



## Anodic Dissolution of Titanium Oxycarbide $\text{TiC}_x\text{O}_{1-x}$ with Different O/C Ratio

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The performance of  $\text{TiC}_x\text{O}_{1-x}$  solid solutions with different O/C ratio serving as the anode in electrolysis cell was investigated in NaCl-KCl molten salt. It was found that the electrochemical dissolution occurs from the same potential for all the  $\text{TiC}_x\text{O}_{1-x}$ . The valance of the dissolved titanium ion depends on the potential applied. Both the dissolution ratio of titanium and the by-product of the anode reaction are dependent on the composition of the anode  $\text{TiC}_x\text{O}_{1-x}$ . For high carbon  $\text{TiC}_x\text{O}_{1-x}$  ( $x > 0.5$ ), all the titanium in  $\text{TiC}_x\text{O}_{1-x}$  dissolves as titanium ions with carbon monoxide (CO) and carbon (C) as the by-products. For low carbon  $\text{TiC}_x\text{O}_{1-x}$  ( $x < 0.5$ ), carbon monoxide and carbon dioxide ( $\text{CO}_2$ ) were detected in anodic gas, titanium partially dissolves as titanium ion and the remaining forms  $\text{Ti}_2\text{O}_3$ . The dissolution ratio of titanium decreases with the increase of oxygen in  $\text{TiC}_x\text{O}_{1-x}$ .

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Titanium is considered to be an extremely valuable metal due to its excellent physical and chemical properties, such as high strength, toughness, durability, low density, corrosion-resistance and biological compatibility. Therefore, it has been widely used in medical treatments, aircraft and automotive production, chemical processing and others. However, the cost is extremely high due to the high cost of the current production method named Kroll process.<sup>1</sup> The development of a titanium production process with low cost has attracted tremendous attentions from 1970s.<sup>2-10</sup> Among the many alternative methods previously investigated, the electrolytic process is expected to be one of the most promising methods for titanium metallurgy,<sup>4-10</sup> such as FFC-Cambridge process,<sup>11-15</sup> calciothermic reduction,<sup>16-18</sup> USTB<sup>19-21</sup> and MER<sup>22</sup> process. The USTB and MER processes are similar in the technical approach. Consumable anode is used in both processes. During the electrolysis, the titanium is dissolved as the titanium ion at the anode, and the titanium metal is deposited at the cathode from the molten salts bath. The difference between USTB and MER processes is in the anode material. In the MER process, the anode material is described as "composite", the mixture of titanium sub-oxide and carbon ( $\text{Ti}_x\text{O}_y + \text{C}$ ), whereas in USTB process, compound of titanium oxycarbide,  $\text{TiC}_x\text{O}_{1-x}$  is required for the consuming anode material. The titanium oxycarbide can be obtained from titanium dioxide by using carbothermal reduction route at temperatures higher than 1400°C.<sup>19,23,24</sup> During the electrolysis process, the anodic reaction for  $\text{TiC}_{0.5}\text{O}_{0.5}$  is



The cathodic reaction is



The valance of dissolved titanium ion,  $n$  varies from 2 to 3 depending on the electrolysis parameters. The dissolution behavior of  $\text{TiC}_x\text{O}_{1-x}$  is crucial for the whole USTB process. Since titanium carbide (TiC) and titanium monoxide (TiO) have the same cubic structure, space group, and similar lattice size, they have the capability to form a continuous series of  $\text{TiC}_x\text{O}_{1-x}$  solid solutions with different  $x$ , all of which have high electronic conductivity and could be used as electrode material.<sup>23</sup> The objective of this investigation is to study whether the content of oxygen and carbon, or the O/C ratio in  $\text{TiC}_x\text{O}_{1-x}$ , would affect their dissolution behavior, which is important for the application

of the USTB process. In the real USTB process, titanium oxycarbide is prepared from  $\text{TiO}_2$  or titanium ore by carbothermal reduction at high temperatures ( $> 1400^\circ\text{C}$ ).<sup>19,24</sup> However, in order to control the precise content of oxygen and carbon, the oxycarbides were prepared from pure TiO and TiC in this paper.  $\text{TiC}_x\text{O}_{1-x}$  solid solutions with different O/C ratio were synthesized by sintering different ratio of titanium carbide and titanium monoxide mixture at 1600°C. A series of electroanalytical test was conducted with a focus on the effect of O/C ratio on the anodic dissolution behavior of  $\text{TiC}_x\text{O}_{1-x}$ .

