



# Kinetics and mechanism of hydrogen evolution reaction on cobalt silicides in alkaline solutions



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## ARTICLE INFO

### Article history:

Received 27 October 2014

Received in revised form 15 February 2015

Accepted 24 February 2015

Available online 24 February 2015

### Keywords:

cobalt silicide

hydrogen evolution reaction

electrochemical impedance

## ABSTRACT

Cathodic polarisation curves and impedance spectra for cobalt silicides  $\text{Co}_2\text{Si}$  and  $\text{CoSi}_2$  in 0.5–2 M KOH at ambient temperature were obtained. It was shown that electrocatalytic activity of both silicides in hydrogen evolution reaction (HER) is higher than that of cobalt. The dependences of equivalent circuit elements on the electrode potential were analysed. The conclusion was made that the atomic hydrogen adsorption on the surface of cobalt silicides is described by the Langmuir isotherm, and hydrogen evolution proceeds through the Volmer–Heyrovsky mechanism (at  $\alpha_1 \neq \alpha_2$  for  $\text{Co}_2\text{Si}$  and  $\alpha_1 = \alpha_2$  for  $\text{CoSi}_2$ ;  $\alpha_1$  and  $\alpha_2$  are the transfer coefficients for the Volmer and Heyrovsky steps respectively). The Heyrovsky reaction is probably the rate-determining step. The values of the kinetic parameters of HER on  $\text{Co}_2\text{Si}$  and  $\text{CoSi}_2$  in 1 M KOH were estimated.

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## 1. Introduction

Studies on the kinetics and mechanism of the hydrogen evolution reaction (HER) on the transition metal silicides are not numerous [1–6]. It has been shown that the electrocatalytic activity of silicides correlates with the activity of the corresponding metals and the highest current densities are observed on platinum and palladium silicides [2,3]. Kinetic data for HER on NiSi in perchlorate solutions (pH 0.04 and 10.8) are presented in [1]. Current densities on NiSi in acidic solution are higher than those on Ni electrode; hydrogen ion discharge is considered to be the rate-determining step (rds) in HER. More detailed information on the kinetics of HER on the silicides of iron group metals in acidic solutions is contained in [4,5]. It has been found [4] that the cathodic current densities on  $\text{Co}_2\text{Si}$  and  $\text{CoSi}$  in 0.5 M  $\text{H}_2\text{SO}_4$  are higher than those on Co electrode. The activity of cobalt silicides in HER in sulfuric acid solution can be increased significantly by anodic treatment of these materials in 0.5 M  $\text{H}_2\text{SO}_4$  or in 1 M NaOH [5].

Tilak et al. [7] showed that hydrogen overvoltage for  $\text{NiSi}_2$  in 15% NaOH + 17% NaCl at 95 °C is one of the lowest among ca. 60 investigated materials. Although high values of the HER rate on nickel silicides in this electrolyte are primarily due to high surface area produced by the leaching of Si from NiSi and  $\text{NiSi}_2$ , the results of [7] indicate that silicides have considerable promise for the HER

electrocatalysis in alkaline media. Acceleration of HER as a result of the leaching of Si from  $\text{NiSi}_2$  is also noted in [8].

There are studies of the kinetics and mechanism of HER on composite materials Ni + Mo + Si, Ni + W + Si, Ni + W + Mo + Si in alkaline solutions by the electrochemical impedance spectroscopy (EIS) method [9,10]. These heterogeneous materials were obtained by electrodeposition of nickel from the electrolyte containing suspensions of W, Mo and Si powders. After their thermal treatment, such silicide phases as NiSi and  $\text{Mo}_5\text{Si}_3$  were found. It was shown [10] that Ni + W + Mo + Si exhibits higher electrochemical activity for HER as compared with the Ni + W coating due to the presence of additional components (in particular silicon) in the composite.

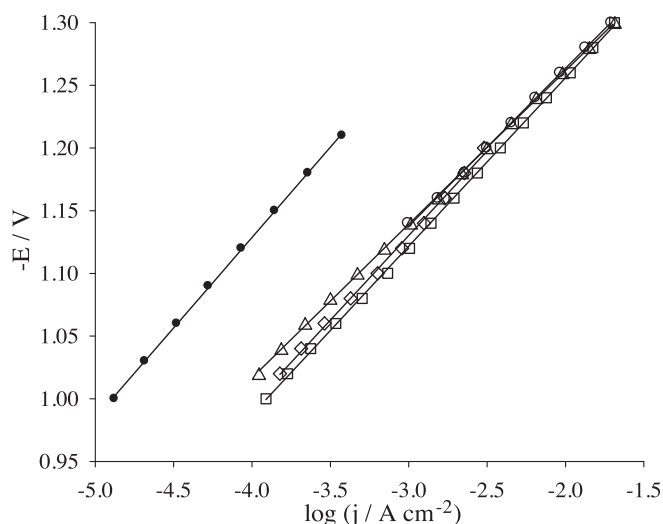
The mechanism of HER on cobalt silicides in alkaline solutions has not been yet studied. In this article we report the results of an investigation of the kinetics and mechanism of HER on two cobalt silicides – one with low content of silicon ( $\text{Co}_2\text{Si}$ ) and the other with high content of silicon ( $\text{CoSi}_2$ ) – in potassium hydroxide solutions using polarisation measurements and EIS. In the analysis of impedance data, we use recently proposed diagnostic criteria for hydrogen evolution mechanisms [11].

## 2. Experimental

Investigated electrodes were made from  $\text{CoSi}_2$  and  $\text{Co}_2\text{Si}$ . These silicides were prepared from silicon (99.99% purity) and electrolytic cobalt (99.98% purity) by Czochralski method (pulling from the melt at speed of 0.4 mm min<sup>-1</sup>). The working electrode surface area was 0.4–0.6 cm<sup>2</sup>. Before measurements, the working electrode

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**Fig. 1.** Polarisation curves for  $\text{Co}_2\text{Si}$  at KOH concentrations ( $\text{mol dm}^{-3}$ ): (○) 2; (△) 1; (□) 0.5; (◇) 0.2. (●) Co in 1 M KOH.

surface was abraded with emery papers 1000 and 2000, cleaned with ethanol and washed in the working solution.

Solutions of KOH were prepared from high-purity reagent and de-ionized water (Milli-Q;  $18.2 \text{ M}\Omega \text{ cm}$ ). The solutions were de-aerated with hydrogen (99.999% purity). The temperature of the solutions was  $21\text{--}23^\circ\text{C}$ .

Electrochemical measurements were carried out in three-electrode electrochemical cell with cathodic and anodic compartments separated with a porous glass diaphragm. Potentials were changed from low to high cathodic polarisations and in reverse direction. Before recording an impedance spectrum at each potential value, the electrode was polarised under potentiostatic conditions until constant value of current was reached. The electrode potentials are given with respect to the SHE.

Impedance measurements were carried out using FRA Solartron 1255 and potentiostat Solartron 1287 (Solartron Analytical) in frequency range from 10 kHz to 0.01 Hz (10 points per decade). The alternating signal amplitude was 10 mV rms. The CorrWare2, ZPlot2 and ZView2 software (Scribner Associates, Inc.) was used for measuring and processing the impedance data.

### 3. Results and discussion

#### 3.1. $\text{Co}_2\text{Si}$ electrode

Cathodic polarisation curves for  $\text{Co}_2\text{Si}$  and Co electrodes are presented in Fig. 1. It can be seen that at a constant electrode potential  $E$  the current densities  $j$  for  $\text{Co}_2\text{Si}$  are significantly higher than for Co. The HER rate for  $\text{Co}_2\text{Si}$  varies insignificantly with the solution concentration in the range 0.2–2.0 M KOH, but the Tafel slopes  $b$  of polarisation curves slightly increase when the concentration decreases (Table 1).

