrode systems at elevated temperature. By contrast, a.c. impedance spectroscopy can provide a wealth of information on the reaction at the porous electrode/electrolyte interface [8]. Armstrong and Henderson [9] and Epelboin et al. [10] have provided mathematical expressions for the a.c. impedance response of the reactions involving intermediate states. It is still necessary, however, to establish the a.c. impedance technique for the complex pathway reaction on the porous electrode.

The present work aims to investigate oxygen reduction on Pt/C porous electrodes by analysing a.c. impedance spectra combined with current-decay transients (chronoamperograms). For this purpose, a.c. impedance spectra and current-decay transients are measured on unwetted and pre-wetted Pt/C electrode specimens in 1 M H₂SO₄ solution at room temperature. The reaction rate constants are determined from a.c. impedance spectra by using a complex, non-linear, least squares (CNLS) fitting method. The changes in impedance

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spectra and current-decay transients with pre-wetting treatment on Pt/C electrode specimens are discussed on the basis of the Epeiboin model [10]. In addition, in order to investigate oxygen reduction under actual PAFC operational conditions, the impedance spectra are obtained from a fresh Pt/C electrode in 85% H_3PO_4 solution at 145 °C, with and without oxygen and air blowings. The effect of oxygen and air on oxygen reduction is compared with that of pre-wetting treatment.

2. Experimental

Specimens of PTFE (polytetrafluoroethylene)-bonded Pt/C electrodes were prepared as follows. First, 10 wt.% Pt-dispersed Vulcan XC-72 carbon black powder (Johnson Matthey, 70 wt.%) and PTFE (30 wt.%) emulsion were mixed in distilled water with ultrasonic agitation. The mixture of Pt-dispersed carbon black powder and PTFE emulsion was pasted onto carbon paper (which is used as a gas supply layer) and then dried in an oven at 120 °C for 24 h with passage of nitrogen gas. This pasted sheet was pressed with 2 MPa pressure. Finally, the Pt/C electrode specimen (15 mm diameter and 0.2 mm thickness) was obtained by sintering at 330 °C for 10 min under a nitrogen atmosphere. The pre-wetted Pt/C specimen was prepared by wetting the freshly sintered Pt/C electrode specimen with 96% H_2SO_4 solution for 8 h before a.c. impedance and current-decay transient measurements. By means of this pre-wetting treatment, electrolyte may infiltrate deeply into the narrow pores of the Pt/C electrode.

Fig. 1 provides a schematic view of the specimen holder. The Pt/C electrode specimen was composed of two layers: (i) an active reaction layer and (ii) a gas-supply layer which was not exposed to the electrolyte.

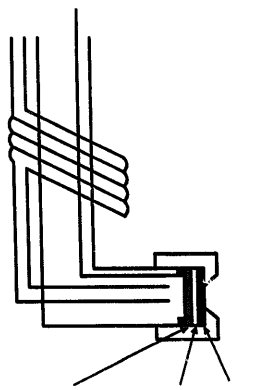


Fig. 1. Schematic view of specimen holder.

The experimental apparatus for measuring a.c. impedance spectra and current-decay transients is presented schematically in Fig. 2. Platinum wire was used as a current collector. 1 M H_2SO_4 and 85% H_3PO_4 solution were used as the electrolytes. It is noted that the current collector was not exposed to the electrolyte. A platinum net and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The reversible hydrogen electrode (RHE) was used as the reference electrode in 85% H_3PO_4 solution at 145 °C. Unless otherwise stated, the potentials in the present work are reported with respect to a RHE. The corrosion potential of the Pt/C carbon electrode specimen in 1 M H_2SO_4 solution amounted to about 0.9 V_{RHE} at room temperature.

