

Exploring the incorporation of nitrogen in titanium and its influence on the electrochemical corrosion resistance in acidic media

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Abstract The role of the nitrogen incorporation into titanium, its chemical nature, the location in the titanium lattice and its electrochemical performance were investigated by a combination of several spectroscopy and microscopy techniques using samples prepared by CVD of NH₃ at different temperatures and successive electrochemically tested in 1 M of HClO₄. We found that nitrogen is incorporated in either the interstitial or substitutional site of the lattice depending on the preparation temperature modifying strongly its corrosion resistance which was ascribed to the N 2p hybridization with the Ti 3d orbitals. It was found that at low temperature the N 2p orbitals were more likely to hybridize with Ti_{3d-t_{2g}} orbitals while higher temperature favours the hybridization with the Ti_{3d-e_g} orbitals. This is responsible for the corrosion resistance shown by the samples prepared at higher temperature.

1. Introduction

There is an increasing effort to use renewable sources of energy because of the social and environmental consequences. However, the energy conversion and/or storage in chemical and electrical energy represent some of the biggest challenges due to the technical complexity [1-5]. One of the promising directions are electrolyzers which convert the electric energy produced, i.e. by solar cells or wind generators, into chemical energy through, for example, splitting water into oxygen and hydrogen [6-9]. However the cost and the durability of these electrolyzers are their major weaknesses [10-13] due to the low stability and corrosion resistance of the electrode in aggressive media. Precious-metal oxides are the most stable under such conditions, however, these elements are expensive and listed among the rarest on earth, limiting their large-scale application.

Nitrogen incorporation in titanium is a highly interesting subject in electro and photocatalysis due to the long-term durability shown by TiN_x and the demonstrated ability of nitrogen-doped titanium to absorb visible light [14, 15]. These properties could be used to produce hydrogen directly from solar light or electrolysis of water into its principal components. One of the most important issues is whether the nitrogen is incorporated by the titanium lattice substitutionally or interstitially [16] modifying its performance as electrode drastically as well as outstanding oxidation behaviors and corrosion resistance [17, 18]. Although there is a lot of literature [19-22] no consensus among the reports on the state of doped nitrogen in N-TiO₂ has been established. A detailed investigation of the thermal reactions between ammonia and titanium will provide valuable information about the related nitrogen incorporation in titanium, which produces the formation of TiN_x and TiO_{x-2}N_x from TiO₂. In addition, the successive characterization after the prolonged electrochemical conditions will provide information about its performance as an electrolyzer and its corrosion resistance.

A systematic preparation/characterization scheme has been conducted in this work. TiN_x samples prepared from the reaction of NH_3 with Ti at different temperatures have been studied with several spectroscopy and microscopy techniques as XPS, NEXAFS, XRD and SEM before and after electrochemical characterization in acidic media. In addition to oxidation state sensitive XPS, bonding geometry sensitive NEXAFS was used to extract local geometry and bonding information. By combining these two techniques we were able to distinguish the formation of nitrogen species and the N 2p hybridization with Ti_{3d} orbitals as t_{2g} or e_g giving valuable information about the nitrogen incorporation in the lattice. This investigation has given rise to the understanding of the stability of these species as substitutional or interstitial as well as the energy levels that are induced by the incorporation of nitrogen. We found that the interstitial (associated with the hybridization of N 2p and Ti 3d- t_{2g} orbitals) nitrogen induces doping but lacks stability under electrochemical conditions. On the other hand, substitutional nitrogen (related to the hybridization of N 2p with the Ti 3d- e_g orbitals) leads to doping and higher stability under aggressive electrochemical environments.

2. Experimental

The nitrification of pristine Ti foil (Grade 1, 50 μm thick from Ankuro International GmbH) was carried out using a cold-wall shower-head CVD reactor at the Fritz-Haber-Institute of the Max Planck Society, Berlin. Pre-cut titanium disks, 10 mm in diameter, were inductively heated at temperatures between 700°C to 1100°C using a graphite plate as a susceptor. All the reactions were performed under a laminar flow of 10% ammonia (purity 99.999% from Westfalen AG) in an argon (200 sccm NH_3 + 1800 sccm Ar) gas mixture at 6 mbar pressure for 10 minutes. The incorporation and the chemical state of titanium were monitored by scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD), and X-ray photoelectron spectroscopy (XPS). The samples were transferred to the spectrometer by a sealed transfer system in order to avoid contact with ambient environment.

