

## Original articles

Research article

<https://doi.org/10.17308/kcmf.2022.24/9058>**The kinetics of cathodic hydrogen evolution on titanium disilicide in a sulphuric acid solution**V. V. Tretyakova, V. V. Panteleeva , A. B. SheinPerm State University,  
15 Bukirev str., Perm 614990, Russian Federation**Abstract**

The kinetics and mechanism of hydrogen evolution reaction on the  $\text{TiSi}_2$  electrode in  $x \text{M H}_2\text{SO}_4 + (0.5 - x) \text{M Na}_2\text{SO}_4$  ( $x = 0.5; 0.35; 0.20; 0.05$ ) solutions were studied using the methods of polarisation and impedance measurements.

The cathodic polarisation curves of  $\text{TiSi}_2$  were characterised by a Tafel section with a slope of 0.116–0.120 V at  $E$  ranging from  $-0.30$  to  $-0.48$  V (SHE). The value of hydrogen evolution overpotential at  $i = 1 \text{ A/cm}^2$  for  $\text{TiSi}_2$  was 0.90–0.96 V. The kinetic parameters of the hydrogen evolution reaction on silicide were close to the theoretical values for the slow stage of charge transfer.

Based on the measurements of the differential capacitance of the  $\text{TiSi}_2$  electrode (at  $f = 10 \text{ kHz}$ ), depending on the cathodic polarisation and acidity of the electrolyte, it was concluded that a thin dielectric film of silicon dioxide ( $\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{H}^+ + 4\text{e}^-$ ) was present on the surface of the silicide. The film was not reduced with low cathodic polarisations.

The impedance spectra of the  $\text{TiSi}_2$  electrode at the potentials of the Tafel region were capacitive semicircles with a misplaced centre. The impedance spectra were described by an equivalent electrical circuit, the Faraday impedance of which consisted of a series-connected charge transfer resistance  $R_1$  and a parallel  $R_2C_2$  chain corresponding to the adsorption of atomic hydrogen on the electrode surface. The impedance of the double layer capacitance was modelled using the constant phase element  $\text{CPE}_1$ . The  $\chi^2$  criterion for the circuit was  $(1.3\text{--}3.7) \cdot 10^{-4}$  (when using data modulus weighting), the sum of square deviations was  $(1.5\text{--}4.1) \cdot 10^{-2}$ , and the error in the determination of the values of circuit parameters did not exceed 10 %.

The experimental values of the slopes of  $\lg R_1, E^-$ ,  $\lg R_2, E^-$ , and  $\lg C_2, E^-$  dependences were close to the theoretical values of the slopes for the discharge-electrochemical desorption mechanism, in which both stages were irreversible and the transfer coefficients of the stages were not equal, when the Langmuir isotherm for adsorbed atomic hydrogen was fulfilled. The reaction of absorption of hydrogen with the kinetic control proceeded at the same time as the hydrogen evolution reaction.

**Keywords:** titanium disilicide  $\text{TiSi}_2$ , hydrogen evolution reaction, sulphuric acid solution, impedance

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## 1. Introduction

The hydrogen evolution reaction (HER) is an electrocatalytic process whose rate considerably depends on the nature and structure of the electrode material as well as the condition of its surface. Therefore, metals, alloys, intermetallic, and metal-like (carbides, silicides, germanides, nitrides, chalcogenides, and composite materials based on them) compounds were studied as HER catalysts [1–16].

The kinetics of HER on transition metal silicides have not been thoroughly studied. The study of HER on transition metal silicides showed [1–4, 7–9, 10, 13–15] that depending on the nature and concentration of metal and silicon in the compound as well as the pH and composition of the medium, silicides can be characterised by lower or higher hydrogen overpotential as compared to the corresponding pure metals, and it was noted [1, 2, 13] that a thin oxide film of silicon dioxide influences the kinetics of hydrogen evolution on silicides in an acidic media with low cathodic polarisations.

The purpose of this work was to establish the kinetics and mechanism of the hydrogen evolution reaction on titanium disilicide ( $\text{TiSi}_2$ ) in sulphuric acid solutions with various concentrations in order to determine the electrochemical activity of  $\text{TiSi}_2$  in HER.

## 2. Experimental

The study was conducted using titanium disilicide ( $\text{TiSi}_2$ ) obtained by the Bridgman method.

