

**DETERMINATION OF THE LANGMUIR ADSORPTION ISOTHERM OF THE OVER-POTENTIALLY DEPOSITED HYDROGEN (OPD H) AT THE POLY-Re/H<sub>2</sub>SO<sub>4</sub> AQUEOUS ELECTROLYTE INTERFACE USING THE PHASE-SHIFT METHOD**

Jang H. Chun,\* Keuk H. Ra, and Nam Y. Kim  
Department of Electronic Engineering, Kwangwoon University, Seoul 139-701, Korea

\* E-mail: jhchun@daisy.kwangwoon.ac.kr

**ABSTRACT**

The phase-shift method for the Langmuir adsorption isotherm of the over-potentially deposited hydrogen (OPD H) for the cathodic H<sub>2</sub> evolution reaction (HER) at the poly-Re/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface has been studied using cyclic voltammetric, differential pulse voltammetric, and ac impedance techniques. The behavior of the phase shift ( $0^\circ \leq -\phi \leq 90^\circ$ ) for the optimum intermediate frequency can be linearly related to that of the fractional surface coverage ( $1 \geq \theta \geq 0$ ) of the OPD H for the cathodic HER at the interface. 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 the Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) of the OPD H for the cathodic HER at the interface. At the poly-Re/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface, the equilibrium constant ( $K$ ) and standard free energy ( $\Delta G_{ads}$ ) of the OPD H are  $5.5 \times 10^{-7}$  and 35.7 kJ/mol, respectively. The Tafel slopes of the OPD H for the cathodic HER at the interface are 60 and 120 mV/decade.

Recently, we have experimentally and consistently found that the phase-shift method can be effectively used to determine the Langmuir and Frumkin adsorption isotherms of the under-potentially deposited hydrogen (UPD H) and the OPD H for the cathodic HER at the electrocatalytic metal (Pt, Rh, Ir, Pd, Au, Ni)/aqueous electrolyte interfaces.<sup>1-8</sup> It is useful and effective for studying the electrode kinetic and thermodynamic parameters, i.e.,  $K$  and  $\Delta G_{ads}$ , of the UPD H and the OPD H, 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 Langmuir adsorption isotherm of the OPD H for the cathodic HER at the poly-Re/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface using the phase-shift method. It concerns essentially the phase-shift method which is useful and effective to determine or estimate the electrode kinetic and thermodynamic parameters, i.e.,  $K$  and  $\Delta G_{ads}$ , of the OPD H for the cathodic HER at the interface.

**REFERENCES**

1. E. Gileadi, *Electrode Kinetics*, pp. 261–271, 291–303, VCH, New York (1993).
2. B. E. Conway and G. Jerkiewicz, Editors, *Electrochemistry and Materials Science of Cathodic Hydrogen Absorption and Adsorption*, The Electrochemical Society, PV 94–21, Pennington, NJ (1995).
3. J. H. Chun and K. H. Ra, *J. Electrochem. Soc.*, **145**, 3794 (1998).
4. J. H. Chun and K. H. Ra, in *Hydrogen at Surfaces and Interfaces*, G. Jerkiewicz, J. M. Feliu, and B. N. Popov, Editors, PV 2000–16, pp. 159–173, The Electrochemical Society, Pennington, NJ (2000).

5. J. H. Chun, K. H. Ra, and N. Y. Kim, *Int. J. Hydrogen Energy*, **26**, 941 (2001).
6. J. H. Chun, S. K. Jeon, and J. H. Lee, *J. Korean Electrochem. Soc.*, **5**, 131 (2002).
7. J. H. Chun, K. H. Ra, and N. Y. Kim, *J. Electrochem. Soc.*, **149**, E325 (2002).
8. J. H. Chun, K. H. Ra, and N. Y. Kim, *J. Electrochem. Soc.*, in press (2003).

**FIGURES**

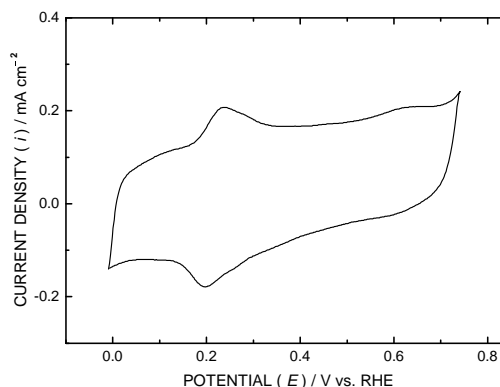


Fig. 1. The cyclic voltammogram at the poly-Re/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface.

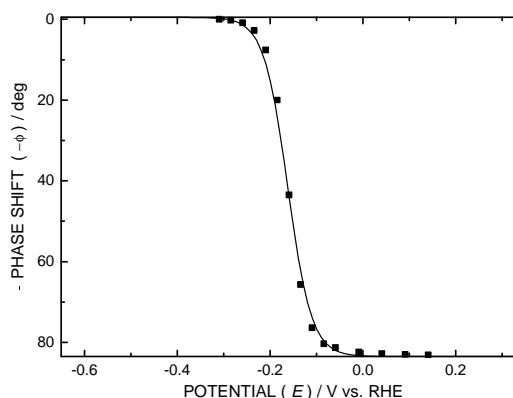


Fig. 2. The phase-shift profile ( $-\phi$  vs.  $E$ ) for the optimum intermediate frequency (ca. 10 Hz) at the poly-Re/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface.

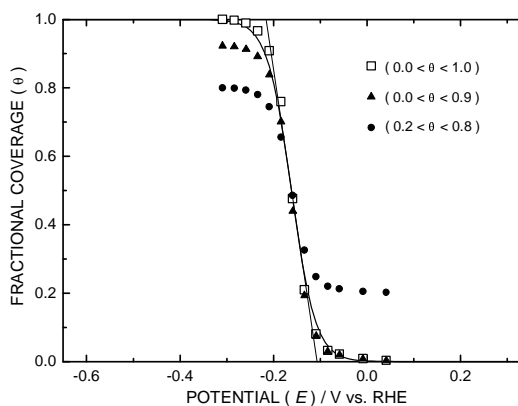


Fig. 3. The comparison of three different ranges of  $\theta$  for the Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) at the poly-Re/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface.