



## 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  $\text{NH}_3$  at different temperatures and successive electrochemically tested in 1 M of  $\text{HClO}_4$ . 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  $\text{Ti}_{3d-t_{2g}}$  orbitals while higher temperature favors the hybridization with the  $\text{Ti}_{3d-e_g}$  orbitals. This is responsible for the corrosion resistance shown by the samples prepared at higher temperature.

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### 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  $\text{TiN}_x$  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– $\text{TiO}_2$  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  $\text{TiN}_x$  and  $\text{TiO}_x - \text{N}_x$  from  $\text{TiO}_2$ . 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.  $\text{TiN}_x$  samples prepared from the reaction of  $\text{NH}_3$  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  $\text{Ti}_{3d}$  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)

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leads to doping and higher stability under aggressive electrochemical environments.

## 2. Experimental

The nitrification of pristine Ti foil (Grade 1, 50  $\mu\text{m}$  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  $^{\circ}\text{C}$  and 1100  $^{\circ}\text{C}$  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  $\text{NH}_3$  + 1800 sccm Ar) gas mixture at 6 mbar pressure for 10 min. 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.

Fig. 1a shows the scanning electron microscopy (SEM) images of nitrified titanium foil at different temperatures indicating the samples nitrified at 800  $^{\circ}\text{C}$  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  $^{\circ}\text{C}$  shows (see Fig. 1a3). Chemical analysis was obtained by element specific XPS measurements (see Fig. 1b). The Ti 2p XP spectra show the spin orbit doublet 2p $_{3/2}$  and 2p $_{1/2}$  peaks with an energy separation,  $\Delta E$ , of 5.6 eV. Titanium presents a peak at 459.2 eV related to  $\text{Ti}^{4+}$  which is associated with  $\text{TiO}_2$ , while the peak at 454.9 eV ( $\text{Ti}^{3+}$ ) indicates the formation of  $\text{TiN}_x$ . Finally the peak at 457.2 eV is usually related to a lack of stoichiometry of  $\text{TiO}_2$ – $\text{TiN}_x$  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  $\text{Ti}^{4+}$  peak resulting from the native oxide. On the other hand, the sample produced from  $\text{NH}_3$  at 800  $^{\circ}\text{C}$  shows an increase in the  $\text{TiO}_x - 2\text{N}_x$  species. Samples nitrified at higher temperatures produced significant reduction of  $\text{Ti}^{4+}$  ( $\text{TiO}_2$ ) into  $\text{Ti}^{3+}$  ( $\text{TiN}_x$ ) as the spectra prove. This interpretation was corroborated by the successive analysis of  $\text{N}_{1s}$  and O 1s XPS spectra. The O 1s XPS spectra of nitrified titanium samples feature a dominant peak at 530.6 eV, depending on the temperature, which is associated with the presence of  $\text{TiO}_2$  [17]. The peak at 530.6 eV decreases and an additional peak at 533.3 eV assigned to  $\text{NO}_x$  [24] species emerges in samples nitrified at 800  $^{\circ}\text{C}$ . The samples produced at higher temperature yield a decrease in the oxygen species which agrees with the increase in the  $\text{Ti}^{3+}$  species shown in  $\text{Ti}_{2p}$  spectrum. The chemical states of the

incorporated nitrogen were characterized by the  $\text{N}_{1s}$  core-level spectra. Based on the binding energies, the  $\text{N}_{1s}$  peaks can be divided into two groups: those at binding energy 397.0 eV and at 400.5 eV, which are assigned to  $\text{TiN}$ -like nitrogen species in the lattice and bound to various surface oxygen sites ( $\text{NO}_x$  like species), respectively [25]. According to this assignment, the N 1s XP spectra show an increase in the  $\text{TiN}_x$  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 $^{\circ}$  Theta and phase analysis was done with DIFFRAC.EVA software from Bruker (Database PDF 2013). Fig. 2 shows the XRD diagram of pristine, nitrified Ti samples at 800 $^{\circ}$  and 1100  $^{\circ}\text{C}$  samples. Pristine samples behave a titanium oxide character as the reflection peaks at 42.2 $^{\circ}$ , 43.2 $^{\circ}$  and 49 $^{\circ}$  indicate, see Fig. 2a. Otherwise, Fig. 2b shows the XRD spectra of samples nitrified at 800  $^{\circ}\text{C}$  which features a strong peak associated with the presence of  $\text{TiN}_{0.26}/\text{TiN}_{0.17}$  species. Finally, samples nitrified at 1100  $^{\circ}\text{C}$  yields peaks at 39.3 $^{\circ}$  and 40.8 $^{\circ}$  related to  $\text{Ti}_2\text{N}$  species (see Fig. 2c) which is ascribed to the formation of a titanium nitride layer. The elimination of the features ascribed to  $\text{TiO}_2$  in the pristine sample at 42.2 $^{\circ}$  and 49 $^{\circ}$  is due to nitrogenation, which is connected to the formation of  $\text{TiO}_x - 2\text{N}_x$  ( $\text{Ti}^{4+}/\text{Ti}^{3+}$ ) from  $\text{TiO}_x(\text{Ti}^{4+})$  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 h in 1 M of  $\text{HClO}_4$ . In Fig. 3 the CV and the CA of pristine, nitrified Ti foil at 800  $^{\circ}\text{C}$  and 1100  $^{\circ}\text{C}$  are shown. SEM and energy dispersive X-ray (EDX) measurements after the electrochemical test show the corrosion of the pristine Ti foil as shown by the change in oxygen signal. Samples nitrified at 800  $^{\circ}\text{C}$  suffer 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  $^{\circ}\text{C}$  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

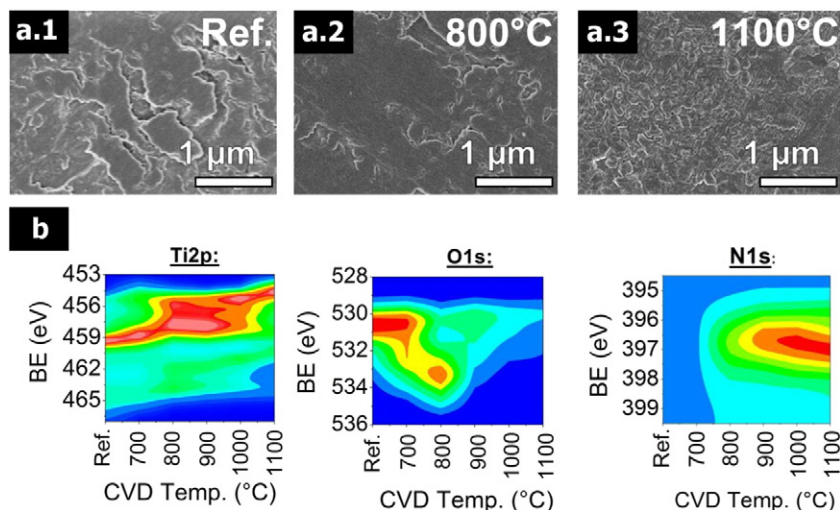


Fig. 1. a) SEM pictures of the CVD of  $\text{TiN}_x$  process fabricated at different temperature. b) Ti 2p, O 1s and N 1s XP spectra vs. temperature.

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