

Article

Formation of Electrode Materials in the Process of Carbothermic Flux Smelting of Ilmenite Concentrate and Hydrothermal Refining of Titanium Slag

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Abstract: The present study demonstrates, for the first time, the fundamental possibility of producing electrode materials for sodium-ion batteries through low-temperature carbothermic smelting of ilmenite concentrate fluxed with calcined soda and diatomite, followed by aqueous refining of titanium slag. The primary phase composition of the slag includes $\text{Na}_2\text{Ti}_3\text{O}_7$ (48.2%), $\text{Na}_{0.23}\text{TiO}_2$ (22.0%), $\text{Na}_2\text{TiSiO}_5$ (11%), and $\text{Na}_{0.67}\text{Al}_{0.1}\text{Mn}_{0.9}\text{O}_2$ (8.5%), which, upon hydrolysis, transform into a monophasic titanium dioxide with intercalated sodium— $\text{Na}_{0.23}\text{TiO}_2$. Thermodynamic analysis of the heat effects of chemical reactions among raw materials and resulting products substantiates the role of silicon and sodium oxides, carbon, oxygen, and water in the formation of various electrode materials during carbothermic flux conversion and aqueous refining. Insights into the mechanisms of thermochemical formation and hydrothermal phase transformations offer a scientific basis for the development of intercalation systems from abundant and low-cost natural raw materials, bypassing the need for expensive precursor synthesis.



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Keywords: ilmenite concentrate; carbothermic flux smelting; titanium slag; refining; intercalation; electrode materials

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are the dominant electrochemical power sources in modern portable electronics and electric vehicles. However, the application of LIBs for many large-scale applications (stationary energy storage, power plant buffer systems, electric passenger transport, etc.) is constrained by the high cost of lithium and the limited and uneven geographical distribution of its raw materials. The development of alternative energy devices, primarily sodium-ion batteries (SIBs) as the closest analog to LIBs, is of paramount importance. The main advantage of SIBs over LIBs is the low cost and wide availability of natural raw materials. SIBs have the longest lifespan among battery energy storage systems. They are effective at high and low temperatures, do not ignite when using water as a solvent, and do not contain harmful minerals such as lithium, cobalt, or nickel. Information on the current state, research directions, achievements, and commercialization of electrode materials and electrolytes for SIBs is most informatively covered in [1–3]. It should be noted that stationary room-temperature SIBs have recently become widespread in large-scale energy systems and smart systems. SIBs use the same sodium storage mechanism as lithium in LIBs, so selecting suitable electrodes with low

cost, satisfactory performance, and high reliability is a crucial factor in the development of SIBs.

Titanium anodes are an ideal material combining excellent corrosion resistance, durability, lightness, non-toxicity, and good electrical conductivity. Numerous studies have been published on the methods of obtaining, morphology, and electrochemical properties of the anode material sodium titanate $\text{Na}_2\text{Ti}_3\text{O}_7$, intended for SIBs, which can reversibly intercalate two Na^+ ions at an average potential of 0.3 V (vs. Na/Na^+), with its theoretical capacity being approximately 200 mAh/g [4–17]. The main methods of its production are solid-state, as well as hydrothermal and sol–gel synthesis methods. Titanium dioxide TiO_2 [4,5,12], metallic titanium powders [10], titanitic acid [13], tetrabutoxytitanate $(\text{C}_4\text{H}_9\text{O})_4\text{Ti}$ [11], and titanium chloride TiCl_3 [14] are used as precursors.

A sandwich-like $\text{Na}_{0.23}\text{TiO}_2/\text{Ti}_3\text{C}_2$ nanocomposite has been created, demonstrating long-term cycling stability (up to 4000 cycles at high rates with almost 100% capacity retention) and remarkable fast-charging capability when used as anodes in LIBs and SIBs [18]. The composite electrode is manufactured by slow etching of titanium aluminum carbide Ti_3AlC_2 powder at 40 °C for 20 h. The separated layered nanosheets of titanium carbide Ti_3C_2 are repeatedly washed with deionized water to pH 6–7 and dried in a vacuum at 60 °C for 8 h. By dispersion using ultrasound, partial oxidation of Ti_3C_2 , and holding for 100 h in a NaOH solution, continuous stirring of the reaction mixture at room temperature forms curly one-dimensional amorphous $\text{Na}_{0.23}\text{TiO}_2$ nanotubes growing on two-dimensional layered Ti_3C_2 nanosheets. The content of $\text{Na}_{0.23}\text{TiO}_2$ in the $\text{Na}_{0.23}\text{TiO}_2/\text{Ti}_3\text{C}_2$ composite is about 75 wt.%. Amorphous $\text{Na}_{0.23}\text{TiO}_2$ nanobelts, capable of withstanding high deformations, play an important role as they contribute to the main capacity of the batteries as an active material. Ti_3C_2 nanosheets improve the electrical conductivity of the $\text{Na}_{0.23}\text{TiO}_2/\text{Ti}_3\text{C}_2$ composite electrode by ensuring the efficiency of electron transfer from the electrode to the nanobelts. The long-term cyclic ability of the anode made of $\text{Na}_{0.23}\text{TiO}_2$ nanoparticles embedded in a carbon network, created by pyrosynthesis using polyol (a carbon source) for SIBs, is confirmed in [19].

A vast class of materials with promising technological applications is represented by titanosilicates, mainly synthesized by hydrothermal synthesis methods [20–27]. Framework titanosilicates with the structure of natural minerals natasite and sitinakite were obtained by hydrothermal–autoclave synthesis for the sorption of radionuclides Cs^{137} , Sr^{90} , Eu^{152} . Finely dispersed high-purity titanosilicate $\text{TiSiO}_4 \cdot n\text{H}_2\text{O}$ was synthesized by the hydrothermal–microwave method. Carbon coating and double nano-size modification improved the electrochemical characteristics of lithium titanosilicate $\text{Li}_2\text{TiSiO}_5$ for lithium-ion batteries, which has a large reversible capacity of $257 \text{ mAh} \cdot \text{g}^{-1}$, high performance, and excellent cycling stability with 90.0% capacity retention at $5000 \text{ mA} \cdot \text{g}^{-1}$ for 4000 cycles.

The above methods for synthesizing titanates and titanosilicates involve the use of expensive, analytically pure precursors, which predetermines a serious problem for the large-scale production of electrode materials.

Below are the results of our research on obtaining promising electrode materials directly from ilmenite concentrate.

2. Materials and Methods

2.1. Raw Materials

This work involved the processing of a difficult-to-enrich ilmenite concentrate (IC) from the sandy–clayey ore of the Satpayev deposit in Eastern Kazakhstan provided by the Ust-Kamenogorsk Titanium and Magnesium Plant (JSC ‘UK TMK’). Fluxing additives included anthracite with a 3.87% ash content, 3.03% technical-grade calcined soda of the highest quality (granulated, grade OKP 21 3111 0220, and powdered, grade OKP 21 3111

0120), with a sodium carbonate (Na_2CO_3) mass fraction of at least 99.4%, an iron content recalculated to Fe_2O_3 of no more than 0.003%, other impurities within trace amounts in accordance with the quality standard GOST 5100-85 [28] for calcined soda, and diatomite (also known as kieselguhr, a sedimentary natural mineral from the Mugaljar deposit in Western Kazakhstan) containing approximately 80% macroporous amorphous silica (SiO_2). Molasses (a byproduct of the sugar industry) was used as a binder at a rate of 3% by weight of the coal charge with IC and fluxing additives.