Taking into account the value of the Tafel slope and weak dependence of HER rate at  $E = \text{const}$  on the alkali concentration,

**Table 1**  
The values of Tafel slopes in KOH solutions.

Electrode	The value of $b$ (V) at KOH concentration ( $\text{mol dm}^{-3}$ )			
	0.2	0.5	1.0	2.0
Co	–	–	0.144	–
$\text{Co}_2\text{Si}$	0.135	0.134	0.123	0.125
$\text{CoSi}_2$	–	0.115	0.105	0.105

one can suppose that hydrogen evolution on  $\text{Co}_2\text{Si}$  takes place in accordance with the mechanism of slow discharge of water molecules (Volmer reaction), but these results can be also explained in the frameworks of slow electrochemical desorption (Heyrovsky reaction) mechanism.

Weak dependence of the current density and the Tafel slope on KOH concentration can be associated with double layer effects. According to [12], the influence of KOH on the structure of the double layer occurs at the concentration of  $1 \text{ mol dm}^{-3}$  and lower. Frumkin [13] showed that in alkaline solutions

$$E = \psi_1 - \frac{RT}{\alpha F} \ln j + \text{const} \quad (1)$$

where  $\psi_1$  is the potential in the point of reactant location,  $\alpha$  is the transfer coefficient for the rate-determining step.

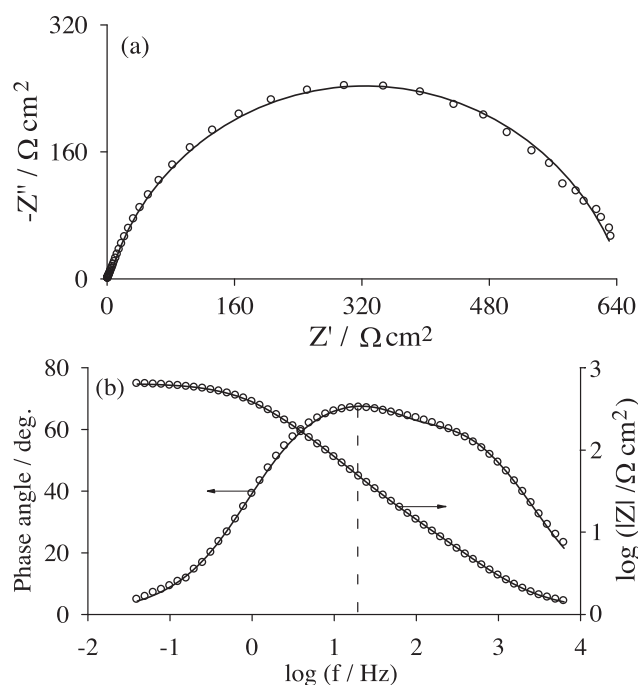
From Eq. (1) one can obtain the expression for the observed Tafel slope

$$b = \frac{2.3RT}{\alpha F} \frac{1}{1 - d\psi_1/dE} \quad (2)$$

Relation  $\psi_1(E)$  is generally not linear, but at small values of  $\psi_1$  potential (that can be expected in 0.2–0.5 M KOH) the function  $\psi_1(E)$  is close to be linear, and the polarisation curve that takes into consideration the influence of double layer structure will be practically straight-line.

A typical impedance diagram for  $\text{Co}_2\text{Si}$  in one of the investigated solutions is presented in Fig. 2. The Nyquist diagram (Fig. 2(a)) looks like slightly distorted capacitive semicircle. However, the impedance spectra can not be correctly described by a simple equivalent circuit that consists of the charge transfer resistance and the double-layer capacitance (or the constant phase element CPE) in parallel, because the Bode phase-angle plot is considerably asymmetric with respect to vertical line drawn through the point of maximum (dashed line in Fig. 2(b)).

For the simulation of the process under study on the basis of experimental impedance spectra, we used the equivalent electrical



**Fig. 2.** Nyquist (a) and Bode (b) plots for  $\text{Co}_2\text{Si}$  in 1 M KOH at  $E = -1.0 \text{ V}$ . Points are the experimental data, solid lines are the results of CNLS fitting to the circuit in Fig. 3(b).

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