

Dependency of Gases Released from the Anode on Perovskite Formed in the Cathode in the Process of the Preparation of Titanium

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Abstract: Perovskite is the inevitable phase formed in the cathode during electrolysis of TiO_2 in molten CaCl_2 by FFC Cambridge process. Dependency of perovskite in the cathode on gases released from the anode in the process of titanium preparation was studied. The results show that three stages are obtained based on the phases formed in the cathode, including formation of perovskite, deoxygenation from perovskite and titanium suboxides to TiO and deoxygenation from TiO to Ti . Perovskite formed in the cathode is closely related to gases released from the anode although the decomposition voltage is lower than that of CaCl_2 . Chlorine release from the anode is due to overvoltage caused by the formation of perovskite in a short time. Amount of chlorine is dependent on the mass of TiO_2 and generation of different titanium suboxides during electrolysis process. The mass ratio of TiO_2 to chlorine is from 9:2 to 9:4 when titanium suboxides are between Ti_3O_5 and TiO at the first deoxygenation stage. The anode has no obvious consumption during chlorine release. Formation of the perovskite and deoxygenation of Ti_2O_3 are the main limited step to prepare titanium by electrolysis process in molten CaCl_2 . The total current efficiency from TiO_2 to Ti is 24.07%. The current efficiency of the first stage is between 22.37%~44.74% and the second stage is between 30.18%~37.72%.

Key words: molten-salt electrolysis; perovskite; anodic gas

The novel process of FFC Cambridge process to extract titanium has been proposed for almost 20 years. Low current efficiency is the restrictive link for realizing the industrialization of the process^[1-5]. One of the reasons causing low current efficiency is formation of the interphases of perovskite. Initially, some researchers thought that CaTiO_3 in the cathode comes from reaction between TiO_2 and CaO which is produced by hydrolysis of CaCl_2 ^[6]. In 2005 Schwandt et al^[7] proposed that titanium oxides including TiO_2 could react with CaO to form CaTiO_3 . Then CaTiO_3 also reacts with TiO form CaTi_2O_4 . In 2010 Bhagat et al reported that CaTiO_3 is only from the reaction between CaO and TiO_2 and CaTiO_3 is the main phase in the beginning stage^[8]. With the electrolysis time increasing CaTiO_3 is also electrolyzed and finally titanium

metal is obtained. The author thought that CaO comes from Ca^{2+} in molten CaCl_2 and O^{2-} deoxygenated from titanium oxides. Namely, formation of CaTiO_3 on the cathode would consume cation of the molten salt. However, where Cl^- is going to, which is balanced with the consumed cations, is not discussed in the paper. And there is report about chlorine released from the anode but no detailed description^[9]. Until now, there is no quantitative study about effect of the interphase CaTiO_3 on the current efficiency.

In the present paper, gases released from the anode were measured and the consumption of molten salt was also calculated. The dependency of gases released from the anode on perovskite formed in the cathode and the current efficiency of different stages were discussed too.

Received date: July 10, 2018

Foundation item: National Natural Science Foundation of China (51674054)

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1 Experiment

Titanium dioxide powder of 98% specified purity was selected as the oxide precursor. The titanium dioxide was uniaxially pressed at 2.5~5 MPa using a 12 mm diameter into 1.3 g preformed cylinders. Then, these cylinders were sintered at 1173 K for 2 h so that the cylinders had sufficient mechanical strength for the experiments.

A dense alumina crucible which 100 mm internal diameter and 100 mm height was placed in the vertical tubular reactor. The crucible contained approximately 600 g of anhydrous CaCl_2 salt. The water-cooled upper end of the reactor was sealed using a stainless-steel cover with silicone-sealed feed. The sealed reactor system was vacuumed and continually flushed with argon gas. Then, the reactor was heated at a rate of 5 K/min to the target temperature. The constant argon flow was approximately 120 mL/min.

The TiO_2 sample was attached to the steel rod to serve as the cathode using tungsten wire. A graphite rod was used as the anode. When the operating temperature was reached, the system was stabilized for 1 h. Thereafter, the sintered TiO_2 sample and graphite rod were slowly lowered into the melt electrolyte. A constant voltage of 3.1 V was applied between the anode and the cathode.

