

Effect of surface groups on the electrocatalytic behaviour of Pt–Fe–Co alloy-dispersed carbon electrodes in the phosphoric acid fuel cell

Su-Il Pyun^{*}, Seung-Bok Lee

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-Dong, Yusong-Gu 305-701, Taejeon, South Korea

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Abstract

Effect of surface group on the electrocatalytic behaviour of 10 wt.% Pt–Fe–Co alloy-dispersed carbon (Pt–Fe–Co/C) electrode has been investigated as functions of applied potential and duration in 85% H_3PO_4 solution of 145°C, using Fourier transform infrared (FTIR) spectroscopy, combined with ac-impedance spectroscopy, potentiostatic current transient technique, and potentiodynamic polarization experiment. It was shown from FTIR spectra that surface group formed in this work mainly comprises carboxyl group and that the formation potential of carboxyl group lies between 600 and 700 mV_{RHE}. From increase of charge transfer resistance (R_{ct}), and decrease of electrocatalytic activity for oxygen reduction with immersion time, it is suggested that above the formation potential of carboxyl group, further formation of carboxyl group on the carbon support around the catalyst particle reduces active surface area of the catalyst particle with immersion time. On the other hand, below the formation potential, dissolution of carboxyl group previously formed on the carbon support raises active surface area of the catalyst particle. In the present study, relationship between electrocatalytic aspect of the electrode, and the amount of carboxyl group formed on the carbon support around the catalyst particle was well discussed with a schematic illustration. The illustrative representation is underlain by formation on and dissolution from the catalyst particle of carboxyl group which cause the rise and fall in circumferential coverage of carboxyl group, respectively and hence the reduction and elevation in active surface area of the catalyst particle. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In a phosphoric acid fuel cell (PAFC), oxidation of hydrogen gas into proton and electron, and consecutive reduction of oxygen gas with the proton and electron into water occur, which then provide electrical energy for the outer load [1–3]. In this sense, PAFC is an electrochemical system in which the chemical energy of a fuel (hydrogen gas) is converted directly into electrical energy with the aid of an oxidant (oxygen gas). This energy conversion takes place without any intermediate: i.e., heat engines are avoided in the production of electrical energy. Thus, much attention [2] has been paid to PAFC due to the increased demand of clean and highly efficient power-generation systems.

The platinum-dispersed carbon (Pt/C), in which the dispersed platinum acts as a catalyst for the oxygen reduc-

tion, has been commonly used as cathode material for PAFC. Nowadays many efforts [4,5] have been made to enhance the performance of the cathode by replacing the Pt/C electrode with alloy catalyst-dispersed carbon electrodes such as Pt–Co/C, Pt–Cr/C, Pt–Ni/C, Pt–Co–Ni/C and Pt–Fe–Co/C. Among these alloy catalysts, Pt–Fe–Co/C has drawn much attention from researchers in this field, since it has a high electrocatalytic activity for oxygen reduction reaction.

It was generally reported [3,6–9] that corrosion of the carbon support in hot phosphoric acid (H_3PO_4) solution leads to the electrochemical formation of the two primary oxidation products, namely, CO_2 and a carbon surface group. Thus, catalyst particles can be detached by the evolution of CO_2 gas, and can be partially covered with the latter reaction product of carbon surface group formed on the carbon support [2].

At the operating potential of cathode in the range of 0.7 to 0.9 V_{RHE}, the final product of the oxygen reduction formed on the dispersed catalyst particle, i.e., water, con-

^{*} Corresponding author. Tel.: +82-42-869-3319; Fax: +82-42-869-3310; E-mail: sipyun@sorak.kaist.ac.kr

tributes to formation of surface groups on the carbon support [3,9–11], resulting in corrosion of the carbon support [1]. Although numerous studies [12] have dealt with the method of Pt/C electrocatalyst preparation, Pt particle size, activation process, wetting of electrode structure and polytetrafluoroethylene (PTFE) content contributing to the steady-state performance and life of cathode in phosphoric acid fuel cells (PAFC), the role of the surface group in the deterioration of the electrode performance has not been addressed in much detail [6–9]. Therefore, the relationship between formation of surface group and the alteration of electrocatalytic activity of the electrode still needs to be clarified.

The present work aims at exploring the effect of the surface group formation on electrocatalytic behaviour of Pt–Fe–Co alloy-dispersed carbon electrode. For this purpose, Fourier transform infrared (FTIR) spectroscopy was exploited to identify the surface group and to estimate its formation potential. In addition, ac-impedance spectra, potentiostatic current transients, and potentiodynamic polarization curves were measured in order to show the dependence of electrocatalytic behaviour of the electrode on applied potential and its duration in 85% H_3PO_4 solution at 145°C. From the comparison of the FTIR spectra with electrochemical experimental results, the dependence of the electrocatalytic activity on the surface groups formed in 85% H_3PO_4 solution at 145°C is discussed in terms of the active surface area of the catalyst particle.

