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# Investigation of the electrochemical reduction of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> in CaCl<sub>2</sub> molten salt



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### A R T I C L E I N F O

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# ABSTRACT

Sodium titanate (Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>), as an intermediate product for producing TiO<sub>2</sub> through alkaline process, was used as precursor to prepare Ti metal successfully by FFC Cambridge Process. For the aim to gain insight into the electro-reduction mechanism, the sintered Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> pellets(~1.83 mm thinkness, open porosity ~20%) were electrolysed using them as cathodes against graphite counter electrode in the molten CaCl<sub>2</sub>. The experiments were carried out at 900 °C and the applied voltage was 3.1V. Partially reduced samples were prepared by terminating the reduction process after different electrolysis times. The obtained samples were characterised by means of X-ray diffraction analysis, SEM and EDS. The results show that Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> reacts easily with molten CaCl<sub>2</sub> as  $2Na_2Ti_3O_7 + 2CaCl_2 \rightarrow Ca_2Ti_2O_6 + 4TiO_2 + 4NaCl and Ca<sub>2</sub>Ti<sub>2</sub>O<sub>6</sub> <math>\rightarrow 2CaTiO_3$ . The electrochemical reduction of sodium titanate proceeds via sequential formation of CaTiO<sub>3</sub>, titanium sub-oxides (such as Ti<sub>4</sub>O<sub>7</sub>, Ti<sub>3</sub>O<sub>5</sub>, Ti<sub>2</sub>O<sub>3</sub> and TiO), CaTi<sub>2</sub>O<sub>4</sub>, Ti-O solid solution and Ti. The whole reduction can be divided into three stages: the first stage is that Ca<sup>2+</sup> ions from electrolyte are inserted into Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> particles leading to the formation of titanium sub-oxides and calcium titanates (CaTiO<sub>3</sub> and CaTi<sub>2</sub>O<sub>4</sub>); the second stage is that calcium titanates are reduced into Ti-O solid solution from outside to inside of the pellets; the third stage is that the formed Ti-O solid solution is further deoxidised to form Ti metal.

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# 1. Introduction

As a promising method for preparing Ti metal, FFC Cambssridge Process has been studied for about twenty years [1-11]. Its main mechanism is oxygen ionisation of cathode oxides in CaCl<sub>2</sub> molten salt under the driving of a voltage that is below the decomposition potential of CaCl<sub>2</sub> but higher than reduction potential of titanium oxides. The ionised oxygen passes into electrolyte from oxide pellets and discharged on graphite anode to evolve CO and CO<sub>2</sub> gas. The whole electro-deoxidation process could be summarized as follows:

Cathode: 
$$TiO_2 + 4e^- \rightarrow Ti + 20^{2-}$$
 (1)

Anode:  $xO^{2-} + C \rightarrow CO_x + 2xe^- (x = 1 \text{ or } 2) (2)$ 

Using TiO<sub>2</sub> as the precursor is one of the advantages comparing

to Kroll process for producing Ti metal, because the transportation and storage of TiO<sub>2</sub> is easier than TiCl<sub>4</sub>. However, the production of TiO<sub>2</sub> by the traditional sulphate process or chloride process is still a highly energy-wasting and high-pollution process. Besides, high purity  $TiO_2$  would be more expensive than  $TiCl_4$  [12]. That is because that, in the pigment industry, TiCl<sub>4</sub> is the precursor to produce TiO<sub>2</sub>. Meanwhile, TiO<sub>2</sub> produced via the traditional sulphate process is priced in the market at similar prices to that of chloride route pigment, which means the TiO<sub>2</sub> produced via the traditional sulphate process could be not cheaper. In recent years, a novel process for preparing TiO<sub>2</sub> was invented, called alkaline process [13-16]. In the process, ilmenite is decomposed in concentrated KOH or NaOH solution into potassium or sodium titanates which can be converted into pigment grade titanium dioxide after further treatments such as acid leaching and calcination. In the process, potassium or sodium titanates, as the intermediate products, are produced more easily than TiO<sub>2</sub>. Therefore, using sodium titanate (Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>) to replace TiO<sub>2</sub> as precursor to prepare Ti metal by FFC Cambridge process was investigated in this paper.





