

ABSTRACT
thesis for the degree of Doctor of Philosophy (PhD)
on specialty “6D072000 – Chemical technology of inorganic substances”
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“Development of a method for producing hydrogen from water in the
presence of a catalyst”

General characteristics of the work. The dissertation work is devoted to the development of methods for hydrogen production from water using a catalyst. It has been shown that, in the presence of mercury ions, aluminum reacts with water, resulting in the formation of hydrogen and aluminum hydroxide. Optimal conditions for the hydrogen evolution process from water at room temperature using an aluminum electrode and a catalyst have been determined, making it possible to develop a hydrogen generator capable of operating under autonomous conditions.

The work presents a detailed study of various experimental parameters, including the influence of cations and anions present in water, as well as the dependence of the hydrogen evolution rate on the catalyst concentration. The process of hydrogen evolution in the presence of various depolarizing metals (Pd, Ni, Fe) and graphite in contact with aluminum is also analyzed. For comparison, the processes of aluminum interaction with water in the presence of sodium hydroxide and certain acids are considered.

The relevance of the study. At present, the world continues to face environmental problems associated with climate change, depletion of the ozone layer, and other anthropogenic phenomena that negatively affect the quality of life. One of the urgent tasks of modern scientific and technological research is the development and improvement of methods for producing affordable, environmentally friendly, and low-cost fuels.

The ability of hydrogen to undergo catalytic oxidation at low temperatures, accompanied by the conversion of the chemical energy of oxidation into electrical energy, opens broad prospects for the widespread application of hydrogen energy technologies. However, the current state of hydrogen technologies and hydrogen production methods does not yet provide the possibility of fully replacing traditional energy sources. This is due to several reasons: hydrogen does not exist in a free state on Earth, and its production requires accessible chemical raw materials and available energy sources.

Producing hydrogen from ordinary water under autonomous conditions is an urgent global problem, as it has not yet been solved worldwide. Hydrogen is an easily oxidizable gas, widely used as a fuel – primarily for combustion to generate heat. Moreover, it is used in internal combustion engines and in fuel cells for electricity generation. Hydrogen is an excellent fuel with significant advantages over other types of fuel. Its combustion does not pollute the environment, since the reaction product is water – a substance naturally present in the environment ($2H_2 + O_2 \rightarrow 2H_2O$).

Thus, based on the above, the development of methods for producing hydrogen is a pressing issue of modern science.

Purpose of the work: To develop a method for producing hydrogen through the interaction of water with aluminum in the presence of a catalyst, as well as during the contact of aluminum with various depolarizing metals.

Research objectives:

- To investigate the influence of the catalyst on the rate of interaction between aluminum and water; to determine the effects of temperature and aluminum electrode surface area on the rate of hydrogen evolution;
- To study the effect of anions and cations on the rate of hydrogen evolution from water in the presence of the catalyst;
- To investigate hydrogen evolution on the surface of an aluminum plate in sodium hydroxide solutions and certain mineral acids (phosphoric, sulfuric);
- To examine the change in aluminum potential during its interaction with water in the presence of the catalyst;
- To study the interaction of aluminum with water when aluminum is in contact with various depolarizing metals and graphite.

Research methods

The study of the influence of various parameters on the rate of hydrogen evolution during the chemical interaction of aluminum with water in the presence of the catalyst; pH measurements; chemical analysis of reaction products; measurement of the aluminum electrode potential; recording voltammograms on a CS 120 Potentiostat (CorrTest Instruments, China) using a thermostated three-electrode cell (Metrohm, Herisau, Switzerland, model 663 VA stand), with data acquisition through the CS Studio5 software installed on a laptop (Slovakia, manufactured for Lenovo, China); X-ray diffraction and elemental analysis of the resulting precipitates using a DRON-4-07 diffractometer and an energy-dispersive X-ray fluorescence spectroscopy system attached to a JSM 6610 LV scanning electron microscope (JEOL, Japan).

