

Evaluation of perspectives for the synthesis of Ti_3AlC_2 in Kazakhstan for supercapacitor application

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With the increasing demand for energy-efficient technologies, there is a growing focus on developing new materials for supercapacitors and other energy devices. MXene $Ti_3C_2T_x$ is known for its unique electrochemical properties and has garnered significant interest in such applications. However, the high cost of synthesizing MXene limits its commercial viability, prompting research into cost-effective methods for synthesizing the MXene precursor, the Ti_3AlC_2 MAX phase. This paper presents a method for synthesizing the MAX-phase Ti_3AlC_2 using local raw materials from Kazakhstan Electrolysis Plant JSC and Ust-Kamenogorsk Titanium-Magnesium Plant JSC. Utilizing local resources significantly reduces production costs. The study investigates the impact of temperature conditions and excess aluminum content on MAX phase formation. Process optimization, including pressing the precursors and coating them with a layer of aluminum oxide, resulted in a Ti_3AlC_2 content of 91.2%. MXene $Ti_3C_2T_x$ derived from the synthesized MAX phase demonstrated electrochemical performance comparable to materials prepared from commercially available MAX phases. An economic assessment revealed that the cost of synthesizing 1 gram of Ti_3AlC_2 from local precursors is \$0.22, more than 19 times lower than similar commercial materials. These findings confirm the cost-effectiveness and competitiveness of the proposed approach, highlighting its potential to create high-performance materials suitable for advanced batteries, supercapacitors, and other energy devices.

Keywords: Ti_3AlC_2 MAX phase synthesis; MXene $Ti_3C_2T_x$; local raw materials; production cost reduction; temperature conditions; process optimization; electrochemical performance; economic assessment.

Қазақстандағы суперконденсаторларда қолдануға арналған Ti_3AlC_2 синтезінің перспективасын бағалау

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Энергияны үнемдейтін технологияларға деген сұраныстың артуымен суперконденсаторлар мен басқа да энергетикалық құрылғыларға арналған жаңа материалдарды әзірлеуге көбірек көңіл бөлінуде. MXene $Ti_3C_2T_x$ өзінің ерекше электрохимиялық қасиеттерімен танымал және мұндай қосымшаларда үлкен қызығушылыққа ие. Алайда, MXene синтезінің жоғары құны оның коммерциялық өміршеңдігін шектейді, бұл MXENE прекурсорының, MAX Ti_3AlC_2 фазасының үнемді синтез әдістерін зерттеуге итермелейді. Бұл мақалада «Қазақстандық электролиз зауыты» АҚ және «Өскемен титан-магний комбинаты» АҚ өндіріс орындарының жергілікті шикізатын пайдалана отырып, Ti_3AlC_2 MAX-фазасын синтездеу әдісі ұсынылған. Жергілікті ресурстарды пайдалану өндіріс шығындарын айтарлықтай төмендетеді. Зерттеу түрлі температура шарттары мен артық алюминийдің MAX-фазасының қалыптасуына әсерін зерттейді. Процесті оңтайландыру, соның ішінде прекурсорларды қысымдау мен оларды алюминий оксиді қабатымен жабу арқылы өнімдегі Ti_3AlC_2 үлесі 91,2%-ға дейін жетті. Синтезделген MAX фазасынан алынған MXene $Ti_3C_2T_x$ коммерциялық қол жетімді MAX фазаларынан алынған материалдармен салыстырарлық электрохимиялық өнімділікті көрсетті. Экономикалық бағалау жергілікті прекурсорлардан 1 грамм Ti_3AlC_2 синтезінің құны 0,22 АҚШ долларын құрайтынын көрсетті, бұл ұқсас коммерциялық материалдардан 19 есе төмен. Бұл нәтижелер ұсынылған тәсілдің экономикалық тиімділігі мен бәсекеге қабілеттілігін растайды, оның заманауи аккумуляторларға, суперконденсаторларға және басқа да энергетикалық құрылғыларға сәйкес келетін жоғары өнімді материалдарды жасау әлеуетін көрсетеді.

Түйін сөздер: Ti_3AlC_2 MAX фазасының синтезі; MXene $Ti_3C_2T_x$; жергілікті шикізат; өнімнің өзіндік құнын төмендету; температура жағдайлары; процесті оңтайландыру; электрохимиялық өнімділік; экономикалық бағалау.

Оценка перспектив синтеза Ti_3AlC_2 в Казахстане для применения в суперконденсаторах

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С ростом спроса на энергоэффективные технологии все больше внимания уделяется разработке новых материалов для суперконденсаторов и других энергетических устройств. MXene $Ti_3C_2T_x$ известен своими уникальными электрохимическими свойствами и привлек значительный интерес для таких устройств. Однако высокая стоимость синтеза MXene ограничивает его рыночную конкурентоспособность, побуждая к исследованию экономически эффективных методов синтеза прекурсора MXene – MAX-фазы Ti_3AlC_2 . В данной статье представлен метод синтеза MAX-фазы Ti_3AlC_2 с использованием местного сырья от АО «Казахстанский электролизный завод» и АО «Усть-Каменогорский титано-магниевый комбинат». Использование местных ресурсов значительно снижает производственные затраты. В исследовании изучается влияние температурных условий и избыточного содержания алюминия на формирование MAX-фазы. Оптимизация процесса, включая прессование прекурсоров и покрытие их слоем оксида алюминия, позволила получить Ti_3AlC_2 чистотой 91,2%. MXene $Ti_3C_2T_x$, полученный из синтезированной MAX-фазы, продемонстрировал электрохимические характеристики, сопоставимые с характеристиками материалов, полученных из коммерчески доступных MAX-фаз. Экономическая оценка показала, что стоимость синтеза 1 грамма Ti_3AlC_2 из местных прекурсоров составляет 0,22 доллара США, что более чем в 19 раз ниже, чем у аналогичных коммерческих материалов. Эти результаты подтверждают экономическую эффективность и конкурентоспособность предлагаемого подхода, подчеркивая его потенциал для создания высокопроизводительных материалов, подходящих для современных аккумуляторов, суперконденсаторов и других энергетических устройств.

Ключевые слова: синтез MAX-фазы Ti_3AlC_2 ; MXene $Ti_3C_2T_x$; местное сырье; снижение себестоимости продукции; температурные условия; оптимизация процесса; электрохимические характеристики; экономическая оценка.



