Oxide-based nanomaterials for fuel cell catalysis: the interplay between supported single Pt atoms and particles

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The concept of single atom catalysis offers maximum noble metal efficiency for the development of low-cost catalytic materials. Among possible applications are catalytic materials for proton exchange membrane fuel cells. In the present review, recent efforts towards the fabrication of single atom catalysts on nanostructured ceria and their reactivity are discussed in the prospect of their employment as anode catalysts. The remarkable performance and the durability of the ceria-based anode catalysts with ultra-low Pt loading result from the interplay between two states associated with supported atomically dispersed Pt and sub-nanometer Pt particles. The occurrence of these two states is a consequence of strong interactions between Pt and nanostructured ceria that yield atomically dispersed species under oxidizing conditions and sub-nanometer Pt particles under reducing conditions. The square-planar arrangement of four O atoms between Pt and nanostructured ceria that yield atomically dispersed species under oxidizing conditions and sub-nanometer Pt particles under reducing conditions. The latter emerge due to either oxygen vacancies or adsorption of reducing agents. The unique properties of the sub-nanometer Pt particles arise from metal-support interactions involving charge transfer, structural flexibility, and spillover phenomena. The abundance of specific adsorption sites similar to those on (100) nanoterraces determines the ideal (maximum) Pt loading in Pt-CeO₂ films that still allows reversible switching between the atomically dispersed Pt and sub-nanometer particles yielding high activity and durability during fuel cell operation.

1. Introduction

Hydrogen powered proton exchange membrane fuel cells (PEMFCs) are considered potential next generation power sources for a variety of small to medium-scale applications, including automotive vehicle propulsion and chip-integrated micro-devices. For PEMFC technology, platinum is the essential catalytic element. Typically, commercial anode catalysts contain about 2-5 mg cm⁻² of the noble metal. The high cost of platinum is the main factor limiting the large-scale application of fuel cell technology. Therefore, great efforts are dedicated to the development of catalytic materials for PEMFCs to meet the standards defined by the US Department of Energy (DOE). The latest developments in fuel cell technology may reduce the total Pt loading in PEMFCs to 0.15 mg cm⁻² which is still above the target value (0.125 mg cm⁻²) set for the year 2017.

In the prospect of further reduction of Pt loading, supported single atom catalysts (SACs) offer ultimate noble metal efficiency by exposing the entire noble-metal content to reactants. The synthesis and performance of SACs in numerous heterogeneous reactions have been recently reviewed in detail. Several key challenges have been identified with respect to the stability and reactivity of the atomically dispersed noble metals. In particular, anchoring of noble metal atoms at appropriate supports requires the presence of...
specific adsorption sites that are capable of stabilizing metal atoms against sintering and agglomeration into particles. Such sites have been identified on the surfaces of graphenes, nitrides, zeolites, and metal oxides. In most cases, atomically dispersed metals are found to be anchored in surface cationic positions of the host oxide. Depending on the oxidation state of the anchored metal atom, spontaneous formation of anionic or cationic vacancies occurs to balance the charge. In some cases, anchoring of the metal atom is achieved through the spatial confinement in pores or open channels of the support. The stability of the anchored metal atoms and their propensity to agglomerate is determined by the energy difference between the states associated with an adsorbed metal atom and a supported metal particle. In this respect, the use of metal oxides allows employing metal-support interactions to achieve a strong binding between the metal and the support. Conceptually, oxide supported noble metal SACs are closely related to noble metal-doped oxides. However, the common disadvantage of the latter is that a substantial amount of the noble metal is atomically dispersed in the bulk. As a result, the density of the noble-metal sites at the surface is low. An increase of the noble metal loading in doped oxides, on the other hand, often gives rise to metallic particles at the surface.

Different strategies are applied to increase the density of the atomically dispersed species at the surface. These include grafting of the atomically dispersed metals, the use of stabilizing ligands, and nanostucturing of the support. In particular, new sites emerge at the surface of the nanostuctured oxides that may anchor atomically dispersed noble metals in a structural environment which is energetically highly favorable with respect to cationic substitution in the doped bulk. Under these circumstances, the segregation of the noble metal is driven thermodynamically, yielding a high density of atomically dispersed noble metal at the surface.

In the following review we summarize the properties of new materials containing atomically dispersed noble metals anchored at surface sites of nanostructured ceria. In particular, the catalytic performance of atomically dispersed platinum supported on nanostructured ceria is discussed in the prospect of applications as anode catalysts for PEMFCs. The remarkable properties of these catalysts involve the interplay between the two states associated with the atomically dispersed noble metal and sub-nanometer particles. The great stability and durability of the prototype anode catalyst arise from reversible switching between these two states under operating PEMFC conditions.

## 2. Supported single atom catalysts in proton exchange membrane fuel cells

### 2.1. High efficiency at ultra-low noble metal loading

The performance of Pt–CeO₂ catalysts with ultra-low Pt loading prepared by means of radio frequency sputtering was tested under relevant PEMFC conditions. The key parameter determining the cost efficiency of the fuel cell catalyst is the specific power (SP), i.e. the power density (PD) per weight of noble metal. The corresponding SPs and PDs achieved using the Pt–CeO₂ catalysts at the anode (Table 1) were compared with those of a commercial Pt nanoparticle catalyst and Pt thin films (Table 2) under identical operation conditions.