Electrochemical measurements were performed at a temperature of 25°C under natural aeration in unstirred solutions of 0.5 M  $\text{H}_2\text{SO}_4$ ; 0.35 M  $\text{H}_2\text{SO}_4$  + 0.15 M  $\text{Na}_2\text{SO}_4$ ; 0.20 M  $\text{H}_2\text{SO}_4$  + 0.30 M  $\text{Na}_2\text{SO}_4$ ; 0.05 M  $\text{H}_2\text{SO}_4$  + 0.45 M  $\text{Na}_2\text{SO}_4$ . The solutions were prepared using deionised water (with water resistivity of 18.2 M $\Omega$  cm and organic carbon content of 4  $\mu\text{g/l}$ ) which was obtained using a Milli-Q water purification system by Millipore (France) and chemically pure reagents  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ . The measurements were conducted using a potentiostat/galvanostat with a built-in Solartron 1280C frequency analyser by Solartron Analytical (Great Britain) in a YASE-2 electrochemical cell with cathode and anode sections separated by a porous glass diaphragm. A saturated silver chloride

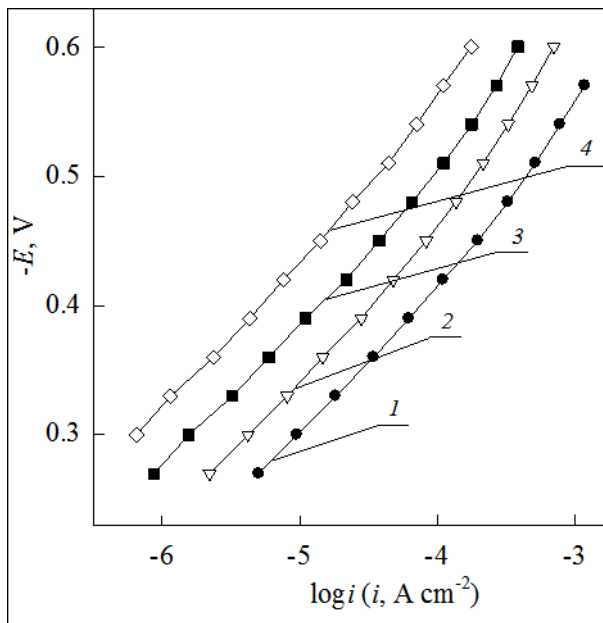
electrode was used as the reference electrode and a platinum electrode was used as the auxiliary electrode. The potentials presented in this work are relative to the standard hydrogen electrode.

Before performing the measurements, the working surface of the electrode was polished with abrasive papers with decreasing grain size, degreased with ethyl alcohol, and rinsed with a working solution. Once the electrode was immersed in the solution, it was subjected to cathodic polarisation with a current density of 0.5 mA/cm<sup>2</sup> for 10 minutes, then held with an open circuit potential until a stable potential was established, and then the impedance spectra were recorded. Before the measurement of the impedance spectra, potentiostatic polarisation of the electrode was conducted at each potential until an almost constant current value was established. After that, the impedance was measured at this value of  $E$  and lower potentials, and the potential was changed with a fixed step. Cathodic potentiostatic curves were plotted based on the obtained values of  $i$  for this value of  $E$ . The range of frequencies  $f(\omega/2\pi)$  used for impedance measurements was from 20 kHz to 0.02 Hz, while the amplitude of the alternating signal was 5–10 mV.

