

Preparation of Titanium by Electro-deoxidation of CaTiO₃ in a Molten CaCl₂-NaCl Salt

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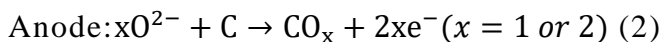
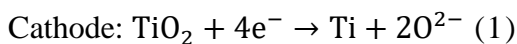
Calcium titanate (CaTiO₃) is the main mineral phase of titanium-bearing blast furnace slag after selective enrichment, growth and separation. It is the titanium-bearing material closest to the primary mineral, titanium. In this study, CaTiO₃ was used as the precursor, and titanium metal was prepared by electro-deoxidation of CaTiO₃ in molten CaCl₂-NaCl salt. The feasibility of preparing titanium from CaTiO₃ was analyzed by calculating the decomposition voltages, energy band structures and densities of states of the raw materials during the process of converting CaTiO₃ into titanium. To understand the reduction mechanism in the process of preparing titanium from CaTiO₃, electrolytic experiments were carried out for different times on a cathode of CaTiO₃ sintered at 1200°C. The research showed that the reduction process of CaTiO₃ was CaTiO₃→Ti₂O₃→TiO/Ti₂O→Ti[O]₆→Ti. Finally, a deoxidation model of CaTiO₃ in CaCl₂-NaCl molten salt was established.

Keywords: Calcium titanate, Electro-deoxidation, Titanium

1. INTRODUCTION

Titanium has been widely used in the aviation, aerospace and shipbuilding industries due to its excellent properties, such as high specific strength, strong corrosion resistance, low thermal conductivity and wide temperature adaptability. With the development of science and technology, various kinds of high-performance titanium have been very successful in applications in automobiles, sports equipment, medical devices and light industry[1]. For decades, titanium metal has been produced by the Kroll method[2], which converts TiO₂ to TiCl₄ and then reduces it by liquid Mg. However, the chlorination process of TiCl₄ is complex, and many toxic gases generated during the production process pollute the environment. Molten salt electro-deoxidation (FFC) is a promising method for preparing titanium metal. With TiO₂ as the cathode, it is reduced to titanium under a voltage lower than the decomposition potential of CaCl₂ but higher than the reduction potential of TiO₂. At the same time, oxygen ions enter the CaCl₂

electrolyte from TiO_2 and discharge after reaching the graphite anode to generate CO and CO_2 gases. The whole electro-deoxidation process can be summarized by reactions (1) and (2)[3]:



Compared with the Kroll method, using TiO_2 as a raw material is one of the advantages of the FFC method for preparing titanium because it is easier to obtain TiO_2 than TiCl_4 . While the FFC method has some disadvantages, the traditional sulfuric acid method or chlorination method used to produce TiO_2 requires high energy consumption and produces large amounts of pollution. High purity TiO_2 is more expensive than TiCl_4 [4]. Moreover, the side reactions of TiO_2 in molten salts result in excessive oxygen content in the product. These shortcomings limit the preparation of titanium from TiO_2 by means of electro-deoxidation of molten salts. Although titanium resources are abundant in the world, most of them exist in the form of vanadium titanomagnetite. Less than 8% of titanium exists in the forms of rutile and anatase titanium dioxide. After the metallurgical process of steelmaking and vanadium extraction, most of the valuable titanium elements in vanadium titanomagnetite enter the slag, forming titanium materials. In the traditional metallurgical process, TiCl_4 can be obtained from titanium-containing materials through a series of steps, such as decomposition, calcination, oxidation and chlorination. Thus, the Kroll method is used to prepare titanium metal, as shown in step (1) of Figure 1. However, this leads to the discharge of wastewater with high concentrations of ammonia-nitrogen and NH_3 .

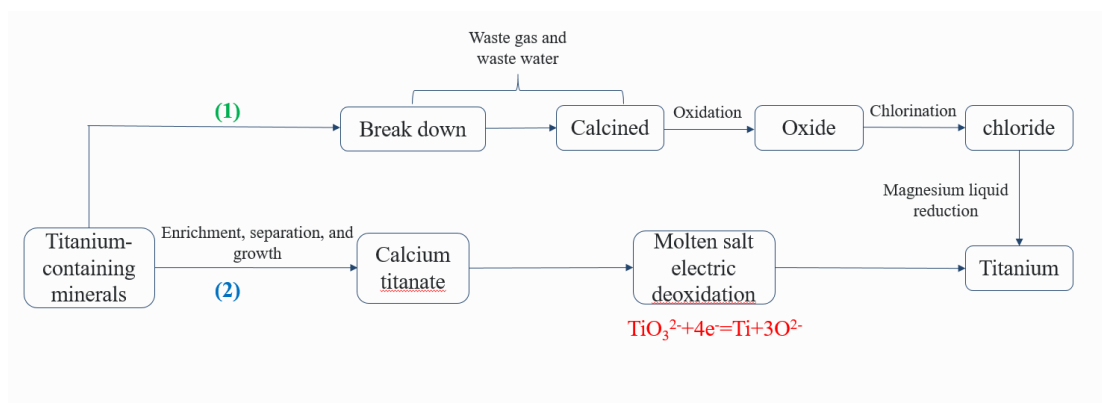


Figure 1. Comparison of traditional metallurgy and electrochemical metallurgy processes

At present, many researchers are investigating the enrichment of titanium materials by selective enrichment, growth and separation, as shown in step (2) of Figure 1. Most of the polyvalent titanium elements in titanium-containing blast furnace slag change into CaTiO_3 [5]. CaTiO_3 is the product of titanium-containing blast furnace slag enrichment, and it is similar to the primary minerals and easier to obtain than TiO_2 or TiCl_4 . If CaTiO_3 is used as a raw material to prepare titanium metal by electro-deoxidation of molten salt, the process can be much shorter and not produce pollutants, which is in line with the current principle of green short process metallurgy and has significant economic benefits.

Peng Yan[6] conducted electrochemical tests on TiO_2 and CaTiO_3 cathodes and found that the reduction potential of the CaTiO_3 cathode was slightly lower than that of TiO_2 , but the reduction step of

CaTiO₃ was relatively simple and did not produce undesired byproducts. Wang[7] also compared TiO₂ and CaTiO₃ in experiments. The researchers mixed TiO₂ with CaO or CaCO₃ powder, pressed the mixture and then heated it in air to 1300°C to obtain a porous CaTiO₃ cathode. The reduction rate of CaTiO₃ was twice as fast as that of TiO₂, and the current efficiency and energy efficiency were also higher. Therefore, it is more advantageous to use CaTiO₃ instead of TiO₂ as a solid cathode to produce titanium metal. However, the deoxidation mechanism of CaTiO₃ to prepare titanium in molten salt is still unclear and needs to be further studied.

