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Determination of the Langmuir adsorption isotherms of under- and over-potentially deposited hydrogen for the cathodic H_2 evolution reaction at poly-Ir/aqueous electrolyte interfaces using the phase-shift method

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Abstract

The Langmuir adsorption isotherms of under-potentially deposited hydrogen (UPD H) and over-potentially deposited hydrogen (OPD H) for the cathodic H_2 evolution reaction (HER) at poly-Ir/0.5 M H_2SO_4 and 0.05 M KOH aqueous electrolyte interfaces have been studied using cyclic voltammetric, differential pulse voltammetric, and ac impedance techniques. The behavior of the lagged phase shift ($0° \leqslant -\phi \leqslant 90°$) for the optimum intermediate frequency can be linearly related to that of the fractional surface coverage ($1 \geqslant \theta \geqslant 0$) of H (UPD H, OPD H) for the cathodic HER at the interfaces. A linear relationship between the phase-shift profile ($-\phi$ vs. E) for the optimum intermediate frequency and the Langmuir adsorption isotherm (θ vs. E) of H (UPD H, OPD H), i.e., the phase-shift method, can be used as a new electrochemical method to determine or estimate the fractional surface coverage (θ), equilibrium constant (K), and standard free energy (ΔG^0_{ads}) of H (UPD H, OPD H) for the cathodic HER at the interfaces. At the poly-Ir/0.5 M H_2SO_4 aqueous electrolyte interface, K and ΔG^0_{ads} of the OPD H for the cathodic HER are 9.9×10^{-5} and 22.8 kJ/mol, respectively. At the poly-Ir/0.05 M KOH aqueous electrolyte interface, K and ΔG^0_{ads} of the UPD H for the cathodic HER are 3.9 and −3.4 kJ/mol, respectively. At the poly-Ir/0.05 M KOH aqueous electrolyte interface, K and ΔG^0_{ads} of the OPD H for the cathodic HER are 5.8×10^{-4} and 18.5 kJ/mol, respectively. The two different Langmuir adsorption isotherms for H (UPD H, OPD H) correspond to two different adsorption sites of H (UPD H, OPD H) on the poly-Ir electrode surface. The two different adsorption sites of UPD H and OPD H act as two distinguishable electroadsorbed H species. The phase-shift method is a simple and efficient tool for determining the adsorption, electrode kinetic, and thermodynamic parameters (θ, K, ΔG^0_{ads}) of H (UPD H, OPD H) for the cathodic HER at the interfaces.

Keywords: Phase-shift method; Langmuir adsorption isotherm; Under-potentially deposited hydrogen; Over-potentially deposited hydrogen; Ir electrode

1. Introduction

For clean environment and energy, the cathodic H_2 evolution reaction (HER) at electrocatalytic metal/aqueous electrolyte interfaces has been extensively and continually studied in electrochemistry and electrochemical hydrogen technology fields. Many electrochemical methods, e.g., cyclic voltammetric and electrochemical impedance spectroscopic methods, have been used to study the adsorption processes of under-potentially deposited hydrogen (UPD H) and over-potentially deposited hydrogen (OPD H) for the cathodic HER at these interfaces [1–10]. However, the kinetics and mechanisms of the cathodic HER have been studied mainly using steady-state polarization experiments

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and so there are very few reliable kinetic and thermodynamic data, i.e., the fractional surface coverage, equilibrium constant, and standard free energy of the OPD H, at these interfaces. In addition, the phase-shift method, i.e., the linear relationship between the phase-shift profile for the optimum intermediate frequency and the Langmuir, the Frumkin, or the Temkin adsorption isotherm, has not been developed or suggested to study the adsorption processes of UPD H and OPD H for the cathodic HER at these interfaces.

The relation, transition, and criterion of UPD H and OPD H have been studied to understand the kinetics and mechanisms of the cathodic HER at noble and transition-metal/aqueous electrolyte interfaces. It is well known that UPD H and OPD H occupy different surface adsorption sites and act as two distinguishable electroadsorbed H species, while only OPD H can contribute to the cathodic HER. However, the relation, transition, and criterion of UPD H and OPD H at these interfaces have been studied from the viewpoint of H_2 evolution and potentials rather than H adsorption sites and processes, i.e., the Langmuir, the Frumkin, or the Temkin adsorption isotherm.