2.2. Main Equipment and Technological Conditions

Thoroughly mixed coal charges with a mass ratio of $\text{IC}:\text{Na}_2\text{CO}_3:\text{SiO}_2 = 1:0.5:0.3$, loaded into press forms, were compacted on a Metallkraft WPP 50M (Guangzhou, China) hydraulic press with a compression force increasing from 100 to 50,000 kg (Figure 1a). The carbothermal melting of the briquettes, placed in graphite crucibles with tightly fitting graphite lids, was carried out in a NOBERTHERM (Laupheim, Germany) muffle furnace at a temperature of $1573 \div 1673$ K for 120 min (Figure 1b). Magnetic separation of the cooled and crushed sintered briquettes in ambient air was performed using a laboratory magnetic separator from “Prodecology–Scientific and Production Company” (Kyiv, Ukraine) with manual adjustment of the magnetic field strength from 80 to 900 Tl (Figure 1c).

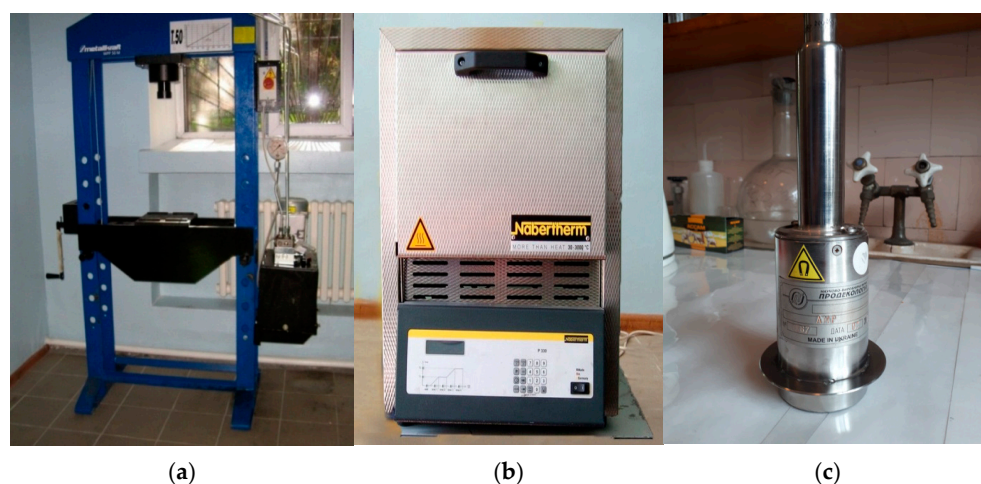


Figure 1. Hydraulic press Metallkraft WPP 50M (a), NOBERTHERM muffle furnace (b), magnetic separator “Prodecology—scientific and production” (c).

The primary titanium slag was refined with water at a solid–liquid ratio of 3:1, at a temperature of $353 \div 363$ K for 4 h with an impeller speed of 500 rpm using a mechanical stirrer ES from the company “Velp–Scientifica” (Usmat, Italy) in thermostated beakers heated through an external jacket with hot water from the circulating thermostat LT–108 from the company “LOIP” (Budapest, Hungary). The alkaline pulp from the water refining of titanium slag was filtered using a vacuum water-jet pump through a Büchner funnel with “blue tape” paper filter.

2.3. Physical and Chemical Studies

The fractional composition of a representative batch of the Satpaev ilmenite concentrate was determined by classification on a vibrating screen with a set of standard sieve fabrics of different sizes. The chemical composition of the concentrate and the obtained products was studied using X-ray fluorescence analysis on a wavelength dispersive spectrometer Venus 200 PANalytical B.V. (Eindhoven, The Netherlands) and X-ray phase analysis (XRD) on a BRUKER D8 ADVANCE (Freiburg, Germany) diffractometer with copper radiation at an accelerating voltage of 36 kV and a current of 25 mA. The alkalinity of the filtrate

from the pulp of the aqueous refining of primary titanium slag was analyzed using pH metric and titrimetric measurements, employing a 1% solution of hydrochloric acid, a 0.1% solution of phenolphthalein as an acid-base indicator, and a 0.1% solution of methyl orange as a pH indicator.

2.4. Thermodynamic Analysis

The numerical values of the thermal effects of individual and total chemical reactions of the carbothermic conversion process of ilmenite concentrate were determined, taking into account the heat capacities ΔC_p° of the reacting substances and the resulting products according to the stoichiometric coefficients of the equation by calculating the enthalpy $\Delta H^\circ T$, entropy $\Delta S^\circ T$, and Gibbs energy $\Delta G^\circ T$ in each temperature interval from 373 to 2273 K using standard reference thermodynamic values at 298 K [29].

3. Results

3.1. Characteristics of Ilmenite Concentrate

The size and mass fraction of the granules of the ilmenite concentrate are presented in Table 1, the content of titanium oxides and the main accompanying elements in Table 2, and the mineral composition is shown in Figure 2.

Table 1. Fractional composition of ilmenite concentrate.

Classes, mm	Mass Fraction, %
−0.5 + 0.315	3.80
−0.315 + 0.2	27.86
−0.2 + 0.074	58.32
−0.074 + 0.044	7.22
−0.044 + 0.0	2.80
Total	100

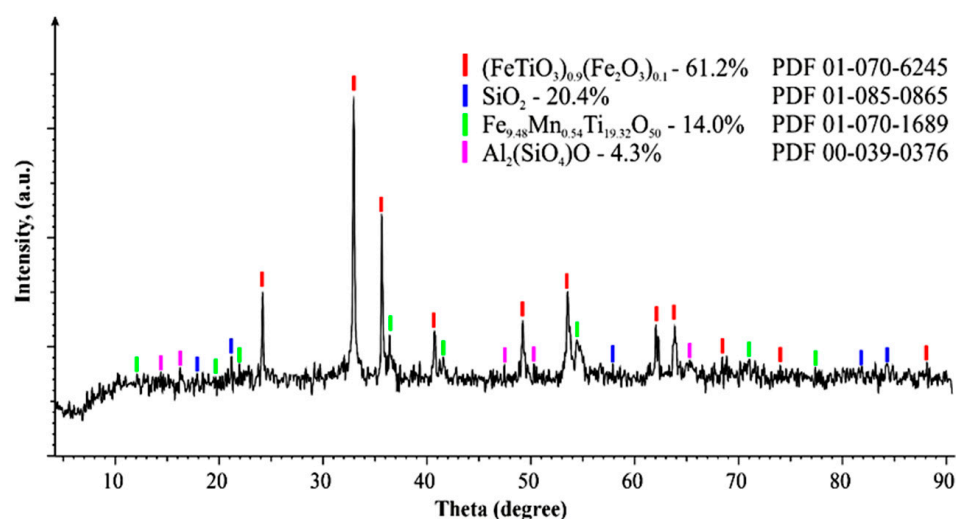


Figure 2. Mineral composition of the crystalline phase of ilmenite concentrate.

Table 2. Chemical composition of ilmenite concentrate.