In this paper, the feasibility of preparing titanium by electrolysis of CaTiO₃ was analyzed theoretically, and the phase and morphology of the electrolytic products of CaTiO₃ cathodes under different sintering temperatures and electrolysis times were compared. The electro-deoxidation process of CaTiO₃ in molten salt was analyzed, and an electro-deoxidation model of CaTiO₃ was established.

2. CALCULATION METHOD AND EXPERIMENT

In this study, by combining theory with experiments, a theoretical method was adopted to analyze the feasibility of preparing titanium metal with CaTiO₃, and an experimental confirmation was carried out.

The standard Gibbs free energy change, ΔG^θ (kJ/mol), was calculated by HSC thermodynamics software, and its standard equilibrium decomposition voltage was calculated by the Nernst equation, U^θ (V). n is the number of electrons transferred in the electrochemical reaction, F (96485 Cmol⁻¹) is the Faraday constant, and the formula for calculating the decomposition voltage is shown as follows[8]:

$$\Delta G^\theta = -nU^\theta F \quad (3)$$

Materials Studio8.0 software was used to analyze the bonding characteristics of the electrolytic raw materials. The energy band structures and densities of states were calculated through the CASTEP module of the software, and the energy convergence accuracy was 1×10^{-6} eV.

All reagents used in this paper were analytically pure. The graphite anode was polished with sandpaper of 600, 1000, 1500 and 2000 grit, drilled, dried, and connected to the electrode leader. The cathode was made by adding 5% PVA into CaTiO₃ and pressing the mixture under 10 MPa. The molded cathode was sintered at 1200°C for 4 h and then cooled to room temperature in a furnace. The connection method between the CaTiO₃ cathode and electrode leader was as follows: the 200-mesh iron net was cut into a wafer of the same size as the cathode sheet; the wafer-like iron net was wound on the cathode with fine copper wire; and then the cathode was connected to the electrode leader.

Before electrolysis, the mixed molten salt CaCl₂-NaCl with a mass ratio of 7:3 was dried in air for 48 h and then transferred to an argon atmosphere for further drying for 24 h. After drying, the temperature was raised to 750°C. After the molten salt completely melted, two polished graphite electrodes were inserted into the molten salt, and pre-electrolysis at 2.5V was performed for 2 h. Then, another graphite electrode that served as the anode and the CaTiO₃ cathode were inserted into the molten salt for the electro-deoxidation process. The connection mode of the electrode is shown in Figure 2. During the electrolysis experiment, the changes in current with time were recorded by a computer. The whole process of pre-electrolysis and electro-deoxidation was carried out in an argon atmosphere. After

the experiment, the electrode was removed from the molten salt and protected by argon gas until it cooled to room temperature. The specific experimental device is shown in Figure 3. The samples were washed with deionized water and anhydrous ethanol and then dried in an empty container and stored for subsequent analysis. The samples were characterized by XRD (D8 Advance, AXS Brook, Germany) and SEM (S-4800, Hitachi, Japan).

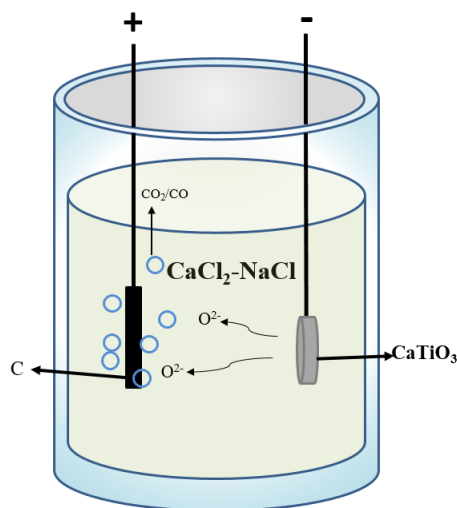


Figure 2. Electrode connection mode during the experiment

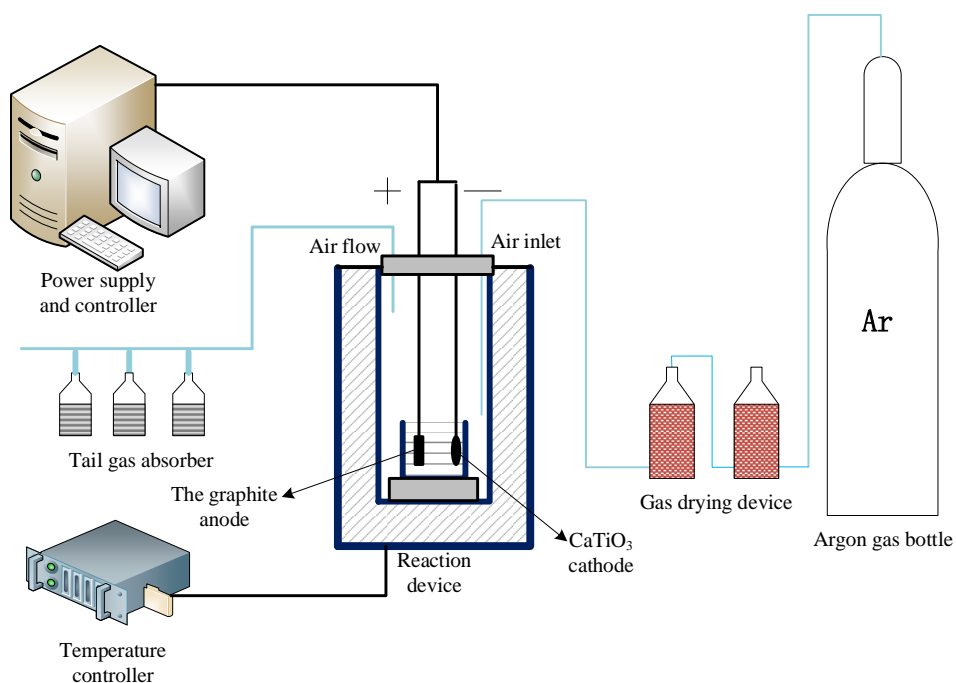


Figure 3. The specific experimental device of the electrolysis process

3. RESULTS AND DISCUSSION

3.1 Thermodynamic Analysis

To determine whether the reaction of reducing CaTiO_3 to titanium in molten salt can be carried out, the decomposition voltages of the possible reaction in the reaction system were calculated by using HSC6.0 software. Figure 4 shows the decomposition voltages of CaCl_2 and NaCl molten salts, and Figure 5 shows the decomposition voltages of CaTiO_3 in possible reaction with molten salts. To simplify the calculation, the anodic products were replaced by CO_2 .

