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Substrate Grain-Dependent Chemistry of Carburized Planar Anodic TiO₂ on Polycrystalline Ti

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3 Supporting Information

ABSTRACT: Mixtures or composites of titania and carbon have gained considerable research interest as innovative catalyst supports for low- and intermediate-temperature proton-exchange membrane fuel cells. For applications in electrocatalysis, variations in the local physicochemical properties of the employed materials can have significant effects on their behavior as catalyst supports. To assess microscopic heterogeneities in composition, structure, and morphology, a microscopic multitechnique approach is required. In this work, compact anodic TiO₂ films on planar polycrystalline Ti substrates are converted into carbon/titania composites or multiphase titanium oxycarbides through carbothermal treatment in an acetylene/argon atmosphere in a flow reactor. The local chemical composition, structure, and morphology of the converted films are studied with scanning photoelectron microscopy, micro-Raman spectroscopy, and scanning electron microscopy and are related with the crystallographic orientations of the Ti substrate grains by means of electron backscatter diffraction. Different annealing temperatures, ranging from 550 to 850 °C, are found to yield different substrate grain-dependent chemical compositions, structures, and morphologies. The present study reveals individual time scales for the carbothermal conversion and subsequent surface re-oxidation on substrate grains of a given orientation. Furthermore, it demonstrates the power of a microscopic multitechnique approach for studying polycrystalline heterogeneous materials for electrocatalytic applications.

1. INTRODUCTION

In catalysis and electrocatalysis, a detailed understanding of the local physicochemical properties of the active materials is of utmost importance to develop optimized functional materials. Many fundamental investigations on catalytic materials are based on the study of single crystalline substrates because their well-defined surfaces facilitate the relation of materials properties to observed processes, such as pathways of catalytic reactions that are promoted on differently oriented crystalline surfaces.1−5 However, real catalyst materials require a high surface area and are synthesized in the form of supported nanoparticles or high-surface-area powders, which in most cases bring about nanoscopically or microscopically heterogeneous physicochemical properties. In view of the important role of the support, which needs to stabilize the catalyst nanoparticles, to ensure electrical conductivity or which under certain conditions can positively influence the overall catalytic performance, it is necessary to devote sufficient research efforts to the investigation of innovative support materials on a microscopic basis. A model system that constitutes a compromise between real high-surface-area powders and a well-defined single crystalline surface with assessable properties is provided by a polycrystalline planar substrate. With the emergence of experimental methods that combine microscopy with comple-

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mentary analysis methods, such as photoelectron or vibrational spectroscopy, diffractometry, or electrochemistry, the investigation of planar polycrystalline materials has opened up new perspectives in materials research.4−7

Hybrid or composite materials of titania and carbon (Ti−O−C) have gained remarkable interest in the search for suitable catalyst support materials for proton-exchange membrane fuel cells, as they may provide a higher corrosion resistance than that of commonly used carbon-based supports in combination with a high electrical conductivity8−10 and may enhance the overall catalytic activity.11−13 Planar model systems consisting of thermally carburized compact anodic titania films on a polycrystalline titanium substrate (Ti poly) provide a flexible model system to study the relationship between the physicochemical properties of Ti−O−C materials, which can be tailored via the synthesis conditions, and their electrochemical and electrocatalytic performances.14−16 In particular, different annealing temperatures during the carbothermal treatment of anodic TiO2 yield significantly different average physicochemical properties of the obtained Ti−O−C films14 which in turn strongly affect the catalytic properties of Ti−O−C-supported Pt nanoparticles (Pt/Ti−O−C) toward the electrochemical oxidation of ethanol in an acidic electrolyte.15 Interestingly, a clear influence of the Ti substrate grains on the local (electro)chemical stability of Pt/Ti−O−C on Ti poly was observed,15 which demonstrates the necessity for the use of microscopic analysis tools to gain a deep understanding of the local property−performance relationships on such model systems. In a previous publication, we have investigated the effect of titanium substrate grain orientations on the crystallization of compact anodic TiO2 and on the reactive decomposition of acetylene during carbothermal treatment with acetylene at a relatively low annealing temperature. A substrate grain-dependent chemical composition and structure of the obtained C/TiO2 composite material has been observed in this study.7 The effect of annealing temperature on the final average composition of Ti−O−C films, prepared at relatively high temperatures, has been explained with a thermodynamic model, where diffusion of carbon and oxygen in the compact anodic TiO2 has been taken into account.14 A common consideration of both substrate grain orientation and annealing temperature is still missing. However, it is necessary to gain a deeper understanding and control of the synthesis of such Ti−O−C systems.

