

Электрохимическая энергетика. 2021. Т. 21, № 3. С. 164–170

Electrochemical Energetics, 2021, vol. 21, no. 3, pp. 164–170

<https://energetica.sgu.ru>

<https://doi.org/10.18500/1608-4039-2021-21-3-164-170>

Article

Influence of impurities of the transitional metals Fe, Ni, and Co on the hydrolysis kinetics of BH_4^- ions in alkaline solutions

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Abstract. The influence of small amounts of the Fe, Co, and Ni impurities on the spontaneous hydrolytic process of borohydride was studied within a temperature range of 60–100°C. The object under study was a simulated solution containing 9.53 M of OH^- ions and 0.14 M of BH_4^- ions, used as a fuel for borohydride fuel cells. The rate constant k of borohydride hydrolysis for a small amount of impurities at different temperature was estimated. The lowest non-accelerating concentrations of the impurities were established (~10 ppm for iron; ~1 ppm for cobalt). The strongest accelerating effect on the hydrolysis of BH_4^- ions was rendered by nickel impurities: self-hydrolysis was accelerated by 1.2 times for 1 ppm Ni. The ambiguous trend of the kinetic curves does not allow to accurately estimate the activation energy; however, the increased temperature enhances the catalytic effect of hydrolysis acceleration according to Arrhenius' equation.

Keywords: borohydride, hydrolysis reaction, rate constant, activation energy

For citation: Gamayunova I. M. The influence of impurities of the transition metals Fe, Ni, and Co on hydrolysis kinetics of BH_4^- ions in alkaline solutions. *Electrochemical Energetics*, 2021, vol. 21, no. 3, pp. 164–170 (in Russian). <https://doi.org/10.18500/1608-4039-2021-21-3-164-170>

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Научная статья

УДК 651.357

ВЛИЯНИЕ ПРИМЕСЕЙ ПЕРЕХОДНЫХ МЕТАЛЛОВ Fe, Ni И Co НА КИНЕТИКУ ГИДРОЛИЗА BH_4^- -ИОНОВ В ЩЕЛОЧНЫХ РАСТВОРАХ

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Аннотация. Исследовалось влияние небольших количеств примесей Fe, Co и Ni на самопроизвольный процесс гидролиза борогидрида в интервале температур 60–100°C. Исследуемый объект представлял собой модельный раствор, содержащий 9.53 М OH^- -ионов и 0.14 М BH_4^- -ионов и используемый в качестве топлива для борогидридных топливных элементов. Оценена константа скорости гидролиза борогидрида k для небольшого количества примесей при разных температурах. Установлены самые низкие не ускоряющие гидролиз концентрации примесей (~10 ppm для железа; ~1 ppm для кобальта). Наибольшее ускоряющее действие на гидролиз BH_4^- -ионов оказали примеси никеля: самогидролиз ускорился в 1.2 раза для 1 ppm Ni. Неоднозначный ход кинетических кривых не позволяет точно оценить энергию активации, однако увеличение температуры усиливает каталитический эффект ускорения гидролиза в полном соответствии с уравнением Аррениуса.

Ключевые слова: борогидрид, реакция гидролиза, константа скорости, энергия активации

Для цитирования: Гамаюнова И. М. Влияние примесей переходных металлов Fe, Ni и Co на кинетику гидролиза BH_4^- -ионов в щелочных растворах // Электрохимическая энергетика. 2021. Т. 21, № 3. С. 164–170. <https://doi.org/10.18500/1608-4039-2021-21-3-164-170>