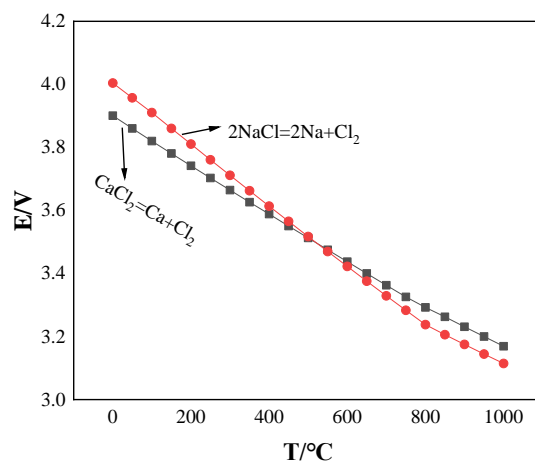


Figure 4. Decomposition voltage of CaCl_2 and NaCl molten salts

According to the analysis, the decomposition voltage of the CaTiO_3 reduction to oxide and titanium and the voltage of titanium oxide reduction to titanium are much lower than the decomposition voltages of CaCl_2 and NaCl . This indicates that CaTiO_3 and titanium oxides can be reduced to metals in CaCl_2 - NaCl mixed molten salts. The decomposition voltages of TiO , Ti , Ti_2O_3 and Ti_3O_5 are 1.04 V, 1.16 V, 1.33 V and 1.74 V, respectively. Because the lower the decomposition voltage of the reaction is, the easier it is to obtain the reaction products[9], CaTiO_3 does not deoxidize directly to titanium in one step but reduces first to an inexpensive titanium oxide, and then the inexpensive titanium oxide slowly deoxidizes to titanium metal. Therefore, from a purely thermodynamic point of view, the theoretical reduction process of CaTiO_3 in molten salt, $\text{CaTiO}_3 \rightarrow \text{TiO} \rightarrow \text{Ti}[\text{O}]_6 \rightarrow \text{Ti}$ ($\text{Ti}[\text{O}]_6$, is necessary in the process of preparing titanium by electrodeoxidation of molten salt[10]). However, the reduction of CaTiO_3 is not under only thermodynamic control; other factors, such as O^{2-} diffusion in the electrolyte and solid mass transfer inside the cathode plate, must be considered[11-12].

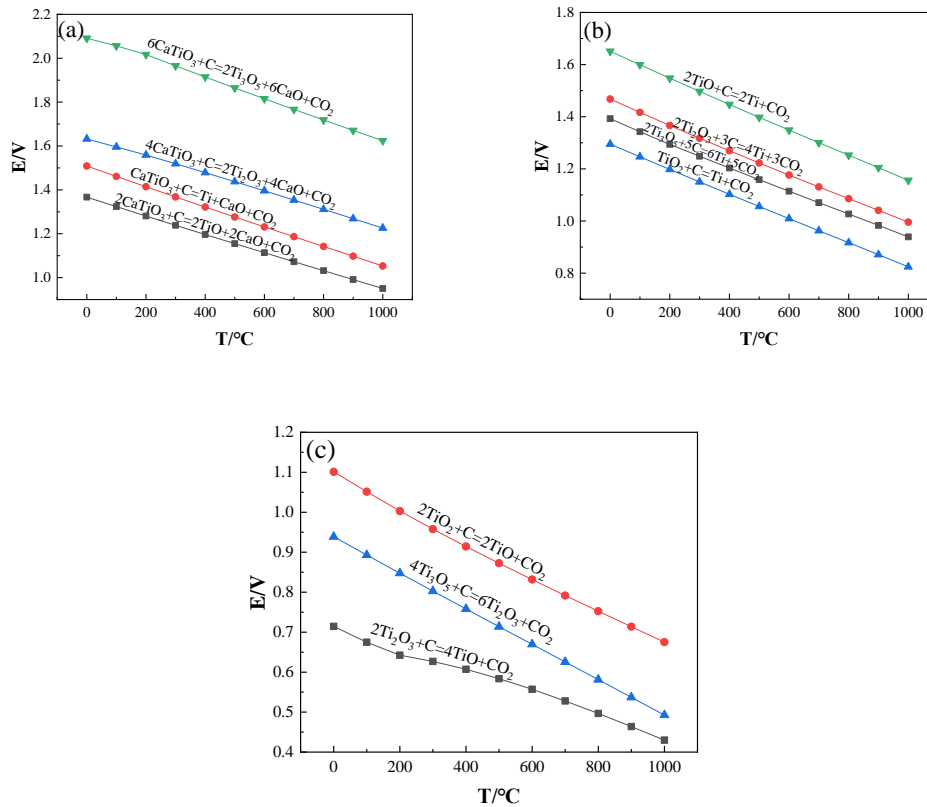
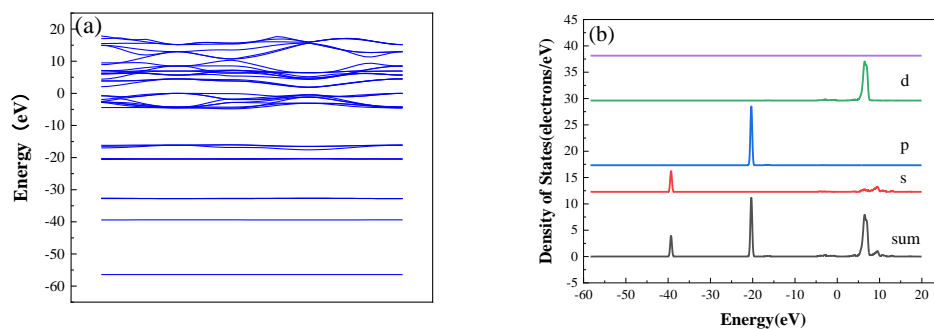


Figure 5. (a) Decomposition voltage of CaTiO₃ into titanium metal or oxide, (b) Decomposition voltage of titanium metal oxide into titanium, (c) Decomposition voltage of titanium high-order oxide into low-order oxide

3.2 Energy band structure and density of states of CaTiO₃ and TiO₂

To analyze the removal of calcium ions in molten salt and the strength of the interactions between atoms, the energy band structure and density of states of the raw material CaTiO₃ were calculated with the aid of first principles and Materials Studio8.0 software. The calculation results are shown in Figure 6.