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### 2. Experiment

Anhydrous CaCl<sub>2</sub> (10005861 Sinopharm) was dried for 4 h at 300 °C under vacuum before use. The CaO content of the dried salt was estimated by acid-base titration method and was found to be about 0.045% wt%. Sodium titanite (98 wt%, Na2Ti3O7, Shanghai Dian Yang Industry co. Ltd) powder was pressed into pellets under the axial pressure of 40 MPa. Then these pellets were sintered for 4 h at 900 °C. The sintered pellets  $(3.00 \pm 0.03g, 28.7 \text{ mm diameter})$ and 1.83 mm thickness), whose porosity was measured by Mercury Porosimeter and is about 20%, were attached to a molybdenum wire (2 mm diameter, 700 mm long) that was employed as the current collector of cathode. A high-purity graphite rod (10 mm diameter, 80 mm long) was used as anode, which was connected with a stainless steel collector. Alumina crucibles (80 mm inner diameter and 120 mm high) were used as containers for molten CaCl<sub>2</sub>. 500g dried CaCl<sub>2</sub> salt was taken in an alumina crucible and placed in a leak tight reactor vessel. Before heated, the vessel was evacuated to 10Pa and then was replenished with high-purity Ar gas. This process was repeated twice. Then Ar gas passed continuously through the reactor vessel at 2L/min until the end of each experiment. The vessel was heated by silicon carbide rods. When the salt was heated to 900 °C, the graphite anode and the sodium titanate pellet were inserted into molten salt through electrode holes at the furnace cover. The applied voltage between the cathode and anode was 3.1V.

The partially reduced samples were obtained after different electrolysis times. After each experiment, the sample was moved out from molten salt and cooled down rapidly at argon atmosphere. Then they were rinsed with flowing tap water to remove the solidified molten salt clinging to the surface of samples and were dried in vacuum oven at room temperature. The microstructure and constituents of samples were analysed by SEM and EDS (S-4800, Hitachi). The phase compositions of the partially reduced samples were analysed by X-ray diffraction analyser (X'Pert Pro MPDDY2094, PANalytical B.V with CuK<sub> $\alpha$ </sub> radiation). The content of oxygen in final product was tested by oxygen/nitrogen analyser (TC500 LECO).

# 3. Results

Fig. 1a presents the XRD spectrum of the precursor material after sintering for 4 h at 900 °C. The main phase is  $Na_2Ti_3O_7$ . The SEM image (in Fig. 1b) shows the  $Na_2Ti_3O_7$  present rod-like particles ranging from 1 µm to 3 µm in length. Fig. 1d is the sectional SEM image of a sodium titanite ( $Na_2Ti_3O_7$ ) pellet after 4 h of submerging in molten CaCl<sub>2</sub> at 900 °C. The particles were still rod-like, but the phase compositions of the pellets had become a mixture of TiO<sub>2</sub>, CaTiO<sub>3</sub> and little Ca<sub>2</sub>Ti<sub>2</sub>O<sub>6</sub> as shown in Fig. 1c. At the same time, it was observed that the space between the particles was filled with electrolyte. Fig. S1 (in the supplementary materials) shows the X-ray diffraction patterns of  $Na_2Ti_3O_7$  pellets submerging in CaCl<sub>2</sub> melted salt for different times at 900 °C.  $Na_2Ti_3O_7$  reacts with molten CaCl<sub>2</sub> easily to form Ca<sub>2</sub>Ti<sub>2</sub>O<sub>6</sub> was transformed into CaTiO<sub>3</sub> completely. The involved reactions are as follows.

 $2Na_2Ti_3O_7 + 2CaCl_2 \rightarrow Ca_2Ti_2O_6 + 4TiO_2 + 4NaCl$ (3)

$$Ca_2Ti_2O_6 \rightarrow 2CaTiO_3$$
 (4)

When a voltage of 3.1V was applied between a  $Na_2Ti_3O_7$  cathode and a graphite anode in molten CaCl<sub>2</sub>, the  $Na_2Ti_3O_7$  pellet transformed into a mixture of CaTiO<sub>3</sub>,  $Ti_2O_3$  and little Ca<sub>2</sub>Ti<sub>2</sub>O<sub>6</sub> in ~ 6min as shown in Fig. 2c(S1). From the experiments, it was found that applying a potential promotes reaction (2). As the reaction time went on, the diffraction peaks of NaCl became weaker and weaker, which indicates the pellets have a good diffusion channel for ions.

