

# Determination of the Langmuir and Temkin Adsorption Isotherms of H for the Cathodic H<sub>2</sub> Evolution Reaction at a Pt/KOH Solution Interface Using the Phase-Shift Method

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**Abstract :** The phase-shift method for determining the Langmuir, Frumkin, and Temkin adsorption isotherms ( $\theta_H$  vs.  $E$ ) of H for the cathodic H<sub>2</sub> evolution reaction (HER) at a Pt/0.1 M KOH solution interface has been proposed and verified using cyclic voltammetric, differential pulse voltammetric, and electrochemical impedance techniques. At the Pt/0.1 M KOH solution interface, the Langmuir and Temkin adsorption isotherms ( $\theta_H$  vs.  $E$ ), the equilibrium constants ( $K_H=2.9 \times 10^{-4} \text{ mol}^{-1}$  for the Langmuir and  $K_H=2.9 \times 10^{-3} \exp(-4.6\theta_H) \text{ mol}^{-1}$  for the Temkin adsorption isotherm), the interaction parameters ( $\varrho=0$  for the Langmuir and  $\varrho=4.6$  for the Temkin adsorption isotherm), the rate of change of the standard free energy of H with  $\theta_H$  ( $r=11.4 \text{ kJ mol}^{-1}$  for  $\varrho=4.6$ ), and the standard free energies ( $\Delta G_{\text{ads}}^\circ=20.2 \text{ kJ mol}^{-1}$  for  $K_H=2.9 \times 10^{-4} \text{ mol}^{-1}$ , i.e., the Langmuir adsorption isotherm, and  $16.7 < \Delta G_\theta^\circ < 23.6 \text{ kJ mol}^{-1}$  for  $K_H=2.9 \times 10^{-3} \exp(-4.6\theta_H) \text{ mol}^{-1}$  and  $0.2 < \theta_H < 0.8$ , i.e., the Temkin adsorption isotherm) of H for the cathodic HER are determined using the phase-shift method. At intermediate values of  $\theta_H$ , i.e.,  $0.2 < \theta_H < 0.8$ , the Temkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) corresponding to the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ), and vice versa, is readily determined using the constant conversion factors. The phase-shift method and constant conversion factors are useful and effective for determining the Langmuir, Frumkin, and Temkin adsorption isotherms of intermediates for sequential reactions and related electrode kinetic and thermodynamic data at electrode catalyst interfaces.

**Keywords:** Phase-shift method, Langmuir, Frumkin, and Temkin adsorption isotherms, H adsorptions, Pt electrode catalyst.

## 1. Introduction

To obtain an environmentally clean energy source, many experimental methods have been used to study the adsorption processes of H for the cathodic H<sub>2</sub> evolution reaction (HER) and OH for the anodic O<sub>2</sub> evolution reaction (OER) in electrochemical systems. The adsorption of H for the cathodic HER at electrode catalyst/aqueous solution interfaces is one of the most extensively studied electrochemical reactions. The relation, transition, and criterion of the adsorption processes of under-potentially deposited hydrogen (UPD H) and over-potentially deposited hydrogen (OPD H) have been studied to understand the kinetics and mechanisms of the cathodic HER in the electrochemical systems. However, it is well known that UPD H and OPD H occupy different surface adsorption sites and act as two distinguishable electroadsorbed H species, and that only OPD H can contribute to the cathodic HER.<sup>1-8)</sup>

At electrode catalyst interfaces, it is preferable to consider the Langmuir, Frumkin, and Temkin adsorption isotherms for H rather than equations of the electrode kinetics and thermodynamics for H, because the Langmuir, Frumkin, and Temkin

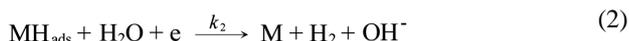
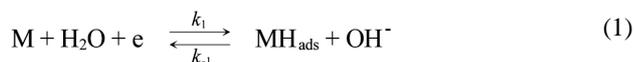
adsorption isotherms can be associated more directly with the atomic mechanism of H adsorption. Although the Langmuir, Frumkin, and Temkin adsorption isotherms may be regarded as classical models and theories in electrochemistry, they are useful and effective for studying the adsorption process of H and related electrode kinetic and thermodynamic data at electrode catalyst interfaces. Thus, there is a technological need for a fast, simple, and reliable method to determine the Langmuir, Frumkin, and Temkin adsorption isotherms for characterizing the adsorption process of H for the cathodic HER at electrode catalyst interfaces.

We have experimentally and consistently found that the behaviors ( $-\varphi$  vs.  $E$ ) of the phase shift ( $0^\circ \leq -\varphi \leq 90^\circ$ ) for the optimum intermediate frequencies can be interpreted as those ( $\theta_H$  vs.  $E$ ) of the fractional surface coverage ( $1 \geq \theta_H \geq 0$ ) of H for the cathodic HER at electrode catalyst/aqueous solution interfaces.<sup>9-24)</sup> It appears that the phase-shift method<sup>1</sup> can be effectively used to determine the Langmuir or the Frumkin adsorption isotherms ( $\theta_H$  vs.  $E$ ) of H for the cathodic HER at these interfaces. However, at first glance, it seems that there is no linear relationship between the phase-shift profiles ( $-\varphi$  vs.  $E$ ) for the optimum intermediate frequencies and the Langmuir or the Frumkin adsorption isotherms ( $\theta_H$  vs.  $E$ ) of H

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for the cathodic HER at these interfaces. But the comments and responses on the phase-shift method confirm that it is an effective way to study adsorption processes of intermediates (H, OH, etc.) for sequential reactions (HER, OER, etc.) at the electrode catalyst interfaces.<sup>25-28)</sup>

In general, the cathodic HER in alkaline solutions can be expressed as follows<sup>2-8)</sup>



where M is an electrode catalyst surface atom, e is an electron, and  $H_{ads}$  is the adsorbed hydrogen on the M. Note that  $H_{ads}$  described in Eq. (1) is the OPD H for the cathodic HER.

For the cathodic HER,  $k_1$ ,  $k_{-1}$ ,  $k_2$ , and  $k_3$  are the electrochemical rate constants. Eqs. (1), (2), and (3) are known as the proton ( $H^+$ ) discharge, electrochemical desorption, and recombination reactions, respectively. For the adsorption process of H, i.e., the proton ( $H^+$ ) discharge reaction, the reverse reactions corresponding to the electrochemical desorption and recombination reactions described in Eqs. (2) and (3) are not considered. The relation, transition, and criterion of UPD H and OPD H for the cathodic HER at platinum group metal/alkaline solution interfaces are described elsewhere.<sup>11,12,21)</sup>

In this paper, we represent the adsorption process of H for the cathodic HER and related Langmuir, Frumkin, and Temkin adsorption isotherms at a Pt/0.1 M KOH solution interface using the phase-shift method. It appears that the phase-shift method is useful and effective for determining the Langmuir, Frumkin, and Temkin adsorption isotherms of intermediates for sequential reactions and related electrode kinetic and thermodynamic data at the Pt electrode catalyst interface. This paper is intended to supplement the previously published papers.<sup>11,12,20,23)</sup>

## 2. Experimental

### 2.1. Preparations

Taking into account the  $OH^-$  concentration and effect of pH,<sup>29)</sup> an alkaline solution was prepared from KOH (Alfa-Aesar, reagent grade) with purified water (resistivity:  $>18 \text{ M}\Omega \text{ cm}$ ) obtained from a Millipore system. The 0.1 M KOH solution was deaerated with 99.999% purified nitrogen gas for 20 min before the experiments.

A standard three-electrode configuration was employed using a saturated calomel electrode (SCE) reference electrode and a Pt wire (Johnson Matthey, purity: 99.998%, 1 mm diameter, estimated surface area: ca.  $0.70 \text{ cm}^2$ ) working electrode. The Pt working electrode was prepared by flame cleaning and then quenched and cooled in Millipore Milli-Q water and in air, sequentially. A Pt wire (Johnson Matthey, purity: 99.95%, 1.5 mm diameter) was used as the counter electrode. To take into account the cathodic HER and its large current distribu-

tion, the working and counter electrodes were separated by ca. 4 cm in the same compartment of a Pyrex cell using Teflon holders.<sup>30)</sup>

### 2.2. Measurements

A cyclic voltammetric (CV) method was used to achieve the steady state of the Pt/0.1 M KOH solution interface. The CV experiments were conducted at a scan rate of 200 mV/s and a scan potential of 0 to -1.0 V vs. SCE for the cathodic HER. This high scan rate ( $>100 \text{ mV/s}$ ) was used to confirm the state of the Pt electrode catalyst at the commencement of the cyclic scan.

