JOURNAL OF MATERIALS SCIENCE **34** (1999) 2015–2022

XPS study of titanium species exposed to molten Li_2CO_3-Na_2CO_3 in the anodic conditions used in molten carbonate fuel cells

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The surface characterization of titanium, titanium oxide and lithium titanate samples exposed to molten Li_2CO_3-Na_2CO_3, in the anodic conditions used in molten carbonate fuel cells, was carried out by X-ray Photoelectron Spectroscopy (XPS). Different elements were identified: Ti(IV), O(-II), Li(I) and Na(I). The amounts of adsorbed sodium and lithium carbonates, as well as inserted lithium were estimated by a semi-quantitative XPS analysis in layers of about 50 Å. A broadening of the Ti $2p_{3/2}$ peak was observed. This effect is probably caused by a distorsion of the Li_2TiO_3 lattice due to the incorporation of lithium within this structure. Li_2TiO_3 compound was detected by X-ray diffraction (XRD) on Ti, TiO_2 as well as Li_2TiO_3 after treatment in the molten carbonate eutectic. *© 1999 Kluwer Academic Publishers*

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1. Introduction

Titanium and titanium oxide are candidate materials for molten carbonate fuel cells (MCFC) operating at 550–750 °C. Titanium is easily covered by an oxide passive layer at high temperature, which is very corrosion resistant and TiO_2 can be used as a protective layer on different metals [1]. The conductivity of this oxide can be increased by the incorporation of alkali species in the TiO_2 lattice, allowing this compound to be possibly used in MCFC's stacks. Titanium-based materials have been very rarely studied, theoretically or experimentally, in molten carbonates [2–4]. In a previous paper [4], thermodynamic predictions of the stability of these species were established under oxidizing ($O_2 : CO_2$, in contact with the MCFC's cathode compartment) and reducing conditions ($H_2 : CO_2 : H_2O : CO$, in contact with the anode compartment). Li_2TiO_3 was found to be the only stable species in both conditions. Experimental evidence is required in order to confirm the presence of lithium titanate and other species at the surface of TiO_2 or Ti/TiO_2 in contact with carbonate melts.

The aim of this paper is to investigate by X-ray Photoelectron Spectroscopy (XPS) the chemical composition and the chemical states of very thin layers on the surface of titanium and titanium dioxide samples before and after treatment in molten Li_2CO_3-Na_2CO_3 at 650 °C under an $H_2/CO_2/H_2O$ atmosphere. The interactions of titanium species with the alkali cations present in the melt, lithium and sodium, were studied in details. The spectroscopic results are also compared with previous thermodynamic predictions.

2. Experimental

Lithium and sodium carbonates, mixed in proportions of 52–48 mol %, were Merck reagents of analytical purity (>98%). The carbonates were previously storred in a dry atmosphere. A mixture of hydrogen and carbon dioxide (80/20), of high purity grade, bubbled in a humidificator containing water heated at 60 °C ($P(H_2O) \approx 0.2$ atm), before being introduced in the melt. The total flow was 50 $cm^3\ min^{-1}$. As it was necessary to eliminate the air contained in the cell before introducing hydrogen, because of the explosion risk at high temperature, only CO_2 bubbled first in the carbonate melt for about one hour.

Each sample was introduced in the electrochemical cell, and exposed for 24 h to the gaseous atmosphere above the melt (time necessary for reaching the gas equilibrium) and subsecuently immersed in the molten carbonate for more than 48 h (until, at least, the measured open-circuit potential became stationary). Then, the sample was removed from the molten mixture, air-cooled and rinsed with de-ionized water before being analyzed by XPS. A similar procedure was described in a previous paper [5].

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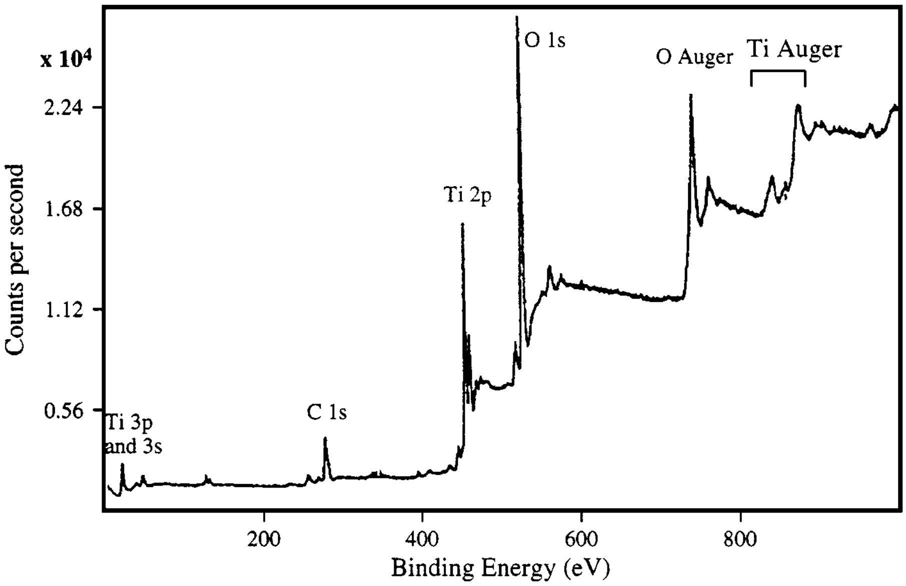


Figure 1 XPS survey spectrum of a titanium foil exposed to molten Li_2CO_3-Na_2CO_3 at 650 °C, under anodic atmosphere (H_2 : CO_2 80 : 20, humidified with water heated at 60 °C).

The cell with the carbonate melt was a compact single-compartment crucible 70×50 mm^2 (Degussa A1 23) contained in another Al 23 250×60 mm^2 crucible hermetically closed by a stainless steel cover with a Viton O-ring. The reference electrode and the auxiliary electrodes were fully described elsewhere [6]. The samples, which constitute the working electrodes, were either metallic titanium foils of $10 \times 10 \times 1$ mm^3, handled by a titanium wire of the same purity grade (99.9%, provided by Goodfellow), or titanium dioxide pellets of 12×4 mm^2, with 99.9% purity grade, provided by Cerac. Temperature control was achieved with a West 3810 Gulton regulator and calibrated chromel-alumina thermocouple.

XPS measurements were performed with a VG ESCALAB Mark II spectrometer using the MgK_α X-ray source. The spectrometer was calibrated using the reference energies of Au $4f_{5/2}$ (83.9 ± 0.1 eV), and Cu $2p_{3/2}$ (932.7 ± 0.1 eV). A take off angle of 90° was used (angle between the surface and the analyser). A binding energy of 285.0 eV was assigned to the C ls peak corresponding to the surface contamination and this was used as an internal reference for correction of charging effects.

XRD experiments were carried out with a Siemens CGR type Thêta 60 diffractometer using a $CoK_{\alpha 1}$ radiation ($\lambda = 1.789$ Å).

3. Results and discussion

The following informations were extracted from XPS experiments: a qualitative analysis of the species present, including their chemical states, within a surface layer of about 50 Å, a semi-quantitative analysis of the proportions of lithium and sodium respectively present in this layer under an adsorbed form or as part of the crystalline structure and an empirical correlation between the presence of lithium and the intensities of the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks.

3.1. Qualitative surface analysis

3.1.1. Metallic titanium

The survey spectrum of a titanium sample treated in molten Li_2CO_3-Na_2CO_3 at 650 °C during 3 days (24 h in the gaseous atmosphere above the melt and 48 h inside the melt) is presented in Fig. 1. It reveals the presence at the surface of the sample of C 1s (corresponding to adsorbed carbonates and/or to a surface contamination), Ti 3p, 3s, 2p and Auger, O 1s and Auger. The high resolution spectra corresponding to Ti 2p and O 1s are reported in Fig. 2. The spectra may originate from different chemical states. The Ti $2p_{3/2}$ and $2p_{1/2}$ peaks can be well fitted by single peaks corresponding to Ti(IV) with known binding energy position and full width at half maximum. The O 1s spectrum exhibits a principal peak at low binding energies, ascribed to O^{2-}, characteristic of the O-Ti bond. The relatively important shoulder at higher energies can be explained by the contribution of two kinds of oxygen: O 1s(OH^-) and O 1s(ads), corresponding respectively to hydroxide ions and to adsorbed molecules of water or carbon dioxide. Sodium is also detected with an Na 1s peak at 1072 eV, as shown in Fig. 3, and two Auger peaks at 263.6 and 302.8 eV respectively. Although the XPS sensivity is very weak with respect to lithium, a small Li 1s peak is also detected at 56 eV, between Ti 3s at 63.7 eV and the satellite titanium peak at 51.8 eV, as shown in Fig. 4.

These results were then compared to those obtained with another titanium foil, which was in contact only with the gaseous anodic atmosphere at 650 °C during about 24 h. The corresponding survey spectrum shows the presence of carbon, oxygen and titanium, whereas no peaks corresponding to lithium or sodium were detected. High resolution spectra allowed us to identify Ti(IV) and the three O 1s peaks previously mentioned O 1s(O^{2-}): 53%, O 1s(OH^-): 37% and O 1s(ads): 10%. It can be observed that O 1s(ads) represents 41% of the total O 1s peak area, which means that the amount of adsorbed gas (H_2O or CO_2) is much larger than for the titanium foil dipped in the carbonate melt.