Therefore, in the present study, the effect of annealing temperature on the substrate grain-dependent physicochemical properties of carburized planar anodic TiO2 films on Ti poly is investigated using both microscopic and spectroscopic

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<th>Table 1. Ranges of Ti Substrate Orientations and Representative Projected Hexagonal Cells</th>
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Figure 1. Scanning electron micrographs of TiOC. High-magnification insets: areas on differently oriented substrate grains (TiOC550 TiOC650 TiOC750) or areas with different TiOC morphologies (TiOC850). Projected hexagonal cells: approximate crystallographic orientation of the Ti substrate grains.
techniques. Ti–O–C films are synthesized via carbothermal treatment with acetylene at four different annealing temperatures, that is, 550, 650, 750, and 850 °C. Scanning electron microscopy (SEM), scanning photoelectron microscopy (SPEM), and micro-Raman spectroscopy results of the carburized films are correlated with the crystallographic orientation of the substrate grains, which is assessed through electron backscatter diffraction (EBSD).

2. RESULTS

EBSD was used to generate crystalline orientation maps of the Ti<sub>poly</sub> substrates, which will be represented as surface-normal projected inverse pole figure orientation maps in the following. From these maps, the orientations of the hexagonal lattice of Ti with respect to the substrate surface, defined by the three Euler angles, are extracted for individual grains.

To define the crystallographic plane parallel to the sample surface, only the two Euler angles, $\Phi$ and $\varphi_2$, need to be considered. Angle $\Phi$ describes the tilt of the c-axis of the hexagonal unit cell with respect to the substrate surface, and $\varphi_2$ describes the azimuthal rotation of the hexagonal unit cell about its c-axis with respect to a reference orientation with $\varphi_2 = 0°$. Because of the hexagonal symmetry, the values of the orientation angles can be restricted to $0° \leq \Phi \leq 90°$ and $0° \leq \varphi_2 \leq 30°$. According to our previous work, it is sufficient to take into account four ranges of tilt angles, $\Phi$, to gain insight into the physicochemical properties of thermally treated planar anodic TiO<sub>2</sub> films. In addition, we subdivide the orientations with $\Phi > 50°$ into $0° \leq \varphi_2 \leq 15°$ and $15° \leq \varphi_2 \leq 30°$. Table 1 lists the five groups of Ti substrate orientations that are considered in the present study and shows the surface-projected hexagonal cells that are used for labeling.

Figure 1 shows scanning electron micrographs of TiOC, synthesized at different temperatures. After the thermal treatments at temperatures of up to 750 °C, the grain boundaries of the Ti substrate are still visible through the TiOC. The morphology of TiOC<sub>550</sub> and TiOC<sub>750</sub> is clearly affected by the crystallographic orientation of the underlying Ti substrate grains. In particular, substrate grains with tilt angles $0° \leq \Phi \leq 40°$ can be easily distinguished from substrate grains with tilt angles $\Phi \geq 50°$, due to apparent differences in the morphologies of the TiOC overlayers. TiOC<sub>850</sub> is characterized...
by a granular morphology with no pronounced substrate grain dependency; only the grain boundaries can be recognized. After carbothermal treatment at 850 °C, the initial grain boundaries of the substrate disappeared and extended areas of uniform morphology formed. No interdependence between morphology and the original substrate grain orientation is visible due to significant substrate grain growth at this temperature.18

The comparison between the morphologies of TiOC750 and TiOC850 suggests that the surface undergoes an ordering at high annealing temperatures. The high-resolution micrographs (insets) of TiOC850 show ordered morphologies, such as triangular shapes (left bottom) or stepped terraces (right top). The phase change of the Ti substrate from α-Ti (hcp structure) to β-Ti (bcc structure) does not happen below 882 °C and can therefore not be responsible for this ordering.19

Figure 2 depicts chemical maps of the Ti 2p1/2 and C 1s core-level electrons extracted from SPEM of TiOC and the corresponding EBSD maps of the Ti substrate. Apparently, the surface chemistry of TiOC550 and TiOC750 is affected by the orientation of the substrate grains: TiOC films on type A and B grains (0° ≤ Φ ≤ 40°, ~Ti(0001)) show a clearly different average brightness in the chemical maps than that of films on type D and E grains (50° ≤ Φ ≤ 90°, ~Ti(hk0)). In the case of TiOC750 several grain boundaries can be identified. On the other hand, the surface of TiOC650 has a relatively homogeneous composition that is independent of the substrate grains in the mapped area. The chemical maps of TiOC650 show several areas with dark spots and less pronounced grain boundaries.

