Reactivity enhancement of oxide skins in reversible Ti-doped NaAlH₄

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The reversibility of hydrogen sorption in complex hydrides has only been shown unambiguously for NaAlH₄ doped with transition metal compounds. Despite a multitude of investigations of the effect of the added catalyst on the hydrogen sorption kinetics of NaAlH₄, the mechanism of catalysis remains elusive so far. Following the decomposition of TiCl₃-doped NaAlH₄ by in-situ X-ray photoelectron spectroscopy (XPS), we link the chemical state of the dopant with those of the hydride and decomposition products. Titanium and aluminium change their oxidation states during cycling. The change of the formal oxidation state of Al from III to zero is partly due to the chemical reaction from NaAlH₄ to Al. Furthermore, aluminium oxide is formed (Al₂O₃), which coexists with titanium oxide (Ti₂O₃). The interplay of metallic and oxidized Ti with the oxide skin might explain the effectiveness of Ti and similar dopants (Ce, Zr . . . ).

The development of reversible solid hydrogen storage requires in-depth knowledge of the stability of the compounds involved¹ - including possible reaction intermediates - i.e. their respective energies of formation and decomposition. Additionally, the kinetics of formation and decomposition should meet specific requirements related to the application of interest. Since the kinetics of a gas-solid reaction is sensitive to the surface properties - i.e. dissociation barrier, chemisorption enthalpy and surface coverage² - and since these properties are in turn sensitive to surface parameters which depend on the application considered - e.g. surface composition/poisoning, texture and microstructure - in-situ information relative to the surface chemistry of the solids involved is of primary importance. These stability and kinetic requirements are particularly demanding in solid-state hydrogen storage because the solid hydride has to be formed and decomposed as quickly and as energetically efficient as possible.¹ The fact that light-weight complex hydrides such as alanates³ and borohydrides⁴ can store hydrogen up to 20 mass % was recognized early,⁵ but non-ideal thermodynamics and slow kinetics at technical conditions hindered their application. The situation changed when Bogdanović showed that the formation and decomposition is reversible under technically applicable conditions, if NaAlH₄ is catalyzed with transition-metal compounds, most efficiently with titanium compounds.⁶,⁷ This finding triggered extensive research using a multitude of experimental and theoretical methods to unravel the mechanism of the formation and decomposition processes - and as such NaAlH₄ can be considered as a model system to test scientific hypotheses explaining complex gas-solid interactions.⁸ In particular, many models have been proposed regarding the catalytic

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activity of Ti in NaAlH₄, and these models can be divided into two categories: the ones that claim this activity to come from the bulk, e.g. Refs. 10–12, and the ones that rather locate it on the surface, e.g. Refs. 13–15. Here again, the importance of gathering reliable in-situ surface information is pointed out. In particular, the change of the intrinsic surface properties by contamination such as oxygen or water is often overlooked or simply ignored. However, this subject has been addressed by several authors regarding intermetallic hydrides. Eventually, the ability of functioning in a technical hydrogen atmosphere proved to be the most important advantage for the applicability of LaNi₅ (or mischmetal nickel hydrides) as a hydrogen storage material, despite the fact that intermetallic hydrides with a higher hydrogen content and proper stability are known. Similar outcomes were found for the hydrogen storage material MgH₂ and hydrogen switchable mirrors. Particularly the latter two examples raise hope that additives (“catalysts”) can be found, which reduce the effect of surface blocking layers from contaminations. Sodium and aluminium are two of the most reactive elements, making surface contaminations likely for the NaAlH₄ system.

In this paper, we follow the decomposition of TiCl₃-doped NaAlH₄ by in-situ XPS and mass spectrometry. With this technique, we are able to link the chemical state of the catalyst with those of the hydride and decomposition products. We find that Ti influences the formation of oxides on the hydride and decomposition products, which cannot be avoided during cycling in technical hydrogen gas. Indeed, the oxidation number of Ti is found to decrease in the oxide skin during hydride decomposition, while atomic oxygen migrates from the bulk to the surface. The same experiments carried out on cycled specimens revealed that this phenomenon is reversible, despite a global increase of the oxide skin thickness at the end of decomposition.