The a.c. impedance measurements were performed with a ZAHNER IM5d impedance spectrum analyzer on the unwetted and pre-wetted Pt/C electrode specimens in 1 M H_2SO_4 solution at various applied cathodic electrode potentials of 250, 300, 350, 450, 500 and 550 mV, namely, below 690 mV (standard electrode potential for the formation of an intermediate state H_2O_2) at room temperature. The impedance spectra were also obtained from a fresh Pt/C electrode in 85% H_3PO_4 solution at 145 °C; the applied cathodic electrode potentials were 250, 300, 350, 450 and 500 mV. An alternating sinusoidal signal of 20 mV peak-to-peak is superimposed on the d.c. potential. The impedance spectra were obtained in the frequency range between 1 mHz and 1 MHz.

In addition, the current-decay transient measurement (chronoamperometry) was conducted with an EG&G potentiostat/galvanostat model 273 on the unwetted and pre-wetted Pt/C electrode specimens in 1 M H_2SO_4 solution. The Pt/C electrode specimen was first exposed to the open-circuit potential for 120 s from which its electrode potential was then

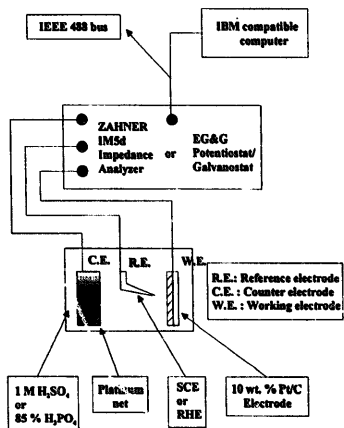


Fig. 2. Schematic representation of the experimental apparatus for measuring a.c. impedance spectra and current-decay transients.

dropped to 250, 350, 450, 550 and 650 mV, i.e., below 690 mV in 1 M H₂SO₄ solution at room temperature. From this moment the resulting current was recorded with time.

3. Results and discussion

Fig. 3 presents the measured impedance in the Nyquist representation for the unwetted Pt/C electrode specimen subjected to 250, 300, 350, 450, 500 and 550 mV in 1 M H₂SO₄ solution. One does not observe the constant phase element (CPE) due to the porous structure of the electrode and that has a theoretical slope of 45° in the high-frequency range of the Nyquist plot. This indicates that the electrolyte does not infiltrate into the narrow pores of the unwetted Pt/C electrode. Thus, oxygen reduction occurring on the surface of the unwetted Pt/C electrode contributes mainly to the resulting cathodic current of the a.c. impedance response. For the unwetted Pt/C electrode subjected to potentials from 250 to 550 mV (Fig. 3), one high-frequency capacitive arc and one low-frequency inductive arc are observed. The occurrence of the low-frequency inductive arc suggests that oxygen reduction proceeds via formation of intermediate states on the unwetted Pt/C electrode specimen. The magnitude of the overall impedance increases with decreasing overpotential for oxygen reduction.

The Nyquist plots for oxygen reduction on the pre-wetted Pt/C electrode specimen subjected to 250, 300, 350, 450, 500 and 550 mV in 1 M H₂SO₄ solution are presented in Fig. 4. In contrast to the unwetted Pt/C electrode specimen, the impedance spectra obtained from the potential range 250 to 550 mV consist of the CPE with a slope of 45°, one high-frequency capacitive arc, and one low-frequency capacitive arc. The appearance of the CPE in the high-frequency range shows that the electrolyte infiltrates into the narrow pores of the pre-wetted Pt/C electrode specimen. Considering that the overall impedance value of the pre-wetted Pt/C electrode specimen is smaller by three orders in magnitude than that of the unwetted Pt/C electrode specimen, oxygen reduction that

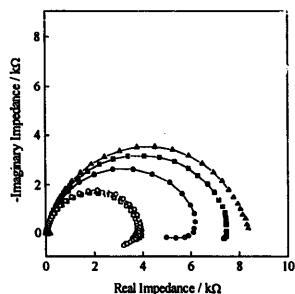


Fig. 3. Nyquist plots for oxygen reduction on unwetted Pt/C electrode in 1 M H₂SO₄ subjected to various applied potentials: (○) 250 mV; (□) 300 mV; (△) 350 mV; (●) 450 mV; (■) 500 mV, and (▲) 550 mV.

