Increasing Complexity Approach to the Fundamental Surface and Interface Chemistry on SOFC Anode Materials

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CONSPECTUS: In this Account, we demonstrate an increasing complexity approach to gain insight into the principal aspects of the surface and interface chemistry and catalysis of solid oxide fuel cell (SOFC) anode and electrolyte materials based on selected oxide, intermetallic, and metal–oxide systems at different levels of material complexity, as well as into the fundamental microkinetic reaction steps and intermediates at catalytically active surface and interface sites. To dismantle the complexity, we highlight our deconstructing step-by-step approach, which allows one to deduce synergistic properties of complex composite materials from the individual surface catalytic properties of the single constituents, representing the lowest complexity level: pure oxides and pure metallic materials. Upon mixing and doping the latter, directly leading to formation of intermetallic compounds/alloys in the case of metals and oxygen ion conductors/mixed ionic and electronic conductors for oxides, a second complexity level is reached. Finally, the introduction of an (inter)metallic(oxy)–(mixed) oxide interface leads to the third complexity level. A shell-like model featuring three levels of complexity with the unveiled surface and interface chemistry at its core evolves. As the shift to increased complexity decreases the number of different materials, the interconnections between the studied materials become more convoluted, but the resulting picture of surface chemistry becomes clearer. The materials featured in our investigations are all either already used technologically important or prospective components of SOFCs (such as yttria-stabilized zirconia, perovskites, or Ni–Cu alloys) or their basic constituents (e.g., ZrO₂), or they are formed by reactions of other compounds (for instance, pyrochlores are thought to be formed at the YSZ/perovskite phase boundary). We elaborate three representative case studies based on ZrO₂, Y₂O₃, and Y-doped ZrO₂ in detail from all three complexity levels. By interconnection of results, we are able to derive common principles of the influence of surface and interface chemistry on the catalytic operation of SOFC anode materials. In situ measurements of the reactivity of water and carbon surface species on ZrO₂- and Y₂O₃-based materials represent levels 1 and 2. The highest degree of complexity at level 3 is exemplified by combined surface science and catalytic studies of metal–oxide systems, oxidatively derived from intermetallic Cu–Zr and Pd–Zr compounds and featuring a large number of phases and interfaces. We show that only by appreciating insight into the basic building blocks of the catalyst materials at lower levels, a full understanding of the catalytic operation of the most complex materials at the highest level is possible.

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## INTRODUCTION

Although solid oxide fuel cells (SOFCs) are part of the prospective energy infrastructure, some challenges in their adaption still remain. Besides the need for lower operating temperatures, fuels that are easier to store, cheaper, and/or more abundant than hydrogen are preferred. While external reformers enable the transformation of various compounds into hydrogen and carbon monoxide,⁵ the environmental footprints of such systems are drastic. Alternatively, the anode can act as an internal reforming catalyst,⁶⁻⁷ allowing to feed the fuel (mixed with either H₂O or CO₂) directly to the anode. At the same time, the dimensions of the whole SOFC unit can be kept as small as possible for nonstationary applications. However, the standard nickel/ytrria-stabilized zirconia (YSZ) anode working well in hydrogen and sufficiently water-enriched reformate gas is not ideally suited for the operation in methane-containing feeds as it is susceptible to deactivation by coking.⁸⁻¹¹ Thus, optimization of internal reforming processes is of prime importance.

In this Account, we demonstrate a typical workflow allowing insight into the fundamental surface chemistry of internal reforming processes by exploiting an increasing material complexity approach using materials on different model-, system- and technology-oriented levels. Figure 1 features a sketch of this workflow encompassing the studied materials and their property relations. Concentric circular shells represent the three material complexity levels. Level 1 deals with the simplest systems, i.e., pure oxides and metals such as ZrO₂ or nickel. Level 2 includes mixed materials in the form of alloys and doped or, generally, compositionally/structurally more complex oxides, such as YSZ or perovskites. Some of these oxide materials are ionic conductors for oxygen anions and are rendered with a black border in the sketch. Finally, a metal/oxide interface is introduced by combining metals and oxides, such as YSZ or perovskites. Some of these oxide materials are ionic conductors for oxygen anions and are rendered with a black border in the sketch.