For each type of substrate grain, X-ray photoelectron (XP) spectra of the Ti 2p1/2 and C 1s core levels are extracted from the photoelectron maps and plotted in Figure 3. Each spectrum is obtained from a rectangular area on a substrate grain and represents the average surface composition of TiOC on that grain. An alternative representation of the XP spectra is given in Figures S1 and S2 in the Supporting Information (SI). The Ti 2p1/2 signals show that all TiOCs contain TiO2 (459 eV)5 and that TiOC650 and TiOC750 additionally contain a considerable fraction of TiC and/or TiO species (454.9 eV)5,20 and some TiOx sub-oxides (456−458 eV, 1 < x < 2)5,14 at the surface.

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In the case of TiOC550, TiOC650, and TiOC750, the pronounced peak in the C 1s spectra, centered at 284.5 eV, is attributed to an sp2-hybridized (graphitic) carbon (C=C) (Figure 3e−g).5,21 The C 1s peak found for TiOC850 (Figure 3h) is shifted toward the binding energy of an sp3-hybridized (diamond-like) carbon (C−C at 285.6 eV),5,21 indicating the presence of amorphous carbon on the surface.22 It can be seen that only TiOC650 and TiOC750 contain a notable amount of carbidic carbon (281.7 eV) within a film depth of ∼1.4−2.3 nm (calculated for TiO2 and C=C), which is analyzed with SPEM.21

Analysis of the XP spectra reveals that carbothermal treatment at 550 °C mainly produces graphitic carbon on top of TiO2. A significant reduction in the anodic TiO2 film is obtained through carbothermal treatments at 650 and 750 °C, generating TiC (TiO) and TiOx species, and the resultant TiOC is covered by a relatively high amount of graphitic carbon. The surface of TiOC850 consists of TiO2 covered by amorphous carbon.

Both chemical maps (Figure 2) and XP spectra (Figure 3) show that the conversion from TiO2 to TiC (TiO) and TiOx depends both on the annealing temperature and substrate texture. On TiOC550 (Figures 2a and 3a,e), the relative amount of graphitic carbon is significantly enhanced and the fraction of TiO2 is small on top of substrate grains of types A and B (~Ti(0001)), with 0° ≤ Φ ≤ 40°. A detailed investigation on the effect of substrate grains on the chemical surface composition of TiOC550 has been published elsewhere.7 The
XP spectra of TiOC$_{650}$ (Figure 3b,f) suggest an exceptional surface chemistry on top of substrate grains of type D (~Ti{1010}), see Table 1): on these grains, the conversion of the anodic film to TiC (TiO) and TiO$_2$ phases is significantly lower and slightly less graphitic carbon is generated on the surface. This is in line with the TiC/TiO$_2$ and C/BG chemical maps (Figure 2c), which show a high density of dark spots and thus a lower average content of TiC (TiO) and carbon in the TiOC on top of these grains. The variation in the surface chemistry on top of the other types of substrate TiOC on top of these grains. The variation in the surface chemistry of TiOC$_{650}$ on top of the other types of substrate grains is less strong. On TiOC$_{550}$ a pronounced substrate grain-dependent oxide film reduction can be observed, with the highest fraction of TiC (TiO) and TiO$_2$ being present on top of substrate grains D and E, with $50^\circ \leq \Phi \leq 90^\circ$ (~Ti{hki0}), and the lowest, on substrate grains A and B, with $0^\circ \leq \Phi \leq 40^\circ$ (~Ti(0001)), which is in accordance with the chemical maps (Figures 3c,g and 2b). At the same time, the total amount of graphitic and carbidic carbon species in TiOC$_{750}$ is slightly higher on substrate grains with 50° $\leq \Phi \leq 90^\circ$ (~Ti{hki0}) than that on substrate grains with 0° $\leq \Phi \leq 40^\circ$ (~Ti(0001)). An intermediate composition is found on substrate grains C, with 40° $\leq \Phi \leq 50^\circ$. No difference is visible in the XP spectra of TiOC$_{650}$ on differently oriented substrate grains, which confirms the homogeneous contrast of its chemical maps (Figures 3d,h and 2d). The highest overall fraction of TiC is found in TiOC$_{750}$ on top of $\sim$Ti{hk0} grains. The highest overall amount of (amorphous or graphitic) carbon is found in TiOC$_{650}$ on top of all substrate grains except for $\sim$Ti{1010} (Figures 3f and S2). Considering only TiOC$_{650}$ and TiOC$_{750}$ an almost opposite chemical surface composition is observed on $\sim$Ti{1010} and $\sim$Ti(0001) substrate grains: TiOC$_{650}$ contains a high amount of TiC and C on $\sim$Ti(0001) and a low amount on $\sim$Ti{1010}, whereas the contrary is found for TiOC$_{750}$.