Figure 1a shows the scanning electron microscopy (SEM) images of nitrified titanium foil at different temperatures indicating the samples nitrified at 800°C have a similar morphology to the pristine samples. However, it is obvious that the titanium surface morphology is strongly influenced by the nitrogen incorporation as the sample prepared at 1100°C shows (see figure 1a3). Chemical analysis was obtained by element specific XPS measurements (see figure 1b). The Ti 2p XP spectra show the spin orbit doublet 2p $_{3/2}$ and 2p $_{1/2}$ peaks with an energy separation, ΔE , of 5.6 eV. Titanium presents a peak at 459.2 eV related to Ti^{4+} which is associated with TiO_2 , while the peak at 454.9 eV (Ti^{3+}) indicates the formation of TiN_x . Finally the peak at 457.2 eV is usually related to a lack of stoichiometry of TiO_2 - TiN_x species with mix oxidation 3+ and 4+ states resulting from the formation of $\text{TiO}_{x-2}\text{N}_x$ [23]. Thus, the pristine Ti foil features a sharp Ti^{4+} peak resulting from the native oxide. On the other hand, the sample produced from NH_3 at 800°C shows an increase in the $\text{TiO}_{x-2}\text{N}_x$ species. Samples nitrified at higher temperatures produced significant reduction of Ti^{4+} (TiO_2) into Ti^{3+} (TiN_x) as the spectra prove. This interpretation was corroborated by the successive analysis of N_{1s} and O_{1s} XPS spectra. The O_{1s} XPS spectra of nitrified titanium samples features a dominant peak at 530.6 eV, depending on the temperature, which is associated with the presence of TiO_2 [17]. The peak at 530.6 eV decreases and an additional peak at 533.3 eV assigned to NO_x [24] species emerges in samples nitrified at 800°C. The samples produced at higher temperature yield a decrease in the oxygen species which agrees with the increase in the Ti^{3+} species shown in Ti_{2p} spectrum. The chemical states of the incorporated nitrogen were

characterized by the N_{1s} core-level spectra. Based on the binding energies, the N_{1s} peaks can be divided into two groups: those at binding energy 397.0 eV and at 400.5 eV, which are assigned to TiN-like nitrogen species in the lattice and bound to various surface oxygen sites (NO_x like species), respectively [25]. According to this assignment, the N 1s XP spectra show an increase in the TiN_x species with increasing nitrification temperature in good agreement with the Ti 2p and O 1s spectra. The binding energies and chemical states associated with each orbital are summarized in Table 1.

In addition, the incorporation of nitrogen in titanium was investigated by XRD, which was performed under out-of-plane grazing incidence geometry (with a Goebel mirror and secondary sollers) at a Bruker D8 Advance (Da Vinci - Design with LynxEye detector), equipped with an eulerian cradle. The incident angle was set to 0.4° Theta and phase analysis was done with DIFFRAC.EVA software from Bruker (Database PDF 2013). Figure 2 show the XRD diagram of pristine, nitrified Ti samples at 800° and $1100^\circ C$ samples. Pristine samples behave a titanium oxide character as the reflection peaks at 42.2° , 43.2° and 49° indicates, see figure 2a. Otherwise, figure 2b shows the XRD spectra of samples nitrified at $800^\circ C$ which features a strong peak associated with the presence of $TiN_{0.26}/TiN_{0.17}$ species. Finally, samples nitrified at $1100^\circ C$ yeals peaks at 39.3° and 40.8° related to to Ti_2N species (see figure 2c) which is ascribed to the formation of a titanium nitride layer. The elimination of the features ascribed to TiO_2 in the pristine sample at 42.2° and 49° are due to nitrogenation, which is connected to the formation of $TiO_{x-2}N_x$ (Ti^{4+}/Ti^{3+}) from $TiO_x(Ti^{4+})$ species as the XPS proved.