Ti-doped NaAlH₄ is prepared by ball-milling NaAlH₄ for 5 min at room temperature with 5 mol. % TiCl₃, resulting in NaAlH₄, Ti species, NaCl and Al. The corresponding XP-overview spectrum is shown in Fig. 1, showing all expected elements in their chemical state which is in good agreement with earlier research. Besides the expected XPS and Auger lines of the two main elements Na and Al present in the specimen, oxygen and carbon contamination are also clearly visible. The Ti 2p orbital from the dopant is also present, intense enough for qualitative and quantitative analysis (to be detailed below). This is not the case for the Cl 2s orbital, whose XPS relative sensitivity factor (RSF) is less intense than Ti 2p by a factor 5, and which fades into the noise. However, as shown by Léon et al., the Cl concentration on the hydride surface is very sensitive to the milling conditions. After survey spectrum acquisition, the specimen has been heated from 310 K to 380 K at 0.25 K/min and its decomposition has been followed in-situ. NaAlH₄ decomposes in two steps, releasing theoretically 5.6 mass % of hydrogen:

\[
3\text{NaAlH}_4 \rightarrow \text{Na}_2\text{AlH}_6 + 2\text{AlH}_3 \rightarrow \text{Na}_2\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \quad (1)
\]

\[
\rightarrow 3\text{NaH} + \text{AlH}_3 + 3\text{Al} + 3\text{H}_2 \rightarrow 3\text{NaH} + 3\text{Al} + \frac{9}{2}\text{H}_2. \quad (2)
\]

Reactions (1) and (2) take place between 420 - 480 K and 470 - 530 K, respectively. The temperatures for hydrogen desorption are significantly reduced by the addition of a few mol. % of Ti catalyst. The hydrogen from NaH is only desorbed at high temperatures at technically relevant pressures (698 K at 1 bar). NaAlH₄, Na₃AlH₆ and NaH are ionic compounds, while hydrogen and Al are not. During decomposition, the formal oxidation states of Al and hydrogen change from III to 0 and from -I to 0, respectively. The qualitative (chemical state) and quantitative (relative amount) analysis of the surface composition is determined by the energy positions and intensities of the XPS lines. Particular emphasis is laid on the change of the Al 2p peak (Fig. 1). The Al 2p peak may be assigned to Al(III) in NaAlH₄ (75.1 to 75.6 eV) or, due to the oxygen contamination on the surface, to Al₂O₃ (74.1 eV to 74.6 eV). During decomposition, metallic Al is formed by both reactions (1) and (2). The corresponding chemical shift is high enough to be distinguished by XPS and a second peak develops during decomposition, indicative of metallic aluminium (72.8 eV, compare also with Ref. 36). In Fig. 2, the atomic percentages of Al(III) and Al(0) are plotted as a function of time. The latter do not follow the hydrogen loss as estimated from the hydrogen pressure in the measurement chamber. The reason for this is the highly reactive specimen: hydrogen desorption takes place already during vacuum transfer. The first decomposition state can therefore only be partly recorded. Indeed, the metallic Al 2p peak is already observable with the first measurement. Furthermore, XPS
probes only the first 2 - 3 nanometers of the approximately 250 µm thick specimen, while the amount of desorbed hydrogen stems from the complete specimen. Apparently, desorption from the surface differs slightly from that of the deeper lying material, explaining the different behavior of metallic Al as measured by XPS and blurring the time-dependence of the two decomposition steps represented by reactions (1) and (2).
Al 2p photoelectrons from NaAlH₄, Na₃AlH₆ and Al₂O₃ all contribute to the Al(III) XPS lines. Although we cannot resolve the difference in chemical shifts in oxides and alanates, a fit of the Al(III) 2p peak reveals a small change of the exact energy position ($\Delta E \approx 500$ meV, see top graph in Fig. 2), while that of the Al(0) 2p peak remains constant ($\Delta E < 100$ meV, not shown). At the fully dehydrogenated state, Al(III) 2p can only originate from oxidized Al. With this we can precise the energy position of Al(III) 2p in NaAlH₄ and oxidized Al to $\geq 75.1$ eV and 74.6 eV, respectively.

