Increasing energy-resource-efficiency of electrochemical processes to obtain inorganic substances by creating new electrode materials

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Relevance of the research topic. The work is devoted to the development of a coating based on lead dioxide modified with metal oxides in order to create anode materials capable of replacing expensive anodes based on platinum group metals and, in particular, ORTA (oxide-ruthenium-titanium anode) in various electrochemical processes. Research on electrode materials, especially those based on lead dioxide (PbO_2), is aimed at reducing energy consumption and cost of processes, as well as at creating anodes with high corrosion resistance and electrocatalytic activity. Such insoluble anodes coated with PbO_2, with additives of TiO_2, SnO_2 and other oxides, can be effectively used in low-current electrochemical processes for the production of inorganic substances, including the synthesis of sodium hypochlorite and sodium chlorate, the production of sodium hydroxide and sulfuric acid. In addition, the use of the developed electrodes in water treatment processes by electroflotation and electrocorrection of pH is relevant. The developed electrode materials must meet the requirements for accessibility and low cost of the materials used in their manufacture, as well as ease of manufacture, which makes them suitable for use in developing countries, in particular in the Republic of the Union of Myanmar.

The aim of the work is to formulate the new electrode materials based on lead dioxide to improve the energy efficiency of electrochemical processes for the production of inorganic substances and wastewater treatment by electroflotation method.

Research Tasks:

1. Choose a suitable electrolyte and substrate for applying lead dioxide coatings that are highly resistant to electrochemical processes as anode materials.

2. Optimize the parameters of obtaining lead dioxide coatings on a titanium substrate from an alkaline plumb electrolyte (1N NaOH, PbO to saturation) with the addition of TiO_2 and SnO_2 powders.

3. To analyze the physico-chemical properties of electrode materials based on PbO_2 modified with additives of TiO_2 and SnO_2 powders, with substrates made of various materials (titanium, stainless steel, lead).

4. To conduct experimental studies of the behavior of PbO_2-based anodes in low-current (up to 5 A/dm^2) processes of electrochemical production of inorganic substances using the example of hypochlorite and sodium chlorate, electroflotation extraction of poorly soluble metal compounds from electrolyte solutions, electrocorrection of pH, membrane desalination to obtain sodium hydroxide and sulfuric acid.

5. To test the stability of the anode material based on PbO_2 in the studied electrochemical processes.

Scientific novelty of the work:

1. For the first time, the possibility of using modified PbO_2-based electrode materials with titanium-based TiO_2 as anodes in the production of hypochlorite and sodium chlorate has been established. It is shown that the use of the developed anode material instead of the ORTA electrode in the process of membrane-free electrolysis of a sodium chloride solution with the addition of sodium dichromate leads to an

increase in the current yield of the most valuable product sodium chlorate from 63% to 89% at an anode current density of 1 A/dm^2.

2. The possibility of using the developed anode material based on PbO_2 with the addition of TiO_2 in the processes of electrochemical membrane desalination of sodium sulfate solutions to obtain solutions of sulfuric acid and sodium hydroxide, electroflotation and electrocorrection of pH, including in solutions with high salinity, is shown.

Theoretical and Practical Significance:

1. The patterns of formation of PbO_2 coatings from alkaline plumbite electrolytes have been established, and the influence of current density, temperature, and electrolyte composition on their morphology, mechanical strength, and adhesion has been determined.
2. Technological modes of the deposition of anode coatings based on PbO_2 with the addition of TiO_2 have been developed, ensuring the production of durable and resistant coatings suitable for industrial use, including in the processes of obtaining hypochlorite and sodium chlorate, wastewater treatment and membrane desalination to produce sulfuric acid and alkali.
3. The theoretical understanding of the behavior of modified PbO_2–based electrodes in the synthesis of inorganic substances - hypochlorite and sodium chlorate, sulfuric acid and sodium hydroxide, as well as in the processes of electroflotation, electrocorrection and membrane electrolysis has been expanded.
4. New data on the influence of the nature and concentration of background salts (Na_2SO_4, NaCl, $NaNO_3$ with concentrations up to 100 g/l) have been obtained, deepening understanding of the influence of the composition of the medium on the overvoltage of anode reactions on electrodes based on PbO_2.

5. The effect of current density and electrolyte composition on the degradation of PbO_2-TiO_2 electrodes in solutions of Na_2SO_4, NaCl, and $NaNO_3$, characteristic of the electrochemical synthesis of hypochlorite and sodium chlorate, sulfuric acid, and alkali, as well as electroflotation, pH correction, and membrane desalination, is analyzed.
6. The mechanisms of degradation of PbO_2-TiO_2 electrodes in various electrochemical processes and environments are systematized, recommendations for extending the service life of the electrodes are given, and the areas of their application are identified. It is shown that the developed electrode demonstrates high electrochemical stability in various processes in the range of anode current densities of 1-5 A/dm^2.
7. The economic feasibility of using the developed anode materials based on PbO_2-TiO_2 is due to the low cost of the material compared to ORTA anodes used in the processes under study: the developed materials are almost 10 times cheaper with a comparable service life in conditions of an anode current density of no more than 5 A/dm^2.

Thesis to be defended:

1. Optimization of the electrochemical process for producing PbO_2-based electrodes: The parameters of the PbO_2 electrodeposition process (current, temperature, modifying additives) have been optimized to improve the structure and strength of the coating. The optimal base material for electrodeposition of lead dioxide (titanium VT-1-00) was selected.

2. Electrochemical synthesis of NaClO/$NaClO_3$: optimal technological parameters of the process were determined, allowing to obtain the most valuable $NaClO_3$ product with 89% W (anode current density of 1 A/dm^2, membrane-free electrolysis with sodium dichromate).

3. Na_2SO_4 electrolysis to produce NaOH and H_2SO_4: the optimal current density for the Na_2SO_4 membrane electrolysis process was determined (output per current (NaOH) 78%, output per current (H_2SO_4) 77%, anode and cathode current density 3 A/dm^2).

4. Environmental processes (electroflotation water treatment and pH correction): the efficiency of electroflotation and pH electrocorretion processes when using PbO_2-based anodes in electrolyzers exceeds the efficiency of processes using electrolyzers with ORTA anodes, which is associated with low overvoltage of anode reactions on PbO_2-based electrodes.

5. Modification of PbO_2 electrodes: for the first time, differences in morphology, composition and mechanical properties (adhesion of the coating to the substrate and hardness of the coating) of PbO_2-based electrodes were revealed when they were modified with TiO_2, SnO_2, etc. powders, as well as when using different materials as the base (stainless steel, lead, titanium). The materials with the best adhesion of the coating to the substrate and hardness are selected - PbO_2 modified TiO_2.

6. Stability tests of electrode materials based on PbO_2-TiO_2 on a titanium substrate were carried out in various electrochemical processes by the CV (cyclic voltammetry) method and tests in the processes of electrochemical synthesis of sodium chlorate and hypochlorite, desalination, electroflotation and electrocorrection of pH at an anode current density of 0.4-5.0 A/dm^2, the test duration was 600 hours. It has been shown that the electrode materials are stable in solutions of Na_2SO_4, NaCl, and $NaNO_3$ with concentrations up to 100 g/l, and can be used instead of ORTA electrodes.