Mass Fraction, %									
TiO ₂	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	Cr ₂ O ₃	MnO	CaO	MgO	P ₂ O ₅	SO ₃
52.3	39.55	4.83	0.95	1.43	1.74	0.08	0.16	0.014	0.014

According to the RFAS, the mineral basis of the concentrate (over 60%) consists of primary ilmenite FeTiO_3 , tightly fused with the platy surface of hematite Fe_2O_3 grains, commonly referred to as hemo-ilmenite, alongside which a polymorphic variety of leucocoxenite ilmenite is present in the form of pseudorutile of non-stoichiometric composition $\text{Fe}_{9.48}\text{Mn}_{0.54}\text{Ti}_{19.32}\text{O}_{50}$, accounting for 14%.

The presence of the rock-forming fine-dispersed aluminosilicate mineral kyanite Al_2SiO_5 , which cements the titanium minerals, and the non-compliance of the chemical composition with the regulated requirements for impurities exclude the possibility of processing the Satpayev ilmenite concentrate by commercial enrichment methods.

By selecting technologically acceptable conditions, we have established that carbothermic smelting with the addition of diatomite and calcined soda to the ilmenite concentrate feed ensures complete rapid reduction of iron and effective stratification of the titanium slag melt and alloyed the entire mass of iron, with significantly lower electricity costs and process duration (see Figures 3 and 4).

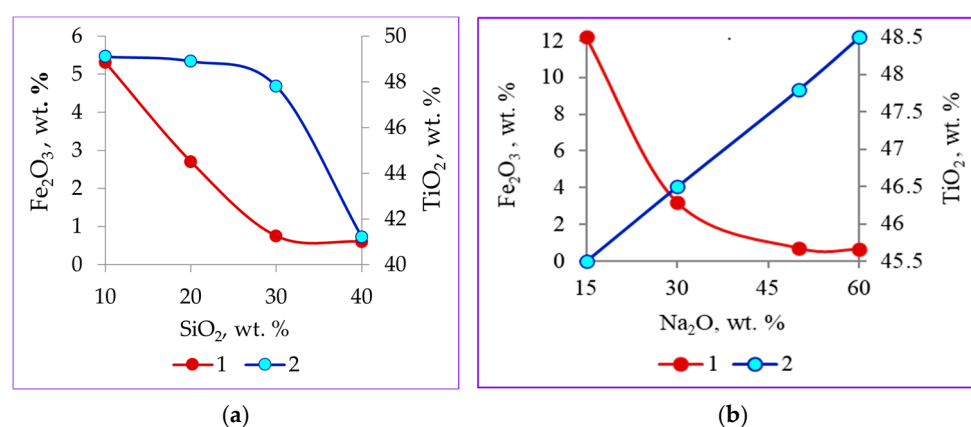


Figure 3. Effect of flux additives SiO_2 (a) and Na_2O (b) on iron reduction and slag enrichment with titanium dioxide.



Figure 4. Titanium slag (a), ingot and reduced iron beads (b).

It should be noted that the degree of enrichment of the slag with titanium dioxide (curve 2), despite the completeness of separation from iron (curve 1), decreases with an increasing mass fraction of diatomite in the coal-ilmenite feed, particularly noticeable when the silicon oxide content exceeds 30%, as clearly observed in Figure 3a. However, the degree of enrichment of the slag, assessed by its TiO_2 content, steadily increases even

with a significantly higher mass fraction of sodium oxide from soda in the feed, as shown in Figure 3b (curve 2).

3.2. Material Composition of Primary and Modified Titanium Slag

It has been found that flux additives not only improve the technical and economic indicators of the carbothermal smelting process of non-conforming raw materials but also ensure the production of primary titanium slag, which is almost 90% a solid-phase mixture of electrode materials, primarily consisting of sodium trititanate $\text{Na}_2\text{Ti}_3\text{O}_7$ (more than 48%), sodium-intercalated titanium dioxide (22%), sodium titanate $\text{Na}_2\text{TiSiO}_5$ (11%), and sodium- and aluminum-intercalated manganese dioxide $\text{Na}_{0.67}\text{Al}_{0.1}\text{Mn}_{0.9}\text{O}_2$ (8.5%) (Figure 5).

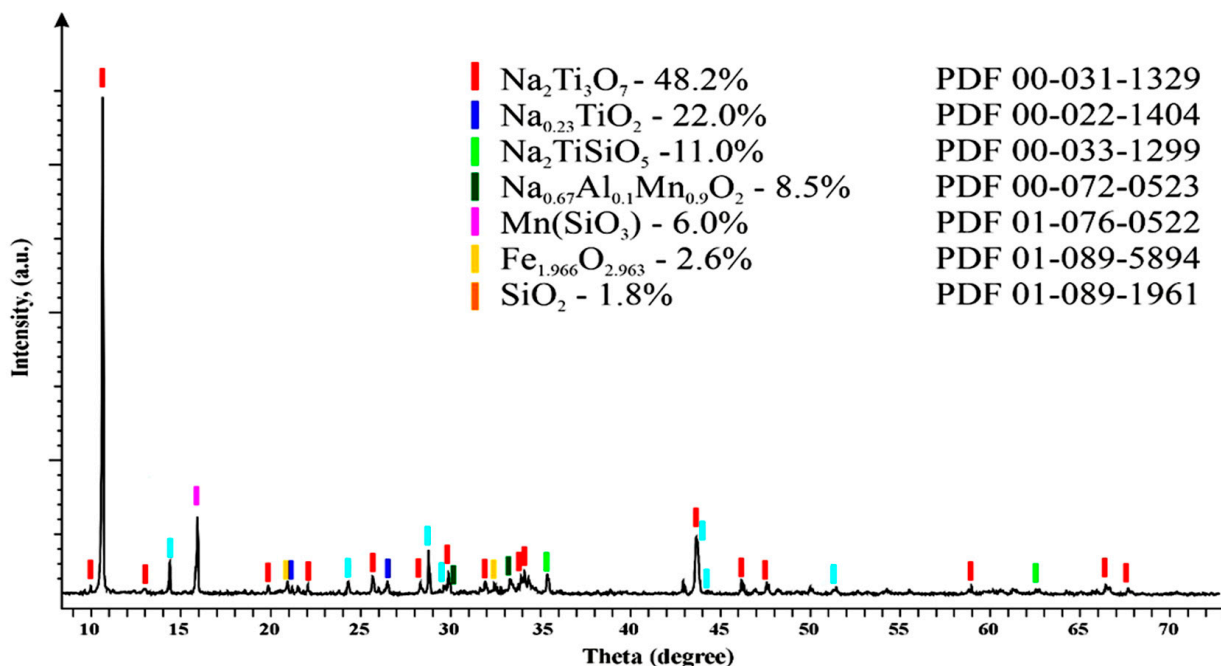


Figure 5. X-ray of primary titanium slag.

The optimization of the technological conditions for refining primary titanium slag with water resulted in a monophasic titanium dioxide with intercalated sodium $\text{Na}_{0.23}\text{TiO}_2$ (Figure 6).

The reproducibility of the laboratory research results has been confirmed by successful tests on the pilot plant of the Experimental and Production Institute of Metallurgy and Ore Beneficiation (PEMP of JSC «IMOB»). Experimental tests of the technological indicators of each key operation were conducted through careful verification of the optimal modes selected by detailed laboratory studies three times. No discrepancies were found in the actually identical results of the analysis. The phase composition and yield of electrode materials in the primary and modified titanium slag are shown in Figures 5 and 6. The extraction of titanium dioxide amounted to no less than 93%.