In the next three sections, we describe a typical procedure in our workflow covering all complexity materials levels from the lowest to the highest, starting from simple systems and subsequently adding more complexity to gain information about reforming processes of carbon-based fuels on SOFC anode materials. As a representative example serving as the recurrent theme, we focus on the understanding of water and carbon reactivity on ZrO₂-related materials in reforming reactions. Specifically, we focused on the fundamental understanding of methane steam/dry as well as methanol steam reforming, covering materials from all complexity levels. In this respect, we show that it is highly essential to cover the entire SOFC-relevant temperature axis. Only by connecting information from all complexity levels at realistic temperatures and under realistic gas phase conditions, a clear picture evolves, allowing generalization and intertransformation of knowledge between different materials and reactions. Moving along the material and property complexity axis, we start from the isolated water and carbon reactivity on comparatively simple oxide surfaces (ZrO₂ and Y₂O₃, level 1) and continue via changes in the water and carbon reactivity on more complex oxides as a function of the doping level (Y-doped ZrO₂, level 2) to the in situ corrosion of complex intermetallic compound/alloy materials in methane dry and methanol steam reforming mixtures (Pd₉Zr/Pd₉Zr, Pd–Zr alloy, and Cu₅Zr₁₄, level 3),

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**Figure 1.** Sketch of the increasing complexity approach. The concentric circles describe the different material complexity levels, with level 1 focusing on the lowest and level 3 representing the highest complexity. Materials with a black border are ionic conductors, and the lines between the different nodes express various connections between the materials in our studies. The colored materials are featured in the three studies presented in this work.

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**AN EXEMPLARY PATH TO UNRAVEL THE SURFACE AND INTERFACE CHEMISTRY OF REFORMING PROCESSES ON SOFC ANODE MATERIALS**

In the next three sections, we describe a typical procedure in our workflow covering all complexity materials levels from the lowest to the highest, starting from simple systems and subsequently adding more complexity to gain information about reforming processes of carbon-based fuels on SOFC anode materials. As a representative example serving as the recurrent theme, we focus on the understanding of water and carbon reactivity on ZrO₂-related materials in reforming reactions. Specifically, we focused on the fundamental understanding of methane steam/dry as well as methanol steam reforming, covering materials from all complexity levels. In this respect, we show that it is highly essential to cover the entire SOFC-relevant temperature axis. Only by connecting information from all complexity levels at realistic temperatures and under realistic gas phase conditions, a clear picture evolves, allowing generalization and intertransformation of knowledge between different materials and reactions. Moving along the material and property complexity axis, we start from the isolated water and carbon reactivity on comparatively simple oxide surfaces (ZrO₂ and Y₂O₃, level 1) and continue via changes in the water and carbon reactivity on more complex oxides as a function of the doping level (Y-doped ZrO₂, level 2) to the in situ corrosion of complex intermetallic compound/alloy materials in methane dry and methanol steam reforming mixtures (Pd₉Zr/Pd₉Zr, Pd–Zr alloy, and Cu₅Zr₁₄, level 3),
leading to active and selective composite Pd/ZrO2 and Cu/ZrO2 systems, respectively. Particular emphasis is given to exemplify how the operation of the most complex Cu/Pd−ZrO2 interface in reforming reactions can only be understood on the basis of the interaction with water as well as with carbon-containing fuels with the individual building blocks.

**LEVEL 1: WATER AND CARBON REACTIVITY ON ZrO2 AND Y2O3: ELUCIDATING THE COMPLEX INTERPLAY BETWEEN (STEAM) REFORMING REACTANTS AND OXIDE SURFACES**

As an example, the interaction of water and methane with the surfaces of the insulating oxides (with respect to both electrons and ions) ZrO2 and Y2O3 was investigated separately using in situ Fourier-transform infrared (FT-IR) spectroscopy and electrochemical impedance spectroscopy (EIS).1–3 Brunauer–Emmett–Teller (BET) surfaces of the powder samples differ (2 m² g⁻¹ (m-ZrO2), 32 m² g⁻¹ (YSZ), (Y2O3)120 m² g⁻¹), but according to Barrett–Joyner–Halenda analysis porosity is essentially absent. For both EIS and FT-IR analysis, pressed powder samples are used. ZrO2 is usually monoclinic (m-), and the tetragonal (t-) polymorph must be stabilized by doping (e.g., YSZ)12,13 or crystallite size effects.14 As the metal (e.g., Cu)−t-ZrO2 interface has been shown to exhibit beneficial reforming properties,1 a sophisticated synthesis routine to phase-pure t-ZrO2, pertaining its structure in oxidative, reductive, or reactive gas environments, as long as the temperature is kept below 723 K, was developed to compare the intrinsic surface-chemical behavior of different ZrO2 polymorphs.15