2. Experimental

The PTFE-bonded Pt–Fe–Co/C electrode specimen was prepared as follows: firstly, Pt–Fe–Co alloy-dispersed Vulcan XC-72 carbon black powder (10 wt.% Pt–Fe–Co/C, N.E. CHEMCAT) in 70 wt.% and PTFE in 30 wt.% emulsion was mixed in distilled water with ultrasonic agitation. The mixture of the platinum-dispersed carbon black powder and PTFE emulsion was pasted on wet-proofed carbon paper and then dried in an oven at 120°C for 24 h under nitrogen atmosphere. This pasted sheet was pressed with 2 MPa pressure, and finally sintered at 330°C for 10 min under nitrogen atmosphere to the Pt–Fe–Co/C electrode specimen with 15 mm diameter and 0.2 mm thickness. It should be noted that the electrode specimen consists of two layers: Pt–Fe–Co/C and carbon paper. The Pt–Fe–Co/C at which the oxygen reduction occurs acts as an active layer exposed directly to the electrolyte. The carbon paper behaves as a gas supply layer which supports the active layer and provides a gas channel to the active layer, so that three-phase contact is established among the solid electrode, liquid electrolyte and the gas.

The usual three electrode cell [3] was adopted for all the electrochemical experiments. The Pt–Fe–Co/C electrode specimen exposed to dry air with the area of 0.8 cm² was used as a working electrode. The specimen was previously

subjected to open circuit potential (OCP) for 1 h in 85% H_3PO_4 solution of 145°C before carrying out all the experiments. Then, the specimen is regarded as a prewetted one [3]. A platinum net and a reversible hydrogen electrode (RHE) were used as counter and reference electrodes, respectively. 85% H_3PO_4 solution at 145°C was used as an electrolyte.

A disc type specimen for FTIR spectroscopy was prepared by the following procedure. The Pt–Fe–Co/C electrode specimen was previously subjected to various applied potentials of 200 to 800 mV_{RHE} in 85% H_3PO_4 solution of 145°C for 1 to 3 h and then dried at 80°C in vacuum oven. The Pt–Fe–Co/C powder collected from the above specimen was mixed in 0.05 wt.% with KBr powder, which was then pressed to the disc type specimen. FTIR spectra (2000–600 cm⁻¹) were collected on a FTIR spectrometer (Nicolet, Model 520) interfaced with an IBM-PC. The resolution of measurement and the number of scans were 4 cm⁻¹ and 45, respectively. The relative amount of the carbon surface groups was qualitatively determined by the resulting peak area in the measured FTIR spectra. To eliminate any contribution of H₂O in air to the FTIR spectra, the equipment was purged with dry air throughout the measurement.

The ac-impedance was measured by using a frequency response analyzer (Solartron, SI 1255 FRA) in conjunction with a potentiostat (Solartron, SI 1286 ECI) with an ac-signal of 10 mV superimposed on dc-potentials of 400 and 800 mV_{RHE} over the frequency range of 10⁻² to 10⁴ Hz.

Potentiostatic current transient was obtained from 10 wt.% Pt–Fe–Co/C electrode specimen at the applied potentials of 300 to 800 mV_{RHE} for 1 h. Potentiodynamic polarization experiments were carried out in the scan range of 600 to 800 mV_{RHE} with a scan rate of 5 mV s⁻¹ on the specimen before and after application of conditioning potentials of 300 to 800 mV_{RHE} for 1 h. The current density at 700 mV_{RHE} obtained from the potentiodynamic polarization experiment before applying conditioning potentials is subtracted from that after applying conditioning potentials, which is regarded as a measure of electrocatalytic activity in the present work. Both electrochemical experiments mentioned above were carried out by using potentiostat (EG and G PAR, Model 263A).

3. Results

It is important to characterise the surface groups, produced during the corrosion process of the carbon support and then to investigate the variation in the amount of surface groups with respect to the applied potential in order to elucidate the role of carbon corrosion in deterioration of electrode performance. Fig. 1 shows FTIR spectra obtained from 10 wt.% Pt–Fe–Co/C electrode in 85% H_3PO_4 solution at 145°C after application of potentials of 200 to 800 mV_{RHE} for 1 h. Surface groups are identified to