The role and stability of the incorporated nitrogen can be discussed further through a comparison before and after electrochemical reactions carried out under chronoamperometry (CA) control at +1.0 V vs Ag/Cl (reference electrode) and Pt (counter electrode) during ~30 hours in 1 M of $HClO_4$. In figure 3 the CV and the CA of pristine, nitrified Ti foil at $800^\circ C$ and $1100^\circ C$ are shown. SEM and energy dispersive X-ray (EDX) measurements after the electrochemical test shows the corrosion of the pristine Ti foil as shown by the change in oxygen signal. Samples nitrified at $800^\circ C$ suffers less severe corrosion or the adsorption of clusters on the surface activated by bias potential than the pristine samples as seen in samples nitrified at $1100^\circ C$ yield higher resistance to corrosion in aggressive medium under anodic oxidation conditions as seen in EDX. However, EDX is not enough to describe the complex electronic structure of such electrodes before and after the anodic oxidation. Consequently, in depth X-ray spectroscopy (XPS/NEXAFS) measurements were performed at the ISS beamline in BESSY II (Helmholtz-Zentrum Berlin) using soft X-ray radiation provided from the tuneable monochromator light source. The measurements were made at $\sim 10^{-8}$ mbar using the Fritz-Haber-Institute end station. The kinetic energy was set to 150 eV for the XPS measurements yielding an electron mean free path of about ~ 0.85 nm providing surface sensitive spectra. The X-ray absorption spectroscopy (XAS) measurements were recorded in total electron yield (TEY) collecting the secondary electrons by grounding the sample with a current pre-amplifier and has a slightly higher information depth than XPS. The energy resolution was 0.1 eV. The possible contamination contribution of atmospheric oxygen was suppressed by the use of an special sealed vacuum transfer system. In addition, no beam damage was detected as confirmed by the successive measurements at the same point. The spectra were normalized to the adsorption pre- and post-edges.

2.1 XPS analysis

Figure 3 shows the electrochemical characterization recorded using the pristine and nitrified Ti foil used as working electrodes. Measurements were performed during ~30 hours CA

control at +1.0 V vs Ag/Cl and Pt counter electrodes in 1 M of HClO₄. Figure 4 displays the XP spectra of Ti 2p, O 1s and N 1s core levels before and after the electrochemical characterization. Thus, Ti_{2p} features three peaks of interest at 459.2 eV, 457.2 eV and 454.9 eV which are assigned to Ti⁴⁺ (TiO₂), TiO_{x-2}N_x and Ti³⁺ (TiN_x), respectively (see figure 4a). The energy separation between the peaks 2p_{3/2} and 2p_{1/2} is $\Delta = 5.6$ eV. Prior to the electrochemical characterization the pristine Ti shows (figure 4a1) an intense peak at 459.2 eV pointing to its TiO₂ nature. After the electrochemical characterization the sample remains unaltered as shown in figure 4a2. On the other hand, samples prepared at 800°C feature a characteristic peak at 457.2 eV revealing its TiO_{x-2}N_x nature (figure 4a3). These species are not stable as the curve in figure 4a4 indicates: the original TiO₂ nature is recovered after the CA control. Finally, the samples prepared at 1100°C feature an intense peak at 454.9 eV associated with the formation of Ti³⁺ (figure 4a5). These species are more stable in aggressive media as the remaining peak at 454.9 eV after CA indicates (figure 4a6).

Figure 4b shows the O 1s spectra featuring four regions of interest: TiO₂ species located at 530.6 eV [26], TiO_{x-2}N_x/NO species at 531.4 eV indicating nitrogen incorporation [24], O₂/H₂O species at 532.5 eV [27] and adsorbed NO_x species at 533.3 eV [28]. The pristine foil has TiO₂ nature as indicates the dominant peak at 530.6 eV, which remains unaltered after the CA (see figures 4b1 and 4b2). Otherwise, Ti foil nitrified from NH₃ at 800°C yields two main peaks located at 530.6 eV and 533.3 eV ascribed to TiO₂ and NO_x bonding to surface species [29] (see figure 4b3). After the CA the adsorbed NO_x nearly vanished and a peak assigned to O₂/H₂O species evolved (see figure 4b4). Nevertheless, samples prepared at 1100°C features residual TiO₂ character (see figure 4b4) with a shoulder at 531.4 eV characteristic of TiO_{x-2}N_x species. The CA control yields the formation of TiO₂ and the adsorption O₂/H₂O species (see figure 4b6).

