

ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD) in the educational program "8D07102 - Chemical Engineering" by Jumadil Kayyrgali Muratuly "Development of the synthesis technology of aluminized titanium carbides as the main precursor for obtaining 2D MXene material"

General characteristics of the work. The dissertation is devoted to the development and optimization of the synthesis technology of aluminum-containing titanium carbides of MAX phases Ti_3AlC_2 and Ti_2AlC , used as precursors for obtaining two-dimensional materials of the MXene family — $\text{Ti}_3\text{C}_2\text{Tx}$ and Ti_2CTx . The work investigates the regularities of formation of target MAX phases depending on the composition of initial precursors, temperature, synthesis time, aluminum excess, the form of loading of the reaction mixture, and protection conditions against oxidation. Conditions for selective leaching of aluminum to obtain MXene were determined, physicochemical and electrochemical characteristics of synthesized materials were studied, and the cost of MAX-phase synthesis using local precursors was evaluated. The obtained results are aimed at creating a more accessible and technologically justified approach to the synthesis of MAX phases and MXene materials.

The relevance of research. MAX phases are layered carbides and nitrides of transition metals with the general formula $\text{M}_{n+1}\text{AX}_n$ and serve as the main precursors for obtaining two-dimensional materials of the MXene family. MXenes belong to a promising class of functional materials of interest for electrochemical energy storage, sensor systems, catalysis, electromagnetic shielding, and other applications. Among them, titanium MXenes such as $\text{Ti}_3\text{C}_2\text{Tx}$ and Ti_2CTx are of greatest interest due to the combination of high electrical conductivity, hydrophilicity, developed surface area, and ability for reversible ion intercalation. However, one of the factors limiting wider practical application of MXenes is their high production cost. According to literature, the cost of 1 g of MXene is about 12.2 USD, with up to 34% of the cost attributed to precursors used in MAX-phase synthesis. Therefore, the development of cost-effective and technologically justified approaches to the synthesis of MAX phases Ti_3AlC_2 and Ti_2AlC , including using local Kazakhstan raw materials, is a relevant task.

The purpose of the study. Optimisation of the synthesis methods for MAX phases Ti_3AlC_2 and Ti_2AlC to increase the yield of the target phases, reduce process costs, and develop a laboratory-scale synthesis process suitable for scaling.

Research objectives.

1. Selection of precursor mixtures for synthesis of MAX phases Ti_3AlC_2 and Ti_2AlC ;
2. Optimization of synthesis parameters including temperature, holding time, mixture loading form, aluminum content, and partial substitution of Al with Sn;
3. Determination of conditions for selective leaching of aluminum to obtain MXene $\text{Ti}_3\text{C}_2\text{Tx}$ and Ti_2CTx ;
4. Physicochemical characterization and electrochemical study of obtained MXene materials;

5. Scaling of synthesis process and cost evaluation;
6. Development of technological scheme.

The object of the study. MAX phases Ti_3AlC_2 and Ti_2AlC and MXene $\text{Ti}_3\text{C}_2\text{Tx}$ and Ti_2CTx .

The subject of the study. The effect of the technological parameters of synthesis and the composition of precursors on the phase composition, purity and yield of MAX phases, as well as on the properties of the obtained MXene.

Research methods. To solve these problems, a complex of modern physico-chemical analysis methods was used: X-ray phase analysis with Rietveld parameter refinement, scanning electron microscopy (SEM/EDX), laser particle size distribution analysis, cyclic voltammetry, and galvanostatic cycling.

Scientific novelty. The scientific novelty lies in establishing the relationship between technological parameters (precursor composition, temperature, aluminum content, synthesis atmosphere, and methods of protecting the reaction mixture) and the formation of MAX phases Ti_3AlC_2 and Ti_2AlC . For the first time, it is shown which of these factors are key to ensuring high phase purity and product yield when adapting the synthesis technique to laboratory conditions. Rational synthesis modes from Kazakhstani raw materials have been developed and experimentally substantiated, enabling the production of Ti_3AlC_2 and Ti_2AlC with yields of up to 91.2% and 71.3%, respectively, at a more than tenfold reduction in cost compared with imported analogues. Optimal conditions for selective etching ($\text{LiF} + \text{HCl}$, 35.0 °C, 24 h) were determined, ensuring the production of MXenes $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x with high suspension concentration, a homogeneous structure, and stable electrochemical characteristics.

Practical significance. The results of the work are of practical importance for the development of laboratory and industrial technologies for the synthesis of MAX phases using readily available precursors. The developed technique enables the production of high-yield, high-purity materials at low cost, opening the possibility of organising low-tonnage production of MXene precursors in Kazakhstan. The resulting MXene can be used as an active material for electrodes in supercapacitors, lithium-ion batteries, and sensor systems.

Provisions to be defended.

1. The optimal synthesis parameters for the Ti_3AlC_2 phase are: a precursor mixture of TiC-Ti-Al , pressing of the reaction mixture into pellets, a temperature of 1350 °C, a holding time of 2 h, the presence of an Al_2O_3 protective coating, and a 60% excess of aluminum, under which the phase purity of the product reaches 91.2%.
2. The optimal synthesis parameters for the Ti_2AlC phase are: a precursor mixture of $\text{Ti-C-Al}_4\text{C}_3$, loading of the reaction mixture in powder form, a temperature of 1350 °C, and a holding time of 2 h, under which the phase purity of the product reaches 71.3%.
3. MXene $\text{Ti}_3\text{C}_2\text{T}_x$, obtained from the synthesized Ti_3AlC_2 phase, in a 6 M NaOH solution at a scan rate of 5 mV/s demonstrates a coulombic efficiency of 99.8% over 1000 cycles, indicating high electrochemical reversibility of the material under the studied conditions.

The main results.

