



# Electrochemical synthesis of titanium oxycarbide in a $\text{CaCl}_2$ based molten salt

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## ABSTRACT

Titanium oxycarbide ( $\text{TiC}_x\text{O}_y$ ) was successfully prepared by an electro-deoxidation of  $\text{TiO}_2/\text{C}$  composite cathode in molten calcium chloride at  $900^\circ\text{C}$ . The composite cathode was prepared by adding an amount of carbon into  $\text{TiO}_2$  powders. By using X-rays diffraction and scanning electron microscopy, it was found that the presence of carbon resulted in changes in reaction mechanism and accelerated the rate of electrochemical reaction. The results suggested that the electrochemical reduction of  $\text{TiO}_2/\text{C}$  composite was the following: firstly titanium dioxide was reduced to  $\text{TiO}_n$  ( $0 < n < 1$ ) along with the formation of  $\text{CaTiO}_3$ . Then,  $\text{TiO}_n$  ( $0 < n < 1$ ) reacted with carbon to  $\text{TiC}_x\text{O}_y$ .

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## 1. Introduction

Titanium oxycarbide was found as an intermediate product in the process of carbothermic reduction of  $\text{TiO}_2$ . It possesses some of metallic properties such as good electrical and thermal conductivity, extreme high hardness and high melting point etc. Some of works have been conducted on the preparation as well as the performance of  $\text{TiC}_x\text{O}_y$  [1–9]. At present,  $\text{TiC}_x\text{O}_y$  has been attracting more and more interest in scientific research due to its wide use in decorative field [1–3] and as an anode for electro-extracting titanium [4–7].

Generally, there are two approaches to prepare  $\text{TiC}_x\text{O}_y$ . One is the carbothermic reduction of  $\text{TiO}_2$  [4,5]. The other involves a heat treatment of  $\text{TiO}$  and  $\text{TiC}$  at a relatively high temperature [6,7]. Both of approaches require high vacuum and high temperature. It was also reported that  $\text{TiC}_x\text{O}_y$  films could be made through several methods such as by a gas–solid combustion [8]. Anyway, the harsh conditions inevitably result in a high cost of production so far. It is necessary to develop an alternative method to prepare titanium oxycarbide with low-cost.

In the late 1990s, an electro-deoxidation technique was discovered by the scientists at University of Cambridge. The process has been used to successfully prepare numerous metals and alloys directly from their respective metal-oxides in  $\text{CaCl}_2$  based molten salts [9–26]. In this process, oxygen in the cathode is ionized and transported to the anode via the electrolyte. If a conventionally carbon anode is used,  $\text{O}^{2-}$  will discharge to form  $\text{CO}$  or  $\text{CO}_2$ .

Recently, it has been reported the electro-deoxidation of  $\text{Nb}_2\text{O}_5$  in the presence of additives such as carbon,  $\text{CaCO}_3$  or  $\text{CaO}$  to increase porosity and the number of the  $\text{O}^{2-}$  vacancies during the sintering process of the solid cathode [25]. The present work is focusing on the preparation of titanium oxycarbide ( $\text{TiC}_x\text{O}_y$ ) by electrolyzing a  $\text{TiO}_2/\text{C}$  composite in molten  $\text{CaCl}_2$  electrolyte. The composite cathode was prepared by adding an amount of carbon into  $\text{TiO}_2$  powders. It is reasonable to expect that the presence of carbon will provide more channels for the transmission of electrons, and electrons accelerating the electrolysis. Thereafter, carbon involved in the reduction process could form  $\text{TiC}_x\text{O}_y$ .

## 2. Experimental

Commercially available  $\text{TiO}_2$  (AR) and carbon powders ( $\geq 99\%$ ) were selected as the starting materials. The powders were mixed using mortar and pestle within a molar proportion of  $\text{TiO}_2:\text{C} = 2:1$ , and thereafter uniaxially pressed into a pre-formed pellet (10 mm in diameter), which was subsequently calcined in argon at  $900^\circ\text{C}$  for 6 h in order to give sufficient mechanical strength for connecting to be an electrode. The cathode was assembled by wrapping  $\text{TiO}_2/\text{C}$  pellet by a nickel–chromium alloy wire (0.5 mm in diameter) and then connecting to a stainless steel rod (6 mm in diameter). A graphite rod with a diameter of 10 mm was used to be anode.