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Introduction

Alkaline solutions of some borohydrides (LiBH_4 , NaBH_4 , and KBH_4) are used as fuel in direct borohydride fuel cells (DBFC) and hydrogen generators (HG) [1–7]. In such devices, borohydrides are used as suspensions or concentrated aqueous solutions with dissolved hydroxides as additives to stabilize the system by preventing BH_4^- hydrolysis as well as to determine and control its chemical and electrochemical activity [8]. During DBFC functioning, borohydrides are oxidized according to the model of fuel transformation at discharging [9], releasing the contained hydrogen and being converted into borates. The performance of such a fuel system is determined by the solubility of their components [10–12]. Nowadays, a large number of papers are devoted to describing the properties of alkaline aqueous solutions of borohydrides [13]. Special attention is paid to the self-destruction of kinetics of BH_4^- ions in solution, as well as to the influence of various factors, such as temperature, pH, and impurities (pollutions) on the hydrolysis rate [14–17]. Studying the acceleration of borohydride hydrolysis is very important for the development of hydrogen storage technologies [18–21]. The key factors of this hydrolytic process acceleration are increased temperatures and the presence of impurities in the borohydride fuel [22, 23]. The borohydride fuel is prepared with the help of industrial equipment and during this process the occurrence of various impurities is possible. The ions of various metals are the most probable type of pollution, which possess catalytic activity and accelerate the borohydride destruction rate.

The present paper is devoted to studying the influence of small quantities of Fe, Co, and Ni on the spontaneous borohydride hydrolytic process within the temperature range of 60–100°C. Direct experimental data of the decomposition rate of solutions containing BH_4^- and OH^- ions with metal impurities measured at several temperatures allowed us to estimate the maximum allowable concentration of impurities of each metal, which does not affect the rate of borohydride self-decomposition.

1. Materials and methods

The object under study was a model solution containing 9.53 M of OH^- ions (11.61 wt%) and 0.14 M of BH_4^- ions (0.15 wt%) used as a fuel for DBFC. The detailed characterization of this solution is given in [17]. The hydrogen storage capacity of this solution is 0.09 wt%. The density of this model solution is $1.3976 \text{ g}\cdot\text{mL}^{-1}$ at 25°C.

The composition of the mixture under study was calculated from the main substance content in the reagents used. Chemically pure NaBH_4 , KBH_4 , NaOH , and KOH (“Ecos” and “Aviabor”, Russian Federation) and distilled water without carbon dioxide were used to prepare original borohydride solutions (the “pure solution”). The composition of the solution was verified by the quantitative chemical analysis (acid-base and iodometric titration).

The content of OH^- , CO_3^{2-} ions and the sum of $\text{BO}_2^- + \text{BH}_4^-$ ions were determined by acid-base titration. For this purpose, a sample of the liquid solution (0.2–0.5 g) was quantitatively transferred into a glass for titration, with further diluting with distilled water up to 50 mL. The titration was done

with a 1 mol·L⁻¹ HCl solution under permanent stirring using a magnetic stirrer. The titrant flow on the sampling was 6–14 mL. The potentiometric titration was started from the initial pH of solution (as ordinarily pH was 11–13) and carried out to pH ≈ 2–3. Titration curves (the integral and differential curves) were processed by computer fitting of experimental and calculated titration curves as described in [24]. The simulated curve of acid-base titration was calculated by the Eq. (1):

$$V_{\text{HCl_fit}} = \frac{V_0 + V_{\text{HCl}}}{N_{\text{HCl}}} \left\{ C_{\text{OH}^-} + C_{\text{BH}_4^- + \text{BO}_2^-} + [\text{H}^+] - [\text{OH}^-] - \left([\text{BH}_4^-] + [\text{BO}_2^-] \right) + [\text{HCO}_3^-] + 2[\text{H}_2\text{CO}_3] \right\} \quad (1)$$

where V_0 is the volume of analyzed solution; V_{HCl} is the volume of titrant; N_{HCl} is the normality of titrant; C_{OH^-} , $C_{\text{BH}_4^- + \text{BO}_2^-}$ are the initial molar concentrations of ions; $[\text{H}^+]$, $[\text{OH}^-]$, $[\text{BH}_4^-]$, $[\text{BO}_2^-]$, $[\text{HCO}_3^-]$ and $[\text{H}_2\text{CO}_3]$ are the current equilibrium molar concentrations of ions.