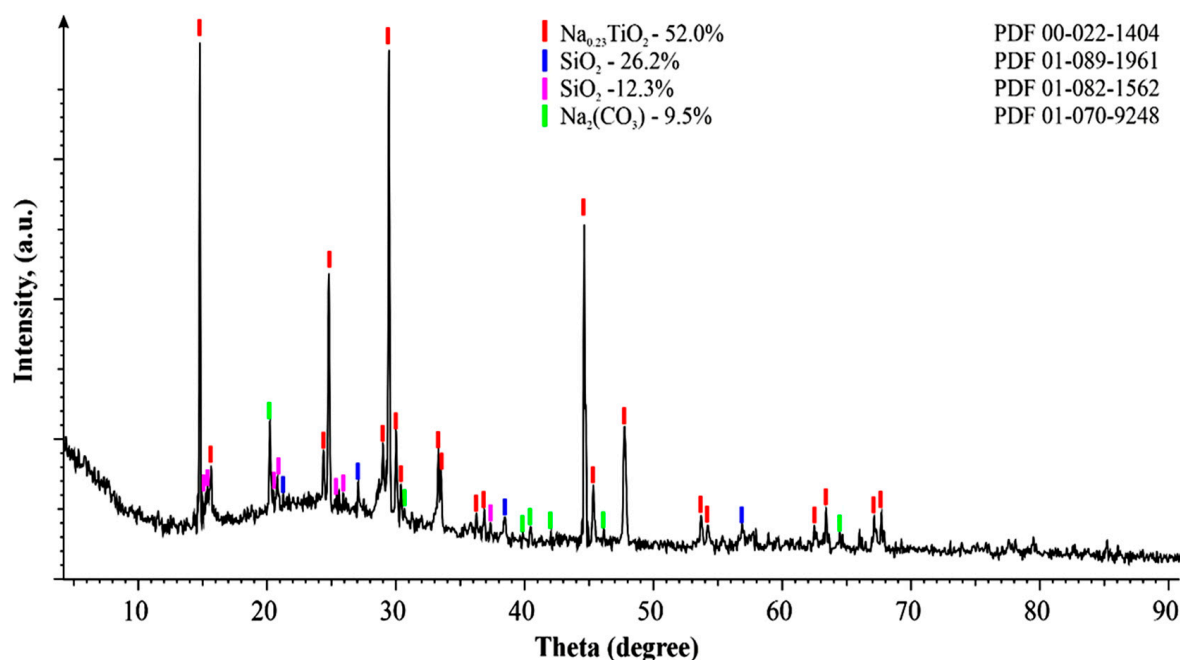


Figure 6. X-ray diffraction pattern of water-modified titanium slag.

4. Mechanism of Formation of Electrode Materials

4.1. Thermodynamics of the Reactions of Calcined Soda Decomposition

To understand the mechanism of electrode material formation, it is essential to first consider the influence of the flux additives calcined soda and diatomite on the carbothermic conversion of ilmenite concentrate.

Soda ash Na_2CO_3 (anhydrous sodium carbonate–natrite), as is known, decomposes into sodium oxide Na_2O and carbon dioxide CO_2 at a temperature of 1000 °C (or 1273 K) [30]. The decomposition of alkali metal carbonates is known to be facilitated by the removal of the generated CO_2 or the elimination of Na_2O from the reaction mixture by adding anhydride, for example, SiO_2 , a very weak but thermally stable silicic acid that forms a silicate salt with the base Na_2O [31].

By calculating the numerical values of the thermal effects of chemical reactions involving the starting substances and the resulting products, it has been established that the key chemical activator for the carbothermic conversion of ilmenite is calcined soda. The catalytic initiator for the decomposition of soda at room temperature is diatomaceous silica. It has been found that the thermal decomposition of crystalline soda (the decahydrate of sodium carbonate, known in modern mineralogy as natron, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), which begins at 573 K, is accelerated by the presence of SiO_2 and shifts to a lower temperature range of 373 K (irreversible reactions (1) and (2) with numerical values of $\Delta H^\circ_T > 0$, $\Delta S^\circ_T > 0$, $\Delta G^\circ_T < 0$ for $T > \Delta H^\circ / \Delta S^\circ$, occurring due to the entropic factor that indicates the tendency of the composite components of the alkali reagent to dissociate, as shown in Figure 7). The catalytic effect of SiO_2 is particularly pronounced on the thermal decomposition of powdered soda (anhydrous sodium carbonate–natrite) (exothermic reaction (3)). The decomposition of natron and natrite is intensified due to the active reactivity of SiO_2 and Na_2O from soda, forming the low-melting metasilicate of sodium, Na_2SiO_3 (acid–base reaction (4) with numerical values of $\Delta H^\circ_T < 0$, $\Delta S^\circ_T < 0$, $\Delta G^\circ_T < 0$ for $T < \Delta H^\circ / \Delta S^\circ$, occurring at any temperature within the studied range due to the enthalpic factor indicating the tendency of SiO_2 and Na_2O to form strong bonds).

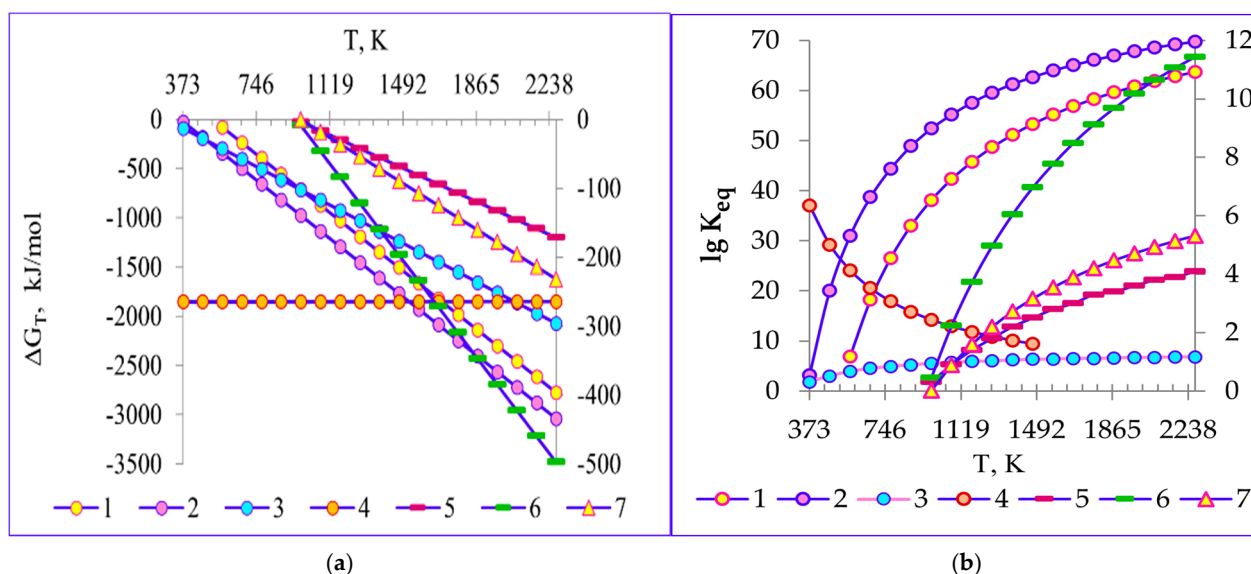
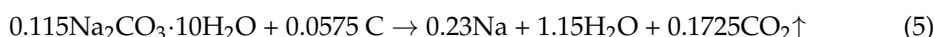
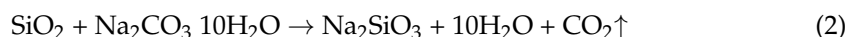
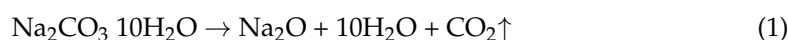


Figure 7. Dependence of the change in ΔG°_T (a) and $\lg K_{eq}$ (b) on the temperature of calcined soda decomposition reactions.

