

# Kinetics of mixed-controlled oxygen reduction at nafion-impregnated Pt-alloy-dispersed carbon electrode by analysis of cathodic current transients

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**Abstract** The effects of Co alloying to Pt catalyst and Nafion pretreatment by  $\text{NaClO}_4$  solution on the rate-determining step (RDS) of oxygen reduction at Nafion-impregnated Pt-dispersed carbon (Pt/C) electrode were investigated as a function of the potential step  $\Delta E$  employing potentiostatic current transient (PCT) technique. For this purpose, the cathodic PCTs were measured on the pure Nafion-impregnated and partially  $\text{Na}^+$ -doped Nafion-impregnated Pt/C and PtCo/C electrodes in an oxygen-saturated 1 M  $\text{H}_2\text{SO}_4$  solution and analyzed. From the shape of the cathodic PCTs and the dependence of the instantaneous current on the value of  $\Delta E$ , it was confirmed that oxygen reduction at the pure Nafion-impregnated electrodes is controlled by charge transfer at the electrode surface mixed with oxygen diffusion in the solution below the transition potential step  $|\Delta E_{\text{tr}}|$  in absolute value, whereas oxygen reduction is purely governed by oxygen diffusion above  $|\Delta E_{\text{tr}}|$ . On the other hand, the RDS of oxygen reduction at the partially  $\text{Na}^+$ -doped Nafion-impregnated electrodes below  $|\Delta E_{\text{tr}}|$  is charge transfer coupled with proton migration, whereas above  $|\Delta E_{\text{tr}}|$ , it becomes proton migration in the Nafion electrolyte instead of oxygen diffusion. Consequently, it is expected in real fuel cell system that the cell performance is improved by Co alloying since the electrode reaches the maximum diffusion (migration) current even at small value of  $|\Delta E|$ , whereas the cell performance is aggravated by Nafion

pretreatment due to the decrease in the maximum diffusion (migration) current.

**Keywords** Oxygen reduction · Change in rate-determining step · Pt-dispersed carbon · PtCo-dispersed carbon · Partially  $\text{Na}^+$ -doped Nafion

## Introduction

Pt-dispersed carbon (Pt/C) has been commonly used as the cathode and anode materials for polymer electrolyte membrane fuel cell (PEMFC). However, the high cost of Pt is one of the main factors that increases the total cost of PEMFC; hence, many research efforts have been focused on the reduction of Pt loading [1]. Recently, it has been reported [2–16] that the alloying of such transition metals as V, Cr, Co, Ti, Fe, and Ni to Pt matrix has been found to exhibit significantly higher electrocatalytic activities for oxygen reduction than does Pt alone. These Pt-alloy catalysts improve both the performance and resistance to sintering of the nanoparticles under the operating condition of PEMFC [1, 17].

There have been many studies of the kinetics of oxygen reduction using PtCr [3, 6], PtCo [4, 12–14, 16], PtNi [7], PtFe [15], and PtV [9] catalysts with rotating disk electrode technique in order to predict the performance of PEMFC and to find the optimum composition from a practical viewpoint. The activity enhancement produced by Pt-alloy catalysts has been ascribed to the geometric factors [1], the dissolution of the alloys [3], changes in surface structure morphology [4], and electronic factors [7].

In addition, it is well known [18] that proton transport through the Nafion electrolyte occurs via the hopping of

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H<sup>+</sup> ions between H<sub>2</sub>O and SO<sub>3</sub><sup>-</sup> sites. Thus, these sites contribute to the enhancement of proton transport. Also, it has been reported [18] that during Nafion pretreatment in a boiling NaClO<sub>4</sub> solution, the protonated form of the Nafion electrolyte is converted to the Na<sup>+</sup> form, which leads to a decrease in the proton concentration within the Nafion electrolyte. Consequently, the hopping sites in the Nafion electrolyte are significantly reduced by Nafion pretreatment by NaClO<sub>4</sub> solution, thus causing less proton conductivity.

Recently, the mechanism of oxygen reduction at the Pt/C electrode has been investigated employing rotating disk voltammetry, linear sweep voltammetry, and PCT technique in an aqueous solution due to its great importance for high power output fuel cell [19–23]. Especially, most of researchers investigated the oxygen reduction kinetics under the mixed diffusion and charge transfer-control appropriately by analysis of the rotating disk voltammograms and linear sweep voltammograms.

In the previous work from our laboratory [23], the oxygen reduction kinetics at the Pt/C electrode was investigated using PCT technique, which is newly adopted in fuel cell system in our laboratory. It has been reported [23, 24] that PCT technique can be used effectively for elucidating the RDS of oxygen reduction. Specifically, PCT technique has many advantages, including easy theoretical treatment and quantitative determination of kinetic parameters.

In our previous work [23], we reported that oxygen reduction at the Pt/C electrode is controlled by charge transfer at the electrode surface mixed with oxygen diffusion in the solution at small negative potential steps, whereas at large negative potential steps, oxygen reduction is purely governed by oxygen diffusion in the solution. In addition, it was suggested that the extrinsic parameters such as Pt loading, Nafion content, and temperature play an important role in the determination of the RDS of oxygen reduction, e.g., mixed diffusion and charge transfer and purely diffusion.

The present work is a further stage of the continuing reports on the collective program of elucidating the RDS of oxygen reduction at the carbon-supported catalysts. In this respect, this work is aimed at investigating the influences of intrinsic parameters such as exchange current for oxygen reduction and proton conductivity on the change in RDS of oxygen reduction using cathodic PCT technique. For this purpose, we first prepared the pure Nafion-impregnated and partially Na<sup>+</sup>-doped Nafion-impregnated Pt/C, and PtCo/C electrodes as model systems. Then, the cathodic PCTs were measured on those electrodes as a function of the negative potential step in an oxygen-saturated 1 M H<sub>2</sub>SO<sub>4</sub> solution. Finally, the change in RDS of the oxygen reduction was discussed at the four kinds of electrodes.

## Experimental

### Preparation of Pt/C and PtCo/C electrodes

For the electrochemical experiments, Pt/C and PtCo/C powders (Johnson Matthey, USA) were used as the catalysts. Catalyst slurries were prepared by mixing each powder with a 10 mL ethanol and deionized water solution (the weight ratio of 1) containing a 5 wt.% Nafion solution using ultrasonic agitator. Here, the weight ratio of catalyst to the Nafion solution was 9. The slurries were coated on the glassy carbon (GC) circular disk electrode (PINE instrument company, USA) with an area of 0.126 cm<sup>2</sup> and then dried in air. The Pt loadings on both electrodes were 40 μg cm<sup>-2</sup>. Prior to coating, the GC disk was mechanically polished successively with 1, 0.3, and 0.05 μm Al<sub>2</sub>O<sub>3</sub> powders, followed by chemical polishing in a concentrated HNO<sub>3</sub> solution (60 wt.%) to remove organic contaminants on the surface of the disk.

Subsequently, the mixture-coated electrodes were coated with a 0.05 wt.% Nafion solution to yield the Nafion film thickness 0.1 μm and then the electrodes were dried at room temperature in air. The 0.05 wt.% Nafion solution was previously prepared by diluting a 5 wt.% Nafion solution with a deionized water. Here, the thickness of the Nafion film was roughly estimated from the volume of the Nafion solution used, the density of dry Nafion, and the surface area of the electrode. Finally, to completely evaporate the residual solvent, the Nafion-coated electrode was dried in a vacuum oven at 70 °C for 2 h. The resulting electrodes are referred to as the “pure Nafion-impregnated Pt/C and PtCo/C electrodes.”

In addition, in order to reduce the proton conductivity of the Nafion electrolyte on purpose, the pure Nafion-impregnated Pt/C and PtCo/C electrodes were previously treated in a boiling 5 wt.% NaClO<sub>4</sub> solution for 2 h. Then, the electrodes were completely washed with deionized water and were dried in a vacuum oven at room temperature for 2 h. The resulting electrodes treated in a NaClO<sub>4</sub> solution are named as the “partially Na<sup>+</sup>-doped Nafion-impregnated Pt/C and PtCo/C electrodes.”

### Electrochemical experiments

A three-electrode electrochemical cell was employed for the electrochemical measurements. A platinum wire and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. In this work, to ensure the accuracy of the electrochemical measurements, a saturated Ag/AgCl electrode was also used as the reference electrode. Deaerated or oxygen-saturated 1 M H<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte. During the electrochemical measurements, a Luggin capil-

lary was used to minimize the Ohmic potential drop due to the uncompensated solution resistance. The cell configuration commonly used was detailed elsewhere [25]. Although the SCE and the saturated Ag/AgCl electrode served as the reference electrodes, all potentials in this work were referred to a reversible hydrogen electrode (RHE).

Prior to the electrochemical experiments, the electrodes were activated by 100 times potential cycling in the potential range of 0 to 1.2  $V_{\text{RHE}}$ . The cyclic voltammograms (CVs) were measured in the potential range of 0 to 1.2  $V_{\text{RHE}}$  with a scan rate of 100  $\text{mV s}^{-1}$  in a 1 M  $\text{H}_2\text{SO}_4$  solution deaerated with purified nitrogen gas. The rotating disk voltammograms were obtained by scanning the applied potential  $E_{\text{app}}$  from 1.0 to 0  $V_{\text{RHE}}$  at a scan rate of 10  $\text{mV s}^{-1}$  in an oxygen-saturated 1 M  $\text{H}_2\text{SO}_4$  solution. During rotating disk voltammetry, the rotation rate was controlled by an EG&G Princeton Applied Research (PARC) Model 636 Electrode Rotator.

