The Effect of the Temperature on Hydrogen Adsorption on PtMo Alloy in Acid Solution

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Abstract

Potentiodynamic studies of the underpotential deposition of hydrogen (H_{upd}) on PtMo electrode in 0.5 mol dm^{-3} HClO_4 aqueous solution at the range of temperature from 274 K to 312 K are made and thermodynamic state functions for the hydrogen adsorption are determined.

Theoretical treatment of the experimental results is derived from H_{upd} electrochemical adsorption isotherm. It is determined that \Delta G_{ads}^{\text{H}_{\text{upd}}} as a function of temperature varies with the surface coverage from –2.3 kJ mol^{-1} (\Theta = 0) to –23.8 kJ mol^{-1} (\Theta = 0.5). The increase of \Delta G_{ads}^{\text{H}_{\text{upd}}} toward less negative value indicates the repulsive interactions between H_{upd} adatoms. From the temperature dependence of the Gibbs energy of adsorption the enthalpy and entropy of adsorption are calculated. The values of these functions are determined to be \Delta H_{ads}^{\text{H}_{\text{upd}}} (\Theta = 0) = 59.0 kJ mol^{-1} and \Delta S_{ads}^{\text{H}_{\text{upd}}} (\Theta = 0) = –224 J K^{-1}mol^{-1}. The value of \Delta H_{ads}^{\text{H}_{\text{upd}}} allows determinations of the bond energy between electrode surface and H_{upd} that is found to be \Delta H_{M-H} = 185 kJ mol^{-1}for \Theta = 0.5. The lateral repulsion interactions are the reason why M-H_{upd} bond energy decreases significantly with increase of coverage so, the saturation coverage is less than 1 in the UPD potential region.

Introduction

In electrochemical surface science two kinds of electroadsorbed H species are recognized: the underpotentially electrodeposited H species (H_{upd}) that takes place above the potential required for the onset of the hydrogen evolution reaction and the overpotentially deposited H (H_{opd}) that takes place at potentials negative with respect to the reversible hydrogen potential. Underpotentially and overpotentially deposited hydrogen occupy different adsorption sites so, their Gibbs energy of adsorption, enthalpies and entropies of adsorption so as bond energies should be different. Cyclic voltammetry measurements on Pt, Pd, Rh and Ir [1-3] show that up to monolayer of underpotentially deposited H is formed on these metal surfaces prior to the onset of hydrogen evolution.

In this work, voltammetric profiles of the PtMo surface in 0.5 mol dm^{-3} HClO_4 aqueous solution obtained at different temperatures with quantification of the temperature effect on the reversible adsorption of the H_{upd} state are presented and the thermodynamic state functions for H adsorption process are calculated. The chemisorption bond energy of the M-H state is estimated in order to establish the relationship between the surface structure and the electrocatalytic activity of PtMo electrodes.

Results and discussion

Series of the cyclic voltammetry adsorption-desorption profiles for the H_{upd} at PtMo electrode from 0.5 mol dm^{-3} HClO_4 aqueous solution, for various temperatures between 274 and 312 K, recorded at the sweep rate of 100 mV s^{-1} are shown in Fig.1. All profiles are symmetric with respect to the potential axis indicating that surface electrochemical process is reversible. All profiles characterize a broad H_{upd} potential region without pronounced peaks on these profiles, similar as at Pt(111) [4].

From the experimental results presented in Fig.1. by integrating the anodic charge under the UPD voltammetric peaks, the adsorption isotherms \Theta vs. E were obtained, at each temperature. By fitting these isotherms to a generalized form of a Temkin-Frumkin isotherm with

Fig.1. CV profiles for PtMo electrode in 0.5 moldm^{-3} HClO_4 solution obtained at different temperatures: --- 274 K, ... 284 K, ...-.-. 294 K, ---312 K

Table 1. Thermodynamic state functions for H_{upd} in 0.5 mol dm^{-3} HClO_4, for \Theta = 0 at PtMo electrode

<table>
<thead>
<tr>
<th>T [K]</th>
<th>\Delta G_{ads}^{\text{H}_{\text{upd}}} [kJ mol^{-1}]</th>
<th>T [K]</th>
<th>\Delta H_{ads}^{\text{H}_{\text{upd}}} [kJ mol^{-1}]</th>
<th>\Delta S_{ads}^{\text{H}_{\text{upd}}} [J mol^{-1} K^{-1}]</th>
<th>D_{M-H} [kJ mol^{-1}]</th>
</tr>
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<tbody>
<tr>
<td>274</td>
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<td>23.8</td>
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References