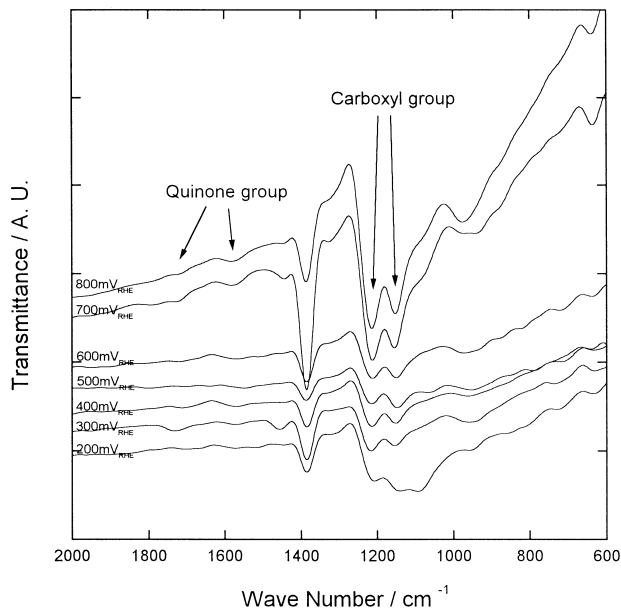
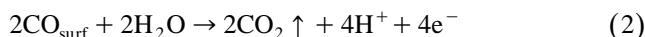
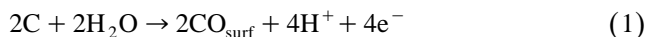


Fig. 1. FTIR spectra obtained from a 10 wt.% Pt-Fe-Co/C electrode after application of potentials of 200, 300, 400, 500, 600, 700 and 800 mV_{RHE} for 1 h.

be carboxyl and quinone groups from the FTIR peaks in the range of 1000 to 1335 cm⁻¹ and those peaks in the range of 1527 to 1712 cm⁻¹, respectively [10,13,14]. Here, the intensity of peaks concerning carboxyl group is much more pronounced than that concerning quinone group, resulting from the relatively low oxygen partial pressure ($P_{O_2} = 0.2$ atm) in dry air as an oxidant gas compared to that in pure oxygen gas which is also used as an oxidant gas. This is in good agreement with the previous report [11] that the amount of carboxyl group is much more than that of quinone group at the low oxygen partial pressure. In this regard, it is suggested that carboxyl group is a main constituent of corrosion product on the carbon support when using dry air as an oxidant gas, which corresponds to general operating condition of PAFC.

Oxidation of carbon, in general, proceeds via the following consecutive reaction pathways [15]:



where CO_{surf} means surface group formed on the carbon support. Under the operating condition of PAFC, formation of surface group on the carbon as per Eq. (1) is dominant over the CO₂ evolution as per Eq. (2). Thus, in exploring carbon corrosion, it is necessary to focus on the electrochemical behaviour of carboxyl group which is a main constituent of surface group. From the above FTIR spectra, it was observed that the peak intensities of carboxyl groups were markedly higher at 700 and 800 mV_{RHE} than at the other potentials. Under these circumstances, it is suggested that the formation potential of carboxyl groups lies between 600 and 700 mV_{RHE}.

Reportedly, carbon corrosion is a kinetically sluggish process under the operating conditions of the PAFC [6]. Thereafter, it is of necessity to investigate the variation in the amount of carboxyl group as a function of elapsed time in the electrolyte in order to determine whether formation or dissolution of carboxyl group occurs at a given potential. We investigated the variations in the amount of car-

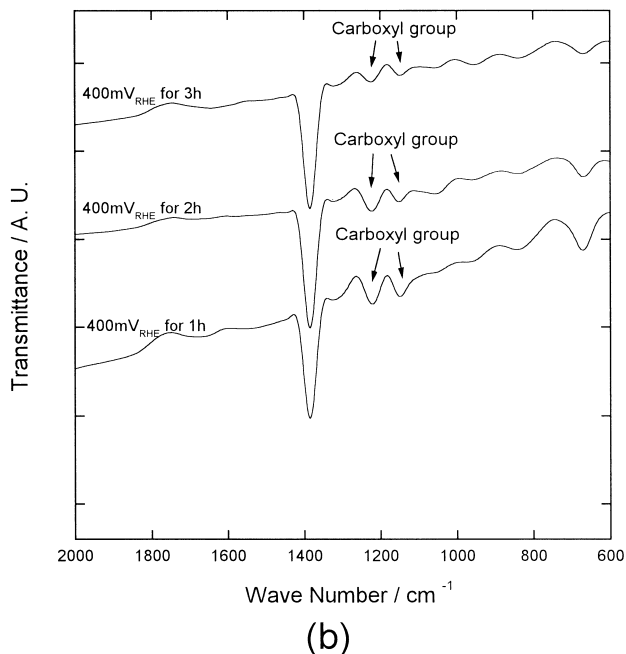
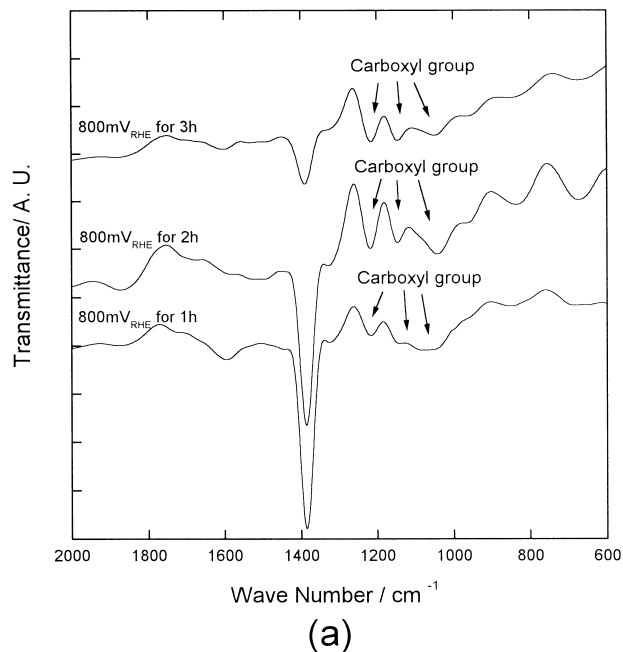