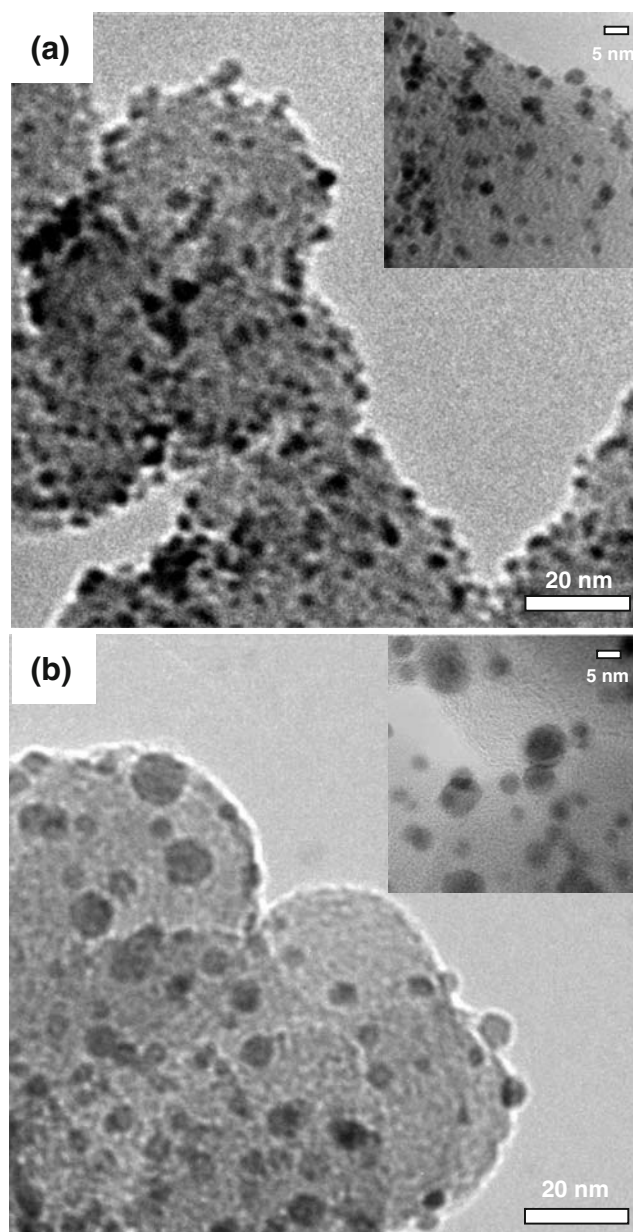
The cathodic PCTs were measured in an oxygen-saturated 1 M  $\text{H}_2\text{SO}_4$  solution by applying the negative potential steps  $\Delta E$  from the open circuit potential (OCP), 1.05  $V_{\text{RHE}}$  to different applied potentials  $E_{\text{app}}$  ranging from 0.1 to 0.7  $V_{\text{RHE}}$ . In the present work, the OCP can be regarded as the electrode potential  $E$ ; hence,  $\Delta E$  means the difference between  $E_{\text{app}}$  and  $E$ , i.e.  $\Delta E = E_{\text{app}} - E$ . All of the electrochemical experiments were conducted using a potentiostat (Zahner IM6e).

## Results

### Characterization of the electrodes

Figure 1a, b show the transmission electron microscopic (TEM) image of the 20 wt.% Pt/C and 20 wt.% PtCo/C catalyst powders, respectively, used in this work. From the TEM images, it was found that the Pt and PtCo particles were almost spherical in shape and were uniformly distributed on the carbon support with a diameter of ca. 50 nm. From the image analysis of the TEM images, it was found that the PtCo particles are slightly larger than the Pt particles, and the former has a wider particle distribution as compared with the latter. But, the diameters of both the Pt and PtCo particles were determined on average to be about 2.5 nm as well.

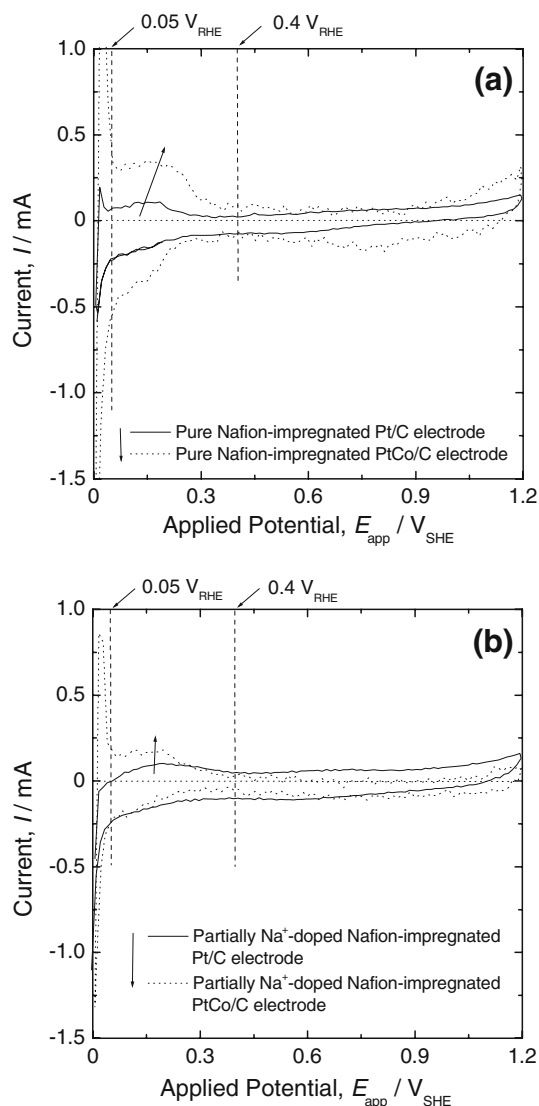
First, to determine the electrochemical active area  $A_{\text{ca}}$ , the cyclic voltammograms (CVs) were measured in the potential range of 0 to 1.2  $V_{\text{RHE}}$  at a scan rate of 100  $\text{mV s}^{-1}$  in a deaerated 1 M  $\text{H}_2\text{SO}_4$  solution on both the pure Nafion-impregnated Pt/C and PtCo/C electrodes and on the partially  $\text{Na}^+$ -doped Nafion-impregnated Pt/C and PtCo/C electrodes. The resulting CVs for the pure Nafion-impregnated and partially  $\text{Na}^+$ -doped Nafion-impregnated electrodes are given in Fig. 2a, b, respectively. In Fig. 2a, b,



**Fig. 1** TEM micrographs of the **a** 20 wt.% Pt/C and **b** 20 wt.% PtCo/C powders

all the CVs show a typical shape, which is similar to the shape of the CVs measured on a polycrystalline bulk Pt electrode [26].

The  $A_{\text{ca}}$  values can be estimated from the hydrogen adsorption/desorption charge of the formation of hydrogen monolayer in the potential range of 0.05 to 0.4  $V_{\text{RHE}}$ . The Pt utilization can be also determined from the ratio of  $A_{\text{ca}}$  to the theoretical active area  $A_{\text{theo}}$ . The calculation methods of the  $A_{\text{ca}}$  value and Pt utilization were detailed in our previous work [23]. The resulting  $A_{\text{ca}}$  values and Pt utilization of the electrodes are listed in Table 1. From Table 1, it was found that the  $A_{\text{ca}}$  value for the PtCo/C electrode is slightly larger than that value for the Pt/C



**Fig. 2** Cyclic voltammograms (CVs) obtained from the **a** pure Nafion-impregnated and **b** partially Na<sup>+</sup>-doped Nafion-impregnated circular Pt/C and PtCo/C disk electrodes in the potential range of 0 to 1.2 V<sub>RHE</sub> at a scan rate of 100 mV s<sup>-1</sup> in a deaerated 1 M H<sub>2</sub>SO<sub>4</sub> solution [exposed electrode area: 0.126 cm<sup>2</sup>]

electrode and that the  $A_{\text{ea}}$  values for both the Pt/C and PtCo/C electrodes are significantly lowered by Nafion pretreatment. The former  $A_{\text{ea}}$  increase by Co alloying results from either the change of the crystal plane [27] or

the enhancement of the catalytic activity of Pt on the PtCo/C electrode due to the synergistic effect of Co atoms. On the other hand, the latter  $A_{\text{ea}}$  decrease by Nafion pretreatment indicates that some Pt becomes inactive as a result of poor proton transport.

Next, it is necessary to find out the oxygen reduction pathway by analysis of the rotating disk voltammograms in order to analyze the cathodic PCTs quantitatively. It is generally known [28–32] that oxygen reduction on the Pt bulk electrode proceeds by the following two pathways: (1) four-electron reduction of oxygen to form water, i.e.,  $\text{O}_2 + 4\text{H}^+ + 4e \rightarrow 2\text{H}_2\text{O}$  and (2) two-electron reduction of oxygen to form hydrogen peroxide, i.e.,  $\text{O}_2 + 2\text{H}^+ + 2e \rightarrow \text{H}_2\text{O}_2$ .

To disclose the oxygen reduction pathway quantitatively, the rotating disk voltammograms were measured on the pure Nafion-impregnated Pt/C and PtCo/C electrodes as a function of the rotation rate  $\omega$  by scanning the applied potential  $E_{\text{app}}$  from 1.2 to 0 V<sub>RHE</sub> at a scan rate of 10 mV s<sup>-1</sup> in an oxygen-saturated 1 M H<sub>2</sub>SO<sub>4</sub> solution. In the measured rotating disk voltammograms, as  $E_{\text{app}}$  decreased, the cathodic current gradually increased in absolute value and then reached a constant value that is generally termed the diffusion-limited current. The diffusion-limited current increased in absolute value with increasing  $\omega$ .

The relationship between the experimentally measured current and  $\omega$  is given by the following Koutecký–Levich equation [23]:

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_f} + \frac{1}{0.62zFA_{\text{geo}}c_{\text{O}_2}D_{\text{O}_2}^{2/3}\nu_s^{-1/6}} \quad (1)$$

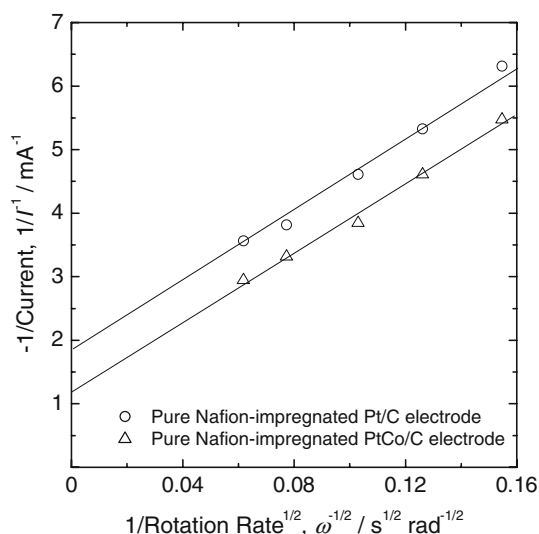
where  $I_k$  [A] is the kinetic current for oxygen reduction,  $I_f$  [A] the diffusion current controlled by oxygen diffusion in the Nafion film,  $z$  [–] the number of transferred electrons during oxygen reduction,  $F$  (96,485 C mol<sup>-1</sup>) the Faraday constant,  $A_{\text{geo}}$  [cm<sup>2</sup>] the geometric area of disk electrode,  $\nu_s$  [cm<sup>2</sup> s<sup>-1</sup>] the kinematic viscosity of the solution (defined as  $(\eta_s/\rho_s)$ ,  $\eta_s$  (g cm<sup>-1</sup> s<sup>-1</sup> ≡ poise) the viscosity of the solution,  $\rho_s$  (g cm<sup>-3</sup>) the density of the solution), and  $c_{\text{O}_2}$  [mol cm<sup>-3</sup>] and  $D_{\text{O}_2}$  [cm<sup>2</sup> s<sup>-1</sup>] denote the oxygen concentration and the oxygen diffusivity in the solution, respectively.

Figure 3 shows the plots of the inverse of current  $I^{-1}$  against the inverse square root of the rotation rate  $\omega^{-1/2}$  obtained from the pure Nafion-impregnated Pt/C and PtCo/C

**Table 1** The electrochemical active area  $A_{\text{ea}}$  and Pt utilization obtained from the cyclic voltammograms (CVs) measured on the pure Nafion-impregnated and partially Na<sup>+</sup>-doped Nafion-impregnated Pt/C and PtCo/C electrodes

Specimen		Electrochemical active area, $A_{\text{ea}}$ [cm <sup>2</sup> ]	Pt utilization [%]
Pt/C electrode	Pure Nafion-impregnated	4.31	73.8
	Partially Na <sup>+</sup> -doped Nafion-impregnated	3.14	53.8
PtCo/C electrode	Pure Nafion-impregnated	4.54	77.7
	Partially Na <sup>+</sup> -doped Nafion-impregnated	3.26	55.8





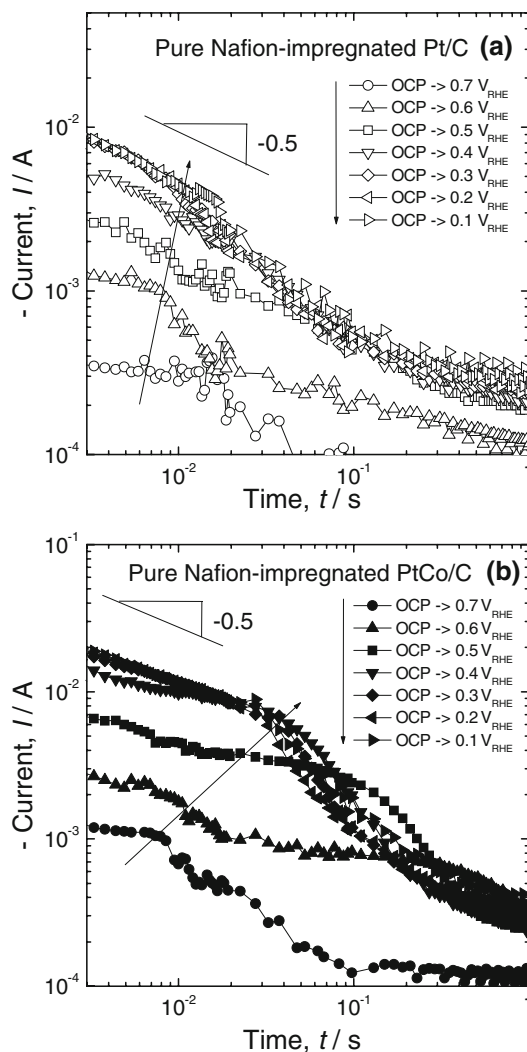
**Fig. 3** Plots of the inverse of current against the inverse square root of the rotation rate  $\omega^{-1/2}$  obtained from the pure Nafion-impregnated circular Pt/C and PtCo/C disk electrodes. Here, the solid line represents the Koutecky–Levich plots fitted with Eq. 1

C electrodes. In Fig. 3, it was found that  $I^{-1}$  was linearly proportional to  $\omega^{-1/2}$ . The  $z$  values were determined by fitting the measured Koutecky–Levich plots of Fig. 3 to Eq. 1 by taking the values of  $c_{O_2}$ ,  $D_{O_2}$ , and  $\nu_s$  as  $1.1 \times 10^{-6}$  mol cm $^{-3}$  [33],  $1.7 \times 10^{-5}$  cm $^2$  s $^{-1}$  [33], and  $9.87 \times 10^{-3}$  cm $^2$  s $^{-1}$  [34], respectively. Data fitting gave the values of  $z$  as 3.6 and 3.5 for the pure Nafion-impregnated Pt/C and PtCo/C electrodes, respectively. From this result, it is confirmed that oxygen reduction at both the pure Nafion-impregnated Pt/C and PtCo/C electrodes occurs predominantly via the direct 4-electron reduction reaction rather than the indirect 2-electron reduction reaction.

Effect of Co alloying to Pt catalyst on the change in rate-determining step of oxygen reduction under mixed charge transfer and diffusion control

It has been reported [23] that when  $\Delta E$  is applied across the electrode, the charging/discharging of the interfacial capacitance and pseudocapacitance concurrently occurs with oxygen reduction; hence, the measured current within those time constant ranges inevitably includes the non-Faradaic current which does not contribute to oxygen reduction. Thus, in order to determine the real oxygen reduction current in value, the charging/discharging capacitive current should be previously subtracted from the total current of the cathodic PCTs experimentally measured from the pure Nafion-impregnated Pt/C and PtCo/C electrodes.

The resulting cathodic PCTs are plotted on a logarithmic scale in Fig. 4a, b. The calculation method for the charging/discharging capacitive current was detailed elsewhere [23]. All the cathodic PCTs shared in shape of three stages: first,



**Fig. 4** Cathodic PCTs on a logarithmic scale experimentally obtained from the pure Nafion-impregnated circular a Pt/C and b PtCo/C disk electrodes in an oxygen-saturated 1 M H $_2$ SO $_4$  solution [exposed electrode area: 0.126 cm $^2$ ]

the cathodic PCTs clearly exhibited a linear relationship between logarithmic current and logarithmic time with an absolute slope between 0 and 0.5 in the first stage. Second, the current abruptly decreased in absolute value with time in the second stage. Finally, the current reached steady-state value in the third stage.

Here, it should be emphasized that as the value of  $E_{app}$  decreased from 0.7 to 0.3 V $_{RHE}$ , the slope of the logarithmic current transient gradually increased to 0.5 in absolute value. Then, at the value of  $E_{app}$  lower than 0.2 V $_{RHE}$ , the cathodic PCTs exhibited a linear relationship between the logarithm of current and the logarithm of time with an absolute slope of 0.5 in the early stage, representing the Cottrell behavior [35]. This means that the oxygen concentration  $c_{O_2}$  at the Pt/C electrode surface is fixed at zero.