Micro-Raman spectroscopy was performed to gain information on the substrate grain-dependent structure and chemical composition of the anodic TiO$_2$ before and after carbothermal treatment at different temperatures. Figure 4 depicts the Raman spectra of as-anodized TiO$_2$ and of TiOC$_{550}$, TiOC$_{650}$ and TiOC$_{750}$ on top of $\sim$Ti{1010} and $\sim$Ti(0001) substrate grains, for which SPEM reveals a clearly different TiOC composition. As the initial grain boundaries of the titanium substrate vanished after carbothermal treatment at 850 °C, Raman spectra of TiOC$_{650}$ were acquired on several spots of different appearance in the optical microscope (black and gray spectra in Figure 4). Photographs of the TiOC surfaces are shown in Figure 4e. An alternative representation of the micro-Raman spectra is given in Figure S3. The peaks at 1350 and 1600 cm$^{-1}$ in Figure 4a,c correspond to the D and G bands of the nanocrystalline graphitic carbon. Figure 4b,d depicts the spectral range of the bands associated with Raman-active TiO$_2$. 

Figure 4. Micro-Raman spectra of TiOC$_{650}$, TiOC$_{650}$ and TiOC$_{750}$ on top of (a, b) $\sim$Ti{1010} and (c, d) $\sim$Ti(0001) and of two spots on TiOC$_{650}$ with different optical appearances (black and gray spectra). Purple spectrum in (a): as-grown anodic TiO$_2$ (b, d) Spectral range marked by the box in (a, c). Baseline correction: (a, c) subtraction of a fourth-order polynomial function; constant shift to a common level at (b) 800 cm$^{-1}$ and (d) 150 cm$^{-1}$.
Figure 5. Schematic representation of the cross-sectional composition of TiOC on top of ~Ti(1010) and ~Ti(0001) substrate grains for the different annealing temperatures. The substrate grain orientations of TiOC_{450} are unknown due to grain growth during the thermal treatment.

The absence of distinct bands associated with crystalline (rutile or anatase) TiO_{2} evidences that the as-grown anodic film is amorphous (purple spectrum in Figure 4a). Carbothermal treatment at 550 °C leads to crystallization of the oxide, generating a mixed phase of rutile and anatase, and to a slight reduction, which is evidenced by the features ascribed to Ti_{2}O_{3}. The highest reduction of rutile is detected on top of ~Ti(0001) (compare Figures 4b,d and S3). There are no bands associated with TiC phases in the spectra of TiOC_{550}. The blue optical appearance of TiOC_{550} indicates that the ~53 nm thick anodic oxide film is only slightly reduced, where the color is most likely a result of interference effects in combination with color centers, for example, due to oxygen vacancies (Figure 4e). Note that the as-grown anodic film has a different blue color, which arises from interference effects only (see the Supporting Information of ref 7).

No graphitic carbon is detected prior to the carbothermal treatment. The carbon bands are intense for TiOC_{550} and continuously decrease with increasing annealing temperature on both types of substrate grains (Figure 4a,c). The Raman signal of the graphitic carbon is notably enhanced for TiOC_{550} on both types of substrate grains (Figure 4a,c). The Raman spectrum of TiC_{0.67} has been associated with TiC_{x} phases of TiOC_{550}, TiOC_{650}, TiOC_{750}, and TiOC_{850}. Instead, Raman-active TiO_{2} bands (in particular, the characteristic low-frequency band of anatase) are not visible in the spectra of TiOC_{550}, TiOC_{650}, and TiOC_{750}. Instead, Raman-active TiO_{2} and TiC phases appear and, at the same time, the optical appearance of TiOC changes to metallic gray (Figure 4e). This indicates that the oxide film is completely converted to a TiO_{2}C_{y} phase, which is mainly a solid solution of TiO and TiC and has been reported to have semi-metallic properties, through carbothermic treatments at 650, 750, and 850 °C. The fraction of TiO_{2} on the surface, detected with SPEM, appears to be too small to considerably contribute to the Raman response. Only the slightly enhanced signal intensity at 447 cm\(^{-1}\) (E\(_{g}\) band of rutile TiO\(_{2}\)) in the gray spectrum of TiOC_{550} with respect to that in the black spectrum may be related to the presence of TiO_{2} (Figures 4b and S3). Without data on well-defined TiO_{2}C\(_{y}\) reference materials, it is not possible to quantify the phase composition and stoichiometry of the TiO_{2}C\(_{y}\) phase in the bulk of TiOC using Raman spectroscopy. Therefore, the observed differences between the Raman responses of TiOC_{550}, TiOC_{650}, and TiOC_{750} can only be interpreted in a qualitative manner and suggest an effect of the annealing temperature on the stoichiometry and/or defectivity of the converted films. In the case of TiOC_{550} and TiOC_{750}, a weak substrate grain orientation effect on the Raman response can also be observed (see Figure S3). A relation of the properties of TiOC_{550} with the initial substrate grains is not possible, but local variations in phase composition are evidenced by notable differences between the black and gray spectra in Figure 4b,d (see also Figure S3).