180 g  $\text{CaCl}_2$  ( $\geq 96.0\%$ ) was weighed and placed in a well sealed vacuum drying oven ( $180^\circ\text{C}$ ) for 24 h. Then, the preliminary prepared salt was melted in an alumina crucible at  $900^\circ\text{C}$ , which was placed inside a vertical cylindrical tube furnace reactor. Throughout the entire melting process, argon, which was used as the protective gas, was constantly passed through the system.

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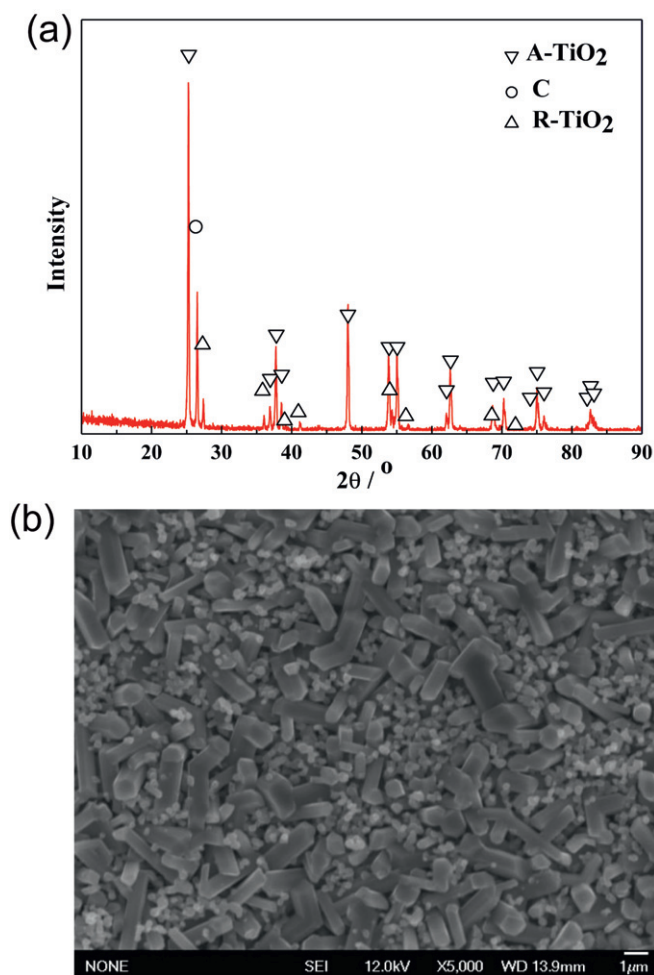


Fig. 1. XRD spectra (a) and SEM image (b) of pellet sintered at 900 °C for 6 h.

After the pre-set temperature was reached, carbon anode was immersed into the molten salt, subsequently the cathodic pellet was slowly lowered into the electrolyte. Electrolysis was carried out with a constant voltage of 3.0 V using a Solatron 1287 working station.

When the electro-deoxidation was terminated, the sample was lifted from the melt into the upper part of the reactor and cooled naturally under the protection of argon. Then, the electrodes were washed by distilled water and acetic acid to remove residual salt within the pores of the cathode, and avoid subsequent fragmentation of the electrodes caused by hydration of the calcium chloride. Finally, the samples were dried and characterized using X-ray diffraction analysis (Model MAC, M21XVHF22) and a scanning electron microscope (JEOL, JSM-6480LV) to identify the phase composition and microstructure of the cathodic products. Meanwhile, the oxygen and carbon content of the products were quantitatively analyzed by using Eltra ONH-2000 analyzer and HORIBA EMIA-820V.

### 3. Results and discussion

Fig. 1a indicates XRD pattern of the sintered composite cathode pellet in which all peaks visible correspond to  $\text{TiO}_2$  and C. The result presents that no new phase is yielded during the sintering process. The SEM photograph of the sintered composite pellet shown in Fig. 1b suggests a compositional homogeneity, with respect to the distribution of  $\text{TiO}_2$  and carbon. Porosity existed in the prepared