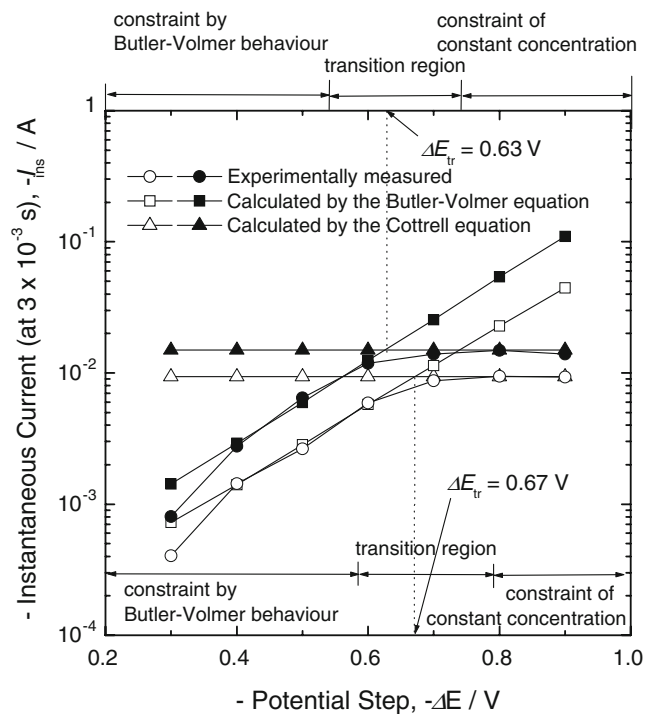
To determine the RDS of oxygen reduction, the instantaneous current  $I_{ins}$  was first taken at  $3 \times 10^{-3}$  s from

Fig. 4a, b. Then, the  $|I_{\text{ins}}|$  values are plotted on a logarithmic scale in Fig. 5 against  $\Delta E$ , where open and closed circles indicate the pure Nafion-impregnated Pt/C and PtCo/C electrodes, respectively. In Fig. 5, the value of  $\log |I_{\text{ins}}|$  linearly increased with rising  $|\Delta E|$ , then it exhibited a transition over a narrow range of  $|\Delta E|$ , and finally, it remained nearly constant regardless of  $|\Delta E|$ . In order to more clearly specify the RDS at the electrode surface during oxygen reduction, the values of  $I_{\text{ins}}$  were theoretically determined under the “constraint of constant concentration” as well as under the “constraint by Butler–Volmer behavior,” and then they were quantitatively compared with that value of  $I_{\text{ins}}$  experimentally measured.

First, in case that a relatively large potential is negatively applied across the electrode, the cathodic current  $I_{\text{cath}}$  was theoretically calculated as a function of  $\Delta E$  under the “constraint by Butler–Volmer behavior” from the following equation [23]:

$$I(\Delta E) = I_{\text{cath}}(\Delta E) = -I_0 \exp\left(-\frac{z\alpha_{\text{cath}}F}{RT} \Delta E\right) \quad (2)$$

where  $I_0$  [A] represents the exchange current,  $\alpha_{\text{cath}}$  [–] the cathodic transfer coefficient for oxygen reduction,  $R$  (8.31 J

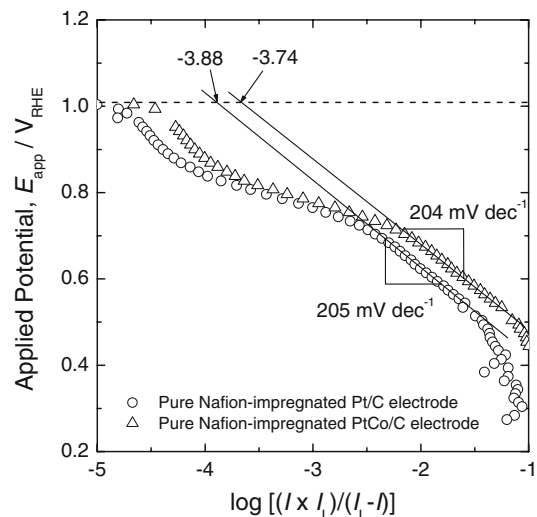


**Fig. 5** Plots of the instantaneous current  $I_{\text{ins}}$  taken at  $3 \times 10^{-3}$  s on a logarithmic scale against the potential step  $\Delta E$  for the pure Nafion-impregnated circular Pt/C and PtCo/C disk electrodes: *open and closed circles*, experimentally measured; *open and closed squares*, calculated from the Butler–Volmer equation (Eq. 3); *open and closed triangles*, calculated by the Cottrell equation (Eq. 4). Here, the *open and closed symbols* indicate the pure Nafion-impregnated Pt/C and PtCo/C electrodes, respectively

$\text{mol}^{-1} \text{K}^{-1}$ ) the gas constant, and  $T$  [K] denotes the absolute temperature.

Consequently,  $|I|$  should exponentially rise in absolute value with increasing  $|\Delta E|$ . Practically, the linear relationship between  $\log |I|$  and  $|\Delta E|$  is one of the crucial experimental evidences that the “constraint by Butler–Volmer behavior” is established at the electrode surface during oxygen reduction. To evaluate the values of  $I_0$  and  $\alpha_{\text{cath}}$ , the cathodic potentiodynamic polarization curves were first measured, and the resulting polarization curves are presented in Fig. 6. From the slope and extrapolation toward the OCV value of the straight line in the potential range of 0.4 to 0.6 V<sub>RHE</sub>, where the current transients were measured, the values of  $I_0$  and  $\alpha_{\text{cath}}$  were quantitatively determined. We then calculated the value of  $I$  by taking the values of  $I_0$  and  $\alpha_{\text{cath}}$  as  $1.32 \times 10^{-4}$  A and 0.07 for the pure Nafion-impregnated Pt/C electrode and as  $2.82 \times 10^{-4}$  A and 0.07 for the pure Nafion-impregnated PtCo/C electrode, respectively. It should be also stressed that the calculation was performed by using the  $z$  values obtained in the preceding Section. The values of  $I_0$  and  $\alpha_{\text{cath}}$  for the Pt/C electrode determined in this work well coincided with those in the literatures [23, 36, 37]. The calculated values of  $|I|$  are also shown on a logarithmic scale as a function of  $\Delta E$  in Fig. 5, where open square and closed square denote the pure Nafion-impregnated Pt/C and PtCo/C electrodes, respectively.

Next, by assuming that the “constraint of constant concentration” is valid over the whole  $\Delta E$  range, the value



**Fig. 6** Potentiodynamic polarization curves experimentally obtained from the pure Nafion-impregnated Pt/C and PtCo/C electrodes in an oxygen-saturated 1 M  $\text{H}_2\text{SO}_4$  solution, which was corrected with a limiting current  $I_L$  under the assumption of a first-order kinetics [exposed electrode area:  $0.126 \text{ cm}^2$ ]

of  $I$  was theoretically determined from the Cottrell equation [35] in the early stage:

$$I(t) = -\frac{zFA_{ca}D_{O_2}^{1/2}\Delta c_{O_2}}{\pi^{1/2}t^{1/2}} \text{ for } x = 0 \text{ at } t \geq 0 \quad (3)$$

where  $\Delta c_{O_2}$  [mol cm<sup>-3</sup>] refers to the difference between the oxygen concentration  $c_{O_2}^{x=\infty}$  [mol cm<sup>-3</sup>] in the bulk solution and the surface oxygen concentration  $c_{O_2}^{x=0}$  [mol cm<sup>-3</sup>] corresponding to  $E_{app}$ , i.e.,  $\Delta c_{O_2} = c_{O_2}^{x=\infty} - c_{O_2}^{x=0}$ , and  $t$  means time. In this work, all the values of  $E_{app}$  correspond to  $c_{O_2}^{x=0} = 0$  and, hence,  $\Delta c_{O_2}$  just equals  $c_{O_2}^{x=\infty}$ . For this reason, it is obvious that the value of  $I_{ins}$  determined under the “constraint of constant concentration” should be a constant value irrespective of the value of  $\Delta E$ .

By taking the values of  $D_{O_2}$  as  $1.7 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> [33] and  $c_{O_2}^{x=\infty}$  as  $2.0 \times 10^{-6}$  mol cm<sup>-3</sup> [33] for both the pure Nafion-impregnated Pt/C and PtCo/C electrodes, we calculated the value of  $I_{ins}$  at  $3 \times 10^{-3}$  s from Eq. 3. The calculation was performed by using the  $A_{ca}$  value obtained from the cyclic voltammograms of Fig. 2. The resulting values of  $|I_{ins}|$  are designated in Fig. 5 as open triangle for the pure Nafion-impregnated Pt/C electrode and closed triangle for the pure Nafion-impregnated PtCo/C electrode.