Fig. 2. (a) FTIR spectra obtained from a 10 wt.% Pt-Fe-Co/C electrode after 1, 2 and 3 h at the applied potential of 800 mV_{RHE} in 85% H₃PO₄ solution at 145°C. (b) FTIR spectra obtained from a 10 wt.% Pt-Fe-Co/C electrode after 1, 2 and 3 h at the applied potential of 400 mV_{RHE} in 85% H₃PO₄ solution at 145°C.

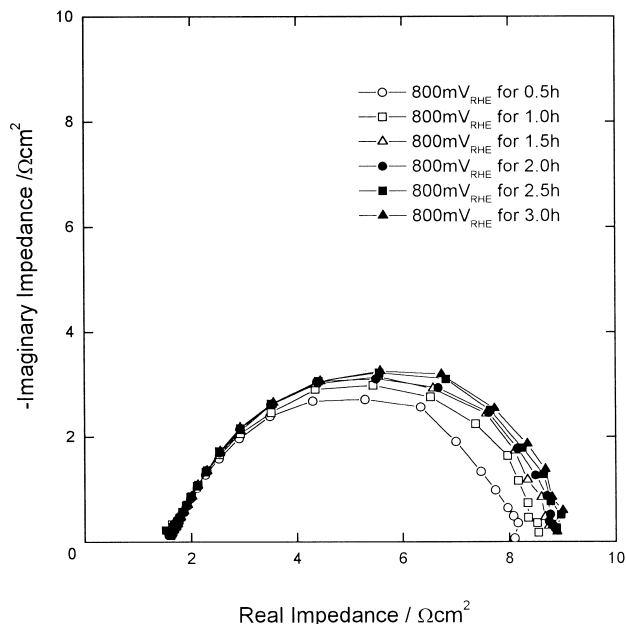


Fig. 3. Impedance spectra obtained from a 10 wt.% Pt–Fe–Co/C electrode subjected to 85% H_3PO_4 solution at 145°C at the applied potential of $800\text{ mV}_{\text{RHE}}$ for various durations of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 h. (exposed area: 0.8 cm^2).

boxyl group with immersion time at two different potentials of 800 and $400\text{ mV}_{\text{RHE}}$. The former potential is above the formation potential of carboxyl group and the latter one is below the formation potential.

Fig. 2(a) and (b) show FTIR spectra obtained from 10 wt.% Pt–Fe–Co/C at the applied potentials of 800 and $400\text{ mV}_{\text{RHE}}$, respectively, as a function of duration of 1, 2 and 3 h in 85% H_3PO_4 solution at 145°C . The peak intensity of carboxyl groups increases with immersion time

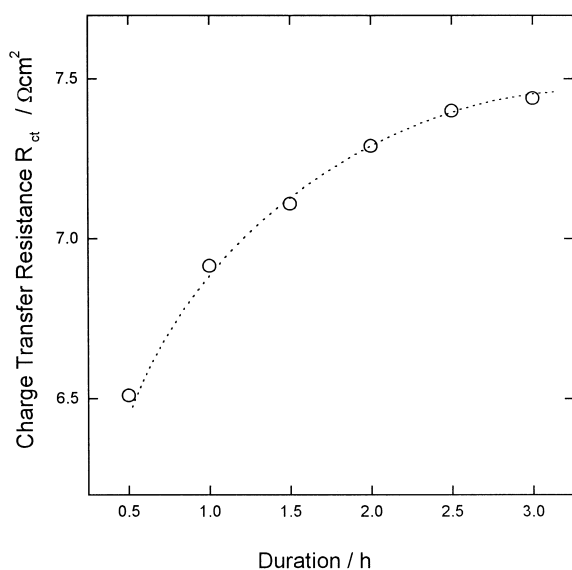


Fig. 4. Plot of the charge transfer resistance (R_{ct}) against time obtained from the analysis of impedance spectra at the applied potential of $800\text{ mV}_{\text{RHE}}$ using complex non-linear least squares (CNLS) fitting method. (exposed area: 0.8 cm^2).