A thorough investigation of TiO_{550} with micro-Raman spectroscopy is reported in ref 7, in which a marked relation between the substrate grain orientations and crystalline phases of TiO_{2} as well as the amount of deposited graphitic carbon was found.

3. DISCUSSION

The presented results show that the final physicochemical properties of carbothermally produced TiOC on Ti_{poly} such as the chemical composition, phase composition, and surface morphology, depend on the annealing temperature and underlying substrate grain orientations. It should be noted that the gas atmosphere during the carbothermal treatment constitutes an important synthesis parameter as well; very similar chemical maps to those of TiOC_{550} are obtained by carburization of planar anodic TiO_{2} films on Ti_{poly} under ultrahigh vacuum conditions using ethylene as a carbon source. To summarize the results obtained with SPEM and micro-Raman spectroscopy, Figure 5 depicts simplified schematic models representing the cross-sectional compositions of TiOC on top of substrate grains with ~Ti(1010) and ~Ti(0001) orientations for the different annealing temperatures. TiO_{2}C\(_{y}\) represents here the solid solution of TiC and TiO_{2} as well as TiO_{2}C\(_{y}\) phases. The different thicknesses of the compact, as-grown anodic TiO_{2} on top of differently oriented substrate grains, which have been reported in the literature, are neglected in the depicted models. The film thickness is
assumed to remain constant for all carbothermal treatments. Compositional gradients are simplified to defined phase boundaries. Carburization at 650 and 750 °C is found to generate TiOC films with an inhomogeneous surface chemistry on individual grains: in the case of TiOC_{650} SPEM reveals micrometer-sized spots on ∼Ti(1010), with compositions that differ from the average (Figure 2c), and in the case of TiOC_{750} a different chemical composition is observed at grain boundaries (Figure 2b). Furthermore, on the nanometric scale, a patched surface composition of TiOC, with carbon, TiO_{x} and TiO_{x}C_{y} (if present) side by side, is possible. For the sake of simplicity, only the grain area-averaged chemical composition is considered in Figure 5. This gives rise to the layered film structure of the models, which is in line with previously performed angle-resolved XPS measurements on TiO_{x}C_{y}−rich TiOC and is supported by the present results of XP and micro-Raman spectroscopies, which reveal that the TiO_{x}C_{y} phase in TiOC_{850} is covered by a TiO_{2} film of at least ∼1.4 nm (estimated from the photoelectron escape depth in TiO_{2}).

Carbothermal treatment at 550 °C yields a C/TiO_{2} composite, with TiO_{2} species in the oxide film and a substrate grain-dependent amount of graphitic carbon on the surface, which is higher on top of ∼Ti(0001) than that on top of ∼Ti{1010}, as reported in ref 7. At 650, 750, and 850 °C, the anodic TiO_{2} film is converted to TiO_{2}C_{x} in the bulk, as suggested by the Raman results (Figure 4), but contains temperature- and substrate grain-dependent fractions of TiO_{2} and carbon at the surface, as seen with SPEM (Figures 2 and 3). The carbon is mainly graphitic (denoted by graphite) on TiOC_{550}, TiOC_{650} and TiOC_{750} and amorphous (denoted by C amorph) on TiOC_{850}. In the case of TiOC_{650} there is more TiO_{2} and less carbon on ∼Ti(1010) than those on ∼Ti(0001). In the case of TiOC_{750} there is less TiO_{2} and more carbon on ∼Ti(1010) than those on ∼Ti(0001). The fractions of TiO_{2} and carbon in TiOC_{650} on ∼Ti(1010) are similar to the respective fractions in TiOC_{750} on ∼Ti(0001), but there is more TiO_{2} and C in TiOC_{650} on ∼Ti(0001) than those in TiOC_{750} on ∼Ti(1010). After carburization at 850 °C, the amount of carbon is significantly lower and the amount of TiO_{2} is significantly higher than those after carburization at 750 and 650 °C.