After the CV experiments, a differential pulse voltammetric (DPV) method was used to study the Tafel slopes of H for the cathodic HER at the Pt/0.1 M KOH solution interface. The DPV experiments were conducted at a scan rate of 1 mV/s, a pulse height of 25 mV, a pulse width of 50 ms, a step/drop time of 2 s, a reversible potential of 0.001 V, and a scan potential of 0 to -1.20 V vs. SCE for the cathodic HER. This slow scan rate ( $<10 \text{ mV/s}$ ) was used to obtain the steady state Tafel plots at the Pt electrode catalyst interface.

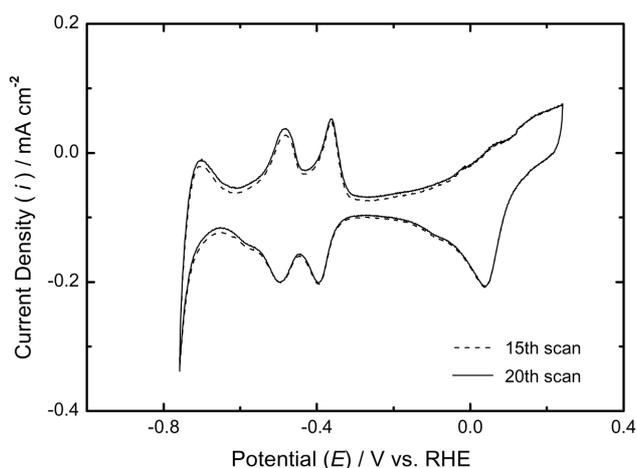
An ac impedance method was used to study the relation between the phase-shift profile ( $-\phi$  vs.  $E$ ) for the optimum intermediate frequency and the corresponding Langmuir, Frumkin, and Temkin adsorption isotherms ( $\theta_H$  vs.  $E$ ) at the Pt electrode catalyst interface. The ac impedance experiments were conducted at a single sine wave, a scan frequency of  $10^4$ -1 Hz, an ac amplitude of 5 mV, and a dc potential of 0 to -1.175 V vs. SCE for the cathodic HER at the Pt/0.1 M KOH solution interface.

The CV and DPV experiments were performed using an EG&G PAR Model 273A potentiostat controlled with the PAR Model 270 software package. The ac impedance experiments were performed using the same apparatus in conjunction with a Schlumberger SI 1255 HF Frequency Response Analyzer controlled with the PAR Model 398 software package. To obtain comparable and reproducible results, all measurements were carried out using the same preparations, procedures, and conditions at room temperature. The international sign convention is used, i.e., cathodic currents and lagged phase shifts or angles are taken as negative. To clarify the hydrogen adsorption in the different aqueous solutions, all potentials are given in the reversible hydrogen electrode (RHE) scale.

## 3. Results and Discussion

### 3.1. Cyclic voltammogram

Fig. 1 shows a typical cyclic voltammogram for the cathodic HER at the Pt/0.1 M KOH solution interface. By comparing the 15th cyclic voltammogram with the 20th cyclic voltammogram shown in Fig. 1, one can interpret that the adsorption process of OPD H for the cathodic HER proceeds at the steady state. Fig. 1 also shows that there is a significant faradaic current at the interface. For an ideally polarizable interface, the anodic and cathodic charging currents should be symmetrical around zero. However, it is not of serious concern for determining the Langmuir, Frumkin, and Temkin adsorption



**Fig. 1.** Typical cyclic voltammogram for the cathodic HER at the Pt/0.1 M KOH solution interface. Scan potential: 0.241 to -0.759 V vs. RHE. Scan rate: 200 mV/s. Number of scans: 20.

isotherms ( $\theta_H$  vs.  $E$ ) of OPD H for the cathodic HER at the interface. For a whole range of  $\theta_H$ , i.e.,  $0 \leq \theta_H \leq 1$ , the double-layer capacitance ( $C_D \approx 24.7 \mu\text{F cm}^{-2}$ ) can be neglected compared to the equivalent capacitance ( $C_P \approx 264.3\text{--}552000 \mu\text{F cm}^{-2}$ ) due to the adsorption process of OPD H and related effects at the interface (refer to Table 1). This is discussed in more detail in the section on the phase-shift profile for the optimum intermediate frequency.

The UPD H peaks, i.e., the hydrogen adsorption peaks, due to the reduction of hydrogen occur at ca. -0.39 and -0.49 V vs. RHE. The hydrogen desorption peaks due to the oxidation of hydrogen occur at ca. -0.38 and -0.48 V vs. RHE. As expected, the reduction and oxidation of hydrogen at the interface are reversible reactions rather than irreversible reactions. The UPD H peaks and the corresponding potentials ( $E$ ) are useful

for verifying the Langmuir, Frumkin, and Temkin adsorption isotherms ( $\theta_H$  vs.  $E$ ) of OPD H for the cathodic HER at the interface. Note that the adsorption process of OPD H proceeds at a more negative potential than that of UPD H. The UPD H and OPD H occupy different surface adsorption sites and act as two distinguishable electroadsorbed H species, and that only OPD H can contribute to the cathodic HER. In the following discussions, the adsorption process of H means that of OPD H for the cathodic HER.

### 3.2. Tafel slopes

The Tafel plots depend on the mechanism of H adsorption for the cathodic HER at the Pt/0.1 M KOH solution interface. It is well known that the Tafel slopes depend on experimental methods or procedures as shown in Figs. 2 and 3. To clarify the validity and effectiveness of the phase-shift method, the potentials on the Tafel plots are expressed in terms of the electrode potential ( $E$ ) rather than the overpotential ( $\eta$ ).

The Tafel slopes for the rate-determining step of the proton ( $\text{H}^+$ ) discharge reaction shown in Figs. 2(a) and 3(a) are 80.1 and 77.8 mV/decade, respectively. The Tafel slopes for the rate-determining step of the electrochemical desorption reaction shown in Figs. 2(b) and 3(b) are 266.8 and 279.1 mV/decade, respectively. In Figs. 2(a) and 3(a), one can conclude that the range of  $E$  for the rate-determining step of the proton ( $\text{H}^+$ ) discharge reaction is ca. -0.70 to -0.83 V vs. RHE. It is useful and necessary to verify the Langmuir, Frumkin, and Temkin adsorption isotherms ( $\theta_H$  vs.  $E$ ) corresponding to the adsorption process of H for the cathodic HER at the interface. This is discussed in more detail in the section on the Langmuir adsorption isotherm.

The effect of  $iR$  on the Tafel slopes for the rate-determining step of the proton ( $\text{H}^+$ ) discharge reaction is not considered. For a wide range of  $\theta_H$ , i.e.,  $0.153 < \theta_H < 0.805$ , the solution resistance ( $R_S \approx 11.7 \Omega \text{ cm}^2$ ) can be neglected compared to

**Table 1.** Measured values of the equivalent circuit elements for the optimum intermediate frequency (ca. 1.0 Hz) and the estimated fractional surface coverage ( $\theta_H$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface

$E$ (V vs. RHE)	$R_S + R_F$ ( $\Omega \text{ cm}^2$ )	$C_P^a$ ( $\mu\text{F cm}^{-2}$ )	$-\varphi^b$ (deg)	$-\varphi$ (deg)	$\theta_H^c$
-0.659	15.3	264.3	88.55	88.5	0
-0.684	45.3	316.4	84.86	84.9	0.041
-0.709	106.4	400.0	75.04	75.0	0.153
-0.734	179.3	872.9	45.49	45.5	0.489
-0.759	93.2	5337.1	17.75	17.7	0.805
-0.784	50.9	28171.4	6.34	6.3	0.934
-0.809	40.9	83928.6	2.66	2.7	0.975
-0.834	37.4	162000.0	1.51	1.5	0.989
-0.859	35.8	262857.1	0.97	1.0	0.994
-0.884	34.2	340142.9	0.78	0.8	0.997
-0.909	32.7	450857.1	0.62	0.6	0.999
-0.934	32.2	552000.0	0.51	0.5	$\approx 1$

<sup>a</sup> $C_P$  practically includes  $C_D$  ( $C_P \gg C_D$  except for low values of  $\theta_H$ ).

<sup>b</sup>Calculated using  $R_S$ ,  $R_F$ ,  $C_P$ , and Eq. (6).

<sup>c</sup>Estimated using the measured phase shift ( $-\varphi$ ).