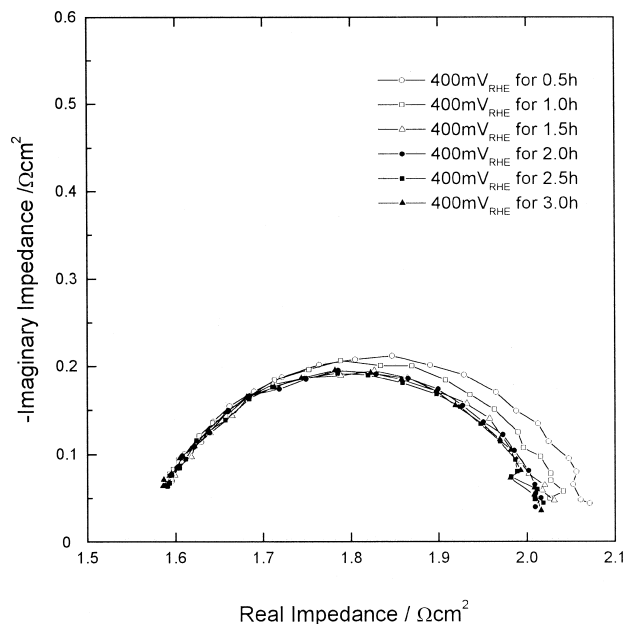


Fig. 5. Impedance spectra obtained from a 10 wt.% Pt–Fe–Co/C electrode subjected to 85% H_3PO_4 solution at 145°C at the applied potential of $400\text{ mV}_{\text{RHE}}$ for 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 h. (exposed area: 0.8 cm^2).

at $800\text{ mV}_{\text{RHE}}$; however, it decreases at $400\text{ mV}_{\text{RHE}}$. This means that carboxyl group is further formed at $800\text{ mV}_{\text{RHE}}$, whereas carboxyl group previously formed at OCP is dissolved at $400\text{ mV}_{\text{RHE}}$. In this respect, it is concluded that the formation of carboxyl groups at OCP is impeded and the dissolution of carboxyl group begins to prevail below the formation potential of carboxyl group. In contrast, further formation of carboxyl group occurs above the

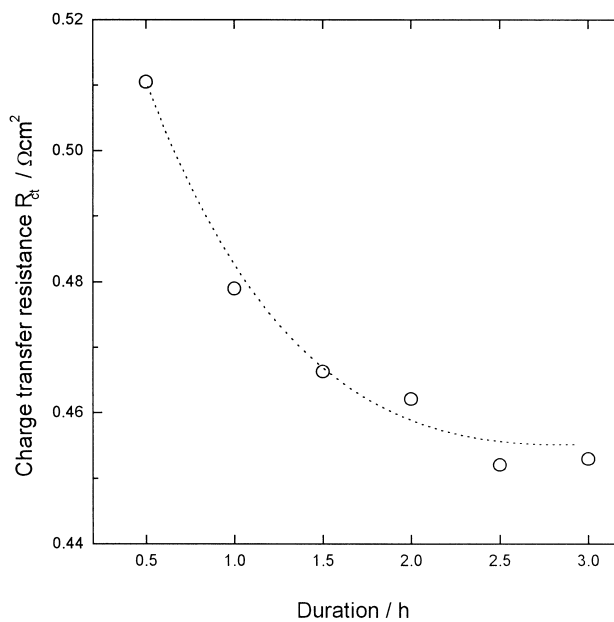


Fig. 6. Plot of charge transfer resistance (R_{ct}) against time obtained from the analysis of impedance spectra at the applied potential of $400\text{ mV}_{\text{RHE}}$ using complex non-linear least squares (CNLS) fitting method. (exposed area: 0.8 cm^2).

formation potential of carboxyl group. These FTIR spectra show that either formation or dissolution of carboxyl groups proceed far 2 to 3 h, since the reaction is a kinetically slow process as mentioned earlier [6].

Until now we examined the dependency of the amount of surface groups on potential and elapsed time. Regarding the electrocatalytic aspects of the electrode in relation to the amount of surface group; Fig. 3 gives impedance