The physicochemical properties of TiOC can be understood as resulting from several parallel processes during and after carburization that are affected by temperature and substrate texture, which will be discussed in the following.

### 3.1. Crystallization of TiO_{2} and Reactive Decomposition of C_{2}H_{2}

During carbothermal treatments at high temperatures, the amorphous anodic TiO_{2} crystallizes to anatase and/or rutile phases before C_{2}H_{2} is added to the process. The crystallization kinetics depends on the temperature and orientation of the Ti substrate, which has consequences for the reaction of the surface with C_{2}H_{2}. Because of the higher activity of anatase TiO_{2} compared to that of amorphous TiO_{2} toward the reactive decomposition of C_{2}H_{2}, the substrate grain-dependent crystallization results in a substrate grain-dependent amount of graphitic carbon on the surface of TiOC_{550}. Also, at higher temperatures, the substrate texture may affect the crystallization of anodic TiO_{2} and thus the reactive decomposition of C_{2}H_{2}. In particular, the peculiar properties of TiOC_{650} on top of ∼Ti(1010), namely, the presence of spots with a lower carbon coverage and a lower fraction of TiC compared to the average, may be ascribed to the formation of a polycrystalline TiO_{2} film on these grains, exposing facets of very different reactivities. Furthermore, the significantly lower amount of carbon on TiOC_{850} could be related to a low reactivity of the, most likely rutile-rich, TiO_{2} film that forms at 850 °C prior to the addition of C_{2}H_{2}. Besides the reactivity of the surface, the sticking coefficient of C_{2}H_{2} on TiO_{2} and the desorption probability of possible reaction intermediates, both of which depend on temperature and surface structure, can play a role in the substrate grain-dependent decomposition efficiency. Because of the concomitant diffusion of carbon into the bulk and generation of TiC at temperatures of 650 °C and higher, the final carbon content at the surface is not determined only by carbon layer formation.

### 3.2. Conversion of TiO_{2} to TiC and Material Transport in TiO_{2} and Ti

To explain the observed temperature-dependent average chemical composition of TiOC, thermodynamic considerations need to be taken into account. First, sufficiently high temperatures are required to convert TiO_{2} into a solid solution of TiC and TiO. Second, the final bulk composition is mostly determined by thermally activated diffusion of both carbon into the compact anodic TiO_{2} and oxygen and carbon into the Ti substrate. The average amount of carbon on the surface decreases from 650 to 850 °C, which can be attributed partly to the higher diffusion kinetics of carbon at higher temperatures and partly to the lower carbon-formation efficiency. It is noteworthy that the amorphous carbon found on TiOC_{850} most likely originates from contamination of TiO_{2} that is not covered by graphitic carbon from the thermal C_{2}H_{2} treatment, after exposure to ambient air. The results obtained with micro-Raman spectroscopy suggest a temperature- and substrate grain-dependent stoichiometry and/or defectivity of the TiO_{2}C_{x} phase in TiOC, which is very likely a consequence of the temperature- and substrate grain-dependent carbon supply and diffusion kinetics. At 850 °C, both oxygen and, in particular, carbon can diffuse into the Ti substrate, promoting the formation of a carbon-poor TiO_{2}C_{y−1} phase.

The main influence of substrate grain orientations on the conversion may be an indirect effect controlled by the initial formation of polycrystalline TiO_{2}, with a substrate grain-dependent phase composition and preferential orientation. First-principles calculations suggest anisotropic migration of carbon in the tetragonal lattices of anatase (c/a = 2.51) and rutile TiO_{2} (c/a = 0.64). Therefore, substrate grain-dependent material transport in TiO_{2} which brings about substrate texture-dependent conversion time scales of the anodic TiO_{2} at a given temperature, may be responsible for the substrate grain-dependent chemical compositions of TiO_{2}C_{650} and TiO_{2}C_{750}. When oxygen and carbon start to diffuse into the Ti substrate, the grain-dependent orientation of the hexagonal Ti lattice (c/a = 1.58) is likely to determine the diffusion kinetics and therewith not only the fractions of C and O that remain in the TiO_{2}C_{x} phase adjacent to the Ti substrate but also the thickness of the TiO_{2}C_{x} layer. In addition, the substrate grain boundaries can affect the conversion of the anodic TiO_{2}. From the chemical maps of TiO_{2}C_{750} (Figure 2b), a different conversion behavior of the anodic film at the boundaries compared to that in the area within the substrate grains can be inferred, suggesting a lower reactivity and/or faster carbon diffusion at the substrate grain boundaries. At 850 °C, substrate grain growth becomes important as well, generating fresh grain boundaries in the oxide film, which can facilitate diffusion of carbon into the bulk.
### 3.3. Surface Re-Oxidation of TiOC<sub>y</sub>.