Fig.1 shows a schematic of the apparatus. The gas exhaust was led into the starch KI solution (100 mL 0.2 g/L soluble starch and 0.08 g/L KI) to detect the released Cl_2 gas. Partial electrolysis was performed for 1, 5, and 10~70 min with a step size of 10 min. Then, the electrodes were removed from the melt into the top of the reactor. At room temperature, the samples of the partial electrolysis were placed in water for several hours to remove the soluble residue CaCl_2 and then dried. The surfaces and fracture surfaces of some dried samples were used for the XRD and SEM analyses. Other samples were inlaid with epoxy resin and ethylenediamine, and the cross-section was obtained for the XRD and SEM analyses.

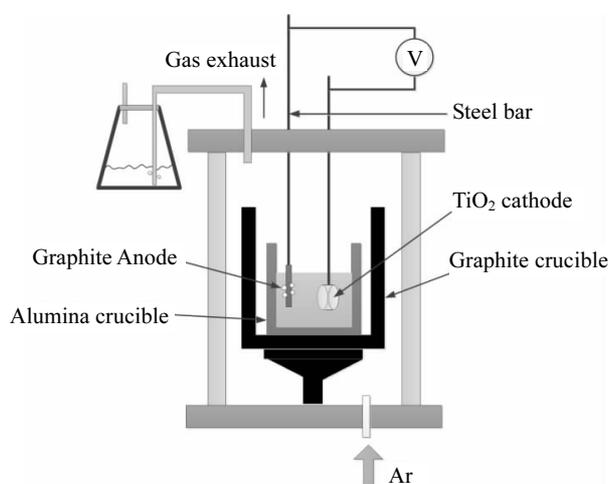


Fig.1 Schematic of the apparatus

The phase composition of the samples was determined through X-ray diffraction analysis (XRD: D/max 2500PC). Each scan was $10^\circ\sim 80^\circ$. The microstructure and chemical composition of the samples were investigated by scanning electron microscopy (SEM, TESCAN VEGA II) and energy-dispersive X-ray analysis (EDS, Oxford INCA Energy 350).

2 Results and Discussion

2.1 Interphases formed on the cathode

Fig.2 shows the morphology of the samples electrolyzed in short time (vertical ordinate, 5~80 min) and in long time (horizontal ordinate, 6~18 h). It can be seen that the morphology of the cathode samples shows obvious changes. Even in 10 min there are some square crystals. With time increasing they become capsules. With further deoxygenation the cathode becomes loose and porous. However, titanium metal is contracted block causing much gaps within the final sample, as shown in Fig.2 (the image is inlaid in Fig.2). Fig.3 shows XRD patterns of the samples electrolyzed at various time. The main phases of titanium oxides which are formed during electrolysis process include TiO_2 , Ti_4O_7 , Ti_2O_3 , TiO , Ti_2O and Ti (Ti-O solid solution) and the main interphases containing calcium are CaTiO_3 , CaO . Based on the phases formed at different times the current curve is divided into three stages, as shown in Fig.4. Stage I includes deoxygenation of TiO_2 and formation of TiO_x and CaTiO_3 . Stage II is deoxygenation from CaTiO_3 and TiO_x to Ti_2O and stage III is deep deoxygenation from Ti_2O to Ti (Ti-O solid solution).

At the end of the stage I there is not TiO_2 found in the cathode. The main phases in the cathode are CaTiO_3 , TiO and a few other titanium suboxides. It can be inferred that there is a proportional relationship among O^{2-} released from TiO_2 , Ca^{2+} from the molten CaCl_2 and the remained TiO_2 . If we con-

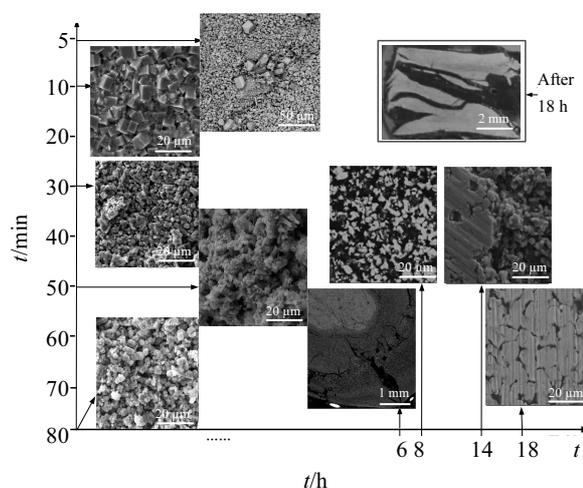


Fig.2 SEM images of the partially reduced sample and the micro picture of TiO_2 electrochemically reduced in molten CaCl_2 for 18 h