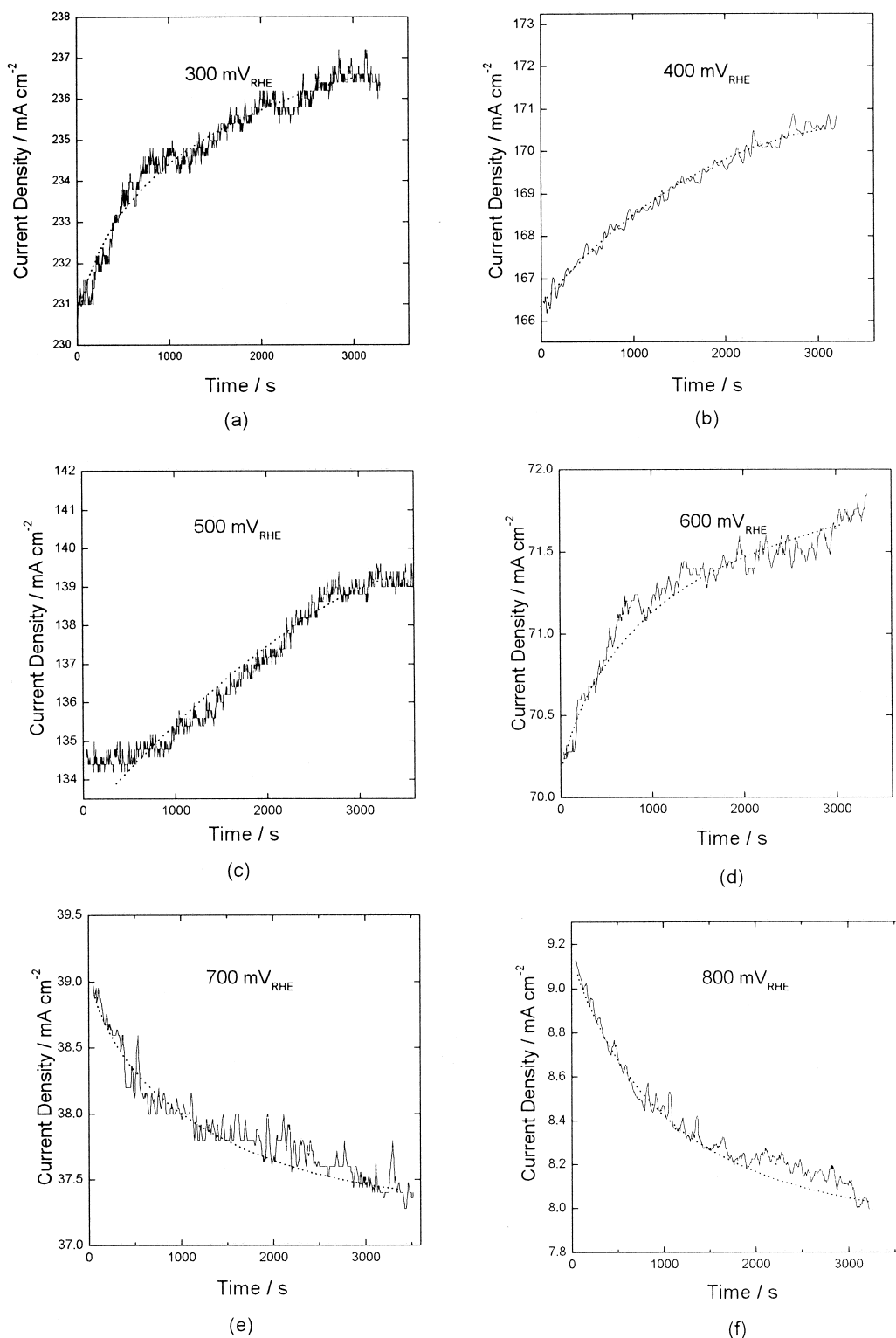


Fig. 7. Potentiostatic current transients obtained from a 10 wt.% Pt-Fe-Co/C electrode in 85% H₃PO₄ solution at 145°C subjected to various applied potentials: (a) 300 mV_{RHE}; (b) 400 mV_{RHE}; (c) 500 mV_{RHE}; (d) 600 mV_{RHE}; (e) 700 mV_{RHE}; (f) 800 mV_{RHE}. (exposed area: 0.8 cm²).

spectra obtained from 10 wt.% Pt–Fe–Co/C electrode subjected to 85% H_3PO_4 solution of 145°C at the applied potential of 800 mV_{RHE} for various durations between 0.5 to 3.0 h. The single arcs on the impedance spectra pertain to charge transfer that is considered to be related to oxygen reduction reaction [16,17]. The arc size increased with immersion time, as shown in this figure. The tendency of charge transfer resistance (R_{ct}) to increase with elapsed time is well illustrated in Fig. 4 which is obtained from the analysis of impedance spectra at the applied potential of 800 mV_{RHE} by using complex non-linear least squares (CNLS) fitting method. It is also shown that increasing rate of R_{ct} with immersion time is slowed down.

It is possible to assume that carboxyl groups are mainly formed on the carbon support around the catalyst particle, i.e., sporadic formation of carboxyl groups, since, the oxygen reduction product (water on the catalyst particle) promotes corrosion of the carbon support near the catalyst particle. Thus, it is suggested that the increase in R_{ct} with immersion time is attributable to decrease in active surface area of the catalyst particle for the oxygen reduction reaction due to formation of carboxyl groups on the carbon support around the catalyst particle. We will discuss the relationship between the decrease in active surface area of the catalyst particle and formation of carboxyl groups on the carbon support later.