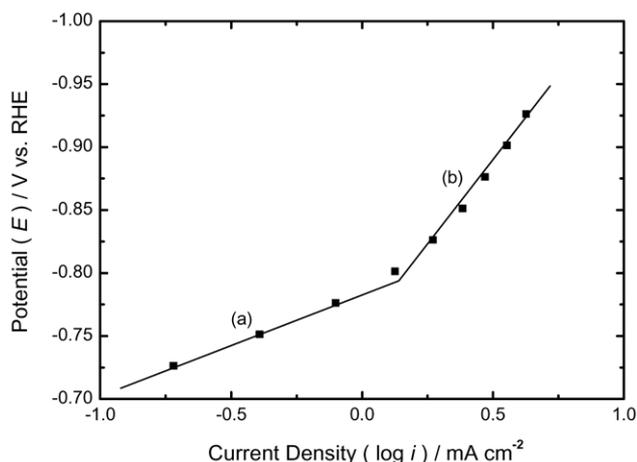


Fig. 2. Tafel plot of H for the cathodic HER at the Pt/0.1 M KOH solution interface. (a) Slope: 80.1 mV/decade and (b) slope: 266.8 mV/decade. The Tafel plot is based on the technique of current impulse vs. potential step.

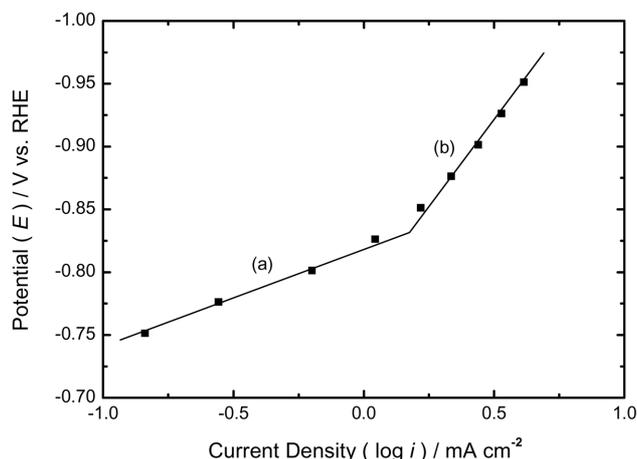


Fig. 3. Tafel plot of H for the cathodic HER at the Pt/0.1 M KOH solution interface. (a) Slope: 77.8 mV/decade and (b) slope: 279.1 mV/decade. The Tafel plot is based on the technique of current step vs. potential step.

the equivalent resistance ( $R_F \approx 81.5\text{--}167.6 \Omega \text{ cm}^2$ ) due to the adsorption process of H and related effects at the interface (refer to Table 1). This is discussed in more detail later.

### 3.3. Phase-shift profile for the optimum intermediate frequency

The equivalent circuit for the adsorption processes of intermediates (H, OH, etc.) for sequential reactions (HER, OER, etc.) at electrode catalyst interfaces is usually expressed as shown in Fig. 4(a).<sup>31,32</sup> Taking into account the various effects, e.g., the relaxation time effect, the surface diffusion effect, the lateral interaction effect, the specific adsorption effect, etc., which are inevitable under the ac impedance experiments, we define the equivalent circuit elements shown in Fig. 4(a).  $R_S$  is the solution resistance,  $R_F$  is the equivalent resistance due to the adsorption process of H and related effects at the Pt

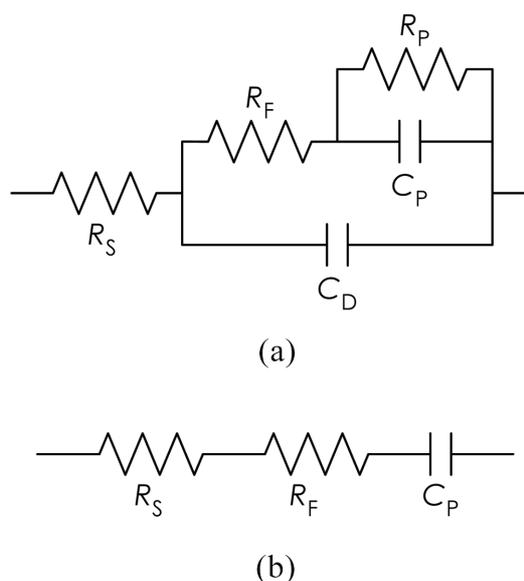


Fig. 4. (a) Equivalent circuit for all frequencies at the Pt/0.1 M KOH solution interface and (b) simplified equivalent circuit for the intermediate frequencies at the interface.

electrode catalyst interface,  $R_P$  is the equivalent resistance due to the recombination reaction,  $C_P$  is the equivalent capacitance due to the adsorption process of H and related effects at the Pt electrode catalyst interface, and  $C_D$  is the double-layer capacitance. The impedance ( $Z$ ) of the equivalent circuit for all frequencies shown in Fig. 4(a) is given by

$$Z = R_S + \left\{ (R_F + R_P + j\omega R_F R_P C_P) / [1 - \omega^2 R_F R_P C_P C_D + j\omega(R_P C_P + R_F C_D + R_P C_D)] \right\} \quad (4)$$

where  $j$  is an operator and is equal to the square root of  $-1$ , i.e.,  $j^2 = -1$ , and  $\omega (=2\pi f)$  is the angular frequency.

The two equivalent circuit elements,  $R_F$  and  $C_P$ , are the equivalent resistance and capacitance associated with the faradaic resistance ( $R_\phi$ ) and the adsorption pseudocapacitance ( $C_\phi$ ) of H, respectively. This implies that the behaviors of  $R_F$  and  $C_P$  vs.  $E$  depend strongly on those of  $R_\phi$  and  $C_\phi$  vs.  $E$ , i.e., the proton ( $H^+$ ) discharge reaction for the cathodic HER. Therefore, the adsorption process of H corresponding to the combination of  $R_F$  and  $C_P$  can be correctly expressed in terms of the phase delay, i.e., the lagged phase shift ( $-\phi$ ). Under the ac impedance experiments,  $R_F$  is smaller than  $R_\phi$  due to the superposition of the surface diffusion and relaxation time effects of the previously adsorbed hydrogen (H), i.e., the increase of  $H^+$  on the Pt electrode catalyst surface. However,  $C_P$  is greater than  $C_\phi$  due to the superposition of the surface diffusion and relaxation time effects of the previously adsorbed hydrogen (H), i.e., the increase of  $H^+$  on the Pt electrode catalyst surface. Because a resistance is inversely proportional to the concentration of charged species ( $H^+$ ), but a capacitance is proportional to the concentration of charged species ( $H^+$ ), the surface diffusion and relaxation time effects of  $R_F$  and  $C_P$  can be cancelled out or compensated together (refer to Eq. (6) and Table 1).

The frequency responses of the equivalent circuit for all frequencies shown in Fig. 4(a) are essential for studying the relationship between the behavior ( $-\varphi$  vs.  $E$ ) of the phase shift ( $0^\circ \leq -\varphi \leq 90^\circ$ ) for the optimum intermediate frequency and that ( $\theta_H$  vs.  $E$ ) of the fractional surface coverage ( $1 \geq \theta_H \geq 0$ ) of H for the cathodic HER at the Pt electrode catalyst interface. At low frequencies, the equivalent circuit for all frequencies shown in Fig. 4(a) can be expressed as a series circuit of  $R_S$ ,  $R_F$ , and  $R_P$ . At high frequencies, the equivalent circuit for all frequencies shown in Fig. 4(a) can be expressed as a series circuit of  $R_S$  and  $C_D$ . At intermediate frequencies, the equivalent circuit for all frequencies shown in Fig. 4(a) can be simplified as the series circuit of  $R_S$ ,  $R_F$ , and  $C_P$  shown in Fig. 4(b). Note that the simplified equivalent circuit shown in Fig. 4(b) is not for the change of the cathodic HER itself but only the intermediate frequency response. In other words, it is only effective and valid for studying the adsorption process of H for the cathodic HER at the Pt electrode catalyst interface.

The impedance ( $Z$ ) of the equivalent circuit for the intermediate frequencies shown in Fig. 4(b) and the corresponding phase shift ( $\varphi$ ) or angle are given by

$$Z = (R_S + R_F) - j/\omega C_P \quad (5)$$

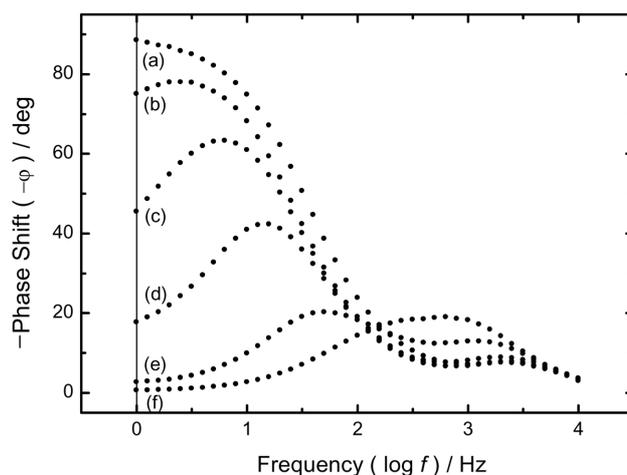
$$\varphi = -\tan^{-1}[1/\omega(R_S + R_F)C_P] \quad (6)$$

$$R_F \propto R_\phi, R_F > R_S, C_P \propto C_\phi, \text{ and } C_P > C_D \text{ (for a wide range of } \theta_H) \quad (7)$$

Note that  $f$ , i.e.,  $\omega = 2\pi f$ , described in Eqs. (5) and (6) is the optimum intermediate frequency for the phase-shift profile ( $-\varphi$  vs.  $E$ ). In addition, both  $R_F$  and  $C_P$  cannot exist unless charge is transferred across the interface. This implies that the behaviors of  $R_F$  and  $C_P$  vs.  $E$  depend strongly on those of  $R_\phi$  and  $C_\phi$  vs.  $E$ , i.e.,  $\theta_H$  vs.  $E$ , at quasi-equilibrium. Therefore, the adsorption process of H corresponding to the combination of  $R_F$  and  $C_P$  can be correctly expressed in terms of the phase delay ( $-\varphi$ ) at the rate-determining steps of the proton ( $H^+$ ) discharge, electrochemical desorption, and recombination reactions.