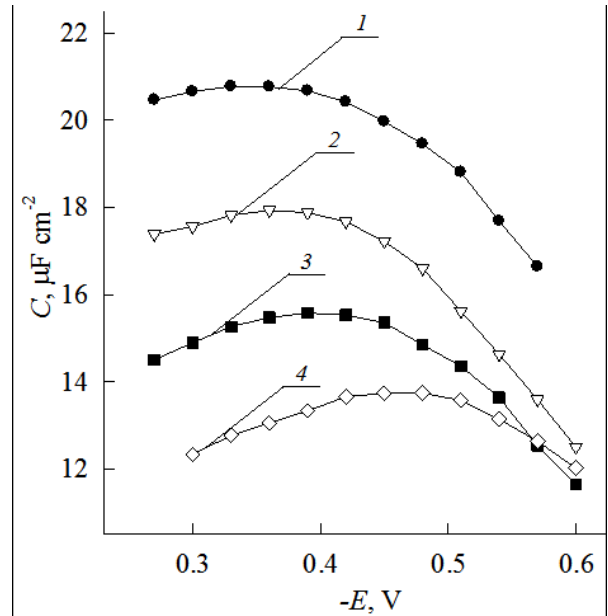
## 3. Results and discussion

The cathodic potentiostatic curves of the  $\text{TiSi}_2$  electrode in sulphuric acid solutions are presented in Fig. 1. There is a linear section with a slope of 0.116–0.120 V on the cathodic silicide curves in the potential region from -0.30 to -0.48 V, and the range of potentials for recording the linear dependence of  $E$  on  $\lg i$  decreases with a decrease in the acidity of the electrolyte (Table 1). The slope increases in the region of  $E < -0.48$  V with an increase in cathodic polarisation. The value of hydrogen evolution overpotential at  $i = 1$  A/cm<sup>2</sup> for  $\text{TiSi}_2$  is 0.90–0.96 V, meaning that in the sulphate electrolyte titanium disilicide refers to materials with high hydrogen evolution overpotential and, as a result, it does not have high electrochemical activity in HER.

The kinetic parameters of the hydrogen evolution reaction on the  $\text{TiSi}_2$  electrode with the potentials of the linear dependence of  $E$  on  $\lg i$  on polarisation curves are close to the theoretical values for the slow stage of charge transfer (Table 1) [17].



**Fig. 1.** Cathodic polarisation curves for the TiSi<sub>2</sub> electrode in solutions: 1 – 0.5 M H<sub>2</sub>SO<sub>4</sub>; 2 – 0.35 M H<sub>2</sub>SO<sub>4</sub> + 0.15 M Na<sub>2</sub>SO<sub>4</sub>; 3 – 0.20 M H<sub>2</sub>SO<sub>4</sub> + 0.30 M Na<sub>2</sub>SO<sub>4</sub>; 4 – 0.05 M H<sub>2</sub>SO<sub>4</sub> + 0.45 M Na<sub>2</sub>SO<sub>4</sub>



**Fig. 2.** The dependence of differential capacitance of the TiSi<sub>2</sub> electrode on the potential at a frequency of 10 kHz in solutions: 1 – 0.5 M H<sub>2</sub>SO<sub>4</sub>; 2 – 0.35 M H<sub>2</sub>SO<sub>4</sub> + 0.15 M Na<sub>2</sub>SO<sub>4</sub>; 3 – 0.20 M H<sub>2</sub>SO<sub>4</sub> + 0.30 M Na<sub>2</sub>SO<sub>4</sub>; 4 – 0.05 M H<sub>2</sub>SO<sub>4</sub> + 0.45 M Na<sub>2</sub>SO<sub>4</sub>

The differential capacitance of the TiSi<sub>2</sub> electrode at an alternating current frequency of  $f = 10$  kHz in the studied region was  $\sim 10$ – $22$   $\mu\text{F}/\text{cm}^2$  and at the potentials of the linear section on the cathodic curves it passed through a mild maximum and decreased with a decrease in the acidity of the medium (Fig. 2). The differential capacitance was determined using the values of the imaginary component of the impedance  $Z''$ :

$$C = -\frac{1}{\omega Z''},$$

where  $\omega$  was the circular frequency of the alternating current ( $\omega = 2\pi f$ ).

In accordance with [18], at room temperature titanium disilicide is a metallic conductor and is characterized by resistivity not exceeding

$20 \mu\Omega \text{ cm}$ . Therefore, the reduced values of the differential capacitance of the TiSi<sub>2</sub> electrode as compared to the capacitance values typical for solid metal electrodes in aqueous electrolyte solutions ( $\sim 20$ – $40 \mu\text{F}/\text{cm}^2$ ) cannot be associated with the nature of conductivity and low concentration of charge carriers in the silicide.

The low values of the silicide capacitance were apparently due to the presence of a thin dielectric film of silicon dioxide on its surface ( $\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{H}^+ + 4\text{e}^-$ ,  $E^0 = -0.86 \text{ V}$  [19]). An oxide film was formed on the silicide at the corrosion potential and was not subject to reduction during cathodic polarisation. The authors [1, 2] also showed that SiO<sub>2</sub> was stable in acidic media with low cathodic polarisations.