Fig. 5 illustrates impedance spectra obtained from 10 wt.% Pt–Fe–Co/C electrode subjected to 85% H_3PO_4 solution of 145°C at the applied potential of 400 mV_{RHE} for 0.5 to 3.0 h. Contrary to the trend of impedance spectra at 800 mV_{RHE} , the size of the arcs pertaining to charge transfer decreased with immersion time. This means that the active surface area for the oxygen reduction reaction increased due to dissolution of carboxyl groups previously formed at OCP around the catalyst particles. The tendency of R_{ct} to decrease with elapsed time is clearly shown in Fig. 6, which shows a plot of R_{ct} against duration at the applied potential of 400 mV_{RHE} using CNLS fitting method.

Fig. 7 depicts potentiostatic current transients obtained from 10 wt.% Pt–Fe–Co/C electrode subjected to various applied potentials of 300 to 800 mV_{RHE} in 85% H_3PO_4 solution at 145°C. Two types of current transients appear. One type of current transient at 700 and 800 mV_{RHE} shows a decrease in current density with time. The other type of current transient at the other potentials, shows current density increasing with time. It is suggested that the decreased oxygen reduction rate with time in the former current transients is attributable to a decrease in active surface area for oxygen reduction reaction by formation of carboxyl group near the catalyst particles. By contrast, increased oxygen reduction rate with time in the latter current transients is ascribed to an increase in active surface area due to dissolution of carboxyl group.

It should be noticed that the type of current transient is changed as the applied potential shifts from 600 to 700 mV_{RHE} . This means that dissolution of carboxyl group

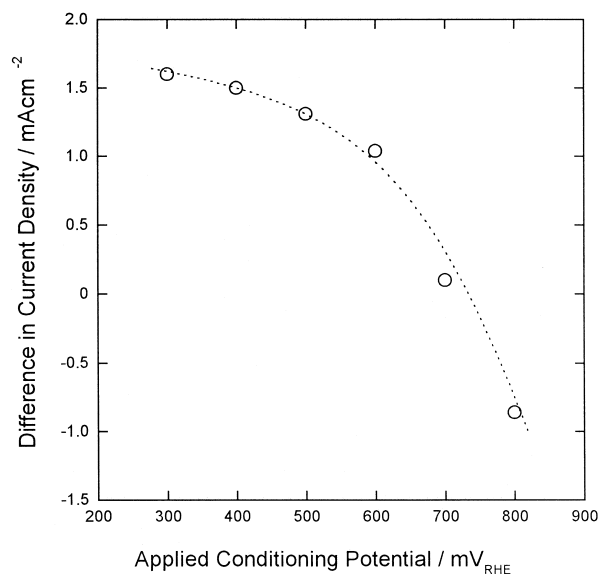


Fig. 8. Influence of the conditioning potential on differences in current densities at 700 mV_{RHE} on potentiodynamic polarization curves before and after applying conditioning potentials of 300, 400, 500, 600, 700 and 800 mV_{RHE} for 1 h to 10 wt.% Pt–Fe–Co/C electrode in 85% H_3PO_4 solution at 145°C.

occurs dominantly below 600 mV_{RHE} ; however formation of carboxyl group occurs above 700 mV_{RHE} . Thus, it is supposed that the formation potential of carboxyl group is between 600 and 700 mV_{RHE} , which agrees well with results of the FTIR spectra as shown in Fig. 1.

Fig. 8 shows the influence of the conditioning potential on discrepancies in the current densities at 700 mV_{RHE} of potentiodynamic polarization curves before and after applying the conditioning potentials of 300 to 800 mV_{RHE} for 1 h to 10 wt.% Pt–Fe–Co/C electrode in 85% H_3PO_4 solution at 145°C. These potentiodynamic polarization experiments were carried out to investigate the effect of carboxyl groups on electrocatalytic activity. That is to say, by changing conditioning potentials, it is possible to change the amount of carboxyl group around the catalyst particles, resulting in a variation in active surface area for oxygen reduction reaction. Thus, current densities before and after applying potentials make a difference. As shown in this figure, the difference in current density, which corresponds to a measure for electrocatalytic activity, increases with falling applied conditioning potential. This indicates that the amount of carboxyl groups around the catalyst particle decreased, so that the active surface area for oxygen reduction increased with falling applied conditioning potential.

4. Discussion

We can establish the relationship between active surface area of the catalyst particle and the amount of carboxyl

group on the carbon support on the basis of the experimental findings combined with the following assumptions.

1. Carbon corrosion is enhanced by the formation of an oxygen reduction product, i.e., water. Carbon oxidation products, namely, carboxyl groups form preferentially at the interface between the catalyst particles and the carbon support, and grow along the surface of the carbon support, so that its layer covers the surface of the carbon support to at the most one or two monolayers (≈ 0.4 nm) in thickness. This leads to sporadic coverage of carboxyl groups at the catalyst particle/carbon support interface at any of the instantaneous immersion time during formation of carboxyl groups.

2. A carboxyl group layer with a thickness of one or two monolayers covers the active surface of the catalyst particle effectively enough to impede the oxygen reduction reaction. Thus, dead active surface area develops on the surfaces of the catalyst particles.