**Water Reactivity**

The different adsorption behavior of ZrO2 and Y2O3 is already visible in FT-IR spectra as a function of H2O partial pressure at 298 K (Figure 2A and B). Whereas for pure m-ZrO2 strongly bonded dissociated water species at the otherwise hydrolysis-inert surface are clearly absent (only terminal and multicoordinated water signals at 3780/3670 cm⁻¹ and a sharp δ(OH) peak at 1645 cm⁻¹, strongly masked by gas phase H2O, are visible at lower water partial pressures1), a simple molecular water adsorption model cannot explain the complex water−Y2O3 interaction, as dissociative water incorporation into the crystal lattice prevails. Also the superimposed molecular water surface adsorption behavior appears much more complex and involves an array of multicoordinated hydroxyl groups. Surface Zr hydroxylation is also prevalent for t-ZrO2 treated in water at 873 K (Figure 2C). Minor surface reduction of Zr takes place, but the majority of Zr species appear in Zr(IV)−OH state (with the Zr 3d3/2 component measured at 182.5 eV).1 This example is of particular importance, as it subsequently allows one to address the reversibly formed reactive OH groups of the

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**Figure 2.** Water reactivity on ZrO2 and Y2O3: (A, B) In situ isothermal FT-IR spectra at variable H2O pressure on m-ZrO2 and Y2O3. (C) Zr 3d XP spectrum on t-ZrO2 after water exposure at 873 K. (D, E) Dynamic water sorption measurements on ZrO2 and Y2O3. (F) In situ temperature-resolved electrochemical impedance spectra on ZrO2 and Y2O3 under water atmosphere. (G) STM image of an ultrathin ZrO2 film on Pt/3Zr after 15 L water exposure at 293 K. (H) Calculation of the water adsorption energy on m-ZrO2 from in situ isothermal and isobaric FT-IR experiments. (I) Multilayer model for the water adsorption on YSZ. Reproduced with permission from ref 1 (A, B, D−F, I), ref 19 (C), and ref 16 (G, H). Copyright 2020 American Chemical Society, 2017 the Royal Chemical Society, and 2018 the Royal Chemical Society, respectively.
Cu–t-ZrO$_2$ interface formed by in situ decomposition of Cu$_{13}$Zr$_{14}$ (cf. Figure 5A). Dynamic sorption measurements on ZrO$_2$ and Y$_2$O$_3$ (presented via the mass change as a function of the water partial pressure in Figure 2D and E) also show vast adsorption and reactivity differences. m-ZrO$_2$ adsorbs ultrathin water layers only at the surface, but Y$_2$O$_3$ adsorbs more than 4% of its mass, revealing a strong adsorption hysteresis effect. In situ EIS data acquired during water adsorption on both samples show only a limited increase in conductivity (Figure 2F). This indicates that, despite their vastly different nature, both the strongly and irreversibly dehydroxylated pure m-ZrO$_2$ (exhibiting unreactive isolated OH groups) and the ice- and polymeric chainlike water layers on Y$_2$O$_3$ hardly show any proton bound state similar to liquid H$_2$O (stable around 500 K). To connect surface and bulk properties, Figure 2G shows a scanning tunneling microscopy (STM) image of an ultrathin ZrO$_2$ film on a Pt$_x$Zr single crystal, exposed to 15 Langmuir equivalents of H$_2$O at 293 K. Water-related species are found preferentially above subsurface dislocation lines (gray areas in the image) showing strong local ordering (yellow triangles). Correlated FT-IR data on m-ZrO$_2$ yield a strikingly similar range for molecular water adsorption energies around 0.57 eV as compared to the complementary surface-science and density functional theory studies, highlighting the strong potential of our dedicated “materials gap-bridging” approach in resolving reactivity issues on structurally strongly different bulk- and surface phases of ZrO$_2$. Figures 2I and 3 summarize the derived general picture and differences of the complex water adsorption on “realistic” oxide surfaces: after a first chemisorbed hydroxylated layer (can be typically stable up to 900 K), strongly bound, physisorbed icedlike ordered water molecules (stable up to T ∼ 500 K) are obtained. A higher coverage leads to chained polymer-like networks (decomposition at T ≤ 500 K) before transitioning to a more weakly bound state similar to liquid H$_2$O (stable around T < 300 K).\textsuperscript{11,17}