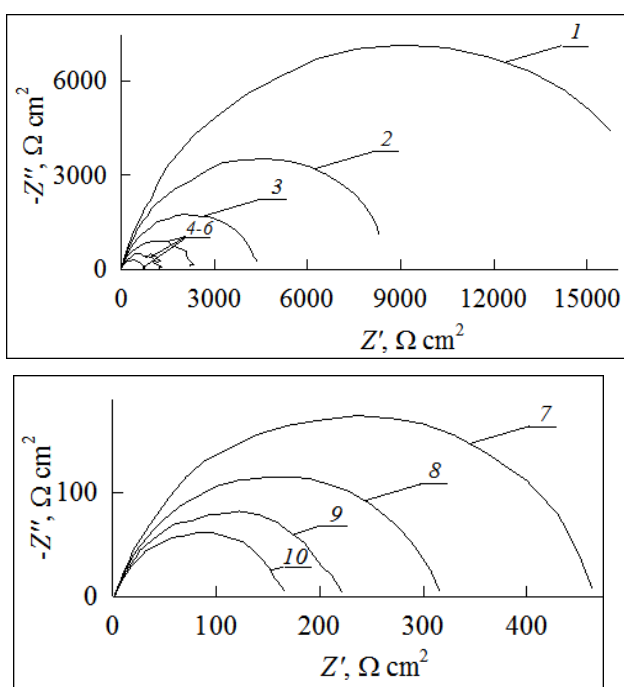
**Table. 1.** Kinetic parameters of hydrogen evolution reaction for the TiSi<sub>2</sub> electrode in sulphuric acid solutions

Solution	$-E, \text{ V}$	$-\left(\frac{\partial E}{\partial \log i}\right)_{c_{\text{H}^+}}, \text{ V}$	$-\eta, \text{ B}$ at $i = 1 \text{ A}/\text{sm}^{-2}$	$\left(\frac{\partial \log i}{\partial \log c_{\text{H}^+}}\right)_E$	$-\left(\frac{\partial E}{\partial \log c_{\text{H}^+}}\right)_i, \text{ V}$
0.5 M H <sub>2</sub> SO <sub>4</sub>	0.30–0.48	0.120±0.003	0.90±0.02	1.01±0.04	0.123±0.005
0.35 M H <sub>2</sub> SO <sub>4</sub> + 0.15 M Na <sub>2</sub> SO <sub>4</sub>	0.30–0.48	0.119±0.003	0.92±0.02		
0.20 M H <sub>2</sub> SO <sub>4</sub> + 0.30 M Na <sub>2</sub> SO <sub>4</sub>	0.33–0.48	0.116±0.004	0.94±0.04		
0.05 M H <sub>2</sub> SO <sub>4</sub> + 0.45 M Na <sub>2</sub> SO <sub>4</sub>	0.36–0.48	0.117±0.003	0.96±0.03		

The decrease in the differential capacitance due to a decrease in acidity of the electrolyte (Fig. 2) may be associated with the lower rate of chemical dissolution of  $\text{SiO}_2$  in solutions with lower acidity. According to [20], the rate of chemical dissolution of various forms of silicon dioxide (quartz or amorphous oxide) was minimal at pH  $\sim(2-3)$  and increased with deviations from this value in both directions. The pH values of the studied electrolytes were 0.4–1.8 and, therefore, correspond to the descending branch of the curve of the dependence of  $\text{SiO}_2$  dissolution rate on the pH of the solution.

The introduction of sodium fluoride (0.005 M) into a solution of 0.5 M  $\text{H}_2\text{SO}_4$  leading to the dissolution of silicon dioxide [20] resulted in an increase in the differential capacity of the silicide by  $\sim 1.3-2.1$  times. The higher values of the differential capacitance of silicide in the presence of fluoride confirmed the assumption about the low capacitance of  $\text{TiSi}_2$  in an acidic fluoride-free solution associated with the presence of a thin oxide film on its surface.

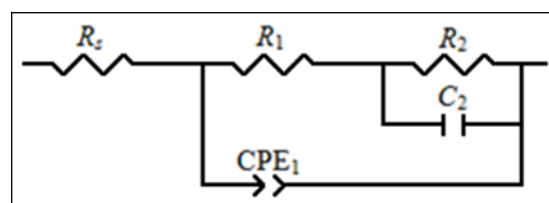
The impedance spectra of the  $\text{TiSi}_2$  electrodes in the studied solutions were capacitive semicircles with a misplaced centre (Fig. 3) which



**Fig. 3.** Impedance spectra of the  $\text{TiSi}_2$  electrode in 0.20 M  $\text{H}_2\text{SO}_4$  + 0.30 M  $\text{Na}_2\text{SO}_4$  at  $E$ , V: 1 – -0.33; 2 – -0.36; 3 – -0.39; 4 – -0.42; 5 – -0.45; 6 – -0.48; 7 – -0.51; 8 – -0.54; 9 – -0.57; 10 – -0.60

corresponded to asymmetric maxima in the graph of the dependence of the phase angle  $\varphi$  on the logarithm of the alternating current frequency  $f$ . The electrode quantity  $|Z|$  changed in accordance with the shape of the polarisation curves in all solutions (Fig. 1).

