UDC 541.138.3

DOI: 10.15372/CSD2023473

EDN: POFZMF

Cathodic Evolution of Hydrogen on Iron Disilicide in Alkaline Electrolyte

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(Received 30.11.22; revised 06.02.23)

Abstract

The kinetics and mechanism of hydrogen evolution on the $FeSi_2$ electrode in 0.25–1.0 M NaOH solutions have been studied by polarisation and impedance measurements. The cathodic polarisation curves of iron disilicide in the studied solutions are characterized by a Tafel region with constants a and b equal to (−0.78)–(−0.72) and (−0.133)–(−0.128) V, respectively. The impedance spectra of $FeSi_2$ at the potentials of the Tafel region represent a capacitive semicircle with a displaced centre, which corresponds to an asymmetric maximum in the graph of phase angle dependence on the logarithm of the alternating current frequency; the magnitude of the electrode impedance in all solutions changes in accordance with the course of the polarization curves. To describe the hydrogen evolution reaction on iron disilicide, an equivalent electrical circuit was used, the Faraday impedance of which consists of series-connected charge-transfer resistances and a parallel circuit responsible for the adsorption of atomic hydrogen on the surface and its diffusion into the depth of the electrode material; the circuit also includes the electrolyte resistance and the double-layer capacitance impedance, which is modelled by a constant phase element. It is shown that the results of polarization and impedance measurements for the $FeSi_2$ electrode are in satisfactory agreement with the discharge-electrochemical desorption mechanism, in which both stages are irreversible and have unequal transfer coefficients; for adsorbed atomic hydrogen, the Langmuir adsorption isotherm is satisfied; simultaneously with the reaction of hydrogen evolution, the reaction of hydrogen absorption by the electrode material proceeds with diffusion control. It has been found that iron disilicide in an alkaline electrolyte is characterised by the low overvoltage of hydrogen evolution, and it is a promising electrode material for the electrolytic production of hydrogen.

Keywords: iron disilicide, hydrogen evolution reaction, electrocatalysis

INTRODUCTION

Hydrogen is used to accumulate, store, transport energy and is currently considered as a promising energy carrier for the development of low-carbon and zero-carbon economics to decrease the anthropogenic effect of climate [1–3]. The major advantages of hydrogen use and energy carrier are the absence of carbon dioxide emissions and the formation of water as a result of combustion, entering the closed cycle of hydrogen production.

The main methods of obtaining hydrogen in industry are steam conversion of methane and its homologues, coal gasification, and electrolysis of water [4]. The electrolytic method of obtaining hydrogen is the most ecologically friendly one. It is characterized by the high purity of resulting hydrogen, the simplicity of technological process, its continuity, flexibility and the possibility to obtain hydrogen directly under pressure [4, 5]. At the same time, electrolysis is characterized by low productivity and high energy consumption. One

of the ways to enhance the efficiency of the electrolytic method is to decrease the overvoltage of hydrogen reaction and thus to decrease the voltage at the electrolysis cell. In view of the catalytic nature of the process (reaction rate is essentially dependent on the nature of electrode material), researchers are actively searching for new materials exhibiting activity in the electrolytic evolution of hydrogen. The substances that were studied as the catalysts for the hydrogen evolution reaction (HER) include metals, alloys, intermetallic compounds, as well as systems containing various compounds of metals with nonmetals (carbides, sulphides, silicides, *etc*.) [6–8]. It has been stressed that in some cases the introduction of a nonmetal into the composition of the metal electrode not only improves its catalytic activity in hydrogen reaction but also enhances the corrosion stability of the material. Investigation of the silicides of transition metals as promising electrode materials for hydrogen power engineering has shown [6, 9–11] that these compounds may be characterized by the lower hydrogen overpotential than initial metals, possess high corrosion stability and favourable performance characteristics.