The thin film of the Pt–CeO₂ catalyst deposited directly on the gas diffusion layer (GDL) yielded a higher PD with respect to the reference PtRu anode catalyst despite the ten-fold lower Pt loading. The use of double-wall (DWCNT), multi-wall (MWCNT), and chemical vapor deposited (CVD-CNT) carbon nanotubes resulted in a further increase of PDs and SPs (see Table 1). With respect to the commercial Pt anode (Table 2a), the Pt–CeO₂ catalyst yielded an around 10²-fold increase of the SP.

Additionally, an increase of the operation temperature of the fuel cell yielded an approximately two-fold increase of the PD and SP. However, the highest PD and SP were obtained with the Pt–CeO₂ catalyst deposited on carbon nanoparticle coated GDL (nanoGDL, also n-GDL).

### Table 1 Power density (PD) and specific power (SP) obtained with the Pt–CeO₂ anode catalyst as a function of Pt loading, the catalyst support, and temperature

<table>
<thead>
<tr>
<th>Catalyst support</th>
<th>Pt loading (µg cm⁻²)</th>
<th>T (K)</th>
<th>PD (mW cm⁻²)</th>
<th>SP (W mg⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDL</td>
<td>2.2</td>
<td>300</td>
<td>4.9</td>
<td>2.5</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>300</td>
<td>10.5</td>
<td>5.4</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>300</td>
<td>12.3</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>313</td>
<td>15.5</td>
<td>12.6</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>300</td>
<td>0.41</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>DWCNT/GDL</td>
<td>1.2</td>
<td>300</td>
<td>43</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>MWCNT/GDL</td>
<td>0.9</td>
<td>348</td>
<td>38</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td>CVD-CNT/GDL</td>
<td>0.9</td>
<td>300</td>
<td>40</td>
<td>44.4</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>342</td>
<td>70</td>
<td>77.8</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>348</td>
<td>74</td>
<td>82.2</td>
<td>43</td>
</tr>
<tr>
<td>n-GDL</td>
<td>4</td>
<td>338</td>
<td>330</td>
<td>82.5</td>
<td>41, 44</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>338</td>
<td>410</td>
<td>205</td>
<td>21, 41</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>338</td>
<td>170</td>
<td>283</td>
<td>41</td>
</tr>
</tbody>
</table>

*a The catalyst contains Sn.*
The morphology of the GDL support has a critical influence on the performance of the Pt–CeO$_2$ catalyst. Scanning electron microscopy (SEM) revealed characteristic differences in the structure of the bare GDL, GDL coated with DWCNTs, MWCNTs, and CVD-CNTs, and n-GDL (see Fig. 1).

The main difference between the CNT-coated GDL supports (Fig. 1b–d) is the diameter of the tubes and their alignment with respect to the surface of GDL. In particular, CVD-CNTs grow perpendicular to the surface of GDL while DWCNTs and MWCNTs deposited by spin-coating are aligned parallel to the surface of GDL.$^{42}$

### 2.2. The composition of the catalysts

The composition of the Pt–CeO$_2$ anode catalysts and the Pt oxidation state were investigated as a function of the information depth.$^{39,40}$ The experimental approach involved a combination of high-resolution synchrotron spectroscopy (SRPES), angle-resolved X-ray photoelectron spectroscopy (AR XPS), and hard X-ray photoelectron spectroscopy (HAXPS).$^{48}$ The information depth achieved with these techniques increases with increasing photon energies ($h\nu$) and $\cos(\alpha)$ with respect to the surface normal from 0.5 nm (SRPES) and 1–2 nm (AR XPS) to 7 nm (HAXPS). The corresponding Pt 4f spectra obtained from the Pt–CeO$_2$ thin films with SRPES, AR XPS, and HAXPS are shown in Fig. 2.

The major contributions in the Pt 4f spectra arise from atomically dispersed Pt$^{2+}$ and Pt$^{4+}$ species. Additionally, traces of metallic Pt$^0$ were identified at the surface of Pt–CeO$_2$ films (Fig. 2, bottom spectrum). The formation of ionic species is typically found for films prepared by magnetron co-sputtering of CeO$_2$ in combination with transition metals.$^{40,49,50}$ The ratio between the Pt$^{2+}$, Pt$^{4+}$, and Pt$^0$ contributions in the Pt 4f is a function of the sampling depth. Accordingly, Pt$^{2+}$ species are located mostly in the bulk while Pt$^{2+}$ and Pt$^0$ reside at the surface.

The relationship between the performance of the Pt–CeO$_2$ catalyst supported on n-GDL and the abundance of Pt$^{2+}$, Pt$^{4+}$, and Pt$^0$ species can be derived from the comparison of the SPs (Table 1) and the shape of the corresponding Pt 4f spectra (Fig. 3a) as a function of Pt loading.

Clearly, the SP is directly related to the Pt$^{2+}$/Pt$^{4+}$ ratio in the films. The highest SP was obtained at the highest Pt$^{2+}$/Pt$^{4+}$ ratio corresponding to the lowest Pt loading (0.6 $\mu$g cm$^{-2}$). However, the PD shows a rather non-linear dependence on the Pt$^{2+}$/Pt$^{4+}$ ratio. Note that a further increase of the Pt loading yielded a lower Pt$^{2+}$/Pt$^{4+}$ ratio and resulted in a substantial decrease of the PD (Table 1). The analysis of the Pt–CeO$_2$ catalyst after running several FC cycles revealed conversion of the Pt$^{4+}$ species to Pt$^{2+}$ and Pt$^0$ (Fig. 3b). As a result, both Pt–CeO$_2$ films with Pt loadings 0.6 and 2 $\mu$g cm$^{-2}$ contain Pt$^{2+}$ species, exclusively. Despite the slightly lower SP, the Pt–CeO$_2$ film with