For a wide range of  $\theta_H$ ,  $R_F$  and  $C_P$  are much greater than  $R_S$  and  $C_D$ , respectively, and so  $-\varphi$  described in Eq. (6) can be substantially determined by the series circuit of  $R_F$  and  $C_P$ . In other words,  $-\varphi$  is substantially characterized by the adsorption process of H, i.e.,  $\theta_H$ . This implies that the behavior ( $-\varphi$  vs.  $E$ ) of the phase shift ( $0^\circ \leq -\varphi \leq 90^\circ$ ) for the optimum intermediate frequency can be linearly related to that ( $\theta_H$  vs.  $E$ ) of the fractional surface coverage ( $1 \geq \theta_H \geq 0$ ) of H, i.e., the Langmuir, the Frumkin, and the Temkin adsorption isotherms ( $\theta_H$  vs.  $E$ ) of H, at the Pt electrode catalyst interface.

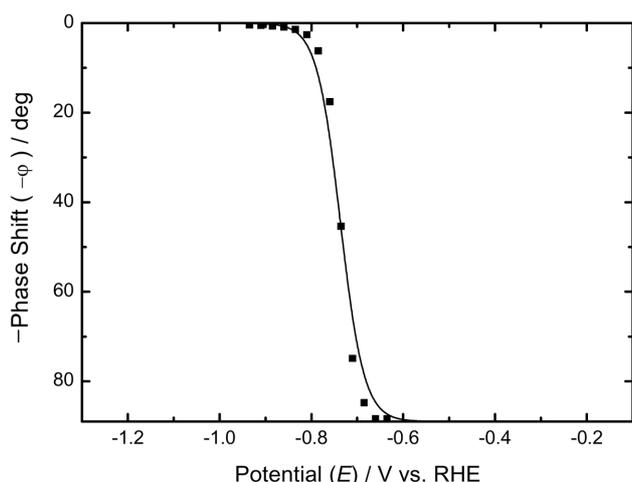
Fig. 5 compares the phase-shift curves ( $-\varphi$  vs.  $\log f$ ) for the different electrode potentials ( $E$ ) at the Pt/0.1 M KOH solution interface. In this figure,  $-\varphi$  and  $-\varphi$  vs.  $\log f$  are markedly different at intermediate frequencies due to the combination of  $R_F$  and  $C_P$  described in Eq. (6), i.e., the adsorption process of H, at the interface. The intermediate frequency, i.e.,



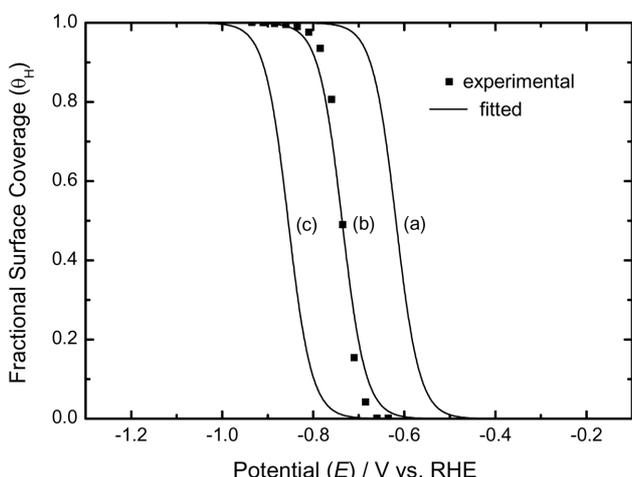
**Fig. 5. Comparison of the phase-shift curves ( $-\varphi$  vs.  $\log f$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface. Vertical solid line: ca. 1.0 Hz; single sine wave; scan frequency:  $10^4$ -1 Hz; ac amplitude: 5 mV; dc potential: (a) -0.659 V, (b) -0.709 V, (c) -0.734 V, (d) -0.759 V, (e) -0.809 V, and (f) -0.909 V vs. RHE.**

a vertical solid line (ca. 1.0 Hz) on the phase-shift curves ( $-\varphi$  vs.  $\log f$ ) shown in Fig. 5, can be set as the optimum intermediate frequency for the phase-shift profile ( $-\varphi$  vs.  $E$ ). Note that the optimum intermediate frequency (ca. 1.0 Hz) indicates a maximum lagged phase shift on the phase-shift curve ( $-\varphi$  vs.  $\log f$ ) shown in Fig. 5(a). At the maximum lagged phase shift ( $-88.5^\circ$ ) for the optimum intermediate frequency (ca. 1.0 Hz), it appears that the adsorption process of H and related effects at the interface are minimized. In other words,  $\theta_H$  can be set to zero, as shown in Table 1. Therefore, using Eq. (6),  $-\varphi$  has a maximum value of  $\leq 90^\circ$ , as shown in Fig. 5(a) or Table 1. At the minimum lagged phase shift ( $0.5^\circ$ ) for the optimum intermediate frequency (ca. 1.0 Hz), it appears that the adsorption process of H and related effects at the interface are maximized or almost saturated. In other words,  $\theta_H$  can be set to unity, as shown in Table 1. Therefore, using Eq. (6),  $-\varphi$  has a minimum value of  $\geq 0^\circ$ , as shown in Fig. 5(f) or Table 1. By comparing the calculated phase shift ( $-\varphi$ ) with the measured phase shift ( $-\varphi$ ) shown in Table 1, one can conclude that the discussions on the simplified equivalent circuit for the optimum intermediate frequency shown in Fig. 4(b) and derived Eqs. (5)-(7) are valid and effective. The determination of the optimum intermediate frequency for the phase-shift profile ( $-\varphi$  vs.  $E$ ) is described elsewhere.<sup>13,14,21-24,28)</sup>

The electrode potentials ( $E$ ) and the corresponding phase shifts ( $0^\circ \leq -\varphi \leq 90^\circ$ ) for the optimum intermediate frequency (ca. 1.0 Hz) shown in Table 1 or Fig. 5 can be plotted as the phase-shift profile ( $-\varphi$  vs.  $E$ ) for the optimum intermediate frequency (ca. 1.0 Hz) shown in Fig. 6. Note that the behavior ( $-\varphi$  vs.  $E$ ) of the phase shift ( $0^\circ \leq -\varphi \leq 90^\circ$ ) for the optimum intermediate frequency (ca. 1.0 Hz) is similar to that ( $\theta_H$  vs.  $E$ ) of the fractional surface coverage ( $1 \geq \theta_H \geq 0$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface (refer to Fig. 7).



**Fig. 6.** Phase-shift profile ( $-\phi$  vs.  $E$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface. The optimum intermediate frequency is ca. 1.0 Hz.



**Fig. 7.** Comparison of the experimental and fitted data for the Langmuir adsorption isotherms ( $\theta_H$  vs.  $E$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface. (a)  $K_H=2.9 \times 10^{-2}$ , (b)  $K_H=2.9 \times 10^{-4}$ , and (c)  $K_H=2.9 \times 10^{-6} \text{ mol}^{-1}$ .

### 3.4. Langmuir adsorption isotherm

We consider the determination of the Langmuir, Frumkin, and Temkin adsorption isotherms ( $\theta_H$  vs.  $E$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface as follows. First, we determine the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) and then find the interaction parameter ( $\psi$ ) for the Frumkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) based on the relevant experimental results, i.e., the Tafel slopes for the rate-determining step of the proton ( $\text{H}^+$ ) discharge reaction, the fractional surface coverage profile ( $\theta_H$  vs.  $E$ ) corresponding to the phase-shift profile ( $-\phi$  vs.  $E$ ) of H for the optimum intermediate frequency, etc. Finally, the applicability of the Temkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) is considered.