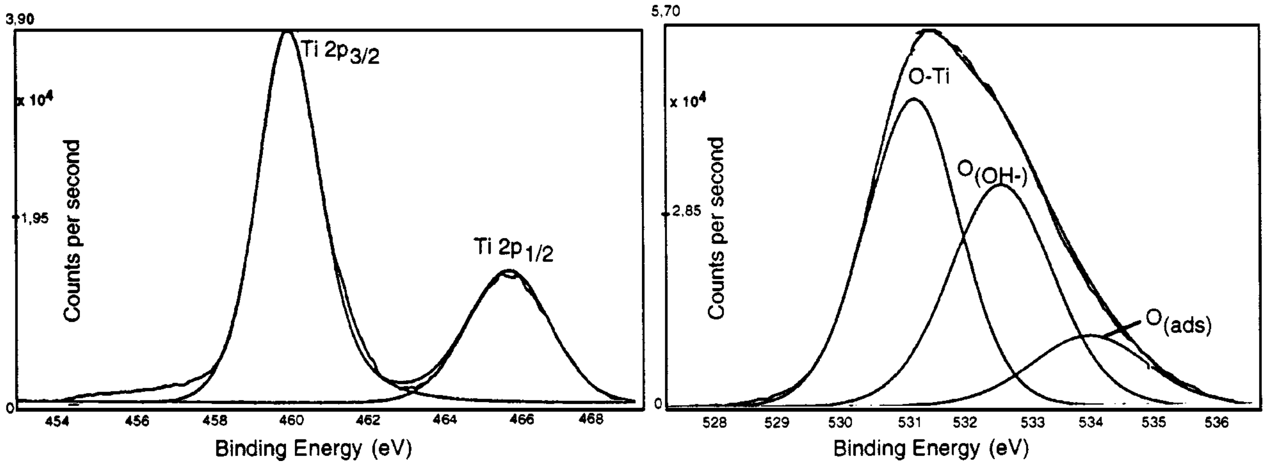


Figure 2 High resolution XPS spectra of Ti 2p and O 1s, relative to a titanium foil exposed to molten Li_2CO_3-Na_2CO_3 at 650 °C, under anodic atmosphere.

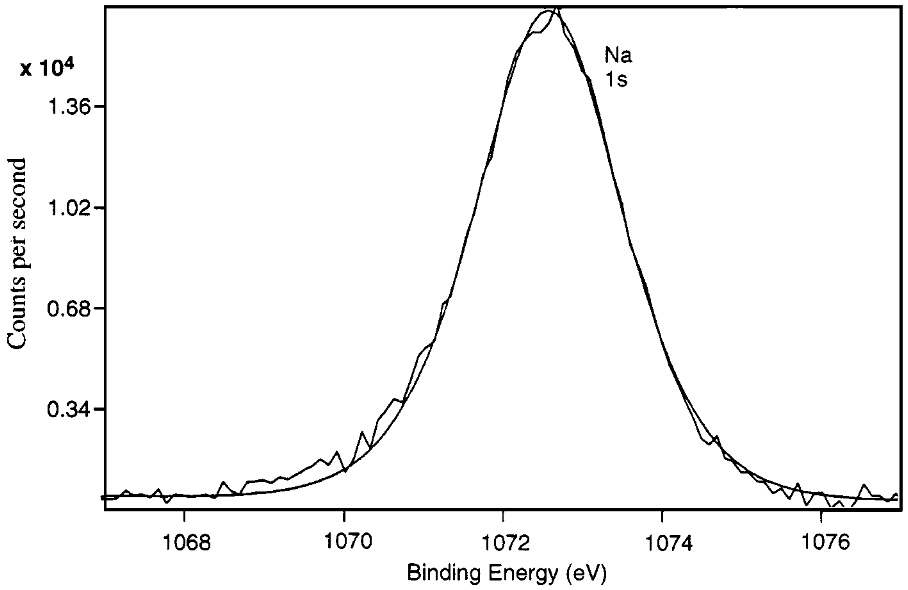


Figure 3 High resolution spectrum of Na 1s, in the same conditions, relative to a titanium foil exposed to molten Li_2CO_3-Na_2CO_3 at 650 °C, under anodic atmosphere.

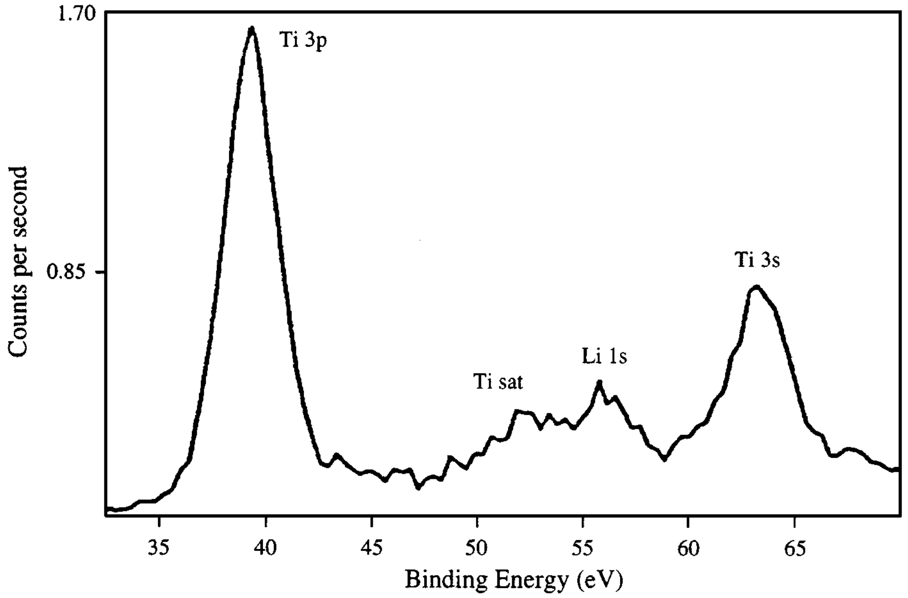


Figure 4 High resolution XPS spectrum showing Li 1s peak, relative to a titanium foil exposed to molten Li_2CO_3-Na_2CO_3 at 650 °C, under anodic atmosphere.

