

Determination of Adsorption Isotherms of Hydrogen on Zirconium in Sulfuric Acid Solution Using the Phase-Shift Method and Correlation Constants

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Abstract : The phase-shift method and correlation constants, i.e., the unique electrochemical impedance spectroscopy (EIS) techniques for studying the linear relationship between the behavior ($-\varphi$ vs. E) of the phase shift ($90^\circ \geq -\varphi \geq 0^\circ$) for the optimum intermediate frequency and that (θ vs. E) of the fractional surface coverage ($0 \leq \theta \leq 1$), have been proposed and verified to determine the Langmuir, Frumkin, and Temkin adsorption isotherms of H and related electrode kinetic and thermodynamic parameters at noble metal (alloy)/aqueous solution interfaces. At a Zr/0.2 M H₂SO₄ aqueous solution interface, the Frumkin and Temkin adsorption isotherms (θ vs. E), equilibrium constants ($K = 1.401 \times 10^{-17} \exp(-3.5\theta) \text{ mol}^{-1}$ for the Frumkin and $K = 1.401 \times 10^{-16} \exp(-8.1\theta) \text{ mol}^{-1}$ for the Temkin adsorption isotherm), interaction parameters ($g = 3.5$ for the Frumkin and $g = 8.1$ for the Temkin adsorption isotherm), rates of change of the standard free energy ($r = 8.7 \text{ kJ mol}^{-1}$ for $g = 3.5$ and $r = 20 \text{ kJ mol}^{-1}$ for $g = 8.1$) of H with θ , and standard free energies ($96.13 \leq \Delta G_0^0 \leq 104.8 \text{ kJ mol}^{-1}$ for $K = 1.401 \times 10^{-17} \exp(-3.5\theta) \text{ mol}^{-1}$ and $0 \leq \theta \leq 1$ and $94.44 < \Delta G_0^0 < 106.5 \text{ kJ mol}^{-1}$ for $K = 1.401 \times 10^{-16} \exp(-8.1\theta) \text{ mol}^{-1}$ and $0.2 < \theta < 0.8$) of H are determined using the phase-shift method and correlation constants. At $0.2 < \theta < 0.8$, the Temkin adsorption isotherm correlating with the Frumkin adsorption isotherm, and vice versa, is readily determined using the correlation constants. The phase-shift method and correlation constants are probably the most accurate, useful, and effective ways to determine the adsorption isotherms of H and related electrode kinetic and thermodynamic parameters at highly corrosion-resistant metal/aqueous solution interfaces.

Keywords : Phase-shift method, Correlation constants, Hydrogen adsorption, Frumkin and Temkin adsorption isotherms, Zirconium, Highly corrosion-resistant metals.

1. Introduction

Zirconium and its alloys have been widely used as highly corrosion-resistant materials due to their excellent corrosion resistances. Also, they have been extensively studied to use hydrogen storage materials, nuclear engineering materials, biomaterials, etc.¹⁻⁹ However, it seems that the adsorption isotherms of hydrogen and related electrode kinetic and thermodynamic parameters at zirconium and its alloy/aqueous solution interfaces have never been reported elsewhere.

At highly corrosion-resistant metal/aqueous solution 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 these adsorption isotherms are associated more directly with the atomic mechanism of H adsorption. Thus, there is a technological need for a simple, accurate, and reliable method to determine the Langmuir, Frumkin, and Temkin adsorption isotherms for characterizing the H adsorptions at highly corrosion-resistant metal/aqueous solution interfaces.

The phase-shift method is the unique electrochemical

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impedance spectroscopy (EIS) technique for studying the linear relationship between the behavior ($-\varphi$ vs. E) of the phase shift ($90^\circ \geq -\varphi \geq 0^\circ$) for the optimum intermediate frequency and that (θ vs. E) of the fractional surface coverage ($0 \leq \theta \leq 1$) at noble metal (alloy)/aqueous solution interfaces.¹⁰⁻²⁸⁾ The behavior (θ vs. E) of the fractional surface coverage ($0 \leq \theta \leq 1$) is well known as the Langmuir or the Frumkin adsorption isotherm. Correspondingly, the phase-shift method is useful and effective for determining the Langmuir, Frumkin, and Temkin adsorption isotherms of H and related electrode kinetic and thermodynamic parameters at these interfaces.

