THE PHASE-SHIFT METHOD FOR THE ADSORPTION ISOTHERMS OF ELECTROADSORBED HYDROGENS AT THE NOBLE AND TRANSITION METAL/AQUEOUS ELECTROLYTE INTERFACES

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ABSTRACT

The phase-shift method for the Langmuir and Frumkin adsorption isotherms of the under-potentially deposited hydrogen (UPD H) and the over-potentially deposited hydrogen (OPD H) for the cathodic H_2 evolution reaction (HER) at the noble and transition metal (Pt, Ir, Pd, Au, Rh, Re, Ni)/aqueous electrolyte interfaces has been studied using cyclic voltammetric, linear sweep voltammetric or differential pulse voltammetric, and ac impedance techniques. The behavior of the phase shift ($0° \leq -\phi \leq 90°$) for the optimum intermediate frequency can be linearly related to that of the fractional surface coverage ($1 \geq \theta \geq 0$) of the UPD H or the OPD H for the cathodic HER at the interfaces. The phase-shift method, i.e., the phase-shift profile ($-\phi$ vs. E) for the optimum intermediate frequency, can be used as a new electrochemical method to determine or estimate the Langmuir and Frumkin adsorption isotherms (θ vs. E) of the UPD H and the OPD H for the cathodic HER at the interfaces. The equilibrium constants (K) and standard free energies (ΔG_{ads}) of the UPD H and the OPD H for the cathodic HER at the interfaces can be effectively determined or estimated using the phase-shift method.

Recently, we have experimentally and consistently found that the phase-shift method can be effectively used to determine or estimate the Langmuir and Frumkin adsorption isotherms of the UPD H and the OPD H for the cathodic HER at the noble and transition metal (Pt, Rh, Ir, Pd, Au, Re, Ni)/aqueous electrolyte interfaces.[1–8] It is useful and effective for studying the relation, transition, and criterion between the UPD H and the OPD H for the cathodic HER at the interfaces.

In this symposium we represent the phase-shift method for the Langmuir and Frumkin adsorption isotherms of the UPD H and the OPD H for the cathodic HER at the noble and transition metal/aqueous electrolyte interfaces. It is useful and effective to determine or estimate the electrode kinetic and thermodynamic parameters, i.e., K and ΔG_{ads}, of the UPD H and the OPD H for the cathodic HER at the interfaces.

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FIGURES

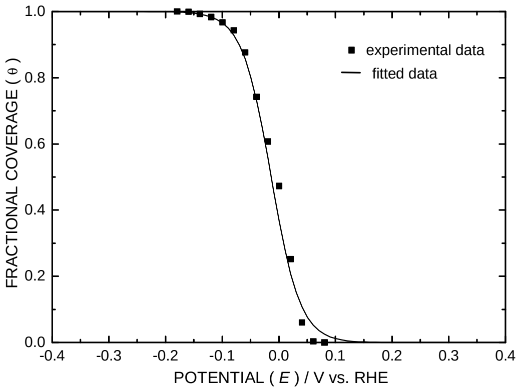

Fig. 1. The comparison of the experimental and fitted data for the Langmuir adsorption isotherm (θ vs. E) at the poly-Pt/0.5 M H_2SO_4 aqueous electrolyte interface.

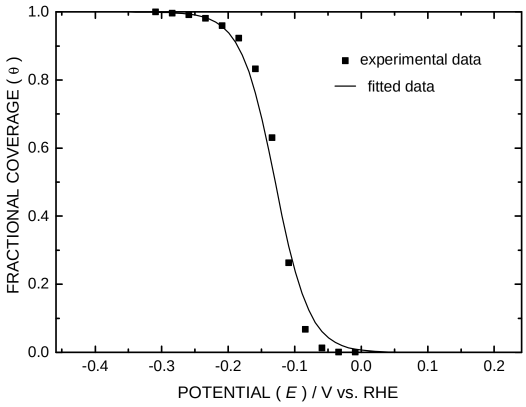

Fig. 2. The comparison of the experimental and fitted data for the Langmuir adsorption isotherm (θ vs. E) at the poly-Au/0.5 M H_2SO_4 aqueous electrolyte interface.

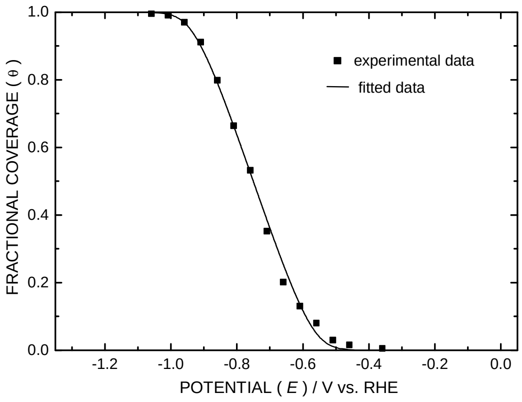

Fig. 3. The comparison of the experimental and fitted data for the Frumkin adsorption isotherm (θ vs. E) at the poly-Ni/0.05 M KOH aqueous electrolyte interface.