TABLE I Values of the binding energies (B.E.) corresponding to Ti $2p_{3/2}$, Ti $2p_{1/2}$ peaks and ΔB.E., the difference between them

Literature data [ ] or experimental results	Titanium oxidation degree	B.E. $2p_{3/2}$ (eV)	B.E. $2p_{1/2}$ (eV)	ΔB.E. (eV)
[7]	0	454.5/453.8	460.5	6.0
[7]	III	457.5	463.1	5.7 ± 0.1
[8]	III	457.4	463.1	5.7
[8]	IV	458.9/459.0	464.6	5.7
[9]	IV	459.2 ± 0.1	465.0 ± 0.1	5.8
Ti treated above the melt	IV	458.1	463.9	5.8
Ti treated in Li-Na	IV	458.9	464.6	5.7
TiO_2 before treatment	IV	458.4	464.1	5.7
TiO_2 treated in Li-Na	IV	458.4	464.2	5.8
Li_2TiO_3 before treatment	IV	458.4	464.2	5.8
Li_2TiO_3 treated in Li-Na	IV	458.4	464.1	5.7

3.1.2. Titanium dioxide

The XPS spectra obtained with an untreated commercial pellet of rutile TiO_2 were used as references for the titanium and the oxygen peaks. Titanium is present in +IV chemical state and the high resolution spectrum of O 1s shows that 82% of the total oxygen peak is bound to titanium (Ti-O), 13% corresponds to hydroxide groups and only 5% to the adsorbed gases.

The spectrum obtained with a TiO_2 pellet after the same treatment of three days in the Li + Na carbonate eutectic is roughly the same than that obtained in Fig. 2 with the Ti foil dipped in the melt. Nevertheless, the proportions of the O 1s components are different: O^{2-}: 18%, O 1s(OH^-): 9% and O 1s(ads): 73%.

In Table I, the binding energies relative to Ti $2p_{3/2}$ and $2p_{1/2}$ and the difference between both values for the mentioned samples are compared to data from the literature concerning titanium in different chemical states. These results confirm the presence of Ti(IV) at the surface of all the studied samples. In Table II are summarized the deconvolution parameters used for the Ti $2p_{3/2}$, Ti $2p_{1/2}$ and O 1s(O-Ti) peaks relative to the different samples.

TABLE II Values of the binding energies (B.E.), the peak areas and the parameters used for the decomposition of the high resolution spectra of Ti $2p_{3/2}$, Ti $2p_{1/2}$ and O 1s (O-Ti) peaks

Samples	B.E. (eV) Ti $2p_{3/2}$, (Ti $2p_{1/2}$) and [O 1s]	Peak area (cts.eV)	FWHM (eV)	G/L
Ti treated above the melt	458.1	17 200	1.5	30
	(463.9)	(8 160)	(2.2)	(60)
	[530.1]	[22 660]	[1.6]	[20]
Ti treated in Li-Na	458.9	66 286	1.5	50
	(464.6)	(31 650)	(2.3)	(30)
	[530.2]	[79 154]	[1.6]	[30]
TiO_2 before treatment	458.4	76 711	1.4	60
	(464.1)	(37 555)	(2.2)	(60)
	[529.7]	[99 397]	[1.5]	[20]
TiO_2 treated in Li-Na	457.6	14 205	1.6	20
	(463.4)	(5 902)	(2.2)	(50)
	[529.0]	[18 888]	[1.6]	[60]
Li_2TiO_3 before treatment	458.4	43 268	1.6	20
	(464.2)	(21 846)	(2.2)	(60)
Li_2TiO_3 treated in Li-Na	458.4	45 126	1.7	20
	(464.1)	(20 101)	(2.1)	(50)

3.1.3. Discussion

XPS spectra (Figs 1 and 2) obtained for the titanium foil treated in the molten carbonate are similar to those corresponding to the TiO_2 pellet. The presence of Ti(IV) and O-Ti shows that the titanium foil was oxidized *in situ*. The hypothesis of this oxidation in the anodic conditions of a molten carbonate fuel cell can be justified by the fact that H_2O and CO_2 are globally stronger oxidizing agents and dominate the reducing power of hydrogen. Indeed, the comparison of the free energies ΔG^* shows that the oxidation reactions of Ti into TiO_2 or Li_2TiO_3 are more favourable than the reduction reaction of Ti into TiH_2 [4] in our working conditions:

$$\mathrm{Ti} + \mathrm{H_2} \rightarrow \mathrm{TiH_2} \quad \Delta G^* = -17.4\,\mathrm{kJ/mol} \tag{1}$$

$$\mathrm{Ti} + 2\mathrm{H_2O} \rightarrow \mathrm{TiO_2} + 2\mathrm{H_2} \quad \Delta G^* = -376.2\,\mathrm{kJ/mol} \tag{2}$$

$$\mathrm{Ti} + \mathrm{Li_2CO_3} + 2\mathrm{H_2O} \rightarrow \mathrm{Li_2TiO_3} + 2\mathrm{H_2} + \mathrm{CO_2} \tag{3}$$

$$\Delta G^* = -435.0\,\mathrm{kJ/mol}$$

The fact that only Ti(IV) is present at the surface of the titanium sample, in contact with the $H_2/CO_2/H_2O$ atmosphere at 650 °C, shows that metallic titanium is oxidized into TiO_2 or Li_2TiO_3 over a layer thickness larger than 50 Å, which is the analysis depth for titanium compounds.