In practice, the theoretical derivation or the numerical calculation of a single equation for $-\varphi$ vs. θ as a function of potential (E) and frequency (f) is complex due to the superposition of various effects, i.e., relaxation time effect, real surface area problems, surface absorption and diffusion processes, inhomogeneous and lateral interaction effects, specific adsorption effect, etc., at the interfaces. This is the reason why the phase-shift method is necessary, useful, and effective.

In this paper, we represent the Frumkin and Temkin adsorption isotherms of H and related electrode kinetic and thermodynamic parameters at a Zr/0.2 M H₂SO₄ aqueous solution interface using the phase-shift method and correlation constants. It appears that the phase-shift method and correlation constants are the most accurate, useful, and effective ways to determine the adsorption isotherms of H and related electrode kinetic and thermodynamic parameters at highly corrosion-resistant metal/aqueous solution interfaces.²⁹⁾

2. Experimental

2.1. Preparations

Taking into account the H⁺ concentration and effects of the diffuse double layer and pH,³⁰⁾ an acidic aqueous solution was prepared from H₂SO₄ (Sigma-Aldrich, reagent grade) with purified water (resistivity: > 18 MΩ cm) obtained from a Millipore system. The 0.2 M H₂SO₄ aqueous solution (pH 0.58) 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 zirconium foil (Johnson Matthey, purity: 99.2%, 1 mm thick, estimated area: ca. 5.43 cm²) working electrode. The Zr foil was polished to

a mirror finish with Al₂O₃ powders, ultrasonically cleaned in the purified water, and finally rinsed with acetone. A platinum wire (Johnson Matthey, purity: 99.95%, 1.5 mm diameter) was used as the counter electrode.

2.2. Measurements

A cyclic voltammetry (CV) technique was used to achieve the steady state at the Zr/0.2 M H₂SO₄ aqueous solution interface. The CV experiments were conducted for 30 cycles, a scan rate of 50 mV s⁻¹, and a scan potential of 0 to -1.240 V vs. SCE for the H adsorption. An EIS technique was used to study the relation between the phase-shift profile ($-\varphi$ vs. E) for the optimum intermediate frequency and the corresponding surface-coverage profile (θ vs. E), i.e., the Langmuir, the Frumkin, or the Temkin adsorption isotherm. The EIS experiments were conducted at a single sine wave, a scan frequency of 3×10^4 to 1 Hz, an ac amplitude of 5 mV, and a dc potential of 0 to -1.350 V vs. SCE for the H adsorption.

The CV experiments were performed using an EG&G PAR Model 273A potentiostat controlled with the PAR Model 270 software package. The EIS 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 H adsorption in the different aqueous solutions, all potentials are given in the reversible hydrogen electrode (RHE) scale. The Gaussian and adsorption isotherm analyses were carried out using the Excel and Origin software packages.

3. Results and Discussion

3.1. The basic concept and description on the phase-shift method

Fig. 1 compares the phase-shift curves ($-\varphi$ vs. $\log f$) for the different potentials (E) at the Zr/0.2 M H₂SO₄ aqueous solution interface. The intermediate frequency, i.e., a vertical solid line (47.55 Hz) on $-\varphi$ vs. $\log f$ shown in Fig. 1, can be set as the optimum intermediate frequency for $-\varphi$ vs. E and θ vs. E . At this frequency (47.55 Hz), the normalized change

