The Effect of the Temperature on Hydrogen Adsorption on Pt_4Mo Alloy in Acid Solution

J.Jaksic Lj.Vracar and N.Krstajic

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Yugoslavia

Abstract

Potentiodynamic studies of the underpotential deposition of hydrogen (H_{upd}) on Pt_4Mo 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 ΔG^{θ}_{ads} (H_{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 $\Delta G^{\theta}_{ads}(H_{upd})$ 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 detemined to be $\Delta H^{\theta}_{ads\ (\theta=0.5)}$ = 59,0 kJ mol^{-1} and $\Delta S^{\theta}_{ads(\theta=0.5)}$ = - 224 J $mol^{-1}K^{-1}$.The value of ΔH^{θ}_{ads} aloweds determinations of the bond energy between electrode surface and H_{upd} that is found to be $\varepsilon_{M\text{-}H}$ = 185 kJ $mol^{-1}$for $\theta = 0.5$. The lateral repulsion interactions are the reason why M-H_{upd} bond energy decreases significantely 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 overpotential deposited H (H_{opd}) that takes place at potentials negativ with respect to the reversible hydrogen potential. Underpotentially and overpotentially deposited hydrogen occupy different adsorption sites so, their Gibs 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 af the Pt_4Mo surface in 0.5 mol dm^{-3} $HclO_4$ aquous 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 Pt_4Mo electrodes.

Results and discussion

Series of the cyclic viltammetry adsorption-desorption profiles for the H_{upd} at Pt_4Mo 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 the respect to the potential axes indicating that surface electrochemical process is reversible. All profiles characterise 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 θ vs.E were obtained, at each temperature. By fitting these isotherms to a generalized form of a Temkin-Frumkin isotherm with assumption of Gibss energy of adsorption vary linearly with surface coverage, and Gibss energies of adsorption were obtained. From the slope of these dependecies the Gibss energy parameters and interaction parameters, at each temperature, are calculated (Table1.). The positive sign of the interaction parameter and its value over the temperature range of 274-312 K indicates highly attractive lateral interactions between H_{upd} adsorbed species on Pt_4Mo surface. The values of all calculated thermodynamic functions are summerized in Table 1.

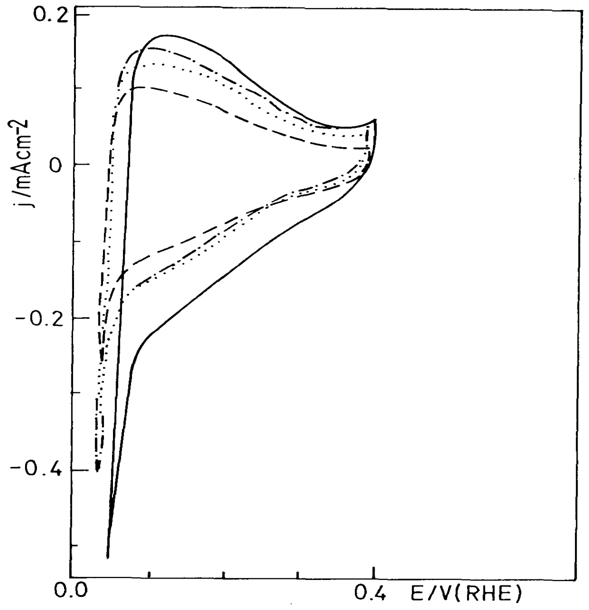

Fig.1. CV profiles for Pt_4Mo electrode in 0.5 moldm^{-3} $HClO_4$ solution obtained at different temperatures: --- 274 K, ... 284 K, .-.-. 294 K, —312 K

Table 1. Thermodynamic state functions for H_{upd} in 0.5 mol dm^{-3} $HClO_4$, for $\theta = 0$ at Pt_4Mo electrode

T [K]	$-\Delta G^{\theta=0}$ [kJ mol^{-1}]	f	$\Delta H^{\theta=0}$ [$kJmol^{-1}$]	$\Delta S^{\theta=0}$ [$Jmol^{-1}K^{-1}$]	$D_{M\text{-}H}$ [$kJmol^{-1}$]
274	22.8	18.4			
283	22.4	12.7			
288	23.0	12.6	-13.0	35	230
294	23.0	12.1			
302	23.0	11.7			
312	23.8	9.0			

References

[1] W.Bold, M.W.Breiter, *Z.Elektrochem,* **64** (1960)897.
[2] M.W.Breiter, B.Kennel, *Z.Elektrochem,* **64** (1960)1180
[3] B.E.Conway, *Theory and Principles of Electrode Processes,* Ronald Press, London (1965).
[4] N.M.Markovic, B.N.Grgur, P.N.Ross, *J.Phys.Chem.,B* **101** (1997) 5405.