ABSTRACT

dissertation for the degree of Doctor of Philosophy (PhD) in the educational program "8D07102 - Chemical Engineering" by Jumanova Raigul Zhumakhanovna on the topic: "Synthesis of nanostructured anode material based on titanium oxide for magnesium-ion batteries"

General Overview of the Work

The dissertation is devoted to the development and investigation of nanostructured anode materials based on titanium dioxide (TiO_2) for magnesium-ion batteries (MIB) as promising energy storage systems. Within the framework of this work, technological approaches were implemented for the formation of various TiO_2 morphologies – nanotubes, nanofibers, and nanorods – with controlled synthesis parameters affecting their phase composition and structural–morphological characteristics. A comprehensive analysis of the physicochemical properties and electrochemical behavior of the obtained structures was carried out, including the evaluation of their capacity characteristics, stability, and the kinetics of Mg^{2+} ion intercalation/deintercalation processes.

Using the COMSOL Multiphysics platform, two-dimensional numerical modeling of the discharge processes of magnesium ions on the TiO_2 nanotubular anode was performed, taking into account the real geometric and physical parameters of the system. The modeling made it possible to determine the optimal geometric ratios of nanotubes that ensure uniform current density distribution, efficient Mg^{2+} ion transport, and an increase in the electrochemical efficiency of the anode material. The work also proposes a technological algorithm for obtaining anode materials, representing a universal scheme that combines all the key stages – from precursor selection and synthesis to structural-morphological and electrochemical characterization, modeling, and optimization. The obtained results form the engineering basis for designing anodes of next-generation magnesium-ion energy storage devices.

Relevance of the Research Topic

The limitations of lithium-ion batteries (LIB), including safety concerns, the depletion of lithium resources in the Earth's crust, and their high cost, have prompted the search for alternative energy storage technologies. Magnesium-ion batteries (MIB), in turn, offer several advantages: magnesium does not form dendrites (enhancing safety), has a low oxidation potential (–2.37 V), a high volumetric capacity (3833 $mA \cdot h/cm^3$), and is environmentally benign and abundantly available in nature [1-3].

However, the main obstacle to the development of MIB remains the lack of effective anode materials capable of reversible intercalation of magnesium ions. Additional complications include corrosion of metallic magnesium in aqueous electrolytes and the formation of a solid electrolyte layer in non-aqueous systems, which reduces cell stability. Furthermore, the strong electrostatic interaction of Mg^{2+} ions with the electrode lattice leads to slow diffusion and reduced intercalation efficiency. To address these issues, it is necessary to develop new strategies for synthesizing anode materials capable of effectively and reversibly intercalating Mg^{2+}

ions. One promising approach is the use of anodes that do not form passive layers. Despite the successful use of alloy-based anodes in LIBs, they do not provide the required efficiency in MIB systems due to the unique chemical properties of magnesium [4].

In recent years, layered intercalation materials such as V_2O_5, VS_4, TiS_2, as well as compounds such as $Li_4Ti_5O_{12}$ and $Na_2Ti_3O_7$, have been studied. However, their capacity and diffusion kinetics with respect to Mg^{2+} ions remain limited, limiting their potential as anode materials [5-9]. The key requirements for an ideal anode are high capacity, fast ionic/electronic conductivity, and high cyclic stability.

Among all possible candidates, titanium oxide (TiO_2) most fully meets these requirements. It has a structure favorable for the intercalation of Mg^{2+}, Li^+, and Na^+ ions, is widely available [9, 10], environmentally safe, and compatible with organic electrolytes [11].

This paper proposes the use of various nanostructured titanium oxide morphologies (nanotubes, nanofibers, nanorods) as anode material. These structures improve the surface and conductive properties of the material, facilitating charge transport:

• Nanotubes promote ion migration and increase mechanical stability;

• Nanofibers ensure continuous electron conductivity, while their high porosity and developed active surface contribute to increased efficiency of electrochemical processes.