Upon contact with carbon, calcined soda decomposes to produce sodium and carbon dioxide (CO_2)—the Deville process (irreversible reactions (5) and (6)). By reacting with the oxygen in the carbon dioxide released during the decomposition of soda, carbon forms carbon monoxide (CO), which accelerates the reduction of iron oxides by penetrating the cracks and pores of ilmenite concentrate minerals (reaction (7)).



4.2. Thermodynamics of Decomposition Reactions of Ilmenite Concentrate

The carbothermic conversion of ilmenite concentrate (IC), triggered by the intense decomposition of Na_2CO_3 in the presence of SiO_2 , begins at 673 K (overall reaction (8) with numerical values $\Delta H^{\circ}_T < 0$, $\Delta S^{\circ}_T < 0$, $\Delta G^{\circ}_T < 0$ for $T < \Delta H^{\circ} / \Delta S^{\circ}$), occurring throughout the studied temperature range due to the enthalpic factor associated with the predominant thermal effect of forming electrode materials $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_{0.23}\text{TiO}_2$, $\text{Na}_2\text{TiSiO}_5$, and $\text{Na}_{0.67}\text{Al}_{0.1}\text{Mn}_{0.9}\text{O}_2$ (Figure 8), identified through X-ray phase analysis of the crystalline phase of primary titanium slag (Figure 5).

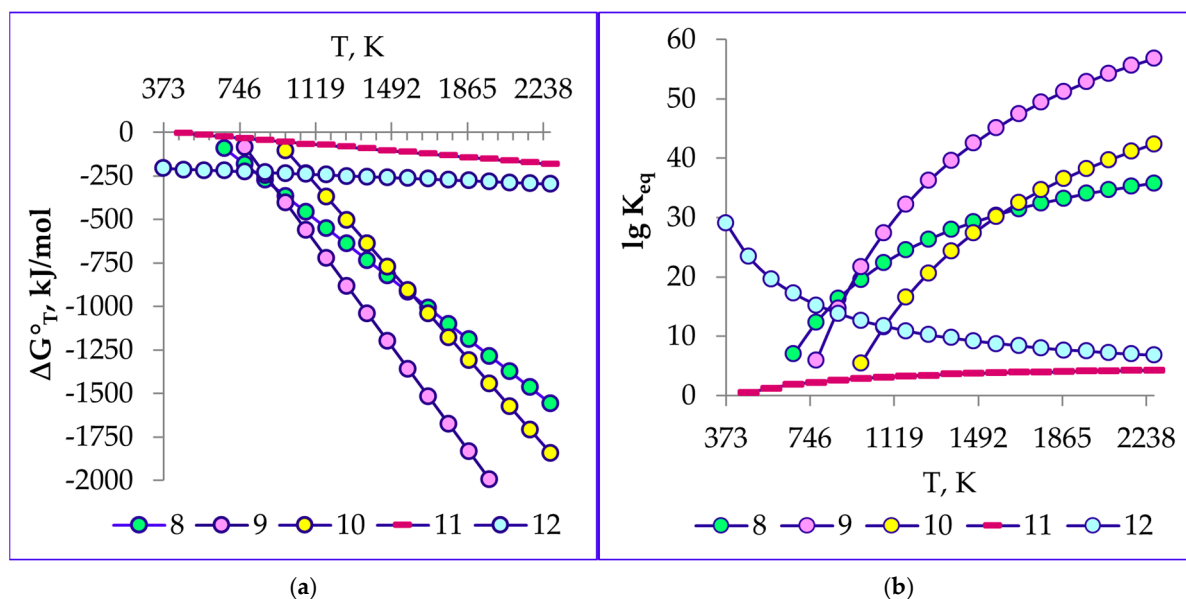
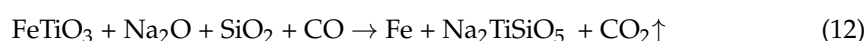
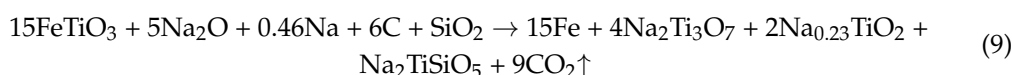
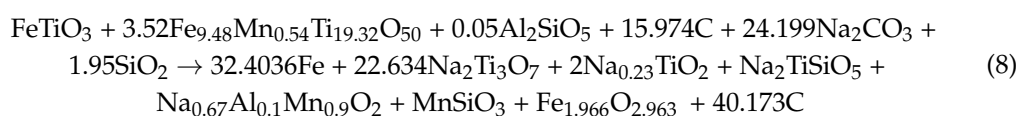


Figure 8. Dependence of the change in ΔG°_T (a) and $\lg K_{eq}$ (b) on the temperature of the carbochemical conversion reactions of ilmenite concentrate.

The raw material source for the first three electrode materials is ilmenite (FeTiO_3)—a widely distributed natural titaniferous iron ore ($\text{FeO} \cdot \text{TiO}_2$)—which forms the mineral basis of the concentrate, along with pseudorutile—a variety of leucoxenized ilmenite with a non-stoichiometric composition $\text{Fe}_{9.48}\text{Mn}_{0.54}\text{Ti}_{19.32}\text{O}_{50}$.

The carbothermic decomposition of ilmenite is accompanied by the formation predominantly of $\text{Na}_2\text{Ti}_3\text{O}_7$ (irreversible reactions (9) and (10) with numerical values $\Delta H^\circ_T > 0$, $\Delta S^\circ_T > 0$, $\Delta G^\circ_T < 0$ for $T > \Delta H^\circ / \Delta S^\circ$, occurring due to the entropic factor). $\text{Na}_{0.23}\text{TiO}_2$ is formed as a result of sodium incorporation into the interlayer space of titanium dioxide released during ilmenite decomposition (reaction (11) with numerical values $\Delta H^\circ_T < 0$, $\Delta S^\circ_T > 0$, $\Delta G^\circ_T < 0$, spontaneously occurring in the temperature range of 473–873 K without decomposing ilmenite, and above 873 K due to entropic destruction of the natural mineral). $\text{Na}_2\text{TiSiO}_5$ is formed under the combined action of Na_2O and SiO_2 (spontaneously occurring reaction (12) with numerical values $\Delta H^\circ_T < 0$, $\Delta S^\circ_T > 0$, $\Delta G^\circ_T < 0$ over a wide temperature range of 373–1473 K).