### Experimental

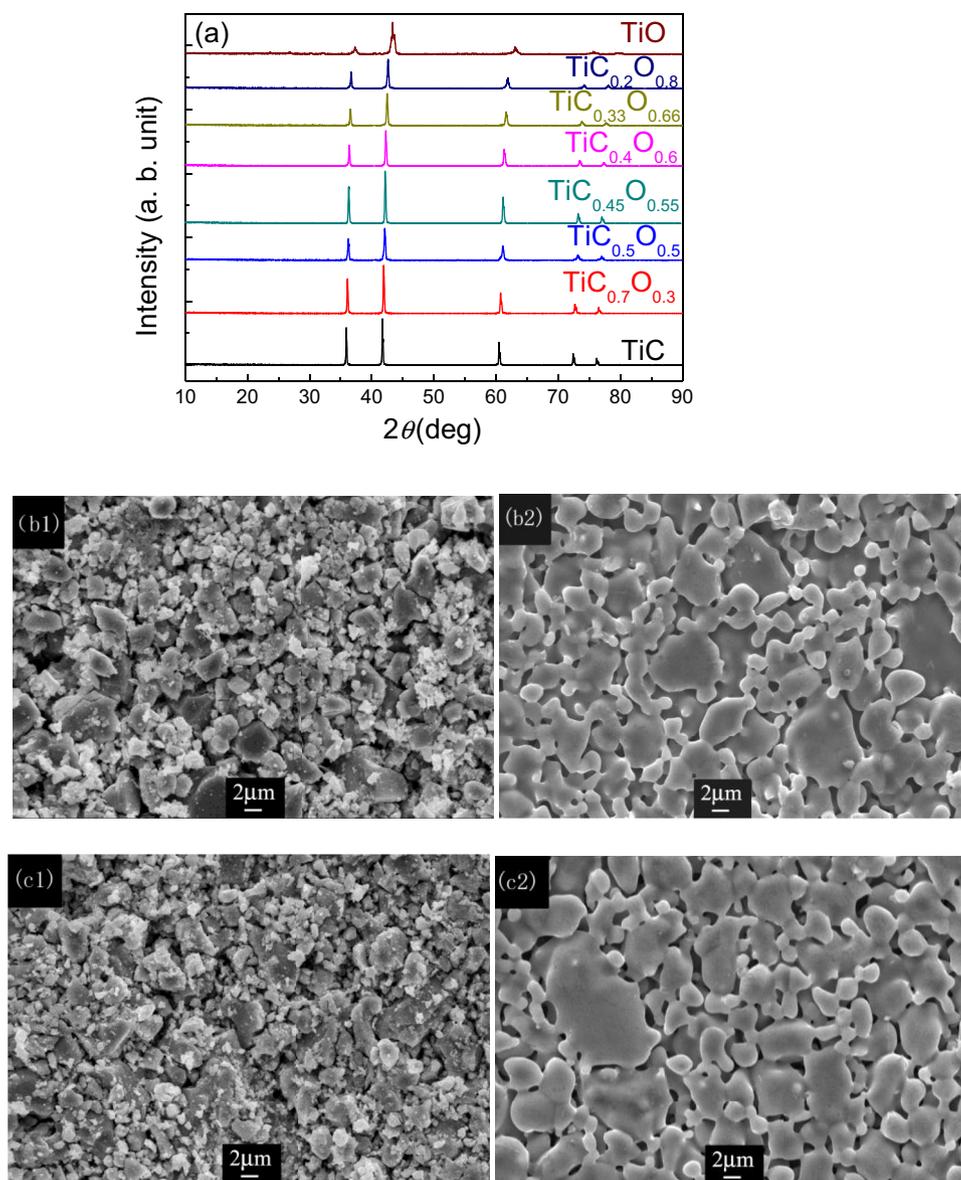
$\text{TiC}_x\text{O}_{1-x}$  with different O/C ratio ( $\text{TiC}_{0.7}\text{O}_{0.3}$ ,  $\text{TiC}_{0.5}\text{O}_{0.5}$ ,  $\text{TiC}_{0.45}\text{O}_{0.55}$ ,  $\text{TiC}_{0.4}\text{O}_{0.6}$ ,  $\text{TiC}_{0.33}\text{O}_{0.67}$  and  $\text{TiC}_{0.2}\text{O}_{0.8}$ ) were synthesized from titanium monoxide (TiO, Beijing Mengtai Corp.) and titanium carbide (TiC, Beijing Mengtai Corp.) with different TiC:TiO ratio (7:3, 1:1, 9:11, 2:3, 1:2 and 1:4). Titanium monoxide and titanium carbide were homogeneously mixed and pressed to form a pellet with 10 mm in diameter and 10 mm in height. The pellet was then sintered at 1600 °C for 4 hrs under Ar atmosphere. The schematic diagram of the whole process is shown in Fig. S1.

The composition, crystal structure, and the morphology of the product before and after being sintered were analyzed by X-ray diffraction (XRD, JEOL JDX-3500, Cu Ka radiation) and scanning electron microscopy (SEM, JEOL JXA-8900M), respectively.

The electrochemical measurement was carried out in an equimolar NaCl - KCl solution (reagent grade, Beijing Chemical Industries). The salt was pre-dried in a graphite crucible under vacuum at the elevated temperature of 300°C for 4 hours to remove moisture. All electrochemical experiments were conducted in a sealed vessel under a dry helium atmosphere at 750°C.

The electrolysis and electrochemical experiments were performed using a potentiostat /galvanostat (EG&G PAR 263 A). A pellet of  $\text{TiC}_x\text{O}_{1-x}$  with 3 mm in diameter is served as a working electrode, and a graphite (6 mm in diameter) rod is served as a counter electrode. The reference electrode was the Ag/AgCl electrode, which consisted of a silver wire (1mm in diameter) in contact with the solution of AgCl (4 wt%) in a NaCl-KCl molten-salt mixture, contained in a Mullite tube. The reference electrode was calibrated against chlorine evolution, and all the potentials were recorded with respect to the potential of  $\text{Cl}_2/\text{Cl}^-$  electrode.

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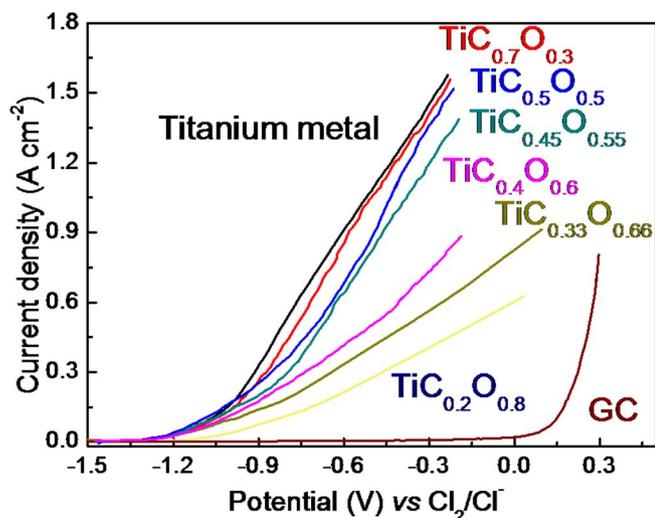
**Figure 1.** XRD pattern of  $\text{TiC}_x\text{O}_{1-x}$  with different O/C ratio (a), the morphology of  $\text{TiC}_x\text{O}_{1-x}$  of different O/C ratio before and after sintering, (b1) (b2)  $\text{TiC}_{0.7}\text{O}_{0.3}$ , (c1) (c2)  $\text{TiC}_{0.2}\text{O}_{0.8}$ .