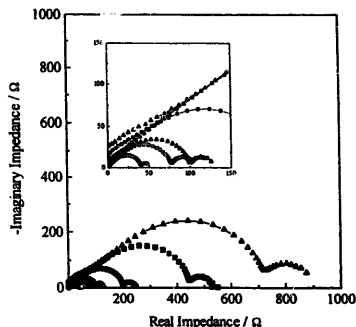
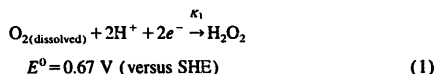


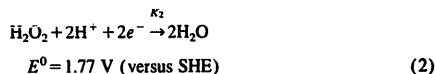
Fig. 4. Nyquist plots for oxygen reduction on pre-wetted Pt/C electrode in 1 M H₂SO₄ subjected to various applied potentials: (○) 250 mV; (□) 300 mV; (△) 350 mV; (●) 450 mV; (■) 500 mV, and (▲) 550 mV.

occurs within the narrow pores contributes mainly to the resulting cathodic current of the a.c. impedance response. The inductive-to-capacitive transition in the impedance spectra with pre-wetting treatment implies a change in the mechanism and the kinetics of oxygen reduction.

It is well known that oxygen reduction occurs via complex pathways that involve the formation of intermediate states [1,4-6]. In the present work, it is postulated that below 0.67 V (versus SHE), oxygen reduction on the unwetted and pre-wetted Pt/C electrode specimens takes place according to following reaction mechanism that involves the intermediate H₂O₂



and



where K_1 and K_2 are the electrochemical rate constants of reactions (1) and (2), respectively, and E^0 is the standard electrode potential.

A mathematical expression for faradaic impedance, Z_f , of a reaction that involves an intermediate state has been advanced by Epelboin et al. [10]. In this work, the faradaic impedance is expressed as follows

$$\frac{1}{Z_f} = \frac{1}{R_i} + \frac{Q}{1 + j\omega\tau}, \quad j = \sqrt{-1} \quad (3)$$

using the abbreviations:

$$\tau = \frac{\beta}{[a_{H^+}]^2(K_1 C_{O_2} + \beta K_2)}$$

$$R_i = \frac{1}{2F[a_{H^+}]^2 \left\{ \frac{dK_1}{dV} C_{O_2} (1 - \theta_s) + \beta \theta_s \frac{dK_2}{dV} \right\}}$$

and

$$Q = - \left(\frac{1}{K_1} \frac{dK_1}{dV} - \frac{1}{K_2} \frac{dK_2}{dV} \right) \times K_1 K_2 [a_{H^+}]^4 C_{O_2}^2 2F(K_1 C_{O_2} - \beta K_2)$$

where R_i represents the charge-transfer resistance, ω the angular frequency, τ the relaxation time, β the maximum concentration of an intermediate state on the electrode surface, $[a_{H^+}]$ the activity of proton, C_{O_2} the concentration of the dissolved oxygen in electrolyte within the narrow pores, F the Faraday constant, V the overpotential, θ_s the coverage of an intermediate state on the electrode surface at a steady state. Q is called the effective impedance and is given as a function of V , $[a_{H^+}]$ and C_{O_2} . Considering Eq. (3), it is generally said that if the Q value is positive, two capacitive arcs emerge in the Nyquist plot. Otherwise if the Q value is negative, one capacitive arc and one inductive arc appear in the Nyquist representation. For the unwetted and pre-wetted Pt/C electrodes, the sign of the value of Q is determined by the sign of the quantities in the first and second parentheses.