The middle graph in Fig. 2 shows the evolution of the O 1s peak (identified at 531.6 eV, in agreement with standard Al₂O₃ powder data³⁷) during hydride decomposition. The observation of an oxide layer on a hydride surface is not surprising, namely in the case of sodium alanate.²⁴ Usually, this oxide layer is seen as a stable hydrogen diffusion barrier, and thereby as a limiting factor in the
dehydrating kinetics.  

But in certain cases, e.g. the decomposition of yttrium hydride, oxygen plays an active role in the decomposition process by effectively participating in the decomposition reaction. The evolution of the O 1s peak in Fig. 2 indeed shows that the surface oxygen content changes during hydride decomposition, firstly slightly decreasing during the first stage of decomposition and then significantly increasing during the second stage. The slight decrease observed in the first stage can be explained by the removal of adsorbed molecular oxygen (531.7 to 532.3 eV) and/or hydroxide (531.1 to 531.3 eV) by hydrogen. We attribute the significant overall increase of the oxygen signal to a migration of atomic oxygen from the bulk - whose presence comes from the combined effect of surface oxidation of the starting powder material and ball milling - to the surface during hydrogen desorption. A similar effect has been reported with nickel-zirconium hydride.

In Ti-doped alanates, the oxidation state of the additive is of particular interest. It was shown by Bogdanović et al. that titanium works as a dehydrogenation/rehydrogenation catalyst irrespective of whether it was added in oxidized (e.g. TiCl 4 ) or metallic form (e.g. Ti nano-particles or Al 2 Ti). After doping reaction, the oxidation state seems to be near Ti(0) as derived from various techniques (e.g. X-ray absorption spectroscopy and XPS). However, it has also been found that different Ti species in oxidized and reduced form are present after doping. These findings make it difficult to correctly describe the catalytically active species and corresponding mechanism.

Let us first focus on the decomposition of as-prepared specimens. In Fig. 1, particular emphasis is put on the chemical state of Ti as derived from its 2p photoelectrons. Two distinct components are identified on the spectrum at 310 K (and thus four peaks in total, taking into account spin-orbit coupling). The lower energy component identified at 454.2 eV is straightforwardly assigned to Ti(0) (Ti metal 2p 3/2: 454.3 eV). The second one identified at 457 eV is too low for Ti(IV) (TiO 2 p 3/2: 458.6 eV) and too high for Ti(II) (TiO 2 p 3/2: 455.9 eV), i.e. it does not fit with the two most common forms of Ti oxide. However, it fits very well with Ti(III) (Ti 2 O 3 p 3/2: 456.9 eV). Hierro-Oliva et al. recently investigated the oxidation of a Ti-Al based alloy by XPS and identified this sub-oxide, the presence of which they attributed to the limited availability of oxygen in their system. The limited availability of oxygen is also a property of our system, where it only exists as a contaminant. In this respect, it makes sense that this compound is found to be the main surface Ti oxide in this study. Taking these peak assignments into account, one can first deduce from Fig. 1 that titanium is in different oxidation states after specimen preparation. As already observed elsewhere, metallic titanium is formed by reaction with NaAlH 4 , but it may also partly remain as TiCl 4 . It forms oxides on the surface as well. As previously shown for the case LiAlH 4 , and as shown above for the case NaAlH 4 (Figs. 1 and 2), the change of the Al XPS-lines is a probe for the state of decomposition of the alinate. Simultaneously, the Ti lines change: the components corresponding to metallic Ti increase between the start and the end of hydride decomposition, while the proportion of Ti 2 O 3 significantly decreases. The evolutions of these Ti compounds during hydride decomposition can be seen in Fig. 3.