3. The oxygen reduction reaction does not occur on the surface of the carbon support, but on the surface of the catalyst particle. Thus, the oxygen reduction rate is in proportion to the active surface area of the catalyst particle.

Taking into account the sporadic coverage of carboxyl groups (assumption 1), it is possible that spherical catalyst particles of 2 to 4 nm in radius embedded in the surface of spherical carbon support are covered with carboxyl groups along their circumference to form a band with height, h and width, w at any of the immersion time, t . This is schematically presented in Fig. 9. This figure is a vertical section across a catalyst particle.

From assumptions 2 and 3, it can be seen that the active surface area depends only on the value of h . It is expected

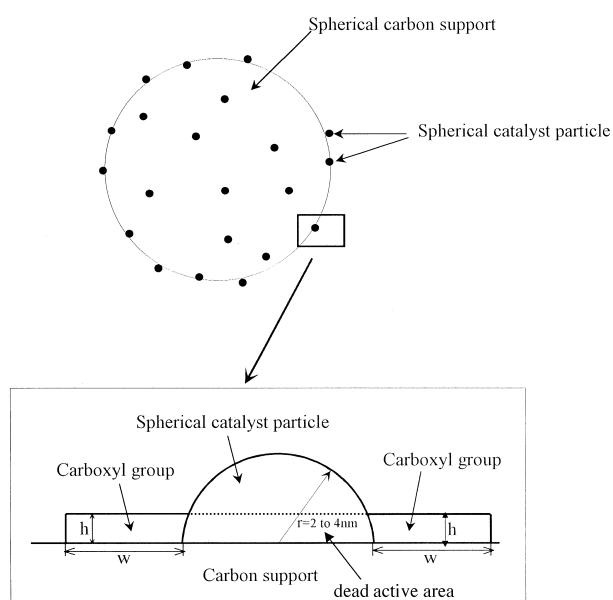


Fig. 9. Schematic representation of coverage of carboxyl groups, at the catalyst particle/carbon support interface at any immersion time t .

that the catalyst particle has been partially or completely covered with carboxyl groups during immersion of the electrode at OCP for 1 h, leading to a non-uniform height along the circumferential band. It is noted that the catalyst particles are covered with carboxyl groups only on the circumferential band, so that the fraction of carboxyl group along the surface of the circumferential band contributes to coverage of carboxyl group. Thus, the average height of the circumferential band provides a benchmark for the coverage of carboxyl group, since the active surface area relies not on the magnitude of w but on the value of h .

Now, we can correlate the sporadic coverage of carboxyl groups to the electrocatalytic activity of the catalyst particle. As formation of carboxyl group proceeds at 800 mV_{RHE}, it is reasonable to consider that the catalyst particles are being further covered with carboxyl groups accompanied by an increase in average height of the band. In contrast, it is probable that as dissolution of carboxyl group occurs at 400 mV_{RHE}, the catalyst particle is progressively stripped of the previously-formed carboxyl group layer sheath with immersion time, thus causing the fall in average height of the band.

In this way, the reduction in the active surface area of the catalyst particle is mainly brought about by the increase in average height of the covering of carboxyl groups. It can be deduced that the decrease in electrocatalytic activity with immersion time above the formation potential of carboxyl group is consistent with the increase in dead active surface area. The opposite is true below the formation potential of carboxyl group. This schematic diagram explains the electrocatalytic aspect of the electrode in relation to the amount of carboxyl group for the electrochemical experiments reported. The above illustrative concept can be reasonably applied to the following research into the effect of the catalyst particle size on the electrocatalytic aspects of the electrode [18].

5. Conclusions

The present work relates electrocatalytic aspects of a Pt–Fe–Co alloy-dispersed carbon electrode closely to the amount of surface groups formed on the carbon support, using FTIR spectroscopy combined with electrochemical experiments. From these experimental results, it is concluded as follows.

1. From the FTIR spectra, it was shown that the surface groups formed in 85% H₃PO₄ solution at 145°C were carboxyl groups and that the formation potential of the carboxyl groups is between 600 and 700 mV_{RHE}.

2. Based upon the increase in R_{ct} , and decrease in the electrocatalytic activity for oxygen reduction with immersion time, it is suggested that on the application of potentials above the formation potential of carboxyl groups, further formation of carboxyl groups on the carbon support

around the catalyst particles decreases the active surface area of the catalyst particles. On the other hand, below the formation potential of carboxyl group, the dissolution of carboxyl groups previously formed on the carbon support around the catalyst particles increases their active surface area.

3. In this work, the relationship between active surface area of the catalyst particle and the amount of carboxyl group above and below the formation potential has been well established with a schematic illustration. This representation involves the reduction and elevation with potential and duration in active surface area of the catalyst particle which are caused by the rise and fall in coverage of carboxyl group along the circumferential band of the catalyst particle in average height, respectively. The coverage is increased and decreased directly by the formation and dissolution of carboxyl group, respectively.

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