The derivation of the practical form of the Langmuir, Frumkin, and Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) of intermediates for sequential reactions at electrode catalyst surfaces is des-

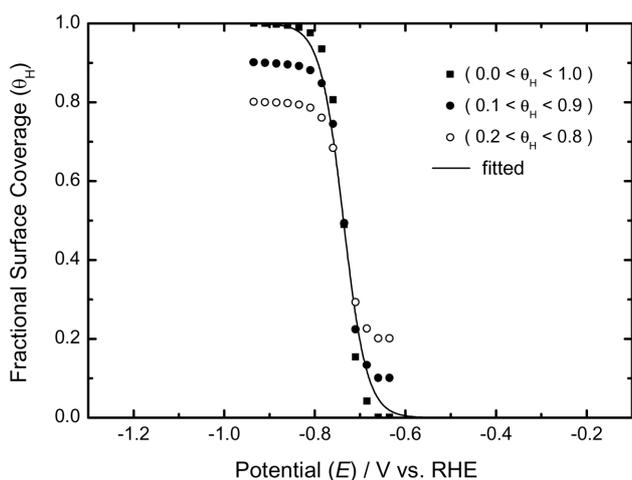
cribed elsewhere.<sup>33-35</sup> The Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) assumes that the electrode catalyst surface is homogeneous and that the lateral interaction effect is negligible. The practical form of the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface can be expressed as

$$[\theta_H/(1 - \theta_H)] = K_H C_{\text{H}^+} [\exp(-EF/RT)] \quad (8)$$

where  $\theta_H$  is the fractional surface coverage of H,  $K_H (=k_1/k_{-1})$  is the equilibrium constant for  $\text{H}$ ,<sup>36)</sup>  $C_{\text{H}^+}$  is the  $\text{H}^+$  concentration in the bulk solution,  $E$  is the electrode potential,  $F$  is the Faraday constant,  $R$  is the gas constant, and  $T$  is the absolute temperature. In Eq. (8),  $E$  is a negative electrode potential as measured against the standard reference electrode, i.e., the SCE.

For the cathodic HER at the Pt/0.1 M KOH solution (pH 12.99) interface, the fitted data, i.e., the numerically calculated Langmuir adsorption isotherms ( $\theta_H$  vs.  $E$ ) using Eq. (8), are shown in Fig. 7. Figs. 7(a), (b), and (c) show the three numerically calculated Langmuir adsorption isotherms ( $\theta_H$  vs.  $E$ ) corresponding to  $K_H=2.9 \times 10^{-2}$ ,  $2.9 \times 10^{-4}$ , and  $2.9 \times 10^{-6} \text{ mol}^{-1}$ , respectively. As expected, the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) shown in Fig. 7(b) can be linearly related to the phase-shift profile ( $-\phi$  vs.  $E$ ) for the optimum intermediate frequency (ca. 1.0 Hz) shown in Fig. 6. From Fig. 7(b), one infers that the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) for  $K_H=2.9 \times 10^{-4} \text{ mol}^{-1}$  is applicable to the formation of H for the cathodic HER at the interface. This implies that the lateral interaction effect of H for the cathodic HER at the interface is negligible. Consequently, it appears that the behavior ( $-\phi$  vs.  $E$ ) of the phase shift ( $0^\circ \leq -\phi \leq 90^\circ$ ) for the optimum intermediate frequency can be linearly related to that ( $\theta_H$  vs.  $E$ ) of the fractional surface coverage ( $1 \geq \theta_H \geq 0$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface.

As shown in Fig. 7, the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) described in Eq. (8) is practically and definitively determined by the value of  $K_H$ , which is defined by the ratio ( $k_1/k_{-1}$ ) between the rate constant ( $k_1$ ) of the forward reaction, i.e., the hydrogen adsorption reaction, and the rate constant ( $k_{-1}$ ) of the reverse reaction, i.e., the hydrogen desorption reaction, in the proton ( $\text{H}^+$ ) discharge reaction described in Eq. (1). Thus, by comparing Fig. 7(b) with Figs. 2(a) and 3(a), one can confirm the validity and effectiveness of the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) at the interface. In other words, the range of  $E$ , ca. -0.70 to -0.83 V vs. RHE, shown in Figs. 2(a) and 3(a) corresponds to the range of  $\theta_H$ , ca. 0.18-0.98, shown in Fig. 7(b). The range of  $\theta_H$ , ca. 0.18-0.98, which corresponds to the portion of the rate-determining step of the proton ( $\text{H}^+$ ) discharge reaction on the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) plot, is sufficiently large to verify the mechanism of H adsorption for the cathodic HER at the interface. Thus, the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) shown in Fig. 7(b) is valid and effective. This implies that the applicability of the Frumkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) is unreasonable or unacceptable at the Pt/0.1 M KOH solution interface. At values of  $\theta_H$ , i.e.,  $\theta_H > 0.98$ , one can interpret that



**Fig. 8.** Comparison of three different ranges of  $\theta_H$  for the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) of H for  $K_H=2.9 \times 10^{-4} \text{ mol}^{-1}$  at the Pt/0.1 M KOH solution interface.

the cathodic HER is determined by the rate-determining step of the electrochemical desorption reaction or the recombination reaction. Finally, considering the high negative values of  $E$  and the rate-determining step of the proton ( $\text{H}^+$ ) discharge reaction corresponding to the range of  $\theta_H$ , one can conclude that the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) shown in Fig. 7(b) is reasonable or acceptable at the Pt/0.1 M KOH solution interface.

Fig. 8 compares three different ranges of  $\theta_H$ , which are estimated using the measured phase shift ( $-\phi$ ) shown in Table 1 and through the previously described procedures, for the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ),  $K_H=2.9 \times 10^{-4} \text{ mol}^{-1}$ , at the Pt/0.1 M KOH solution interface. In contrast to the different values of  $K_H$  shown in Fig. 7, the different ranges of  $\theta_H$  are not of serious concern for determining the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) as shown in Fig. 8.

### 3.5. Frumkin adsorption isotherm

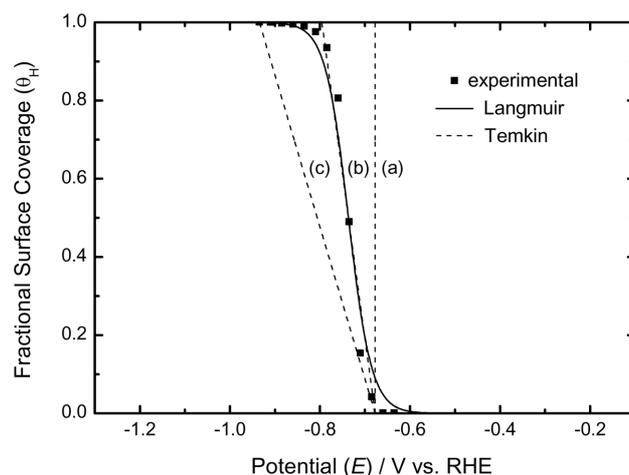
The Frumkin adsorption isotherm ( $\theta$  vs.  $E$ ) assumes that the electrode catalyst surface is inhomogeneous or that the lateral interaction effect is not negligible.<sup>33-35</sup> The practical form of the Frumkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface can be expressed as follows

$$[\theta_H/(1-\theta_H)] \exp(\mathcal{G}\theta_H) = K_{o(H)} C_H^+ [\exp(-EF/RT)] \quad (9)$$

$$\mathcal{G} = r/RT \quad (10)$$

$$K_H = K_{o(H)} \exp(-\mathcal{G}\theta_H) \quad (11)$$

where  $\mathcal{G}$  is the interaction parameter for the Frumkin adsorption isotherm,  $K_{o(H)}$  is the equilibrium constant for H at  $\mathcal{G}=0$ , and  $r$  is the rate of change of the standard free energy of H with  $\theta_H$ , i.e.,  $0 \leq \theta_H \leq 1$ . Note that  $\mathcal{G}=0$  in Eq. (9) is the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) described in Eq. (8).



**Fig. 9.** Comparison of the experimentally determined Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) of H for  $K_H=2.9 \times 10^{-4} \text{ mol}^{-1}$  shown in Fig. 7(b) and three numerically calculated Temkin adsorption isotherms ( $\theta_H$  vs.  $E$ ) of H for  $K_{o(H)}=2.9 \times 10^{-3} \text{ mol}^{-1}$  at the Pt/0.1 M KOH solution interface. (a)  $\mathcal{G}=0$ , (b)  $\mathcal{G}=4.6$ , and (c)  $\mathcal{G}=10$  for  $K_{o(H)}=2.9 \times 10^{-3} \text{ mol}^{-1}$ . Note that Fig. 9(b) shows the Temkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) of H for  $K_H=2.9 \times 10^{-3} \exp(-4.6\theta_H) \text{ mol}^{-1}$ . The Temkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) is only valid and effective at  $0.2 < \theta_H < 0.8$ .