Previously we studied [12] the electrocatalytic activity of iron disilicide ($FeSi_2$) in the reaction of hydrogen evolution in 1.0 M NaOH solution and the effect of various methods of surface layer treatment on its activity in hydrogen reaction. It has been determined that the anodic and high-temperature chemical etching of $FeSi_2$ in alkaline electrolyte causes an increase in HER rate; the latter was explained by the development and change of the composition of electrode surface due to the dissolution of silicon and silicon dioxide under the effect of alkaline medium. In the present work, for the purpose of determining the effect of the alkaline electrolyte concentration on the kinetic regularities of HER and on electrochemical activity, the cathode behaviour of $FeSi_2$-electrode in 0.25–1.0 M NaOH solutions is investigated.

EXPERIMENTAL

Iron disilicide $FeSi_2$ (α-phase) synthesized using Bridgman method in vacuum in a resistive furnace with graphite heater was chosen as the material for investigation. The synthesized samples were cylindrical. Synthesis procedure and the materials under investigation have been described in [13, 14].

To carry out electrochemical measurements, the samples were placed into specially manufactured fluoroplastic holders and embedded in polymerized epoxy resin, only leaving free the disc-shaped working electrode surface 0.3 cm^2 in the area. All specific values given in the work are presented per unit geometric area of the electrode surface.

Electrochemical measurements were carried out at a temperature of 20 °C under the conditions of natural aeration in non-mixed NaOH solutions with the concentration 0.25–1.0 M. The solutions were prepared from deionised water (electrical resistivity 18.2 MOhm · cm, organic carbon content 4 μg/L) obtained with the help of the Milli-Q water purification system (Millipore, France), and NaOH (chemically pure grade). Measurements were carried out with a potentiostat-galvanostat with the embedded frequency analyzer Solartron 1280C (Solartron Analytical, UK) in the YaSE-2 electrochemical cell with cathode and anode compartments separated from each other with a porous glass diaphragm. The saturated silver chloride electrode was used as a reference electrode, while the platinum electrode was used as auxiliary. The potentials are given with respect to the standard hydrogen electrode.

Before measurements, the working surface of the electrode was polished with abrasive paper sheets with concurrently decreased grain size, ungreased with ethyl alcohol, and rinsed with the working solution. After immersion in the solution, the electrode was subjected to cathode polarization at the current density (i) equal to 0.5 mA/cm^2 for 10 min, then kept at the open-circuit potential (E) till the steady value was established, and finally impedance (Z) spectra were recorded. Before measuring impedance spectra, potentiostatic polarization of the electrode was carried out at each potential value until almost constant current value was established, and then impedance measurements were carried out at a given E and lower potential; the potential was changed in a definite step. On the basis of the obtained i values for a definite E value, cathode potentiostatic curves were plotted. The range of alternate current frequencies f ($\omega/2\pi$) involved in impedance measurements, where ω is the angular frequency (rad/s), was 20 kHz to 0.02 Hz (10 points per decade with the uniform distribution over the logarithmic scale), the amplitude of the alternate signal was 5–10 mV.

Measurements and data processing involved the software CorrWare2, ZPlot2, ZView2 (Scribner Associates, Inc.). Confidence intervals were calculated with the confidence level equal to 0.05.

