

ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
on educational program «8D07104 – Chemical technology
of inorganic substances»

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«Development of methods for obtaining anticorrosive coatings based on titanium oxide and stearic acid»

The relevance of the study. Corrosion of metals and electrode materials remains one of the most significant problems of modern materials science. The economic losses from corrosion damage in industrialised countries are estimated at 3–6% of gross domestic product. In addition to direct material losses, corrosion poses a threat to the safety of structures, equipment and energy systems.

Among the existing methods of metal surface protection, electrochemical coating occupies a special place owing to the possibility of precise thickness control, uniform deposition and coating formation at low temperatures. A promising direction for the development of this method is the production of composite electrochemical coatings (CEC), in which dispersed particles (oxides, carbides, sulfides) are incorporated into a metallic matrix. Such coatings combine the mechanical strength of the metal with the functional properties of the dispersed phase, providing enhanced corrosion resistance, hardness and wear resistance compared with single-component galvanic coatings.

Titanium dioxide TiO_2 is of particular interest as a dispersed phase for CEC due to its high chemical inertness, thermal stability and availability. However, systematic studies of the effect of electrodeposition parameters on the composition and corrosion properties of coatings and powders in the Ni– TiO_2 , Cu– TiO_2 and other systems remain insufficient. General patterns governing the incorporation of TiO_2 particles into various metallic matrices from aqueous solutions have not been established. Alongside the protection of metallic surfaces, the prevention of corrosion degradation of electrode materials in aqueous-electrolyte-based electrochemical energy storage systems is also an urgent task. The anode material $\text{NaTi}_2(\text{PO}_4)_3$ with a NASICON structure possesses a high theoretical capacity (133 mAh/g) and structural stability; however, its application in aqueous electrolytes is limited by intense self-discharge due to parasitic reactions with dissolved oxygen and water (a corrosion process). Existing methods for surface protection of this material (atomic layer deposition, conductive polymer coatings, surfactant additives) are either technologically complex and expensive or fail to sufficiently suppress side reactions. In this context, the search for simple and effective ways to form protective barriers on the surface of electrode materials is an urgent task.

Thus, the development of anti-corrosion coatings based on oxide and organic compounds – both for the protection of metallic surfaces by electrodeposition methods and for the stabilisation of electrode materials in aggressive aqueous media – constitutes an important scientific and practical problem.

The aim of the study: to develop methods for obtaining anti-corrosion coatings based on the oxide compound TiO_2 within composite electrochemical coatings and powders with metallic matrices of Ni and Cu, and an organic compound (stearic acid) as a protective barrier for the anode material $\text{NaTi}_2(\text{PO}_4)_3/\text{C}$; to establish the patterns

of the effect of preparation conditions on the composition, structure and corrosion resistance of the resulting coatings and materials.

The following tasks were set to accomplish the aim of the work:

- 1) To study the effect of Ni–TiO₂ electrodeposition parameters (TiO₂ concentration, current density, electrolyte concentration) on achieving optimal TiO₂ mass values in CEC and high corrosion resistance;
- 2) To determine the corrosion resistance of the obtained Ni–TiO₂ -based CEC and compare it with that of the pristine Ni coating;
- 3) To determine the effect of Cu–TiO₂ electrodeposition parameters (TiO₂ concentration, current density, electrolyte concentration, H₂SO₄ concentration, stirring rate) on achieving optimal TiO₂ mass values in CEC;
- 4) To synthesise and characterise the NTP/C anode material;
- 5) To develop a method for applying a protective coating onto the NTP/C anode material using stearic acid;
- 6) Physicochemical characterisation of NTP/C modified with stearic acid;
- 7) To determine the electrochemical performance (cyclability, reversibility, charge/discharge rate, corrosion rate) of NTP/C modified with stearic acid.

The objects of the study: Ni–TiO₂ and Cu–TiO₂ composite electrochemical coatings; Ni–TiO₂ composite powders; NaTi₂(PO₄)₃/C anode material modified with stearic acid.

The methods of research: galvanostatic electrolysis; potentiodynamic polarisation (cyclic and linear voltammetry, acquisition of Tafel curves for determining corrosion parameters); gravimetric method for corrosion resistance evaluation; scanning electron microscopy (SEM); energy-dispersive X-ray spectroscopy (EDS); X-ray diffraction analysis (XRD); Fourier-transform infrared spectroscopy (FTIR); laser particle size analysis; atomic absorption spectrometry (AAS); contact angle measurement; galvanostatic charge–discharge cycling; open circuit potential (OCP) measurement.