The theoretical decomposition potential of CaCl<sub>2</sub> at 900 °C is 3.137V, which is calculated from thermodynamic data according to Nernst equation [17]. In experiments, the observed decomposition potential of CaCl<sub>2</sub> agrees well with the calculated value. Fig. 2a shows the typical current vs. time (I-t) curve during the electrochemical reduction experiments performed with a Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> pellet as the cathode and a graphite rod as the anode under an applied voltage of 3.1V. The current jumped to about 3A in the moment the voltage was applied and then decreased sharply in 1 min, which could be attributed to the double layer charging and the accumulation of adatoms on the electrode. In the next minutes, the current increased quickly again to about 3A. According to 3PIs (three-phase interlines) propagation models in initial phase of electrodeoxidation, that could be due to the expansion of the 3PIs [18]. After passing through the maximum value, the current decayed with time. Until about 4 h later, the current levelled out at about 0.7A. The decreasing again of the current occurred after about 16 h. Finally the current decreased to about 0.3A in 22 h. Curves of current against time for an experiment are closely related to the rate of reaction, with a faster rate corresponding to a higher current. And the rate of reaction could be again related with the phase compositions of electrode. For the experiments here, the sudden change of the current tends to imply the possible change of the phase compositions of cathode pellets. On the I-t curve, two peaks (A, B), two inflection points (C and D) and two shoulders (E and F) appeared successively. Thereby these time points were chose as the terminating time points of polarisation.

Table 1 lists the experiment conditions and the corresponding results. After about 6min of polarisation, the sample (S1) was found to be predominantly composed of CaTiO<sub>3</sub> and Ti<sub>2</sub>O<sub>3</sub>. Magneli phases, such as  $Ti_4O_7$  and  $Ti_3O_5$ , were not detected here. But they were detected in the sample quenched after 10min of polarisation when cutting down the voltage to 2.8V, as shown in Fig. S2 (in the supplementary materials). Prolonging the polarisation time to about 10min, the sample (S2) consisted of CaTiO<sub>3</sub>, Ti<sub>2</sub>O<sub>3</sub> and little TiO; to ~37min, the sample (S3) was mainly comprised of CaTiO<sub>3</sub>, Ti-O solid solution (Ti<sub>2</sub>O) and little CaTi<sub>2</sub>O<sub>4</sub>; and to 4 h, the sample (S4) consisted mainly of Ti-O solid solution (Ti<sub>3</sub>O) and little CaTiO<sub>3</sub>. Fig. 2c shows the XRD patterns of the partially reduced samples. During around 6–37min of polarisation, CaTiO<sub>3</sub> was much more than other phases and decreased slightly with electrolysis times; titanium suboxides gradually disappeared; Ti-O solid solution and CaTi<sub>2</sub>O<sub>4</sub> began to form. During around 0.6-4 h of polarisation, CaTi<sub>2</sub>O<sub>4</sub> disappeared completely, CaTiO<sub>3</sub> diminished dramatically and Ti-O solid solution (Ti<sub>3</sub>O) increased substantially. After about 16 h of polarisation, the sample (S5) was reduced into Ti metal but the oxygen content was up to 1.6 wt%. Prolonging the polarisation time to 22 h, the oxygen content of the sample (S6) decreased to about 0.6 wt%. At the same time, it was found that the pellets became thinner and thinner with the step-by-step reduction of the pellets.

Fig. 2b shows the SEM images of the cross sections of S1-S6. The samples began to delaminate after 6min of polarisation. The outer layer is the reduced region and the core is the less reduced region. As the polarisation time went on, the outer layer grew thick and the core shrunk progressively. The pellets were gradually reduced from outside to inside. After 4 h of polarisation, the reduced region was found to be porous and sintered slightly, and the less reduced region was sintered fast and finally became a compact metal sheet of about 0.7 mm in thickness.