Besides the temperature- and grain-dependent conversion of TiO<sub>2</sub> to TiO<sub>C</sub><sub>y</sub>, the final composition of TiOC is affected by the subsequent re-oxidation of the TiC, TiO, and TiO<sub>x</sub> species near the surface to TiO<sub>2</sub> and graphitic carbon, due to their relative thermodynamic instability at room temperature and in the presence of oxygen. Re-oxidation was reported to happen during exposure of TiO<sub>C</sub><sub>y</sub>-rich films to ambient air and even during cooling down in reducing atmosphere at the end of a carbothermal treatment, when the temperature dropped below a certain threshold value. As the intrinsic inertsness toward re-oxidation depends on the chemical composition of TiOC (in particular, on the stoichiometry of the TiO<sub>C</sub><sub>y</sub> phase), a substrate grain effect on the re-oxidation rate can be expected for TiOC<sub>650</sub> and TiOC<sub>750</sub>. In the case of TiOC<sub>850</sub>, for which local variations in chemical composition that cannot be related to initial substrate grain orientations are observed, the intrinsic inertsness is likely to vary accordingly on areas of different compositions. A high amount of graphitic carbon on the surface of TiO<sub>2</sub> after carburization could retard the re-oxidation process, as carbon doping or carbon coating of TiO<sub>2</sub> is known to suppress the crystalline phase transformations of TiO<sub>2</sub> and reduce TiO<sub>2</sub> crystallite growth, both of which are processes that require atomic re-organization, as does re-oxidation. This provides a possible explanation for the observation that there is less TiO<sub>2</sub> on TiOC<sub>650</sub> and TiOC<sub>750</sub> than that on TiOC<sub>850</sub>. Furthermore, the inverse trend of carbon and TiO<sub>2</sub> at the substrate grain-dependent fraction of TiO<sub>2</sub> observed on those substrate grains on which TiOC contains a high fraction of carbon. Therefore, not only the TiO<sub>2</sub> conversion time scale but also the TiOC re-oxidation time scale is effectively determined by the substrate texture. Independent of the substrate texture, the surface oxide of TiOC<sub>550</sub> is almost stoichiometric within the depth that can be analyzed with SPEM so that no substrate grain-dependent intrinsic stability can be deduced here. It is noteworthy that the substrate grain-dependent fraction of TiO<sub>2</sub> observed with SPEM on TiOC<sub>550</sub> is a consequence of the substrate grain-dependent thickness of the carbon layer, which attenuates photoelectrons from the covered TiO<sub>2</sub>.<sup>7</sup>

### 4. CONCLUSIONS

The presented results on the annealing temperature and substrate grain-dependent conversion of compact anodic TiO<sub>2</sub> on Ti<sub>poly</sub> to TiOC reveal that both annealing temperature and substrate texture majorly influence this process. By means of a spectromicroscopic multimodal approach, employing EBSD, SEM, SPEM, and micro-Raman spectroscopy, it was found that the anodic films on top of differently oriented substrate grains have individual conversion and re-oxidation time scales. A combination of temperature- and substrate grain-dependent processes, such as crystallization, reactive carbon deposition, conversion to TiO<sub>C</sub><sub>y</sub>, and re-oxidation of the surface, plays a major role in the definition of the heterogeneous physicochemical properties of TiOC films. A deep understanding of such an interplay constitutes an essential point toward the development of novel transition metal oxy-carbide-based synergistic supports for use in (electro)catalytic systems with improved performance. On the basis of the present findings, the spatially selective degradation of Pt/TiOC<sub>750</sub>/Ti<sub>poly</sub> during ethanol electro-oxidation<sup>10</sup> can be ascribed to the substrate grain-dependent chemical composition of TiOC<sub>750</sub> which determines the overall chemical stability of the catalytic system in concentrated phosphoric acid at elevated temperatures.