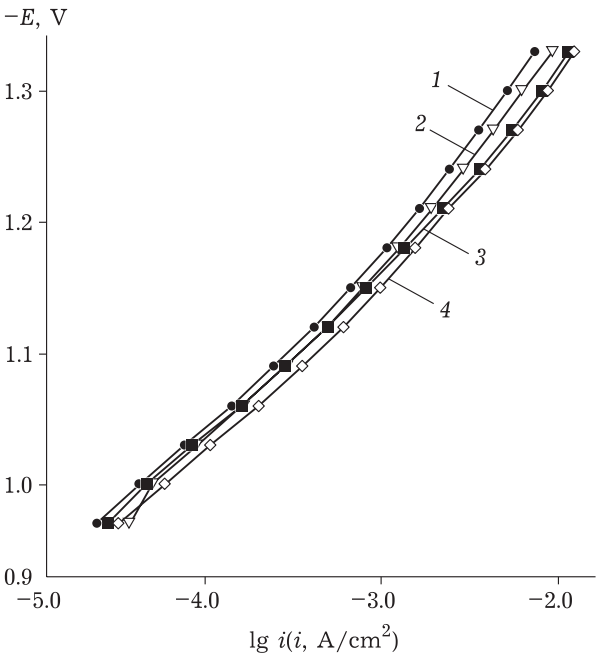

Fig. 1. Cathodic potentiostatic curves for $FeSi_2$-electrode in NaOH solutions with the concentration 0.25 (*1*); 0.5 (*2*); 0.75 (*3*); 1.0 M (*4*).

RESULTS AND DISCUSSION

The cathode potentiostatic curves for the $FeSi_2$-electrode in 0.25−1.0 M NaOH solutions (Fig. 1) are of the same type and contain the Tafel region at potential E values from −1.0 to −1.24 V with the slope b from −0.133 to −0.128 V (Table 1); at lower E an increase of the slope of E,lg$i$-curves was observed with an increase in cathode polarisation. The constant a in the Tafel equation for $FeSi_2$ in these solutions varies from −0.78 to −0.72 V, that is, according to the classification presented in [15], iron disilicide in the alkaline electrolyte relates to the materials with medium hydrogen evolution overvoltage.

The kinetic parameters of HER at the $FeSi_2$-electrode in 0.25−1.0 M NaOH solutions, the values of exchange current (i_0) and transfer coefficient (α) calculated from polarisation measurements for the limiting stage of the process are listed in Table 1. The kinetic parameters of HER on the $FeSi_2$-electrode at the Tafel-region potential values are close to theoretical ones for the slowed-down stage of charge transfer (see Table 1) [15, 16].

A decrease in the overvoltage of hydrogen evolution on iron disilicide with an increase in electrolyte concentration, as well as a slight excess of the calculated kinetic parameters over the values predicted by the theory, escalating with an increase in cathode polarisation (see Table 1), are likely due to the change of the morphology and composition of the electrode surface layer with changes in solution concentration. For instance, it is demonstrated by the authors of [17] that the electrode surface develops and gets enriched with the metal component of the alloy in the alkaline electrolyte as a consequence of selective dissolution of silicon from the silicide sublattice; the higher is electrolyte concentration, the stronger is this effect. For the $FeSi_2$-electrode, the latter is also confirmed by the results of capacitance measurements. The differential capacitance of silicide, measured at the alternate current frequency of 10 kHz, increases from 37.8 to 56.4 μF/cm² (at E = −1.05 V) with an increase in NaOH concentration from 0.25 to 1.0 M.

TABLE 1

Kinetic parameters of the reaction of hydrogen evolution on $FeSi_2$-electrode in 0.25−1.0 M NaOH solutions

Solution	$-a$, V	$-b$, V	$\left(\frac{\partial \lg i}{\partial \lg a_{\pm NaOH}}\right)_E$ *	$\left(\frac{\partial E}{\partial \lg a_{\pm NaOH}}\right)_i$, V*	α	$i_0 \cdot 10^6$, A/cm²
0.25 M NaOH	0.78±0.01	0.133±0.002	0.19 (E = −1.05 V) / 0.24 (E = −1.15 V)	0.024 (i = 0.1 mA/cm²) / 0.032 (i = 1 mA/cm²)	0.44±0.01	1.38±0.17
0.5 M NaOH	0.76±0.02	0.131±0.002	0.19 (E = −1.05 V) / 0.24 (E = −1.15 V)	0.024 (i = 0.1 mA/cm²) / 0.032 (i = 1 mA/cm²)	0.45±0.02	1.65±0.28
0.75 M NaOH	0.74±0.02	0.128±0.002	0.19 (E = −1.05 V) / 0.24 (E = −1.15 V)	0.024 (i = 0.1 mA/cm²) / 0.032 (i = 1 mA/cm²)	0.46±0.01	1.73±0.34
1.0 M NaOH	0.72±0.02	0.129±0.001	0.19 (E = −1.05 V) / 0.24 (E = −1.15 V)	0.024 (i = 0.1 mA/cm²) / 0.032 (i = 1 mA/cm²)	0.46±0.01	2.72±0.22

Note. $a_{\pm NaOH}$ − the mean ion activity of NaOH solution; α − transfer coefficient for the limiting stage of the process; i_0 − the density of exchange current.