\section*{Carbon Reactivity}
Essentially important for the fundamental understanding of carbon-fuel–catalyst interaction at high temperatures, the carbon reactivity is exemplified by the interaction of methane with clean Y$_2$O$_3$ and CO$_2$ with m-/t-ZrO$_2$.\textsuperscript{5,11,18} Figure 4A shows, via correlated in situ FT-IR and EIS measurements, the distinct change of the surface at 1023 K by forming carbon deposits on the pure oxide surface (a common feature for all studied oxides), as indicated by both a drastic increase in conductivity by forming percolated carbon islands and an associated total decrease in IR transmission. Structurally, the carbon deposits are graphic in nature, encapsulating grains and forming rosette-like morphologies (Figure 4B). Frequency-dependent EIS measurements (Figure 4C) reveal these carbon islands to be extremely dynamic, potentially also migrating to the metal–oxide interface in complexer systems, thus contributing to the overall reactivity of a combined metal–oxide catalyst entity. Similar interactions are observed for other C$_x$ molecules. Exemplified for t-ZrO$_2$, as shown in Figure 4D and E, a surface-carburizing high temperature treatment at 1273 K in CO$_2$ allows preservation of a complete surface-near ZrO$_2$C$_x$ layer in an electron-conductive (oxy)carbidic-like state. Although the sample consists of >90 wt % m-ZrO$_2$ after the treatment, such a surface carburization is not obtained starting from m-ZrO$_2$ directly. Starting from t-ZrO$_2$, which is highly surface and bulk structurally defective (e.g., exhibiting coordinatively unsaturated sites essentially arising from the synthesis procedure), hydroxylated, and more reactive, apparently strongly promotes these surface modifications. These studies further highlight the technological importance of understanding the interaction of simple SOFC entities with fuel components.\textsuperscript{19} Even though coking is usually associated with the Ni content in traditional SOFC anodes,\textsuperscript{10,11} our studies have revealed that at technologically relevant temperatures above ~1000 K the oxidic component (i.e., YSZ, but also ZrO$_2$ and Y$_2$O$_3$) is not exempt from this phenomenon either.\textsuperscript{7,3}

In summary, these fundamental data on the adsorption and decomposition behavior of the basic constituents of reforming reactions on simple oxides already provide a foundation for subsequent stages in the experimental procedure, to explain reactivities obtained from catalytic testing in reforming reactions and to be used to project hypotheses onto compounds further along the complexity axis in the materials domain.

\section*{LEVEL 2: WATER AND CARBON REACTIVITY ON Y-DOPED ZrO$_2$: INFLUENCE OF THE Y-CONTENT ON REACTIVITY, SURFACE CONDUCTION AND CHEMISTRY IN C$_1$ GASES}

On YSZ, chemically viewed simply as a solid solution of Y$_2$O$_3$ in ZrO$_2$, the surface-near water adsorption as a function of partial pressure is considerably more complex compared to that on simple ZrO$_2$ (Figure 5A), and also the multilayer water sorption is strongly different (Figure 5B). Above 80% relative humidity, an almost 10-fold increase in the amount of bound water is observed, whereas below that threshold the process is completely reversible without hysteresis, and only about 1% mass increase is observed (in contrast to pure ZrO$_2$, where only a mass change of 0.25% has been observed at close to 100% relative humidity). In due course, ZrO$_2$ appears rather hydrophobic, as it is much less hydroxylated than 8-YSZ (ZrO$_2$ stabilized with 8 mol % Y$_2$O$_3$), which not only lowers the amount of water in the icedlike layers, but essentially changes its binding mode. The higher amount of water in the icedlike layer on YSZ can be attributed to the higher amount of OH groups and defects on the surface compared to ZrO$_2$. The scattered OH groups on the latter are, referenced to YSZ, too isolated to stabilize a total hydrogen-bound wetting of the surface. In contrast, on YSZ, pronounced stabilization of the
OH-covered surface in the icelike layers is likely, increasing the capacity of water uptake in this specific layer relative to ZrO₂. It should be noted that different specific BET surface areas of these oxides lead to different mass changes and thus the absolute values cannot be compared. Nevertheless, the qualitative differences in the sorption experiments are representative, also corroborated by normalization of the water sorption to the respective surface area. Correlated in situ FT-IR and EIS data in 24 mbar water on 8-YSZ, referenced to measurements in dry He and single- and polycrystalline YSZ to separate annealing and water adsorption effects, indicate removal of water multilayers directly contributing to increased protonic conductivity, in vast difference to its pure oxidic counterparts, where the proton hopping mechanism proposed on YSZ is clearly absent.