The fitting of experimental and calculated titration curves allows us to define the quantity of components (n_{OH^-} , $n_{\text{BH}_4^- + \text{BO}_2^-}$, $n_{\text{CO}_3^{2-}}$) in probe. The content of BO_2^- ions was calculated by the difference of “general boron” minus borohydride:

$$n_{\text{BO}_2^-} = n_{\text{BH}_4^- + \text{BO}_2^-} - n_{\text{BH}_4^-} \quad (2)$$

The content of BH_4^- ions was determined by iodometric titration selectively.

Chemically pure salts $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 12\text{H}_2\text{O}$ (“Ecos” and “Aviabor”, Russian Federation) were used as the sources of metal impurities into the “pure solution”. All the solutions were prepared counting on the mass content of the metal ion. At first, the borohydride solution with 1 wt. % of the metal ion as the impurity was prepared and then it was diluted by adding a certain quantity of the filtrate to prepare borohydride solution with a certain amount of the impurities. For example, 2 g of the borohydride solution with 1 wt. % Fe were mixed with 18 g of the original solution to prepare 20 g of the

fuel mixture with 0.1 wt. % Fe. The weighing was done on a VLT-150-P laboratory electronic digital balance with the accuracy of ±0.001 g.

Each solution was kept at room temperature for ~20 min. 30 g of each solution was placed into a hermetically sealed Teflon® pot. The solutions were stored at a fixed temperature in a SNOL58/350 thermobox. The temperature range 60–100°C was chosen because of practical reasons. Below 60°C, hydrolysis in the alkaline solution proceeds with a low rate whose exact determination becomes very difficult. Heating above 100°C results in very intense decomposition and significant scattering of replicate experiments due to the fact that sampling may be accompanied by water evaporation and carbon dioxide absorption from the air by the hot concentrated alkaline solution.

The samples were periodically taken from each pot for chemical analysis. The first sample was taken in 30 min, further sampling was usually done 1 or 2 times per day (the schedule was adjusted depending on the hydrolysis rate). The whole cycle of observations could last several weeks. The boiling temperatures of the solutions considerably exceeded 100°C, so water evaporation from any pot did not exceed 50 mg per day at the highest temperature. The pots were weighed before and after every sampling, the loss of weight was taken into account to correct the composition. Sampling and sample preparation for iodometric titration (~10 min) and the iodometric titration itself (~2 min) were performed at room temperature; hence, borohydride self-hydrolysis was negligible.

Iodometric titration was used for borohydride analysis. The liquid sample of 0.2–0.5 g was quantitatively transferred into a 100 mL flask and brought to the mark with a 1 mol·L⁻¹ NaOH solution. Then, a 5 mL aliquot was sampled, transferred into a glass for titration, brought to 50 mL with a 1 mol·L⁻¹ NaOH solution with further titration with a 0.1 mol·L⁻¹ standard iodine solution. Titration was conducted by means of an automatic titrator ATP-02 (“Aquilon”,

Russian Federation) with a platinum indicator electrode, a glass reference electrode, and a magnetic stirrer. Precise titrant feed in the course of titration (an accuracy of $\pm 1 \mu\text{L}$) with computer recording of titration curves and computer fitting of experimental and calculated curves of acid-base and iodometric titrations provided the high reliability of our results [24].

2. Results and discussion

The detailed mathematical description of the kinetic curves of borohydride hydrolysis is presented in [17]. Three parts can be resolved on the kinetic curves of borohydride decomposition in the pure solution and the solution with impurities. Our experimental data completely correspond to the regularities reported in [17]. They are:

- the part characterizing the initial fast linear decomposition (Fig. 1, *a*), according to

$$\frac{v_0 - v}{v_0} = k\tau; \quad (3)$$

- the part characterizing the subsequent retarded decomposition by the logarithmic law (Fig. 1, *b*), according to

$$\ln \frac{v_0}{v} = k\tau; \quad (4)$$

- the part characterizing the further slower decomposition (Fig. 1, *c*), according to

$$\frac{1}{\tau} \ln \frac{v_0}{v} = k - h\tau, \quad (5)$$

where τ is the storage period; v is the mol number of borohydride at the instant τ ; v_0 is the mol number of borohydride at the initial instant of time $\tau = 0$; k is the kinetic constant; h is the correction parameter.