**Fig. 1.** (a) X-ray diffraction spectrum of the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> pellets after sintering in air at 900 °C for 4 h, showing Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> ((A), ICDD: 00-031-1329), little Na<sub>2</sub>Ti<sub>5</sub>O<sub>11</sub> ((B), ICDD: 00-011-0289) and Na<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> ((C), ICDD: 01-075-2497); (b) SEM image of the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> pellets after sintering in air at 900 °C for 4 h; (c) X-ray diffraction spectrum of the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> pellets after submerging in molten CaCl<sub>2</sub> at 900 °C for 4 h, showing TiO<sub>2</sub> ((A), ICDD: 01-073-2224), CaTiO<sub>3</sub> ((B), ICDD: 01-076-2400), little Ca<sub>2</sub>Ti<sub>2</sub>O<sub>6</sub> ((C), ICDD: 00-040-0103); and the non-ascribed peaks mainly corresponds to CaCl<sub>2</sub>·4H<sub>2</sub>O and CaCl<sub>2</sub>·6H<sub>2</sub>O). (d) the sectional SEM image of the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> pellets after submerging in molten CaCl<sub>2</sub> at 900 °C for 4 h

(9)

# 4. Discussion

From the XRD analysis of the partially reduced samples, the possible reactions occurred on cathodes during polarisation are as followed [3,7].

 $5Na_{2}Ti_{3}O_{7} + 7Ca^{2+} + 4e^{-} \rightarrow 2Ti_{4}O_{7} + 7CaTiO_{3} + 10Na^{+}$ (5)

$$4\text{Ti}_4\text{O}_7 + \text{Ca}^{2+} + 2e^- \rightarrow 5\text{Ti}_3\text{O}_5 + \text{Ca}\text{Ti}\text{O}_3 \tag{6}$$

$$3\text{Ti}_3\text{O}_5 + \text{Ca}^{2+} + 2\text{e}^- \rightarrow 4\text{Ti}_2\text{O}_3 + \text{Ca}\text{Ti}\text{O}_3$$
 (7)

$$2Ti_2O_3 + Ca^{2+} + 2e^- \rightarrow 3TiO + CaTiO_3$$
 (8)

$$CaTiO_3 + TiO \rightarrow CaTi_2O_4$$

$$CaTi_2O_4 + Ca^{2+} + 2e^- \rightarrow 2TiO + 2CaO$$
 (10)

$$\mathrm{TiO} + (1-\delta)\mathrm{Ca}^{2+} + 2(1-\delta)\mathrm{e}^{-} \to \mathrm{Ti}[\mathrm{O}]_{\delta} + (1-\delta)\mathrm{CaO}$$
(11)

$$\label{eq:cational} \begin{split} \text{CaTi}_2\text{O}_4 + (3\text{-}2\delta)\text{Ca}^{2+} + 2(3\text{-}2\delta)\text{e}^- \rightarrow 2\text{Ti}[\text{O}]_\delta + (4\text{-}2\delta)\text{Ca}\text{O} \eqno(12) \end{split}$$

$$CaTiO_3 + (2-\delta)Ca^{2+} + 2(2-\delta)e^- \rightarrow Ti[O]_{\delta} + (3-\delta)CaO$$
(13)

$$Ti[O]_{\delta} + \delta Ca^{2+} + 2\delta e^{-} \rightarrow Ti + \delta CaO$$
(14)

The reduction process is similar with that of  $TiO_2$  the electroreduction mechanism of which was determined by Schwandt, C.