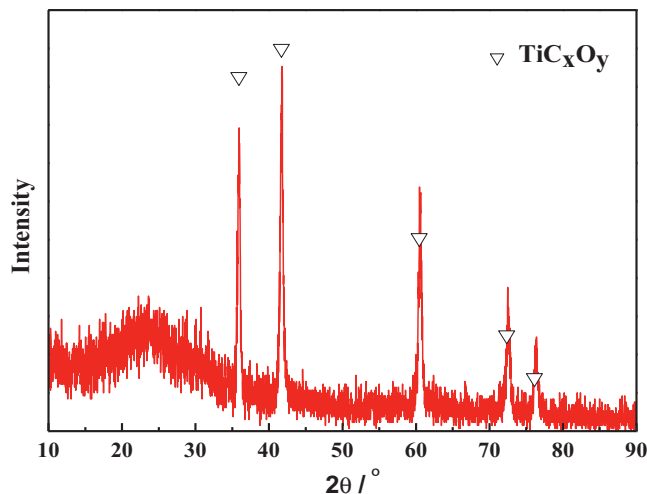


Fig. 2. XRD pattern of electrolyzed cathode for 12 h.

$\text{TiO}_2/\text{C}$  composite pellet, which is favorable for the penetration of molten salts and the diffusion of ionized  $\text{O}^{2-}$  during electrolysis.

On the basis of precisely controlling the molar ratio of  $\text{TiO}_2:\text{C}$  as 2:1, it can be speculated that pure  $\text{TiC}_x\text{O}_y$  ( $x=y=0.5$ ) could be synthesized through electrolysis of  $\text{TiO}_2/\text{C}$  composite pellet. Indeed, the oxygen and carbon content in the final cathodic product was measured, and the result reveals that the titanium oxycarbide synthesized is  $\text{TiC}_{0.5}\text{O}_{0.5}$ . The XRD result shown in Fig. 2 confirms that almost single phase  $\text{TiC}_x\text{O}_y$  is prepared after electrolysis for 12 h [4–7].

A series of interrupted experiments were conducted to investigate the electrolysis mechanism of  $\text{TiO}_2/\text{C}$  composite cathode, with the electrolyzing durations ranging from 0 min to 12 h. Fig. 3 shows that the XRD patterns of those as-prepared products obtained with different electrolysis durations. XRD pattern (a) presents that a small amount of  $\text{CaTiO}_3$  appeared in the sample quenched after 30 min of immersion without electrolysis. The results disclose that some CaO remained in the molten  $\text{CaCl}_2$  even the salt has been purified by a pre-melt process. It is known by the corresponding

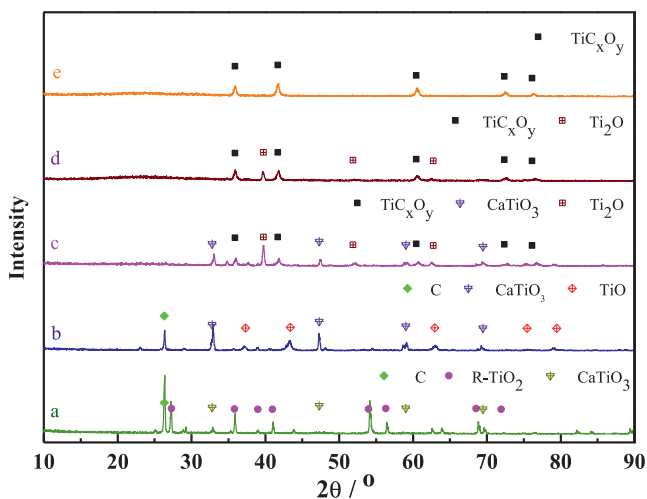


Fig. 3. The XRD patterns of pellets electrolyzed for different durations. (a) With 30 min of immersion without electrolysis; (b) with 5 min electrolysis; (c) with 1.5 h electrolysis; (d) with 8 h electrolysis; (e) with 12 h electrolysis.

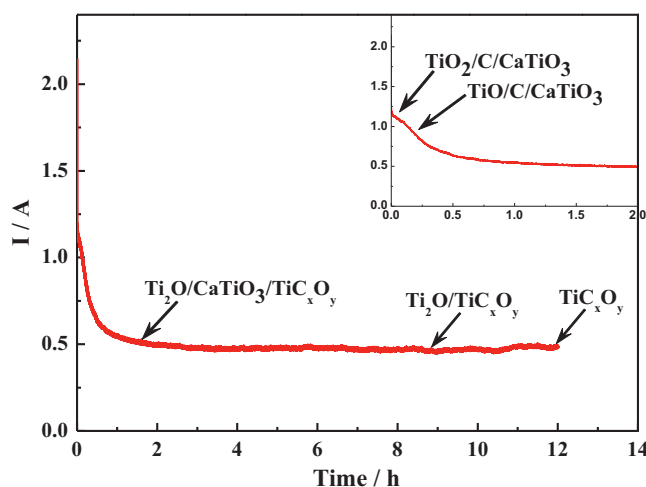
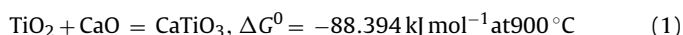
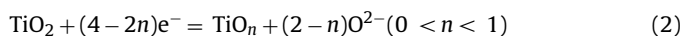


