ANNOTATION
of doctoral dissertation
(PhD)

6D072000 – Chemical technology of inorganic substances

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Electrochemical processes on Mg-anode in chemical current sources

The thesis is devoted to the study of metallic magnesium corrosion in aqueous electrolytes, development of a method for synthesizing modified anode material based on intercalated magnesium and research of the physical and chemical parameters of the proving material, as well as testing of magnesium-ion batteries (such as "swage lock cell") based on synthesized anode material. In the course of this work, a model of film formation during magnesium oxidation is proposed, the composition of the film is determined, and new methods for synthesizing intercalation anode material for magnesium-ion batteries are proposed.

All studies were carried out for the first time, the results are presented as a 1 article in journals with a non-zero impact factor according to the information database of Thomson Reuters and Scopus, 3 articles in journals recommended by the Committee for Control of Education and Science, and also in the form of 8 abstracts in international, national scientific-practical conferences and symposia.

Relevance of the research topic.

The development of technology in the last decade has led to a sharp development of energy-saving tools. Chemical current sources are the most important means of storing energy.

Batteries should be safe, inexpensive, made from components common in the earth's crust, and, most importantly, demonstrate a long cycle. Lithium batteries are used as an energy source with the highest specific power and energy density. However, lithium metal is expensive due to its low prevalence in the earth's crust. In this regard, as an alternative to lithium power sources, we have proposed magnesium power sources with high energy density and from environmentally friendly components.

The electrochemical characteristics of chemical power sources are determined by the properties of the electrode used. The surface of magnesium metal is rapidly corroded by electrolytes. New classes of electrolytes are being investigated to solve the surface problems of magnesium. However, many electrolytes are corrosive and volatile. To solve this problem, it is necessary to know the laws of formation and growth of a passive film on a magnesium electrode under the action of simple electrolytes, as well as the charge transfer in it.

Moreover, one of the important issues for the wide application of a magnesium current source is the optimization of the anode material that can be

used in conventional electrolytes. To solve the problem of magnesium in the metallic state, it is advisable to use an alternative anode. Based on recent research, d elements are used as an alternative anode, which can easily form an intermetallic compound with magnesium. Bismuth metal, which has a high ability to form intermetallide with magnesium due to its rhombohedral structure, was chosen as the active material in this work. As a result of intercalation of the magnesium ion into bismuth, Mg_3Bi_2 is formed. Although there is worldwide evidence of magnesium intercalation in research, no studies are supporting a complete interpretation of the mechanism of electrochemical reversible formation of the Mg_3Bi_2 phase.

In this regard, the study of processes occurring on a magnesium anode and optimization of the anode material is relevant both from a theoretical and practical point of view.

The purpose of the dissertation.

Analysis of the functioning of magnesium in two forms: a magnesium anode in the metallic state in primary power sources and an intercalation magnesium anode in secondary power sources.

To achieve this goal, the following tasks were set:

- establishment of regularities of corrosion processes of the magnesium electrode for primary chemical power sources by gravimetric and electrochemical methods.
- drawing up an electrical equivalent diagram of the corrosion process in magnesium.
- development of a model of the magnesium corrosion process in an aqueous environment.
- synthesis and optimization of intercalation material for the anode.
- study of morphological, structural, and electrochemical characteristics of the synthesized anode material.
- testing of the obtained anode material and determination of electrochemical characteristics.

Objects of study:

A metallic magnesium electrode for primary power sources and a bismuth electrode intercalated with magnesium ions for secondary power sources.

The subject of scientific research.

The process of formation, growth, and charge transfer in a corrosive film during the polarization of a magnesium electrode. The process of intercalation of magnesium ion in a bismuth-based composite material.

Research methods.

Preparative synthesis, gravimetry, linear (SV) and cyclic (CV) voltammetry, impedance spectroscopy (IES), electron microscopy (SEM), x-ray spectral

microanalysis (RSA), x-ray diffraction analysis (XRD), optical emission spectroscopy.