During the potentiostatic electrolysis, the emitted gas from the anode was analyzed online using a mass spectrometer. Electrochemical experiments including linear polarization and square-wave voltammetry were performed under the same conditions as the electrolysis. For these measurements a tungsten disk electrode with 0.1 mm in diameter was used as a working electrode. The tungsten disk electrode was prepared by sealing a tungsten wire into a quartz tube, and polishing the bottom part as the electrode surface. A schematic diagram of the electrochemical cell and the tungsten disk electrode is shown in Fig. S2(a) and S2(b). The anodic gas generated during dissolution was monitored by mass spectrometer with a special instrument shown in Fig. S2(c) and (d). The  $\text{TiC}_x\text{O}_{1-x}$  solid solution pellet was connected to a platinum wire as working electrode. A quartz sheath with 10mm in diameter and 50mm in height was used as a shell of the anode, and the anodic gas generated during the electrolysis was collected inside the shell. An alumina tube (3.2mm in diameter, 99.8%, McDanel Advanced Ceramic Technologies) with double bores (1mm in diameter) was used to hold the working electrode. One bore is used for the passing through of platinum wire as the current lead whereas the other one for the anodic gas to flow to the mass spectrometer. As

shown in Fig. S2(c), some space between the quartz sheath and the alumina tube allows the helium gas to flow into the anode chamber. The anodic gas released during electrolysis was sampled through the alumina tube. The sampled anodic gas was analyzed for the concentration of CO, CO<sub>2</sub>, and O<sub>2</sub> by online gas mass spectrum (MS, HPR20, Hidden Analytical).

## Results and Discussion

XRD was used to provide composition and assignment of crystal structure information of  $\text{TiC}_x\text{O}_{1-x}$ . The XRD patterns of  $\text{TiC}_x\text{O}_{1-x}$  with different O/C ratio are shown in Fig. 1a and Fig. S3. From Fig. 1a, it is clear that the peak positions of TiC,  $\text{TiC}_{0.7}\text{O}_{0.3}$ ,  $\text{TiC}_{0.5}\text{O}_{0.5}$ ,  $\text{TiC}_{0.45}\text{O}_{0.55}$ ,  $\text{TiC}_{0.4}\text{O}_{0.6}$ ,  $\text{TiC}_{0.33}\text{O}_{0.67}$  and  $\text{TiC}_{0.2}\text{O}_{0.8}$  shifted with the changing of O/C ratio in  $\text{TiC}_x\text{O}_{1-x}$ . With the increasing of O/C ratio in  $\text{TiC}_x\text{O}_{1-x}$ , the peaks shifted step by step from that of TiC to TiO. It indicates that all these  $\text{TiC}_x\text{O}_{1-x}$  solid solution are formed after sintering, and they have the same structure as TiC and TiO. This is confirmed by the SEM analysis (Fig. 1, and Fig. S4).

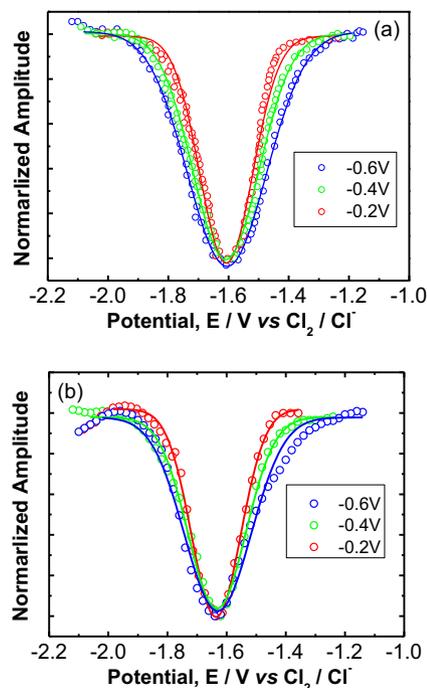


**Figure 2.** The anodic polarization curve of  $\text{TiC}_x\text{O}_{1-x}$  in NaCl-KCl at  $750^\circ\text{C}$ , scan rate  $100 \text{ mV s}^{-1}$ .

Figure 1 (b1) and (c1) presented SEM images of the raw materials (TiC-TiO mixture) with different ratio, 7:3, and 1:4, respectively. Figure 1 (b2) and (c2) are the corresponding samples after the sintering. Compared with the comparatively coarse and heterogeneous raw materials, the  $\text{TiC}_x\text{O}_{1-x}$  solid solutions are homogenous and compact, indicating the complete formation of  $\text{TiC}_x\text{O}_{1-x}$  solid solution. And the significant particle size growth was also observed from the raw materials TiC and TiO to the  $\text{TiC}_x\text{O}_{1-x}$  solid solution.