The comparison of the peak intensities relative to O 1s(ads) and C 1s(CO_3^{2-}), obtained for TiO_2 before and after treatment in Li_2CO_3-Na_2CO_3, shows that a large amount of carbonate is adsorbed at the surface of the sample in contact with carbonates. Fig. 5 shows the high resolution spectra of C 1s.

In order to determine the structure of thicker layers of about 1 μm, XRD experiments were carried out on metallic titanium and TiO_2 after treatment in molten carbonate. XRD spectra of the surface of metallic titanium and TiO_2 are presented in Fig. 6. In the case of metallic titanium, two crystalline structures were identified: mainly $Li_2Ti(IV)O_3$ and also $LiTi_2O_4$ (which is a bronze with Ti(IV) and Ti(III)). As no Ti(III) was detected by XPS, it can be concluded that the upper layer (<50 Å) is constituted by Li_2TiO_3, which is thermodynamically the most stable form of titanium in MCFC conditions [4], and the inner layer (>50 Å) by $LiTi_2O_4$. In the case of TiO_2, again two structures were

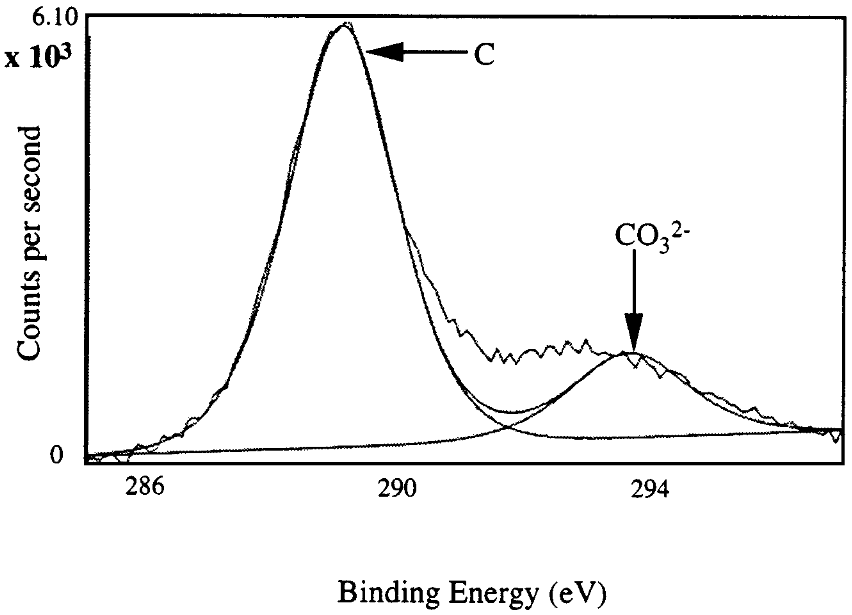
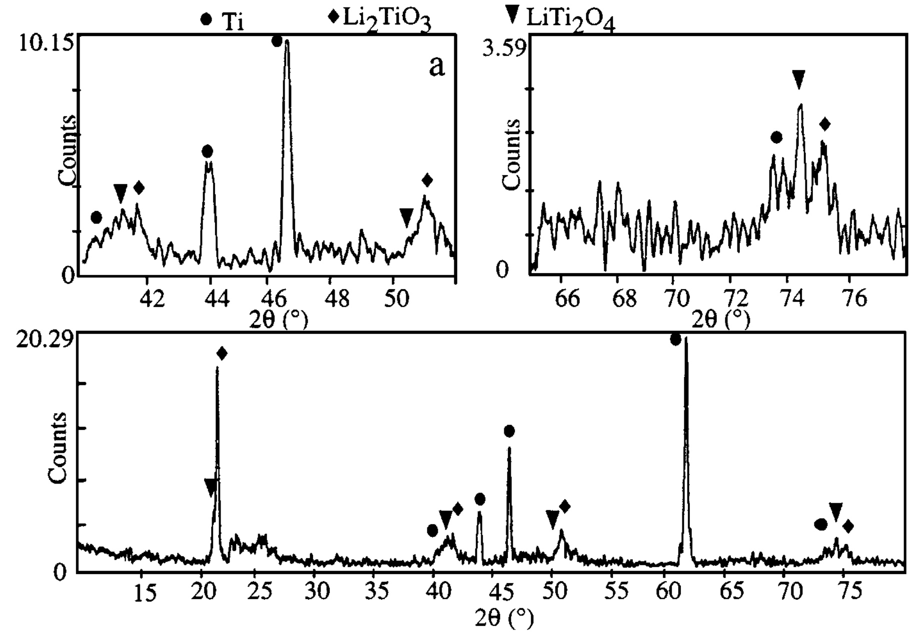


Figure 5 High resolution XPS spectrum showing C 1s peak, relative to a titanium foil exposed to molten Li_2CO_3-Na_2CO_3 at 650 °C, under anodic atmosphere.



(a)

Figure 6 XRD patterns, after exposure to molten Li_2CO_3-Na_2CO_3 at 650 °C, under anodic atmosphere, of the following samples: (a) Metallic titaniuma and (b) TiO_2.