• Nanorods accelerate Mg^{2+} diffusion through directed channels and improve the cyclic stability of the material.

Similar morphologies have previously proven their effectiveness in similar systems: nanotubes have demonstrated high results in lithium-ion batteries due to accelerated Li^+ diffusion and structural stability [12], while nanofibers and nanorods composed of various oxides (MnO_2, V_2O_5, etc.) have demonstrated good electrochemical characteristics and stability [13, 14]. These data confirm that such structures are universal and promising for the intercalation of multivalent ions.

Research Objective

Creation of new nanostructured anode materials for magnesium-ion batteries.

Research Tasks

1. Production of various nanostructured titanium oxide-based materials and study of their morphological, structural, and elemental characteristics using modern instrumental methods.

2. Study of the electrochemical properties of the synthesized anode materials using cyclic voltammetry and galvanostatic methods, determining the kinetic parameters of Mg^{2+} ion intercalation/deintercalation processes.

3. Determination of the dependence of Mg^{2+} ion intercalation/deintercalation processes on various anode material structures and evaluation of their effectiveness for use in Mg-ion systems.

4. Numerical simulation of magnesium ion discharge in TiO_2 nanotubes using COMSOL Multiphysics.

5. Design of a universal technological algorithm for the synthesis and investigation of anode materials to improve the efficiency of magnesium-ion batteries.

Object of the Study

Nanostructured titanium oxide-based anode materials (nanotubes, nanofibers, and nanorods) for magnesium-ion batteries.

Subject of the Study

Electrochemical properties of nanostructured TiO_2-based anodes synthesized by different methods, including the intercalation and deintercalation behavior of Mg^{2+} ions during charge/discharge processes and the influence of material morphology and structure on these processes.

Research Methods

Electrochemical anodization, hydrothermal and solid-state synthesis; X-ray diffraction (XRD), contact angle measurements, energy-dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), cyclic voltammetry, and galvanostatic charge/discharge testing.

Scientific Novelty

1. For the first time, various nanostructured forms of TiO_2 were studied as anode materials for magnesium-ion batteries, and their applicability was determined. The relationship between TiO_2 morphology and Mg^{2+} intercalation/deintercalation processes was demonstrated.

2. For the first time, a numerical model of magnesium ion discharge in TiO_2 nanotubes was constructed using COMSOL Multiphysics. The model takes into account real-world geometric characteristics, mass transfer processes, and electrochemical reaction kinetics, allowing for the identification of key factors limiting the effectiveness of the anode material.

Theoretical Significance of the Work

The dissertation investigated the intercalation processes of magnesium ions (Mg^{2+}) in nanostructured titanium oxide-based materials. This is of great importance for the theoretical justification of MIB systems. Numerical modeling of mass transfer and charge transport processes was carried out, taking into account the morphology of nanomaterials, their geometric characteristics, and reaction kinetics. The results obtained provide opportunities for a scientific understanding of the behavior of multivalent ions in solid-phase structures and make it possible to substantiate the choice of effective and stable phase and structural forms of TiO_2 as an anode material.

Practical Significance of the Work

The growing global demand for energy and escalating environmental challenges necessitate the development of efficient, safe, and economically viable energy storage systems. Magnesium-ion batteries are considered an environmentally friendly and cost-effective alternative to lithium-ion systems. Within the framework of this research, nanostructured anode materials based on TiO_2 have been developed, providing a stable and efficient medium for Mg^{2+} ion intercalation. The ability to control material morphology through different synthesis methods broadens the scope of practical applications of these materials.

The synthesized materials can serve as a foundation for the creation of rechargeable magnesium batteries. Given Kazakhstan's rich natural reserves of titanium and magnesium – including resources from the Ust-Kamenogorsk Titanium and Magnesium Plant – the findings of this work open opportunities for the production of battery components based on domestic raw materials. This would contribute to reducing import dependence and promoting scientific-industrial cooperation within the country. The developed materials can be applied in medicine, electric transport, and renewable energy storage systems. The research holds practical importance for strengthening Kazakhstan's scientific and technological potential and supporting the transition to a "green" economy.