Now, we can define the transition potential step  $|\Delta E_{tr}|$ , which is the  $|\Delta E|$  value needed for the occurrence of the change in RDS, at which the plot of  $|I_{ins}|$  versus  $|\Delta E|$  calculated from the Butler–Volmer equation (Eq. 2) intersects that plot calculated from the Cottrell equation (Eq. 3). Accordingly, the values of  $|\Delta E_{tr}|$  were determined to be 0.67 V for the pure Nafion-impregnated Pt/C electrode and to be 0.63 V for the pure Nafion-impregnated PtCo/C electrode from Fig. 5. The resulting values of  $|\Delta E_{tr}|$  are listed in Table 2. It can be seen from Fig. 5 and Table 2 that in the first place, in the value of  $|\Delta E|$  smaller than  $|\Delta E_{tr}|$ , the measured  $|I_{ins}|$  was almost identical to  $|I_{cath}|$  calculated from the Butler–Volmer equation, which means that the “constraint by Butler–Volmer behavior” is effective at the electrode surface for oxygen reduction. In the second place, for values of  $|\Delta E|$  greater than  $|\Delta E_{tr}|$ , the measured  $|I_{ins}|$  coincided fairly well with  $|I_{ins}|$  calculated from the Cottrell equation, implying that the RDS of oxygen reduction is purely oxygen diffusion in the solution.

Now, let us consider oxygen reduction under the “constraint by Butler–Volmer behavior.” To clearly demonstrate the “constraint by Butler–Volmer behavior,” it is necessary to introduce the transient of the oxygen concentration profile across the electrolytic solution. Following the hydrogen concentration profile transient during hydrogen desorption [24, 38], the oxygen concentration profile transients analogized under the purely diffusion control and purely charge transfer control are plotted in Fig. 7a, b, respectively. The oxygen concentration profile transient analogized under the “constraint by Butler–Volmer behavior” by using Eq. 2 is also plotted in Fig. 7c. In Fig. 7,  $c_{O_2}^{x=0}$  means the oxygen concentration at the electrode surface,  $c_{O_2}^{x=L}$  the oxygen concentration at  $x=L$  which corresponds to  $c_{O_2}^{x=\infty}$  in Eq. 3, and  $L$  denotes the diffusion layer thickness.

If oxygen reduction is purely controlled by oxygen diffusion,  $c_{O_2}^{x=0}(t)$  and  $c_{O_2}^{x=L}(t)$  are fixed at zero and a finite value, respectively, over the whole time as shown in Fig. 7a. On the other hand, if oxygen reduction is purely governed by charge transfer, there is no concentration gradient of oxygen across the electrolytic solution in the diffusion direction from bulk solution to electrode as shown in Fig. 7b. However, in the concentration profile transient of Fig. 7c,  $c_{O_2}^{x=0}(t)$  decreases in value with time from  $c_{O_2}^{x=L}(t = 0)$  over  $f(t)$  finally to zero at  $t = \infty$  and  $c_{O_2}^{x=L}(t \geq 0)$  remains constant. The concentration gradient of oxygen is formed across the electrolytic solution due to the transport limitation induced by oxygen diffusion. This means that the value of the electrode potential  $E$  involved in  $\Delta E$  of Eq. 2 is not fixed at zero, but it varies with time depending upon the oxygen concentration at the electrode surface.

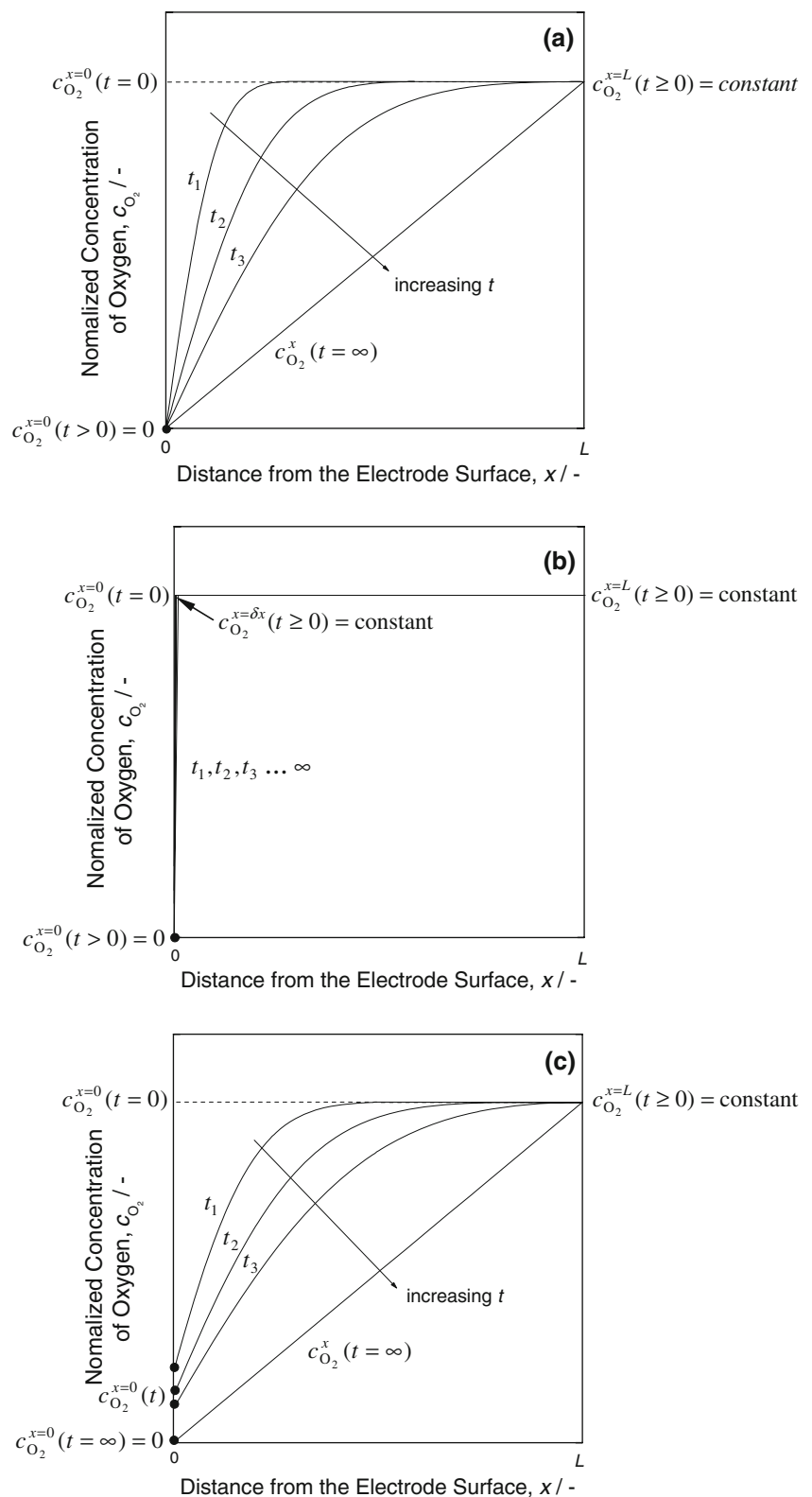
From the above result, it was concluded that the Butler–Volmer equation involves the concentration-dependent electrode potential; hence, the “constraint by Butler–Volmer behavior” means the condition where oxygen diffusion is kinetically coupled with charge transfer. The Butler–Volmer equation involving the concentration-dependent electrode potential has been widely adopted in the theoretical models for diffusion process coupled with interfacial charge transfer under the impermeable boundary condition  $(\partial c/\partial x)_{x=0}$  or  $(\partial c/\partial x)_{x=L}$  depending upon which interface is the impermeable boundary [24, 38].

**Table 2** The transition potential step  $\Delta E_{tr}$

Specimen		Transition potential step, $\Delta E_{tr}$ [V]
Pt/C electrode	Pure Nafion-impregnated	0.67
	Partially Na <sup>+</sup> -doped Nafion-impregnated	0.59
PtCo/C electrode	Pure Nafion-impregnated	0.63
	Partially Na <sup>+</sup> -doped Nafion-impregnated	0.60

The potential step needed for the occurrence of the change in RDS, evaluated from the analysis of the cathodic PCTs measured on the pure Nafion-impregnated and partially Na<sup>+</sup>-doped Nafion-impregnated Pt/C and PtCo/C electrodes

**Fig. 7** Plots of the transients of the oxygen concentration profile over the electrolytic solution analogized under the **a** purely diffusion control  $c_{\text{O}_2}^{x=0}(t \geq 0) = 0$  and  $c_{\text{O}_2}^{x=L}(t \geq 0) = \text{constant}$ , **b** purely charge transfer control  $c_{\text{O}_2}^{x=0}(t \geq 0) = 0$  and  $c_{\text{O}_2}^{x=\delta x}(t \geq 0) = \text{constant}$ , and **c** “constraint by Butler–Volmer behavior”  $c_{\text{O}_2}^{x=0}(t \geq 0) = \text{variable}$  and  $c_{\text{O}_2}^{x=L}(t \geq 0) = \text{constant}$ . Here,  $L$  means the diffusion layer thickness of electrolytic solution



Furthermore, the difference between the  $|\Delta E_{\text{tr}}|$  values for the pure Nafion-impregnated Pt/C and PtCo/C electrodes originates from the  $I_0$  value. In the case of the PtCo/C electrode, charge transfer is promoted by the catalytic effect

of Co; hence, the “Butler–Volmer current” of the PtCo/C electrode is higher than that of the Pt/C electrode. Therefore, the two currents, i.e., the “Butler–Volmer current” and “Cottrell current” intersect even at small  $|\Delta E|$ .