The main provisions of the research to be defended:

1. The incorporation of chemically inert TiO₂ particles into a nickel matrix by electrodeposition from an aqueous sulfate electrolyte result in a reduction of the corrosion rate of the resulting composite coatings in a 3% NaCl solution compared to a single-component nickel coating across the entire investigated range of cathodic current densities of 100–800 A/m².
2. The deposition of stearic acid from an ethanol solution onto the surface of the NaTi₂(PO₄)₃/C anode material leads to hydrophobization of the electrode surface - an increase in the contact angle with the aqueous electrolyte from 69° for the pristine material to ~145° for the modified one.
3. Surface modification of the NaTi₂(PO₄)₃/C anode material with stearic acid at a content of 2% provides a Coulombic efficiency of galvanostatic cycling of the electrode of 99.0% at a 2C rate in a 1 M NaClO₄ aqueous electrolyte.

The main results of the research:

1. A fundamental dependence of the dispersed phase incorporation efficiency on the nature of the metallic matrix has been revealed. The maximum TiO₂ content was achieved in the nickel matrix (0.97 wt%), whereas in the copper matrix it does not exceed 2.55%. This pattern is explained by the difference in electrocrystallisation

overpotentials: at higher overpotentials, the crystal growth rate slows down, providing longer contact time between particles and the surface and their more effective entrapment by the growing deposit.

2. A nonlinear dependence of the corrosion rate of Ni and Ni-TiO₂ coatings on the deposition current density of 100–800 A/m² was established. The lowest corrosion rate values are achieved at 300 A/m², where the inclusion of TiO₂ particles in the nickel matrix provides a 1.45-fold reduction in the corrosion rate (0.31 mm/year for Ni-TiO₂ versus 0.45 mm/year for pure Ni).

3. A transition from the formation of compact coatings to the generation of dispersed composite powders upon exceeding the limiting diffusion current in the Ni-TiO₂ system at 4000–5000 A/m² has been discovered and investigated. The powders exhibit magnetic properties and enhanced oxidation resistance, which is attributed to the barrier effect of TiO₂ particles blocking oxygen access to the active metallic surface.

4. A method for surface modification of the NaTi₂(PO₄)₃/C anode material with stearic acid by deposition from an ethanol solution has been implemented. The formation of a conformal organic coating on the surface of NTP/C particles, which does not alter the NASICON crystal structure of the parent material, was confirmed by XRD, FTIR spectroscopy, SEM and TEM.

5. It was established that stearic acid modification leads to a significant increase in the hydrophobicity of electrode surfaces: the contact angle increases from 69.1° (hydrophilic surface) to ~145° (hydrophobic surface) already at 1 wt% of the modifier.

6. Electrochemical methods (CV, GCD, long-term cycling) demonstrated that the hydrophobic barrier of stearic acid effectively suppresses parasitic reactions in aqueous electrolyte (1 M NaClO₄). The Coulombic efficiency of the NTP/C–2% sample at a rate of 2C reaches 99.0% by the 100th cycle, which is substantially higher than that of the pristine NTP/C (96.5%). At a lower rate of 0.5C, where the relative contribution of parasitic processes increases, the modified electrode achieves CE = 93%, while the pristine NTP/C shows a maximum of only ~75%. The self-discharge test (OCV) revealed an increase in self-discharge time of 13.3% (from 71 to 80 h) upon modification with 1 wt% stearic acid, corresponding to a ~12% reduction in self-discharge current.

The scientific novelty of the research

1. A systematic comparative study of the electrodeposition of CEC with a TiO₂ dispersed phase in two metallic matrices (Ni, Cu) from aqueous solutions under varying electrolysis parameters has been carried out. It was confirmed that the mechanism of TiO₂ particle incorporation in all investigated systems is non-Faradaic (electrophoretic and adsorptive) in nature.

2. The patterns of the effect of electrodeposition parameters (concentrations of NiSO₄·7H₂O and TiO₂ in the electrolyte, and cathodic current density) on the mass content of TiO₂ in Ni-TiO₂ CEC obtained by sequential electrolysis have been established. It was shown that the dispersed phase content in the coating is determined by the competing effect of the matrix deposition rate and the intensity of TiO₂ particle incorporation, and the optimal process parameters were identified (NiSO₄·7H₂O – 200 g/l, TiO₂ – 10 g/l, $i = 400$ A/m²).

3. It was established that the introduction of a dispersed TiO₂ phase into a nickel

matrix ensures a systematic reduction in the corrosion rate of Ni–TiO₂ composite coatings in a 3% NaCl solution over the entire studied range of cathodic deposition current densities of 100–800 A/m² compared to a single-component nickel coating.