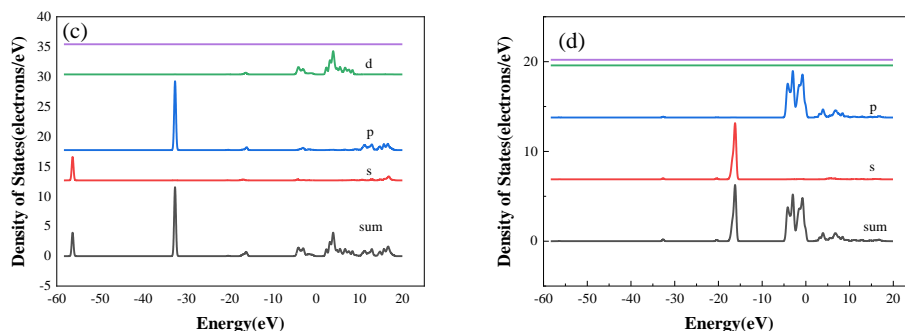


Figure 6. (a) Band structure of calcium titanate; (b), (c), (d) the density of states of calcium ion, titanium ion and oxygen ion in CaTiO_3 and the partial density of states in each orbit

As shown in Figure 6, the band structure of the CaTiO_3 crystal is relatively flat, and there is a wide band gap near the Fermi level with a value of approximately 2.184 eV. This is similar to the results reported in other documents[13]. From the density of states diagram, as shown in Figure 7(b)~(d), Ti (p) and a small amount of O (sp) are mainly formed in the range of -35 eV ~-32 eV, Ca (p) and O (s) are mainly formed in the range of -21 eV~-15 eV, O (p) and Ti (d) are mainly formed in the range of -5 eV ~-0 eV, and bonds formed between Ti (d) and O (p) and between Ti (d) and Ca (d) in the interval from 2 eV to 8 eV. Therefore, the Ti-O interaction in the CaTiO_3 crystal, especially the bonding between the O (p) and Ti (d) orbitals, is much stronger than that O-Ca and Ti-Ca bonds. Therefore, the O-Ca and Ti-Ca bonds easily break, and the calcium ions are easily removed during the electrolysis of CaTiO_3 . The key to the success of the electrolysis experiment is to break the Ti-O bonds and remove the oxygen ions.

Similarly, the energy band structure and density of states of TiO_2 , which is the traditional raw material for electro-deoxidation of molten salt, are also calculated, and the results are shown in Figure 7. Table 1 compares the bond energy ranges of CaTiO_3 and TiO_2 .

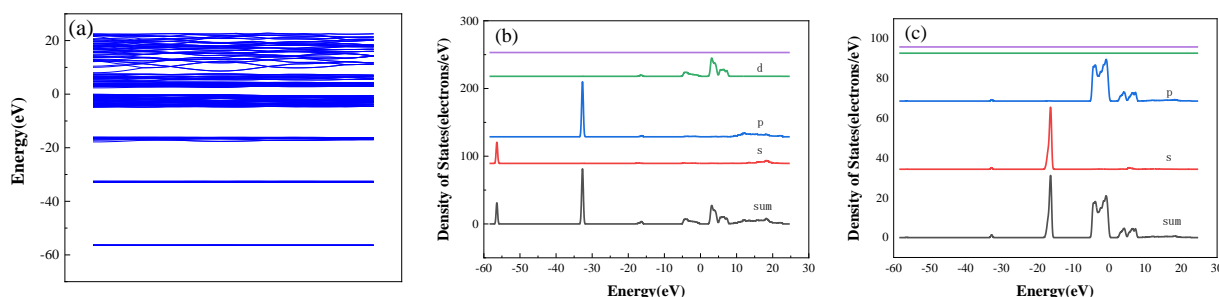


Figure 7. (a) the energy band structure of TiO_2 ; (b) (c) the density of states of titanium ions and oxygen ions in titanium dioxide and the partial density of states in each orbit.

Table 1. Comparison of bonding energy range of CaTiO₃ and TiO₂

Bonding energy range	CaTiO ₃	Bonding energy range	TiO ₂
-35eV~-32eV	Ti(p) and a small amount of O(sp)	-35eV~-32eV	Ti(p) and a small amount of O(sp)
-21eV~-15eV	Ca(p) and a small amount of O(s)	19eV~-15eV	A small amount of Ti(sd) and O(s)
-5eV~-0eV 2eV~8eV	O(p) and Ti(d) Ti(d) and a small amount of O(p), a small amount of Ti(d) and Ca(d)	-5eV~10eV	O(p) and Ti(d)

The preparation of titanium metal by electro-deoxidation using TiO₂ as a raw material in molten salt was first performed by Fray and Chen [3,14-15]. By analyzing the band structure and density of states of TiO₂ crystals, the band gap near the Fermi level was found to be approximately 2.359 eV, slightly higher than that of CaTiO₃, while the band structure of pure titanium metal has no band gap (the calculation results are shown in Figure 8 (a)). According to the density of states diagram in Figure 8, Ti (p) and a small amount of O (sp) are mainly formed in the range of -35 eV ~-32 eV, Ti (s) and O (s) are mainly formed in the range of -19 eV~-15 eV, and O (p) and Ti (d) are mainly formed in the range of -5 eV ~10 eV. In TiO₂ crystal, O (p) and Ti (d) are the mainly formed bands, while the energy range of the bands is wider, so the Ti-O interaction in TiO₂ is slightly stronger than that in CaTiO₃. Overall, CaTiO₃ is more easily deoxidized to titanium than TiO₂.

Finally, the energy band structure and density of states of the final titanium product are calculated, and the results are shown in Figure 8. Because the product is a metal, there is no band gap near the Fermi level of its energy band structure. It is easier to obtain titanium from CaTiO₃ with a lower band gap than from TiO₂. The calculation is:

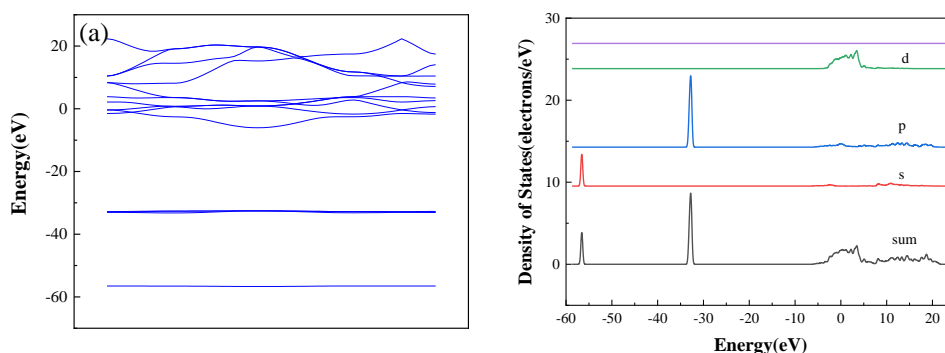


Figure 8. (a) the energy band structure of titanium; (b) the density of states of metallic titanium and the partial density of states in each orbit

3.3 Reduction process of CaTiO_3 in molten salt

Figure 9 shows XRD patterns of the CaTiO_3 raw material and CaTiO_3 cathode sintered at 1200°C for 4 h. The composition of CaTiO_3 did not change significantly before and after sintering, and no other phases were produced.