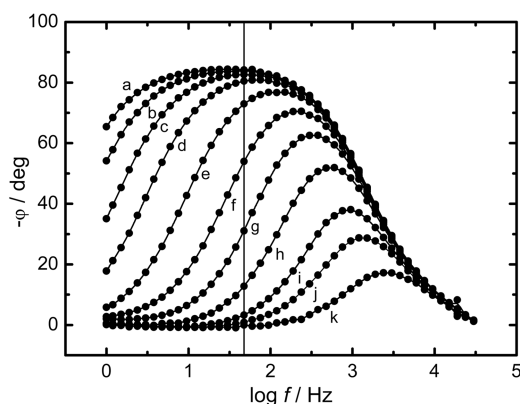


Fig. 1. Comparison of the phase-shift curves ($-\phi$ vs. $\log f$) at the Zr/0.2 M H_2SO_4 aqueous solution interface. Vertical solid line: 47.55 Hz; single sine wave; scan frequency: 3×10^4 to 1 Hz; ac amplitude: 5 mV; dc potential: (a) -0.509 V, (b) -0.609 V, (c) -0.659 V, (d) -0.709 V, (e) -0.759 V, (f) -0.809 V, (g) -0.859 V, (h) -0.909 V, (i) -0.959 V, (j) -1.009 V, and (k) -1.109 V vs. RHE.

rate of $-\phi$ vs. E , i.e., $\Delta(-\phi)/\Delta E$, corresponds to that of θ vs. E , i.e., $\Delta\theta/\Delta E$, and vice versa. Both $\Delta(-\phi)/\Delta E$ and $\Delta\theta/\Delta E$ are maximized at $\theta \approx 0.5$, decrease symmetrically with E at other values of θ , and are minimized at $\theta \approx 0$ and 1 (see Fig. 4(c)). Note that this is a unique feature of the Langmuir or the Frumkin adsorption isotherm.¹⁰⁻²⁹⁾

At the maximum lagged phase shift shown in Fig. 1(a), it appears that the H adsorption and superposition of various effects are minimized, i.e., $\theta \approx 0$. At $\theta \approx 0$, both $\Delta(-\phi)/\Delta E$ and $\Delta\theta/\Delta E$ are minimized. At the minimum lagged phase shift shown in Fig. 1(k), it appears that the H adsorption and superposition of various effects are maximized or almost saturated, i.e., $\theta \approx 1$. At $\theta \approx 1$, both $\Delta(-\phi)/\Delta E$ and $\Delta\theta/\Delta E$ are also minimized. At the medium lagged phase shift shown in Figs. 1(f) and (g), it appears that both $\Delta(-\phi)/\Delta E$ and $\Delta\theta/\Delta E$ are maximized, i.e., $\theta \approx 0.5$. At other lagged phase shifts shown in Figs. 1(c)-(f) and (g)-(i), i.e., at other values of θ , it appears that both $\Delta(-\phi)/\Delta E$ and $\Delta\theta/\Delta E$ decrease symmetrically with E (see Fig. 4(c)).

Based on $-\phi$ vs. $\log f$ shown in Fig. 1, the linear relationship between $-\phi$ vs. E and θ vs. E for the optimum intermediate frequency,¹⁰⁻²⁹⁾ and the unique feature of electrosorption,^{31,32)} the basic concept and description on the phase-shift method are summarized in Table 1. Table 1 shows the changes of $-\phi$ vs. E and θ vs. E for the optimum intermediate frequency (47.55 Hz) with 50 mV increment changes in negative

Table 1. Measured values of the phase shift ($-\phi$) for the optimum intermediate frequency (47.55 Hz), the estimated fractional surface coverage (θ) of H, and the normalized change rates ($\Delta(-\phi)/\Delta E$, $\Delta\theta/\Delta E$) at the Zr/0.2 M H_2SO_4 aqueous solution interface