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1. Introduction

Research on batteries and supercapacitors is actively being conducted today, as these devices are crucial for energy storage due to the growing demand for electric vehicles and portable electronics. Two-dimensional (2D) materials have become promising candidates for electrode materials in metal-ion batteries and supercapacitors due to their large surface-area-to-volume ratios and substantial internal surface areas, which provide high energy density [1]. 2011 marked the discovery of a new class of two-dimensional transition metal carbides, nitrides, and carbonitrides, known as MXenes [2].

MXene are layered materials with the general formula $M_{n+1}X_nT$, where M is a transition metal (Ti, Mo, V, Cr, and others), X is carbon or nitrogen, and T are surface groups (usually Cl, F, OH, O) formed during its synthesis process [3]. MXenes are derived from MAX phases, where M and X are the specified elements, and A is an element (typically Al) that binds them. The A atoms are removed from the MAX phases via etching, forming the desired 2D material. To date, over 40 MXenes have been synthesized, with computational modeling suggesting the stability of over 100 more [4]. The metallic properties of the M layer offer excellent pseudocapacitance characteristics, while the X layer is characterized by abundant active sites and conductivity similar to that of graphene. Compared with conventional materials, the existence of various functional groups on the surface of MXenes gives them stronger hydrophilicity and higher wettability in aqueous electrolytes, which, combined with their diverse frame structures and functional group combinations, significantly augment their applicability for energy storage devices [5].

The most well-known and widely used MXene in electrochemical energy storage devices (supercapacitors) is titanium carbide (Ti_3C_2) [6-8]. Ti_3C_2 is produced from the corresponding MAX phase Ti_3AlC_2 by etching aluminum using hydrofluoric acid or fluoride [9]. The MAX phase is synthesized using a high-temperature method from the respective elemental powders (Al, C, Ti) or binary compounds (such as titanium carbide, titanium hydride, and aluminum carbide) [10-12]. However, converting MXene into practical products faces several challenges, including high synthesis costs. For instance, 1 g of MXene costs approximately \$12.20 [13]. According to Zaed *et al.*, the most significant contribution to the cost of MXene, accounting for 34% (\$4.20), comes from the total cost of raw precursors required to synthesize 1 g of MAX phase: Ti powder is \$3,38, Al powder is \$0,045, and C powder is \$0,77 according to the prices of Sigma Aldrich sales. However, considering a 60% yield of MXene from the initial MAX phase, the actual cost of 1 g of MXene increases to \$20.33. This highlights the need to reduce production costs to achieve economic efficiency in the large-scale commercial production of MXene.

Therefore, recent research was focused on improving the economic efficiency of the MAX phase synthesis process, including exploring alternative methods using cheaper precursors. For example, recycling used car tires through a simple sulfonation process and subsequent low-temperature pyrolysis can be an affordable carbon source, costing less than 50% of the price of graphite carbon [14]. Other carbon sources include petroleum coke, cotton, coconut shells, and other materials [15,16]. Jolly S. *et al.* used titanium oxide, which is 50% cheaper than metallic titanium, and recycled aluminum

scrap instead of commercially pure aluminum, significantly reducing the product's cost and environmental impact [17,18]. It was previously believed that Ti_3AlC_2 could not be synthesized from the TiO_2 -Al-C system. However, Li *et al.* demonstrated the possibility of forming Ti_3AlC_2 with the corrected stoichiometry and temperature from such precursors [19]. Another affordable source of titanium compared to metallic titanium is TiH_2 , a semi-product of Ti production, which costs 10% less on average [10].

This study used local resources from Kazakhstan manufacturers JSC "Kazakhstan Electrolysis Plant" and JSC "Ust-Kamenogorsk Titanium-Magnesium Plant" to synthesize the MAX phase Ti_3AlC_2 . The cost assessment of the precursors for synthesizing 1 g of MAX phase was based on the following prices: Ti – \$0.04, Al – \$0.008, and TiC – \$0.11. These prices are significantly lower than the market prices for similar precursors [20-22].

MXene $Ti_3C_2T_x$ derived from the synthesized MAX phase exhibited high electrochemical characteristics comparable to those of materials obtained from the commercially available MAX phase [20] (Carbon-Ukraine). The cost calculation for synthesizing 1 g of MAX phase Ti_3AlC_2 using local precursors showed that the total cost amounts to \$0.22, with the precursors' cost accounting for 74.02% of the total expenditure. These results highlight the economic efficiency of the proposed method and confirm its potential for producing high-performance, cost-effective materials for energy storage applications.

2. Experiment

When synthesizing Ti_3AlC_2 , it is essential to consider that aluminum, with a melting point of about 660°C, undergoes significant losses (due to sublimation) when reaching synthesis temperatures in the 1100-1350°C range. This fact, well documented in the literature [6], necessitates using excess aluminum in preparing precursors. Our study used 20% excess aluminum as a starting point to compensate for its losses during synthesis.

For the synthesis of Ti_3AlC_2 , the powders of Ti (99.5 wt.%, UKTMP, Kazakhstan), Al (99.5 wt.%, KEP, Kazakhstan), and TiC (99.5 wt.%, UKTMP, Kazakhstan) were used in molar ratios of 1.0 Ti: 2.0 TiC: (1.2-1.6) Al. The phase purity of precursors was confirmed with the XRD analysis. The precursor mixtures were homogenized in a ball mill (Fritsch Pulverisette 7) for 2 hours at 400 rpm with the addition of hexane. After homogenization, the mixture was dried under vacuum at 200°C for 4 hours to remove the residuals of solvent and oxygen.

After drying, the material was loaded into alumina crucibles in three different ways: as a powder, as a pellet (9 mm diameter) pressed at 703 t/m², and as the same pellet freely powder-covered with a layer of Al_2O_3 to suppress diffusion of the trace oxygen presented in the inert gas into the pellet. The crucibles were then placed in a tube furnace. The heating was carried out in an Ar/H₂ (95:5 vol. %) atmosphere at a heating

rate of 5°C/min until the temperature reached 1150-1350°C. Once the final temperature was achieved, the samples were sintered for 2 hours and then cooled to room temperature naturally.