The N 1s (figure 4c) spectra show three peaks associated to TiO_{x-2}N_x (396.5 eV), TiN_x (397.0 eV) and 400.5 eV related to the presence of TiO_{x-2}N_x species [24]. Pristine samples (figure 4c1 and 4c2) do not show the presence of nitrogen. Otherwise, samples prepared at 800°C feature two peaks at 396.5 eV and 400.5 eV characteristic of TiO_{x-2}N_x and NO_x, respectively (figure 4c3). After the CA control the NO_x species decreased in samples prepared at 800°C while the TiO_{2-x}N_x species vanished (figure 4c4). Samples produced at 1100°C yielded one main peak at 396.5 eV with a shoulder at 397.0 eV associated to TiN_x species (see figure 4c5). After the electrochemical characterization these species remained stable with a slight increase of the peak associated to the TiO_{x-2}N_x species.

Figure 5 shows the valence band of these samples collected before and after the electrochemical test. It is well known that the incorporation of nitrogen creates a large concentration of vacancies inducing noticeable doping [30]. This is the so-called red shift effect due to the ability of TiN_x to absorb visible light. Therefore, a carefully investigation of the valence band can elucidate the role of the N incorporation in the doping of titanium [25]. Figure 5a shows the valence band measurements of the samples before the electrochemical test. Pristine samples show an estimated gap of 3.2 eV referred to the Fermi level position (figure 5a1). On the other hand the nitrification of the titanium samples at 800°C and 1100°C with NH₃ induces the formation of additional energy levels which narrow the gap yielding gaps of 2.4 eV and 2.0 eV respectively. After the electrochemical test the band remained the same for the pristine samples 3.2 eV (figure 5b1) while for the two nitrified samples they increased to 2.5 eV and 2.9 eV, respectively (figure 5b2 and 5b3). The XPS measurements indicated a decrease in the Ti³⁺ and the increase in the Ti⁴⁺ species which is ascribed to the formation at the interface of TiO_{x-2}N_x and TiO_x species. This fact explains the broader gap observed in the nitrified samples after the electrochemical test.

2.2 NEXAFS analysis

The complex structure of the Ti L-edge NEXAFS spectra of TiO₂ is due to the combination of atomic interaction and crystal field effects as a result of the static electric field produced by the surrounding anion neighbors (charge distribution) [31]. The interaction between the ligands and the transition metal is caused by the attraction of positively charged metal cations and non-bonding electrons of the ligands [32]. It follows the change in energy in the transition metal d-orbitals when they are surrounded by an array of ligand charges because some of them will be closer to the d-orbitals. The electrons in the d-orbitals and those in the ligand repel each other by means of electrostatics repulsion between charges. It implies that the d-electrons closer to the ligand present higher bond energy than the others resulting in d-orbital energy splitting (t_{2g} and e_g) [33] yielding larger separations at higher oxidation states (see figure 6). Figure 7 shows the XA spectra collected in TEY of TiN_x films produced at different temperatures under the presence of NH₃ in the CVD reactor.