| E / V vs. RHE | $-\phi$ / deg | θ ($0 \leq \theta \leq 1$) | $\Delta(-\phi), \Delta\theta/\Delta E$ |
|---------------|---------------|-------------------------------------|--|
| -0.509 | 84.2 | ≈ 0 | - |
| -0.559 | 84.0 | 0.002375 | 0.028504 |
| -0.609 | 83.7 | 0.005938 | 0.042755 |
| -0.659 | 82.6 | 0.019002 | 0.156770 |
| -0.709 | 80.5 | 0.043943 | 0.299287 |
| -0.759 | 73.0 | 0.133017 | 1.068884 |
| -0.809 | 54.0 | 0.358670 | 2.707838 |
| -0.859 | 31.0 | 0.631829 | 3.277910 |
| -0.909 | 12.8 | 0.847981 | 2.593824 |
| -0.959 | 3.3 | 0.960808 | 1.353919 |
| -1.009 | 0.9 | 0.989311 | 0.342043 |
| -1.059 | 0.3 | 0.996437 | 0.085511 |
| -1.109 | 0 | ≈ 1 | 0.042755 |

potential (E). These changes of $-\phi$ vs. E and θ vs. E for 47.55 Hz are plotted in Figs. 2 and 3, respectively. The changes of $-\phi$ vs. E and θ vs. E for other frequencies (1 Hz, 23.83 Hz, 75.36 Hz, 475.5 Hz) plotted in Figs. 2 and 3, respectively, are also obtained through the same procedures summarized in Table 1. Table 1 also shows that both $\Delta(-\phi)/\Delta E$ and $\Delta\theta/\Delta E$ for the optimum intermediate frequency (47.55 Hz) are exactly the same.

Figs. 2 and 3 compare the phase-shift profiles ($-\phi$ vs. E) and surface-coverage profiles (θ vs. E) for five different frequencies at the Zr/0.2 M H_2SO_4 aqueous solution interface, respectively. Note that θ vs. E shown in Fig. 3 corresponds to $-\phi$ vs. E shown in Fig. 2 and vice versa. In Fig. 3, it is understood that only one adsorption isotherm can be fitted to θ vs. E for the optimum intermediate frequency.

Fig. 4 compares the normalized change rates of $-\phi$ vs. E and θ vs. E , $\Delta(-\phi)/\Delta E$ and $\Delta\theta/\Delta E$, for five different frequencies at the Zr/0.2 M H_2SO_4 aqueous solution interface. Both $\Delta(-\phi)/\Delta E$ and $\Delta\theta/\Delta E$ shown in Fig. 4 are plotted based on $-\phi$ vs. E and θ vs. E shown in Figs. 2 and 3, respectively. The Gaussian profile shown in Fig. 4(c) is plotted based on $\Delta(-\phi)/\Delta E$ and $\Delta\theta/\Delta E$ for the optimum intermediate frequency (47.55 Hz) summarized in Table 1. Similarly, the Gaussian profiles for 1 Hz, 23.83 Hz, 75.36 Hz, and 475.5 Hz shown in Figs. 4(a), (b), (d), and (e), respectively, are plotted through the same procedures summarized in Table 1. At the optimum intermediate frequency (47.55 Hz)

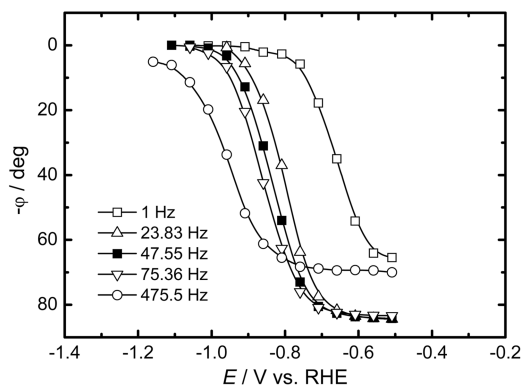


Fig. 2. Comparison of the phase-shift profiles ($-\phi$ vs. E) for five different frequencies at the Zr/0.2 M H_2SO_4 aqueous solution interface. The optimum intermediate frequency is 47.55 Hz.