Key Findings Defended in the Dissertation:

1. Anatase-phase TiO_2 nanotubes and nanofibers provide reversible intercalation of magnesium ions in the potential range of 1,2-1,9 V, accompanied by pronounced charge-discharge peaks, which confirms their electrode activity and makes them effective anode materials for magnesium-ion batteries.

2. The highest cyclic stability of TiO_2 anodes is achieved with nanotubular morphology, characterized by a specific capacity of 0,40 $mA \cdot h \cdot g^{-1}$ and complete retention of discharge capacity after 50 cycles, whereas for nanofibers (13,21 $mA \cdot h \cdot g^{-1}$) and nanorods (~380 $mA \cdot h \cdot g^{-1}$) the capacity decreases to 11,33% and 5,29%, respectively, due to the degradation of active zones and the destruction of the anatase lattice.

3. Under optimized conditions of magnesium deposition (i_0 = 0,665 A/m^2, $D_{Mg2+} = 1{,}13 \cdot 10^{-9}$ m^2/s, E = -0,36, -0,3 V), a uniform current distribution is achieved, whereby deep nanotubes (~850 nm) are filled in ~80 ms and short ones (450 nm) in ~40 ms, which contributes to the preservation of the electrode's active surface and an increase in specific capacity.

Presentation of Experimental Results

The results of the work were presented in the form of reports at three international conferences: "INESS – 2022" (Kazakhstan, 2022), "Mediterranean Geosciences Union – 2023" (Turkey, 2023), and "Mediterranean Geosciences Union – 2024" (Spain, 2024).

Relevance of the Dissertation Topic to Research Projects and Government Programs

The dissertation was carried out within the framework of the research plan of the Department of Analytical, Colloid Chemistry and Rare Elements Technology of Al-Farabi Kazakh National University, as well as under the projects of the Center for Physicochemical Research and Analysis Methods.

The research was also supported by the following government-funded grant projects:

1. IRN AR09260383 "Development of a reversible anode for magnesium-ion batteries" (2020–2023) – participation as a research staff member;

2. IRN AP22686263 "Improving the diffusion properties of anode material for magnesium-ion batteries" (2024–2026) – participation as project leader.

Publications

Based on the results of the work, the following have been published: – 2 articles in peer-reviewed scientific journals indexed in the Web of Science (Q3) and Scopus databases (CiteScore not lower than 50% in the subject area of the dissertation); 1 article is under review.

Description of the doctoral candidate's contribution to the preparation of each publication:

1. Rakhymbay G., Avchukir Kh., Konysbay Y., Vacandio F., **Jumanova R.**, Bakhytzhan Y., Abildina A., Argimbayeva A. Influence of LiCl on the kinetics of Mg^{2+} insertion into TiO_2 prepared by solid-state chemical reaction // Journal of Solid State Electrochemistry. - 2023. V.28. – P.1-12 doi.org/10.1007/s10008-023-05742-0. Doctoral candidate's contribution: interpretation of the results, writing of individual subsections.

2. Jumanova R., Rakhymbay G., Abildina A., Avchukir Kh., Bakhytzhan Ye., Vacandio F., Argimbayeva A. Nanostructured TiO_2 as anode material for magnesium-ion batteries // Journal of Solid State Electrochemistry. - 2023. – **27**. - P. 223–233 https://doi.org/10.1007/s10008-022-05307-7. Doctoral candidate's contribution: conducting experiments, interpreting the results, writing and editing the article.

Structure and Scope of the Dissertation

The dissertation is presented on 122 pages (excluding appendices) and consists of: an introduction, 3 main chapters, a conclusion, a list of references containing 171 sources, as well as 9 tables, 53 figures and 6 schemes.