The Ti L-edges XAS-TEY spectrum of reference pristine Ti foil samples are shown in figure 7a1. The L₃ region corresponds to the transition O 2p_{3/2}- Ti 3d and the L₂ to O 2p_{1/2}- Ti 3d [34]. Both bands feature a crystal field splitting of the 3d band into t_{2g} and e_g . Since e_g orbitals are pointed directly toward the 2p orbitals surrounding O atoms, this band is sensitive to the local environment. After the electrochemical test the sample features the same behaviour (see figure 7a2) as the subtraction of spectrum 1 from spectra 2 confirms. The Ti_{2p} XAS on samples produced by the nitrification with NH₃ at 800°C is similar to that of the TiO₂ suggesting the influence of N on Ti is limited (figure 7a3). It indicates that Ti remains highly oxidized with a small amount of bound nitrogen. After the CA control the samples prepared at 800°C feature a slight increase in the t_{2g} peak intensity (see figure 7a 4-3). Samples produced at higher temperature feature broader t_{2g} and e_g peaks as a result of the lower oxidation state (Ti³⁺) and is corroborated by the XP spectra. One small difference is visible: the energy splitting for the centre of Ti t_{2g} - e_g at the L₃ edge is smaller in TiN_x (1.1 eV) than in TiO₂ (1.6 eV) (figure 7a5). The splitting between the t_{2g} and e_g is smaller for the samples with smaller concentration of oxygen atoms pointing out the presence of reduced Ti atoms. This fact is proved by the lower oxidation state (Ti³⁺) observed in the XPS. In addition, samples prepared at higher temperature feature unaltered spectra after the CA control due to the higher stability of the incorporated nitrogen at this temperature.

The O K-edge XA spectra are shown in figure 7b. For pristine Ti foil (figure 7b1) the first doublet located at 531 eV and 534 eV correspond to the O 2p states hybridized with the empty split Ti_{3d} bands, t_{2g} and e_g [35]. The sharpness of these two peaks reflects high ionic or covalent bonding between the O and Ti. The peaks between 537 eV and 550 eV are due to the delocalized antibonding O_{2p} states coupled to Ti_{4sp} with principally O 2p character. The origin for the σ^* bands are related to the Ti 2p, 4s and 4p states hybridized with the O 2p orbitals [36]. The pristine film features the same spectrum after the electrochemical test indicating that the sample remains oxidized with its TiO₂ nature (figure 7b2). Samples prepared at 800°C show the peaks merge to a sharp e_g peak and form a new peak at 533.6 eV in the shoulder (figure 7b3). The Ti e_g orbitals, directed towards the oxygen, show stronger coupling with the O 2p. Nevertheless, an increment of the peak intensities in the oxygen edge corresponding to the antibonding O 2p transition was observed and is probably associated with a smaller Ti-O interaction. After the CA, the samples prepared at 800°C recovered the t_{2g} and e_g orbitals characteristic of TiO₂ species. While we can confirm this fact for single crystal TiO₂, the width and asymmetry requires the inclusion of a third peak near e_g for a correct deconvolution

(figure 7b4) [37]. Finally samples prepared at higher temperature features residual oxygen resembles slightly the TiO₂ spectrum (figure 7b5). These features are likely related to the formation of residual surface TiO₂. After the CA control the sample remains unaltered as confirmed by the residual presence of oxygen (figure 7b6).

Figure 7c shows the N K-edge spectra, the first two spectral features below 403 eV are assigned to unoccupied N 2p states hybridized with Ti 3d orbitals in TiN_x, and the features between 403 and 415 eV to unoccupied N_{2p} states hybridized with Ti 4sp orbitals resembling the shape of the O K-edge [38]. Figure 7c1 and 7c2 shows the absence of nitrogen in the pristine samples. TiN_x grown at 800°C presents a strong t_{2g} peak as well as a weaker e_g peak. It is due to the O 2p hybridization with the e_g orbitals (figure 7b3) which hinders the formation of stronger coupled N 2p orbitals with e_g implying that the nitrogen is added mainly to the Ti interstitially (figure 7c3). Therefore, the doublets are further disrupted compared with samples prepared at higher temperatures suggesting the local bonding environment of this sample is different. After the electrochemical treatment the nitrogen remains residually in the samples prepared at 800°C (figure 7c4). Samples prepared at 1100°C resemble d-orbital splitting in energy (t_{2g} and e_g) pointing out the formation of hybridized N 2p states with Ti 3d (figure 7c5). It implies that the Ti e_g orbitals are directed towards the nitrogen showing a stronger coupling with the N 2p states revealing its substitutional character. After the CA control the spectrum is unaltered (figure 7c6) indicating higher corrosion resistance than the samples prepared at lower temperature.