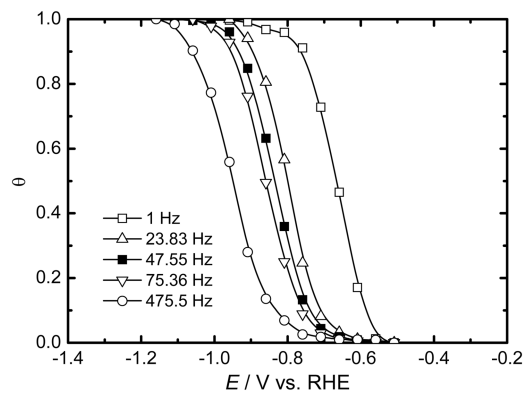


Fig. 3. Comparison of the surface-coverage profiles (θ vs. E) for five different frequencies at the Zr/0.2 M H_2SO_4 aqueous solution interface. The optimum intermediate frequency is 47.55 Hz.

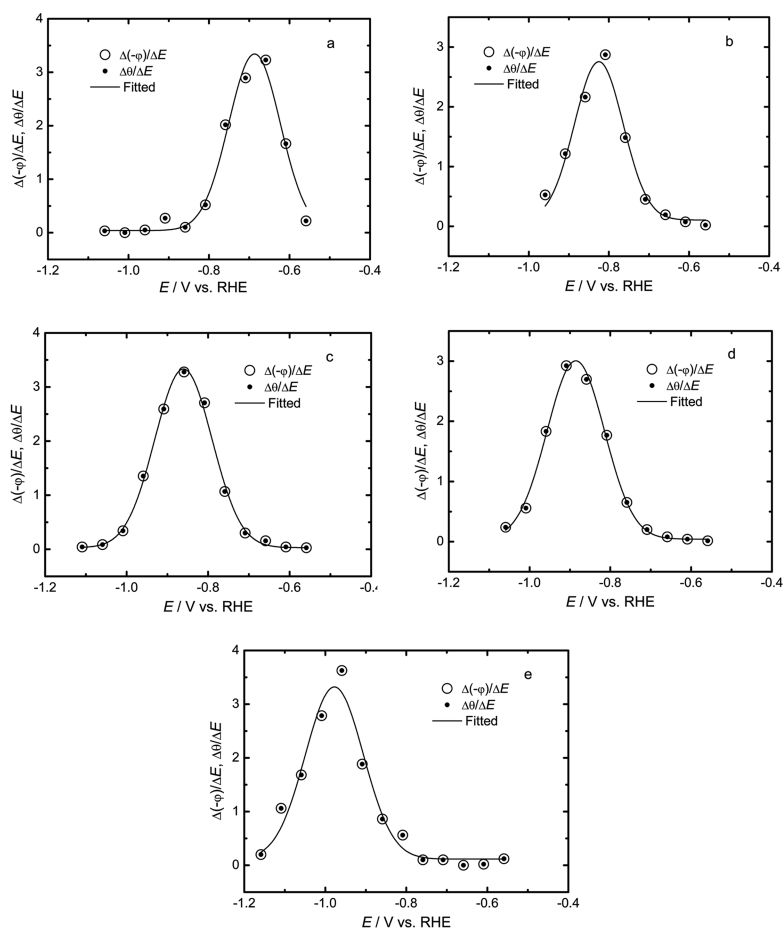


Fig. 4. Comparison of the normalized change rates of $-\phi$ vs. E and θ vs. E , $\Delta(-\phi)/\Delta E$ and $\Delta\theta/\Delta E$, for five different frequencies at the Zr/0.2 M H_2SO_4 aqueous solution interface. (a) 1 Hz, (b) 23.83 Hz, (c) 47.55 Hz, (d) 75.36 Hz, and (e) 475.5 Hz. Note that the optimum intermediate frequency is 47.55 Hz. The fitted curves are all Gaussian profiles.