### Table 2  Power density (PD) and specific power (SP) obtained with anode catalysts based on a commercial Pt nanoparticle catalyst (a) and thin Pt films (b and c) as a function of noble metal loading, the catalyst support, and temperature

<table>
<thead>
<tr>
<th>Anode catalyst</th>
<th>Pt loading (µg cm$^{-2}$)</th>
<th>T (K)</th>
<th>PD (mW cm$^{-2}$)</th>
<th>SP (W mg$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Pt/GDL</td>
<td>2000</td>
<td>338</td>
<td>440</td>
<td>0.22</td>
<td>41</td>
</tr>
<tr>
<td>(b) Pt/GDL</td>
<td>21.45</td>
<td>300</td>
<td>2.4</td>
<td>0.12</td>
<td>40</td>
</tr>
<tr>
<td>(c) Pt/n-GDL</td>
<td>2</td>
<td>338</td>
<td>75</td>
<td>37</td>
<td>41</td>
</tr>
</tbody>
</table>

Fig. 1  SEM images of bare (a) and DWCNT (b), MWCNT (c), CVD-CNT (d) coated GDL, and n-GDL (e). (a) Reprinted from ref. 45 with permission from John Wiley & Sons, Inc. Copyright 2016 by John Wiley & Sons, Inc. (b) Adapted from ref. 40, Copyright 2009, The Electrochemical Society. (c) Reprinted from ref. 46 with permission from John Wiley & Sons, Inc. Copyright 2010 by John Wiley & Sons, Inc. (e) Reprinted from ref. 47, Copyright 2015, with permission from Elsevier.

Fig. 2  Pt 4f spectra obtained from the Pt–CeO$_2$ film by means of SRPES ($h\nu = 180$ eV, $\alpha = 0^\circ$), AR XPS ($h\nu = 1486$ eV, $\alpha = 60^\circ$ and $0^\circ$), and HAXPS ($h\nu = 5946$ eV, $\alpha = 0^\circ$). Reproduced with permission from ref. 39, Copyright 2009, The Electrochemical Society.

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a Pt loading of 2 μg cm\(^{-2}\) shows a significantly higher PD with respect to the film with a Pt loading of 0.6 μg cm\(^{-2}\). Under these conditions, the PD increases with the density of Pt\(^{2+}\) species. From the perspective of volumetric power densities, the Pt–CeO\(_2\) catalyst with a Pt loading of 2 μg cm\(^{-2}\) is therefore the most suitable for a compact design of the FC.

The presence of metallic Pt\(^0\) deteriorated the catalyst performance (see Fig. 3 and Table 1 for a Pt loading of 4 μg cm\(^{-2}\)). It follows that the excellent performance of the Pt–CeO\(_2\) catalyst is associated with the high density and the enhanced stability of Pt\(^{2+}\) species.

2.3. Parameters controlling proton exchange membrane fuel cell performance

The main parameter that controls the abundance of Pt\(^{2+}\) species on the Pt–CeO\(_2\) catalyst is the morphology of the support. The SEM images obtained from Pt–CeO\(_2\) deposited on CNT-coated GDL and n-GDL are shown in Fig. 4. The morphology of the Pt–CeO\(_2\) anode catalyst corresponds to a porous columnar structure\(^{52}\) that varies as a function of the support with respect to the width and height of the crystallites. The degree of nanostructuring increases for films deposited on CNT-coated GDLs (Fig. 4a–c) and n-GDLs (Fig. 4d) with respect to the bare GDL.

The parameters controlling the growth of Pt–CeO\(_2\) films have been systematically investigated with respect to the microstructure of the carbon films, the pressure and the temperature. It was found that the major process giving rise to the porous structure of the Pt–CeO\(_2\) films is associated with the etching of the carbon films by oxygen plasma.\(^{52-55}\) The corresponding mechanism involves the formation of nucleation centers, e.g. Pt–Ce\(_x\) or Ce–C particles which mask the carbon substrate partially and, thus, prevent etching.\(^{53,55}\) The density and the mobility of these nucleation centers determine the width of the columns. Additional parameters are the deposition rate\(^{55}\) and thickness\(^{56}\) of the Pt–CeO\(_2\) films, temperature, and the composition of the reactive gas.\(^{54,55}\)
2.4. Preparation of the nanostructured Pt–CeO₂ films

Besides radio frequency magnetron sputtering,²¹,²⁹–⁴⁴ the nanostructured Pt–CeO₂ films can be prepared by a variety of other techniques including pulsed laser deposition⁵⁷ and chemical vapor deposition techniques.⁵⁸–⁶¹ The preparation of nanostructured Pt–CeO₂ films by means of physical vapor co-deposition of Pt and Ce in an oxygen atmosphere requires low deposition temperature.²¹ For some methods, e.g. pulsed laser deposition, the degree of the nanostructuring of the Pt–CeO₂ films depends on the morphology, i.e. roughness of the support.⁵⁷

2.5. Identification of the surface sites on the nanostructured CeO₂ support

The degree of the nanostructuring of the Pt–CeO₂ films determines the density of the Pt²⁺ species and is closely related to the number of Ce³⁺ cations.⁴²,⁵² For instance, the Pt⁷⁷/Pt⁴⁺ ratio is much higher in the Pt–CeO₂ films deposited under glancing angle (GLAD) conditions.⁴⁶ In contrast, normal deposition (ND) yielded mainly Pt⁴⁺ species accompanied by a low number of Ce³⁺ cations.⁶² It was found that Ce³⁺ sites are located predominantly at the surface steps and edges of the nanostructured Pt–CeO₂ films.⁴²

The surface of the Pt–CeO₂ films was investigated by means of high-resolution transmission electron microscopy (HRTEM). There, the Pt–CeO₂ nanoparticles terminated by the {111} and {100} facets were identified in the Pt–CeO₂ films supported on CNT-coated GDL,⁴²,⁴³ n-GDL,⁴¹,⁴⁴ and silicon wafers.⁴²,⁶³ Typical HRTEM images obtained from the Pt–CeO₂ films supported on n-GDL are shown in Fig. 5 for two different Pt loadings.