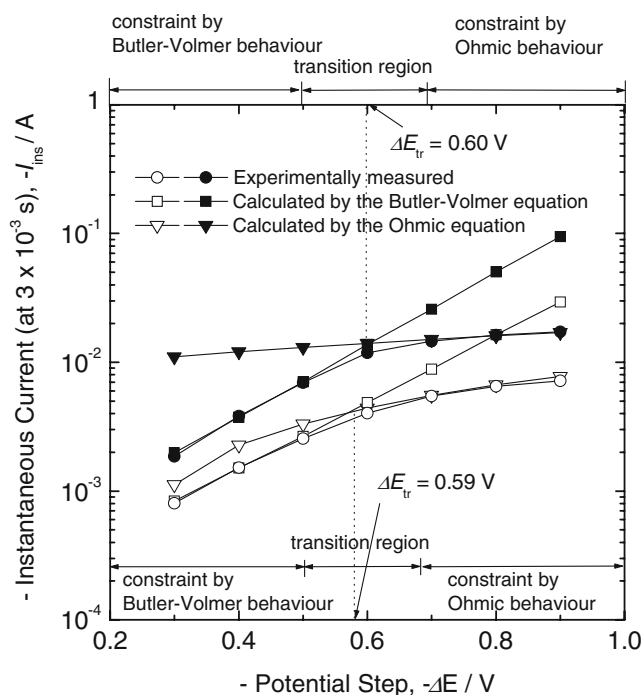
This result can be extended to other alloying catalyst. Based upon the results in the literature [39], the  $|\Delta E_{tr}|$  value was calculated to be 0.65 V from Eq. 2 by taking  $I_0$  as  $2.07 \times 10^{-4}$  A ( $5.18 \text{ A } g_{Pt}^{-1}$ ) for both the Pt<sub>3</sub>Ni/C and Pt<sub>3</sub>Co/C electrodes under the assumption of the same Pt loading. The decreases of the  $|\Delta E_{tr}|$  value for the Pt<sub>3</sub>Ni/C and Pt<sub>3</sub>Co/C electrodes result from the increase of  $I_0$ . These tendencies are well consistent with that tendency observed for the PtCo/C electrode in the present work, but the  $|\Delta E_{tr}|$  values of the Pt<sub>3</sub>Ni/C and Pt<sub>3</sub>Co/C electrodes are larger than that of the PtCo/C electrode due to the lower  $I_0$  value.

Effect of Nafion pretreatment by NaClO<sub>4</sub> solution on the change in rate-determining step of oxygen reduction under the mixed charge transfer and migration control

Let us consider the effect of Nafion pretreatment by NaClO<sub>4</sub> solution on the change in RDS of oxygen reduction at the Pt/C and PtCo/C electrodes. From the cathodic PCTs experimentally obtained from the partially Na<sup>+</sup>-doped Nafion-impregnated Pt/C and PtCo/C electrodes, it was found that all the cathodic PCTs exhibited nearly the same shape as those PCTs in Fig. 4a, b, but they showed different values.

Similarly to the preceding section (“Effect of Co alloying to Pt catalyst on the change in rate-determining step of oxygen reduction under mixed charge transfer and diffusion control”), the  $|I_{ins}|$  values are plotted on a logarithmic scale against  $\Delta E$  in Fig. 8, where open and closed circles denote the partially Na<sup>+</sup>-doped Nafion-impregnated Pt/C and PtCo/C electrodes, respectively. For all of the electrodes, it was observed that in the small  $|\Delta E|$  range, the value of  $\log |I_{ins}|$  linearly increased with rising  $|\Delta E|$ , while in the large  $|\Delta E|$  range, the value of  $|I_{ins}|$  was linearly proportional to  $|\Delta E|$ . Over a narrow range of the intermediate  $|\Delta E|$ , a transition occurred of the linear relation between  $\log |I_{ins}|$  and  $|\Delta E|$  to that linear relation between  $|I_{ins}|$  and  $|\Delta E|$ .

First, to specify the RDS of oxygen reduction, the  $I_{cath}$  value was theoretically calculated as a function of  $\Delta E$  under the “constraint by Butler–Volmer behavior” in the same manner as described in the preceding section (“Effect of Co alloying to Pt catalyst on the change in rate-determining step of oxygen reduction under mixed charge transfer and diffusion control”). The values of  $I_0$  and  $\alpha_{cath}$  were first determined by analyzing the cathodic potentiodynamic polarization curves in the same manner as seen in Fig. 6, and then the values of  $I_{ins}$  were theoretically calculated from Eq. 2 by taking the values of  $I_0$  as  $1.40 \times 10^{-4}$  A and  $\alpha_{cath}$  as 0.07 for the partially Na<sup>+</sup>-doped Nafion-impregnated Pt/C electrode and the values of  $I_0$  as  $2.70 \times 10^{-4}$  A and  $\alpha_{cath}$  as 0.08 for the partially Na<sup>+</sup>-doped Nafion-impregnated PtCo/C electrode. From the coinci-



**Fig. 8** Plots of the instantaneous current  $I_{ins}$  taken at  $3 \times 10^{-3}$  s on a logarithmic scale against the potential step  $\Delta E$  for the partially Na<sup>+</sup>-doped Nafion-impregnated circular Pt/C and PtCo/C disk electrodes: open and closed circles, experimentally measured; open and closed squares, calculated from the Butler–Volmer equation (Eq. 3); open and closed inverted triangles, calculated by the Ohmic equation (Eq. 5). Here, the open and closed symbols indicate the partially Na<sup>+</sup>-doped Nafion-impregnated Pt/C and PtCo/C electrodes, respectively

dence of the measured values of  $|I_{ins}|$  with those values of  $|I_{cath}|$  theoretically calculated from Eq. 2, it is recognized that the “constraint by Butler–Volmer behavior” is effective at the electrode surface in the small  $|\Delta E|$  range.

Next, let us consider the large  $|\Delta E|$  region where  $|I_{ins}|$  is linearly proportional to  $|\Delta E|$ . From the linear relationship between  $|\Delta E|$  and  $|I_{ins}|$ , we newly introduced the “constraint by Ohmic behavior,” which implies that oxygen reduction is purely controlled by proton migration through the Nafion electrolyte. By assuming that the “constraint by Ohmic behavior” is valid over the whole  $\Delta E$  range, the value of  $I_{ins}$  was theoretically determined from the Ohmic equation in the early stage [40]:

$$I(\Delta E) = -\frac{zFA_{ca}}{RT} D_{H^+} c_{H^+} \Delta E \text{ for } x = 0 \text{ at } t \geq 0 \quad (4)$$

where  $D_{H^+}$  [ $\text{cm}^2 \text{ s}^{-1}$ ] and  $c_{H^+}$  [ $\text{mol cm}^{-3}$ ] refer to the diffusivity and concentration of proton in the Nafion electrolyte, respectively.

To calculate the  $I_{ins}$  value under the purely migration control, the  $D_{H^+} c_{H^+}$  values were first evaluated from the straight line of the measured impedance spectra as a function of  $\Delta E$  at high frequencies. Then, we calculated the value of  $I_{ins}$  at  $3 \times 10^{-3}$  s from Eq. 4 by taking the value of  $D_{H^+} c_{H^+}$  as

$2.31 \times 10^{-5} \text{ mol cm}^{-1} \text{ s}^{-1}$  for the partially  $\text{Na}^+$ -doped Nafion-impregnated Pt/C electrode and the value of  $D_{\text{H}^+} c_{\text{H}^+}$  as  $2.19 \times 10^{-5} \text{ mol cm}^{-1} \text{ s}^{-1}$  for the partially  $\text{Na}^+$ -doped Nafion-impregnated PtCo/C electrode. The resulting values of  $I_{\text{ins}}$  are designated in Fig. 8 as open inverse triangle for the partially  $\text{Na}^+$ -doped Nafion-impregnated Pt/C electrode and as closed inverse triangle for the partially  $\text{Na}^+$ -doped Nafion-impregnated PtCo/C electrode.

From the coincidence of the measured values of  $|I_{\text{ins}}|$  with those values of  $|I_{\text{cath}}|$  theoretically calculated from Eq. 4, it is confirmed that oxygen reduction at the partially  $\text{Na}^+$ -doped Nafion-impregnated electrode is purely governed by proton migration in the Nafion electrolyte in the large  $|\Delta E|$  range.

The  $|\Delta E_{\text{tr}}|$  values were also defined from the intersection point at which the plot of  $|I_{\text{ins}}|$  versus  $|\Delta E|$  calculated from the Butler–Volmer equation intersects that plot calculated from the Ohmic equation. The values of  $|\Delta E_{\text{tr}}|$  were determined to be 0.59 V for the partially  $\text{Na}^+$ -doped Nafion-impregnated Pt/C electrode and 0.60 V for the partially  $\text{Na}^+$ -doped Nafion-impregnated PtCo/C electrode from Fig. 8. The resulting values of  $|\Delta E_{\text{tr}}|$  are also listed in Table 2. From Table 2, it was noted that the  $|\Delta E_{\text{tr}}|$  value was markedly reduced by Nafion pretreatment by  $\text{NaClO}_4$  solution.