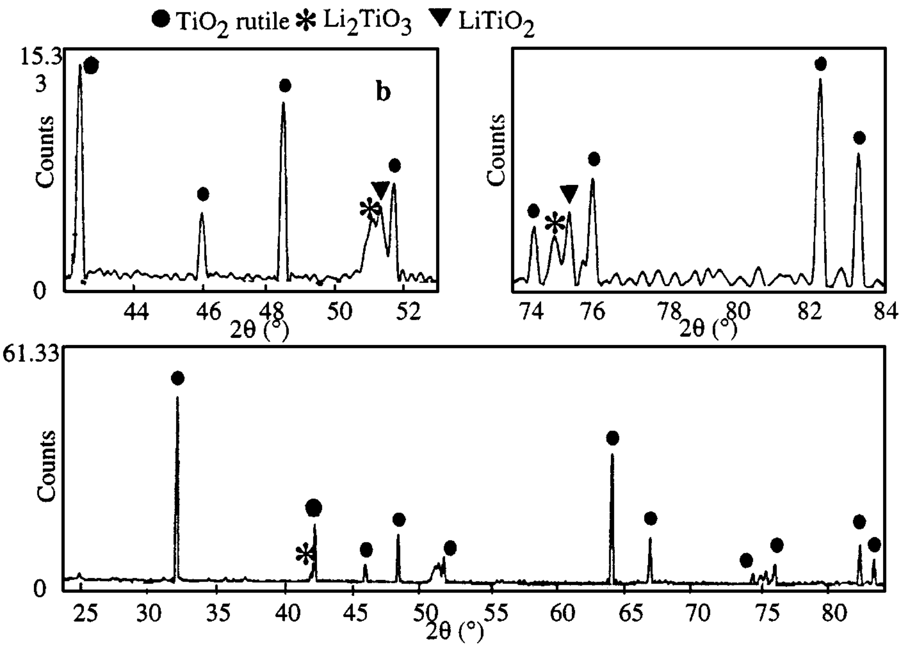
identified: mainly $Li_2Ti(IV)O_3$ and also $LiTi(III)O_2$. The first compound, corresponding to Ti(IV), is also present in the surface layer analyzed by XPS, whereas the second one, containing Ti(III) is only present in subjacent layers deeper than 50 Å. A thorough description of the structures determined by XRD will be given in a forthcoming paper.

3.2. Semi-quantitative analysis

Lithium and sodium were detected on all the samples exposed to molten carbonate. The presence of these elements at the surface of the samples after their contact with the melt can be due either to lithium or sodium incorporation in the oxide layer, or to the adsorption of lithium and sodium carbonates.

In order to determine if alkali cations are incorporated in the surface layers of the samples, a semi-quantitative analysis was carried out. As carbon corresponding to adsorbed carbonates is detected at the surface, an homogeneous layer of the adsorbed carbonate eutectic was considered as the top layer. It was then possible to determine the contribution of the adsorbed lithium and sodium to the respective peak intensities of these species. The following relation, explained in the Appendix, was used, considering that the proportion of lithium and sodium at the surface of the samples is equal to their proportion in the molten carbonate:

$$\frac{D_A^S}{D_B^S} = \frac{I_A^S}{I_B^S} \cdot \frac{Y_B}{Y_A} \cdot \frac{\lambda_B^S}{\lambda_A^S} \qquad (4)$$



(b)

Figure 6 (*Continued*).

TABLE III Intensities of incorporated sodium and comparative ratio of lithium with respect to titanium in Li_2TiO_3 layers

Samples	Li_2TiO_3 before treatment	Ti treated in Li-Na	TiO_2 treated in Li-Na	Li_2TiO_3 treated in Li-Na
I(Na(inc))	—	23738 cts.eV	—	9190 cts.eV
I(Li(inc))	—	5692 cts.eV	4469 cts.eV	11 430 cts.eV
$\frac{I(\text{Li(inc)})}{I(\text{Ti})}\cdot\frac{Y(\text{Ti})}{Y(\text{Li})}$	7.35	8.87	20.3	13.93

where D_i^S represents the density of the atom i inside the solid; I_i^S, peak area of i, represents the intensity emitted by i in a solid of infinite thickness with respect to λ; Y_i represents the experimental XPS yield relative to i; and λ_i^S represents the inelastic mean free path in the solid of the emitted electrons.

The composition of the carbonate eutectic being: Li_2CO_3-Na_2CO_3 52–48 mol %, the ratios of sodium and lithium with respect to carbon in the top layer are the following:

$$\frac{D\left(\text{Na}_{\text{CO}_3^{2-}}\right)}{D(\text{C})} = 2 \times 0.48 = 0.96$$

$$\frac{D\left(\text{Li}_{\text{CO}_3^{2-}}\right)}{D(\text{C})} = 2 \times 0.52 = 1.04$$

Therefore, the intensities emitted respectively by adsorbed lithium and sodium were determined and substracted from their total intensities, allowing to deduce the amounts of these species incorporated within the Li_2TiO_3 lattice. Sodium was considered incorporated when the resulting intensity of this species was >0. In order to determine the incorporation of lithium, the ratios of the resulting lithium intensity with respect to titanium, corrected for the experimental XPS yields, were calculated for each treated sample and compared with pure Li_2TiO_3.

The values of the alkali intensities corresponding respectively to adsorbed and incorporated species are presented in Table III.