Research objects: hydrogen, aluminum, water, catalyst (mercury nitrate), depolarizing metals (palladium, nickel, iron), graphite, alkaline solutions, acid solutions (phosphoric, sulfuric), sodium chloride.

Subject of the research: the reaction of aluminum with water in the presence of the catalyst (mercury nitrate), as well as the interaction of the aluminum electrode in contact with depolarizing metals (palladium, iron, nickel) and graphite.

Main provisions submitted for defense:

1. When the concentration of Hg^{2+} in the “aluminum-water” system is increased from 0.5 to 10.0 g/L, the rate of hydrogen evolution increases by more than 100 times.
2. When a depolarizing metal (Pd, Ni, Fe) or graphite is introduced into the “aluminum-water-mercury” system, the hydrogen evolution rate increases by 1.4-2.4 times due to the reduction of hydrogen evolution overpotential on their surfaces and the acceleration of cathodic water reduction.
3. In the “aluminum-water-mercury” system, the metallic mercury formed by Hg^{2+} reduction successively amalgamates the aluminum, repeatedly destroys the oxide film, and initiates new cycles of its interaction with water.

Scientific novelty

– It has been established that, in the “aluminum – water – Hg^{2+} ” system, an aluminum activation mechanism occurs directly during the reaction. In this mechanism, Hg^{2+} ions are reduced to metallic mercury on the aluminum surface, accompanied by the destruction of the passive oxide film. An increase in the Hg^{2+} concentration leads to a sharp increase in the rate of hydrogen evolution, which is associated with the intensification of oxide-film destruction and aluminum activation processes.

– It has been shown for the first time that the interaction of aluminum with water in the presence of Hg^{2+} proceeds in a non-stationary, cyclic mode caused by the alternation of activation and passivation stages on the surface, and has a self-sustaining character.

– It has been shown that the introduction of a depolarizing metal (Pd, Ni, Fe) or graphite into the “aluminum – water – Hg^{2+} ” system increases the rate of hydrogen evolution by 1.4-2.4 times due to a decrease in the overpotential of the hydrogen evolution reaction and the acceleration of cathodic water reduction.

– It has been established that the identified mechanism of aluminum activation, which occurs directly during the reaction and is accompanied by a cyclic regime, is fundamentally different from known stationary systems in which activation is achieved through the preliminary formation of amalgam coatings.

Theoretical significance

The results of the study expand scientific knowledge in the field of hydrogen energy, including methods for hydrogen generation from water, and provide new insights into the possibility of obtaining hydrogen under autonomous conditions in the presence of a catalyst and during the contact of aluminum with depolarizing metals.

Practical significance

The development of a new method for hydrogen production contributes to solving the problem of obtaining hydrogen fuel under autonomous conditions. Hydrogen combustion produces water – a substance naturally present in the environment – and does not release pollutants harmful to human health or the environment. When hydrogen burns, the flame propagation rate is eight times higher than that of hydrocarbon fuels. The results of this study contribute significantly to hydrogen energy and the development of methods for autonomous hydrogen production. Furthermore, hydrogen, being a light chemical element, is used as a reducing agent in many chemical technologies, and demand for hydrogen is increasing each year. Hydrogen is used in deep oil refining, in the chemical industry for ammonia and nitrogen fertilizer production, and in ferrous metallurgy as a reducing agent.

Relation of the research topic to scientific research plans. This topic is aligned with global programs devoted to developing methods for producing hydrogen from renewable energy sources, with particular interest in autonomous methods of hydrogen production. In the Address of the President of the Republic of Kazakhstan Kassym-Jomart Tokayev to the people of Kazakhstan dated September 1, 2021, “The Unity of the People and Systemic Reforms Are the Solid Basis of the

Country's Prosperity," a task was set to achieve carbon neutrality by 2060. Highlighting the need for a transition to nuclear energy, the President emphasized the prospects of producing "green" hydrogen and developing hydrogen energy. The dissertation was carried out as an exploratory study at the Department of General and Inorganic Chemistry of Al-Farabi Kazakh National University in accordance with the objectives set forth in the Address of the President and other documents.