The pellets were ground and analyzed through powder X-ray diffraction (XRD) using an XRD diffractometer Tongda TD-3700. The diffractometer was equipped with a copper X-ray source ($\lambda_{CuK\alpha1}=1.54056 \text{ \AA}$ and $\lambda_{CuK\alpha2}=1.54439 \text{ \AA}$). The structural, compositional, and semi-quantitative analysis of the samples on the diffraction patterns was done using the Rietveld method with the GSAS-II software [23]. The particle size of the Max phases was determined using a Partica LA-960 (HORIBA) laser analyzer in an aqueous medium.

To obtain delaminated $Ti_3C_2T_x$, the etching of Al from Ti_3AlC_2 was carried out using the standard method employing a mixture of HCl and LiF [9]. 1 g of Ti_3AlC_2 was added gradually to a total of 20 mL of 32% HCl solution mixed with 1.6 g of LiF. The etching process was done for 48 hours while stirring at 42°C in a sand bath. The solid product was separated from the etchant solution by decantation with centrifugation at 3500 rpm and washed with deionized water multiple times until reaching a pH of ~ 5.0-5.5. Then, the solid product was immersed in 50 ml of deionized water and subjected to ultrasonic treatment at 900 W for 5 min for delamination. The obtained suspension of $Ti_3C_2T_x$ flakes was separated from the residual precipitate via centrifugation at 5000 rpm for 5 min.

To obtain free-standing $Ti_3C_2T_x$ films, the resulting aqueous suspension was vacuum filtered using a PVdF filter (d=4 cm) with a pore size of 0.45 μm . The vacuum filtration was carried out using a Buchner-type vacuum filter. After filtration, the obtained film disk was dried in the vacuum oven at 110°C for 12 hours. After drying, the $Ti_3C_2T_x$ film was easily peeled from the filter, maintaining its integrity and uniform structure.

Scanning electron microscopy (SEM) using a Quanta 200i 3D (FEI™) instrument was employed to study the microstructure and surface morphology.

Electrochemical measurements were performed by cyclic voltammetry using a potentiostat-galvanostat Biologic SP-300. A three-electrode system (Swagelok-type cell) was used in the experiments, where a $Ti_3C_2T_x$ free-standing film (disc of 6 mm in diameter) was obtained as the working electrode, a silver chloride electrode (3.5 M KCl) was used as a reference electrode, and carbon cloth was used as an auxiliary electrode. A saturated aqueous solution of LiCl (~ 14 M) was used as the electrolyte to suppress the parasitic hydrogen evolution reaction.

3. Results and Discussion

The study systematically analyzed the influence of temperature conditions and excess aluminum content on the formation of Ti_3AlC_2 from local raw materials. Initial experiments were conducted on a powder mixture loaded into a crucible and placed in a high-temperature synthesis furnace. Upon completion of the synthesis, an X-ray diffraction analysis was carried out to determine the phase composition of the resulting

sample. The phase diagram in Figure 1a illustrates the changes that occur during the synthesis of the Ti_3AlC_2 MAX phase at different temperatures.

At 1150°C, a predominance of the low-temperature phase Ti_2AlC (32.5%) and TiC (52.1%) is observed, while Ti_3AlC_2 (6.7%) and Al_2O_3 (8.8%) are formed as impurity phases. Since the precursors were carefully examined for impurities and no traces of oxygen were found, the relatively constant Al_2O_3 impurity source remains unclear. However, it is essential to note that any residual Al_2O_3 formed during this process is naturally eliminated during the preparation of the MXene phase and has no adverse effect on the resulting material. When the temperature increases to 1200°C, the Ti_3AlC_2 content rises to 18.3%, the Ti_2AlC content decreases to 22.5%, and TiC decreases to 49.9%, while the Al_2O_3 content is 9.3%. A further increase in temperature to 1250°C leads to the complete disappearance of the Ti_2AlC phase, a decrease in the TiC phase content to 35.1%, and an increase in the Ti_3AlC_2 content to 57.1%, while the amount of Al_2O_3 is 7.8%. Upon reaching 1300°C, the Ti_3AlC_2 phase content reaches 63.1%, while the TiC content continues to decrease to 29.4% and Al_2O_3 is 7.5%. When the temperature increases to 1350°C, the content of Ti_3AlC_2 increases to 73.7%, TiC's decreases to 19.1%, and Al_2O_3 is 7.2%. With a further increase in temperature to 1400 °C, a decrease in the Ti_3AlC_2 content to 60.1% is observed, while the TiC content increases to 31.7%, and the amount of Al_2O_3 is 8.2%. These final changes may be associated with the thermodynamic instability of the Ti_3AlC_2 MAX phase at higher temperatures.

The presented data shows that at lower temperatures, the Ti_2AlC phase is formed, and an increase in temperature promotes the interaction between Ti_2AlC and TiC, which leads to the formation of Ti_3AlC_2 . The maximum content of Ti_3AlC_2 (73.7%) is reached at a temperature of 1350°C, after which a further increase in temperature causes its decomposition with the formation of TiC. These results are consistent with previously published data on synthesizing the Ti_3AlC_2 MAX phase in the

temperature range of 1300-1500°C [25] and confirm the possibility of synthesizing this phase based on local precursors.

Titanium carbide was found in the final product after synthesis, likely due to unreacted residues caused by the significant loss of aluminum through sublimation and reaction with trace oxygen in the gas phase. To reduce these losses, we proposed sintering a mixture of precursors as a compressed pellet to minimize the contact area with the gas phase. One of the pellets was coated with a layer of aluminum oxide to prevent excessive oxygen diffusion.

Figure 1b shows a phase diagram illustrating the changes in the composition of the samples. The amount of MAX phase Ti_3AlC_2 in the uncoated pellet increased to 78.3% compared to the powder (73.7%), while the TiC content decreased from 19.1% to 14.3%. The best result was achieved with the pellet coated with aluminum oxide: the Ti_3AlC_2 phase increased to 81.1%, the TiC content decreased to 11.8%, and the aluminum oxide content was 7%.

Since titanium carbide was still detected in the final product, indicating an insufficient amount of aluminum in the initial precursor mixture and its incomplete reaction with titanium carbide to form the MAX phase, it was hypothesized that increasing the aluminum content could facilitate a more efficient synthesis process of the Ti_3AlC_2 phase.