The kinetic curves in the $\frac{v_0 - v}{v_0}$ vs. τ coordinates (Fig. 1, *a*) represent straight lines leaving zero with their slope equal to the kinetic constant k at small degrees of borohydride decomposition (until 10–15 wt. %). The linear dependence in the $\ln \frac{v_0}{v}$ vs. τ coordinates (Fig. 1, *b*) with the k slope was observed at 40–50 wt. % of borohydride decomposition. The hydrolytic borohydride process in the pure

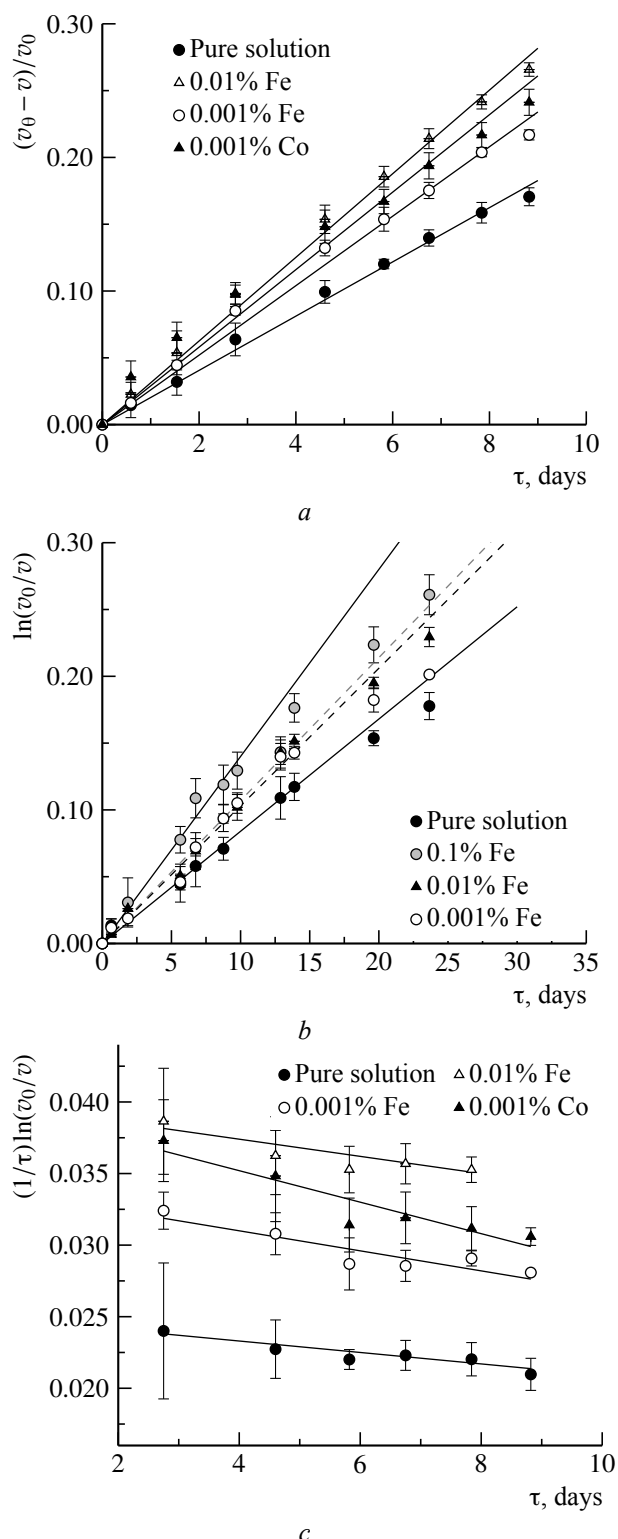


Fig. 1. Time dependences of the borohydride decomposition degree: *a* – the linear dependence at 80°C according to Eq. (3); *b* – the semi-logarithmic dependence at 60°C, the straight lines correspond to Eq. (4); *c* – the linear dependences at 80°C according to Eq. (5)

solution and the solution with impurities was slowed down at high degrees of borohydride decomposition (> 50 wt. %).