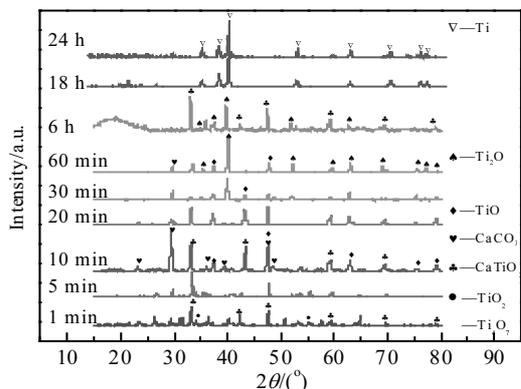


Fig.3 XRD patterns of the samples electrolyzed for different time

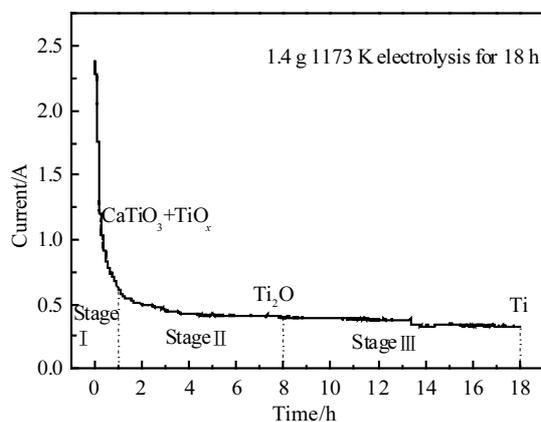


Fig.4 Curve of the current with the electrolysis time increasing

sider that CaO reacts completely with the remained TiO_2 at 1:1 molar no TiO_2 remains in the cathode. During stage II the main processes include deoxygenation and decalcification of CaTiO_3 and deoxygenation of titanium suboxides. At this stage calcium leaves from the cathode as CaO. CaO can be dissolved in CaCl_2 . Sometimes CaO stays the cathode due to limit of the dissolution rate which shows in the form of CaCO_3 in XRD results because of the reaction between CaO and CO_2 in air or water. The main product of stage II is Ti_2O . The final stage is deoxygenation from Ti_2O to TiO (Ti-O solid solute).

In the first stage Ca^{2+} from the molten salt takes part in the reaction on the cathode and forces Cl^- which is balanced with Ca^{2+} to move to the anode.

2.2 Gases released from the anode

KI solution shows blue in the short time of electrolysis and it is no more changed after stage I. At the first stage CO/CO_2 are not obviously detected. This means that at the initial stage the chemical reaction among TiO_2 , Ca^{2+} and O^{2-} is the main behavior. Maybe there are no oxygen ions deviated from the cathode to

the anode. During this stage the current in the molten salt is provided by the ions moving of Ca^{2+} and Cl^- . Ca^{2+} is consumed by the chemical reaction with O^{2-} on the cathode. Cl^- balanced with this consumed Ca^{2+} will constantly move to the anode and pile up, which is finally released from the anode as chlorine. This issue was clarified by ways of the controlled experiment. About 6 g of TiO_2 was processed in molten CaCl_2 (about 600 g). When the outside power switched on the starch KI solution in a gas bottle, which was connected with the anode gas outlet and another gas bottle contained alkaline solution, the solution became blue in a short time which strongly depended on the mass of the TiO_2 . However, the voltage for continuous electrolysis of CaCl_2 is not exceeded. The result proves that formation of CaO and CaTiO_3 is easier than deoxidation of titanium oxides in this stage. In the second stage there is not chlorine released and starch KI solution keeps clear. It means that after stage I there is no more chlorine gas released from the anode. It also deduces that CaTiO_3 just forms in stage I.