On the latter figure, it indeed appears that, while about 30% of the Ti atoms present on the hydride surface before decomposition correspond to Ti 2 O 3 , this percentage decreases by almost a factor 3 upon hydride decomposition. These observations are in good agreement with previous studies, usually claiming Ti to substitute for Na atoms in the alinate. But since we showed here that oxygen is diffusing towards the hydride surface during decomposition, it could also be considered whether its transfer from Ti 2 O 3 to Al 2 O 3 would also be activated by hydrogen transport and temperature, which indeed makes sense from a thermodynamic point of view. However, the effect shown in Fig. 3 can also partly be explained by the formation of metallic Ti from TiCl 4 remainders, although this would not fit well with the Ti (III) species that we see at 457 eV (TiCl 2 p 3/2: 458.5 eV). Thus, we repeated the measurement using Ti-doped NaAlH 4 previously cycled three times (desorbed at 125°C and 0.1 mbar and rehydrated at 125°C and 90 bar H 2 ). In this case, we can fully exclude that oxidized Ti is unreacted TiCl 4 . Fig. 4 summarizes these observations by showing the evolutions of the respective percentages of metallic and oxidized Al and Ti for the cycled specimen. Here again, the atomic percentage of Ti 2 O 3 starts from about 30% before hydride decomposition and is decreased by about a factor 3 upon decomposition. Consequently, it can be deduced that Ti 2 O 3 is reversibly formed and decomposed during every cycle of hydride formation/decomposition.

Coming back to the evolution of the Al formal oxidation states, the same behavior is qualitatively observed in Fig. 4 as compared to Fig. 2, with the expected reformation of metallic Al upon hydride
decomposition. However, quantitatively, a substantial difference is observed, i.e. the percentage of Al in metallic form at the end of decomposition is decreased by a factor 2 for the cycled specimen. This does not mean that the decomposition is not complete at 380K, but simply that the thickness of the oxide layer present at the surface at the end of hydride decomposition is increasing from cycle to cycle. Nevertheless, the surface oxygen atomic concentration before hydride decomposition does not follow this trend (28% for the as-prepared specimen and 24% for the cycled specimen, as derived from standard quantitative analysis\cite{52}), suggesting that oxygen is diffusing back to the bulk upon rehydriding.

In the present study, the changes of the surface oxidation states of Ti and Al as a function of the stage of hydrogenation, together with the change of the surface oxygen concentration, evidence a mobility of oxygen near the surface. An explanation of this effect comes from an energetic analysis of the surface termination. Wang et al. studied the oxygen adsorption on the related system TiAl\cite{53}. The authors find that the surface termination depends on the chemical potential of oxygen and of aluminium. A surface with more Al atoms on the top layer is more stable on the Al-rich condition (high chemical potential of Al), while the surface with more Ti (and O) atoms on the top layer becomes stable with the decrease of the chemical potential of Al. In our case, the chemical potential of oxygen is low, but finite, while the chemical potential of aluminium is a function of the state of hydrogenation: Al is formed during decomposition of NaAlH\textsubscript{4} and consumed during re-hydrogenation. With small amounts of metallic Al, the oxygen is with the Ti, at maximum amount of Al the Ti is reduced. Rehydrogenation changes the situation back to oxygen with Ti, which is indeed observed. The general reasoning of this effect is due to the fact that the surface energies of O:Ti and O:Al, and the corresponding interaction energies are relatively similar. This is a peculiarity, and explains the almost unique existence of a hydrogenation catalyst for alanates.

Besides the important surface oxygen mobility observed in this study, the absence of water and hydroxide as decomposition products is also a crucial aspect. In this UHV system, oxygen is only present as a contaminant and stabilized in the form of mobile solid oxide species. As a matter of fact, our XPS data do not show any signal where surface water would be expected (533.3 eV on a similar
FIG. 4. Bottom: evolution of the atomic percentages of Al(0) and Al(III) as a function of time for a specimen previously cycled three times, as extracted from the Al 2p region shown in Fig. 1. Top: evolution of the atomic percentages of Ti metal and Ti oxidized as a function of time for a specimen previously cycled three times, as extracted from the Ti 2p region shown in Fig. 1.