Assuming that the rates of reactions (1) and (2) obey the Tafel law, the electrochemical rate constants K_1 and K_2 are expressed, respectively, as

$$K_1 = k_1 \exp(b_1 V) \quad \text{and} \quad K_2 = k_2 \exp(b_2 V) \quad (4)$$

where k_1 and k_2 are the chemical rate constants, and b_1 and b_2 are the inverse of the Tafel slopes of reactions (1) and (2), respectively. The Q value is then given by

$$Q = -(b_1 - b_2) K_1 K_2 [a_{H^+}]^4 C_{O_2}^2 2F(K_1 C_{O_2} - \beta K_2) \quad (5)$$

Now let us determine the sign of the first and second parentheses. The applied potential is more cathodic with respect to the standard potential of reaction (2) than with respect to the standard potential of reaction (1) during the a.c. impedance measurement. Therefore, it is expected that the rate of reaction (2) approaches the higher cathodic current in the combined Tafel and limiting current regions owing to the higher applied cathodic potential with respect to reaction (2). This means the value b_2 is much smaller than the value b_1 in the potential range of this work. Hence, the sign of the quantity in the first parenthesis is always positive for the unwetted and pre-wetted specimens, irrespective of the values of V , $[a_{H^+}]$ and C_{O_2} employed in this work.

The sign of the second parenthesis is determined by the values of K_1 , K_2 , β and C_{O_2} employed in this work. The values of K_1 and K_2 depend mainly upon the value of V .

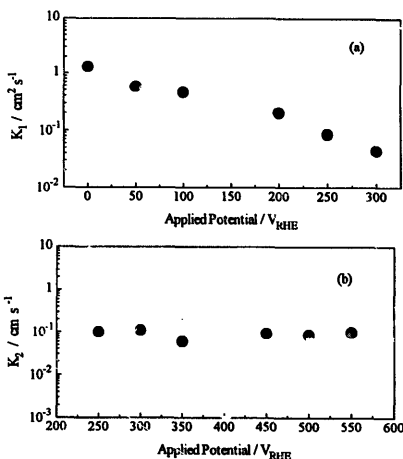


Fig. 5. Fitted parameters of (a) K_1 and (b) K_2 as a function of applied potential for unwetted Pt/C electrode specimen.

The value of β is assumed to have a half of the theoretical value of adsorbed hydrogen on palladium [8]. The C_{O_2} value in the bulk electrolyte is taken as the solubility limit of oxygen in 1 M H_2SO_4 solution [8]. On the other hand, the C_{O_2} value in the electrolyte within the narrow pores is calculated by considering the double-layer capacitance and cathodic current determined from the a.c. impedance spectra and cathodic polarization curves of this work, respectively.

The CNLS (complex non-linear least squares) fitting method was applied on the measured impedance spectra to determine the values of K_1 and K_2 . Fig. 5 shows the potential dependence of fitted values of K_1 and K_2 for the unwetted Pt/C electrode specimen. The value of K_1 increases with decreasing applied potential. The value of K_2 , however, is independent of applied potential. This is probably due to the very small value of b_2 . As shown in Fig. 6, the values of K_1 and K_2 for the pre-wetted specimen are smaller and exhibit less potential dependence than those for unwetted specimen, which arises from the activation effect (elimination of impurities, passivating surface oxide, etc.) of pre-wetting treatment in highly concentrated sulfuric acid. The orders of magnitude of K_1 and K_2 are in good agreement with reported values that have been evaluated by the RRDE technique [11].

In order to determine the sign of the second parenthesis term, we take the reasonable values of $K_1 = 6.0 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ [11] for the unwetted and pre-wetted specimens, $K_2 = 1.45 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$ [11] for the unwetted and pre-wetted specimens, $\beta = 3.95 \times 10^{-7} \text{ mol cm}^{-2}$ for the unwetted and pre-wetted specimens, $C_{O_2} = 1 \times 10^{-6} \text{ mol cm}^{-3}$ for the unwetted specimen, and $C_{O_2} = 1 \times 10^{-8} \text{ mol cm}^{-3}$ for the pre-wetted specimen. As a result, the unwetted specimen