shown in Fig. 4(c), $\Delta(-\varphi)/\Delta E$ corresponds to $\Delta\theta/\Delta E$ and vice versa. Both $\Delta(-\varphi)/\Delta E$ and $\Delta\theta/\Delta E$ are maximized at $\theta \approx 0.5$, decrease symmetrically with E at other values of θ , and are minimized at $\theta \approx 0$ and 1. Correspondingly, both $\Delta(-\varphi)/\Delta E$ and $\Delta\theta/\Delta E$ obey a Gaussian distribution. Note that the Gaussian profile shown in Fig. 4(c) is the unique feature of the Frumkin adsorption isotherm (θ vs. E). The whole procedure of the phase-shift method for determining the adsorption isotherms of hydrogen and hydroxide is described elsewhere.²⁶⁾

3.2. The Frumkin, Langmuir, and Temkin adsorption isotherms

The derivation of the practical forms of the electrochemical Langmuir, Frumkin, and Temkin adsorption isotherms is described elsewhere.^{33,34)} The Frumkin adsorption isotherm assumes that the electrode surface is inhomogeneous or that the lateral interaction effect is not negligible. The Frumkin adsorption isotherm (θ vs. E) of H at the Zr/0.2 M H₂SO₄ aqueous solution interface can be expressed as follows³³⁾

$$[\theta/(1 - \theta)] \exp(g\theta) = K_0 C_H^+ [\exp(-EF/RT)] \quad (1)$$

$$g = r/RT \quad (2)$$

$$K = K_0 \exp(-g\theta) \quad (3)$$

where θ ($0 \leq \theta \leq 1$) is the fractional surface coverage of H, g is the interaction parameter for the Frumkin adsorption isotherm, K_0 is the equilibrium constant for H at $g = 0$, C_H^+ is the H⁺ concentration in the bulk solution, E is the potential, F is Faraday's constant, R is the gas constant, T is the absolute temperature, r is the rate of change of the standard free energy of H with θ , and K is the equilibrium constant for H. The dimension of K is described elsewhere.³⁵⁾ Note that $g = 0$ in Eqs. (1)-(3) implies the Langmuir adsorption isotherm. For the Langmuir adsorption isotherm, the inhomogeneous and lateral interaction effects on the H adsorption are negligible.

For the H adsorption at the Zr/0.2 M H₂SO₄ aqueous solution interface, the fitted data, i.e., the numerically calculated Frumkin adsorption isotherms using Eq. (1), are shown in Fig. 5. Figs. 5(a), (b), and (c) show the three numerically calculated Frumkin adsorption isotherms corresponding to $g = 0, 3.5,$ and 10.5 for $K_0 = 1.401 \times 10^{-17} \text{ mol}^{-1}$, respectively. The Frumkin adsorption isotherm, $K = 1.401 \times 10^{-17} \exp(-3.5\theta) \text{ mol}^{-1}$, shown in Fig. 5(b) is applicable to the H adsorption.

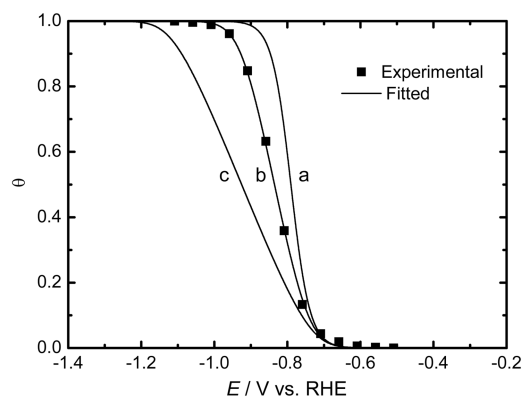


Fig. 5. Comparison of the experimental and fitted data for the Frumkin adsorption isotherms (θ vs. E) at the Zr/0.2 M H₂SO₄ aqueous solution interface. (a) $g = 0$, i.e., Langmuir adsorption isotherm, (b) $g = 3.5$, and (c) $g = 10.5$ for $K_0 = 1.401 \times 10^{-17} \text{ mol}^{-1}$.