### 5. EXPERIMENTAL SECTION

#### 5.1. Sample Preparation.

Disks of 1 mm thickness and 10–15 mm diameter were cut from a 20 mm diameter Ti<sub>poly</sub> rod (99.6% purity, temper annealed; Advent Ltd., England). One side of the disks was mechanically and electrochemically polished, following the procedure described in refs 7 and 14. The areas of investigation were marked with a cross-scratch on the samples using a tungsten needle. The electropolished Ti disks were thoroughly cleaned in an ultrasonic bath with ethanol (technical grade), isopropanol (high purity), and deionized (DI) water and dried in an argon (Ar 4.8; Linde, Germany) stream.

Carbothermal treatment was conducted in a tubular quartz reactor under controlled gas flow. For carburization, the following procedure was applied: (i) purging for 2 h with a high flow of Ar to remove air, (ii) heating at a constant rate to T = 550, 650, 750, or 850 °C in 200 standard cubic centimeters per minute (sccm) Ar, (iii) dwelling for 60 min at T, (iv) addition of 0.5 flow % of acetylene (C<sub>2</sub>H<sub>2</sub>, solvent-free; Linde, Germany) for 5 min, (v) dwelling for 60 min at T in Ar, (vi) cooling to room temperature. The carburized anodic films are termed TiOC<sub>y</sub> throughout the text, where T represents the annealing temperatures 550, 650, 750, and 850 °C.

#### 5.2. EBSD and SEM.

The crystallographic orientation of the electropolished Ti substrate was mapped by EBSD using a FEI XL30 scanning electron microscope operated at a 20 kV accelerating voltage and equipped with a TSL-EDAX EBSD detector, which was low enough to avoid chemical modifications or sample damage during the selected exposure times. Backscattered EBSD signals were recorded with a resolution of about 1 cm<sup>−1</sup> from 2000 to 146 cm<sup>−1</sup> (lower wavenumbers were cut off by the notch filter), with an acquisition time of 1 x 50 s, and from 800 to 146 cm<sup>−1</sup>, with an acquisition time of 2 x 100 s. For baseline correction (background fluorescence), a fourth-order polynomial function
was subtracted from the raw data of the extended spectra and the small-range spectra were only shifted to a common background level.

5.4. SPEM. SPEM was performed at the ESCAmicroscopy beamline at the Elettra Synchrotron Facility in Trieste, where the X-ray photon beam was demagnified by a Zone Plate to a submicron spot of about 150 nm onto the sample, which was then rastered to produce an image by detecting the photoelectrons generated from the sample. In this work, the photon energy was set to 756 eV. The incident X-ray beam was normal to the sample surface, whereas angle \( \theta \) between the hemispherical electron analyzer (HEA) and the sample surface was 30°, providing high surface sensitivity. Photoelectron maps of 50 × 50 \( \mu \)m\(^2\) were recorded by sampling the surface with a step of 0.2 \( \mu \)m and a dwell time of 60 ms per pixel. The HEA was equipped with a multichannel electron detector, which simultaneously acquires 48 maps (channels), each tuned at a specific photoelectron energy within a selected energy window. This allowed to (i) extract XP spectra from selected areas of the acquired photoelectron micrograph, with an energy window of 7.8 eV and a step of 0.164 eV and (ii) to remove the topographic contributions to the photoelectron micrographs and extract the chemical contrast. The chemical contrast micrographs (chemical maps) were obtained by choosing two sets of maps from the recorded 48 maps that were acquired either in the energy range of a photoelectron peak or in the energy range of the background signal, integrating them to obtain two effective maps corresponding to the photoelectron signal in the two spectral ranges and obtaining their ratio. In that way, peak over background (C/BG, TiO\(_2\)/BG) or peak A over peak B (TiC/TiO\(_2\), TiO\(_2\)/TiO\(_3\)) chemical maps were obtained from the photoelectron maps acquired in the spectral regions of the C 1s and Ti 2p\(_{3/2}\) core levels.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00472.

Alternative representation of the XP spectra; alternative representation of the micro-Raman spectra (PDF)

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Notes

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ABBREVIATIONS

SEM, scanning electron microscopy; SPEM, scanning photoelectron microscopy; EBSD, electron backscatter diffraction; XP, X-ray photoelectron spectroscopy

REFERENCES

(4) Yoon, T. H. Applications of Soft X-Ray Spectromicroscopy in Material and Environmental Sciences. 
(9) Kim, D.-Y.; Han, S.-B.; Lee, Y.-W.; Park, K.-W. Core–Shell Nanostructure Supported Pt Catalyst with Improved Electrocatalytic Stability in Oxygen Reduction Reaction. 