3. Discussion

There seems to be no consensus among the reports on the state of the art of doped nitrogen in N–TiO₂ even though it is considered to be in the anionic form [39,40]. While some authors argued that the narrowing of the band gap is due to the formation of oxygen vacancies [41,42] other groups related this effects to the substitution the oxygen by nitrogen [14]. XPS probes the core level binding energies of the constituent species, and the value of the binding energy is a reflection of the valence state and charge density around of the atoms. Finding a solution requires the interpretation of NEXAFS which can provided details about the electronic structure determining the LUMO orbitals around the parent atom. The formation of differently incorporated nitrogen species depends strongly in the sample preparation temperature. Consequently, as the nitrogen is incorporated in the structure it drastically effects its stability as the electrochemical tests proved. The XPS measurement of the samples produced by CVD of NH₃ at different temperatures indicated the formation of different species depending strongly on preparation temperature. In principle, nitrogen could be either at the substitutional positions of the lattice or embedded in the interstitial positions. With this as a starting point, the incorporation of nitrogen atoms into the lattice was investigated with XPS and NEXAFS spectroscopies.

It was found that at 800°C, the nitrogen is incorporated in the form of TiO_{x-2}N_x or absorbed as NO_x species. It is corroborated by the inclusion of a strong O1s XP peak at 533.3 eV associated to NO_x species and another peak at 531.4 eV related to the TiO_{x-2}N_x species. They are directly associated with the peaks at 400.5 eV and 396.5 eV in the N_{1s} spectra. NEXAFS measurements proved that the incorporation of nitrogen in the titanium structure is predominantly interstitial as the stronger t_{2g} at the N K-edge indicated. The incorporation of nitrogen at 800°C from NH₃ yields doping indicated by the narrowing of the gap referred to the Fermi level position. However, the incorporated nitrogen suffers from a lack of stability in acidic environment as the O and N K-edges spectra indicated. The species associated with TiO_x increased after the electrochemical test as the O 1s spectrum shows (peak at 530.6 eV).

Meanwhile, in samples nitrified at higher temperature the nitrogen is incorporated mainly substitutionally as shown the intense e_g peak in the N K-edge spectrum. Furthermore, it is clear that the Ti 2p XP spectra present a reduction of Ti^{4+} states and an increase in the Ti^{3+} which supports the fact that the N substitutes the oxygen in the lattice. The electrochemical test reveals that TiN_x produced from NH_3 at higher temperatures is more stable as the unaltered N K-edge NEXAFS spectrum indicated. Only a portion of the TiN_x is converted into $TiO_{x-2}N_x$ as the slightly reduction in the e_g peak intensity indicated and the XPS corroborated (peak at 396.5 eV). Thus, the higher rate of electrochemical oxidation to form the inert nature and the passive surface are the better proposed model for samples nitrified at higher temperature. Finally, valence band measurements suggested narrower gap than in samples nitrified at lower temperature. After the electrochemical tests, the oxidation explains the broader gap observed in the nitrified samples.

4. Conclusions

The interrelationships between the nitrogen incorporation, the chemical nature and the location of N in the TiO_2 lattice was discussed in terms of a combination of XPS and NEXAFS measurements of samples prepared from CVD of ammonia at different temperatures. The nitrogen is incorporated into the lattice as interstitial or substitutional which depends strongly on the temperature and present different stabilities under electrochemical conditions which affect drastically the corrosion resistance. The samples grown at low temperature induce doping but suffer from low stability in acidic media while the samples nitrified at higher temperature yield higher corrosion resistance. The electrochemical stability depends strongly on the nature of the incorporated nitrogen (interstitial or substitutional) where the TiN_x electronic structure is described by the hybridization of the N 2p with the Ti 3d orbitals. At low temperature the N p-orbitals are more likely to hybridize with the $Ti_{3d-t_{2g}}$ orbitals indicating an interstitial nature. Meanwhile, samples nitrified at higher temperature show N 2p hybridization with the Ti_{3d-e_g} orbitals revealing the nitrogen substitutional nature. This finding provides clear understanding in the corrosion resistance and doping effect of nitrogen incorporation in titanium which dominates the electrochemical performance of the electrode.

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