Our results of determination of the effective kinetic constant k using Eq. (4) are summarized in Table 1 and presented in Fig. 2 in the Arrhenius ($\ln(k)$ vs. $1/T$) coordinates according to

$$\ln k = \ln k_0 - \frac{E_a}{RT}, \quad (6)$$

where E_a is the activation energy, R is the gas constant, T is absolute temperature, k_0 is the pre-exponential factor.

The temperature dependence of k is satisfactorily described by Eq. (6) for all the solutions studied; the approximating equations are shown in Fig. 2. As it should be expected, the chemical stability of any solution decreases with the temperature increasing and the concentration of metal impurities. All the impurities raised the activation energy E_a of the BH_4^- hydrolysis from 32 up to 40–50 $\text{kJ}\cdot\text{mol}^{-1}$ (Table 1).

No increase in the borohydride hydrolysis rate can be reliably recorded for the solution with 10 ppm Fe in comparison with the original one. The increase in the Fe concentration in

the solution up to 100 ppm promotes the decomposition of BH_4^- ions appreciably. The borohydride self-destruction is accelerated by 1.5–4 times for 1000 ppm Fe.

The catalytic activity of Co influences the hydrolysis rate much more strongly in comparison with Fe. For example, the borohydride solution with 1000 ppm Co decomposes completely at the temperature of 100°C after 20 h of storage. The concentration of BH_4^- ions in the solution with the same content of Co decreases twice at 25°C at once after solution preparation in comparison with the original solution. The least accelerating effect on the hydrolysis of BH_4^- ions was rendered by the 1 ppm Co impurity. The borohydride self-destruction was accelerated by 1.4–2 times for 10 ppm Co.

The strongest accelerating effect on the hydrolysis of BH_4^- ions was rendered by nickel impurities: the total self-destruction of BH_4^- was finished at the temperature of 70°C after 24-h storage of the solution with 1000 ppm Ni. The minimal content of nickel accelerates the borohydride decomposition by 1.3 times for 1 ppm Ni. The 10-fold increase in the Ni concentration promoted the hydrolysis process of BH_4^- by 1.7 times.