Scientific novelty:

This dissertation for the first time:

- a new model of the mechanism of film formation on the magnesium surface is proposed.
- a theory describing the electrochemical parameters of anomalous magnesium dissolution is proposed.
- synthesized bismuth-based anode material. Intercalation/deintercalation of magnesium in the synthesized anode material and changes in the crystal lattice of the matrix are studied.
- optimized and proposed technological scheme for the synthesis of modified anode material.

The theoretical significance of the study.

The theoretical significance of the work is to develop a model of magnesium electrode corrosion in sulphate electrolytes. In this regard, the surface of the passive layer formed as a result of magnesium metal corrosion, as well as the stages and mechanism of the magnesium corrosion process, are studied.

As an alternative to pure magnesium anode, the mechanism of intercalation of magnesium ion on the synthesized bismuth electrode was investigated and confirmed experimentally.

Practical significance.

The practical significance lies in the fact that for primary power sources, it is possible to describe and predict the state of the magnesium electrode in chemical power sources based on the proposed corrosion model. An intercalation material based on bismuth was synthesized. Since the synthesized material has a good volumetric capacity, it allows it to be used as an anode material for a current storage device in portable or other electronic equipment.

The main provisions to be defended:

- a new model of the magnesium corrosion process in aqueous solutions.
- electrical equivalent circuit of the magnesium corrosion process.

a modified method for the synthesis of intercalation material based on bismuth.

- technological scheme for the synthesis of intercalation material.

The main results of the dissertation research are published in 12 scientific papers, including:

- in one paper published in an international scientific journal having a non-zero impact factor according to the information base of the companies Scopus and Thomson Reuters;

- in three papers published in journals recommended by the Committee for the Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;
- in eight abstracts of reports at foreign and national, international conferences and symposia.

The structure and scope of the dissertation.

The dissertation includes an introduction, three sections, a conclusion, as well as a list of sources used containing 127 items. The dissertation is presented on 104 pages, contains 66 figures and 11 tables.

Based on the results of the dissertation research, the following conclusions were made:

1. The regularity of the corrosion process of a magnesium electrode for primary chemical power sources is determined using gravimetric and electrochemical methods. Electron microscopy and x-ray spectral analysis revealed that a complex surface film is formed during magnesium corrosion.
2. an electrical equivalent diagram of the corrosion process in magnesium is drawn up.
3. a model of the corrosion process is proposed. It was found that the formation of a film on the magnesium surface occurs due to the hydrolysis reaction of natural magnesium oxide.
4. the method of manufacturing the intercalation material for the anode is optimized. A technological scheme for the synthesis of the optimal anode material for magnesium ion batteries is proposed.
5. morphological, structural, and electrochemical characteristics of the synthesized anode material are Investigated. X-ray phase analysis proved the formation of Mg_3Bi_2 as a result of the interaction of a bismuth-based anode material with a magnesium ion.
6. calculated capacity (114 mAh/d) synthesized anode material and its coulomb efficiency (~40%) was determined.

Assessment of the completeness of solutions to the tasks set.

The goals and tasks set in the dissertation are fully solved:

- regularities of corrosion processes of the magnesium electrode for primary chemical power sources are established by gravimetric and electrochemical methods.
- an electrical equivalent diagram of the corrosion process in magnesium has been drawn up.
- a model of the magnesium corrosion process in an aqueous environment has been developed.
- synthesized and optimized bismuth-based intercalation material for the anode of magnesium-ion batteries.

- morphological, structural, and electrochemical characteristics of the synthesized composite material were studied.
- the resulting anode material was tested and its electrochemical characteristics were determined.

Assessment of technical and economic efficiency proposed in the dissertation. In Kazakhstan, which is an industrial country, the problem of the production of chemical power sources is very relevant and research in this area is most promising.

The solutions proposed in this paper for studying the corrosion process on a magnesium electrode are important for regulating the parameters of its use in chemical current sources. The replacement of corrosive magnesium metal with an intercalation composite material is of practical significance. Carrying out research and development of an effective anode material with subsequent practical use will significantly reduce the import dependence of our Republic and establish the production of domestic batteries.