To conclude, we showed that mobility of surface oxygen is a crucial parameter for the reversibility of NaAlH$_4$, as indicated by the observed migration of atomic oxygen from bulk to surface. The low mobility in pure alanate leads to the formation of stable and inert oxide layers on the hydride and aluminium grains, hence limiting the reversibility of the pure system. In the doped system, the presence of Ti$_2$O$_3$ on the surface allows oxygen atoms to reversibly migrate from bulk to surface or from surface to bulk depending on whether the hydride is being formed or decomposed, and therefore depending on the applied hydrogen pressure (a sketch of this mechanism is shown in Fig. 5). Based on the reduced (i.e. Al and Ti) and oxidized (i.e. Al$_2$O$_3$ and Ti$_2$O$_3$) chemical species identified in the present study, we propose the following redox reaction to describe this oxygen migration:
FIG. 5. Schematic representation of the proposed mechanism for Ti catalytic activity in NaAlH₄. Ti acts as a hydrogen pump on the oxidized surface, while surface Ti oxides enhance oxygen mobility and allow oxygen to reversibly migrate from surface into bulk. The spillover model, here represented by Pd-clusters on the oxide surface, explains the enhancement of the dissociation of molecular hydrogen, but not its transport through thick oxide layers.

\[
2Aℓ^0 + 3O^{2-} \rightleftharpoons Al^{3+}O_{3}^{2-} + 6e^-, \tag{3}
\]

\[
Ti^{2+}O_{3}^{2-} + 6e^- \rightleftharpoons 2Ti^{0} + 3O^{2-}, \tag{4}
\]

\[
2Aℓ^0 + Ti^{2+}O_{3}^{2-} \rightleftharpoons Al^{3+}O_{3}^{2-} + 2Ti^{0}, \tag{5}
\]

where the oxygen atoms in reactions (3) and (4) do not change their oxidation states since they migrate from one metal oxide to the other. Hydrogen does not enter the formulas directly, but upon hydrogenation metallic Al is removed, thereby shifting the equilibrium to the left side. Similarly, decomposing sodium alanate by reducing the hydrogen pressure (reactions (1) and (2)) results in a shift to right side of reaction (5). However, the surface oxide layer thickness steadily increases upon cycling, showing that the reversibility of this mechanism is finally diminished, as already observed by Bogdanović et al.⁵⁷ It should be mentioned here that the analysis of the reversibility of this mechanism still requires complementary experimental investigations, since the investigation of the rehydrogenation cannot be followed in-situ by XPS.

Our finding of the crucial role of oxygen contaminations is in good agreement with recent NMR studies in NaAlH₄, NaH and MgH₂, showing increased hydrogen mobility after O-doping.⁵⁸–⁶⁰ Following our line of argumentation, breaking the surface oxide skin should have a similar effect on hydrogen sorption. Indeed, Na₃AlH₆ and NaAlH₄ can both be formed by ball milling of NaH and Al at moderate hydrogen pressures and room temperature.⁶¹ Furthermore, the oxygen mobility model as presented here explains the effectiveness of other additives such as Ce-halides.³ Ce compounds are not reduced to metallic state, but the implementation of Ce into oxides may have a similar effect as observed when using Ti. The mechanism shown in Fig. 5 also suggests that titanium oxides are preferential pathways for hydrogen transport in the oxide skin, which is well founded given the fact that the diffusivity of hydrogen in alumina⁶² is 5 orders of magnitude below that of titanium oxides⁶³ in the temperature range [310 - 380 K] as considered here.

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1. L.E. Klebanoff and J.O. Keller, Int. J. Hydrogen Energy 38, 4533–4576 (2013).
2. G.G. Froment, K.B. Bischoff, and J. DeWilde, Chemical Reactor Analysis and Design, third ed. (Wiley, Hoboken, 2010).
3. B. Bogdanović, U. Eberle, M. Felderhoff, and F. Schüth, Scripta Mater. 56, 813 (2007).
4. A. Züttel, A. Borgschulte, and S.I. Orimo, Scripta Mater. 2007(56), 823-828 (2007).
5. H.I. Schlesinger et al., J. Am. Chem. Soc. 75, 186-190 (1953).
6. K.L. Lindsay and B. Rouge, “Preparation of Alkali Metal Hydrides,” US pat. 3,505,036 (1967).
7. B. Bogdanović and M. Schwickardti, J. Alloys Compd. 253, 1-9 (1997).
A. Marashdeh, R.A. Olsen, O.M. Løvvik, and G.J. Kroes, J. Phys. Chem. C 112, 2164-2178 (2012).