The personal contribution of the author of the study lies in defining research objectives, conducting experiments, collecting literary data, and summarizing the obtained results.

The main results of the dissertation research have been published in 12 scientific papers, namely, in 1 article published in an international scientific journal, which, according to the Scopus and Web of Science databases, has a percentile of 39, quartile Q3; in 3 articles published in journals recommended by the Committee for Control in the Field of Education and Science of the Ministry of Higher Education and Science of the Republic of Kazakhstan, in 1 article published in the International Scientific and Practical Journal "Global Science and Innovation 2020: Central Asia", in 6 articles and abstracts in collections of international conferences held abroad and in nearby regions; and in 1 patent for a utility model of the Republic of Kazakhstan was received (PM No. 6276 published on July 30, 2021).

PhD student's contribution to scientific publications writing

1. Bayeshova A., Bayeshov A., Molaigan S. Obtaining hydrogen by aluminum interaction with water // Journal of Chemical Technology and Metallurgy . – 2019 . – Vol. 54(3). – P. 639–642 – conducting experiments, collecting literature, processing results, description, formatting, editing.

2. Bayeshova A.K., Molaygan S., Bayeshov A.B. A comparative description of some known and new methods of obtaining hydrogen from water // Bulletin of Abai Kazakh National Pedagogical University Series "Natural science and Geography". – 2018. – No. 2 (56). – P. 22-27. – performing experiments, collecting literature, processing results, description, design, editing.

3. Bayeshova A.K., Molaigan S., Bayeshov A.B. Hydrogen energetics current state and hydrogen production methods // Proceedings of the National Academy of Sciences of the Republic of Kazakhstan, Series of Chemistry and Technology – 2018. – No. 5. – P. 107-116 – conducting experiments, collecting literature, processing results, description, formatting, editing.

4. Bayeshov A., Bayeshova A.K., Molaigan S., Turlybekova M.N., Leska B. The role of depolarizers in hydrogen evolution processes from water on the surface of aluminum amalgam // News of the Sciences of the Republic of Kazakhstan JSC "DV Sokolsky institute of Fuel, catalysis and Electrochemistry", Chemistry and Technology series. – 2023. – No. 1(454). – P.15-26 – conducting experiments, collecting literature, processing results, description, formatting, editing.

5. Bayeshova A.K., Molaigan S., Bayeshov A. Study of the process of hydrogen evolution from aqueous solutions during aluminum dissolution in the presence of cations // Collection of articles based on the results of the International Scientific and Practical Conference on May 12, 2018. Sterlitamak, Russian Federation, Agency

for International Research. – 2018. – P.83-85 – performing experiments, collecting literature, processing results, description, design, editing.

6. Bayeshova A.K., Bayeshov A., Molaigan S. The study of aluminum and its properties in the context of the fourth industrial revolution // Proceedings of the International Scientific and Practical Conference “Science, Education and Production in the Context of the Fourth Industrial Revolution”. – Karaganda. – 2018. – P. 154-156 – conducting experiments, collecting literature, processing results, description, formatting, editing.

7. Molaigan S., Bayeshova A.K. Experimental results of aluminum and thermodynamic studies // International scientific and practical journal “Global Science and Innovation 2020: Central Asia”, No. 5(10). August 2020, “Chemical Sciences” series. – P.17-21 – conducting experiments, collecting literature, processing results, description, formatting, editing

8. Bayeshova A.K., Bayeshov A., Turlybekova M.N., Molaigan S. Method for producing hydrogen // Patent for utility model of the Republic of Kazakhstan No. 6276 based on application No. 2021/0284.2 dated 07/30/2021 – conducting experiments, performing a patent research, processing the results, preparing the patent application, and formatting the document for submission.

The structure and volume of the dissertation

The dissertation consists of an introduction, a literature review, five chapters, a conclusion, and a list of 166 references. The work is presented on 142 pages and includes 61 figures, 18 tables, and appendices.