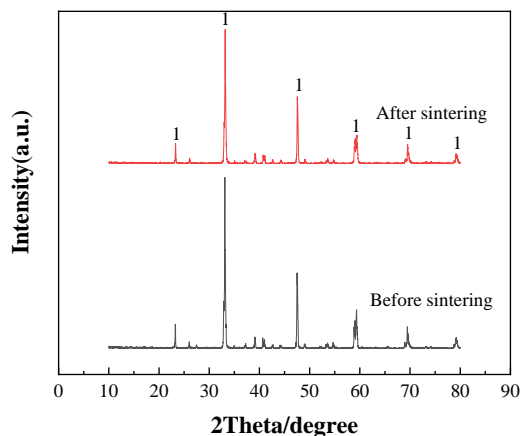


Figure 9. XRD Patterns of CaTiO_3 raw material and sintered cathode

Figure 10 shows SEM images of the CaTiO_3 cathode before and after sintering at 1200°C . Before sintering, the cathode particles were small, and the particle size distribution was not uniform; the larger particles were composed of small particles aggregated by PVA. Some small particles were sintered to form large particles during the sintering process, thus forming some pores that were conducive to the molten salt entering the cathode and achieving dissociation reduction deep inside the CaTiO_3 cathode. Thus, sintering provides a certain strength for the cathode, which is conducive to the connection between the cathode sheet and wire.

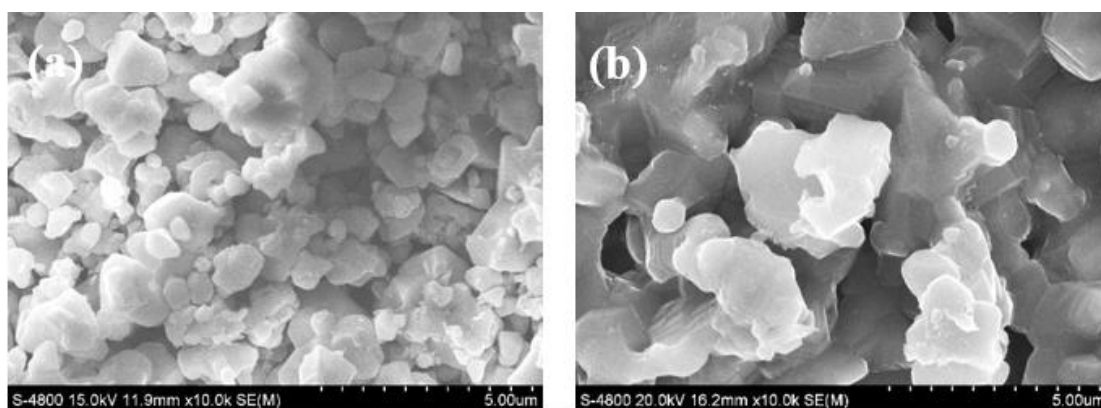


Figure 10. (a) before sintering and (b) after sintering at 1200°C the morphology of the cathode sheet

To analyze the reduction process of CaTiO₃ in CaCl₂-NaCl molten salt, experiments were performed on the CaTiO₃ cathode in CaCl₂-NaCl molten salt at 750°C and 3.2 V for 2 h, 4 h, 6 h, 8 h, 12 h, and 24 h. Figure 11 shows the XRD patterns of the CaTiO₃ cathode sintered at 1200°C and electrolyzed at 750°C and 3.2 V for different times in CaCl₂-NaCl molten salt. The relationship between the electrolysis time and products is shown in Table 3.

After electrolysis for 2 h, CaTiO₃ first deoxidized and decalcified, undergoing reduction to Ti₂O₃. After 4 h of electrolysis, part of the Ti₂O₃ was reduced to TiO. With increasing electrolytic time, all of the Ti₂O₃ was reduced to TiO and a small amount of Ti₂O. After 12 h of electrolysis, TiO and Ti₂O continued to deoxidize to form Ti[O]₆ (a solid solution of oxygen dissolved in titanium). After 24 h of electrolysis, the whole cathode completely changed into titanium metal and a small amount of unreacted CaTiO₃. According to the thermodynamic analysis of 3.1, the decomposition voltage of CaTiO₃ reduction to TiO is lower, but it is reduced to Ti₂O₃ first. This is because the transmission of electrons inside the CaTiO₃ cathode is hindered by solid transfer. It is more inclined to get an electron first and turn it into a high-priced oxide of titanium, and then continue to get electrons to turn it into a low-priced oxide of titanium until the metal titanium. This deoxidization mode of gradually decreasing the valence state of target metal ions is similar to the result obtained by Du when U was prepared from U₃O₈[16].

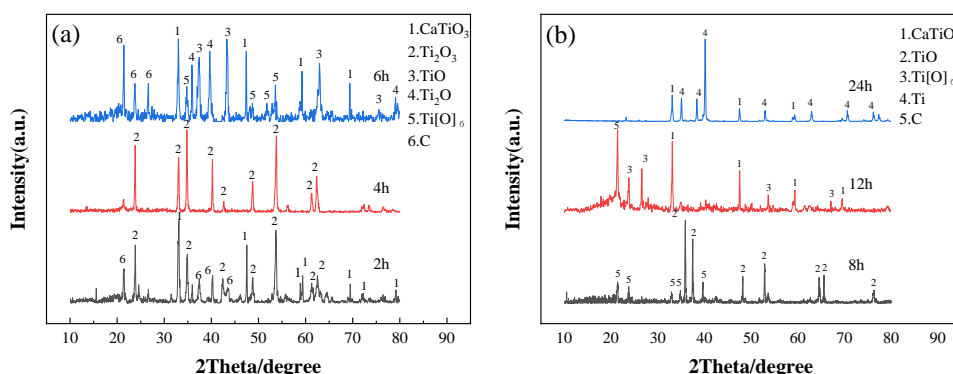


Figure 11. XRD patterns of the cathode sheet products at different times of electrolysis

Table 2. Electrolysis time and corresponding products

Electrolysis time	The main product except unreacted CaTiO ₃
2h	Ti ₂ O ₃
4h	Ti ₂ O ₃ , TiO
6h	TiO, a small amount Ti ₂ O, Ti[O] ₆
8h	TiO
12h	Ti[O] ₆
24h	Ti

It is worth noting that carbon impurities are present in all electrolytic products for the following reasons. The CO₂ formed by O²⁻ diffusing to the C anode after CaTiO₃ cathode deoxidization is not

discharged quickly, but the O^{2-} diffusing to the C anode in molten salt continues to form CO_3^{2-} . Under the influence of the concentration difference of CO_3^{2-} between the anode and cathode, CO_3^{2-} diffuses to the cathode. After reaching the cathode, CO_3^{2-} competes with $CaTiO_3$ to undergo reduction, leaving C impurities in the cathode products[17]. This is one of the main causes of current loss in the process of electro-deoxidation[18].