An equivalent electrical circuit presented in Fig. 4 was used to simulate HER on the  $\text{TiSi}_2$  electrode at potentials of linear dependence of  $E$  on  $\lg i$  on cathodic polarisation curves in the studied solutions. The circuit includes the following:  $R_s$  is the electrolyte resistance,  $R_1$  is the charge transfer resistance, while resistance  $R_2$  and capacitance  $C_2$  describe the adsorption of atomic hydrogen on the electrode surface and the  $\text{CPE}_1$  element simulates double layer capacitance on the inhomogeneous surface of the solid electrode.



**Fig. 4.** The equivalent electrical circuit for the  $\text{TiSi}_2$  electrode in sulphuric acid solutions over the range of hydrogen evolution potentials

The impedance of the constant phase element was:

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

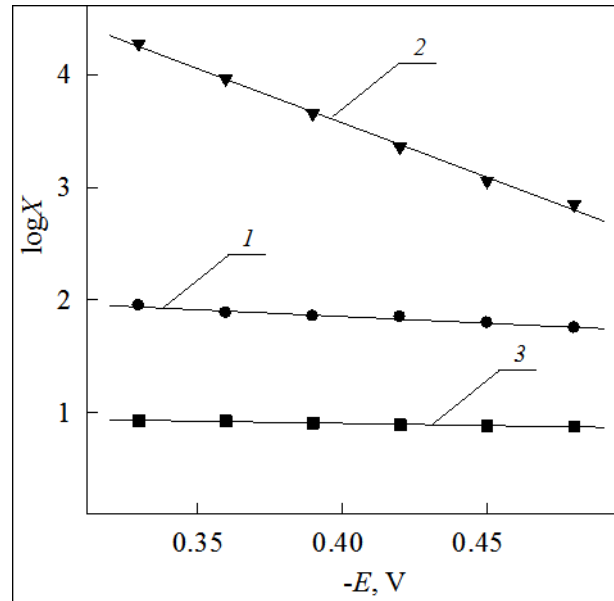
In this ratio with  $p = 1 - \gamma$  the constant phase element is non-ideal capacitance and  $\gamma$  is the value significantly less than 1 (typically  $\gamma < 0.2$ ) [21].

The use of the non-linear least squares method (ZView2 program) showed that the equivalent circuit in Fig. 4 presented a satisfactory description of the experimental impedance spectra of the  $\text{TiSi}_2$  electrode obtained with  $E$  ranging from -0.30 to -0.48 V. The  $\chi^2$  criterion calculated for this circuit using ZView2 was  $(1.3-3.7) \cdot 10^{-4}$ , the sum of square deviations was  $(1.5-4.1) \cdot 10^{-2}$ , and the error in determining the values of the circuit parameters did not exceed 5% and reached 10% only for the value of  $R_1$ . The latter seemed to be associated with the difficulty of the determination of small values of  $R_1$  as compared to the large values of  $R_2$ . The values of the equivalent circuit parameters for the 0.20 M

$\text{H}_2\text{SO}_4 + 0.30 \text{ M Na}_2\text{SO}_4$  solution are presented in Table 2.

The results of the determination of the numerical values of  $R_1$ ,  $R_2$ , and  $C_2$  parameters of the equivalent circuit in Fig. 4 for the  $\text{TiSi}_2$  electrode in the studied solutions were analysed depending on the potential in semi-logarithmic coordinates (Fig. 5, Table 3). In the potential region from  $-0.30$  to  $-0.48 \text{ V}$ , the  $\lg X, E$  dependences, where  $X = R_1, R_2, C_2$ , were linear, which confirmed that the Langmuir adsorption isotherm for adsorbed atomic hydrogen was fulfilled [22]. The experimental values of the slopes  $(\partial \lg X / \partial E)_{c_{\text{H}^+}}$  were close to the theoretical values of the slopes for the discharge-electrochemical desorption mechanism, in which both stages were irreversible and the transfer coefficients of the stages were not equal [22].