etc. [3,7]. But compared the reduction with TiO<sub>2</sub>, more CaTiO<sub>3</sub> formed during the reduction process of Na2Ti3O7. Some CaTiO3 was reduced according to reaction (7)-(9). The rest was reduced directly into Ti-O solid solution as reaction (11). The proof is that only CaTiO<sub>3</sub> and Ti-O solid solution were detected in the sample (S4) after 4 h of polarisation. From these reactions, the whole reduction process of Na2Ti3O7 pellets can be divided into three stages. The first stage is the transformation of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> to calcium titanates (CaTiO<sub>3</sub> and CaTi<sub>2</sub>O<sub>4</sub>) and titanium sub-oxides (Ti<sub>4</sub>O<sub>7</sub>, Ti<sub>3</sub>O<sub>5</sub>, Ti<sub>2</sub>O<sub>3</sub> and TiO) and occurred during ~30min of polarisation. The involved are reaction (3)–(7). This stage is mainly the insertion of  $Ca^{2+}$  into pellets and no CaO or  $O^{2-}$  ions are released, which means the amount of oxygen in pellet during the first is changeless. This stage processed very quickly. The second stage is the transformation of calcium titanates and TiO formed in first stage to Ti-O solid solution and occurred during 0.2 ~ 4 h of polarisation. During this stage, amounts of CaO are released and reaction (8)-(11) are involved. From the I-t curves in Fig. 2, the reduction slowed down gradually with polarisation time during the second stage. The third stage is the deoxidation of Ti-O solid solution and processed during about 4-22 h of polarisation. Reaction (12) is involved. This stage processed very slowly. At the same time, it was found that the thicknesses of the pellets just decreased by about 2% in the first two stages of the reduction. But during around 4-22 h of polarisation, the thickness of the pellets decreased to about 40% of the initial. Combined with the XRD analysis, the sinter occurred mainly during the transformation of Ti-O solid solution to Ti metal. From our unreported data, though the sample was reduced into Ti<sub>6</sub>O (Ti-O



**Fig. 2.** (a) Current vs. time curve of an electro-deoxidation experiment under a voltage of 3.1V at 900 °C. Electrolyte: calcium chlotide; cathode: Sodium titanate pellets ( $3 \pm 0.05g$ ); anode: graphite rod (10 mm diameter, 80 mm long); anode-to-cathode distance: 6 cm; atmosphere: Ar gas; (b) the sectional SEM images of the samples quenched after different times of electrolysis, showing the decreasing thicknesses with the extension of electrolysis times: the sample (S1) after 6min of electrolysis: 1.83 mm thickness; the sample (S2) after 10min of electrolysis: 1.83 mm thickness; the sample (S3) after 37min of electrolysis: 1.83 mm thickness; the sample (S4) after 4 h of electrolysis: 1.79 mm thickness; the sample (S5) after 16 h of electrolysis: 0.9 mm thickness; and the sample (S6) after 22 h of electrolysis: 0.7 mm thickness; (c) X-ray diffraction spectrums of the sample quenched after different times of electrolysis; 0.9 mm thickness; and the sample (S6) after 22 h of electrolysis: 0.7 mm thickness; (c) X-ray diffraction spectrums of the sample quenched after different times of electrolysis; 0.9 mm thickness; and the sample (S6) after 22 h of electrolysis: 0.7 mm thickness; (c) X-ray diffraction spectrums of the sample quenched after different times of electrolysis; 0.9 mm thickness; and the sample (S6) after 22 h of electrolysis: 0.7 mm thickness; (c) X-ray diffraction spectrums of the sample quenched after different times of electrolysis; 0.9 mm thickness; de sample (S1) after 6 min of electrolysis showing CaTiO<sub>3</sub> ((A), ICDD:01-076-2400), Ti<sub>2</sub>O<sub>3</sub>((B), ICDD: 01-071-1053) and Ta<sub>2</sub>O<sub>6</sub> ((C), ICDD: 00-008-0117); the sample (S2) after 10 min of electrolysis showing CaTiO<sub>3</sub> ((A), ICDD:01-076-2400), Ti<sub>2</sub>O<sub>3</sub>((B), ICDD: 01-074-1952); the sample (S4) after 4 h of electrolysis showing CaTiO<sub>3</sub> ((A), ICDD:01-076-2400), Ti<sub>2</sub>O<sub>3</sub> ((B), ICDD: 01-074-1952); the sample (S4) after 4 h of electrolysis showing Ti ((A), ICDD: 01-078-1583); the sample (S5) after 16 h of electrolysis showing Ti ((A), ICDD: 01-089-4893)