Linear sweep voltammetry was used to explore the anodic dissolution behavior of  $\text{TiC}_x\text{O}_{1-x}$  solid solution, and the corresponding results are shown in Fig. 2. The anodic polarization curves of Ti metal,  $\text{TiC}_{0.7}\text{O}_{0.3}$ ,  $\text{TiC}_{0.5}\text{O}_{0.5}$ ,  $\text{TiC}_{0.45}\text{O}_{0.55}$ ,  $\text{TiC}_{0.4}\text{O}_{0.6}$ ,  $\text{TiC}_{0.33}\text{O}_{0.67}$  and  $\text{TiC}_{0.2}\text{O}_{0.8}$  indicated the similar dissolving phenomena. With the swept of potential less than  $-1.2 \text{ V vs. Cl}_2/\text{Cl}^-$ , the current were almost zero, indicating no electrochemical reaction taking place. As the potential is raised beyond  $-1.2 \text{ V vs. Cl}_2/\text{Cl}^-$ , the current density increased rapidly, attributed to the occurrence of electrochemical dissolution of  $\text{TiC}_x\text{O}_{1-x}$  solid solution. With respect to  $\text{TiC}_x\text{O}_{1-x}$ , the current density on glassy carbon electrode gradually increases when the potential is higher than  $0 \text{ V vs. Cl}_2/\text{Cl}^-$ , which corresponds to the generating of  $\text{Cl}_2$  gas. These results proved that  $\text{TiC}_x\text{O}_{1-x}$  has the similar anodic dissolution behavior as titanium metal. However, the slopes of anodic polarization curves of Ti metal,  $\text{TiC}_{0.7}\text{O}_{0.3}$ ,  $\text{TiC}_{0.5}\text{O}_{0.5}$ ,  $\text{TiC}_{0.45}\text{O}_{0.55}$ ,  $\text{TiC}_{0.4}\text{O}_{0.6}$ ,  $\text{TiC}_{0.33}\text{O}_{0.67}$  and  $\text{TiC}_{0.2}\text{O}_{0.8}$  are different. The slopes of the anodic polarization curves of Ti metal,  $\text{TiC}_{0.7}\text{O}_{0.3}$ ,  $\text{TiC}_{0.5}\text{O}_{0.5}$  are similar, whereas from  $\text{TiC}_{0.45}\text{O}_{0.55}$  the slope decreases gradually with the increase of oxygen content in the oxycarbide.

In order to investigate the effect of O/C ratio in  $\text{TiC}_x\text{O}_{1-x}$  on the dissolving product including titanium ions and the anodic gas, the electrochemical methods and mass spectrometer were both used. Because titanium ions can exist in multiple valence state, titanium ions with different valence states could be dissolved into melt under various potentials. Square wave voltammetry (SWV) was adopted to analyze the valence of dissolved titanium ions during electrolysis.  $\text{TiC}_x\text{O}_{1-x}$  solid solutions were electrochemically dissolved into melts at different potentials of  $-0.6 \text{ V}$ ,  $-0.4 \text{ V}$  and  $-0.2 \text{ V vs. Cl}_2/\text{Cl}^-$ , respectively, and each dissolution of the  $\text{TiC}_x\text{O}_{1-x}$  solid solutions lasts the same time, i.e., 1.5 hrs. Figure 3 presents the square wave voltammograms recorded in the salts after electrochemically dissolving  $\text{TiC}_x\text{O}_{1-x}$  solid solutions under various potentials. The exchange electron number calculated according the square wave voltammograms is shown in Table I. It is evident that the average exchange electron number changes from 2.0 to 2.3 with the increase of electrolysis potential. This implies that  $\text{TiC}_x\text{O}_{1-x}$  has been dissolved into the melt during electrolysis mostly as



**Figure 3.** Square wave voltammograms (dot) and corresponding fitting result (line) after electrolysis of  $\text{TiC}_{0.5}\text{O}_{0.5}$  (a) and  $\text{TiC}_{0.4}\text{O}_{0.6}$  (b) at different potential. Frequency  $5 \text{ Hz}$ .

$\text{Ti}^{2+}$  ions at  $-0.6 \text{ V}$ , and partially as  $\text{Ti}^{3+}$  when the electrode potential is raised. Clearly, the electrolysis potential demonstrated significant effect on the valence state of titanium ion, whereas the composition of  $\text{TiC}_x\text{O}_{1-x}$  (O/C ratio) does not provide any contribution to that of titanium ion. However, the O/C ratio might affect the anodic tail gas. According to our previous results,<sup>19-21</sup> it was discovered that the anode reaction of  $\text{TiC}_{0.5}\text{O}_{0.5}$  can be described as Eq. 1, during which Ti dissolves into chloride melt as  $\text{Ti}^{n+}$  ( $n = 2\sim 3$ ), while C and O forms CO without any C or O left in anode. It would be ideal if during the anode reaction of  $\text{TiC}_x\text{O}_{1-x}$  with different composition (C/O ratio), all Ti dissolves as titanium ion,  $\text{Ti}^{n+}$ , while C and O leaves as C, CO,  $\text{CO}_2$ , and  $\text{O}_2$  without any residual. Based on this ideal assumption, the anode reaction of  $\text{TiC}_x\text{O}_{1-x}$  could be described as follows, depending on the O/C ratio.

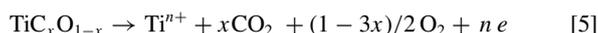
$\text{O/C} \leq 1, x \geq 0.5$  (typically as  $\text{TiC}_{0.7}\text{O}_{0.3}$  and  $\text{TiC}_{0.5}\text{O}_{0.5}$ )



$1 < \text{O/C} \leq 2, 0.33 \leq x < 0.5$  (typically as  $\text{TiC}_{0.45}\text{O}_{0.55}$ ,  $\text{TiC}_{0.4}\text{O}_{0.6}$  and  $\text{TiC}_{0.33}\text{O}_{0.67}$ )