In all the cases:

$$I(\text{Na}) = I\left(\text{Na}_{\text{CO}_3^{2-}}\right) + I(\text{Na}_{\text{inc}}) > I\left(\text{Na}_{\text{CO}_3^{2-}}\right)$$

where I(Na) is the total intensity of the sodium peak, $I(\text{Na}_{\text{CO}_3^{2-}})$ the determined intensity corresponding to Na_2CO_3 and $I(\text{Na}_{\text{inc}})$ the intensity emitted by the sodium incorporated in Li_2TiO_3.

Moreover:

$$\frac{I(\text{Li}_{\text{inc}})\cdot Y(\text{Ti})}{I(\text{Ti})\cdot Y(\text{Li})} > \frac{I\left(\text{Li}_{\text{Li}_2\text{TiO}_3}\right)\cdot Y(\text{Ti})}{I(\text{Ti})\cdot Y(\text{Li})}$$

where $I(\text{Li}_{\text{inc}})$ is the intensity emitted by lithium incorporated in the oxide layer and $I(\text{Li}_{\text{Li}_2\text{TiO}_3})$ the intensity of lithium in pure Li_2TiO_3. The corresponding values are presented in Table III.

It can be concluded that, for all the considered samples, lithium and sodium are incorporated inside Li_2TiO_3.

3.3. Correlation between the ratio of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peak areas and inserted lithium

The ratio, r, between Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peak areas is theoretically equal to the ratio $\frac{2j+1}{2j+1}$, where j is the

TABLE IV Ratio of the Ti $2p_{3/2}$ and the Ti $2p_{1/2}$ peak areas as a function of lithium at the surface of the samples

Samples	$r = \frac{I(2p_{3/2})}{I(2p_{1/2})}$	Presence of additional lithium	Detection techniques
Ti treated above the melt	2.1		
Ti treated in Li-Na	2.2	×	XRD, XPS, FTIR[a]
TiO_2	2.0		
Li_2TiO_3	2.0		
TiO_2 treated in Li-Na	2.4	×	XRD, XPS
Li_2TiO_3 treated in Li-Na	2.3	×	XPS

[a] Fourier transform infrared spectroscopy.

quantum number $j = l \pm s$ with $j > 0$, l being the orbital quantum number and s, the spin quantum number [7]. For Ti 2p electrons, $l = 1$ and $s = \pm 1/2$; therefore, $j = 3/2$ or 1/2 and $r = 2$. The ratios r, measured after the deconvolution of titanium peaks, are presented in Table IV. The value of r is equal to the theoretical value of 2 only in the case of TiO_2 and pure Li_2TiO_3. It appears that this ratio increases with the amount of incorporated lithium in the surface layer. The proportion of incorporated lithium within the lithium titanate structure, estimated from XPS spectra, is represented by the ratio $D_{\mathrm{Li}}^{\mathrm{inc}}/D_{\mathrm{Ti}}$. For both Ti and TiO_2 samples, the value of r increases after treatment in the molten carbonate melt. In fact, Soedergren *et al.* [12], in a recent publication, have found an increase of the full width at half maximum, FWHM, of the Ti 2p peaks when lithium was electrochemically intercalated in nanoporous anatase TiO_2. The full width at half maximum being directly proportional to the peak area, we have determined the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peak areas presented in this paper and found that the ratio $I(2p_{3/2})/I(2p_{1/2})$ was 2.1 for pure TiO_2, 2.5 for TiO_2 after lithium intercalation and again 2.1 when lithium was deintercalated. The following hypotheses were given by these authors:—the double injection of lithium ions and electrons may lead to distorsion of the TiO_2 lattice, resulting in a slight shift and a broadening of the Ti 2p components,—TiO_2 is not homogeneously intercalated, which means that the stoichiometry of the Li-intercalated TiO_2 is not well-defined. By analogy, our results seem to confirm the influence of lithium incorporation within the Li_2TiO_3 lattice (probably provoking a distorsion), on the broadening of Ti 2p peak and in particular Ti $2p_{3/2}$. The formula of the compound formed could be: $Li_{2+x}TiO_3$ (or $Li_{2+x}Ti_x(III)Ti_{1-x}(IV)O_3$). This lithium incorporation should be balanced by the presence of Ti(III), which was not detected by XPS, probably because of the instability of this species after the removal of the samples from the molten carbonate and the water treatment. A more detailed explanation of this process and its correlation with the broadening of the Ti $2p_{3/2}$ peak is impossible at this stage of our work; nevertheless, a similar chemical intercalation of lithium has been described by other authors in a $Li_2Ti_3O_7$ lattice, yielding $Li_{2+x}Ti_3O_7$ [13].

4. Conclusion

XPS analysis allowed us to identify the chemical states of the elements present at the surface of Ti or TiO_2 samples in contact with molten Li_2CO_3-Na_2CO_3: Ti(IV), O(-II), Li(I) and Na(I). Metallic titanium was covered by TiO_2 at 650 °C in the H_2/CO_2 (80/20) (humidified with water $P(H_2O) \approx 0.2$ atm) atmosphere and by Li_2TiO_3 in the molten carbonate under the same atmosphere. Semi-quantitative analysis of the measured XPS intensities showed that both lithium and sodium are incorporated in the $LiTi_2O_3$ lattice provoking, in particular, an increase of the ratio of the intensities of the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks, associated with a broadening of the $2p_{3/2}$ signal.