The structure of the Pt–CeO₂ films is identical to the structure of bare CeO₂ films and does not depend on the choice of the preparation technique. For instance, nanoparticles of CeO₂ and Pt–CeO₂ terminated predominantly by the {111} and {100} facets have been identified in films prepared by magnetron sputtering,⁵⁶,⁶⁴ chemical vapor deposition,⁶⁰ and pulsed laser deposition.⁵⁷ It follows that with respect to the nature of Pt²⁺ surface species, either the {111} or {100} facets or edge and step sites connecting these facets provide the adsorption sites that anchor atomically dispersed Pt atoms.

3. Stability of single atom catalysts

3.1. Anchoring noble metal atoms at surface sites of nanostructured ceria

The capacity of the nanostructured ceria to anchor atomically dispersed noble metals at the {111} and {100} facets was analyzed by means of density functional calculations.²¹ A Ce₄₀O₈₀ nanoparticle model⁶⁵,⁶⁶ featuring a truncated octahedral shape with O-terminated {111} and very small {100} facets was identified as a representative model for nanostructured ceria.⁶⁷ This particle structure, displayed in Fig. 6, emerged from an exhaustive global optimization search.⁶⁵,⁶⁶,⁶⁸ The polar (100) surface corresponding to the {100} nanofacets of the ceria particles is known to be less stable than the {111} surface of ceria.⁶⁹ Each of these {100} nanofacets is terminated by four surface O²⁻ ions in a square planar arrangement with O–O distances of 315–320 pm forming a so-called O₄ pocket.

The binding of Pt atoms adsorbed on the regular CeO₂(111) surface in the form of Pt⁰ or Pt⁺ is associated with a low diffusion barrier along the surface.²¹ The formation of Pt₃ dimers is therefore kinetically facile and strongly exothermic (by 369 kJ mol⁻¹)⁷² giving rise to rapid nucleation of Pt particles.⁷³ In turn, the oxidation state and adsorption energy of Pt atoms on the surface of ceria nanoparticles drastically depend on the local structure of the adsorption sites. A moderately strong binding of atomic Pt on edge sites between {111} facets of the Ce₄₀O₈₀ nanoparticle yields Pt⁰ and Pt⁺ species with the adsorption energies of ~273 and ~303 kJ mol⁻¹, respectively.²¹ Similar adsorption energies were calculated for Pt⁰ (~256 kJ mol⁻¹) and Pt⁺ species (~226 kJ mol⁻¹) on the regular CeO₂(111) surface.⁷¹ This adsorption strength of atomic Pt is typical also for regular surfaces of more inert non-reducible metal oxides, such as MgO(001).⁷⁴ In contrast, the adsorption of Pt atoms on the (100) nanofacet yields Pt²⁺ species with an extraordinarily large binding energy of ~678 kJ mol⁻¹,²¹ which is ~100 kJ mol⁻¹ more in magnitude than that for Pt atoms anchored to neutral oxygen vacancies of the MgO(001) surface.⁷⁵ In these calculations the formal oxidation state of the adsorbed Pt atom was determined by the number of Ce³⁺ centers formed via electron transfer into the 4f orbitals of Ce⁴⁺. Consequently, the formation of Pt⁺ or Pt²⁺ species is accompanied by the reduction of one or two Ce⁴⁺ cations to Ce³⁺, respectively (Fig. 6).

Strong interactions of metal atoms with oxide surfaces are indicative of surface coordination compounds, in which the support acts as a polydentate ligand.⁷⁶ Indeed, the O₄ site provides an ideal coordination environment to host the Pt²⁺ (d⁰) species yielding a square planar PtO₄ moiety.⁷⁷ Remarkably, the adsorption energy of the anchored Pt²⁺ ion exceeds in magnitude the cohesive energy of bulk Pt (~564 kJ mol⁻¹).⁷⁸ As a consequence, Pt²⁺ species are thermodynamically stable against sintering. The structure of the resulting PtO₄ moiety is consistent with the interatomic distances and
coordination numbers of Pt atoms determined by means of extended X-ray absorption fine structure (EXAFS) studies on real Pt/ceria catalysts.79

With respect to sintering and re-dispersion processes, the DFT calculations suggest that the O4 sites are even able to abstract Pt atoms from supported Pt particles21 (Fig. 6). This pathway was calculated to be exothermic for Pt9 and Pt8 particles on Ce40O80, where the migration of Pt atoms from the metal particle to the {100} nanofacets of ceria leads to their transformation into strongly bound Pt2⁺ species. Furthermore, the anchored Pt2⁺ species do not serve as a stable nucleation site for a second Pt atom. Accordingly, no local minimum corresponding to a Pt–Pt2+/O4 moiety was found and during geometry optimization a supported Pt2 di- mer dissociated into a Pt2+/O4 complex and a neutral Pt atom adsorbed nearby. This finding implies that the anchored Pt2⁺ species can actually coexist with Pt particles without being buried by excess Pt.