As for ZrO₂ and Y₂O₃ above ~1000 K, a strong interaction of C gases with the YSZ surface was verified. Treatment in methane at 1173 K causes the formation of mostly graphitic deposits as revealed by transmission electron microscopy (TEM; Figure 5D). Raman spectroscopy on different spots on the surface allows the identification of a limited amount of nanotube-like features, indicating a considerable lateral heterogeneity of the carbon deposits across the surface (Figure 5E).

Combined admission of water and methane to simulate internal reforming gas atmospheres reveals a considerable larger amount of nanotube-like features, mostly due to the easier detachment of the carbon deposits from the YSZ grains (Figure 5F). In consequence, this leads to considerably different reactivity and surface chemical properties, as confirmed by corresponding FT-IR and EIS experiments.

Extension of these ideas and experiments to other doping levels to assess the entire ZrO₂—Y₂O₃ phase diagram reveals both similar features and vast differences. Carbon deposition during treatment in CH₄ at high temperatures T ≥ 1023 K is a common feature, irrespective of the Y content (Figure 5G).

However, for all Y-doped samples temperature regions with different charge carrier activation energies could be identified, perfectly corresponding to significant changes in surface chemistry. Due to the different degree of hydroxylation and the different ability to chemisorb methane (but also CO and CO₂), the influence of the surface chemistry on the elec-
chemical properties and the amount of deposited carbon is varying strongly as a function of Y-content (Figure 5H).

LEVEL 3: THE IMPORTANCE OF WATER AND CARBON REACTIVITY ON Pd/ZrO₂ AND Cu/ZrO₂ METAL–OXIDE SYSTEMS DERIVED FROM IN SITU DECOMPOSED Pd₂Zr/Pd₃Zr AND Cu₂Zr INTERMETALLIC COMPOUNDS AND ALLOY MATERIALS

The most complex systems described in this Account comprise Pd/ZrO₂ and Cu/ZrO₂ metal–oxide materials, obtained via controlled in situ decomposition of Pd₂Zr/Pd₃Zr bulk intermetallic compounds and a surface-near Pd–Zr alloy,⁵⁸–⁶¹ as well as Cu₂Zr intermetallic compounds in methane dry (DRM) and methanol steam reforming (MSR).⁶²–⁶⁴