– Stepwise optimization of synthesis parameters showed that the maximum content of the Ti_3AlC_2 phase is achieved at a temperature of 1350 °C and a holding time of 2 h. It was established that pressing the reaction mixture into pellets, applying an Al_2O_3 protective coating, and introducing a 60% excess of aluminum increase the Ti_3AlC_2 content up to 91.2%. Increasing the temperature above 1350 °C leads to a decrease in the Ti_3AlC_2 content and an increase in the TiC fraction.

– For the Ti_2AlC phase, it was found that optimal synthesis conditions are realized in the Ti–C– Al_4C_3 system at a temperature of 1350 °C and a holding time of 2 h. When the reaction mixture is loaded in powder form, the content of the target phase reaches 71.3%. It was shown that the additional introduction of excess aluminum in this system is impractical, since Al_4C_3 exhibits higher resistance to oxidation and sublimation compared to metallic aluminum.

– The effect of partial substitution of aluminum with tin on the formation of MAX phases Ti_3AlC_2 and Ti_2AlC was investigated. It was established that the introduction of Sn does not increase the yield of target phases and is accompanied by the formation of secondary compounds.

– Conditions for selective leaching of aluminum from synthesized MAX phases to obtain MXene $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x were determined. It was shown that the most effective etching agent is the LiF + HCl system, which ensures the formation of stable suspensions and freestanding MXene films. Under these conditions, the concentration of $\text{Ti}_3\text{C}_2\text{T}_x(\text{syn})$ suspension reaches 14 mg/mL, while that of $\text{Ti}_2\text{CT}_x(\text{syn})$ reaches 8 mg/mL.

– Electrochemical tests demonstrated that the synthesized MXenes exhibit characteristics comparable to commercial analogues. The specific capacity of $\text{Ti}_3\text{C}_2\text{T}_x(\text{syn})$ is 25.8–34 $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$ (for $\text{Ti}_3\text{C}_2\text{T}_x(\text{com})$: 22.6–33 $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$), while for $\text{Ti}_2\text{CT}_x(\text{syn})$ it is 41–46 $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$ (for $\text{Ti}_2\text{CT}_x(\text{com})$: 37–44.2 $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$), confirming the potential of these materials for application in electrochemical energy storage devices.

– The synthesis process of MAX phases Ti_3AlC_2 and Ti_2AlC was scaled in the range of 1–100 g. It was shown that with increasing batch mass, the yield of target phases slightly decreases: for Ti_3AlC_2 from 91.2% to 84.8%, and for Ti_2AlC from 71.3% to 67.8%, which is associated with limitations in heat transfer and diffusion in larger batches.

– The cost assessment of laboratory synthesis showed that the production cost of 1 g of Ti_3AlC_2 from Kazakhstan raw materials is 0.22 USD, while for Ti_2AlC it is 0.38 USD, which is lower than the cost of commercial analogues used for comparison. This indicates the potential for reducing the cost of MAX-phase synthesis through the use of local precursors.

The relationship of the thesis topic with research projects and government programs. The dissertation work was carried out within the framework of the research plan of the Department of Analytical, Colloidal Chemistry and Technology of Rare Elements of the al-Farabi Kazakh National University, as well as within the framework of the state grant financing project.:

1. 14871554 "Optimization of an innovative method for the synthesis of aluminized titanium carbides as the main material for the production of 2D MXene materials (Ti_3C_2 , Ti_2C)
2. The results of the work have been implemented in the research and development activities of the Institute of Batteries LLC, where the applicability of the synthesized Ti_3AlC_2 material for obtaining MXene with electrochemical properties comparable to commercial analogues has been confirmed.

Personal contribution of the author. It consists of directly synthesising the studied MAX phases and MXene materials, preparing and conducting experiments, processing and interpreting experimental data, and analysing the results obtained, as well as formulating the main scientific provisions submitted for defence. All the key results of the dissertation work were obtained personally by the author with his direct participation.

Publications. Based on the dissertation's main results, 4 articles were published, including 3 in international journals with impact factors and 1 in a journal recommended by the KKSON.

1) Zhumadil K.M., Kan T. V., Malik S.D., Skakov M.K., Miniyazov A.Z., Mukhamedova N.M., Zhanbolatova G.K., Malchik F.I. Multilevel optimization of Ti_2AlC synthesis process using precursors of Kazakhstan origin // NNC RK Bulletin. - 2025. - Is. 2. - P. 88–95.

2) Zhigalenok Y., Abdimomyn S., Zhumadil K., Lepikhin M., Starodubtseva A., Kiyatova M., Shpigel N., Malchik F. A practical guide for separator selection, characterization, and electrochemical evaluation for supercapacitor application // Applied Physics Reviews. - 2024. - Vol. 11, Is. 3.

3) Malchik F., Maldybayev K., Kan T., Kokhmetova S., Chae M.S., Kurbatov A., Galeyeva A., Kaupbay O., Nimkar A., Bergman G., Levi N., Zhang H., Jin Q., Lin Z., Shpigel N., Mandler D. Boosting the capacity of MXene electrodes in neutral aqueous electrolytes // Cell Reports Physical Science. - 2023. - Vol. 4, Is. 7. - P. 101507.

4) Malik S., Zhumadil K., Avchukir K., Skakov M., Miniyazov A., Mukhamedova N., Zhanbolatova G., Malchik F. Enhancing electrochemical performance of LaNi_5 anodes using MXene as a multifunctional additive for Ni-MH batteries // Journal of Electroanalytical Chemistry. – 2025. – Vol. 996. – P. 119409.

The structure and scope of the dissertation. The dissertation is 105 pages long and includes an introduction, three chapters, a conclusion, a list of references from 126 sources, and 3 appendices. The work contains 42 figures and 19 tables.