A very similar local PtO4 structure emerges upon Pt adsorption at the steps of the CeO2(IJ111) surface.22 The thermodynamics of segregation and the corresponding atomic and electronic structures of Pt on stepped CeO2(111) were investigated by density functional calculations.22 Different adsorption sites were considered (Fig. 7) including oxygen vacancies (a), regular sites (b) and Pt clusters (c) on the CeO2(111) terrace, and the two low-energy one-monolayer-high steps labeled as step I (d, f) and step II (e, g) on stoichiometric (denoted S) and non-stoichiometric (with excess of oxygen, denoted O) surfaces. Structures I and II represent the preferred types of steps at the CeO2(111) surfaces at temperatures below 1000 K.80,81

Pt adsorption at step I-S yields Pt2⁺ species coordinated by four lattice O atoms in a characteristic PtO 4 planar unit (Fig. 7d) similar to that identified on the (100) facets of the Ce40O80 nanoparticle.21 Consequently, two Ce3⁺ centers are formed in the proximity of the Pt2⁺ (Fig. 7d). The resulting adsorption energy of Pt2⁺ is ~5.0 eV. In contrast, the different atomic structure of the step II-S edge prevents the formation of the PtO4 moiety and yields a weakly oxidized Pt 2+ Δ⁺ species accompanied by the emergence of one Ce3⁺ center (Fig. 7e).

The presence of excess oxygen at the steps triggers restructuring and yields Pt2⁺ in the characteristic square-planar PtO4 surface arrangement. At step I, the excess oxygen leads to the oxidation of Ce3⁺ centers to Ce4⁺ while Pt2⁺
retains its oxidation state. At step II, the oxidation of the Pt\(^{4+}\) species to Pt\(^{2+}\) is accompanied by the oxidation of one Ce\(^{3+}\) to Ce\(^{4+}\). Remarkably, the resulting binding energies of Pt\(^{2+}\) species in excess of oxygen are \(\sim 1.6\) eV higher (i.e. more strongly bound) with respect to that calculated for Pt adsorption on stoichiometric step sites. These results demonstrate that stable PtO\(_4\) moieties with Pt\(^{2+}\) species can be formed at step sites of ceria upon oxidation of Pt\(^0\) to Pt\(^{2+}\) and that the formation of such Pt\(^{2+}\) species does not necessarily involve the formation of Ce\(^{3+}\) ions.\(^{22}\)

The calculations predict the preferential adsorption of Pt atoms at steps I and II regardless of their local geometry and stoichiometry. This prediction is consistent with the higher density of Pt\(^{2+}\) species on ceria surfaces featuring higher step density. Furthermore, it implies that the same square-planar arrangement of PtO\(_4\) moieties is formed on different nanostructured ceria supports including stepped surfaces and nanoparticles.

The capacity of the \{100\} sites on nanostructured ceria to anchor atomically dispersed Pt suggests that other transition metals could interact with the O\(_4\) site of Ce\(_{40}\)O\(_{80}\) in a similar way. In this respect, the adsorption of metal atoms (M) including the 3d (Fe, Co, Ni, Cu), 4d (Ru, Rh, Pd, Ag) and 5d (Os, Ir, Pt, Au) metals of groups 8–10 was investigated.\(^{82}\) The calculated adsorption energies are shown in Fig. 8 in comparison with the calculated adsorption energy of an edge metal atom of a M\(_{79}\) nanoparticle of the corresponding metal.

The adsorption of the metal atom M at the \{100\} site results in the oxidation of the adsorbed atom, accompanied by the reduction of Ce\(^{4+}\) cations to Ce\(^{3+}\). In all cases, the adsorption of the metal atom on the O\(_4\) site of the ceria nanoparticle is stronger than the binding of edge metal atoms in the M\(_{79}\) models. Interestingly, all calculated oxidation states of metal atoms of groups 8–11 are also observed experimentally in metal–ceria systems.\(^{21,26,65,79,83–97}\) However, only the metals of group 10 yield cationic species of the same oxidation state, i.e. Pt\(^{2+}\), Pd\(^{2+}\), and Ni\(^{2+}\). This similarity is associated with the d\(^8\) electronic configuration of the M\(^{2+}\) cations in the group 10 metals adsorbed in the square planar arrangement. The metals of group 11 are found in multiple oxidation states in the M\(_{79}\) models. For instance, Cu\(^{2+}\) in the square planar coordination is just slightly more stable than the Cu\(^{+}\) in a distorted linear arrangement with two short and two long Cu–O distances. Similarly, atomic Ag was found as Ag\(^{+}\) or Ag\(^{3+}\) species. Atomic Au can also be adsorbed as Au\(^{+}\) and Au\(^{3+}\), with the latter being more stable.

Clear trends emerge along the rows and groups of the periodic table (Fig. 8). Binding energies of M both on the ceria nanoparticle and in the M\(_{79}\) nanoparticles generally decrease...
in magnitude, when moving from the left to the right of the period. This indicates that metals with less occupied d bands form stronger metal–metal bonds and also bind more strongly to the oxide support. With the exception of Au, 5d metals form the strongest bonds with the O\textsubscript{3} site of ceria, whereas 4d metals form the weakest bonds, with the exception of Ru. Regardless of the overall strength of the interaction of the different metal atoms with the ceria nanoparticle, the resulting adsorption energies indicate that the \{100\} sites are able to stabilize atomically dispersed species of a wide range of metals.