As expected, the activator of the thermal decomposition of ilmenite is sodium alkali oxide (from soda), which initially binds titanium dioxide in the near-surface, and later in the deeper lattice nodes of the mineral's crystal structure, forming $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{TiSiO}_5$ in conjunction with silicon oxide (Figure 9, reactions (13) and (15), with numerical values of $\Delta H^\circ_T < 0$, $\Delta S^\circ_T > 0$, $\Delta G^\circ_T < 0$ —the first reaction proceeds spontaneously from 373 to 1673 K,

and the second at any temperature). The titanium dioxide released from the ilmenite crystal lattice during the reduction of iron oxides is further bound by sodium metasilicate formed via reaction (4) (an entropy-driven reaction (16), with numerical values of $\Delta H^\circ_T > 0$, $\Delta S^\circ_T > 0$, $\Delta G^\circ_T < 0$ at $T > \Delta H^\circ / \Delta S^\circ$, starting from 673 K).

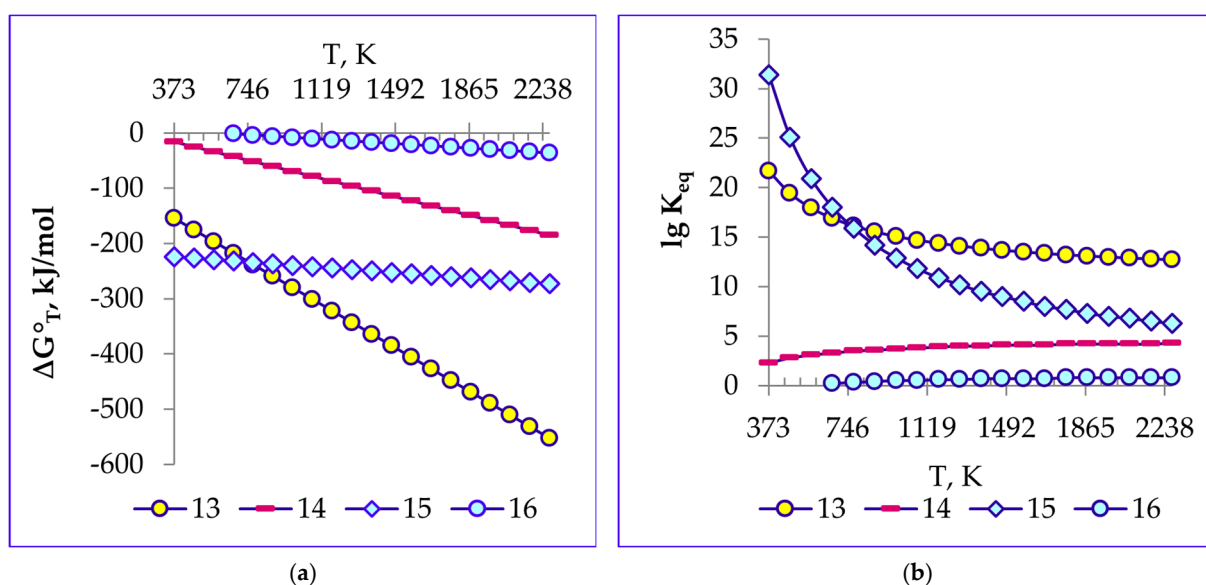
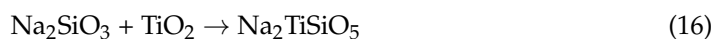
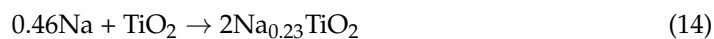


Figure 9. Dependence of the change in ΔG°_T (a) and $\lg K_{eq}$ (b) on the temperature of the reactions forming titanium oxide and silicon–titanium oxide electrode materials.

The binding of titanium dioxide with sodium and silicon oxides, as well as with sodium metasilicate, prevents the formation of high-melting, rapidly crystallizing lower titanium oxides such as Ti_2O_3 (melting point 2403 K), Ti_3O_5 (melting point 2473 K), and TiO (melting point 2293 K). The formation of low-melting compounds such as sodium metasilicate Na_2SiO_3 (melting point 1361–1362 K), sodium titanate $\text{Na}_2\text{Ti}_3\text{O}_7$ (melting point 1401 K), and sodium titanium silicate $\text{Na}_2\text{TiSiO}_5$ (melting point 1173–1303 K) accelerates the reduction of iron and ensures the efficiency of the spontaneous separation of free-flowing melts of metallic iron and titanium slag with significantly lower energy costs and reduced process duration.

For example, the temperature of the carbothermic melting of ilmenite concentrate, which has been previously subjected to oxidizing roasting at 1090 °C (1363 K) according to the technology of the canadian company Quebec Iron and Titanium (QIT), the largest producer of titanium slag in the province of Quebec, North America, is 1700 °C (1973 K). To improve the quality, low-grade primary titanium Sorel slag undergoes modernization through repeated oxidative roasting and carbothermic melting in similar temperature regimes [32]. The South African company Richards Bay Minerals (RBM), a leading producer of titanium slag, pig iron, rutile, and zircon, employs an adapted technology developed by the Canadian company QIT, which also involves a high-temperature carbothermic melting process of pre-oxidized ilmenite concentrate extracted from the Zululand coast in the northern region of KwaZulu-Natal province [33]. In Kazakhstan, at the Ust-Kamenogorsk

Titanium and Magnesium Plant, which holds a leading position in the global market for premium-class [34] titanium sponge, titanium slag is produced from coal-ilmenite charge at a temperature of 1600 °C (1873 K) over a period of 8 h.

Flux additives introduced into the carbonaceous charge of the ilmenite concentrate exert a similar effect on the decomposition of pseudorutile (Figure 10, reaction (17), with numerical values of $\Delta H^\circ_T < 0$, $\Delta S^\circ_T < 0$, $\Delta G^\circ_T < 0$ at $T < \Delta H^\circ / \Delta S^\circ$, occurring in the low-temperature range of 373–1073 K due to the dominant enthalpic effect of the formation of sodium trititanate $\text{Na}_2\text{Ti}_3\text{O}_7$ and manganese metasilicate MnSiO_3 —a synthetic analog of the natural mineral rhodonite).