In addition, carbon anode consumption depends largely on the electrolysis time, as shown in Fig.5. The surface of the carbon anode submerged in molten salt shows no obvious change except slight consumption at the bottom after electrolysis for 8 h. The surface of the anode begins to be consumed after electrolysis for 10 h and the anode is seriously consumed when the electrolysis time increases to 12 h. This means that decalcification from CaTiO_3 to TiO_x is the main process. Namely, little O^{2-} arrives to the anode during deoxidation of CaTiO_3 . The possible reason is that CaTiO_3 is electrolyzed to CaO and TiO_x slowly in the stage II. Some CaO is dissolved in molten salt and the others stay in the cathode which need long time to dissolve. In these processes little O^{2-} moves to the anode and the current curve is almost horizontal. The anode consumption between 10 and 12 h is much heavy and after 14 h the interdependent relationship between the anode consumption and electrolysis time is decreasing. It can be deduced that deoxidization of Ti_2O is relatively slow.

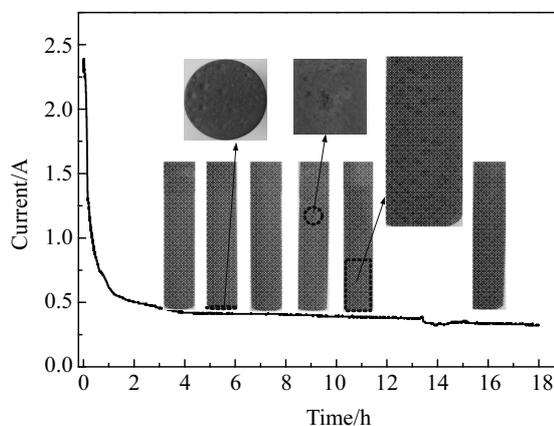


Fig.5 Current-time change curve of anode consumption

In the second stage, the main anodic reaction is the discharge of oxide ions, resulting in the generation of either CO or CO₂. The third stage is the deoxidation stage and the consumption of the anode is heavy.

2.3 Current efficiency

Based on above discussion it can be concluded that formation of CaTiO₃ in the cathode is closely related to gases released from the anode. In addition, amount of O²⁻ deoxidized from TiO₂ is equal to amount of Ca²⁺ and forms the same amount of CaTiO₃ in cathode at stage I. Various titanium suboxides are produced in stage I, such as Ti₄O₇, Ti₂O₃, TiO. To obtain the current efficiency and deoxygenation limit step the following calculation is completed. TiO_x in the first stage is thought the single phase of Ti₃O₅, Ti₂O₃, TiO.

If the main phase of titanium suboxide is Ti₂O₃ at the first stage, the relationship is as follows.

$$1 \text{ mol TiO}_2 = \frac{1}{3} \text{ mol Ti}_2\text{O}_3 + \frac{1}{3} \text{ mol O}^{2-} + \frac{1}{3} \text{ mol TiO}_2 \quad (1)$$

$$\frac{1}{3} \text{ mol O}^{2-} + \frac{1}{3} \text{ mol Ca}^{2+} = \frac{1}{3} \text{ mol CaO} \quad (2)$$

$$\frac{1}{3} \text{ mol CaO} + \frac{1}{3} \text{ mol TiO}_2 = \frac{1}{3} \text{ mol CaTiO}_3 \quad (3)$$

The total electric quantity is 3774.625 C in 1 h, 14965.835 C in 8 h, 28062.335 C in 18 h.

$$Q_1 = \int_0^{1 \text{ h}} Idt = 3774.635 \text{ C} \quad (4)$$

$$Q_2 = \int_0^{8 \text{ h}} Idt = 14965.835 \text{ C} \quad (5)$$

$$Q_3 = \int_0^{18 \text{ h}} Idt = 28062.335 \text{ C} \quad (6)$$

The mass of TiO₂ sample in this study is 1.4 g and the total effective electric quantity from TiO₂ to Ti is 6775 C.

$$n_{\text{TiO}_2} = \frac{1.4 \text{ g}}{80} = 0.0175 \text{ mol} \quad (7)$$

$$Q_{18 \text{ h}} = nzF = 0.0175 \times 4 \times 96500 = 6755 \text{ C} \quad (8)$$

Where, Q is the total electric quantity; n is the number of moles of reduced TiO₂; z is the number of transferred electrons; F is the Faraday constant (96500).

So the total current efficiency in 18 h is 24.07%.

$$\eta_{18 \text{ h}} = \frac{Q_{18 \text{ h}}}{Q_3} \times 100\% = \frac{6755}{28062.335} \times 100\% = 24.07\% \quad (9)$$

The current efficiency of stage I, stage II and stage III is 29.83%, 35.21%, 12.89%, respectively.