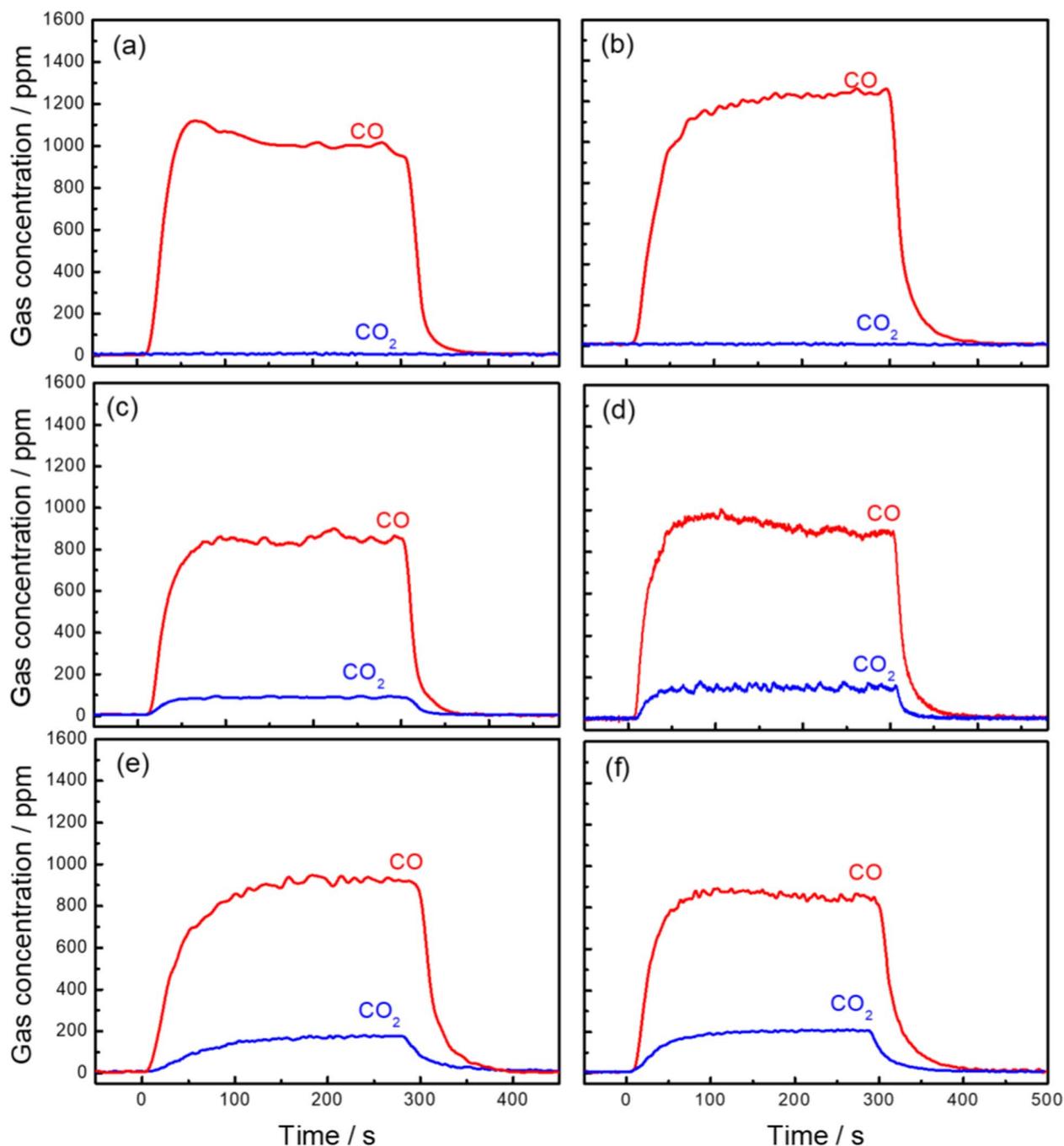
$\text{O/C} > 2, x < 0.33$  (typically as  $\text{TiC}_{0.2}\text{O}_{0.8}$ )



To test the above assumption on the anodic dissolution mechanism, the anode gas during the electrolysis was analyzed by the mass

**Table I.** The valence of titanium ion after electrolysis of  $\text{TiC}_x\text{O}_{1-x}$  at different potential.

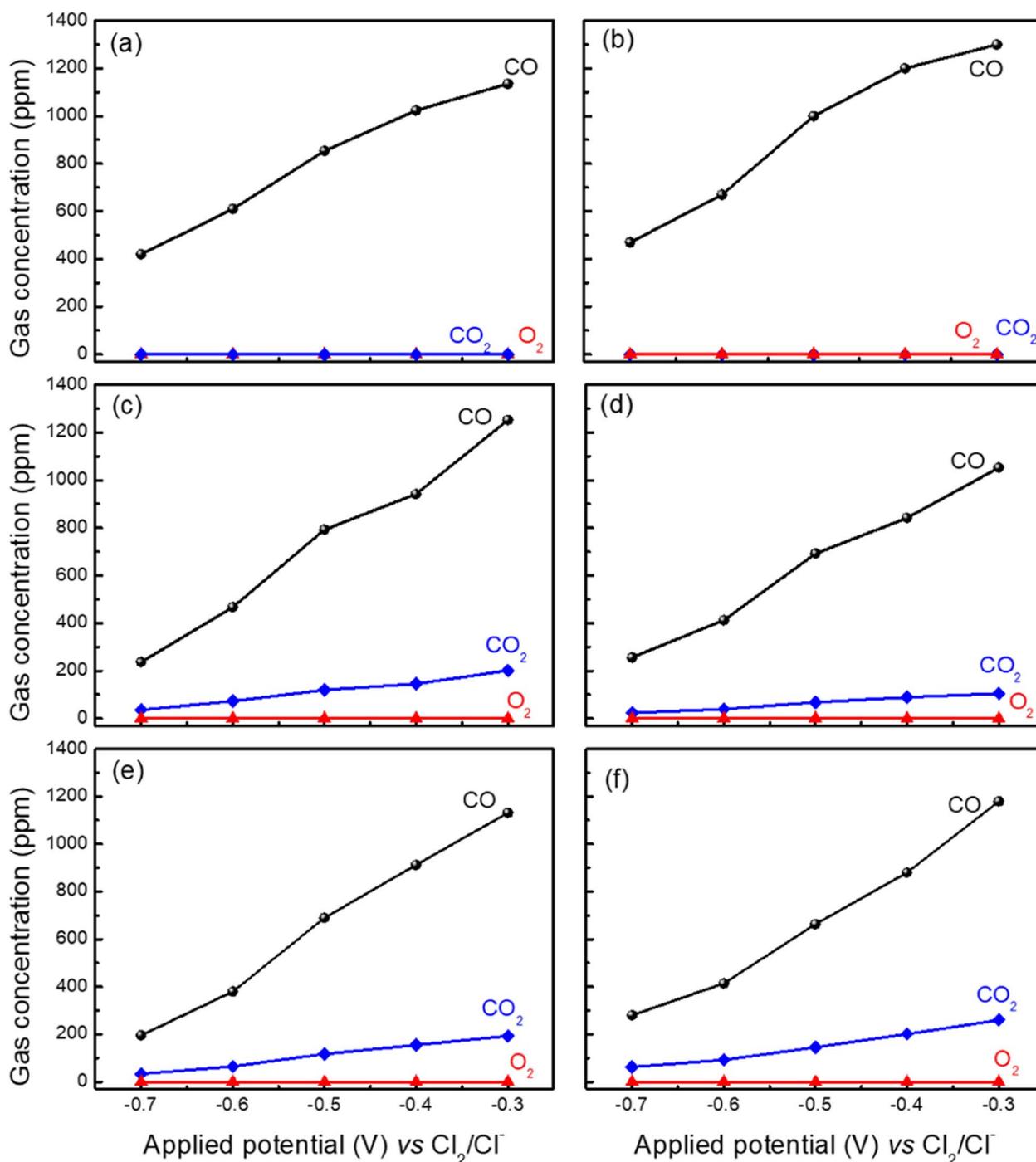
		Electrolysis Potential (V vs $\text{Cl}_2/\text{Cl}^-$ )		
		-0.60	-0.40	-0.20
$\text{TiC}_{0.5}\text{O}_{0.5}$	$n$	2.02	2.15	2.78
$\text{TiC}_{0.4}\text{O}_{0.6}$	$n$	2.08	2.21	2.83