10. O. Palumbo, A. Paolone, R. Cantelli, C. Jensen, and R. Ayabe, Mater. Sci. Eng. A 442, 75-78 (2006).

11. A. Borgschulte et al., Phys. Chem. Chem. Phys. 10, 4045-4055 (2008).

12. S. Singh et al., Acta Mater. 55, 5549-5557 (2007).

13. E. Ivanov, I. Konstanchuk, A. Stepanov, and V. Boldyrev, J. Less Comm. Met. 131, 25-16 (1987).

14. A. Marashdeh, R.A. Olsen, O.M. Løvvik, and G.J. Kroes, J. Phys. Chem. C 111, 8206-82013 (2007).

15. J. Iñiguez and T. Yildirim, Appl. Phys. Lett. 86, 103109/1-3 (2005).

16. P.E. de Jongh, Nature Mater. 10, 265-266 (2011).

17. L. Schlaphab, “Surface properties and activation,” in Hydrogen in Intermetallic Compounds II, edited by L. Schlaphab (Springer Verlag, Berlin, 1992).

18. C. Wu, A. Borgschulte, U. Frischknecht, Y. Yan, F. Yang, L. Luo, Y. Chen, and A. Züttel, J. Alloys Compd. 580, S156-S158 (2013).

19. H. C. Siegmann, L. Schlaphab, and C. R. Brundle, Phys. Rev. Lett. 40, 972-975 (1978).

20. M. Park, J.-H. Shin, Y.-S. Lee, Y.H. Im, and Y.W. Cho, J. Alloys Compd. 375, 393-398 (2013).

21. A. Borgschulte, M. Bielmann, A. Züttel, G. Barkhordarian, M. Domrèm, and R. Bormann, Appl. Surf. Sci. 254, 2377-2384 (2008).

22. J. N. Huiberts, R. Giessen, J. H. Rector, J. P. Dekker, D. G. de Groot, and N. J. Koeman, Nature 380, 231-234 (1996).

23. A. Borgschulte, R. J. Westerwaal, J. H. Rector, B. Dam, R. Giessen, and J. Schoenes, Phys. Rev. B 70, 155414/1-8 (2004).