From the analysis of the cathodic PCTs obtained from the partially  $\text{Na}^+$ -doped Nafion-impregnated Pt/C and PtCo/C electrodes, it is concluded that the change in RDS from the mixed charge transfer and migration to purely proton migration rather than to purely oxygen diffusion occurs at the value of  $|\Delta E_{\text{tr}}|$  by Nafion pretreatment. It should also be emphasized that for the partially  $\text{Na}^+$ -doped Nafion-impregnated electrode, the boundary condition of the “constraint by Butler–Volmer behavior” means that charge transfer is kinetically coupled not with oxygen diffusion but with proton migration. Furthermore, the  $|\Delta E_{\text{tr}}|$  values for the partially  $\text{Na}^+$ -doped Nafion-impregnated electrodes are correspondingly lowered as compared with those for the pure Nafion-impregnated electrodes by Nafion pretreatment.

## Discussion

According to the literatures [23, 41–43] on the oxygen reduction kinetics at the Pt/C electrodes under the mixed charge transfer and transport control, the current-time relation is given as follows:

$$I(t) = I_{\text{st}} - 2I_{\text{st}}(1 + \Lambda) \times \sum_{n=1}^{\infty} \frac{b_n \cos b_n}{(\Lambda^2 + \Lambda + b_n^2) \sin b_n} \exp\left(-\frac{b_n^2}{R_t C_{\text{dl}} l_t^2} t\right) \quad (5)$$

where  $I_{\text{st}}$  [A] represents the steady-state current,  $\Lambda$  [–] the dimensionless parameter denoting the ratio of  $R_t$  to the sum

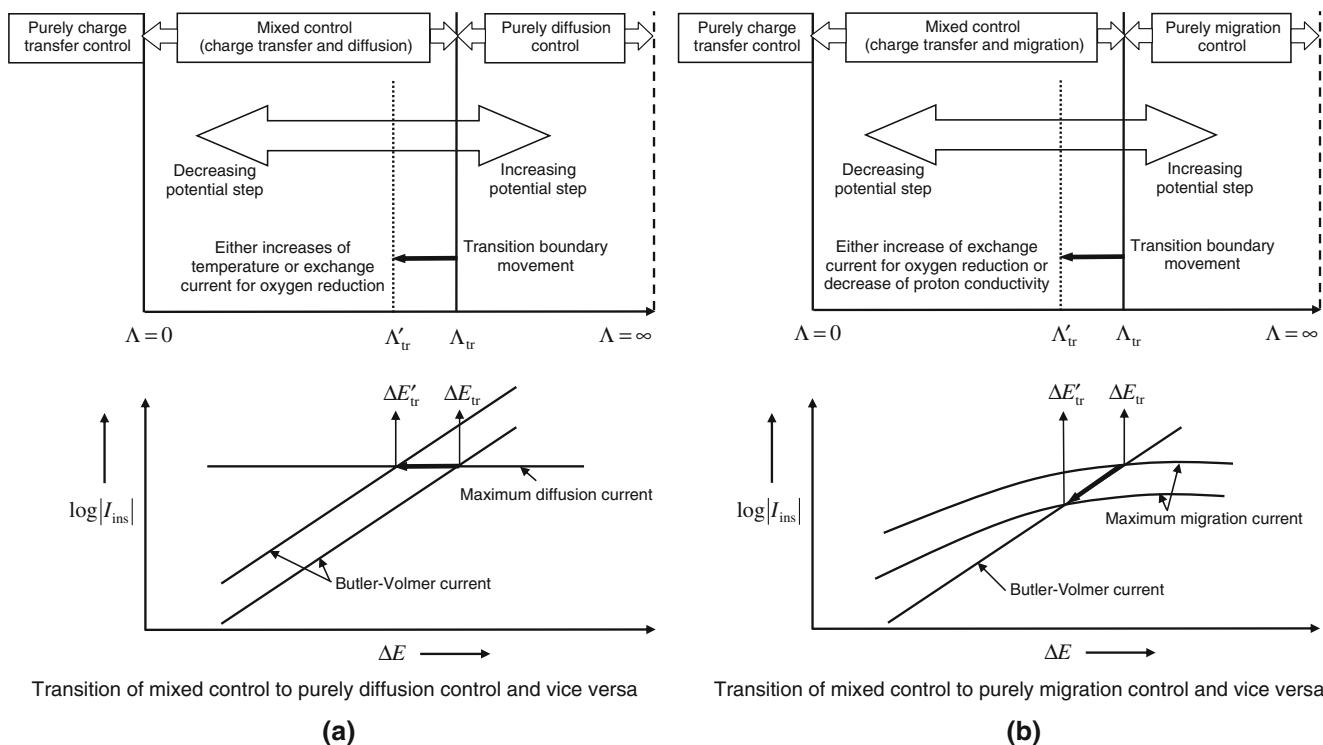
of  $R_s$  and  $R_{\text{ct}}$ , i.e.  $\Lambda = R_t / (R_{\text{ct}} + R_s)$ ,  $R_s$  [ $\Omega$ ] the solution resistance between the reference electrode and the front surface of the Pt electrode and  $b_n$  [–] means the  $n$ th root of “ $b \cot b + \Lambda = 0$ ”. Here,  $R_t$  [ $\Omega$ ] is the transport resistance, which means either the migration resistance  $R_m$  or diffusion resistance  $R_d$  depending upon whether proton migration or oxygen diffusion may occur.

From Eq. 5, it is confirmed that oxygen reduction is purely controlled by charge transport at the electrode surface in the case of  $\Lambda = 0$ , whereas oxygen reduction is purely governed by transport of electroactive species, i.e., proton or oxygen, through the transport media in case that the  $\Lambda$  value exceeds the transition value of  $\Lambda_{\text{tr}}$ . It is also noted that since the potential dependence of  $R_{\text{ct}}$  differs from that of  $R_t$ , the value of  $\Lambda$  is changed by the applied negative or positive potential step  $\Delta E$ , and hence the RDS is correspondingly changed.

Furthermore, based upon the results reported in this work and in the previous work [23], it is concluded that the value of  $\Lambda_{\text{tr}}$  shifts in negative direction with increasing either temperature  $T$  or exchange current for oxygen reduction  $I_0$  in case that charge transfer is mixed with oxygen diffusion. Similarly, it shifts to lower  $\Lambda$  with either increasing  $I_0$  or decreasing proton conductivity in case that charge transfer is mixed with proton migration. This means that the transition boundary of mixed control to purely diffusion (migration) control shifts in negative direction, and hence the mixed control region obviously shrinks. The change in RDS of oxygen reduction is visualized as a function of  $\Lambda$  ( $\Lambda = R_t / (R_{\text{ct}} + R_s)$ ) in the top of Fig. 9 and is also schematically illustrated in the bottom of Fig. 9 as the plot of the logarithmic instantaneous current  $\log |I_{\text{ins}}|$  against the potential step  $|\Delta E|$ .

In real fuel cell system, it is suggested that the cell performance is improved by Co alloying since the electrode reaches the maximum diffusion (migration) current even at small potential step. On the other hand, the cell performance is aggravated by Nafion pretreatment due to the decrease in the maximum current even though the electrode reaches the maximum diffusion (migration) current at small potential step  $|\Delta E|$ . Consequently, it strongly depends upon the intrinsic parameters such as  $I_0$  and proton conductivity as well as upon the extrinsic parameters such as  $T$  and  $|\Delta E|$ , which mechanism of the overall oxygen reduction reaction is operative.

This transition behavior can be adopted in real gas diffusion electrode used for PEMFC. In the previous work from our laboratory [33, 44], we reported that oxygen reduction in the gas diffusion electrode proceeds under the condition where proton migration through the Nafion electrolyte is kinetically mixed with charge transfer at the three-phase boundary. As either  $I_0$  increases in value or proton conductivity decreases, the RDS of oxygen reduc-



**Fig. 9** Schematic diagram of the change in RDS of oxygen reduction in the cases of **a** the transition of mixed control to purely diffusion control and **b** the transition of mixed control to purely migration control

tion moves in the mixed control region toward the purely migration.

It is also extended to the electrochemical reaction which occurs under the constraint of the mixed transport and charge transfer-control. For instance, the change in RDS of hydrogen transport through the Pd, Pd alloy, and metal hydride electrodes occurs at  $|\Delta E_{tr}|$  from the mixed diffusion and charge transfer to purely diffusion. As either  $I_o$  increases in value or the hydrogen diffusivity decreases, the value of  $|\Delta E_{tr}|$  shifts to smaller value of  $|\Delta E|$  [24, 38, 45, 46].