Figure 6A displays XP spectra obtained on Cu₃Zr₁₄ after various catalytic runs in methanol steam reforming. The high CO₂ selectivity (referenced to both clean Cu and pure ZrO₂),²⁴⁴ evident from the temperature-programmed catalytic profiles in Figure 6B, clearly goes along with differently reactive Zr-bound OH groups, whose binding energy matches those of t-ZrO₂ discussed previously. The overall Zr intensity diminishes as the Cu intensity increases. The structural reason for this is the complete decomposition of Cu₃Zr₁₄ in the water/methanol mixture, creating highly dispersed Cu particles at the surface in a matrix mostly consisting of t-ZrO₂ (Figure 6C). The initial intermetallic compound is therefore self-activating, and its corrosion product is highly CO₂ selective, which by in situ X-ray photoelectron spectroscopy (XPS) measurements has been attributed to the reversible formation of reactive surface-bound hydroxylated Zr(OH)ₓ species. Thus, the in situ “selective” corrosion of the precatalyst’s intermetallic compound state to at least partly form a metal/oxide system is a generally viable preparation pathway to active and selective catalyst materials, whose properties could only be fully understood once the
specific water reactivity of the oxidic component, as a prerequisite to CO$_2$ selective methanol steam reforming, has been assessed on previous levels of the work flow. For Pd–ZrO$_2$, the composite metal–oxide state was obtained either by in situ decomposition of a Pd$_2$Zr/Pd$_3$Zr bulk intermetallic compound mixture or by forming a subsurface Pd–Zr alloy by reductive dissolution of chemical vapor-deposited ZrO$_x$ species into a Pd foil.  The reactivities of both systems in the dry reforming of methane (DRM) reaction are vastly different: the CO formation rate is significantly higher on the bulk-derived Pd/ZrO$_x$ system (peaking at about 8.5 hPa min$^{-1}$, Figure 7A) than on the on the subsurface alloy (0.3 hPa min$^{-1}$, cf. referenced to the reactivity on clean Pd and ZrO$_2$ also shown in both graphs, Figure 7A and C). The latter barely exceeds the activity of pure ZrO$_2$. *Operando* near-ambient-pressure XPS (Figure 7B and D) indicates a characteristic carbon morphology on Pd/ZrO$_2$ followed by in situ decomposition of Pd$_2$Zr/Pd$_3$Zr. Exclusively for the latter, a carbide Pd component (green labeled in the deconvoluted Pd 3d and C 1s spectra) is visible in different CH$_4$/CO$_2$ mixtures. This is attributed to the different Pd grain sizes: for the subsurface alloy, the active phase exhibits a large interface to a bulk Pd foil acting as a quasi-infinite reservoir to store carbon. Any carbon formed due to decomposition of methane is immediately dissolved into the bulk, whereas the small Pd nanoparticles present in the decomposed bulk intermetallic compound have a limited storage capacity for carbon, leading to fast saturation. Thus, the observed higher activity can be explained by a catalytic spillover effect, as displayed in the inset in Figure 7A. Methane is decomposed on the Pd surface, essentially leading to the dissolution of reactive carbon into Pd and its effective migration to the Pd/ZrO$_2$ interface, reacting there with adsorbed/activated CO$_2$ via the reverse Boudouard reaction. Without carbon supersaturation of Pd, the statistical probability of the latter process will be negligibly small. By this means, the reduced Pd dimensions invoke higher CO formation rates on Pd$_2$Zr/Pd$_3$Zr, characterized by smaller Pd nanoparticles in contact with ZrO$_2$ (formed in situ), relative to the subsurface alloy. An at least limited reducibility of ZrO$_2$ by carbon around 1000 K at the interface is required for the proposed assistance of Zr(ox) sites in CO$_2$ activation and the transfer of CO$_2$-derived oxygen to the latter (following fast supply of reactive C atoms toward the phase boundary), which was essentially derived on level 1 for pure ZrO$_2$.  

We have shown how the knowledge derived on levels 1 and 2 with respect to the material and catalytic properties can help to elucidate reaction mechanisms on materials of the highest complexity, featuring interfaces between metals, oxides, and, in the case of only partial decomposition, also alloys/intermetallic compounds. As the latter represent structurally highly dynamic systems, decomposing at least partly into a metal–oxide composite, knowledge about the constituting entities is imperative, directly validating our increasing complexity approach.
Although only two examples are presented on level 3, the possibilities in using selected intermetallic compounds to act as catalyst precursors to prepare highly active and CO\textsubscript{2}\textsubscript{-}selective reforming catalyst entities by controlled \textit{in situ} decomposition can be generalized. An obvious prerequisite is the at least partial mutual solubility to form alloys or even intermetallic compounds. Prominent examples fulfilling these requirements include CuZn\textsuperscript{26}, GaPd\textsuperscript{27}, Cu\textsubscript{2}In\textsuperscript{28}, or ZnPd\textsuperscript{29}. The common feature of all systems is the combination of a noble metal, which eventually remains in its metallic state, with an unnoble/depassivated metal that is likely to be oxidized upon decomposition, thus forming the metal\textendash oxide interface. The overall activation process, thus, corresponds to the classical picture of “selective corrosion” of an intermetallic compound or alloy surface and bulk structure and is accompanied by the \textit{in situ} formation of much more complex catalyst entities. These rearrangements can be present in the form of a complete destruction of the intermetallic compound bulk structure (Cu\textsubscript{51}Zr\textsubscript{14})\textsuperscript{4,24}, the formation of an metal/oxide (Cu\textsubscript{51}Zr\textsubscript{14}) or intermetallic compound/oxide (ZnPd, Cu\textsubscript{2}In, CuZn) interface, or the intertransformation of intermetallic compounds with varying composition (Pd\textsubscript{2}Zr) during decomposition. A common leading theme is also the intrinsic reactivity of the resulting oxide (or the metal\textendash oxide interface) in the metal\textendash oxide system.\textsuperscript{30\textendash35} Surface chemical aspects, including the discussed propensity to adsorb (and activate) water e.g. for steam reforming or form reactive carbon species in dry reforming govern the catalytic properties of the oxide and thus, influence the catalytic performance of the entire catalyst detrimentally or beneficially. Other obvious key criteria include the oxidation propensity and general thermodynamic stability of the chosen intermetallic compound/alloy or the metastability of the evolving oxide polymorph that is formed upon decomposition.