24. A. Léon, D. Schild, and M. Fichtner, J. Alloys Compd. 404-406, 766-770 (2005).

25. C. Ronge, I. Llamas-Jansa, S. Oswald, L. Schultz, and O. Gutfleisch, Acta Mater. 57, 5563-5570 (2009).

26. M.P. Seah, I.S. Gilmore, and S.J. Spencer, J. Elec. Spec. 120, 93-111 (2001).

27. T.N. Dymova, Yu.M. Dergachev, V.A. Sokolov, and N.A. Grechanaya, Dokl. Akad. Nauk SSSR. 224, 591-592 (1975).

28. J. A. Diits and E. C. Ashby, Inorg. Chem. 11, 1230-1236 (1972).

29. H. Yao, H. Kawasaki, S. Isobe, Y. Wang, N. Hashimoto, and S. Ohnuki, Mater. Trans. 51, 1016-1019 (2010).

30. S. Isobe, H. Yao, Y. Wang, H. Kawasaki, N. Hashimoto, and S. Ohnuki, Int. J. Hydrogen Energy 35, 7563-7567 (2010).

31. X. Ke and I. Tanaka, Phys. Rev. B 71, 024117/1-16 (2005).

32. G.E. McGuire, G.K. Schweitzer, and T.A. Carlson, Inorg. Chem. 12, 2450-2453 (1973).

33. Y. Okamoto, T. Adachi, A. Maezawa, and T. Imanaka, Bull. Chem. Soc. Jpn. 64, 233-242 (1991).

34. K. Arata and M. Hino, Appl. Catal. 59, 197-204 (1990).

35. R. Hauert, J. Patscheider, M. Tobler, and R. Zehringr, Surf. Sci. 292, 121-129 (1993).

36. P.B. Amna, J.T Grant, P.J. Shamberger, A.A. Voevodin, and T.S. Fisher, J. Phys. Chem. C 116, 21886-21894 (2012).

37. B.R. Strohmeier, Surf. Sci. Spectra 3, 135-140 (1994).

38. G. Steppura, V. Rosenband, and A. Gany, J. Alloys Compd. 513, 159-164 (2012).

39. W. Chen, L. Wang, and S. Lu, J. Alloys Compd. 469, 142-145 (2009).

40. M. Yan, Y. Liu, G.B. Schaffer, and M. Qian, Scripta Mater. 68, 63-66 (2013).

41. A. Pashutski, A. Hoffmann, and F. Folman, Surf. Sci. 208, L91-L97 (1989).

42. C.D. Wagner, D.E. Passoja, H.F. Hillery, T.G. Kinisky, H.A. Six, W.T. Jansen, and J.A. Taylor, J. Vac. Sci. Technol. 21, 933-944 (1982).

43. A. Roustita, J. Chène, and C. Sèverac, Int. J. Hydrogen Energy 32, 5026-5032 (2007).

44. S. Chaudhuri, J. Graetz, A.Y. Ignatov, J.J. Reilly, and J.T. Mackerman, J. Am. Chem. Soc. 128, 11404-11415 (2006).

45. J. Graetz, J.J. Reilly, J. Johnson, A.Y. Ignatov, and T.A. Tyson, Appl. Phys. Lett. 85, 500-502 (2004).

46. G. Stepura, V. Rosenband, and A. Gany, Surf. Interface Anal. 11, 563-568 (1988).

47. C. Sleigh, A.P. Pipers, A. Jaspers, B. Coussens, and R.J. Meier, J. Elec. Spec. 77, 41-57 (1996).

48. H.F. Franzen, M.X. Umana, J.R. McCreary, and R.J. Thorn, J. Solid State Chem. 18, 363-368 (1976).

49. C.M. Chang, S. Trigwell, and T. Duerig, Surf. Interface Anal. 15, 349-354 (1990).

50. M. Hierro-Oliva, A.M. Gallardo-Moreno, and M.L. González-Martín, Metall. Mater. Trans. A 45A, 6285-6290 (2014).

51. I. Bari, Thermodenital Meta of Pure Substances, third ed. (Wiley, Weinheim, 1995).

52. N. Fairley and A. Carrick, The Casa Cookbook - Part 1: Recipes for XPS Data Processing (Acolyte Science, Knutsford, 2005).

53. L. Wang, J.-X. Shang, F.-H. Wang, Y. Chen, and Y. Zhang, Acta Mater. 61, 1726-1738 (2013).

54. I. Giner, M. Maxisch, C. Kunze, and G. Grundmeier, Appl. Surf. Sci. 283, 145-153 (2013).

55. G. Busca, Catal. Today 226, 2-13 (2014).

56. U. Diebold, Surf. Sci. Rep. 48, 53-229 (2003).

57. R. Bogdanović, A. Brand, A. Marjanović, M. Schwickardi, and J. Tölle, J. Alloys Compd. 302, 36-58 (2000).

58. E. G. Sorte et al., J. Phys. Chem. A 117, 8105-8113 (2013).

59. E. G. Sorte et al., J. Phys. Chem. C 117, 23575-23581 (2013).

60. R. L. Corey et al., J. Phys. Chem. C 112, 19784-19790 (2008).

61. N. Eigen, M. Kunowski, T. Klassen, and R. Bormann, J. Alloys Compd. 430, 350-355 (2007).

62. S. Serra, J. Am. Ceram. Soc. 88, 15-18 (2005).

63. G. C. Yu, Phys. Stat. Sol. A 198, 302-311 (2003).