To test this hypothesis, the MAX phase was synthesized with various aluminum excesses (1.2-1.6). As a result of the experiments, it was established (Figure 1c) that the maximum yield of the MAX phase is achieved with an aluminum content of 60% excess. In this case, the share of the Ti_3AlC_2 phase reaches 91.2%, the TiC phase completely disappears, and the Al_2O_3 impurity phase remains 8.8%. Subsequently, when Al is leached from Ti_3AlC_2 , a stable aqueous suspension of single and poly flakes of $Ti_3C_2T_x$ is formed; the settled unreacted components and the unlaminated part precipitate and are separated when washing the final phase, so the Al_2O_3 impurity does not affect the quality of the product.

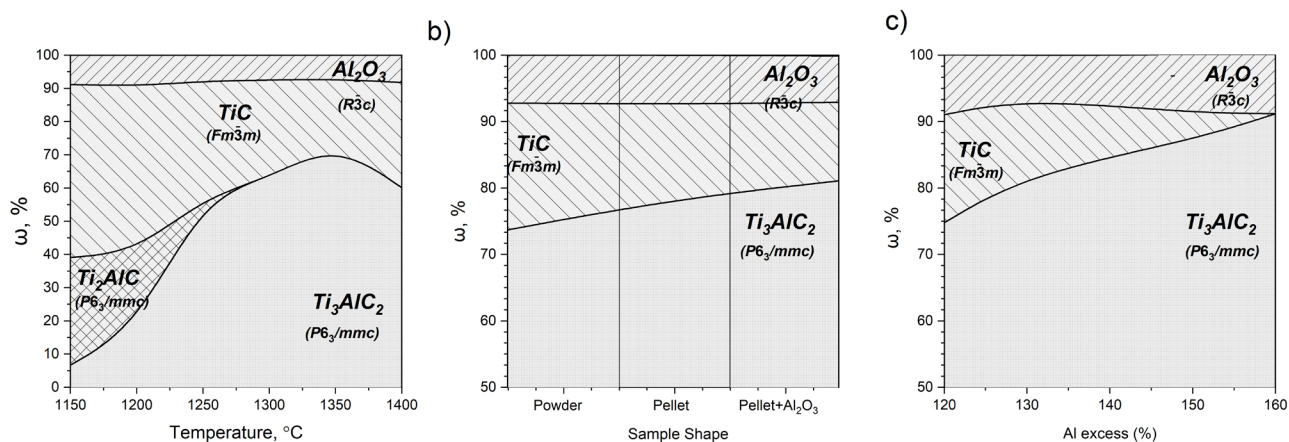


Figure 1 – Phase diagrams showing the changes in the composition of samples obtained: a) as a result of the synthesis of the initial precursors Ti:2TiC:1.2Al at different temperatures: b) with different forms of precursor mixture loading at 1350°C; c) with varying aluminum excess at 1350°C

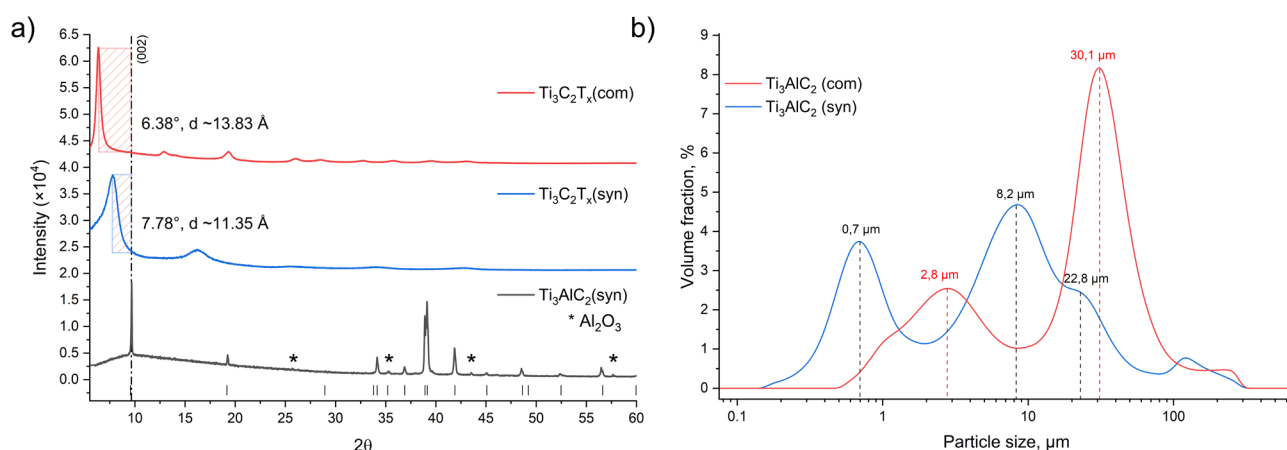


Figure 2 – a) X-ray diffraction pattern of the MAX phase Ti_3AlC_2 powder and the MXene $\text{Ti}_3\text{C}_2\text{T}_x$ disk obtained from it
b) particle size distribution of the commercial and synthesized MAX phases

The diffraction pattern of the resulting $\text{Ti}_3\text{AlC}_2(\text{syn})$ phase was indexed in the space group $P6_3/mmc$ with unit cell parameters: $a=3.0756(4)\text{ \AA}$, $c=18.5757(3)\text{ \AA}$, $Vol.=152.176(8)\text{ \AA}^3$, which is in a good agreement with Chen *et al.* [24] (ICSD 182475).

To determine the possibility of forming MXene $\text{Ti}_3\text{C}_2\text{T}_x(\text{syn})$ from the resulting MAX phase $\text{Ti}_3\text{AlC}_2(\text{syn})$, aluminum was etched to delaminate and form an aqueous suspension. The concentration of the resulting suspension with a loading of the 18 mg/ml MAX phase reached 14 mg/ml, corresponding to a yield of 77.77%. Similarly, an MXene $\text{Ti}_3\text{C}_2\text{T}_x(\text{com})$ suspension was obtained from a commercial MAX phase (Carbon-Ukraine). The obtained concentration of the suspension with the same loading of the 18 mg/ml MAX phase reached only 10 mg/ml, corresponding to a yield of 55.55%.