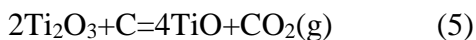
A comparative analysis shows that the reduction of $CaTiO_3$ can be divided into four stages. In the first stage, $CaTiO_3$ removes Ca^{2+} and O^{2-} to form Ti_2O_3 . In the second stage, Ti_2O_3 formed in the first stage is deoxidized to form TiO and a small amount of Ti_2O . In the third stage, TiO and a small amount of Ti_2O continue to deoxidize to form $Ti[O]_6$. The fourth stage is the slow deoxidation of $Ti[O]_6$ into titanium.

The specific reaction involved in the reduction of $CaTiO_3$ cathode into titanium metal in molten salt:

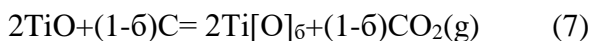
The first stage:



The second stage:



The third stage:



The fourth stage:



The reduction process of $CaTiO_3$ is similar to that of $Na_2Ti_3O_7$. When $Na_2Ti_3O_7$ is reduced to titanium in molten $CaCl_2$ salt, $Na_2Ti_3O_7$ first is reduced to inexpensive oxides of titanium (such as Ti_4O_7 , Ti_3O_5 , Ti_2O_3 and TiO), then reduced to $Ti[O]_6$, and finally, slowly reduced to titanium metal[19].

Figure 12 shows SEM images of cathodes after electrolysis for different times.

According to Figure12(a), square particles appeared in the products after electrolysis for 2h. Combined with the SEM image before electrolysis and XRD analysis, these square particles can be inferred as Ti_2O_3 . When the electrolysis time was 4h, the cathode electrolysis product was basically square Ti_2O_3 . With the extension of electrolysis time, as shown in Figure12(c), the square Ti_2O_3 will gradually sintered into large particles, and there will be some holes in the large particles. These holes were formed by the continuous deoxidation of Ti_2O_3 into lower oxides of titanium (TiO , Ti_2O). With the progress of electrolysis time, as shown in Figure12(d), Ti_2O_3 gradually deoxidizes to form long strip TiO , and then TiO continues to deoxidize to form $Ti[O]_6$, whose morphology was fine granular, as shown in Figure12(e). At the later stage of electrolysis, the granular $Ti[O]_6$ is slowly deoxidized until the powdered titanium is formed finally.

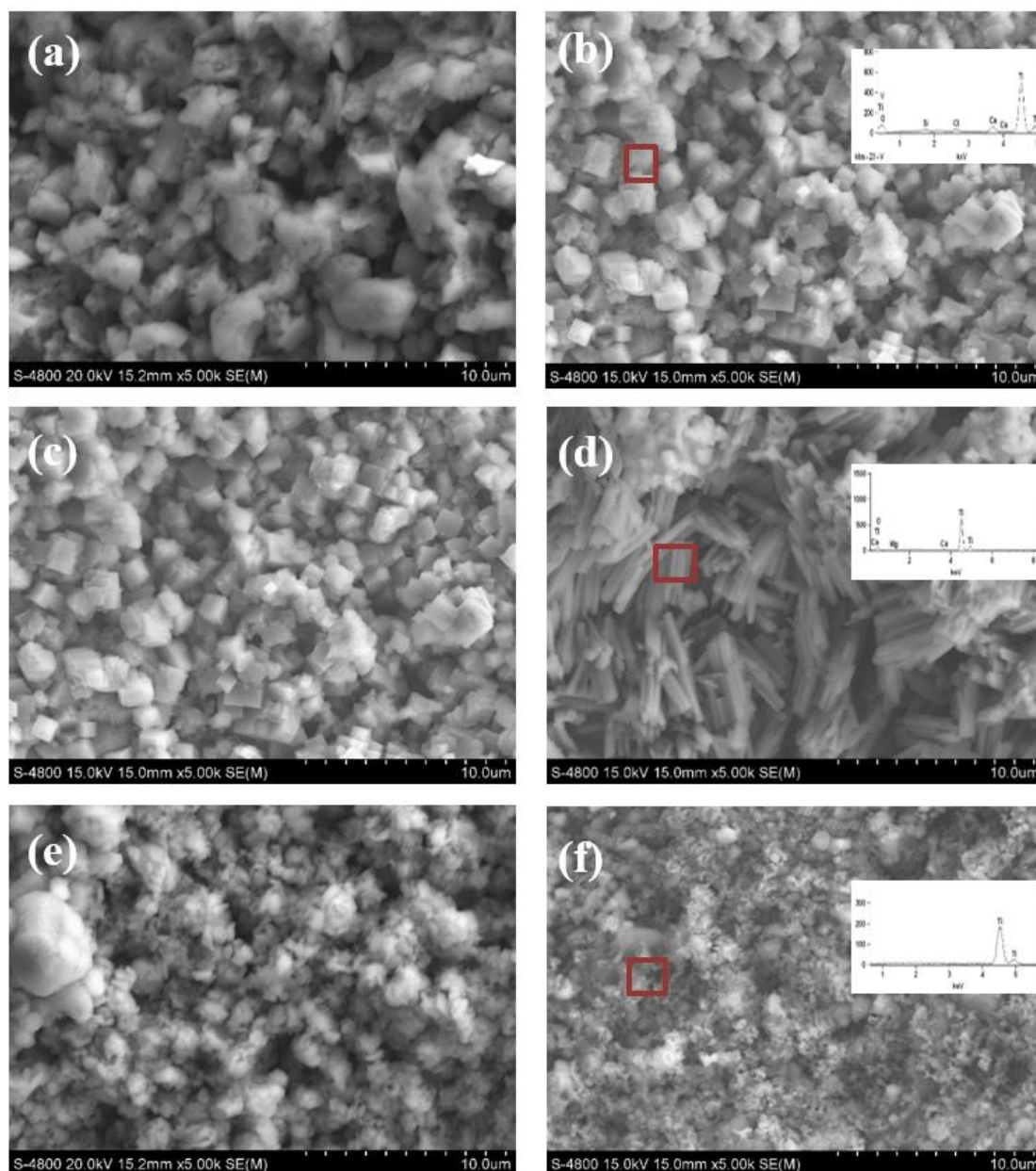


Figure 12. SEM images of cathode sheet products at different times of electrolysis (a.2h, b.4h, c.6h, d.8h, e.12h, f.24h)