**Figure 4.** The gas analysis result during electrolysis at  $-0.4$  V vs  $\text{Cl}_2/\text{Cl}^-$ , (a)  $\text{TiC}_{0.7}\text{O}_{0.3}$ , (b)  $\text{TiC}_{0.5}\text{O}_{0.5}$ , (c)  $\text{TiC}_{0.45}\text{O}_{0.55}$ , (d)  $\text{TiC}_{0.4}\text{O}_{0.6}$ , (e)  $\text{TiC}_{0.33}\text{O}_{0.67}$ , (f)  $\text{TiC}_{0.2}\text{O}_{0.8}$ .

spectrometer online when the  $\text{TiC}_x\text{O}_{1-x}$  was under electrolysis by applied a constant potential step. Figure 4 shows the monitored concentration of CO and  $\text{CO}_2$  in anode chamber before, during and after the electrolysis at the potential of  $-0.4$  V vs  $\text{Cl}_2/\text{Cl}^-$ , for the  $\text{TiC}_x\text{O}_{1-x}$ . In Fig. 5, the average concentration of CO and  $\text{CO}_2$  during the electrolysis is plotted against the applied potential. CO was the only anode gas during dissolution for  $\text{TiC}_{0.7}\text{O}_{0.3}$  and  $\text{TiC}_{0.5}\text{O}_{0.5}$ . With the change of O/C ratio in  $\text{TiC}_x\text{O}_{1-x}$ , both of CO and  $\text{CO}_2$  were detected for  $\text{TiC}_{0.45}\text{O}_{0.55}$ ,  $\text{TiC}_{0.4}\text{O}_{0.6}$ ,  $\text{TiC}_{0.33}\text{O}_{0.67}$  and  $\text{TiC}_{0.2}\text{O}_{0.8}$ . During the electrolysis of all  $\text{TiC}_x\text{O}_{1-x}$  solid solution, no  $\text{O}_2$  was found in the anodic gas. It is important to note that both CO and  $\text{CO}_2$  were found simultaneously even at very low potential. The concentrations of both

CO and  $\text{CO}_2$  in the anode increase with the increase of the applied potential. This corresponds well with the current rise in the polarization curve in Fig. 2. As we only see the gas generation of CO in  $\text{TiC}_{0.7}\text{O}_{0.3}$  and  $\text{TiC}_{0.5}\text{O}_{0.5}$ , the anodic reaction of high carbon content  $\text{TiC}_x\text{O}_{1-x}$  ( $\text{O}/\text{C} \leq 1$ ,  $x \geq 0.5$ ) most likely follow the Eq. 3. However, for the high oxygen content  $\text{TiC}_x\text{O}_{1-x}$  ( $\text{O}/\text{C} > 2$ ,  $x < 0.33$ ), the anode reaction obviously does not follow the Eq. 5 since we have never seen  $\text{O}_2$  generation. In the middle range of carbon content,  $1 < \text{O}/\text{C} \leq 2$ ,  $0.33 \leq x < 0.5$ , both CO and  $\text{CO}_2$  were detected, corresponding with Eq. 4. However, the concentration of  $\text{CO}_2$  in the anode gas was far lower than that of CO. CO was always the major component in the anodic gas in the entail range of oxygen content in  $\text{TiC}_x\text{O}_{1-x}$ , even for

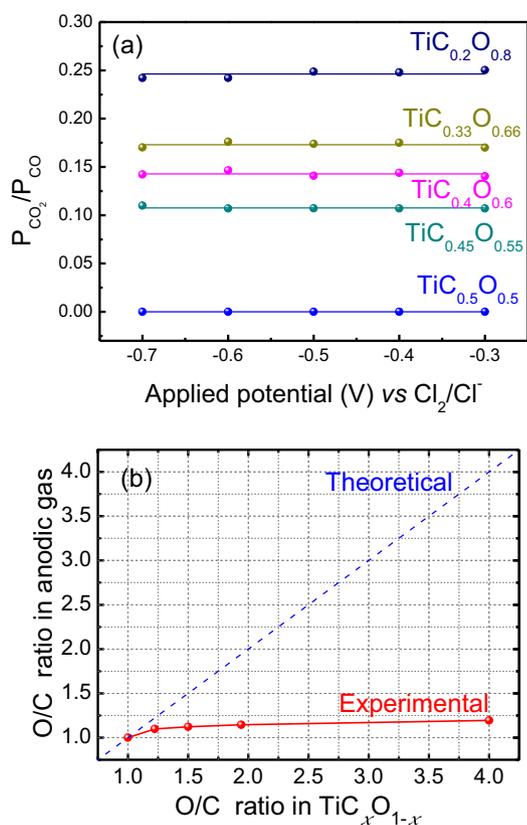


**Figure 5.** The potential dependence of the anode gas concentration during the electrolysis of TiC<sub>x</sub>O<sub>1-x</sub> (a) TiC<sub>0.7</sub>O<sub>0.3</sub>, (b) TiC<sub>0.5</sub>O<sub>0.5</sub>, (c) TiC<sub>0.45</sub>O<sub>0.55</sub>, (d) TiC<sub>0.4</sub>O<sub>0.6</sub>, (e) TiC<sub>0.33</sub>O<sub>0.67</sub>, (f) TiC<sub>0.2</sub>O<sub>0.8</sub>.