Films were formed from the resulting suspensions using vacuum filtration for subsequent analysis. X-ray diffraction analysis was then performed to confirm the phase composition of the films. Figure 2a shows the X-ray diffraction patterns of the synthesized $\text{Ti}_3\text{AlC}_2(\text{syn})$ phase powder, the $\text{Ti}_3\text{C}_2\text{T}_x(\text{syn})$ film derived from it, and the $\text{Ti}_3\text{C}_2\text{T}_x(\text{com})$ film obtained from the commercial MAX phase. After aluminum leaching and delamination, the original MAX phase completely disappears, which confirms the purity of the resulting MXene phase. The main peak of the X-ray diffraction pattern of $\text{Ti}_3\text{C}_2\text{T}_x(\text{syn})$ is located at 7.78° (corresponds to $\sim 11.35\text{ \AA}$ between TiC layers, peak (002), according to the structural model of Naguib *et al.* [2]) and is shifted towards larger angles compared to the similar peak of the MXene $\text{Ti}_3\text{C}_2\text{T}_x(\text{com})$ film at position 6.38° (corresponds to $\sim 13.83\text{ \AA}$ between the TiC layers).

Since Al leaching is a heterogeneous process, the morphology of the MAX particles may play a crucial role. To test the assumption, we determined and compared the particle sizes of the MAX phases $\text{Ti}_3\text{AlC}_2(\text{syn})$ and $\text{Ti}_3\text{AlC}_2(\text{com})$ using the laser dispersion method (Figure 2b). The weight population analysis shows that the commercial MAX phase consists of

micro-sized particles with median sizes of 2.8 and $30.1\text{ }\mu\text{m}$, while the MAX phase synthesized in this work has sizes of 0.7, 8.2, and $22.8\text{ }\mu\text{m}$. With smaller sizes of the initial MAX phase, the Al leaching and delamination process is likely to proceed more efficiently, leading to the denser packing of layers in the MXene structure. Apparently, such a difference is enough to result in smaller interplanar spacing for $\text{Ti}_3\text{AlC}_2(\text{syn})$.

The morphology of MXene $\text{Ti}_3\text{C}_2\text{T}_x(\text{syn})$ and $\text{Ti}_3\text{C}_2\text{T}_x(\text{com})$ films was additionally studied using scanning electron microscopy. Figure 3 shows microphotographs of cross-sections of the resulting films. Individual layers of $\text{Ti}_3\text{C}_2\text{T}_x$ are visible and uniformly deposited on top of each other while filtering the $\text{Ti}_3\text{C}_2\text{T}_x$ -containing suspension.

Electrochemical tests were conducted on the synthesized $\text{Ti}_3\text{C}_2\text{T}_x(\text{syn})$ film to compare its electrochemical behavior with the commercial $\text{Ti}_3\text{C}_2\text{T}_x(\text{com})$. Since MXene stores charge primarily through the electrical double-layer mechanism with some contribution from surface reactions (oxidation/reduction of O/OH groups), cyclic voltammetry was performed at a high sweep rate of 5 mV/s across different potential ranges (Figure 4). In the narrow potential range from -1 to 0 V, the $\text{Ti}_3\text{C}_2\text{T}_x(\text{syn})$ film exhibited a capacity of 25.77 mAh/g, compared to 22.55 mAh/g for the $\text{Ti}_3\text{C}_2\text{T}_x(\text{com})$ film. When the potential window was expanded from -1 to 0.4 V, the capacities increased to 34 mAh/g and 33 mAh/g, respectively. The obtained cyclic voltammetry (CV) curves are consistent in shape and capacity with previously published data [12,25].

A pronounced redox reaction is observed in a wider potential window, increasing the material's capacity by 20-25%. Wang *et al.* explain this reaction by the incorporation of Li^+ without desolvation into the $\text{Ti}_3\text{C}_2\text{T}_x$ layers, which is observed only when using superconcentrated water-in-salt (WIS) electrolytes [12]. During intercalation/deintercalation of a solvated lithium ion, reversible changes occur in the interlayer space $\text{Ti}_3\text{C}_2\text{T}_x$, expressed as a pseudo-Faraday reaction with

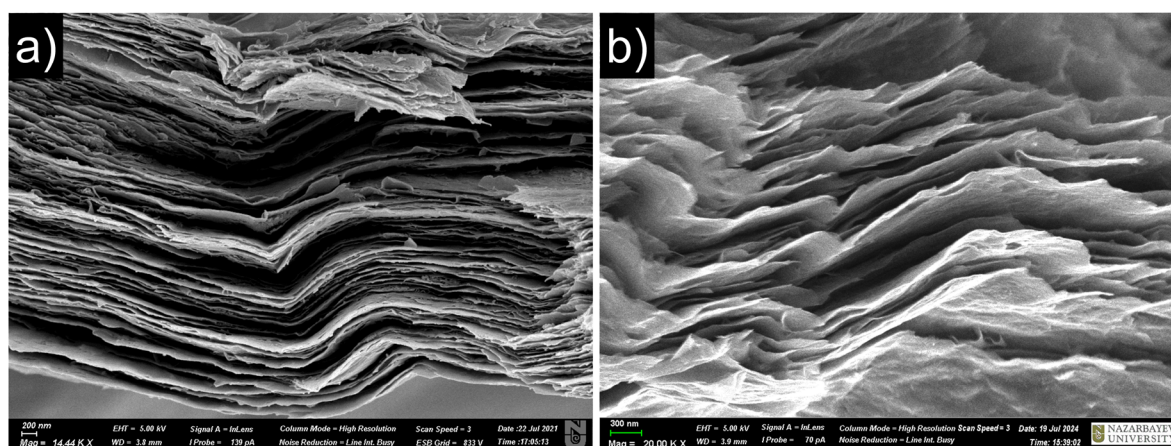


Figure 3 – SEM images of obtained MXene phases: a) $\text{Ti}_3\text{C}_2\text{T}_x(\text{com})$; b) $\text{Ti}_3\text{C}_2\text{T}_x(\text{syn})$