* Numerator and denominator show the values of parameters at the corresponding potential (E) and current density (i), indicated in parentheses.

The impedance spectra for the $FeSi_2$-electrode in 0.25–1.0 M NaOH solutions at E in the Tafel region represent a capacity semi-circle with a biased centre, related to an asymmetric maximum on the dependence of phase angle on the logarithm of alternate current frequency (Fig. 2). The value of electrode impedance in all solutions changes in agreement with the polarisation curves.

The appearance of impedance plots (see Fig. 2) points to the stage nature of HER; not less than two time constants are necessary to describe these stages. Relying on the kinetic parameters of HER, obtained for $FeSi_2$ on the basis of direct-current measurements (see Table 1), the process of hydrogen evolution on silicide may proceed along the routes: discharge – electrochemical desorption, or discharge – recombination with decelerated discharge stage, or along the route: discharge – electrochemical desorption with decelerated stage of electrochemical desorption. In addition, within the entire potential region under study, the hydrogen reaction on silicide may be complicated by adsorption, lateral diffusion of atomic hydrogen, *etc.*

To simulate HER on the $FeSi_2$-electrode, equivalent electric circuits were used as shown in Fig. 3. In the scheme presented in Fig. 3, *a*: R_s is electrolyte resistance; R_1 is the charge transfer resistance; resistance R_2 and capacity C_2 describe the adsorption of atomic hydrogen H_{ads} on electrode surface; C_1 is the capacitance of the electric double layer. In the circuit shown in Fig. 3, *b* the constant-phase element CPE_1 is used instead of the capacitance of the electric double layer, providing a more precise description of electric double layer charging on the non-uniform surface of the solid electrode [18].

The impedance of CPE is equal to [18]:

$$Z_{CPE} = Q^{-1}(j\omega)^{-p}$$

where Q is the numerical value of admittance at $\omega = 1$ rad/s, p is the parameter characterising the phase angle of CPE.

Equivalent circuits shown in Fig. 3, *c*, *d* describe the HER complicated by hydrogen absorption reaction [19]. The physical sense of elements R_s, R_1, R_2, C_2 and CPE_1 in these circuits is the same as that for circuits in Fig. 3, *a*, *b*; R_{abs} is the resistance of hydrogen transfer from the adsorbed state into absorbed one (H_{abs}), Z_d is the impedance of hydrogen diffusion in the solid phase.

The final impedance of diffusion is determined by equation [18]:

$$Z_d = R_d \frac{\text{th}\sqrt{j\omega\tau_d}}{\sqrt{j\omega\tau_d}}$$

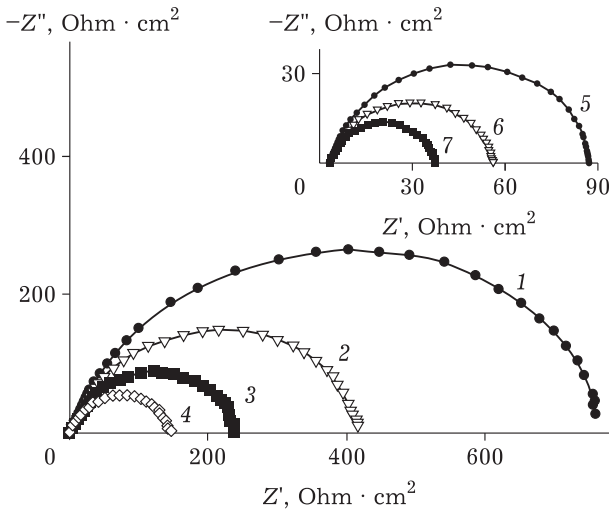

Fig. 2. Impedance spectra of $FeSi_2$-electrode in 0.5 M NaOH solution at $-E$, V: 1.03 (*1*); 1.06 (*2*); 1.09 (*3*); 1.12 (*4*); 1.15 (*5*); 1.18 (*6*); 1.21 (*7*).