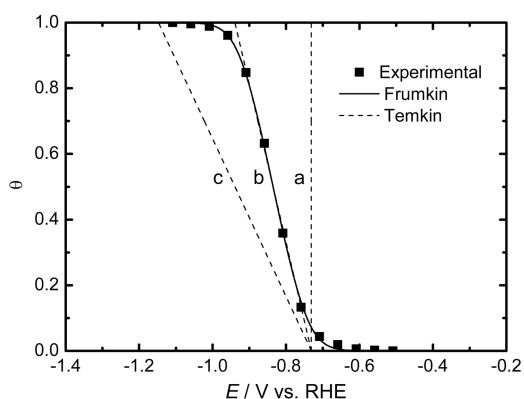


Fig. 6. Comparison of the experimentally determined Frumkin adsorption isotherm and three fitted Temkin adsorption isotherms (θ vs. E) at the Zr/0.2 M H₂SO₄ aqueous solution interface. (a) $g = 0$, (b) $g = 8.1$, and (c) $g = 16.2$ for $K_0 = 1.401 \times 10^{-16} \text{ mol}^{-1}$.

Using Eq. (2), r is 8.7 kJ mol^{-1} . Note that the value of K_0 for Zr is $\sim 10^{10}$ – 10^{13} times less than that of the noble metals (alloys).¹⁰⁻²⁸⁾ Regarding the H adsorption, Zr is a highly corrosion-resistant metal in aqueous solutions but is not a suitable metal itself for the cathodic H₂ evolution in aqueous solutions.

At intermediate values of θ , i.e., $0.2 < \theta < 0.8$, the pre-exponential term, $[\theta/(1 - \theta)]$, varies little with θ compared to the variation of the exponential term, $\exp(g\theta)$ (see Eq. (1)). Under the approximate conditions, the Temkin adsorption isotherm can be simply derived from the Frumkin adsorption isotherm. The Temkin adsorption isotherm (θ vs. E) of H at the

Table 2. Comparison of the standard free energies (ΔG_0^0) of H and the equilibrium constants (K) for the Frumkin and Temkin adsorption isotherms (θ vs. E) of H at the Zr/0.2 M H₂SO₄ aqueous solution interface.

| Adsorption isotherm | $\Delta G_0^0 / \text{kJ mol}^{-1}$ | K / mol^{-1} | θ |
|----------------------|--------------------------------------|---|------------------------|
| Frumkin ^a | $96.13 \leq \Delta G_0^0 \leq 104.8$ | $1.401 \times 10^{-17} \geq K \geq 4.231 \times 10^{-19}$ | $0 \leq \theta \leq 1$ |
| Temkin ^b | $94.44 < \Delta G_0^0 < 106.5$ | $2.773 \times 10^{-17} > K > 2.149 \times 10^{-19}$ | $0.2 < \theta < 0.8$ |

^a $K = 1.401 \times 10^{-17} \exp(-3.5\theta) \text{ mol}^{-1}$.

^b $K = 1.401 \times 10^{-16} \exp(-8.1\theta) \text{ mol}^{-1}$. Note that the Temkin adsorption isotherm is only valid and effective at $0.2 < \theta < 0.8$.

Zr/0.2 M H₂SO₄ aqueous solution interface can be expressed as follows³³⁾

$$\exp(g\theta) = K_0 C_{\text{H}}^+ [\exp(-EF/RT)] \quad (4)$$

Fig. 6 shows the determination of the Temkin adsorption isotherm correlating with the Frumkin adsorption isotherm shown in Fig. 5(b). In Fig. 6(b), K_0 and g for the fitted Temkin adsorption isotherm using Eq. (4) are $1.401 \times 10^{-16} \text{ mol}^{-1}$ and 8.1, i.e., $K = 1.401 \times 10^{-16} \exp(-8.1\theta) \text{ mol}^{-1}$, respectively. Note that the Temkin adsorption isotherm shown in Fig. 6(b) is only valid and effective at $0.2 < \theta < 0.8$. Using Eq. (2), r is 20 kJ mol^{-1} .