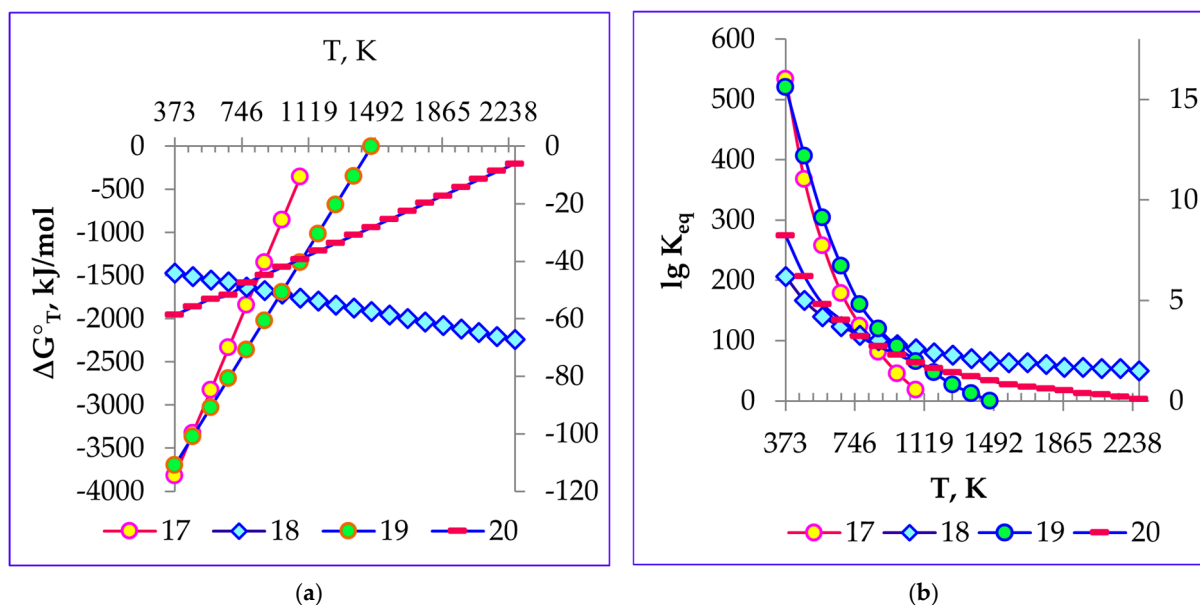
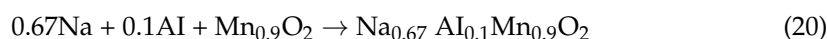
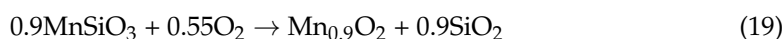
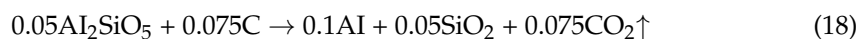
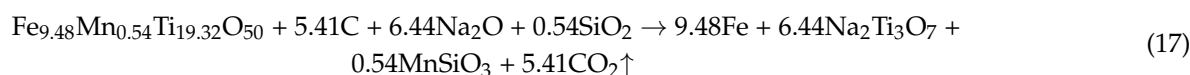


Figure 10. Dependence of the change in ΔG°_T (a) and $\lg K_{eq}$ (b) on the temperature of the reactions forming manganese dioxide intercalated with sodium and aluminum atoms.

The rock-forming aluminosilicate mineral of the ilmenite concentrate, kyanite (Al_2SiO_5), decomposes under the action of carbon, which reduces chemically active aluminum (reaction (18), which proceeds spontaneously with $\Delta H^\circ_T < 0$, $\Delta S^\circ_T > 0$, $\Delta G^\circ_T < 0$ at any temperature).

The byproduct of pseudorutile decomposition, manganese metasilicate MnSiO_3 , decomposes under the influence of evaporating water vapor, which oxidizes divalent manganese, converting it into its most stable tetravalent oxide form (reaction (19), with $\Delta H^\circ_T < 0$, $\Delta S^\circ_T < 0$, $\Delta G^\circ_T < 0$ at $T < \Delta H^\circ / \Delta S^\circ$, proceeding in the temperature range of 373–1473 K due to the enthalpic factor).

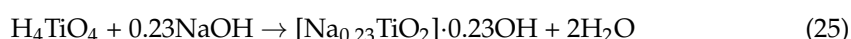
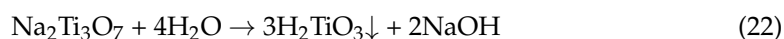
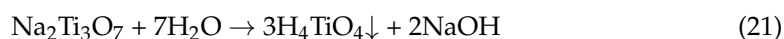
The incorporation of sodium and aluminum into the tunnel structure of manganese dioxide represents the final stage in the formation of the intercalate $\text{Na}_{0.67}\text{Al}_{0.1}\text{Mn}_{0.9}\text{O}_2$, with the initial stage being pseudorutile decomposition and the intermediate stage being the oxidation of Mn^{2+} (enthalpic reaction (20)).



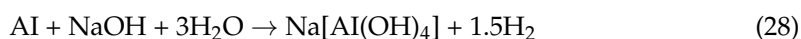
Considering the size of the intercalated sodium atom (190 pm), the manganese dioxide intercalate $\text{Na}_{0.67}\text{Al}_{0.1}\text{Mn}_{0.9}\text{O}_2$ is most likely a polymorphic modification of cryptomelane ($\alpha\text{-MnO}_2$) or birnessite ($\delta\text{-MnO}_2$), which possess either large open-channel or weakly bonded layered structures. These structures easily accommodate large-radius cations such as Na^+ (116 pm), Ba^+ (149 pm), and K^+ (152 pm) with a coordination number of 6.

4.3. Thermodynamics of Titanium Slag-Refining Reactions with Water

The refining of titanium slag with water is of great practical significance for the production of intercalation systems based on titanium dioxide. The process is thermodynamically justified by the hydrolytic decomposition in the low-temperature range of 293–373 K, converting the entire mass of sodium titanate and sodium titanium silicate into ortho- (H_4TiO_4) and meta- (H_2TiO_3) titanic acids—that is, into hydrated titanium dioxide ($\text{TiO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{TiO}_2 \cdot \text{H}_2\text{O}$) (enthalpic reactions (21), (23), (24) and spontaneous reaction (22), Figure 11). The hydrothermal destruction involving the breaking of chemical bonds in the crystal lattice of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{TiSiO}_5$ is initiated by the alkaline sodium oxide present in their composition, which reacts vigorously with water to form sodium hydroxide (caustic soda). In this process, chemically active sodium atoms, which readily donate electrons, are ionized by water. Upon gaining a positive electric charge, Na^+ cations replace hydrogen ions, which are displaced from water molecules as H_2 , resulting in the formation of sodium hydroxide, a highly alkaline compound. The interaction of sodium with water is a substitution reaction of an exothermic type. Due to sodium's high chemical reactivity, its interaction with water occurs almost instantly. The rapidly proceeding hydrolytic deformation of the primary anode materials $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{TiSiO}_5$, obtained from ilmenite concentrate, is accompanied by the incorporation of highly mobile Na^+ cations into the layered mesoporous structure of hydrated titanium dioxide. This facilitates the rapid formation of a stable intercalate in an aggressive alkaline environment— $[\text{Na}_{0.23}\text{TiO}_2] \cdot 0.23\text{OH}$ (enthalpic reaction (25) and spontaneous reaction (26)).



Thermodynamic analysis revealed that the manganese dioxide intercalate $\text{Na}_{0.67}\text{Al}_{0.1}\text{Mn}_{0.9}\text{O}_2$, formed during the carbothermic flux conversion of ilmenite concentrate, is unstable in an aqueous alkaline solution. This is explained by the fact that both aluminum and manganese dioxide, according to literature sources, undergo similar substitution reactions with water as sodium does [30,31]. Aluminum, slowly oxidizing in the presence of oxygen and displacing hydrogen ions from water molecules, forms sodium aluminate (NaAlO_2), which is soluble in water [35,36], and in a strongly alkaline medium, it forms sodium tetrahydroxoaluminate ($\text{Na}[\text{Al}(\text{OH})_4]$) (spontaneous reactions (27) and (28), Figure 12). Manganese dioxide undergoes disproportionation in water to form sodium manganate (Na_2MnO_4) (reaction (29)—enthalpic at 273 K, and spontaneous as the temperature increases).