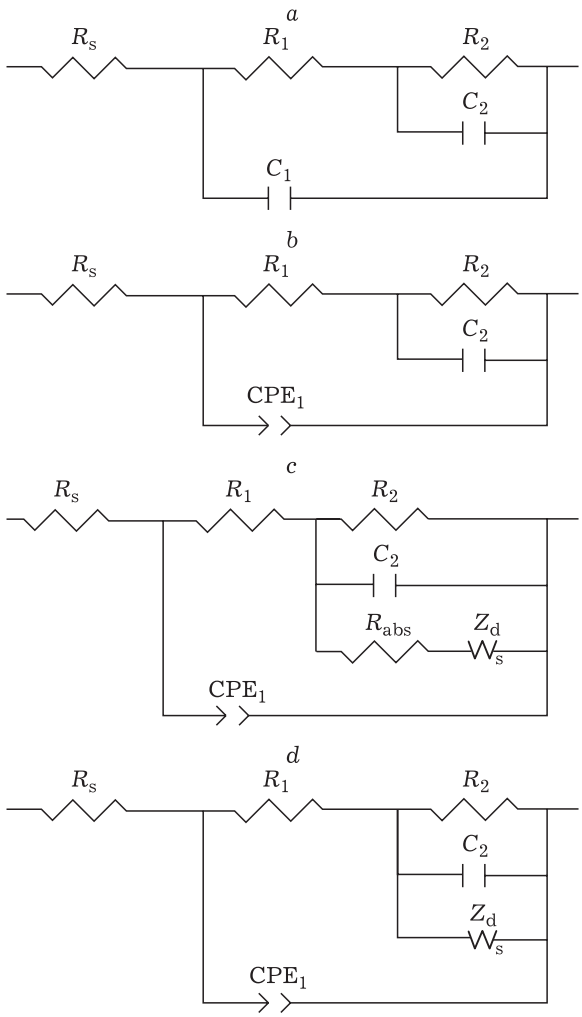

Fig. 3. Equivalent electric circuits for $FeSi_2$-electrode in 0.25–1.0 M NaOH solutions in the potential region of hydrogen evolution.

TABLE 2

Parameters of the equivalent circuit (Fig. 3, *d*) for $FeSi_2$-electrode in 0.5 M NaOH solution

$-E$, V	R_1, Ohm · cm^2	R_2, Ohm · cm^2	R_d, Ohm · cm^2	τ_d, s	$C_2 \cdot 10^5$, F/cm^2	$Q_1 \cdot 10^4$, F · cm^{-2} · s$^{(p_1-1)}$	p_1
1.03	35.5	795.0	9595	3.85	0.63	2.33	0.818
1.06	25.9	428.0	5645	1.52	0.88	1.92	0.838
1.09	16.1	233.0	3875	0.58	0.80	1.81	0.841
1.12	14.0	137.0	1820	0.15	0.88	1.74	0.843
1.15	11.7	80.3	843	0.13	1.25	1.33	0.874
1.18	8.8	48.6	496	0.065	1.48	1.25	0.877
1.21	6.4	30.1	274	0.041	1.41	1.07	0.899

where R_d is the diffusion resistance, τ_d is the characteristic time of diffusion.

The absence of element R_{abs} in the circuit shown in Fig. 3, *d* is reasonable in the case if the hindrance in $H_{ads} \rightarrow H_{abs}$ transition is small.