Fig. 4. Correspondence between composition of products and current–time curve of electrolyzing  $\text{TiO}_2/\text{C}$ .

thermodynamic calculations. This suggests that  $\text{TiO}_2$  can react with  $\text{CaO}$  at  $900^\circ\text{C}$  to form  $\text{CaTiO}_3$ .



The product obtained with a 5 min of electrolysis is found to consist predominantly of  $\text{CaTiO}_3$  and carbon, as well as a large quantity of  $\text{TiO}$  (seen in pattern b). It suggests that  $\text{TiO}_2$  inside of the composite cathode could be directly reduced to be  $\text{TiO}$ . With prolonging the electrolysis time as 1.5 h, a significant result is found that the product mainly comprises  $\text{Ti}_2\text{O}$ ,  $\text{CaTiO}_3$  and a new phase  $\text{TiC}_x\text{O}_y$  (seen in pattern c). Two issues are noteworthy to mention: firstly,  $\text{TiC}_x\text{O}_y$  shows up with respect to the disappearance of carbon. Secondly, carbon could not be involved in reaction until  $\text{TiO}_2$  is further reduced to be  $\text{Ti}_2\text{O}$ . The result suggests the following reactions:



The electrolysis mechanism of  $\text{TiO}_2/\text{C}$  composite cathode has been confirmed by further prolonging electrolysis time up to 12 h. The XRD results seen from pattern (d,e) shown in Fig. 3 indicates that, with increasing the electrolysis time, the amount of  $\text{Ti}_2\text{O}$  and  $\text{CaTiO}_3$  gradually declined with more  $\text{TiC}_x\text{O}_y$  being identified. Finally,  $\text{TiC}_x\text{O}_y$  is the almost single phase after electrolysis of 12 h.

Fig. 4 presents a typical current–time curve recorded during the potentiostatic electrolysis at an applied voltage of 3 V, with the molar ratio of  $\text{TiO}_2$  to C being set as 2:1. The curve indicates that the current rapidly declines within 1.5 h following an initial peak, then it continues to decline slowly until the electrolysis was terminated. The typical shoulder trend may be attributed to the ionization of oxygen in  $\text{TiO}_2$  to oxygen ions, corresponding to the  $\text{TiO}_2$ – $\text{TiO}$ – $\text{Ti}_2\text{O}$  reduction process shown in the inset of Fig. 4. The process can be described by Eq. (2). On the other hand, the ionized  $\text{O}^{2-}$  dissolved in the melt and transferred via the melt to the carbon anode, on which it combined with carbon to form  $\text{CO}_2/\text{CO}$ .



The results suggest, in comparison of  $\text{TiO}_2$  electro-deoxidation [17–19], that the existence of carbon causes the reduction mechanism and the rate of electrochemical reaction have been

changed. With the addition of carbon, Magnéli phases such as  $\text{Ti}_4\text{O}_7$ ,  $\text{Ti}_3\text{O}_5$  and  $\text{Ti}_2\text{O}_3$  are rapidly skipped, and  $\text{TiO}_2$  is reduced to be  $\text{TiO}$  directly. The rate of electro-reduction of the pellet was accelerated greatly.

#### 4. Conclusions

The preparation of  $\text{TiC}_x\text{O}_y$  directly from the electrochemical reduction of  $\text{TiO}_2/\text{C}$  composite cathode in molten calcium chloride at  $900^\circ\text{C}$  was achieved. Compared with the electro-deoxidation of pure  $\text{TiO}_2$ , the electrolysis of solid  $\text{TiO}_2/\text{C}$  composite cathode was significantly accelerated by addition of carbon. With a molar ratio of  $\text{TiO}_2$  to carbon being 2:1, the single phase  $\text{TiC}_{0.5}\text{O}_{0.5}$  can be obtained via electro-deoxidation of  $\text{TiO}_2/\text{C}$  composite cathode. A series of experiment, where samples were quenched experiments were conducted to investigate the mechanism of the whole reduction process. It was found that the reduction of the cathode can be divided into two steps: firstly titanium dioxide was reduced to  $\text{TiO}_n$  ( $0 < n < 1$ ) along with the formation of  $\text{CaTiO}_3$ . Then,  $\text{TiO}_n$  ( $0 < n < 1$ ) was converting to be  $\text{TiC}_x\text{O}_y$  by reaction with carbon.