This work constitutes an attempt to define the evolution of surface layers on titanium and titanium oxide in the anodic conditions of MCFC. The present characterization should be pursued in order to clarify some points. The insertion of lithium in the Li_2TiO_3 structure should induce the presence of Ti(III), however this species was not clearly identified by XPS, which could be done by electron spin resonance spectroscopy (ESR). The composition depth profile of the samples is also an important aspect in order to analyze the diffusion of lithium within these materials. This could be followed by secondary ion mass spectroscopy (SIMS).

Acknowledgements

Gaz de France (GDF/CNRS/ENSCP 414) and the European Community (Joule No. JOE3CT950024) are greatly acknowledged for financial support. Professor N. Baffier is gratefully acknowledged for helpful discussions and J. M. Sifre for technical support.

Appendix [7, 10, 11]

The intensity $I_{\mathrm{A}}^{\mathrm{S}}$ of the signal emitted by an element A in a solid S of infinite thickness is given by the following equation:

$$I_{\mathrm{A}}^{\mathrm{S}} = k \cdot D_{\mathrm{A}}^{\mathrm{S}} \cdot Y_{\mathrm{A}} \cdot \lambda_{\mathrm{A}}^{\mathrm{S}} \cdot \sin\theta \qquad \text{(A1)}$$

where k is a constant characteristic of the spectrometer; Y_{A}, characteristic of the element, constant whatever the chemical state of the element A is inside a metallic or an oxide structure, was determined from [7]; θ, the emission angle is equal, in our condition, to 90°; and λ, the inelastic mean free path, was determined from an empirical relation of Seah and Dench [11]. This equation, expressed for elements A and B, leads to relation (4) given in the text.

The binding energy for Ti 2p(IV) was considered as the mean energy of the doublet (Ti $2p_{3/2}$, Ti $2p_{1/2}$): $E_{\mathrm{b}}^{\mathrm{Ti}} = 461.8$ eV. Therefore, $E_{\mathrm{c}}^{\mathrm{Ti}} = 787.8$ eV.

The following values of M (molecular weight), n (number of atom in the molecule) and ρ (volumic weight in g/dm^3) were used:

- for Li_2TiO_3:
  $\rho(Li_2TiO_3) = 2.13.10^3$ g/dm^3
  $n = 6$
  $a = 0.24$ nm

TABLE V Values of the experimental XPS yield (Y) [7] and the mean inelastic free path (λ) inside the solids Li_2TiO_3 and TiO_2 [11]

	Ti $2p_{3/2}$	Na 1s	Li 1s	C 1s
λ_A (nm) in Li_2TiO_3	2.38	1.15	2.93	2.62
λ_A (nm) in TiO_2	2.09	1.01	2.57	2.30
λ_A (nm) in Li_2CO_3–Na_2CO_3 (52–48 mol %)	2.78	1.34	3.42	3.07
Y_A	1.1	2.51	0.012	0.205

- for TiO_2:
  $\rho(TiO_2) = 4.26.10^3$ g/dm^3
  $n = 3$
  $a = 0.22$ nm

The values of Y_A and λ_A parameters are given in Table V.

References

1. P. C. INNOCENZI, M. GUGLIELMI, M. GOBBIN and P. COLOMBO, *J. Eur. Ceram. Soc.* **10** (1992) 431.
2. I. N. OZERYANAYA, S. D. FINKEL'STEIN, T. I. MANUKHINA, O. P. PENYAGINA and M. V. SMIRNOV, *Zaschita Metallov* **3** (1967) 581.
3. I. N. OZERYANAYA, T. I. MANUKHINA, O. P. PENYAGINA and M. V. SMIRNOV, *Int. Soc. Electrochem.* **30** (1979) 112.
4. V. CHAUVAUT, M. CASSIR and Y. DENOS, *Electrochim. Acta* **43** (1998) 1991.
5. B. MALINOWSKA, M. CASSIR and J. DEVYNCK, *J. Power Sources* **63** (1996) 27.
6. B. MALINOWSKA, M. CASSIR, F. DELCORSO and J. DEVYNCK, *J. Electroanal. Chem.* **21** (1995) 389.
7. W. M. RIGGS, L. E. DAVIS, J. F. MOULDERAND and G. E. MULLENBERG, in "Handbook of X-ray Photoelectron Spectroscopy," edited by C. D. Wagner (Perkin-Elmer Corporation, 6509 Flying Cloud Drive, Eden prairie, Minnesota 55344).
8. J. POUILLEAU, D. DEVILLIERS, H. GROULT and P. MARCUS, *J. Mater. Sci.* **32** (1997) 5645.
9. T. LE MERCIER, J. M. MARIOT, F. GOUBARD, M. QUARTON, M. F. FONTAINE and C. F. HAGUE, *J. Phys. Chem. Solids* **58** (1997) 679.
10. D. BRIGGS and M. P. SEAH, "Practical Surface Analysis," 2nd ed. Vol. 1 (Wiley, 1990).
11. M. P. SEAH and W. A. DENCH, *Surface and Interface Analysis* **1**(1) (1979) 2.
12. S. SOEDERGREN, H. SIEGBAHN, H. RENSMO, H. LINDSTROEM, A. HAGFELDT and S. E. LINDQUIST, *J. Phys. Chem. B.* **101** (1997) 3087.
13. S. GARNIER, C. BOHNKE, O. BOHNKE and J. L. FOURQUET, *Solid State Ionics* **83** (1996) 323.

Received 22 October
and accepted 16 November 1998