The application of the nonlinear least squares method (ZView2 software) has shown that the equivalent circuit in Fig. 3, *d* provides a reasonable description of the experimental impedance spectra for the $FeSi_2$-electrode. The χ^2 criterion, calculated in ZView2 (using the statistical weights expressed through the reciprocal scalar impedance), for the circuit shown in Fig. 3, *d* is equal to $(2.9-5.1) \cdot 10^{-5}$; the sum of square deviations is $(1.9-4.2) \cdot 10^{-3}$; error in determination of R_s, R_2 and CPE_1 does not exceed 3–5 %; R_1 and C_2 – 8–10 %; R_d and τ_d – 10–12 %. With a simpler equivalent circuit that does not take into account the volume solid-phase diffusion of atomic hydrogen in silicide (see Fig. 3, *b*), the χ^2 criterion increases to $(0.6-1.8) \cdot 10^{-4}$; the sum of square deviations increases to $(0.4-1.2) \cdot 10^{-2}$.

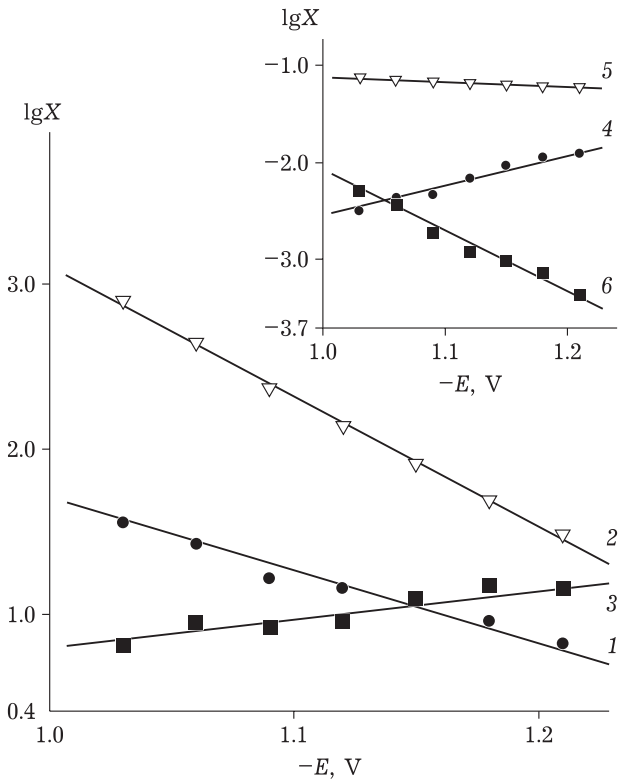

Fig. 4. Dependences of lg*X* (where $X = R_1$ (*1*); R_2 (*2*); C_2 (*3*); iR_1 (*4*); iR_2 (*5*); R_2C_2 (*6*)) on the potential of $FeSi_2$-electrode in 0.5 M NaOH solution. R_1 and R_2 – resistance, Ohm · cm^2; C_2 – capacity, μF/cm^2; iR_1, iR_2 – the products of current density and resistance, V; R_2C_2 – the product of resistance and capacity, s.

The values of parameters for the equivalent circuit shown in Fig. 3, *d* for the $FeSi_2$-electrode in 0.5 M NaOH solution are presented in Table 2.

Results of the determination of numerical values of R_1, R_2, C_2 for the equivalent circuit shown in Fig. 3, *d*, and the products iR_1, iR_2, R_2C_2 for all studied solutions were analysed depending on potential in semi-logarithmic coordinates (Fig. 4, Table 3). Within the studied potential range, experimental slopes $(\partial \lg X/\partial E)_{\alpha_{\pm NaOH}}$, where $X = R_1$, R_2, C_2, iR_1, iR_2, R_2C_2, are close to theoretical values for the mechanism discharge – electrochemical desorption, in which both stages are irreversible and are characterised by unequal transfer coefficients [20, 21]. The linearity of $\lg(R_1, R_2, C_2)$,*E*-dependences provides evidence that adsorption follows the Langmuir isotherm for adsorbed atomic hydrogen. The transfer coefficients for the limiting stage, determined on the basis of impedance measurements [20], are in reasonable agreement with the coefficients obtained from polarisation data (see Table 1). For 0.25, 0.5, 0.75 and 1.0 M NaOH solutions, α is equal to 0.44±0.01, 0.46±0.02, 0.47±0.02 and 0.49±0.01, respectively.