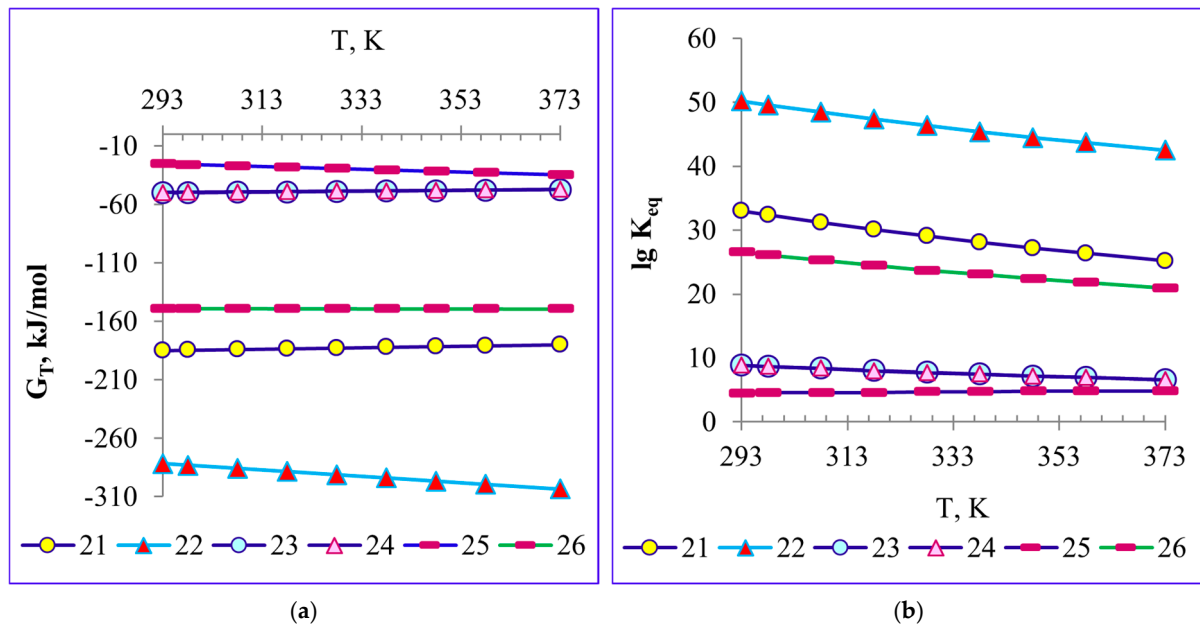


Figure 11. Dependence of the change in ΔG°_T (a) and $\lg K_{eq}$ (b) on the temperature of the hydrothermal formation reactions of sodium-intercalated titanium dioxide.

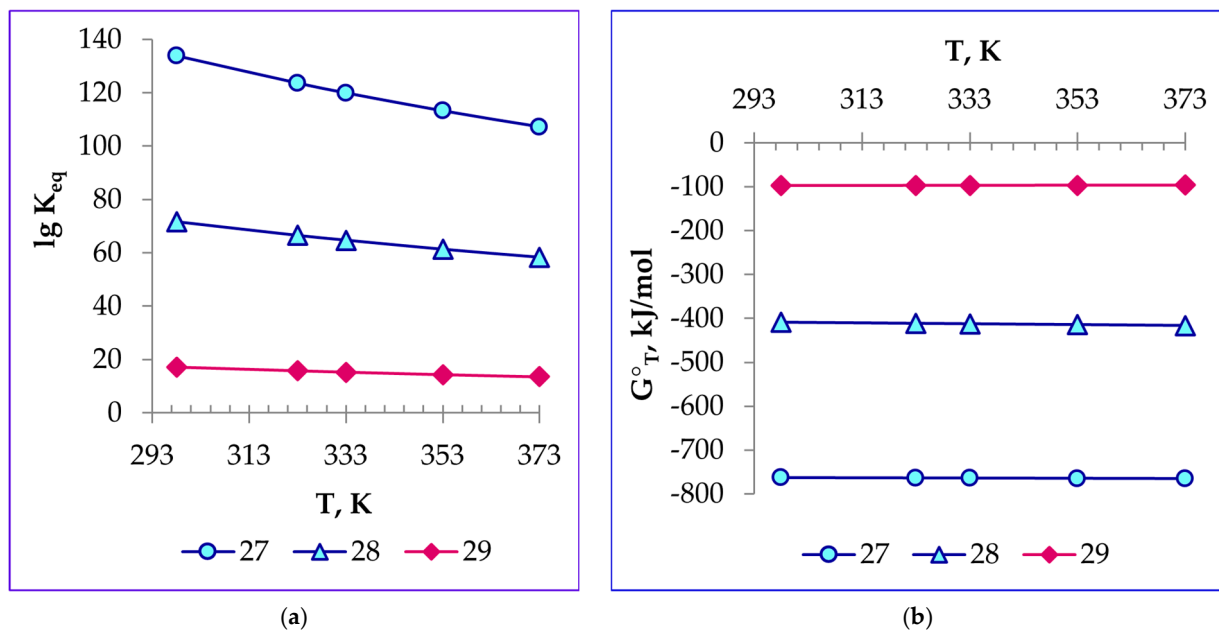


Figure 12. Dependence of the change in ΔG°_T (a) and $\lg K_{eq}$ (b) on the temperature of hydrothermal decomposition reactions of manganese dioxide intercalate.

The desiliconization of water-modified titanium slag using ammonium bifluoride confirmed the possibility of concentrating the content of titanium oxide intercalate. Research aiming at creating pure electrode materials from natural raw materials with specified electrochemical properties is ongoing.

5. Conclusions

The production of the anodic intercalate of titanium dioxide by carbothermic smelting of ilmenite concentrate fluxed with diatomite and calcined soda, followed by the refining of titanium slag with water, represents an innovative technical solution for the large-scale production of cheap sodium-ion batteries.

The regulation of the composition of coal–ilmenite charge with fluxes is a key technological condition for the creation of electrode materials. The formation of electrode materials is accelerated by the presence of diatomaceous silica, which catalytically initiates the decomposition of calcined soda, breaking down into sodium oxide and sodium upon contact with coal, as well as sodium oxide from soda, which activates the destruction of ilmenite and its leucoxene analog, pseudorutile, through individual binding with titanium dioxide and in conjunction with silicon oxide. Due to the reactive properties of sodium and silicon oxides, the formation of lower-melting-point titanium oxides is prevented, iron reduction is accelerated, the separation of titanium slag melts and alloyed cast iron is facilitated, and energy costs are significantly reduced.

The refining of titanium slag with water ensures complete hydrolytic cleavage of sodium titanate and sodium titanosilicate formed during the carbothermic flux conversion of ilmenite concentrate, instant ionization of sodium acquiring a positive electric charge, and rapid formation of a monophase stable intercalate of mesoporous titanium dioxide $\text{Na}_{0.23}\text{TiO}_2$, purified from water-soluble byproducts in an aggressive alkaline environment.

The manganese dioxide intercalate $\text{Na}_{0.67}\text{Al}_{0.1}\text{Mn}_{0.9}\text{O}_2$ lacks structural strength due to the high reactivity of its aluminum and manganese components.

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