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#### References

- [1] M.T. Mathew, E. Ariza, L.A. Rocha, A.C. Fernandes, F. Vac, Tribology International 41 (2008) 603.
- [2] A.C. Fernandes, P. Carvalho, F. Vaz, S. Lanceros-Méndez, A.V. Machado, N.M.G. Parreira, J.F. Pierson, N. Martin, Thin Solid Films 515 (2006) 866.
- [3] F. Santerre, M.A.E.I. Khakani, M. Chaker, J.P. Dodelet, Applied Surface Science 148 (1999) 24.
- [4] S.Q. Jiao, H.M. Zhu, Journal of Materials Research 21 (2006) 2172.
- [5] S.Q. Jiao, H.M. Zhu, Journal of Alloys and Compounds 438 (2007) 243.
- [6] S.Q. Jiao, X.H. Ning, K. Huang, H.M. Zhu, Pure and Applied Chemistry 82 (2010) 1691.
- [7] X.H. Ning, H.Y. Liu, H.M. Zhu, Electrochemistry 78 (2010) 513.
- [8] T. Hashishin, T. Yamamoto, M. Ohyanagi, Z.A. Munir, Journal of the American Ceramic Society 86 (2003) 2067.
- [9] G.Z. Chen, D.J. Fray, T.W. Farthing, Nature 407 (2000) 361.
- [10] D.J.S. Hyslop, A.M. Abdelkader, A. Cox, D.J. Fray, Acta Materialia 58 (2010) 3124.
- [11] G.Z. Chen, E. Gordo, D.J. Fray, Metallurgical and Materials Transactions B 35 (2004) 223.
- [12] A.M. Abdelkader, D.J. Fray, Electrochimica Acta 55 (2010) 2924.
- [13] W. Chen, S.B. Wang, J.B. Ge, S.Q. Jiao, H.M. Zhu, Intermetallics 25 (2012) 66.
- [14] S.Q. Jiao, D.J. Fray, Metallurgical and Materials Transactions B 41 (2010) 74.
- [15] A.M. Abdelkader, D.J. Fray, Electrochimica Acta 64 (2012) 10.
- [16] E. Juzeliunas, A. Cox, D.J. Fray, Electrochemistry Communications 12 (2010) 1270.
- [17] D.T.L. Alexander, C. Schwandt, D.J. Fray, Electrochimica Acta 56 (2011) 3286.
- [18] C. Schwandt, D.T.L. Alexander, D.J. Fray, Electrochimica Acta 54 (2009) 3819.
- [19] C. Schwandt, D.J. Fray, Electrochimica Acta 51 (2005) 66.
- [20] Y. Deng, D.H. Wang, W. Xiao, X.B. Jin, X.H. Hu, G.Z. Chen, Journal of Physical Chemistry B 109 (2005) 14043.
- [21] S.Q. Jiao, L.L. Zhang, H.M. Zhu, D.J. Fray, Electrochimica Acta 55 (2010) 7016.
- [22] X.B. Jin, P. Gao, D.H. Wang, X.H. Hu, G.Z. Chen, Angewandte Chemie International Edition 43 (2004) 733.
- [23] W. Xiao, X.B. Jin, Y. Deng, D.H. Wang, X.H. Hu, G.Z. Chen, ChemPhysChem 7 (2006) 1750.
- [24] W. Xiao, X.B. Jin, Y. Deng, D.H. Wang, G.Z. Chen, Chemistry – A European Journal 13 (2007) 604.
- [25] Q. Xu, L.Q. Deng, Y. Wu, T. Ma, Journal of Alloys and Compounds 396 (2005) 288.
- [26] W. Xiao, X.B. Jin, Y. Deng, D.H. Wang, G.Z. Chen, Journal of Electroanalytical Chemistry 639 (2010) 130.