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

C. Hitz and A. Lasia
Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, J1K 2R1, Canada

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 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:

\[ \text{M} + \text{H}_2\text{O} + e^- = \text{MH} + \text{OH} \quad \text{(Volmer)} \]  

(1)

\[ \text{MH} + \text{H}_2\text{O} + e^- = \text{M} + \text{H}_2 + \text{OH} \quad \text{(Heyrovsky)} \]  

(2)

application of the current step to the electrode is described by a system of two differential equations:

\[ \frac{d\eta}{dt} = \frac{F}{C_{dl}} (\eta_1 - \eta_2) \]  

(3)

\[ \frac{d\eta}{dt} = \frac{F}{C_{dl}} (\eta_1 + \eta_2 - \frac{j}{F}) \]  

(4)

where \( \eta_1 \) and \( \eta_2 \) are the rates of Volmer and Heyrovsky reactions:

\[ \eta_1 = k_1 \left( 1 - \theta \right) e^{\beta \eta_1}/\eta - k_2 \theta e^{(\beta - \beta_1)/\eta} \]  

(5)

\[ \eta_2 = k_2 \theta e^{\beta_2}/\eta - k_1 \left( 1 - \theta \right) e^{(\beta - \beta_1)/\eta} \]  

(6)

\( k_1 \) and \( k_2 \) are the forward and backward rate constants, \( \theta \) is the surface coverage by adsorbed hydrogen, \( C_{dl} \) the charge necessary for a monolayer coverage by adsorbed hydrogen, \( j \) is the applied current density, \( C_{dl} \) 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.

Acknowledgments
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Table 1. Rate constants of the HER obtained on polycrystalline Ni in 1 M NaOH at 25°C by the galvanostatic step method.

<table>
<thead>
<tr>
<th>( k_1 )</th>
<th>( k_2 )</th>
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<tr>
<td>((3.14 \pm 0.19) \times 10^{-4} \text{ mol cm}^{-2} \text{s}^{-1})</td>
<td>((1.19 \pm 0.12) \times 10^{-7} \text{ mol cm}^{-2} \text{s}^{-1})</td>
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Fig. 1. Dependence of overpotential on the logarithm of time for the polycrystalline nickel electrode in 1 M NaOH at 25°C.

Fig. 2. Dependence of overpotential on the logarithm of time for the porous nickel electrode Ni-Zn (50/50%) in 1 M NaOH at 25°C.

References