Stage I:

$$Q_{1 \text{ h}} = nzF = 0.0175 \times \frac{2}{3} \times 1 \times 96500 = 1125.833 \text{ C} \quad (10)$$

$$\eta_{1 \text{ h}} = \frac{Q_{1 \text{ h}}}{Q_1} \times 100\% = \frac{1125.833}{3774.635} \times 100\% = 29.83\% \quad (11)$$

Stage II :

$$Q_{8 \text{ h}} = (n_1z_1 + n_2z_2) \cdot F \quad (12)$$

$$= (0.0175 \times \frac{1}{3} \times 3 + 0.0175 \times \frac{2}{3} \times 2) \times 96500 = 3940.42 \text{ C}$$

$$\eta_{1-8 \text{ h}} = \frac{Q_{1-8 \text{ h}}}{Q_2 - Q_1} \times 100\% = \frac{3940.42}{14965.835 - 3774.635} \times 100\% = 35.21\% \quad (13)$$

Stage III:

$$Q_{8-18 \text{ h}} = nzF = 0.0175 \times 1 \times 96500 = 1688.75 \text{ C} \quad (14)$$

$$\eta_{8-18 \text{ h}} = \frac{Q_{8-18 \text{ h}}}{Q_3 - Q_2} \times 100\% = \frac{1688.75}{28062.335 - 14965.835} \times 100\% = 12.89\% \quad (15)$$

The consumption of the molten CaCl₂ is 0.65 g when 1.4 g TiO₂ is used as the cathode. About 0.41 g Cl₂ is released from the anode when TiO_x in stage I is Ti₂O₃.

$$n_{\text{Cl}_2} = n_{\text{TiO}_2} \times \frac{1}{3} = 0.0175 \times \frac{1}{3} = 0.0058 \text{ mol} = 0.41 \text{ g} \quad (16)$$

$$m_{\text{CaCl}_2} = n_{\text{CaCl}_2} \times 111 = 0.65 \text{ g} \quad (17)$$

$$m_{\text{TiO}_2} : m_{\text{Cl}_2} = 1.4 \text{ g} : 0.41 \text{ g} = 17 : 5 \quad (18)$$

In a similar way the current efficiency can be obtained at different stages if the titanium suboxide is Ti₃O₅ or TiO.

If the main phase of titanium suboxide is Ti₃O₅ at the first stage, the current efficiency of the different stages are 22.37%, 37.72% and 12.89%.

$$\text{Stage I: } \eta_{1 \text{ h}} = \frac{Q_{1 \text{ h}}}{Q_1} \times 100\% = \frac{844.375}{3774.635} \times 100\% = 22.37\% \quad (19)$$

$$\text{Stage II: } \eta_{1-8 \text{ h}} = \frac{Q_{1-8 \text{ h}}}{Q_2 - Q_1} \times 100\% = \frac{4221.875}{14965.835 - 3774.635} \times 100\% = 37.72\% \quad (20)$$

$$\text{Stage III: } \eta_{8-18 \text{ h}} = \frac{Q_{8-18 \text{ h}}}{Q_3 - Q_2} \times 100\% = \frac{1688.75}{28062.335 - 14965.835} \times 100\% = 12.89\% \quad (21)$$

The consumption of the molten salt is about 0.49 g and Cl₂ is about 0.31 g when TiO_x of the stage I is Ti₃O₅.

$$n_{\text{Cl}_2} = n_{\text{TiO}_2} \times \frac{1}{3} = 0.0175 \times \frac{1}{4} = 0.0044 \text{ mol} = 0.31 \text{ g} \quad (22)$$

$$m_{\text{CaCl}_2} = n_{\text{CaCl}_2} \times 111 = 0.49 \text{ g} \quad (23)$$

$$m_{\text{TiO}_2} : m_{\text{Cl}_2} = 1.4 \text{ g} : 0.31 \text{ g} = 9 : 2 \quad (24)$$

If the main phase of titanium suboxide is TiO at the first stage, the current efficiency of the different stages are 44.74%, 30.18% and 12.89%.

$$\text{Stage I: } \eta_{1 \text{ h}} = \frac{Q_{1 \text{ h}}}{Q_1} \times 100\% = \frac{1688.75}{3774.635} \times 100\% = 44.74\% \quad (25)$$

$$\text{Stag II: } \eta_{1-8 \text{ h}} = \frac{Q_{1-8 \text{ h}}}{Q_2 - Q_1} \times 100\%$$

$$= \frac{3377.5}{14965.835 - 3774.635} \times 100\% = 30.18\% \quad (26)$$

$$\text{Stage III: } \eta_{8-18h} = \frac{Q_{8-18h}}{Q_3 - Q_2} \times 100\% \\ = \frac{1688.75}{28062.335 - 14965.835} \times 100\% = 12.89\% \quad (27)$$