The morphology of CaTiO_3 cathode will show different states with the progress of electrolysis time. This is because various titanium oxides formed by the deoxidation of CaTiO_3 will produce secondary sintering phenomenon in the molten salt of $\text{CaCl}_2\text{-NaCl}$ at 750°C [19]. Due to the different sintering properties of various intermediate products, they show different shapes such as square and long strip.

3.4. Electro-deoxidation model of CaTiO_3

The three phase Boundary (3PI) model was first proposed in solid fuel cell research [20-22], and was later used by researchers to describe the FFC process of cathode reduction in molten salt [23].For

the non-conductive CaTiO_3 cathode, the reduction reaction of the cathode is carried out at 3PI (the reaction site) of the metal conductor / CaTiO_3 / electrolyte through electron conduction. The 3PI diagrams of electrons, O^{2-} and Ca^{2+} are shown in Figure 13. When the cathode connected to the conductor, the electronic first passed to the interface of metal conductor and CaTiO_3 , the CaTiO_3 cathode will release O^{2-} , Ca^{2+} , O^{2-} , Ca^{2+} through the interface of CaTiO_3 and electrolyte, respectively, and transferred to the anode. Finally, CaTiO_3 cathode reduced to titanium metal, and the metal formed a new 3PI (titanium/ CaTiO_3 /electrolyte). The 3PI gradually moves to the interior of the CaTiO_3 cathode until the entire cathode is completely transformed into metal.

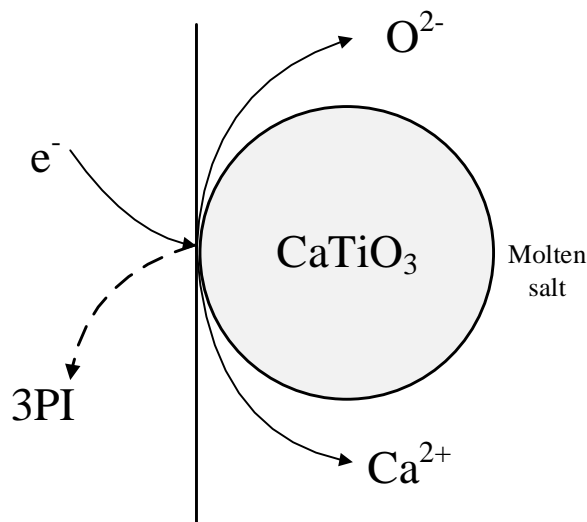


Figure 13. The transmission of electrons, O^{2-} and Ca^{2+} at 3PI

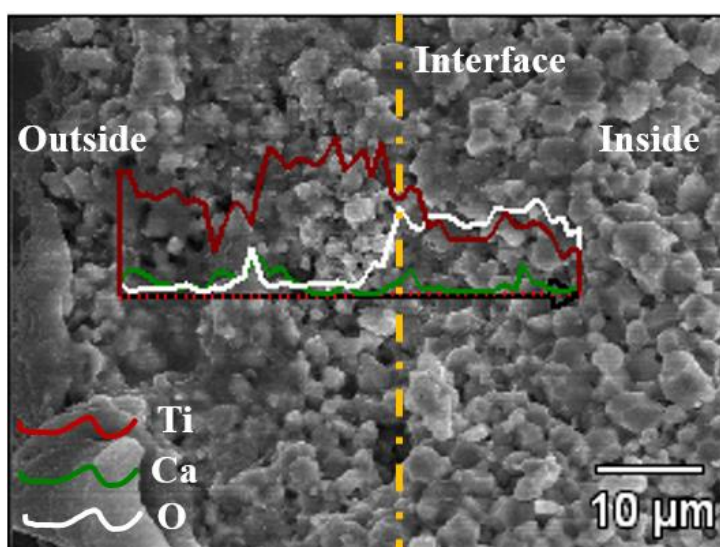


Figure 14. SEM-EDS image of the cross section of the CaTiO_3 cathode sheet after 6 hours of electrolysis

Figure 14 is the SEM-EDS image of CaTiO_3 cathode cross section after 6h of electrolysis. As can be seen from the figure, on the side near the wire, there is more titanium and less oxygen. This is because the deoxidation of CaTiO_3 is carried out from the outside to the inside, while the content of calcium is less, and there is little difference between the inside and the outside of the cathode plate. According to the calculation results of 3.2, Ca^{2+} in CaTiO_3 is easier to be removed than O^{2-} , indicating that Ca^{2+} in the cathode sheet has been basically removed in the early electrolysis stage.

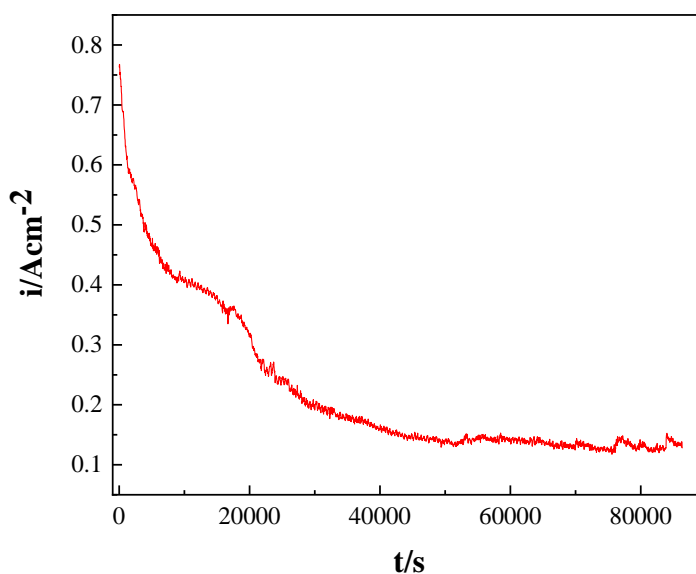


Figure 15. I-t curve of the cathode sintered at 1200°C for 24h under 3.2V voltage

