Determination of the kinetics of hydrogen evolution by the galvanostatic step technique

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Introduction

Determination of the detailed kinetics of the hydrogen evolution reaction (HER) is a complex task and quite few reliable data exist in the literature. Notoya and Matsuda[1-3] used the galvanostatic step technique to determine the kinetics of the HER, however, they considered only low overpotentials, and used the Butler-Volmer equation to approximate its mechanism.

The purpose of our paper was to develop the galvanostatic step technique and to determine the detailed kinetics of the HER on polycrystalline and porous Ni electrodes in alkaline solutions. In this method current step is applied to the electrode at equilibrium potential and the overpotential is followed as a function of time. The results obtained were compared with those obtained by the open circuit potential decay and electrochemical impedance spectroscopy combined with Tafel curves.

Theory

Assuming Volmer-Heyrovsky mechanism of HER:

$$M + H_2O + e^- = MH + OH^- \qquad \text{(Volmer)} \qquad (1)$$

$$MH + H_2O + e^- = M + H_2 + OH^- \qquad \text{(Heyrovsky)} \qquad (2)$$
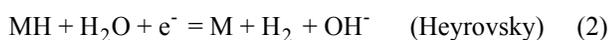
application of the current step to the electrode is described by a system of two differential equations:

$$\frac{d\theta}{dt} = \frac{F}{\sigma_1}(v_1 - v_2) \qquad (3)$$

$$\frac{d\eta}{dt} = \frac{F}{C_{dl}}\left(v_1 + v_2 - \frac{j}{F}\right) \qquad (4)$$

where v_1 and v_2 are the rates of Volmer and Heyrovsky reactions:

$$v_1 = k_1(1-\theta)e^{-\beta_1 f\eta} - k_{-1}\theta e^{(1-\beta_1)f\eta} \qquad (5)$$

$$v_2 = k_2\theta e^{-\beta_2 f\eta} - k_{-2}(1-\theta)e^{(1-\beta_2)f\eta} \qquad (6)$$

k_i and k_{-i} are the forward and backward rate constants, θ is the surface coverage by adsorbed hydrogen, σ_1 the charge necessary for a monolayer coverage by adsorbed hydrogen, j is the applied current density, C_{dl} is the double-layer capacitance, β is the symmetry coefficient, η is the overpotential and $f = F/RT$.

Results and discussion

This method was applied to HER on polycrystalline and porous nickel electrodes Ni-Zn (50/50%, prepared by pressing Ni and Zn powders followed by leaching Zn) in alkaline solutions. The experimental curves were fitted to the numerical solution of Eqs. (3) and(4). Fig. 1 shows the experimental curves overpotential vs. logarithm of time for the polycristalline Ni electrode and Fig. 2 shows such curves for porous Ni, obtained in 1 M NaOH at 25ºC (points) together with the corresponding approximations (continuous lines). Similar curves were obtained at 70°C. All the approximations were good and the values of the rate constants are obtained with low errors (see Tables 1). Moreover, these results are in good agreement with those determined by the open circuit potential decay and electrochemical impedance spectroscopy combined with Tafel curves. The apparent electrochemical activity towards the HER of porous electrodes found here was much larger than that of smooth polycrystalline one. However, the intrinsic activity of the porous electrodes was lower than that of polycrystalline electrodes. There might have been some residual zinc hydroxides formed deep in the pores which influenced the electrode activity.

The determination of the double-layer capacitance was possible from the analysis of the initial part of η-t curves. Approximations in the large overpotential range are less sensitive to changes of C_{dl} and values which depended on the applied current pulse were obtained.

The advantage of this method lies in fact that the current pulse may be applied for a short time until stabilization of the potential and problems of deposition of impurities are greatly avoided.

Table 1. Rate constants of the HER obtained on polycristalline Ni in 1 M NaOH at 25ºC by the galvanostatic step method.

k_1 = $(3.14 \pm 0.19) \, 10^{-8}$ mol cm^{-2} s^{-1}
k_{-1} = $(3.29 \pm 0.17) \, 10^{-7}$ mol cm^{-2}s^{-1}
k_2 = $(1.19 \pm 0.12) \, 10^{-11}$ mol cm^{-2} s^{-1}
k_{-2} = $(1.13 \pm 0.11) \, 10^{-12}$ mol cm^{-2} s^{-1}

References

[1] A. Matsuda and R. Notoya, *J. Phys. Chem.*, **93**, 5521 (1989).

[2] R. Notoya, Elektrokhimiya, 29 (1993) 53.

[3] R. Notoya, Electrochem. Acta, 42 (1995) 899.
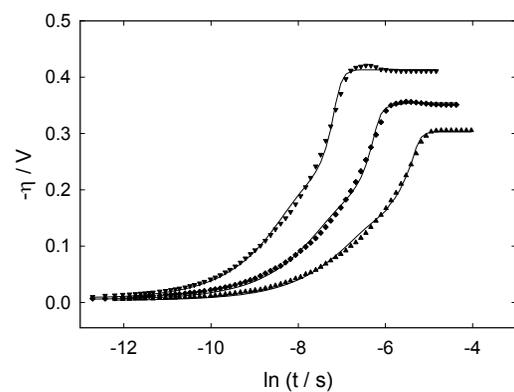
Fig. 1. Dependence of overpotential on the logarithm of time for the polycrystalline nickel electrode in 1 M NaOH at 25ºC for the applied current j = 15.77 (▲), 31.54 (♦) and 63 mA cm^{-2} (▼).
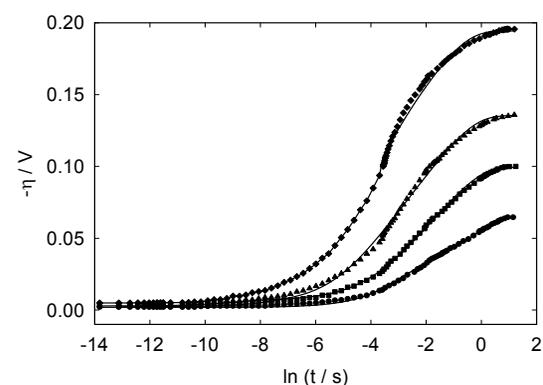
Fig. 2. Dependence of overpotential on the logarithm of time for the porous nickel electrode Ni-Zn (50/50%) in 1 M NaOH at 25ºC for the applied current j = 13.77 (●), 27.54 (■), 55.10 (▲) and 137.7 mA cm^{-2} (♦).