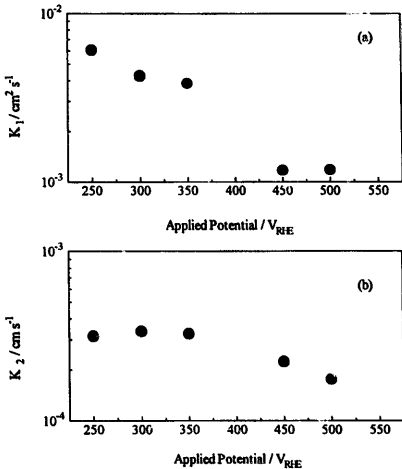


Fig. 6. Fitted parameter of (a) K_1 and (b) K_2 as a function of applied potential for pre-wetted Pt/C electrode specimen.

gives a positive sign for the second parenthesis term. By contrast, the pre-wetted specimen provides a negative sign.

It should be noted that the C_{O_2} value from the pre-wetted specimen is lower than that from the unwetted specimen by two orders in magnitude. This indicates the limited supply of the dissolved oxygen through the electrolyte within the narrow pores of that specimen. The rate of proton diffusion from the bulk electrolyte to the narrow pores is considered to be much faster than that of the dissolved oxygen. Thus, there is an unlimited supply of protons for oxygen reduction.

Finally, it is concluded that the Q value has a positive sign for the unwetted specimen in the V , $[a_{\text{H}^-}]$ and C_{O_2} ranges investigated. On the other hand, the Q value has a negative sign for the pre-wetted specimen. The occurrence of one capacitive arc and one inductive arc at the unwetted Pt/C electrode specimen, and two capacitive arcs at the pre-wetted Pt/C electrode specimen, can be accounted for in terms of the sign of the Q value based upon the proposed model. The sign and magnitude of the Q value determine the feature and size of the a.c. impedance spectra, as determined by the applied potential.

The Nyquist plots for oxygen reduction on the fresh Pt/C electrode specimen subjected to 250, 300, 350, 450 and 500 mV in 85% H_3PO_4 solution at 145 °C, with and without oxygen and air blowings, are shown in Fig. 7. The Pt/C electrode was satisfactorily wetted in 85% H_3PO_4 solution at 145 °C. The high-frequency capacitive arc and the low-frequency inductive arc appear in the presence of oxygen and air. By contrast, the two capacitive arcs appear in the absence of oxygen and air. By comparison with the impedance spectra obtained in 1 M H_2SO_4 solution at room temperature, the

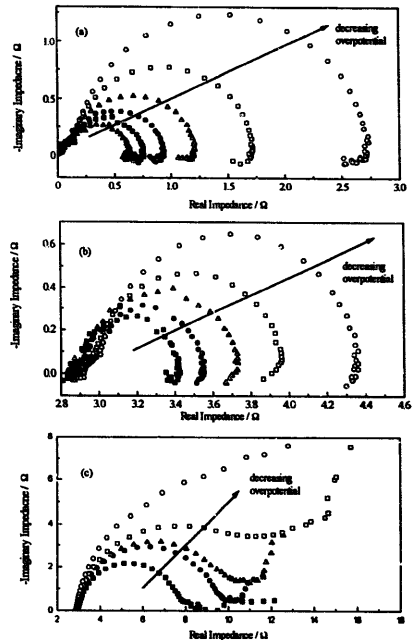


Fig. 7. Nyquist plots for oxygen reduction on fresh Pt/C electrode subjected to various applied potentials: (○) 250 mV; (□) 300 mV; (△) 350 mV; (●) 450 mV, and (■) 500 mV; 85% H_3PO_4 solution at 145 °C with (a) oxygen blowing, (b) air blowing, and (c) without gas (oxygen or air) blowing.

effect of oxygen or air blowings on oxygen reduction in 85% H_3PO_4 solution at 145 °C seems to be the same as that effect of using the unwetted specimen in 1 M H_2SO_4 solution at room temperature. This result strongly supports the conclusion that limited supply of oxygen through narrow pores gives an inductive arc instead of a capacitive arc. From this result, it is thought that with oxygen and air blowings, the concentration of dissolved oxygen in the narrow pores is more or less sufficient to transform the inductive arc into the capacitive arc in the resulting Nyquist plots.