3.2. Stability as a function of noble metal loading

The stability of the ceria supported single atom catalysts is a function of numerous parameters including the metal loading\textsuperscript{96}, the structural and chemical environment of the adsorption site,\textsuperscript{32} the oxidation state of the substrate, i.e. the density of Ce\textsuperscript{3+} centers\textsuperscript{21} and oxygen vacancies,\textsuperscript{89,99} and the ambient atmosphere.\textsuperscript{89}

For instance, the adsorption energy of the Pt\textsuperscript{2+} species at \{100\} sites decreases from 7.02 eV to 6.59 eV when the Pt coverage increases from one to four Pt\textsuperscript{2+} species per Ce\textsubscript{40}O\textsubscript{80} NP due to the increase of Ce\textsuperscript{3+} density.\textsuperscript{99} With respect to the limited capacity of the Ce\textsubscript{40}O\textsubscript{80} NP (only 4 Pt atoms can be adsorbed in the form of Pt\textsuperscript{2+} since there are only four \{100\} nanofacets each exposing one O\textsubscript{3} site), the stepped CeO\textsubscript{2}(111) surface allows a higher density of Pt\textsuperscript{2+} species to be obtained by assembling PtO\textsubscript{4} units along the steps in close proximity to each other (see Fig. 9).

The maximum coverage of the stable Pt\textsuperscript{2+} species at step I-S is 2/3 (Fig. 9a). A further increase of the Pt coverage to 3/3 (1 Pt atom per 1 Ce step edge atom) triggers the nucleation of metallic Pt clusters due to the large strain built up in the long row of interconnected PtO\textsubscript{4} units at the I-S step (Fig. 9b). On step II-S, reduction of Pt\textsuperscript{2+} species gives rise to Pt dimers already at coverages exceeding 1/3 (Fig. 9c). In summary, on samples with stoichiometric steps I and II, the calculations predict low Pt\textsuperscript{2+} coverage at the steps (<33% of the step-edge sites). In contrast, the calculated maximum coverage of Pt\textsuperscript{2+} at the O-rich steps I-O and II-O is 3/3 (Fig. 9e and g), as interconnected assemblies of PtO\textsubscript{4} units fit to the periodicities of both steps I and II (Fig. 7f, g and 9d–g).

The stability of PtO\textsubscript{4} moieties was investigated more quantitatively by evaluating the Gibbs free energy of Pt\textsuperscript{2+} adsorbed at the \{100\} site of a Ce\textsubscript{2}O\textsubscript{4} particle as a function of ambient temperature and partial pressure of oxygen.\textsuperscript{89} The relative stability of oxygen vacancies or excess oxygen species evolves progressively with changing pressure and temperature (Fig. 10). Under oxidizing conditions, the adsorption of one oxygen atom in the proximity of the Pt\textsuperscript{2+} species is favored and leads to the re-oxidation of two Ce\textsuperscript{3+} centers to Ce\textsuperscript{4+}. Under reducing conditions, the adsorption energy of the Pt\textsuperscript{2+} species at the \{100\} site decreases with increasing number of oxygen vacancies. At higher temperature, the onset of vacancy formation shifts to higher oxygen pressure and approaches the onset of oxygen adsorption, thus narrowing the region of the Pt\textsuperscript{2+} stability.

![Fig. 9](image-url) Capacity of the CeO\textsubscript{2}(111) step edges to accommodate Pt\textsuperscript{2+} ions obtained from DFT calculations. Calculated top views of Pt atoms bound to steps I-S (a and b), II-S (c), I-O (d and e) and II-O (f and g) for Pt step coverage 2/3 (a, c, d and f) and 1 (b, e and g). At step I-S, the limiting coverage of Pt\textsuperscript{2+} is 2/3 (a), additional Pt attaches to the step edge as Pt\textsuperscript{0} (b). At step II-S, the Pt\textsuperscript{2+} coverage is 0. Pt atoms attach as weakly ionized Pt\textsuperscript{4+} and readily form metallic dimers (c) and clusters. On both steps I-O and II-O, excess oxygen can stabilize ionic Pt\textsuperscript{2+} at step edges as single ions appearing isolated or in groups up to 100% step coverage (d–g). Reproduced with permission from ref. 22, Copyright 2016, Nature Publishing Group.

The theoretically predicted behavior of atomically dispersed Pt was examined using appropriate model systems based on well-defined surfaces prepared under UHV conditions.\textsuperscript{21,22,98} In particular, Pt\textsuperscript{2+} species were prepared either on the surface of nanostructured ceria films\textsuperscript{21} or on stepped CeO\textsubscript{2}(111) surfaces.\textsuperscript{22} The first approach employed co-deposition of Pt and Ce metal in an oxygen atmosphere onto a well-ordered CeO\textsubscript{2}(111) buffer layer at low temperature. The use of a 1.5 nm thick buffer layer was necessary to minimize the influence of the Cu(111) substrate on the structure of the Pt–CeO\textsubscript{2} film.\textsuperscript{100} The procedure yielded three-dimensional Pt–CeO\textsubscript{2} particles with an average diameter of approximately 3 nm and a typical height of around 0.4 nm (see Fig. 11a and b).\textsuperscript{21}

After annealing to 700 K, some aggregates reveal a faceted shape, suggesting an epitaxial relationship between the supported Pt–CeO\textsubscript{2} nanoparticles and the CeO\textsubscript{2}(111) buffer layer. The chemical state of Pt in the Pt–CeO\textsubscript{2} film was investigated by means of SRPES with high surface sensitivity. Two
types of species associated with Pt$^{2+}$ and Pt$^{4+}$ ions were identified in the Pt 4f spectra obtained from the Pt–CeO$_2$ films as deposited (Fig. 11c and d). In the limit of low Pt loading, the Pt$^{2+}$ species in the Pt–CeO$_2$ films demonstrate exceptional thermal stability upon annealing up to 750 K (see Fig. 11c). At the same time, less stable Pt$^{4+}$ species were readily converted to Pt$^{2+}$. The critical role of providing the appropriate number of surface sites to anchor Pt becomes evident when the Pt–CeO$_2$ films with higher Pt loading were annealed (Fig. 11d). Consequently, the Pt atoms anchored at less favorable sites are bound too weakly to resist sintering to metallic particles.