**Conclusions**

The present work considers the change in RDS of oxygen reduction at the Pt/C electrodes by Co alloying to Pt catalyst and Nafion pretreatment by  $\text{NaClO}_4$  solution employing PCT technique. The results are summarized as follows:

1. From the comparison of the instantaneous current  $I_{ins}$  taken at  $3 \times 10^{-3}$  s from the cathodic PCTs experimentally measured on the pure Nafion-impregnated Pt/C and PtCo/C electrodes with those values of  $I_{ins}$  theoretically calculated, it was found that oxygen reduction at both electrodes proceeds under the condition where charge transfer at the electrode surface is kinetically coupled with oxygen diffusion in the

solution below the transition potential step  $|\Delta E_{tr}|$  in absolute value. In contrast, above  $|\Delta E_{tr}|$ , oxygen reduction is purely controlled by oxygen diffusion in the solution. In addition, the  $|\Delta E_{tr}|$  value for the pure Nafion-impregnated PtCo/C electrode is significantly lower than that value for the Pt/C electrode due to the exchange current for oxygen reduction  $I_o$  increased by Co alloying.

2. From the comparison of the cathodic PCTs experimentally measured on the partially  $\text{Na}^+$ -doped Nafion-impregnated electrodes to those measured on the pure Nafion-impregnated electrodes, it was confirmed that below  $|\Delta E_{tr}|$ , oxygen reduction at the partially  $\text{Na}^+$ -doped Nafion-impregnated electrodes proceeds under the constraint of charge transfer mixed with proton migration in the Nafion electrolyte. However, above  $|\Delta E_{tr}|$ , oxygen reduction is purely governed by proton migration rather than by oxygen diffusion. Furthermore, the values of  $|\Delta E_{tr}|$  for the partially  $\text{Na}^+$ -doped Nafion-impregnated electrodes are slightly lower than those for the pure Nafion-impregnated electrodes due to the proton conductivity reduced by  $\text{Na}^+$  doping to Nafion electrolyte.
3. From the experimental results, it is expected under the operating condition that the cell performance such as power density is improved by Co alloying since the electrode reaches the maximum diffusion (migration)

current even at small potential step  $|\Delta E|$ . However, the cell performance is aggravated by Nafion pretreatment due to the decrease in the maximum diffusion (migration) current even though the electrode reaches the maximum diffusion (migration) current at small  $|\Delta E|$ . This strongly indicates that the intrinsic parameters such as  $I_0$  and proton conductivity as well as the extrinsic parameter such as  $\Delta E$  play an important role in the determination of the cell performance as well as the RDS of oxygen reduction.

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## References

- De Souza A, Gonzalez ER (2003) *J Solid State Electrochem* 7:651. doi:10.1007/s10008-003-0363-2
- Beard BC, Ross PN (1986) *J Electrochem Soc* 133:1839. doi:10.1149/1.2109033
- Paffett MT, Berry GJ, Gottesfeld S (1988) *J Electrochem Soc* 135:1431. doi:10.1149/1.2096016
- Beard BC, Ross PN (1990) *J Electrochem Soc* 137:3368. doi:10.1149/1.2086223
- Mukerjee S, Srinivasan S (1993) *J Electroanal Chem* 357:201. doi:10.1016/0022-0728(93)80380-Z
- Watanabe M, Tsurumi K, Mizukami T, Nakamura T, Stonehart P (1994) *J Electrochem Soc* 141:2659. doi:10.1149/1.2059162
- Toda T, Igarashi H, Uchida H, Watanabe M (1999) *J Electrochem Soc* 146:3750. doi:10.1149/1.1392544
- Min M, Cho J, Cho K, Kim H (2000) *Electrochim Acta* 45:4211. doi:10.1016/S0013-4686(00)00553-3
- Antolini E, Passos RR, Ticianelli EA (2002) *Electrochim Acta* 48:263. doi:10.1016/S0013-4686(02)00644-8
- Paulus UA, Scherer GG, Wokaun A, Schmidt TJ, Stamenkovic V, Radmilovic V, Markovic NM, Ross PN (2002) *J Phys Chem B* 106:4181. doi:10.1021/jp0134421
- Antolini E, Salgado JRC, Giz MJ, Gonzalez ER (2005) *Int J Hydrogen Energy* 30:1213. doi:10.1016/j.ijhydene.2005.05.001
- Remita H, Siril PF, Mbomekalle IM, Keita B, Nadjo L (2006) *J Solid State Electrochem* 10:506. doi:10.1007/s10008-005-0005-y
- Li X, Colon-Mercado HR, Wu G, Lee JW, Popov BN (2007) *Electrochem Solid-State Lett* 10:B201. doi:10.1149/1.2777009
- Koh S, Yu C, Mani P, Srivastava R, Strasser P (2007) *J Power Sources* 172:50. doi:10.1016/j.jpowsour.2007.01.002
- Luna AMC, Bonesi A, Triaca WE, Baglio V, Antonucci V, Arico AS (2008) *J Solid State Electrochem* 12:643. doi:10.1007/s10008-007-0334-0
- Lee MH, Wang PS, Do JS (2008) *J Solid State Electrochem* 12:879. doi:10.1007/s10008-007-0477-z
- Gasteiger HA, Kocha SS, Sompalli B, Wagner FT (2005) *Appl Catal B-Environ* 56:9
- O'Hayre RP, Cha SW, Colella W, Prinz FB (2006) *Fuel Cell Fundamentals*. Wiley, Hoboken, pp 112–121
- Scharifker BR, Zelenay P, JO'M Bockris (1987) *J Electrochem Soc* 134:2714. doi:10.1149/1.2100276
- Zecevic SK, Wainright JS, Litt MH, Gojkovic SL, Savinell RF (1997) *J Electrochem Soc* 144:2973. doi:10.1149/1.1837946
- Eikerling M, Kornyshev AA (1999) *J Electroanal Chem* 475:107. doi:10.1016/S0022-0728(99)00335-6
- Lee SJ, Pyun SI (2007) *Electrochim Acta* 52:6525. doi:10.1016/j.electacta.2007.04.081
- Lee SK, Pyun SI, Lee SJ, Jung KN (2007) *Electrochim Acta* 53:740. doi:10.1016/j.electacta.2007.07.042
- Lee JW, Pyun SI (2005) *Electrochim Acta* 50:1777. doi:10.1016/j.electacta.2004.08.046
- Lee SJ (2008) Ph.D. Thesis, Chapter 3, Korea Advanced Institute of Science and Technology, Daejeon
- Ayad A, Naimi Y, Bouet J, Fauvarque JF (2004) *J Power Sources* 130:50. doi:10.1016/j.jpowsour.2003.11.064
- Biegler T, Rand DAJ, Woods R (1971) *J Electroanal Chem* 29:269. doi:10.1016/S0022-0728(71)80089-X
- Hoare JP (1974) In: Bard AJ (ed) *Encyclopedia of the Electrochemistry of the Elements*, vol II. Marcel Dekker, New York, p 191
- Tarasevich MR, Sadkovski A, Yeager E (1983) In: Conway BE, Bockris JO'M, Khan SVM, White RE (eds) *Comprehensive Treatise of Electrochemistry*, Vol. 7. Plenum, New York, p 301
- Yeager E (1984) *Electrochim Acta* 29:1527. doi:10.1016/0013-4686(84)85006-9
- O'Sullivan EJM, Calvo EJ (1987) In: Compton RG (ed) *Comprehensive Chemical Kinetics*, vol 27. Elsevier, Amsterdam, p 247
- Pletcher D, Sotiropoulos S (1993) *J Electroanal Chem* 356:109. doi:10.1016/0022-0728(93)80514-I
- Floriano JB, Ticianelli EA, Gonzalez ER (1994) *J Electroanal Chem* 367:157. doi:10.1016/0022-0728(93)03007-C
- Mello RMQ, Ticianelli EA (1997) *Electrochim Acta* 42:1031. doi:10.1016/S0013-4686(96)00282-4
- Wen CJ, Boukamp BA, Huggins RA, Weppner W (1979) *J Electrochem Soc* 126:2258. doi:10.1149/1.2128939
- Perez J, Gonzalez ER, Ticianelli EA (1998) *Electrochim Acta* 44:1329. doi:10.1016/S0013-4686(98)00255-2
- Jiang J, Yi B (2005) *J Electroanal Chem* 577:107. doi:10.1016/j.jelechem.2004.11.022
- Han JN, Seo M, Pyun SI (2001) *J Electroanal Chem* 499:152. doi:10.1016/S0022-0728(00)00506-4
- Paulus UA, Wokaun A, Scherer GG, Schmidt TJ, Stamenkovic V, Markovic NM, Ross PN (2002) *Electrochim Acta* 47:3787. doi:10.1016/S0013-4686(02)00349-3
- Bard AJ (2000) *Electrochemical Methods*, 2nd edn. Wiley, New York, p 163
- Montella C (2002) *J Electroanal Chem* 518:61. doi:10.1016/S0022-0728(01)00691-X
- Kim JS, Pyun SI, Lee JW, Song RH (2007) *J Solid State Electrochem* 11:117. doi:10.1007/s10008-005-0080-0
- Kim JS, Pyun SI (2008) *J Electrochem Soc* 155:B8. doi:10.1149/1.2799084
- Lee SJ, Pyun SI (2008) *J Electrochem Soc* 155:B1274. doi:10.1149/1.2987944
- Lee JW, Pyun SI, Filipek S (2003) *Electrochim Acta* 48:1603. doi:10.1016/S0013-4686(03)00085-9
- Lee SJ, Pyun SI, Lee JW (2005) *Electrochim Acta* 50:1121. doi:10.1016/j.electacta.2004.08.009