# Table 1 A lists the experiment conditions and the corresponding results.

Test No.	Porisity	Voltage	Time	Results	
				Thickness of the reduced pellets (mm)	Phases(the size of the particles*)
S1	23%	3.1V	6 min	1.8	CaTiO <sub>3</sub> (5.8 nm), Ti <sub>2</sub> O <sub>3</sub> , Ca <sub>2</sub> Ti <sub>2</sub> O <sub>6</sub>
S2			10min	1.8	CaTiO <sub>3</sub> (28.6 nm), Ti <sub>2</sub> O <sub>3</sub> , TiO
S3			37min	1.8	CaTiO <sub>3</sub> (41.5 nm), Ti <sub>2</sub> O(44.6 nm), CaTi <sub>2</sub> O <sub>4</sub>
S4			4 h	1.75	Ti <sub>3</sub> O(50.2 nm), CaTiO <sub>3</sub>
S5			16 h	0.9	Ti(20.3 nm), TiC
S6			22 h	0.7	Ti(23.8 nm)
S7		2.8V	10min		CaTiO <sub>3</sub> (31.0 nm), Ti <sub>4</sub> O <sub>7</sub> , Ti <sub>3</sub> O <sub>5</sub>

\* The particle sizes were estimated from the XRD patterns according to Scherrer equation.

solid solution containing about 5% oxygen) under a more positive potential at 900 °C, it still was not sintered visually. That indicates that the Ti-O solid solution with a high content of oxygen (more than 5 wt%) is hard to be sintered on macro point.

Fig. 3a shows the SEM image of the core of S3. From the EDS analysis, the cracked region is the solidified electrolyte and the fine particle region is mainly composed of calcium titanates and/or Ti-O solid solution. Fig. 3b shows the SEM image of the core of S4. The EDS analysis indicates that there are amounts of CaO, which agrees well with the result of the XRD analysis (Fig. 3d(I)) obtained from the core of S4 that was tested without the treatment of washing or pickling. By comparison, the CaCl<sub>2</sub> (which was converted to CaClOH because of its famous water absorption) is very little. So much CaO remaining in the inner layer of S4 indicates that the reduction rate of calcium titanates is much higher than the diffusion rate of CaO from inside to outside of the pellets. The phase diagram of CaO-CaCl<sub>2</sub>, as shown in Fig. S3, displays the solubility of CaO in molten

CaCl<sub>2</sub> at 900 °C is about 12.6 wt% [19]. Excess CaO will precipitate and occupies the pores in pellets. That will block up the channel for electrolyte (molten CaCl<sub>2</sub>) entering the inner of the pellets. According to the reaction (8)–(11), the lack of Ca<sup>2+</sup> will slow down the reduction. That might be the reason leading to a lower reduction rate in second stage. Fig. 3c shows the SEM image of the outer layer of S4 and Fig. 3d(II) shows the XRD pattern of the out layer of S4, which indicated the outer layer was reduced into Ti-O solid solution (Ti<sub>3</sub>O). From the SEM image, the finer Ti-O solid solution particles were sintering together. Meanwhile, some macrovoid form. Fig. 2b(S4) also shows that the out layer of S4 presents a porous structure on a macroscale. Those indicated that the electrolyte had a good diffusion channel in the out layer of the samples during polarisation.

With the prolongation of the polarisation time to 16 h, the pellet was reduced and sintered into a compact metal sheet of about 0.9 mm thickness. The thickness decreased by about 50%. Fig. 4a–d



**Fig. 3.** (a) The sectional SEM image of the core of the sample (S3) quenched after 37 min of electrolysis, Zone I corresponding to the solidified electrolyte and Zone II corresponding to a mixture of calcium titanates and/or Ti-O solid solution; (b) the sectional SEM image of the core of the sample (S4) quenched after 4 h of electrolysis, showing amounts of CaO; (c) the sectional SEM image of the out layer of the sample (S4) quenched after 4 h of electrolysis, showing Ti-O solid solution and macropore; (d) the X-ray diffraction spectrums of the core and the out layer of the sample (S4) quenched after 4 h of electrolysis, the core (I) showing CaO ((A), ICDD: 01-075-0264), CaTiO<sub>3</sub> ((B), ICDD: 01-078-1013), Ti<sub>2</sub>O ((C), ICDD: 01-073-1116) and CaClOH ((D), ICDD: 00-036-0983), the non-ascribed peaks corresponding to Ca(OH)<sub>2</sub>; the out layer (II) showing Ti<sub>3</sub>O ((E), ICDD; 01-076-1644).