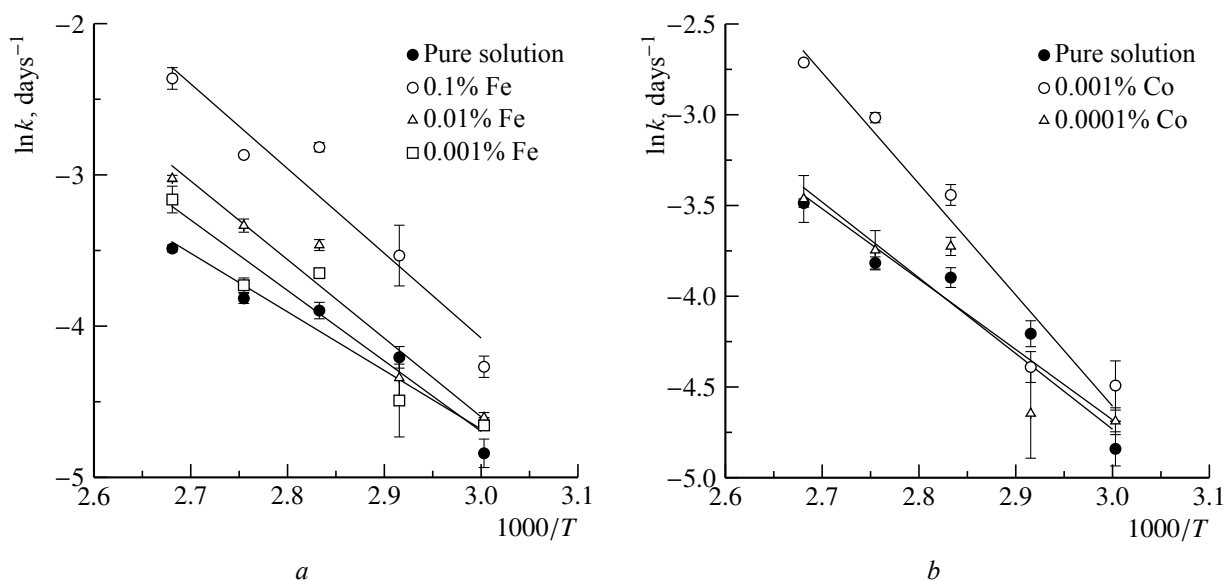


Fig. 2. Temperature dependences of the effective rate constant of BH_4^- hydrolysis in the different solutions: *a* – impurities Fe, *b* – impurities Co

Таблица 1

Characterization of the solutions under study: Their composition, effective constants of the hydrolysis rate k at several temperatures and kinetic parameters

Solution	Rate constant k [day^{-1}] at several temperatures [$^{\circ}\text{C}$]					$\ln k_0$	E_a ($\text{kJ}\cdot\text{mol}^{-1}$)
	60	70	80	90	100		
Pure solution	0.0079 ± 0.0007	0.0149 ± 0.0011	0.0203 ± 0.0011	0.0220 ± 0.0007	0.0306 ± 0.0007	6.9 ± 0.7	32 ± 2
Fe, 1000 ppm	0.0140 ± 0.0008	0.029 ± 0.006	0.060 ± 0.002	0.0568 ± 0.0007	0.094 ± 0.006	12.7 ± 0.3	46.6 ± 0.8
Fe, 100 ppm	0.0100 ± 0.0003	0.013 ± 0.002	0.0313 ± 0.0011	0.0356 ± 0.0014	0.0486 ± 0.0009	11.0 ± 0.4	43 ± 1
Fe, 10 ppm	0.0095 ± 0.0003	0.011 ± 0.003	0.0260 ± 0.0007	0.0240 ± 0.0010	0.042 ± 0.004	9.3 ± 0.4	39 ± 1
Co, 10 ppm	0.0112 ± 0.0016	0.0124 ± 0.0011	0.032 ± 0.002	0.0490 ± 0.0014	0.0664 ± 0.0003	14 ± 1	51 ± 3
Co, 1 ppm	0.0092 ± 0.0007	0.010 ± 0.002	0.0241 ± 0.0013	0.024 ± 0.003	0.031 ± 0.004	8 ± 1	35 ± 3
Ni, 10 ppm	–	0.0267 ± 0.0014	–	–	–	–	–
Ni, 1 ppm	–	0.0188 ± 0.0015	–	–	–	–	–

Conclusions

The catalytic effect of the impurities of Fe, Co, and Ni on the borohydride hydrolytic process acceleration was established. The catalytic activity of these metals takes place without changing the kinetic regularities of the hydrolysis of BH_4^- ions and increases in the row $\text{Fe} \ll \text{Co} < \text{Ni}$. The rate constant k of borohydride hydrolysis for several impurities at various temperatures has been estimated. The lowest non-accelerating concentrations of impurities were established (~ 10 ppm for Fe; ~ 1 ppm for Co). The concentrations of the

impurities which significantly accelerate the hydrolysis of BH_4^- ions were also established too (~ 100 ppm for Fe; ~ 10 ppm for Co). The strongest accelerating effect on the hydrolysis of BH_4^- ions was rendered by nickel impurities: the self-destruction was accelerated by 1.3 times for 1 ppm Ni and by 1.8 times for 10 ppm Ni. The 75–87% fraction of borohydride decomposes during the first day of storage at 70°C at the Ni content of 100 ppm. The increased temperatures enhance the catalytic effect of hydrolysis acceleration in the fair conformity with Arrhenius' equation.

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