TiC<sub>0.33</sub>O<sub>0.67</sub> and TiC<sub>0.2</sub>O<sub>0.8</sub>. Obviously, for the high oxygen content TiC<sub>x</sub>O<sub>1-x</sub> (O/C > 1, x < 0.5) part of oxygen content does not leave as the gas product.

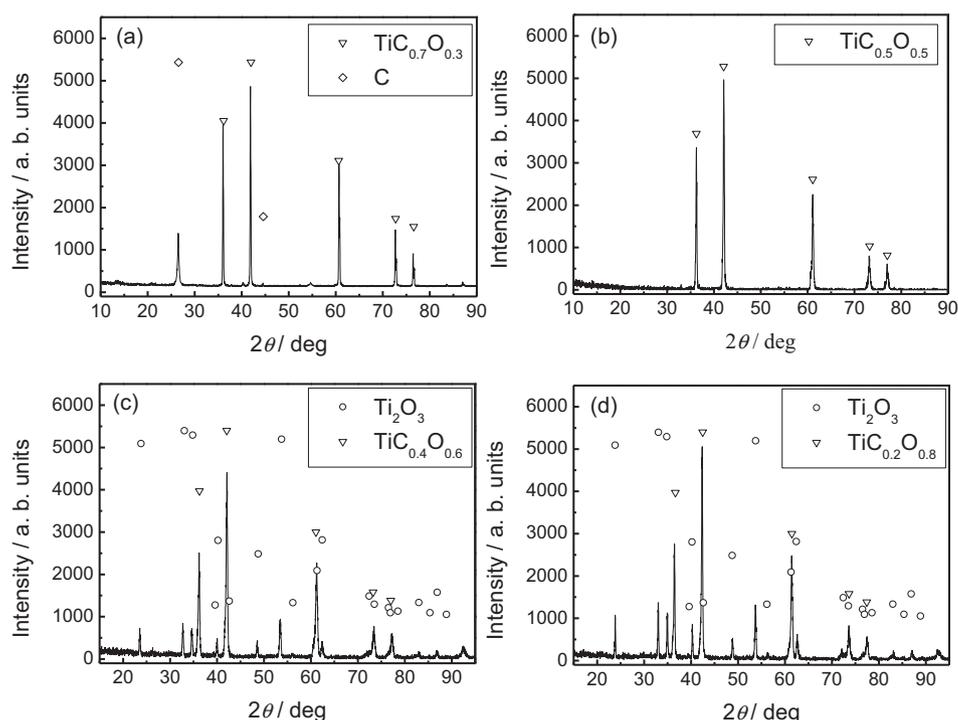
In Fig. 6a the concentration ratio of CO<sub>2</sub> to CO in anodic gas is shown as the function of the applied potential during the electrolysis. It is interesting that the CO<sub>2</sub>/CO ratio is always kept around the same value for a certain carbon (oxygen) content TiC<sub>x</sub>O<sub>1-x</sub>, regardless of the applied potential. However, the O/C ratio in TiC<sub>x</sub>O<sub>1-x</sub> played a significant role on the CO<sub>2</sub>/CO ratio in the anodic gas. CO<sub>2</sub>/CO ratio increases with the increase of O/C ratio in TiC<sub>x</sub>O<sub>1-x</sub> anode material

itself. In Fig. 6b, O/C ratio in anodic gas (CO, CO<sub>2</sub>) is plotted as the function of the O/C ratio in TiC<sub>x</sub>O<sub>1-x</sub> anode material. In this figure, the blue dot line shows the theoretical value if the anode reaction follows the Eqs. 3–5. Other than the point of O/C = 1:1, the O/C ratio in anodic gas is always smaller than that in TiC<sub>x</sub>O<sub>1-x</sub> anode material, and such deviation becomes even larger as the ratio increases further. This implies that O in TiC<sub>x</sub>O<sub>1-x</sub> is consumed incompletely in the range of O/C ratio higher than 1:1. In order to analyze the by-product other than the gas species during the anode reaction, a four-hour electrolysis was carried out on TiC<sub>0.7</sub>O<sub>0.3</sub>, TiC<sub>0.5</sub>O<sub>0.5</sub>, TiC<sub>0.4</sub>O<sub>0.6</sub> and TiC<sub>0.2</sub>O<sub>0.8</sub>.



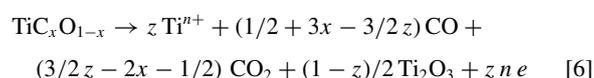
**Figure 6.** (a) The ratio of CO<sub>2</sub> to CO in anode gas during dissolution at different potential (b) The O/C ratio in anodic gas for different TiC<sub>x</sub>O<sub>1-x</sub> solid solution.

The anode after electrolysis was analyzed by XRD, and the results are shown in Fig. 7. Carbon was seen after long time electrolysis for TiC<sub>0.7</sub>O<sub>0.3</sub>. This result confirms again that for high carbon content TiC<sub>x</sub>O<sub>1-x</sub> ( $O/C \leq 1$ ,  $x \geq 0.5$ ), the anode reaction follows the Eq. 3, and



**Figure 7.** The XRD pattern of the residual anode production after the electrolysis for 4 hrs of (a) TiC<sub>0.7</sub>O<sub>0.3</sub>, (b) TiC<sub>0.5</sub>O<sub>0.5</sub>, (c) TiC<sub>0.4</sub>O<sub>0.6</sub>, (d) TiC<sub>0.2</sub>O<sub>0.8</sub>.