### 3.6. Temkin adsorption isotherm

At intermediate values of  $\theta_H$ , i.e.,  $0.2 < \theta_H < 0.8$ , the pre-exponential term,  $[\theta_H/(1-\theta_H)]$ , varies little with compared to the variation of the exponential term,  $\exp(\mathcal{G}\theta_H)$ . Under the approximate conditions, the Temkin adsorption isotherm ( $\theta$  vs.  $E$ ) can be simply derived from the Frumkin adsorption isotherm ( $\theta$  vs.  $E$ ).<sup>33-35</sup> The practical form of the Temkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) of H for the cathodic HER can be expressed as follows

$$\exp(\mathcal{G}\theta_H) = K_{o(H)} C_H^+ [\exp(-EF/RT)] \quad (12)$$

Fig. 9 shows the determination of the Temkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) corresponding to the Langmuir adsorption isotherm ( $\theta_H$  vs.  $E$ ) shown in Fig. 7(b). This implies that the Langmuir and Temkin adsorption isotherms ( $\theta_H$  vs.  $E$ ) can be converted to each other even though their adsorption conditions or processes are different. Note that this capability is attributed to maximum values of  $R_\phi$  and  $C_\phi$  vs.  $E$  at  $\theta_H=0.5$ , which cannot be measured at the interface, and maximum rates of change of  $-\phi$  and  $\theta_H$  vs.  $E$  for the optimum intermediate frequency at  $\theta_H \approx 0.5$  (refer to Table 1). In Fig. 9(b), the equilibrium constant ( $K_{o(H)}$  at  $\mathcal{G}=0$ ) and the interaction parameter ( $\mathcal{G}$ ) for the Temkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) are  $2.9 \times 10^{-3} \text{ mol}^{-1}$  and 4.6, i.e.,  $K_H=2.9 \times 10^{-3} \exp(-4.6\theta_H) \text{ mol}^{-1}$ , respectively. Using Eq. (10), the rate ( $r$ ) of change of the standard free energy of H with  $\theta_H$  is  $11.4 \text{ kJ mol}^{-1}$  for  $\mathcal{G}=4.6$ .

The equilibrium constants ( $K_H$ ) corresponding to the Langmuir, Temkin, and Frumkin adsorption isotherms ( $\theta_H$  vs.  $E$ ) and fractional surface coverages ( $\theta_H$ ) at the Pt/0.1 M KOH solution interface are summarized in Table 2. In the table, note that the equilibrium constant ( $K_H$ ) for the Langmuir adsorption

**Table 2.** Comparison of the equilibrium constants ( $K_H$ ) corresponding to the electrochemical adsorption isotherms (Langmuir, Temkin, Frumkin) and fractional surface coverages ( $\theta_H$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface.

Adsorption isotherm	$K_H$ (mol <sup>-1</sup> )		
	$0 \leq \theta_H \leq 1$	$0.2 < \theta_H < 0.8$	$\theta_H = 0.5$
Langmuir <sup>a</sup>	$2.9 \times 10^{-4}$	$2.9 \times 10^{-4}$	$2.9 \times 10^{-4}$
Temkin <sup>b</sup>	$2.9 \times 10^{-3} \geq K_H \geq 2.9 \times 10^{-5}$	$1.2 \times 10^{-3} > K_H > 7.3 \times 10^{-5}$	$2.9 \times 10^{-4}$
Frumkin	-	-	-

<sup>a</sup> $\varrho = 0$  for  $K_{\theta(H)} = 2.9 \times 10^{-4}$  mol<sup>-1</sup>, i.e.,  $K_H = 2.9 \times 10^{-4}$  mol<sup>-1</sup>.

<sup>b</sup> $\varrho = 4.6$  for  $K_{\theta(H)} = 2.9 \times 10^{-3}$  mol<sup>-1</sup>, i.e.,  $K_H = 2.9 \times 10^{-3} \exp(-4.6\theta_H)$  mol<sup>-1</sup>.

Note that the Temkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) is only valid and effective at  $0.2 < \theta_H < 0.8$ .

isotherm ( $\theta_H$  vs.  $E$ ) is exactly same as that ( $K_H$ ) for the Temkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) at  $\theta_H = 0.5$ . As stated above, this capability is attributed to maximum values of  $R_\phi$  and  $C_\phi$  vs.  $E$  at  $\theta_H = 0.5$ , which cannot be measured at the interface, and maximum rates of change of  $-\phi$  and  $\theta_H$  vs.  $E$  for the optimum intermediate frequency at  $\theta_H \approx 0.5$ . Table 2 also verifies the validity and effectiveness of the phase-shift method.

### 3.7. Constant conversion factors

At the intermediate values of  $\theta_H$ , i.e.,  $0.2 < \theta < 0.8$ , the Langmuir and Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) of intermediates (H, OH) for sequential reactions (HER, OER) are converted to each other even though their adsorption conditions or processes are different (refer to Fig. 9). This is attributed to maximum values of  $R_\phi$  and  $C_\phi$  vs.  $E$  at  $\theta = 0.5$ , which cannot be measured at the interfaces, and maximum rates of change of  $-\phi$  and  $\theta$  vs.  $E$  at  $\theta \approx 0.5$  rather than the adsorption conditions or processes. Similarly, the Frumkin and Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) of intermediates (H, OH) for sequential reactions (HER, OER) are converted to each other. This implies that the Temkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) of H corresponding to the Langmuir or the Frumkin adsorption isotherm ( $\theta_H$  vs.  $E$ ) of H, and vice versa, can be readily determined using the constant conversion factors.<sup>20,23,28)</sup>

The Langmuir adsorption isotherms ( $\theta$  vs.  $E$ ) of intermediates (H, OH) for the sequential reactions (HER, OER) are always parallel to each other (refer to Fig. 7). This implies that the slopes of the Langmuir adsorption isotherms ( $\theta$  vs.  $E$ ) of intermediates (H, OH) for sequential reactions (HER, OER) are all the same at  $0.2 < \theta < 0.8$ . Thus, the interaction parameters ( $\varrho$ ) for the Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) corresponding to the Langmuir adsorption isotherms ( $\theta$  vs.  $E$ ) are all the same, i.e., ca.  $\varrho = 4.6$ , as shown in Fig. 9. In other words, the interaction parameters ( $\varrho$ ) for the Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) are consistently ca. 4.6 greater than those ( $\varrho$ ) for the corresponding Langmuir adsorption isotherms ( $\theta$  vs.  $E$ ). Similarly, one can conclude that the interaction parameters ( $\varrho$ ) for the Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) are consistently ca. 4.6 greater than those ( $\varrho$ ) for the corresponding Frumkin adsorption isotherms ( $\theta$  vs.  $E$ ).<sup>20,28)</sup> Finally, one can confirm that the equilibrium constants ( $K_\theta$ ) for the Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) are consistently ca. 10 times greater than those ( $K$ ) for the corresponding Langmuir or Frumkin adsorption isotherms ( $\theta$  vs.  $E$ ) (refer to Fig. 9 or Table 2).<sup>20,23,28)</sup> Consequently, it appears that these numbers (ca.

10 times and 4.6) can be taken as constant conversion factors between the Temkin and the Langmuir or the Frumkin adsorption isotherms ( $\theta$  vs.  $E$ ) at electrode catalyst interfaces. The Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) corresponding to the Langmuir or the Frumkin adsorption isotherms ( $\theta$  vs.  $E$ ), and vice versa, can be readily determined using the constant conversion factors. The constant conversion factors between the Temkin and the Langmuir or the Frumkin adsorption isotherms ( $\theta$  vs.  $E$ ) also verify the validity and effectiveness of the phase-shift method. However, this aspect was overlooked or not well interpreted in our previously published papers.

### 3.8. Standard free energy

The standard free energy of H is given by the difference between the standard molar Gibbs free energy of H and that of a number of water molecules on the adsorption sites of the electrode catalyst surface. Under the Langmuir adsorption conditions, the relation between the equilibrium constant ( $K_H$ ) and the standard free energy ( $\Delta G_{\text{ads}}^\circ$ ) is given as follows<sup>33)</sup>

$$2.3RT \log K_H = -\Delta G_{\text{ads}}^\circ \quad (13)$$

The definition of  $\Delta G_{\text{ads}}^\circ$  is described elsewhere.<sup>37,38)</sup> At the Pt/0.1 M KOH solution interface, using Eq. (13),  $\Delta G_{\text{ads}}^\circ$  of H for the cathodic HER shown in Fig. 7(b) is 20.2 kJ mol<sup>-1</sup> for  $K_H = 2.9 \times 10^{-4}$  mol<sup>-1</sup>. As expected, the adsorption process of H for the cathodic HER at the Pt/0.1 M KOH solution interface is an endothermic reaction, i.e.,  $\Delta G_{\text{ads}}^\circ > 0$ .