The decreased values of $(\partial \lg X/\partial E)_{\alpha_{\pm NaOH}}$ derivatives, where $X = R_1$, R_2, C_2, for the $FeSi_2$-electrode in comparison with the values reported in [20] for the route discharge – electrochemical desorption, according to [22], may be connected with the fact that absorption of atomic hydrogen by electrode material proceeds simultaneously

TABLE 3

The slopes $(\partial \lg X/\partial E)_{a_{\pm NaOH}}$ (where $X = R_1$, R_2, C_2, iR_1, iR_2, R_2C_2) for $FeSi_2$-electrode in 0.25–1.0 M NaOH solutions

Solution	$\left\{\frac{\partial \lg R_1}{\partial E}\right\}_{a_{\pm NaOH}}$, V^{-1}	$\left\{\frac{\partial \lg R_2}{\partial E}\right\}_{a_{\pm NaOH}}$, V^{-1}	$\left\{\frac{\partial \lg C_2}{\partial E}\right\}_{a_{\pm NaOH}}$, V^{-1}	$\left\{\frac{\partial \lg iR_1}{\partial E}\right\}_{a_{\pm NaOH}}$, V^{-1}	$\left\{\frac{\partial \lg iR_2}{\partial E}\right\}_{a_{\pm NaOH}}$, V^{-1}	$\left\{\frac{\partial \lg R_2C_2}{\partial E}\right\}_{a_{\pm NaOH}}$, V^{-1}
0.25 M NaOH	5.7±0.2	7.5±0.2	−1.2±0.2	−1.9±0.2	0.15±0.2	6.3±0.3
0.5 M NaOH	4.4±0.4	7.9±0.2	−1.9±0.3	−2.9±0.3	0.53±0.3	6.0±0.3
0.75 M NaOH	4.5±0.4	8.0±0.3	−1.1±0.2	−3.2±0.3	0.29±0.2	6.9±0.2
1.0 M NaOH	4.2±0.3	8.4±0.3	−1.1±0.2	−2.7±0.2	0.71±0.2	7.3±0.2

with the reaction of hydrogen evolution. The satisfactory completion of the equivalent circuit shown in Fig. 3, *d* in the simulation of experimental impedance spectra of iron silicide agrees with this statement and provides evidence that the process determining the rate of hydrogen absorption is withdrawal of atomic hydrogen from the surface deep into the electrode material (solid-phase diffusion of atomic hydrogen). The authors of [12, 23], who studied the cathode evolution of hydrogen on FeSi and $FeSi_2$ in 1.0 M NaOH, also determined that HER on silicides is complicated by the process of hydrogen absorption.

CONCLUSION

It is determined on the basis of polarisation and impedance measurements that the reaction of hydrogen evolution on the $FeSi_2$-electrode in 0.25–1.0 M NaOH solutions proceeds along the route: discharge – electrochemical desorption, in which both stages are irreversible and are characterised by unequal transfer coefficients; for adsorbed atomic hydrogen, the Langmuir adsorption isotherm is fulfilled; simultaneously with HER, the reaction of hydrogen absorption proceeds under diffusion control. It is discovered that the overvoltage of hydrogen evolution decreases with an increase in electrolyte concentration; the latter circumstance is explained by the development and change of the composition of electrode surface layer, caused by selective dissolution of silicon. It is revealed that iron disilicide in the alkaline electrolyte within the studied concentration range is characterised by rather low overvoltage of hydrogen evolution and thus this is a promising electrode material for the electrolytic hydrogen evolution.

Acknowledgements

The work was carried out with financial support from the Perm Research and Education Centre "Rational Subsurface Management", 2022.

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