The reduced values of derivatives  $(\partial \lg X / \partial E)_{c_{\text{H}^+}}$  according to [23], may be associated with the reaction of absorption of atomic hydrogen by the electrode material proceeding at the same time with the hydrogen evolution reaction. The absence of an additional time constant characterising the hydrogen absorption in the impedance spectra of the  $\text{TiSi}_2$  electrode (Fig. 3) with the potentials of linear dependence of  $E$  on  $\lg i$  on the polarisation curves indicated that the transition of hydrogen from an



**Fig. 5.** Dependences of  $\lg X$  ( $X$ : 1 –  $R_1$ , 2 –  $R_2$ , 3 –  $C_2$ ) on the potential of the  $\text{TiSi}_2$  electrode in a solution of  $0.20 \text{ M H}_2\text{SO}_4 + 0.30 \text{ M Na}_2\text{SO}_4$ . Units of measurement:  $R_1$  and  $R_2$  in  $\text{Ohm} \times \text{cm}^2$ ,  $C_2$  in  $\mu\text{F}/\text{cm}^2$

adsorbed state to an absorbed state was probably the rate-determining process in the absorption of hydrogen. In this case, the resistance  $R_2$  in the equivalent circuit in Fig. 4 was expressed through the adsorption resistance  $R_{\text{ads}}$  and the absorption resistance  $R_{\text{abs}}$ :  $R_2 = \frac{R_{\text{ads}} R_{\text{abs}}}{R_{\text{ads}} + R_{\text{abs}}}$

**Table 2.** The values of the equivalent circuit parameters in Fig. 4 for the  $\text{TiSi}_2$  electrode in a solution of  $0.20 \text{ M H}_2\text{SO}_4 + 0.30 \text{ M Na}_2\text{SO}_4$

$-E, \text{V}$	$R_1, \Omega \text{ cm}^2$	$R_2, \Omega \text{ cm}^2$	$C_2 \cdot 10^6, \text{F} \cdot \text{sm}^{-2}$	$Q_1 \cdot 10^4, \text{F} \cdot \text{sm}^{-2} \cdot \text{s}^{(p_1-1)}$	$p_1$
0.33	89.2	18818	8.51	1.39	0.817
0.36	76.4	9145	8.43	1.50	0.821
0.39	71.7	4507	8.11	1.59	0.803
0.42	70.4	2263	7.83	1.66	0.798
0.45	62.4	1134	7.65	1.65	0.795
0.48	56.5	704.2	7.53	1.66	0.792

**Table 3.** Slope values  $(\partial \lg X / \partial E)_{c_{\text{H}^+}}$  ( $X = R_1, R_2, C_2$ ) for the  $\text{TiSi}_2$  electrode in sulphuric acid solutions

Solution	$-E, \text{V}$	$\left(\frac{\partial \log R_1}{\partial E}\right)_{c_{\text{H}^+}}, \text{V}^{-1}$	$\left(\frac{\partial \log R_2}{\partial E}\right)_{c_{\text{H}^+}}, \text{V}^{-1}$	$\left(\frac{\partial \log C_2}{\partial E}\right)_{c_{\text{H}^+}}, \text{V}^{-1}$
$0.5 \text{ M H}_2\text{SO}_4$	0.30–0.48	$0.9 \pm 0.5$	$9.1 \pm 0.5$	$0.35 \pm 0.03$
$0.35 \text{ M H}_2\text{SO}_4 + 0.15 \text{ M Na}_2\text{SO}_4$	0.33–0.48	$1.5 \pm 0.2$	$8.3 \pm 0.4$	$0.23 \pm 0.05$
$0.20 \text{ M H}_2\text{SO}_4 + 0.30 \text{ M Na}_2\text{SO}_4$	0.33–0.48	$1.2 \pm 0.3$	$9.4 \pm 0.6$	$0.37 \pm 0.03$
$0.05 \text{ M H}_2\text{SO}_4 + 0.45 \text{ M Na}_2\text{SO}_4$	0.36–0.48	$1.4 \pm 0.2$	$8.8 \pm 0.3$	$0.25 \pm 0.04$



#### 4. Conclusions

It was established that the hydrogen evolution reaction on titanium disilicide in a sulphuric acid electrolyte proceeded according to the discharge-electrochemical desorption path, both stages were irreversible, and the transfer coefficients of the stages were not equal. The Langmuir isotherm for adsorbed atomic hydrogen was fulfilled. It was suggested that HER was complicated by the hydrogen absorption reaction with the electrode material proceeding with kinetic control (over the whole range of the studied potentials). It was found that titanium disilicide in a sulphuric acid electrolyte is a material with a high hydrogen evolution overpotential and did not have a high electrochemical activity in HER. The presence of a thin oxide film was noted on the electrode surface at low cathodic polarisations.

#### Author contributions

All authors made an equivalent contribution to the preparation of the publication.

#### Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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