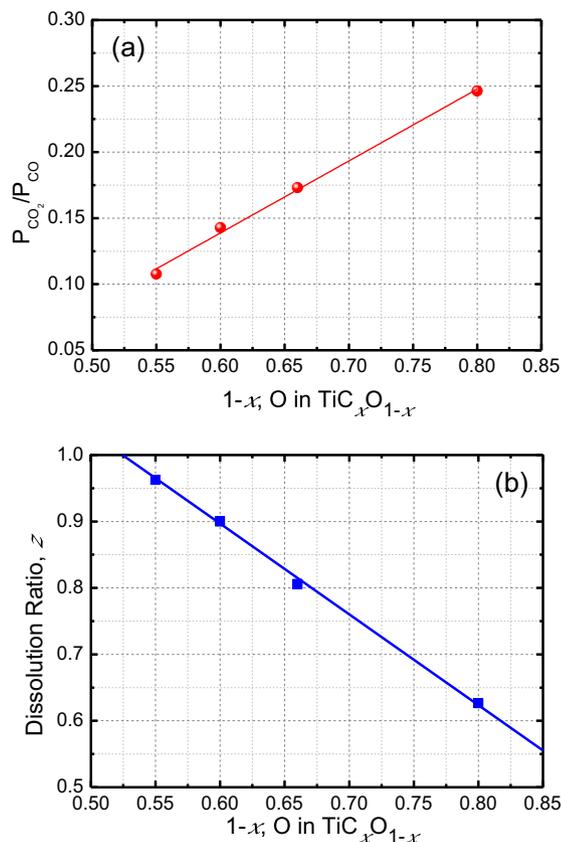
that all Ti dissolves as titanium ion Ti<sup>n+</sup>, while carbon and oxygen form as CO and C. For the low carbon (high oxygen) content anode TiC<sub>x</sub>O<sub>1-x</sub> ( $O/C > 1$ , TiC<sub>0.4</sub>O<sub>0.6</sub> and TiC<sub>0.2</sub>O<sub>0.8</sub>), Ti<sub>2</sub>O<sub>3</sub> was observed as the by-product after the electrolysis. This means that part of Ti in TiC<sub>x</sub>O<sub>1-x</sub> has not dissolved as ion, and, at the same time, part of oxygen has not left as gas species. The anode reaction for low carbon content TiC<sub>x</sub>O<sub>1-x</sub> ( $O/C > 1$ ) does not follow Eqs. 4 and 5. According to the results above and the mass balance of the elements, the anode reaction for low carbon, high oxygen content TiC<sub>x</sub>O<sub>1-x</sub> ( $O/C > 1$ ) could be described as follow, where  $z$  is the dissolution ratio of titanium as ion.



The valance of dissolved titanium ion,  $n$  is electrode potential dependent, the higher the potential applied, the higher the valance ion dissolved. However,  $n$  is not the function of the anode material composition. On the other hand, the anode material composition, and O/C ratio in TiC<sub>x</sub>O<sub>1-x</sub>, shows the significant effect on the anode gas composition. As seen in Fig. 6a, the concentration ratio of CO<sub>2</sub> to CO, is not potential dependent, but is a function of composition of the anode TiC<sub>x</sub>O<sub>1-x</sub>. Figure 8a shows CO<sub>2</sub>/CO ratio as the function of O (TiO) concentration in TiC<sub>x</sub>O<sub>1-x</sub>. The CO<sub>2</sub>/CO ratio increases almost linearly with O concentration in the anode material. The dissolution ratio,  $z$  can be calculated from the CO<sub>2</sub>/CO ratio, and is shown in Fig. 8b. The dissolution ratio decreases linearly with the increase of the oxygen content.

## Conclusions

TiC<sub>x</sub>O<sub>1-x</sub> solid solutions with different O/C ratio demonstrated the similar dissolution behavior under electrolysis in NaCl-KCl. During the electrolysis, Ti was dissolved into molten salt as titanium ion, Ti<sup>n+</sup>, and the valance of the dissolved titanium ion,  $n$  is dependent on the applied potential. Carbon and oxygen were released as carbon, carbon monoxide and carbon dioxide depending on the O/C ratio in TiC<sub>x</sub>O<sub>1-x</sub>. For high carbon content TiC<sub>x</sub>O<sub>1-x</sub> ( $x \geq 0.5$ ,  $O/C \leq 1$ ), all titanium dissolved as the titanium ion, whereas carbon and carbon monoxide CO were the by-product of the anode reaction. For low



**Figure 8.** (a) The ratio of  $\text{CO}_2$  to  $\text{CO}$  in anode gas, (b) The dissolution ratio of  $\text{TiC}_x\text{O}_{1-x}$ , as the function of the oxygen content in  $\text{TiC}_x\text{O}_{1-x}$  solid solution.

carbon content  $\text{TiC}_x\text{O}_{1-x}$  ( $x < 0.5$ ,  $O/C > 1$ ), the anode gas contained  $\text{CO}$  and  $\text{CO}_2$ , most of the titanium dissolved as titanium ion, whereas part of titanium formed as  $\text{Ti}_2\text{O}_3$  without dissolution. For the same content,  $\text{TiC}_x\text{O}_{1-x}$ , the concentration ratio of carbon dioxide to carbon

monoxide,  $\text{CO}_2/\text{CO}$ , stayed constant regardless of the applied potential. With the increase of  $\text{O}$  in  $\text{TiC}_x\text{O}_{1-x}$  the  $\text{CO}_2/\text{CO}$  ratio increases and the dissolution ratio of titanium as titanium ion,  $z$ , decreases linearly.

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