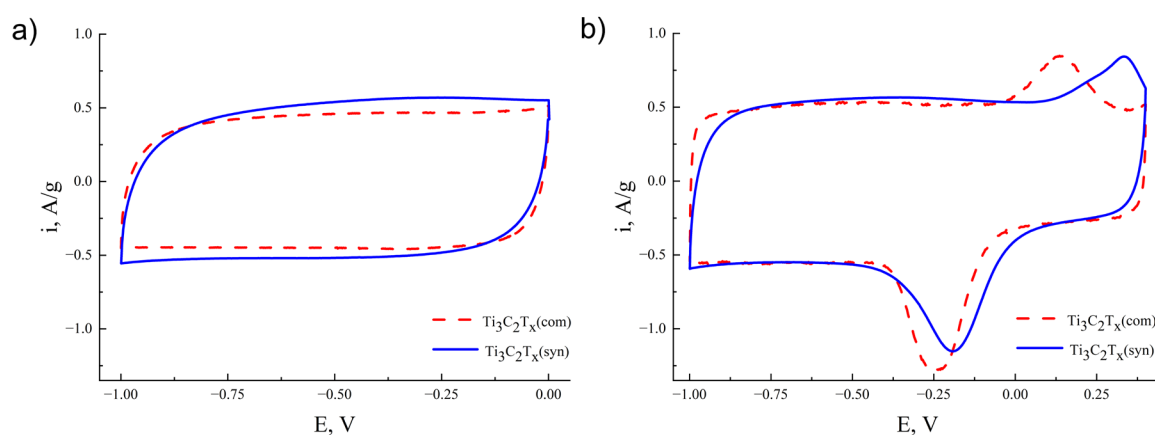


Figure 4 – CV curves of 2 cycles of synthesized and commercial MXene $\text{Ti}_3\text{C}_2\text{T}_x$ at a scan rate of 5 mV/s: a) 1 to 0 V range; b) -1 to 0.4 V range

peaks and a wide hysteresis in potential between them. For $\text{Ti}_3\text{C}_2\text{T}_x(\text{syn})$, cathode and anodic peaks appear in the potential region at -0.16 and 0.25 V, and $\text{Ti}_3\text{C}_2\text{T}_x(\text{com})$ at -0.24 and 0.14 V. The observed shift of the redox process to an area of greater positive potentials for $\text{Ti}_3\text{C}_2\text{T}_x(\text{syn})$ is probably due to the smaller interplanar distance, which complicates the intercalation of the solvated lithium cation.

Thus, the study confirmed that the MXene $\text{Ti}_3\text{C}_2\text{T}_x$ material obtained from the MAX phase we synthesized exhibits electrochemical behavior similar to the commercially available material.

The cost of the MAX phase precursor was analyzed to compare the economic component of the synthesis of MXene from local precursors. All stages, including the cost of precursors, energy and gas costs, and labor costs, were included in the calculation. Zaed *et al.* indicate that 1 g of MAX phase Ti_3AlC_2 may cost \$4.20 [13]. The cost of Ti_3AlC_2 at the Carbon-Ukraine production, from which we obtained the MXene material for comparing electrochemical properties, is \$4.35. In

this study, we calculate the cost of 1 g of the Ti_3AlC_2 phase obtained from local Kazakhstan raw materials. The total cost of precursors for synthesizing 1 g of MAX phase was \$0.16 (Table 1).

Table 1 – Costs of precursors to obtain 1 g of MAX phase

Precursor	Molar ratio	Mass, g	Price per 1 kg, \$	Cost, \$
Ti (powder)	1	0,2461	164,6	0,04
TiC (powder)	2	0,6154	180,7	0,11
Al (powder)	1,6	0,2215	35,6	0,01
Total				0,16

Total energy costs include using a planetary mill, drying oven, ovens, and analytical equipment. During the synthesis of the MAX phase, gas costs are also taken into account. The basis for calculating labor costs was the average salary of a researcher

in Kazakhstan, which is \$575.3 per month. The calculation of costs associated with human efforts is carried out according to the following equation:

$$HEE = \frac{HR/WD}{HD} \cdot t \cdot m$$

HHE is the human effort expense, *HR* is the research assistant hourly rate, *WD* is the working days per month, *HD* is the hours per day, *t* is the working time, and *m* is the mass of the MAX phase product. Additional costs include overhead costs for using the laboratory. The final cost of synthesizing 1 g of MAX phase using Kazakhstan precursors was \$0.22 (Table 2). This is significantly lower than the cost of similar commercially available materials, 19.44 and 20.14 times, respectively [13,20].

The cost analysis revealed that precursor expenses account for 71.2% of the total production cost. Therefore, reducing precursor costs can significantly decrease overall production costs, underscoring the cost-effectiveness of utilizing local resources. As a result, producing the MAX phase Ti₃AlC₂ using Kazakhstan precursors is more economical and competitive in the international market.

Table 2 – The total cost of synthesis of 1 g Ti₃AlC₂ from Kazakhstan precursors

Expenditure	Cost, \$	Cost share
Precursors	0,16	71,2%
Energy costs	0,04	17,8%
Gas costs	0,01	4,4%
Supporting materials	0,01	4,4%
Human effort expense	0,005	2,2%
Total	0,225	100%

4. Conclusion

This study assessed the possibility of synthesizing the MAX-phase Ti₃AlC₂ using local raw materials from Kazakhstan Electrolysis Plant JSC and Ust-Kamenogorsk Titanium-Magnesium Plant JSC. The results showed that a temperature of 1350°C is optimal for the synthesis of the MAX phase, providing a maximum yield of the target phase of 73.7%. Pressing precursors into tablets and coating them with aluminum oxide helps to increase the yield of Ti₃AlC₂ to 81.1% and reduce the content of impurity compounds. Additionally, increasing the aluminum content in the initial precursor mixture by 60% enabled a Ti₃AlC₂ content of 91.2%. MXene Ti₃C₂T_x films were obtained from the synthesized MAX phase, which demonstrated electrochemical behavior comparable to commercially available analogs, confirming the quality of the synthesized material.

An economic assessment showed that the cost of synthesizing 1 g of Ti₃AlC₂ MAX phase using local precursors is \$0.22, significantly lower than similar materials, reaching \$4.20 and \$4.35, respectively. This confirms the economic efficiency and competitiveness of the production of the MAX-phase Ti₃AlC₂ from local Kazakhstan resources in the international arena. Due to its unique properties and cost-effective production, this material shows significant potential for developing high-performance batteries, supercapacitors, and other energy devices, such as flexible electronics and renewable energy systems.