3.3. Correlation constants between the adsorption isotherms

At $0.2 < \theta < 0.8$, the two different adsorption isotherms, i.e., the Temkin and Langmuir or Frumkin adsorption isotherms, appear to fit the same data regardless of their adsorption conditions. These adsorption isotherms are readily determined using the correlation constants.^{22,24-29)} As shown in Fig. 6, the Temkin adsorption isotherm, $K = 1.401 \times 10^{-16} \exp(-8.1\theta) \text{ mol}^{-1}$, correlating with the Frumkin adsorption isotherm, $K = 1.401 \times 10^{-17} \exp(-3.5\theta) \text{ mol}^{-1}$, and vice versa, is readily determined using the correlation constants.

3.4. Standard free energy of adsorption

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 Zr electrode surface. Under the Frumkin adsorption conditions, the relation between the equilibrium constant (K) and the standard free energy (ΔG_0^0) of H is given as follows^{31,33)}

$$2.3RT \log K = -\Delta G_0^0 \quad (5)$$

At the Zr/0.2 M H₂SO₄ aqueous solution interface, using Eqs. (3) and (5), ΔG_0^0 of H is $96.13 \leq \Delta G_0^0 \leq$

$104.8 \text{ kJ mol}^{-1}$ for $K = 1.401 \times 10^{-17} \exp(-3.5\theta) \text{ mol}^{-1}$ and $0 \leq \theta \leq 1$. The standard free energies (ΔG_0^0) of H and the equilibrium constants (K) for the Frumkin and Temkin adsorption isotherms of H are summarized in Table 2.

4. Conclusions

At the Zr/0.2 M H₂SO₄ aqueous solution interface, the Frumkin and Temkin adsorption isotherms (θ vs. E), equilibrium constants ($K = 1.401 \times 10^{-17} \exp(-3.5\theta) \text{ mol}^{-1}$ for the Frumkin and $K = 1.401 \times 10^{-16} \exp(-8.1\theta) \text{ mol}^{-1}$ for the Temkin adsorption isotherm), interaction parameters ($g = 3.5$ for the Frumkin and $g = 8.1$ for the Temkin adsorption isotherm), rates of change of the standard free energy ($r = 8.7 \text{ kJ mol}^{-1}$ for $g = 3.5$ and $r = 20 \text{ kJ mol}^{-1}$ for $g = 8.1$) of H with θ , and standard free energies ($96.13 \leq \Delta G_0^0 \leq 104.8 \text{ kJ mol}^{-1}$ for $K = 1.401 \times 10^{-17} \exp(-3.5\theta) \text{ mol}^{-1}$ and $0 \leq \theta \leq 1$ and $94.44 < \Delta G_0^0 < 106.5 \text{ kJ mol}^{-1}$ for $K = 1.401 \times 10^{-16} \exp(-8.1\theta) \text{ mol}^{-1}$ and $0.2 < \theta < 0.8$) of H are determined using the phase-shift method and correlation constants. The inhomogeneous or the lateral interaction effect on the H adsorption is not negligible.

At $0.2 < \theta < 0.8$, the Temkin adsorption isotherm, $K = 1.401 \times 10^{-16} \exp(-8.1\theta) \text{ mol}^{-1}$, correlating with the Frumkin adsorption isotherm, $K = 1.401 \times 10^{-17} \exp(-3.5\theta) \text{ mol}^{-1}$, and vice versa, is readily determined using the correlation constants. The two different adsorption isotherms appear to fit the same data regardless of their adsorption conditions.

The phase-shift method and correlation constants are the most accurate, useful, and effective ways to determine the adsorption isotherms of H and related electrode kinetic and thermodynamic parameters at highly corrosion-resistant metal/aqueous solution interfaces.

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