4. It was found that at cathodic current densities of 4000–5000 A/m² in a dilute electrolyte, a dispersed Ni–TiO₂ composite powder with a spherical particle morphology is formed, which is fundamentally different from the dendritic morphology of pure nickel powder. This is attributed to the role of TiO₂ particles as additional nucleation centres that suppress anisotropic crystal growth.

5. The patterns of the effect of electrodeposition parameters (cathodic current density, concentrations of TiO₂, H₂SO₄, Cu²⁺, and stirring rate) on the TiO₂ content in Cu–TiO₂ CEC from sulfuric acid electrolyte have been established. It was shown that increasing the current density leads to a monotonic decrease in TiO₂ content in the copper matrix, which is explained by the mass transfer mechanism of Cu²⁺ ions (electromigration) and TiO₂ particles (convective diffusion) at 100% current efficiency.

The theoretical and practical significance of the dissertation.

The experimental data obtained in this work extend the understanding of the patterns governing the formation of composite electrochemical coatings with an oxide dispersed phase from aqueous solutions. The results of the comparative study of two metallic matrices (Ni, Cu) confirm the adsorption–electrophoretic mechanism of TiO₂ particle incorporation into the growing metallic deposit, as described by the Guglielmi model, and demonstrate the dependence of co-deposition efficiency on the nature of the metallic matrix and the current regime.

The established non-linear dependence of the corrosion resistance of Ni–TiO₂ coatings on the deposition current density contributes to the understanding of the relationship between electrocrystallisation conditions, structural defectiveness of coatings and their protective properties in aggressive chloride media.

The results of NaTi₂(PO₄)₃/C modification with stearic acid substantiate the applicability of the hydrophobic organic barrier concept for suppressing interfacial parasitic reactions in aqueous electrochemical systems and supplement the theoretical understanding of the mechanisms of corrosion degradation and kinetic stabilisation of phosphate anode materials with the NASICON structure.

Reliability and validity of the results and data obtained have been confirmed by the use of selective, accurate and modern analytical methods, adherence to the scientific method and rigorous scientific principles. To ensure reproducibility and reliability, all experiments were performed in multiple parallel measurements.

Relevance of the dissertation to priority areas of the development of science and state programs: The research was carried out within the framework of the project funded by the Ministry of Science and Higher Education of the Republic of Kazakhstan, «Development of fundamentally new technologies for complex processing of polymetallic raw materials» (No. BR19777171, 2023–2025) under the priority direction «Geology, extraction and processing of mineral and hydrocarbon raw materials, new materials, technologies, safe products and structures»; «Electrochemical extraction of lithium from solutions of lithium-ion battery recycling» (No. AP25794557, 2025–2027) under the priority direction «Ecology, environment and rational nature management».

Publications (with a description of the personal contribution of the Ph.D. candidate):

Tazhibayeva Aigerim Shotaevna, Bayeshova Azhar Kospanovna, Bayeshov Abduali, Osińska Małgorzata. Electrodeposition of nickel-titanium dioxide coatings and powders from aqueous sulfate solutions // Polyhedron 277 (2025) 117571 <https://doi.org/10.1016/j.poly.2025.117571> **Q2** (Contribution: Writing the original draft, Visualisation, Methodology, Investigation, Formal analysis, Conceptualisation).

Aigerim Tazhibayeva, Altynai Tanash, Yaroslav Zhigalenok, Saken Abdimomyn, Kaiyrgali Zhumadil, Fyodor Malchik. Stearic acid induced hydrophobic protection of $\text{NaTi}_2(\text{PO}_4)_3$ for long-term operation in aqueous Na-ion systems // Journal Of Electroanalytical Chemistry. – 2025 <https://doi.org/10.1016/j.jelechem.2025.119550> **Q1** (Contribution: Writing the original draft, Visualisation, Methodology, Investigation, Formal analysis)

A. Bayeshov, **A.Sh. Tazhibayeva**, A.K. Bayeshova, M. Osińska, A.A. Zharmenov. Electrodeposition of composite coatings based on copper matrix included titanium dioxide in sulfuric acid solutions // International Journal of Biology and Chemistry. – 2023. – Vol.16, No. 1. – P. 87-95. <https://doi.org/10.26577/ijbch.2023.v16.i1.09> **Q4** (Contribution: Writing the original draft, Visualisation, Methodology, Investigation, Formal analysis, Conceptualis