\section*{SUMMARY AND PERSPECTIVE}
Exemplifying the use of SOFC anode materials and their surface and bulk chemistry relevant for different (internal) reforming processes, we have demonstrated a comprehensive workflow using a knowledge-based survey of the materials space, sampling different levels of complexity. Complexity in this case refers to chemical composition, applied experimental techniques, and catalytic reactions.

ZrO\textsubscript{2}, Y\textsubscript{2}O\textsubscript{3}, and YSZ (representing complexity levels 1 for ZrO\textsubscript{2}/Y\textsubscript{2}O\textsubscript{3} and 2 for YSZ) were exemplarily investigated with respect to their behavior upon water adsorption and carbon chemistry/methane reactivity. By considering the fundamental building blocks of reforming catalysts, it was shown that the
water and carbon reactivity are very different among these materials, leading to different adsorbate species. These encompass chemisorbed H$_2$O, physisorbed icelike layers and almost liquidlike water, as well as different carbon morphologies as a function of atmosphere and doping level. In fact, also the isolated oxide materials are prone to coking and have the ability to form carbon filament- and nanotube-like features, causing in part deactivation at typical operating temperatures above 1073 K. This is especially important for the use of conventional SOFC Ni/YSZ cermet anodes, where coking is essentially attributed to the nickel species (exhibiting a higher coking propensity than oxides$^8$).

Increasing the complexity also along the experimental axis, starting from fundamental studies on the single and isolated components, subsequently lifting the restriction of focusing on the effect of a single component, leads to a deeper knowledge about the catalytic properties of more complex materials. Moving to the highest complexity level 3, the common activity and selectivity descriptor in methane dry and methanol steam reforming over metal–oxide systems derived from in situ corrosion of intermetallic compounds and alloys is the specific water-, CO$_2$-, and carbon-activating function of the individual components, providing the connection to the reactivity studies described on level 1. With respect to water reactivity, the studies in methanol steam reforming not only directly help in interpreting the adsorbed OH features at lower temperatures, but our studies also showed that some water species even persist on the oxide surface at reforming- and/or SOFC-relevant temperatures, with strikingly different properties than those present at lower temperatures. With respect to the up to now unknown surface reducibility of ZrO$_2$ (either via carburization to an (oxy)carbide or in hydrogen (not shown in detail, but equally possible$^{36}$) and the associated defect chemistry for water activation and CO$_2$ reforming, we provided another example for the knowledge transfer between the levels: only by assessment of the pure oxide-bound surface and interface surface reduction can a “carbothermal” defect chemistry at the phase boundary be postulated for the methane dry reforming reaction and the carbon source pinpointed at Pd–only the combination of both will eventually yield a complete picture of the reaction mechanism. Elucidating the reactivity of the phase boundary of a metal to a doped oxide by using the knowledge of level 2, would be the next logical step in the direct knowledge transfer between levels 2 and 3.

Entangled with the workflow regarding material complexity, we emphasize the necessity for the use of in situ and operando structure-determining and spectroscopic techniques, such as in situ X-ray diffraction, in situ X-ray absorption spectroscopy, or in situ FT-infrared and in situ electrochemical impedance spectroscopy. Only the combination of such methods allows one to derive a clear picture of the interplay of reactants and surfaces and its structural, morphological, or catalytic consequences. We have chosen one illustrative example of water and carbon reactivity relevant for SOFC anode chemistry on different levels of materials complexity, but by taking in the principles worked out for this particular example, generalization to more complex materials or reactions is possible.
of SOC electrodes/materials at high temperatures, combined with online electrical impedance (EIS) electrode characterization.

### Abbreviations

DRM, dry reforming of methane; EDX, energy-dispersive X-ray spectroscopy; EIS, electrochemical impedance spectroscopy; FTIR, Fourier transform infrared spectroscopy; MSR, methanol steam reforming; SOEC, solid oxide electrolysis cell; SOFC, solid oxide fuel cell; SRM, steam reforming of methane; (S)TEM, (scanning) transmission electron microscopy; XRD, X-ray diffraction; YSZ, yttria-stabilized zirconia.

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