As can be seen from the I-T curve of the electrolysis process in Figure 15, the current is in a gradual decreasing trend. The current value starts to decrease from 0.76 Acm^{-2} and approaches to a background current after 12h, at which time the current is about 0.14 cm^{-2} . This is different from other studies in which the current increases and then decreases with time[24]. The reason for this trend is that: since the cathode is covered with iron mesh, the reaction area of 3PI is the largest at the beginning of electrolysis, and the current is also the largest at this time. As time goes on, 3PI migrates to the inside of the cathode plate. With the reduction of the reaction area, the current also begins to decrease. When the reaction reaches 12h, the surface of the cathode has changed to $\text{Ti}[\text{O}]_6$. The deoxidation of $\text{Ti}[\text{O}]_6$ is a very slow process, so the current does not change much at this time, but tends to be close to a background current. The cathode precursors in other studies are drilled into the cathode, which leads to the minimum 3PI reaction area at the beginning of electrolysis. As time goes on, the 3PI reaction area spreads to the entire cathode surface and then decreases. The current also changes with the change of 3PI reaction area. The I-T curve of this trend is consistent with the typical 3PI model, and is also consistent with the EDS line scan results in the Figure 18 above.

For the actual electro-deoxidation of CaTiO_3 , since CaTiO_3 does not directly generate titanium metal and many intermediate products will be generated, the deoxidation model of CaTiO_3 will have multiple 3PIs simultaneously. At the beginning of electrolysis, the reaction starts from the 3PI of metal conductor/ CaTiO_3 / electrolyte, CaTiO_3 near 3PI will first become titanium low oxide and other

intermediate products, then reaction interface becomes metal conductor $/\text{Ti}_x\text{O}_y/$ electrolyte. As time goes on, the low-price oxide of titanium becomes $\text{Ti}[\text{O}]_6$, and the reaction interface becomes $\text{Ti}_x\text{O}_y/\text{Ti}[\text{O}]_6/$ electrolyte. Finally, $\text{Ti}[\text{O}]_6$ is gradually deoxidized into titanium metal, at which time 3PI becomes $\text{Ti}/\text{Ti}[\text{O}]_6/$ electrolyte. In summary, 3PI is formed by two solid phase transitions. The reduction of CaTiO_3 first occurs in metal conductor/ $\text{CaTiO}_3/$ electrolyte, which makes CaTiO_3 reducing to intermediate products and release O^{2-} and Ca^{2+} into molten salt at the same time. The subsequent reduction will be carried out at the newly formed reaction interface, making multiple 3PI migrate to the interior of CaTiO_3 cathode, until the entire cathode completely reduced to titanium. This model, in which multiple 3PIs migrate from the outside to the inside at the same time, is suitable for most molten salt electro-deoxidation reactions caused by the solid phase transition of the non-conductor[25-27]. Figure 16 shows the schematic diagram of the generation and migration of 3PI in the electro-deoxidation process of a quarter of CaTiO_3 cathode sheet.

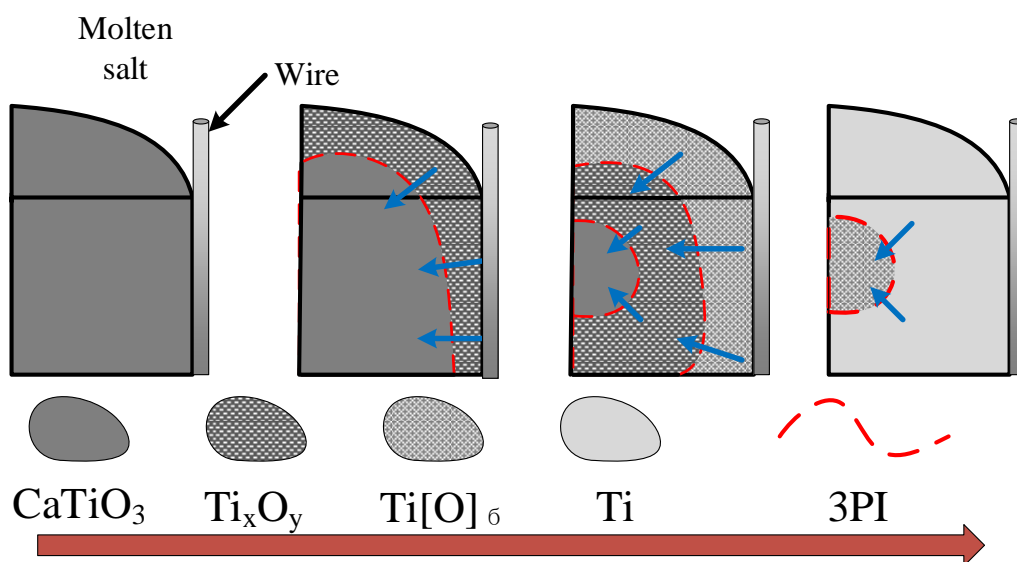


Figure 16. Schematic diagram of 3PI gradual migration

4. CONCLUSION

In this study, the process of reduction of CaTiO_3 to titanium in molten $\text{CaCl}_2\text{-NaCl}$ salt was explained theoretically and experimentally. According to thermodynamic calculations, the decomposition voltages of the CaTiO_3 reduction to titanium and titanium oxides are much lower than that of $\text{CaCl}_2\text{-NaCl}$ molten salt, so CaTiO_3 can be reduced to titanium in this molten salt system. The reduction of CaTiO_3 to titanium has a lower decomposition voltage, so its reduction process should be a multistep reduction process. By comparing the energy band structures and densities of states of CaTiO_3 and TiO_2 , we found that CaTiO_3 more easily forms titanium, and Ca^{2+} in CaTiO_3 is easily removed. The electrolysis experiments of CaTiO_3 at 750°C and 3.2 V for different times show that the deoxidation process of CaTiO_3 in molten $\text{CaCl}_2\text{-NaCl}$ salt is as follows: $\text{CaTiO}_3 \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{TiO}$, $\text{Ti}_2\text{O} \rightarrow \text{Ti}[\text{O}]_6 \rightarrow \text{Ti}$.

The deoxidation process of CaTiO_3 is carried out by the migration of multiple 3PIs. The migration process of 3PI is as follows: metal wire/ CaTiO_3 /electrolyte \rightarrow metal wire/ Ti_xO_y /electrolyte \rightarrow $\text{Ti}_x\text{O}_y/\text{Ti}[\text{O}]_6$ /electrolyte \rightarrow $\text{Ti}/\text{Ti}[\text{O}]_6$ /electrolyte.

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