In line with the density functional calculations$^{82}$ described in section 3.1, Pd$^{2+}$ and Ni$^{2+}$ species were also anchored on the surface of nanostructured ceria following a similar experimental approach. These films were characterized under similar conditions to the Pt–CeO$_2$ films by means of SRPES (see Fig. 12 and 13, respectively).

The formation of both Pd$^{2+}$ and Ni$^{2+}$ species was accompanied by additional oxide phases, namely PdO and NiO, that resulted from the lack of a sufficient number of {100} sites on the nanostructured ceria films (see Fig. 12 and 13). Note that the formation and decomposition of the NiO phase can be identified by the presence of two satellite features, i.e. I and II in the spectra of Ni 2p in Fig. 13. The abundance of the additional phases, e.g. oxide and metal particles is a function of metal loading. Thus, in the limit of the low metal loading, the most stable Pd$^{2+}$ and Ni$^{2+}$ species can be isolated from the less stable oxide phases by annealing in UHV (see Fig. 12a and b and 13a and b). Both PdO and NiO phases decompose via dissolution in the CeO$_2$(111) buffer layer upon annealing.

Higher Pd loading in the films results in a low stability of atomically dispersed Pd$^{2+}$ species (see Fig. 12d and e). Similar to the Pt$^{2+}$, atomically dispersed Pd$^{2+}$ species are converted into metallic particles upon annealing in UHV.

However, the characteristic difference between the Pt$^{2+}$ and Pd$^{2+}$ species is that Pt$^{2+}$ is preferentially stabilized at the oxygen pockets at the surface, whereas Pd can be stabilized both at the surface and in the bulk in a similar square planar arrangement.$^{94}$ This property facilitates the diffusion of Pd$^{2+}$ species into the bulk upon annealing. In sharp contrast to
both Pt–CeO$_2$ and Pd–CeO$_2$ formation of metallic Ni particles was not observed in Ni–CeO$_2$, even at high metal loading. This observation is in agreement with the calculated data suggesting that the formation of metallic Ni from ionic Ni$^{2+}$ is strongly disfavored energetically.

Interestingly, the atomically dispersed metals of group 10 yielded different concentrations of Ce$^{3+}$ centers. This again demonstrates the diversity of mechanisms involved in the anchoring. In contrast to the Pt–CeO$_2$ films, the Pd–CeO$_2$ films maintain a considerably higher degree of reduction even at low dopant concentrations. The decomposition of PdO and NiO phases during annealing results in re-oxidation of Ce$^{3+}$.

An alternative approach to form Pt$^{2+}$ species involves the deposition of Pt onto stepped CeO$_2$$(111)$ surfaces in UHV. Under these conditions, the availability of the adsorption sites capable of anchoring Pt$^{2+}$ species is the most critical parameter. The Pt deposition on CeO$_2$$(111)$ surfaces with a low density of steps and surface oxygen vacancies (Fig. 14a) yields metallic Pt$^0$ clusters in combination with ionic Pt$^{2+}$ species (Fig. 14b and c).

Subsequent annealing of the films to 700 K increases the amount of Pt$^{2+}$ species at the expense of Pt$^0$. Interestingly, this process was not accompanied by the reduction of the CeO$_2$$(111)$ surface. This implies the involvement of another oxidizing agent such as excess oxygen atoms. In the UHV environment, one possible source of excess oxygen is water adsorbing in sub-monolayer amounts from the background and undergoing dissociation on reduced ceria and Pt/ceria substrates.$^{101,102}$ In the real Pt–CeO$_2$ catalysts, excess O atoms may also be incorporated during the synthesis that proceeds in air.$^{103,104}$

Most importantly, it was found that the relative abundance of the Pt$^{2+}$ and Pt$^0$ species depends on the density of steps and the number of oxygen vacancies in the CeO$_2$$(111)$ film. In particular, the amount of Pt$^{2+}$ species scales linearly with the step density.

The presence of oxygen vacancies does not promote the dispersion of Pt$^{2+}$ species but, instead, leads to the formation of small metallic particles (Fig. 14e and f). According to density functional calculations, oxygen vacancies are not the favorable sites for Pt$^{2+}$ formation.$^{22,89}$ Based on the analysis of the adsorption energies of Pt, formation of metallic clusters is preferred on reduced ceria nanoparticles.$^{89}$

3.3. Identification of the oxidation state of the supported catalyst by CO adsorption

The straightforward identification of Pt sites under reaction conditions is important to understand and tune the structure and stability of Pt–CeO$_2$ films. CO is commonly used as a
probe molecule in combination with infrared absorption spectroscopy (IRAS) for identification of adsorption sites in heterogeneous catalysts.\textsuperscript{105–108}

The factors that influence the vibrational frequency of CO adsorbed on Pt particles in Pt–CeO\textsubscript{2} systems include the local structure of the adsorption site (on-top, bridge, and hollow), the oxidation state and coordination number of the Pt adsorption center, the CO coverage, and the stoichiometry of the support. For instance, the vibrational frequency of CO adsorbed in the on-top configuration on Pt surfaces increases as a function of the coordination number of the Pt atom. The effect was demonstrated for Pt(111) and unsupported Pt particles as well as for ceria-supported Pt particles of different sizes\textsuperscript{109,110} (Fig. 15).