Fig. 8(a)–(e) presents cathodic current-decay transients obtained from the pre-wetted Pt/C electrode specimen subjected to 250, 350, 450, 550 and 650 mV, respectively, in 1 M H_2SO_4 solution. The resulting cathodic current decreases down to the current minimum at the time, t_{min} , and then increases with time, followed by attaining the steady-state value. The t_{min} value decreases with decreasing applied potential. It should be noted that a local current minimum was observed in the initial current decay in Fig. 7(c)–(e). This is probably due to noise that originates from non-uniform distribution of the electrolyte within the narrow pores.

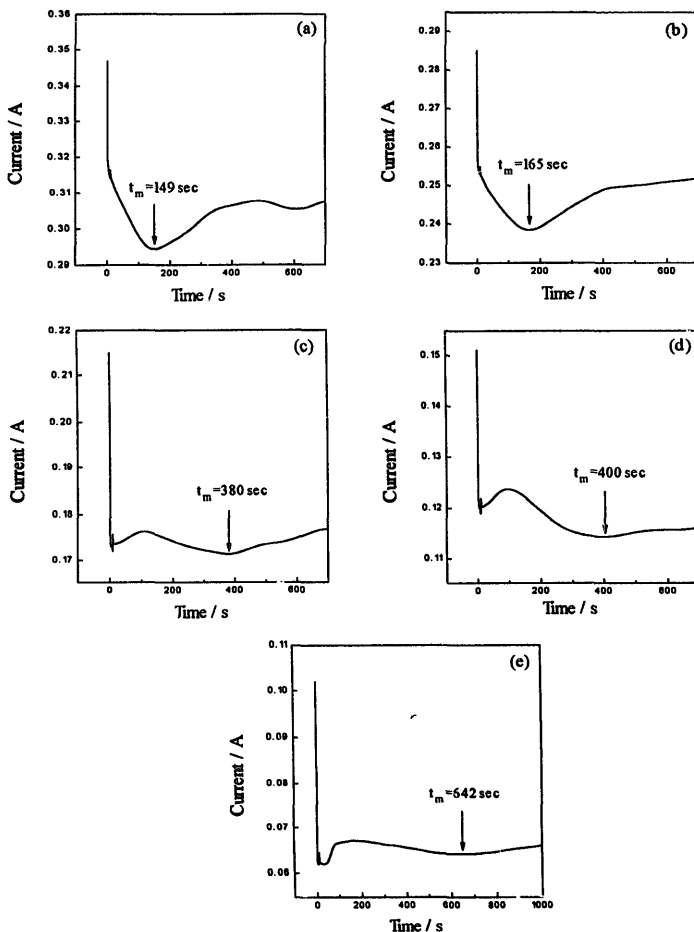


Fig. 8. Current-decay transients obtained from pre-wetted Pt/C electrode in 1 M H_2SO_4 subjected to various applied potentials: (a) 250 mV; (b) 350 mV; (c) 450 mV; (d) 550 mV, and (e) 650 mV.

The occurrence of the current minimum can be explained in terms of the limited supply of the dissolved oxygen to the narrow pores in the following way. At the early stage of the current decay, i.e. before $t = t_m$, the dissolved oxygen is depleted within the narrow pores because of the restricted diffusion and, thus, the cathodic current decreases with time. At a later stage, i.e. $t > t_m$, the dissolved oxygen is replenished within the pores to give a steady-state oxygen concentration

in the electrolyte within the pores and, thus, the cathodic current increases progressively. The current-decay transient with a current minimum is in accordance with the observed a.c. impedance with two capacitive arcs, as already discussed in terms of the sign of the Q value.