The consumption of the molten salt is about 0.97 g and Cl_2 is about 0.62 g when TiO_x of the stage I is TiO .

$$n_{\text{Cl}_2} = n_{\text{TiO}_2} \times \frac{1}{2} = 0.0175 \times \frac{1}{2} = 0.00875 \text{ mol} = 0.62 \text{ g} \quad (28)$$

$$m_{\text{CaCl}_2} = n_{\text{CaCl}_2} \times 111 = 0.97 \text{ g} \quad (29)$$

$$m_{\text{TiO}_2} : m_{\text{Cl}_2} = 1.4 : 0.62 = 9 : 4 \quad (30)$$

In summary, the main phases formed in the cathode at the stage I include TiO_x and CaTiO_3 . If we that TiO_x is the mixture of Ti_3O_5 , Ti_2O_3 and TiO , the current efficiency of the stage I from TiO_2 to TiO_x and CaTiO_3 is 22.37%~44.74%, it is between 30.18%~37.72% in stage II from TiO_x and CaTiO_3 to Ti_2O , and 12.89% from Ti_2O to Ti in stage III. The mass ratio of CaCl_2 consumed to TiO_2 is 35:100~69:100. The mass ratio of Cl_2 released on the anode to TiO_2 is between 2:9~4:9. The TiO_2 increases the consumption of the molten salt and the released Cl_2 amount. Consumption of molten salt and emission of Cl_2 is inevitable when using TiO_2 as the precursor to prepare metal Ti by FFC process although these behaviors just take place in the first stage.

3 Conclusions

1) Deoxygenation from TiO_2 to Ti by FFC process can be divided into three stages, including from TiO_2 to CaTiO_3 and TiO_x ($0 < x < 2$), from CaTiO_3 and TiO_x to Ti_2O and from Ti_2O to Ti .

2) Chlorine is just released from the anode in the first stage.

CO/CO_2 is the main gas emitted from the anode in the second stage and the third stage.

3) The drastic chemical reaction between CaO and TiO_2 makes Cl^- move to the anode and pile up which causes chlorine released due to overvoltage. Chlorine released from the anode is closely related to CaTiO_3 formed in the cathode. When CaTiO_3 begins to deoxidize there is no more chlorine released.

4) The current efficiency of stage I is 22.37%~44.74%, stage II is between 30.18%~37.72%, stage III is 12.89%. The mass ratio of CaCl_2 consumed to TiO_2 is between 35:100~69:100. The mass ratio of Cl_2 released on the anode to TiO_2 is 2:9~4:9.

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制钛过程中阴极钙钛矿的形成与阳极溢出气体间的关系

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摘要: 采用FFC剑桥工艺在熔融 CaCl_2 中电解二氧化钛时, 钙钛矿是阴极上不可避免形成的相。研究了在制备钛的过程中, 阴极钙钛矿的形成与阳极释放气体的关系。结果表明, 阴极上相的形成主要有3个阶段, 包括钙钛矿的形成、钙钛矿的脱氧及钛的低价氧化物脱氧为 TiO 和 TiO 到 Ti 的脱氧。尽管分解电压低于 CaCl_2 , 但阴极形成的钙钛矿与从阳极释放的气体密切相关。由于短时间内钙钛矿的形成造成过电压, 因而阳极释放出氯气, 氯气的量取决于 TiO_2 和电解过程中产生的不同低价钛的量。当钛的低价氧化物介于 Ti_3O_5 和 TiO_2 之间时, 在第1脱氧阶段 TiO_2 和氯气的质量比为9:2到9:4。在氯气释放的过程中阳极没有明显的消耗。钙钛矿的形成和 Ti_2O 的脱氧是在熔融 CaCl_2 中电解制备钛的主要限制性环节。从 TiO_2 到 Ti 的总电流效率是24.07%。目前第1阶段的电流效率在22.37%~44.74%之间, 第2阶段在30.18%~37.72%之间。

关键词: 熔盐电解; 钙钛矿; 阳极气体

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