Under the Frumkin or the Temkin adsorption conditions, the relation between the equilibrium constant ( $K_H$ ) and the standard free energy ( $\Delta G_\theta^\circ$ ) is given as follows<sup>33)</sup>

$$2.3RT \log K_H = -\Delta G_\theta^\circ \quad (14)$$

In contrast to  $\Delta G_{\text{ads}}^\circ$  described in Eq. (13),  $\Delta G_\theta^\circ$  depends on  $\theta_H$ , i.e.,  $0 \leq \theta_H \leq 1$  and  $0.2 < \theta_H < 0.8$  for the Frumkin and Temkin adsorption isotherms, respectively. At the Pt/0.1 M KOH solution interface, using Eqs. (11) and (14),  $\Delta G_\theta^\circ$  of H for the cathodic HER shown in Fig. 9(b) is  $16.7 < \Delta G_\theta^\circ < 23.6$  kJ mol<sup>-1</sup> for  $1.2 \times 10^{-3} > K_H > 7.3 \times 10^{-5}$  mol<sup>-1</sup>, i.e.,  $K_H = 2.9 \times 10^{-3} \exp(-4.6\theta_H)$  mol<sup>-1</sup> and  $0.2 < \theta_H < 0.8$ . The standard free energies ( $\Delta G_{\text{ads}}^\circ, \Delta G_\theta^\circ$ ) corresponding to the equilibrium constants ( $K_H$ ) and fractional surface coverages ( $\theta_H$ ) of H at the Pt/0.1 M KOH solution interface are summarized in Table 3.

**Table 3.** Comparison of the standard free energies ( $\Delta G_{\text{ads}}^{\circ}$ ,  $\Delta G_{\theta}^{\circ}$ ) corresponding to the equilibrium constants ( $K_{\text{H}}$ ) and fractional surface coverages ( $\theta_{\text{H}}$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface.

Adsorption isotherm	$\Delta G_{\text{ads}}^{\circ}$ , $\Delta G_{\theta}^{\circ}$ (kJ mol <sup>-1</sup> )	$K_{\text{H}}$ (mol <sup>-1</sup> )	$\theta_{\text{H}}$
Langmuir	20.2	$2.9 \times 10^{-4}$	$0 \leq \theta_{\text{H}} \leq 1$
Temkin	$16.7 < \Delta G_{\theta}^{\circ} < 23.6$	$1.2 \times 10^{-3} > K_{\text{H}} > 7.3 \times 10^{-5}$	$0.2 < \theta_{\text{H}} < 0.8$
Frumkin	-	-	-

### 3.9. Complementary statements

The Langmuir and Temkin adsorption isotherms ( $\theta_{\text{H}}$  vs.  $E$ ) of H for the cathodic HER at the Pt/0.1 M KOH solution interface can be practically determined using the phase-shift curves ( $-\phi$  vs.  $\log f$ ) and the phase-shift profile ( $-\phi$  vs.  $E$ ) for the optimum intermediate frequency. Note that the other steps or procedures in this paper are only used to verify the validity and effectiveness of the phase-shift method and constant conversion factors. It appears that the phase-shift method and constant conversion factors are useful and effective for determining the Langmuir, Frumkin, and Temkin adsorption isotherms ( $\theta_{\text{H}}$  vs.  $E$ ) and related electrode kinetic and thermodynamic data ( $K$ ,  $g$ ,  $r$ ,  $\Delta G_{\text{ads}}^{\circ}$ ,  $\Delta G_{\theta}^{\circ}$ ) at the interface.

The linear relationship between the phase-shift profile ( $-\phi$  vs.  $E$ ) for the optimum intermediate frequency and the corresponding Langmuir, Frumkin, and Temkin adsorption isotherms ( $\theta_{\text{H}}$  vs.  $E$ ) at the Pt electrode catalyst interface, i.e., the phase-shift method, is proposed based on purely empirical relationships. A single equation for  $\phi$  vs.  $\theta_{\text{H}}$  as a function of potential ( $E$ ) and frequency ( $f$ ) might be represented theoretically or numerically at the interface. At present, the various effects on the adsorption process of H for the cathodic HER at the Pt electrode catalyst interface have not been combined into a single equation for the linear relationship. Therefore, it seems difficult or time consuming to obtain a linear relationship based on theoretical derivations or numerical calculations.<sup>28)</sup>

## 4. Conclusions

The phase-shift method and constant conversion factors for determining the Langmuir and Temkin adsorption isotherms ( $\theta_{\text{H}}$  vs.  $E$ ) of H for the cathodic HER at a Pt/0.1 M KOH solution interface are proposed and verified. At the Pt/0.1 M KOH solution interface, the Langmuir and Temkin adsorption isotherms ( $\theta_{\text{H}}$  vs.  $E$ ), the equilibrium constants ( $K_{\text{H}}=2.9 \times 10^{-4}$  mol<sup>-1</sup> for the Langmuir and  $K_{\text{H}}=2.9 \times 10^{-3} \exp(-4.6\theta_{\text{H}})$  mol<sup>-1</sup> for the Temkin adsorption isotherm), the interaction parameters ( $g=0$  for the Langmuir and  $g=4.6$  for the Temkin adsorption isotherm), the rate of change of the standard free energy of H with  $\theta_{\text{H}}$  ( $r=11.4$  kJ mol<sup>-1</sup> for  $g=4.6$ ), and the standard free energies ( $\Delta G_{\text{ads}}^{\circ}=20.2$  kJ mol<sup>-1</sup> for  $K_{\text{H}}=2.9 \times 10^{-4}$  mol<sup>-1</sup>, i.e., the Langmuir adsorption isotherm, and  $16.7 < \Delta G_{\theta}^{\circ} < 23.6$  kJ mol<sup>-1</sup> for  $K_{\text{H}}=2.9 \times 10^{-3} \exp(-4.6\theta_{\text{H}})$  mol<sup>-1</sup> and  $0.2 < \theta_{\text{H}} < 0.8$ , i.e., the Temkin adsorption isotherm) of H for the cathodic HER are determined using the phase-shift method. At the intermediate values of  $\theta_{\text{H}}$ , i.e.,  $0.2 < \theta_{\text{H}} < 0.8$ , the Temkin adsorption isotherm ( $\theta_{\text{H}}$  vs.  $E$ ) corresponding to the Langmuir adsorption isotherm ( $\theta_{\text{H}}$  vs.  $E$ ), and vice versa, is readily determined using the constant conversion factors. The phase-shift method and constant conversion

factors are useful and effective for determining the Langmuir, Frumkin, and Temkin adsorption isotherms of intermediates for sequential reactions and related electrode kinetic and thermodynamic data at electrode catalyst interfaces.

### Footnotes

1. A linear relationship between the behaviors ( $-\phi$  vs.  $E$ ) of the phase shift ( $0^{\circ} \leq -\phi \leq 90^{\circ}$ ) for the optimum intermediate frequencies and those ( $\theta_{\text{H}}$  vs.  $E$ ) of the fractional surface coverage ( $1 \geq \theta_{\text{H}} \geq 0$ ) of H at electrode catalyst/aqueous solution interfaces has been proposed and verified using cyclic voltammetric, linear sweep voltammetric or differential pulse voltammetric, and electrochemical impedance spectroscopic techniques. The behaviors ( $\theta$  vs.  $E$ ) of the fractional surface coverage ( $1 \geq \theta \geq 0$ ) of intermediates (H, OH) for sequential reactions (HER, OER) are well known as the Langmuir, Frumkin, and Temkin adsorption isotherms ( $\theta$  vs.  $E$ ).

2. Thermodynamic equilibrium constants are dimensionless because they are expressed in terms of activities rather than concentrations. The convention in chemical kinetics is to use concentrations rather than activities. Therefore, the equilibrium constant  $K_{\text{H}}$  described in the Langmuir, Frumkin, and Temkin adsorption isotherms ( $\theta_{\text{H}}$  vs.  $E$ ) is the empirical equilibrium constant. This constant is not dimensionless and must be multiplied by the concentration of the reference state to be made equal to the thermodynamic equilibrium constant. Nevertheless, to maintain consistency with the conventions of chemical kinetics, such constant as  $K_{\text{H}}$  is referred to as the thermodynamic equilibrium constant in the Langmuir, Frumkin, and Temkin adsorption isotherms ( $\theta_{\text{H}}$  vs.  $E$ ).