In contrast, it is confirmed that the current-decay transient obtained from the unwetted Pt/C electrode specimen obeys the usual logarithmic rate law, similar to that from the smooth

platinum electrode. There is an almost unlimited supply of the dissolved oxygen from the bulk electrolyte to the electrode surface for oxygen reduction on the unwetted specimen.

4. Conclusions

The present work is concerned with analysis of impedance spectra of oxygen reduction on unwetted and pre-wetted PTFE-bonded Pt/C electrode specimens at various applied cathodic potentials in 1 M H₂SO₄ solution at room temperature, and in 85% H₃PO₄ solution at 145 °C. The current-decay transients (chronoamperograms) in 1 M H₂SO₄ solution at room temperature are measured in order to clarify the effect of the porous structure of the electrode specimen on the resulting impedance spectra. The porous structure is embodied by previously wetting the Pt/C electrode specimen. The following conclusions are drawn.

1. From analysis of the a.c. impedance measurements based on the Epelboin model [10], it is concluded that the impedance spectra change from a capacitive arc and an inductive arc to two capacitive arcs, as depletion of dissolved oxygen within the narrow pores becomes appreciable. This results in changes in the mechanism and the kinetics of oxygen reduction on the electrode in 1 M H₂SO₄ solution at room temperature.
2. The orders of magnitude and potential dependence of fitted values of K_1 and K_2 are in good agreement with reported values that have been obtained with the RRDE technique. From these results, it is considered that the Epelboin model of the electrochemical reaction with an intermediate state describes satisfactorily the oxygen reduction on Pt/C electrode.
3. In 85% H₃PO₄ solution at 145 °C, two capacitive arcs appear in the absence of oxygen and air blowings. By contrast, one capacitive and one inductive arc appear in the presence of oxygen and air. From this result, it is confirmed that the transition of the capacitive arc to an inductive arc is caused by the limited supply of dissolved oxygen within the narrow pores.
4. Current-decay transients obtained from the pre-wetted Pt/C electrode specimen showed a current minimum that is probably due to the restricted diffusion of the dissolved oxygen through the electrolyte within the narrow pores. The transition in current-decay transients with pre-wetting treatment is consistent with the inductive to capacitive transition in the a.c. impedance spectra.

Acknowledgements

The receipt of a research grant under the program 'Development of Fuel Cell Technology 1993-1994' from the Ministry of Commerce and Industry (MOCI), South Korea, is gratefully acknowledged.

References

- [1] J. O'M. Bockris and S. Srinivasan, *Fuel Cells: Their Electrochemistry*, McGraw-Hill, New York, 1969, pp. 412-466.
- [2] A.J. Appleby, *J. Electrochem. Soc.*, **117** (1970) 328.
- [3] J.C. Huang, R.K. Sen and E. Yeager, *J. Electrochem. Soc.*, **126** (1979) 786.
- [4] A. Damjanovic, M.A. Genshaw and J. O'M. Bockris, *J. Electrochem. Soc.*, **114** (1967) 466.
- [5] W.E. O'Grady, E.J. Taylor and S. Srinivasan, *J. Electroanal. Chem.*, **132** (1982) 137.
- [6] J.-D. Kim, S.-I. Pyun, T.-H. Yang and J.-B. Ju, *J. Electroanal. Chem.*, **383** (1995) 161.
- [7] A.S. Arico, V. Alderucci, V. Antonucci, S. Ferrara, V. Recupero, N. Giordano and K. Kinoshita, *Electrochim. Acta*, **37** (1992) 523.
- [8] K. Kinoshita, *Electrochemical Oxygen Technology*, Wiley, New York, 1992, pp. 19-66.
- [9] R.D. Armstrong and M. Henderson, *J. Electroanal. Chem.*, **39** (1972) 81.
- [10] I. Epelboin, M. Keddam and J.C. Lestrade, *Trans. Faraday Soc.*, **75** (1973) 264.
- [11] K.-L. Hsueh, *Ph.D. Thesis*, Clarkson College of Technology, Nebraska, NE, USA, 1983.