At interfaces, it is preferable to consider the adsorption isotherm for H rather than an equation of the electrode kinetics and thermodynamics for H, because the adsorption isotherm can be associated more directly with the atomic mechanism of H adsorption. The Langmuir, Frumkin, and Temkin adsorption isotherms are useful and effective for characterizing the relation, transition, and criterion between UPD H and OPD H for the cathodic HER at interfaces. Although the adsorption isotherms may be regarded as a classical model and theory in physical electrochemistry, it is useful and effective to study the adsorption sites and processes of UPD H and OPD H for the cathodic HER. Thus, there is a technological need for a fast, simple, and reliable method to determine the adsorption isotherms for characterizing the relation, transition, and criterion between UPD H and OPD H for the cathodic HER at interfaces.

Recently, we have experimentally and consistently found that the phase-shift method can be effectively used to determine the Langmuir or the Frumkin adsorption isotherms of UPD H and OPD H for the cathodic HER at noble and transition-metal (Pt, Ir, Pd, Au, Rh, Pt–Rh alloy, Re, Ni)/aqueous electrolyte interfaces [11–19]. For the cathodic HER in electrochemical systems, the current–potential relationship is determined completely by the electrode potential (E) dependence of the fractional surface coverage (θ) of H. Thus, one can interpret that the electrode kinetic parameters for H will depend on the corresponding adsorption isotherm (θ vs. E) of H, which relates the surface concentration of H to the bulk concentration of H and to the electrode potential. At limited values of θ, i.e. $\theta \approx 0$ and 1, the distinction between the adsorption isotherms (Langmuir, Frumkin, Temkin) of H is very difficult or impossible. At low and high values of θ, e.g., $\theta < 0.2$ and $0.8 < \theta$, the distinction between the adsorption isotherms of H is difficult or complicated. At intermediate values of θ, e.g. $0.2 < \theta < 0.8$, the distinction between the adsorption isotherms of H is easy or clear.

Considering the determination of the suitable adsorption isotherm (Langmuir, Frumkin, Temkin) of H at these interfaces, first of all, the Langmuir adsorption isotherm should be determined and then find the interaction parameter (g) for the Frumkin adsorption isotherm based on the relevant experimental results, e.g., the fractional surface coverage for the electrode potential, the phase-shift profile for the optimum intermediate frequency, etc. Finally, the applicability of the Temkin adsorption isotherm at these interfaces can be considered or confirmed (refer to Fig. 15). This is described elsewhere [4,11,14]. However, the phase-shift method is useful and effective for determining the Langmuir, Frumkin, and Temkin adsorption isotherms of H at these interfaces. Also, this method is a useful and effective way to study the H adsorption sites and processes for the cathodic HER, the relation, transition, and criterion between UPD H and OPD H, the electrode kinetics and thermodynamics at these interfaces.

In this paper, we represent the Langmuir adsorption isotherms of UPD H and OPD H for the cathodic HER at poly-Ir/0.5 M H_2SO_4 and 0.05 M KOH aqueous electrolyte interfaces using the phase-shift method. This paper is intended to supplement the previously published paper [12].

2. Experimental

2.1. Preparations

Taking into account H^+ concentrations and effects of diffuse double layer and pH [20], acidic and alkaline aqueous electrolytes were prepared from H_2SO_4 (Sigma-Aldrich, reagent grade) and KOH (Alfa Aesar, reagent grade) with purified water (resistivity: > 18 MΩ cm) obtained from a Millipore system. The 0.5 M H_2SO_4 and 0.05 M KOH aqueous electrolytes were 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 polycrystalline iridium (poly-Ir) wire (Alfa Aesar, purity: 99.8%, 1 mm diameter, estimated surface area: ca. 0.93 cm^2 for the 0.5 M H_2SO_4 and 0.71 cm^2 for the 0.05 M KOH) working electrode. The poly-Ir working electrode was prepared by flame cleaning and then quenched and cooled in Millipore Milli-Q water and in air, sequentially. A Pt wire (Alfa Aesar, purity: 99.95%, 1.5 mm diameter) was used as a counter electrode. Taking into account the OPD H and its large current distribution [21], the working and counter electrodes were separately by ca. 4 cm in the same compartment of a Pyrex cell using Teflon holders.

2.2. Measurements

A cyclic voltammetric (CV) method was used to observe the UPD H peaks, which are useful and important for