Acknowledgment

The authors thank the Ministry of Science and Higher Education of the Republic of Kazakhstan (project AP14871554) for financial support and Nazarbayev University Core Facilities for instrumental support.

CRedit authorship contribution statement

A.A. Starodubtseva – Investigation, Methodology, Writing - Original Draft; T.V. Kan – Investigation, Data curation; D.M. Eskozha – Investigation; M.Ye. Yegamkulov – Investigation; F.I. Malchik – Investigation, Data curation; I.A. Trussov – Conceptualization, Methodology, Writing - Review & Editing.

Declaration of competing interests

The authors declare no conflict of interest.

References (GOST)

- Jayakumar S., Santhosh P.C., Ramakrishna S., Radhamani A.V. 2D (Ti₃C₂T_x) MXene: A comprehensive review of advancements in synthesis protocols, applications in supercapacitors, sustainability targets and future prospects // *Journal of Energy Storage*. – 2024. – Vol. 97. – P. 112741.
- Naguib M., Kurtoglu M., Presser V., Lu J., Niu J., et al. Two-Dimensional Nanocrystals Produced by Exfoliation of Ti₃AlC₂ // *Advanced Materials*. – 2011. – Vol. 23, Is. 37. – P. 4248-4253.
- Zhang X., Zhang Z., Zhou Z. MXene-based materials for electrochemical energy storage // *Journal of Energy Chemistry*. – 2018. – Vol. 27, Is. 1. – P. 73–85.
- Zhu J., Ha E., Zhao G., Zhou Y., Huang D., et al. Recent advance in MXenes: A promising 2D material for catalysis, sensor and chemical adsorption // *Coordination Chemistry Reviews*. – 2017. – Vol. 352. – P. 306–327.
- Wang R., Young Jang W., Zhang W., Venkata Reddy C., et al. Emerging two-dimensional (2D) MXene-based nanostructured materials: Synthesis strategies, properties, and applications as efficient pseudo-supercapacitors // *Chemical Engineering Journal*. – 2023. – Vol. 472. – P. 144913.

- 6 Naguib M., Barsoum M.W., Gogotsi Y. Ten Years of Progress in the Synthesis and Development of MXenes // *Advanced Materials*. – 2021. – Vol. 33, Is. 39. – .
- 7 Al-Hamadani Y.A.J., Jun B.-M., Yoon M., Taheri-Qazvini N., Snyder S.A., Jang M., Heo J., Yoon Y. Applications of MXene-based membranes in water purification: A review // *Chemosphere*. – 2020. – Vol. 254. – P. 126821.
- 8 Gao L., Li C., Huang W., Mei S., Lin H., et al. MXene/Polymer Membranes: Synthesis, Properties, and Emerging Applications // *Chemistry of Materials*. – 2020. – Vol. 32, Is. 5. – P. 1703–1747.
- 9 Ghidui M., Lukatskaya M.R., Zhao M.-Q., Gogotsi Y., Barsoum M.W. Conductive two-dimensional titanium carbide ‘clay’ with high volumetric capacitance // *Nature*. – 2014. – Vol. 516, Is. 7529. – P. 78–81.
- 10 Li L., Zhou A., Xu L., Li Z., Wang L. Synthesis of high pure Ti₃AlC₂ and Ti₂AlC powders from TiH₂ powders as Ti source by tube furnace 2013. – Vol. 28, Is. 5. – P. 882–887.
- 11 Gauthier-Brunet V., Cabioch T., Chartier P., Jaouen M., Dubois S. Reaction synthesis of layered ternary Ti₂AlC ceramic // *Journal of the European Ceramic Society*. – 2009. – Vol. 29, Is. 1. – P. 187–194.
- 12 Wang X., Mathis T.S., Sun Y., Tsai W.-Y., Shpigel N., et al. Titanium Carbide MXene Shows an Electrochemical Anomaly in Water-in-Salt Electrolytes // *ACS Nano*. – 2021. – Vol. 15, Is. 9. – P. 15274–15284.
- 13 Zaed M.A., Tan K.H., Abdullah N., Saidur R., Pandey A.K., Saleque A.M. Cost analysis of MXene for low-cost production, and pinpointing of its economic footprint // *Open Ceramics*. – Elsevier Ltd, 2024. – Vol. 17, Is. December 2023. – P. 100526.
- 14 Naskar A.K., Bi Z., Li Y., Akato S.K., Saha D., Chi M., Bridges C.A., Paranthaman M.P. Tailored recovery of carbons from waste tires for enhanced performance as anodes in lithium-ion batteries // *RSC Advances*. – 2014. – Vol. 4, Is. 72. – P. 38213.
- 15 Mandegari M., Nasouri K., Ghasemi-Mobarakeh L. Synthesis of low-cost Ti₃AlC₂-Ti₂AlC dual MAX phase with high-electrical conductivity using economical raw materials and novel compositions // *Materials Today Communications*. – 2023. – Vol. 36. – P. 106868.
- 16 Kewate O.J., Punniyakoti S. Ti₃AlC₂ MAX phase and Ti₃C₂T_x MXene-based composites towards supercapacitor applications: A comprehensive review of synthesis, recent progress, and challenges // *Journal of Energy Storage*. – 2023. – Vol. 72. – P. 108501.
- 17 Jolly S., Paranthaman M.P., Naguib M. Synthesis of Ti₃C₂T_x MXene from low-cost and environmentally friendly precursors // *Materials Today Advances*. – 2021. – Vol. 10. – P. 100139.
- 18 Capuzzi S., Timelli G. Preparation and Melting of Scrap in Aluminum Recycling: A Review // *Metals*. – 2018. – Vol. 8, Is. 4. – P. 249.
- 19 Li C., Kota S., Hu C., Barsoum M.W. On the synthesis of low-cost, titanium-based mxenes // *Journal of Ceramic Science and Technology*. – 2016. – Vol. 7, Is. 3. – P. 301–306.
- 20 Shuck C.E., Sarycheva A., Anayee M., Levitt A., Zhu Y., et al. Scalable Synthesis of Ti₃C₂T_x MXene // *Advanced Engineering Materials*. – 2020. – Vol. 22, Is. 3. – P. 1-8.
- 21 Ashok A., Saseendran S.B., Asha A.S. Synthesis of Ti₃C₂T_x MXene from the Ti₃AlC₂ MAX phase with enhanced optical and morphological properties by using ammonia solution with the in-situ HF forming method // *Physica Scripta*. – 2022. – Vol. 97, Is. 2. – P. 025807.
- 22 Feng A., Yu Y., Wang Y., Jiang F., Yu Y., Mi L., Song L. Two-dimensional MXene Ti₃C₂ produced by exfoliation of Ti₃AlC₂ // *Materials & Design*. – 2017. – Vol. 114. – P. 161–166.
- 23 Toby B.H., Von Dreele R.B. GSAS-II: the genesis of a modern open-source all purpose crystallography software package // *Journal of Applied Crystallography*. – 2013. – Vol. 46, Is. 2. – P. 544-549.
- 24 Chen Y., Chu M., Wang L., Bao X., Lin Y., Shen J. First-principles study on the structural, phonon, and thermodynamic properties of the ternary carbides in Ti–Al–C system // *physica status solidi (a)*. – 2011. – Vol. 208, Is. 8. – P. 1879-1884.
- 25 Malchik F., Shpigel N., Levi M.D., Mathis T.S., Mor A., Gogotsi Y., Aurbach D. Superfast high-energy storage hybrid device composed of MXene and Chevrel-phase electrodes operated in saturated LiCl electrolyte solution // *Journal of Materials Chemistry A*. – 2019. – Vol. 7, Is. 34. – P. 19761-19773.

