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 is devoted to the development of methods for producing hydrogen from water using a catalyst. For the first time, it is shown that in the presence of mercury ions, aluminum reacts with water to form hydrogen and aluminum hydroxide. Optimal conditions for hydrogen release from water at room temperature using an aluminum electrode and a catalyst have been determined, enabling the creation of a hydrogen generator capable of operating under autonomous conditions. The work provides a detailed investigation 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 concentration of the catalyst. 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 interactions of aluminum with water in the presence of sodium hydroxide and certain acids are examined.

The relevance of the study. Today, environmental challenges associated with climate change, ozone layer depletion, and other technogenic phenomena continue to negatively affect the quality of life. One of the urgent issues of modern scientific and technological research is the development and improvement of methods for obtaining accessible, environmentally clean, and inexpensive types of fuel.

Hydrogen's ability to undergo catalytic oxidation at low temperatures with the conversion of oxidation chemical energy into electrical energy opens the way for the widespread use of hydrogen energy. However, the current state of hydrogen technologies and hydrogen production methods does not yet allow for a complete replacement of traditional energy sources. The reasons for this include the absence of free hydrogen on Earth and the need for accessible chemical raw materials and energy sources for its production.

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. In the “aluminum-water-mercury” system, due to the difference in electrode potentials between Al and Hg^{2+}, a redox process occurs, resulting in metallic mercury and Al^{3+} ions. An amalgam is formed that destroys the natural oxide film, activates the aluminum, and enables its reaction with water with the evolution of hydrogen. Increasing the Hg^{2+} concentration in the “aluminum-water-mercury” system from 0.5 to 2.5 g/L increases the hydrogen evolution rate by more than 100-fold.

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 upon the introduction of mercury nitrate into the solution, due to the difference in potentials, a redox reaction occurs between aluminum and mercury ions, forming aluminum ions and elemental mercury. As a result, the aluminum surface undergoes electrochemical corrosion, forming an amalgam (with a negative potential), meaning that aluminum becomes freed from the oxide film, becomes active, and, as a negative metal, reacts with water with hydrogen evolution. It is noted that under normal conditions aluminum does not react with water due to the durable oxide film constantly present on its surface;
- It has been found that the formation of aluminum amalgam and hydrogen evolution is cyclic; that is, the catalyst is not consumed but repeatedly participates in the hydrogen formation reaction and in the electrochemical interaction of water with aluminum. The reaction proceeds with hydrogen formation until the aluminum electrode is completely dissolved;
- For the first time, it is shown that the volume and rate of hydrogen evolution depend on the concentration of the catalyst (mercury ions) and on the nature of the depolarizing metal in contact with aluminum. It has been determined that when using metals and graphite with hydrogen evolution overpotentials lower than those of aluminum and its amalgam, the hydrogen evolution rate increases by 1.4-2.4 times.

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 fnd 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 work consists of an introduction, a literature review, five chapters, a conclusion. The list of references includes 163 sources, among which are references to publications co-authored by the PhD student. The content of the work is 139 pages, containing 61 figures and 18 tables, and appendices.