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### References

1. E. Gileadi (Ed.), "Electrosorption", Plenum Press, New York, 1967.
2. E. Gileadi, E. Kirova-Eisner, and J. Penciner, "Interfacial electrochemistry", Addison-Wesley Pub. Co. Reading, MA, 1975.
3. S. Trasatti, "Advances in electrochemical science and engineering", Vol. 2, pp. 185, in: H. Gerischer and T. Tobias (Eds.), VCH, New York, 2000.
4. E. Gileadi, "Electrode kinetics", VCH, New York, 1993.
5. J. O'M. Bockris and S. U. M. Khan, "Surface electrochemistry", Plenum Press, New York, 1993.
6. B. E. Conway and G. Jerkiewicz (Eds.), "Electrochemistry and materials science of cathodic hydrogen absorption and adsorption",

- PV 9421, The Electrochemical Society, Pennington, NJ, 1995.
7. G. Jerkiewicz, "Hydrogen sorption at/in electrodes", *Prog. Surf. Sci.*, **57**, 137 (1998).
  8. G. Jerkiewicz, J. M. Feliu, and B. N. Popov (Eds.), "Hydrogen at surface and interfaces", PV 2000-16, The Electrochemical Society, Pennington, NJ, 2000.
  9. J. H. Chun and K. H. Ra, "The phase-shift method for the Frumkin adsorption isotherms at the Pd/H<sub>2</sub>SO<sub>4</sub> and KOH solution interfaces", *J. Electrochem. Soc.*, **145**, 3794 (1998).
  10. J. H. Chun and K. H. Ra, "Hydrogen at surface and interfaces", in: G. Jerkiewicz, J. M. Feliu, B. N. Popov (Eds.), PV 2000-16, pp. 159-173, The Electrochemical Society, Pennington, NJ, 2000.
  11. J. H. Chun, K. H. Ra, and N. Y. Kim, "The Langmuir adsorption isotherms of electroadsorbed hydrogens for the cathodic hydrogen evolution reactions at the Pt(100)/H<sub>2</sub>SO<sub>4</sub> and LiOH aqueous electrolyte interfaces", *Int. J. Hydrogen Energy*, **26**, 941 (2001).
  12. J. H. Chun, S. K. Jeon, and J. H. Lee, "The phase-shift method for the Langmuir adsorption isotherms of electroadsorbed H for the cathodic H<sub>2</sub> evolution reactions at the poly-Pt electrode interfaces", *J. Korean Electrochem. Soc.*, **5**, 131 (2002).
  13. J. H. Chun, K. H. Ra, and N. Y. Kim, "Qualitative analysis of the Frumkin adsorption isotherm of the over-potentially deposited hydrogen at the poly-Ni/KOH aqueous electrolyte interface using the phase-shift method", *J. Electrochem. Soc.*, **149**, E325 (2002).
  14. J. H. Chun, K. H. Ra, and N. Y. Kim, "Langmuir adsorption isotherms of over-potentially deposited hydrogen at poly-Au and Rh/H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interfaces: Qualitative analysis using the phase-shift method", *J. Electrochem. Soc.*, **150**, E207 (2003).
  15. J. H. Chun, K. H. Ra, and N. Y. Kim, Abstracts of the 203rd Electrochemical Society (ECS) Meeting, Vol. 2003-01, Abstract 1270, April 27-May 2, The Electrochemical Society, Paris, France, 2003.
  16. J. H. Chun, S. K. Jeon, and N. Y. Kim, Abstracts of the 203rd Electrochemical Society (ECS) Meeting, Vol. 2003-01, Abstract 2332, The Electrochemical Society, April 27-May 2, Paris, France, 2003.
  17. J. H. Chun and S. K. Jeon, "Determination of the equilibrium constant and standard free energy of the over-potentially deposited hydrogen for the cathodic H<sub>2</sub> evolution reaction at the Pt-Rh alloy electrode interface using the phase-shift method", *Int. J. Hydrogen Energy*, **28**, 1333 (2003).
  18. J. H. Chun, "Methods for estimating adsorption isotherms in electrochemical systems", *U.S. Patent*, **6613218** (2003).
  19. J. H. Chun and N. Y. Kim, "Hydrogen treatment of materials. Proceedings of the 4th international conference: HTM-2004", pp. 387-393, International Scientific Committee on Hydrogen Treatment of Materials (HTM), May 17-21, Donetsk-Svyatogorsk, Ukraine, 2004.
  20. J. H. Chun, S. K. Jeon, and J. Y. Chun, "Constant correlation factors between Temkin and Langmuir or Frumkin adsorption isotherms in electrochemical systems", *J. Korean Electrochem. Soc.*, **7**, 194 (2004).
  21. J. H. Chun, S. K. Jeon, B. K. Kim, and J. Y. Chun, "Determination of the Langmuir adsorption isotherms of under- and over-potentially deposited hydrogen for the cathodic H<sub>2</sub> evolution reaction at poly-Ir/ aqueous electrolyte interfaces using the phase-shift method", *Int. J. Hydrogen Energy*, **30**, 247 (2005).
  22. J. H. Chun, S. K. Jeon, K. H. Ra, and J. Y. Chun, "The phase-shift method for determining Langmuir adsorption isotherms of over-potentially deposited hydrogen for the cathodic H<sub>2</sub> evolution reaction at poly-Re/aqueous electrolyte interfaces", *Int. J. Hydrogen Energy*, **30**, 485 (2005).
  23. J. H. Chun, S. K. Jeon, N. Y. Kim, and J. Y. Chun, "The phase-shift method for determining Langmuir and Temkin adsorption isotherms of over-potentially deposited hydrogen for the cathodic H<sub>2</sub> evolution reaction at the poly-Pt/H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface", *Int. J. Hydrogen Energy*, **30**, 1423 (2005).
  24. J. H. Chun and N. Y. Kim, "The phase-shift method for determining adsorption isotherms of hydrogen in electrochemical systems", *Int. J. Hydrogen Energy*, **31**, 277 (2006).
  25. K. Kvastek and V. Horvat-Radosevic, "Comment on the paper 'Langmuir adsorption isotherms of over-potentially deposited hydrogen at poly-Au and Rh/H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interfaces: Qualitative analysis using the phase-shift method' ", *J. Electrochem. Soc.*, **151**, L9 (2004).
  26. J. H. Chun, K. H. Ra, and N. Y. Kim, "Response to comment on 'Langmuir adsorption isotherms of over-potentially deposited hydrogen at poly-Au and Rh/H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interfaces: Qualitative analysis using the phase-shift method' ", *J. Electrochem. Soc.*, **151**, L11 (2004).
  27. A. Lasia, "Comments on 'The phase-shift method for determining Langmuir adsorption isotherms of over-potentially deposited hydrogen for the cathodic H<sub>2</sub> evolution reaction at poly-Re/aqueous electrolyte interfaces. Hydrogen Energy, 30 (2005) 485-499' ", *Int. J. Hydrogen Energy*, **30**, 913 (2005).
  28. J. H. Chun, S. K. Jeon, N. Y. Kim, and J. Y. Chun, "Response to comments on 'The phase-shift method for determining Langmuir adsorption isotherms of over-potentially deposited hydrogen for the cathodic H<sub>2</sub> evolution reaction at poly-Re/aqueous electrolyte interfaces. Hydrogen Energy, 30 (2005) 485-499' ", *Int. J. Hydrogen Energy*, **30**, 919 (2005).
  29. E. Gileadi, E. Kirowa-Eisner, and J. Penciner, "Interfacial electrochemistry", pp. 6, 72-73, Addison-Wesley Pub. Co. Reading, MA, 1975.
  30. D. M. Macarthur, "Characterization of solid surfaces", pp. 181-201, in: P. F. Kane and G. B. Larrabee (Eds.), Plenum Press, New York, 1978.
  31. E. Gileadi, E. Kirowa-Eisner, and J. Penciner, "Interfacial electrochemistry", pp. 86-93, Addison-Wesley Pub. Co. Reading, MA, 1975.
  32. E. Gileadi, "Electrode kinetics", pp. 293-303, VCH, New York, 1993.
  33. E. Gileadi, "Electrode kinetics", pp. 261-280, VCH, New York, 1993.
  34. J. O'M. Bockris and S. U. M. Khan, "Surface electrochemistry", pp. 280-283, Plenum Press, New York, 1993.
  35. J. O'M. Bockris, A. K. N. Reddy, and M. Gamboa-Aldeco, "Modern electrochemistry", 2nd Ed., Vol. 2A, pp. 1193-1194, Kluwer Academic/Plenum Pub. Co. New York, 2000.
  36. D. W. Oxtoby, H. P. Gillis, and N. H. Nachtrieb, "Principles of modern chemistry", 5th Ed., p. 446, Thomson Learning Inc. 2002.
  37. E. Gileadi, "Electrosorption", pp. 1-18, in: E. Gileadi (Ed.), Plenum Press, New York, 1967.
  38. E. Gileadi, "Electrode kinetics", pp. 307-318, VCH, New York, 1993.