References

- 1 Jayakumar S, Santhosh PC, Ramakrishna S, Radhamani AV (2024) *J Energy Storage* 97:112741. <http://doi.org/10.1016/j.est.2024.112741>
- 2 Naguib M, Kurtoglu M, Presser V, Lu J, Niu J, Heon M, et al. (2011) *Adv Mater* 23:4248–4253. <http://doi.org/10.1002/adma.201102306>
- 3 Zhang X, Zhang Z, Zhou Z (2018) *J Energy Chem* 27:73–85. <http://doi.org/10.1016/j.jechem.2017.08.004>
- 4 Zhu J, Ha E, Zhao G, Zhou Y, Huang D, Yue G, et al. (2017) *Coord Chem Rev* 352:306–327. <http://doi.org/10.1016/j.ccr.2017.09.012>
- 5 Wang R, Young Jang W, Zhang W, Venkata Reddy C, Kakarla RR, Li C, et al. (2023) *Chem Eng J* 472:144913. <http://doi.org/10.1016/j.cej.2023.144913>
- 6 Naguib M, Barsoum MW, Gogotsi Y (2021) *Adv Mater*. <http://doi.org/10.1002/adma.202103393>
- 7 Al-Hamadani YAJ, Jun B-M, Yoon M, Taheri-Qazvini N, Snyder SA, Jang M, et al. (2020) *Chemosphere* 254:126821. <http://doi.org/10.1016/j.chemosphere.2020.126821>
- 8 Gao L, Li C, Huang W, Mei S, Lin H, Ou Q, et al. (2020) *Chem Mater* 32:1703–1747. <http://doi.org/10.1021/acs.chemmater.9b04408>
- 9 Ghidui M, Lukatskaya MR, Zhao M-Q, Gogotsi Y, Barsoum MW (2014) *Nature* 516:78–81. <http://doi.org/10.1038/nature13970>
- 10 Li L, Zhou A, Xu L, Li Z, Wang L (2013) 28:882–887. <http://doi.org/10.1007/s11595-013-0786-2>
- 11 Gauthier-Brunet V, Cabioch T, Chartier P, Jaouen M, Dubois S (2009) *J Eur Ceram Soc* 29:187–194. <http://doi.org/10.1016/j.jeurceramsoc.2008.05.039>

- 12 Wang X, Mathis TS, Sun Y, Tsai W-YY, Shpigel N, Shao H, et al. (2021) ACS Nano 15:15274–15284. <http://doi.org/10.1021/acsnano.1c06027>
- 13 Zaed MA, Tan KH, Abdullah N, Saidur R, Pandey AK, Saleque AM (2024) Open Ceram 17:100526. <http://doi.org/10.1016/j.oceram.2023.100526>
- 14 Naskar AK, Bi Z, Li Y, Akato SK, Saha D, Chi M, et al. (2014) RSC Adv 4:38213. <http://doi.org/10.1039/C4RA03888F>
- 15 Mandegari M, Nasouri K, Ghasemi-Mobarakeh L (2023) Mater Today Commun 36:106868. <http://doi.org/10.1016/j.mtcomm.2023.106868>
- 16 Kewate OJ, Punniyakoti S (2023) J Energy Storage 72:108501. <http://doi.org/10.1016/j.est.2023.108501>
- 17 Jolly S, Paranthaman MP, Naguib M (2021) Mater Today Adv 10:100139. <http://doi.org/10.1016/j.mtadv.2021.100139>
- 18 Capuzzi S, Timelli G (2018) Metals (Basel) 8:249. <http://doi.org/10.3390/met8040249>
- 19 Li C, Kota S, Hu C, Barsoum MW (2016) J Ceram Sci Technol 7:301–306. <http://doi.org/10.4416/JCST2016-00042>
- 20 Shuck CE, Sarycheva A, Anayee M, Levitt A, Zhu Y, Uzun S, et al. (2020) Adv Eng Mater 22:1–8. <http://doi.org/10.1002/adem.201901241>
- 21 Ashok A, Saseendran SB, Asha AS (2022) Phys Scr 97:025807. <http://doi.org/10.1088/1402-4896/ac4c53>
- 22 Feng A, Yu Y, Wang Y, Jiang F, Yu Y, Mi L, et al. (2017) Mater Des 114:161–166. <http://doi.org/10.1016/j.matdes.2016.10.053>
- 23 Toby BH, Von Dreele RB (2013) J Appl Crystallogr 46:544–549. <http://doi.org/10.1107/S0021889813003531>
- 24 Chen Y, Chu M, Wang L, Bao X, Lin Y, Shen J (2011) Phys status solidi 208:1879–1884. <http://doi.org/10.1002/pssa.201127020>
- 25 Malchik F, Shpigel N, Levi MD, Mathis TS, Mor A, Gogotsi Y, et al. (2019) J Mater Chem A 7:19761–19773. <http://doi.org/10.1039/c9ta08066j>