**Fig. 4.** (a) The sectional SEM image of the outermost layer of the samples quenched after 16 h of electrolysis; (b) the sectional SEM image of the secondary outer layer of the sample quenched after 16 h of electrolysis; (c) the sectional SEM image of the tertiary outer layer of the sample quenched after 16 h of electrolysis; (d) the sectional SEM image of the core of the sample quenched after 16 h of electrolysis; (e) the sectional SEM image of the sample retrieved after 22 h of electrolysis; showing Ti.

show the SEM images of S5 from outside to inside. The sample has a sponge-like microstructure. From inside to outside of the sample, the particles were sintered more and more severely and the oxygen content was lower and lower. That proves that the higher the oxygen content of Ti-O solid solution particles is, the harder it is to be sintered. From Fig. 2b, the thickness of the pellet decreased further about 0.7 mm after about 22 h of polarisation. At this time, the sample became very compact as shown in Fig. 4e. The EDS analysis indicates the pellet has completely transformed into Ti metal.

From the above discussion, a schematic of the progress of electrochemical reduction occurring on Na2Ti3O7 pellets placed in CaCl<sub>2</sub> melt has been depicted in Fig. 5. Driven by a potential which is close but positive to calcium metal deposition, Na2Ti3O7 pellets can be reduced into Ti metal step by step. The reduction could be divided into three stages. In the first stage of electrolysis,  $Ca^{2+}$  ions from electrolyte are inserted into Na2Ti3O7 particles leading to the formation of Ca-Ti-O compounds and titanium sub-oxides. The involved are reaction (3)-(7) whose potentials are more positive. At the same time, there are enough  $Ca^{2+}$  ions in the pellets for these reactions in this stage. Thus this process goes very fast. On continued polarisation, the formed calcium titanates and titanium sub-oxides (the main is TiO) are reduced into Ti-O solid solution from outside to inside. Meanwhile, amounts of CaO are released. The formed CaO could not move out timely but precipitates inside the pellets. That blocks up the channel for electrolyte entering the inner of the pellets, leading to the lack of Ca<sup>2+</sup> ions for reaction (8)–(11). Thus the reduction at second stage goes slowly. During the last stage, the formed Ti-O solid solution is further deoxidised to form Ti metal particles which will be sintered together quickly. From the experiments, this is the most time-consuming process. The main reason might be that the diffusion of oxygen in Ti-O solid solution is very slow.

From the above, the second stage is an electrochemical process controlled by the mass transfer of  $O^{2-}$  ions to the outside of the

pellet and it could be described by the Cottrell equation (Eq. (13)) [20].

$$i = nFCA \left(\frac{D}{\pi t}\right)^{1/2} \tag{15}$$

where, *i*, current; *n*, number of electrons involved; *F*, Faraday constant; *D*, diffusion coefficient; *C*, concentration of species in the bulk and *t*, time. Fig. 6a shows the *i*- $t^{-1/2}$  curves of four electrolysis experiments which correspond to Test.S3-S6 shown in Table 1. The curves have similar trends and can be divided into three zones. The zone I corresponds to the double layer charging and the accumulation of adatoms on the electrode which occurred in 1 min after potential switch; the zone II corresponds to the reduction of Ca-Ti-O compounds into Ti-O solid solution, the rate of which is controlled by mass transfer of Ca<sup>2+</sup> ions. The relationship between *i* and  $t^{-1/2}$  in zone III is approximatively linear, which indicates that the second stage can be described by the Cottrell equation. After linear fitting towards the curves in zone III, the slopes can be obtained and are about 43, 48, 47 and 55 respectively.

In addition, if considering the expansion of the 3PIs in zone II as a nucleation and growth process of Ti or Ti-O solid solution, the electro-deoxidation could be explained be Scharifker-Hill model which is an effective diagnostic tool for the evaluation of the dependence of current on time for nucleation with diffusioncontrolled growth [21,22]. According to the models, there are two limiting nucleation mechanisms which are given as follows:

For the instantaneous nucleation:

$$\left(\frac{i}{i_m}\right)^2 = \frac{1.9542}{t/t_m} \{1 - exp[-1.2564(t/t_m)]\}^2$$
(16)

For the progressive nucleation:



**Fig. 5.** A schematic showing the progress of electro-deoxidation of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> pellets in molten CaCl<sub>2</sub>. At first, Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> particles are decomposed into calcium titanates (including CaTiO<sub>3</sub>, Ca2Ti2O6 and CaTi2O4) and titanium suboxides (Ti<sub>4</sub>O<sub>7</sub>, Ti<sub>3</sub>O<sub>5</sub>, Ti<sub>2</sub>O<sub>3</sub> and TiO). Then all titanium suboxides and slight amounts of calcium titanates are reduced into Ti-O solid solution. Meanwhile slight amounts of CaO are released. Next, all the calcium titanates were reduced into Ti-O solid solution. Meanwhile amounts of CaO form in the pellets, which could block up the channel for electrolyte entering the inner of the pellets and influence the reduction rate. The last step is that the Ti-O solid solution is further deoxidised into Ti metal. Meanwhile the pellets are sintered and shrink greatly.



Fig. 6. (a) Current vs. inverse square root of polarisation time curves of four electrolysis experiments which correspond to Test.S3-S6 shown in Table 1; (b) Normalized transients  $(i/i_m)^2$  vs.  $t/t_m$  curves when  $t/t_m$  is in 0–10 range which corresponds to the first two stages of an electro-deoxidation experiment. The full lines correspond to the curves obtained from the four electrolysis experiments; the black dot dash line corresponds to the calculated curve for the instantaneous nucleation and diffusionlimited growth according to Eq. (14); and the red dot dash line corresponds to the calculated curve for progressive nucleation and diffusion-limited growth according to Eq. (15). (c) Normalized transients  $(i/i_m)^2$  vs.  $t/t_m$  curves when  $t/t_m$  is in 10–160 range which corresponds to the last stages of an electro-deoxidation experiment. The full line correspond to the curve obtained from Expt.3; the black dot dash line corresponds to the calculated curve for the instantaneous nucleation and diffusion-limited growth according to Eq. (14); and the red dot dash line corresponds to the calculated curve for progressive nucleation and diffusion-limited growth according to Eq. (15). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

$$\left(\frac{i}{i_m}\right)^2 = \frac{1.2254}{t/t_m} \left\{ 1 - \exp\left[-2.3367(t/t_m)^2\right] \right\}^2$$
(17)

where  $i_m$  and  $t_m$  are the maximum coordinates of *i* transient. Fig. 6b show the  $(i/i_m)^2 - t/t_m$  curves of the four experiments, comparing with the curves calculated from Eqs. (14) and (15). The four experimental curves of the electro-deoxidation have similar trends and follow mostly the progressive nucleation, which agrees well with C. Osarinmwian's study [22].

Fig. 6c shows the  $(i/i_m)^2 - t/t_m$  curves of Expt.3 when  $t/t_m$  is in 20–160 range. When  $t/t_m$  is greater than 30, which corresponds to the third stage of the electro-deoxidation, the curve of the experiment deviates obviously from those calculated from Eqs. (14) and (15). That is mainly due to the electro-deposition of Ca metal and C on the surface of cathode and the low diffusion rate of O in Ti-O solid solution.

#### 5. Conclusion

In present paper, Ti metal was prepared successfully using the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> pellets as precursor through FFC Cambridge Process. After 22 h of polarisation at 900 °C, a compact Ti metal sheet was obtained. Its oxygen content was about 0.6 wt%. The reduction proceeded via sequential formation of CaTiO<sub>3</sub>, titanium sub-oxides (such as Ti<sub>4</sub>O<sub>7</sub>, Ti<sub>3</sub>O<sub>5</sub>, Ti<sub>2</sub>O<sub>3</sub> and TiO), CaTi<sub>2</sub>O<sub>4</sub>, Ti-O solid solution and Ti. During the reduction, the pellets sintered seriously, which occurs mainly during the transformation of Ti-O solid solution to Ti metal. Besides, it was found that Ti-O solid solution containing more than 5% oxygen is hard to be sintered, which is advantageous to the out diffusion of CaO during the second stage of reduction. In spite of this, the second stage is one of the control steps of the reduction because of the low diffusion rate of CaO in pellets. That might be improved by increasing the porosity of precursors. Another control step during the reduction is the transformation of Ti-O solid solution to Ti metal. That is due to the low diffusion rate of oxygen in Ti-O solid solution.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.electacta.2019.06.072.

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