As under-coordinated sites have characteristic IRAS fingerprints and the relative number of these sites depends on particle size, the trends derived from Fig. 15 allow estimating particle sizes on the basis of the measured CO vibrational frequencies (and vice versa).\textsuperscript{111} For example, the size of Pt particles under electrochemical working conditions in Pt–ceria electrocatalysts was determined by comparing the experimental frequency shifts in IRAS with calculated shifts, both on free and ceria-supported Pt particles of varying size.\textsuperscript{109}

The calculated vibrational frequencies of CO adsorbed in the on-top configuration on Pt species with different oxidation states and coordination numbers of Pt atoms found in several structural Pt–CeO\textsubscript{2} models\textsuperscript{110} are summarized schematically in Fig. 16. A quick inspection of these data reveals a high degree of overlap between CO frequencies calculated for the different structures. However, general trends indicate that the vibrational frequency of the CO molecule in the on-top configuration depends on the distance between Pt and the nearest oxygen atom of ceria at which the platinum atom is bound to, and that CO vibrational frequencies increase as a function of the oxidation state of atomically dispersed Pt on ceria.\textsuperscript{110} In addition, an increase in CO coverage leads to a widening of the CO frequency range for adsorption on supported Pt\textsubscript{8} clusters and to an increase of the frequency on Pt\textsuperscript{2+} species.

This scenario suggests that an assignment of platinum species based exclusively on the vibrational frequency might be misleading or inconclusive. When probing metal species...
with CO and IRAS, it is therefore necessary to monitor the coverage dependent changes in the spectra carefully. In addition, it appears that the adsorption energy of CO is a critical parameter. For example, the adsorption of CO on the Pt$^{2+}$ cation of the PtO$_4$ moiety is rather weak ($\sim -0.61$ eV) and also involves a significant reconstruction, suggesting that this is an activated and not very favorable process. Similarly, the vibrational frequency calculated for CO adsorption on Pt$^{4+}$ comes from a rather unstable system, where excess O atoms have been added to obtain the Pt$^{4+}$ state. This model is probably not very representative of sites one would find in experiments on Pt–ceria systems, but it is nevertheless useful as a tool to explore how the CO frequency changes with the oxidation state of Pt. CO does not adsorb under pertinent experimental conditions on Pt$^{2+}$ and Pt$^{4+}$ species based on the calculated stability of the resulting adsorption complexes.

As a complementary tool, SRPES allows direct determination of the oxidation state of Pt as well as the adsorption site of molecular surface species. The changes in the oxidation state of atomically dispersed Pt species caused by annealing in UHV were reliably identified from their Pt 4f spectra.$^{112}$ In particular, comparison of the intensities of the Pt 4f spectra before and after CO adsorption at 110 K indicated the presence of metallic Pt clusters which served as adsorption sites for CO.

The development of the Pt 4f spectra obtained from Pt–CeO$_2$ films with different Pt loadings are shown in Fig. 17. CO adsorption on the surfaces containing Pt$^{2+}$ and Pt$^{4+}$ exclusively does not attenuate the corresponding contributions (I–II) in the Pt 4f spectra. This suggests that neither Pt$^{2+}$ nor Pt$^{4+}$ serve as adsorption sites for CO in line with the calculated instability of CO on these sites. In contrast, small metallic Pt particles formed at high Pt loading (see Fig. 17c) readily adsorb CO. The emergence of metallic particles yielded distinct differences between Pt 4f spectra before (black) and after (green) CO adsorption (Fig. 17). In particular, the contribution from metallic Pt (IV) in the Pt 4f spectra is attenuated and a new component (V) emerges in the Pt 4f spectra upon CO adsorption. Peak V is identified as a shifted component of peak IV, which is consistent with the core level shift expected upon CO adsorption on metallic Pt.

The development of the C 1s spectra upon CO adsorption on Pt–CeO$_2$ films with different Pt loadings is shown in Fig. 18 in comparison with the Pt-free nanostructured CeO$_2$ film. The C 1s spectra reveal the presence of CO-derived species on the three films. The dominant species formed on all surfaces are tridentate (A) and bidentate (B) carbonates. The emergence of the second tridentate carbonate (C) and carbonite (D) contributions indicates the presence of oxygen vacancies in the films. The formation of carbonite species is not associated with the formation of the tridentate carbonate species at oxygen vacancies (C) suggesting that the two species are formed at structurally different types of oxygen vacancies.

The emergence of a wide range of adsorbed molecular surface species including carbonates, carbonites, and formates, whose stability and spectroscopic signatures strongly depend on the structure and oxidation state of the adsorption site is in line with the results of DFT studies of CO adsorption on a Ce$_2$O$_{3+x}$ particle.$^{113}$

The changes in the relative abundance of species A–D in Fig. 18 are consistent with restructuring of the films upon annealing. The morphological changes induced by the
annealing of the 12% and 25% Pt–CeO\textsubscript{2} mixed oxides are similar to the changes of the Pt-free CeO\textsubscript{2} film and occur above 300 K. The observed reduction of Pt\textsuperscript{2+} to metallic Pt particles on the 25% Pt–CeO\textsubscript{2} film is also associated with restructuring causing a decrease in the number of stable sites that can anchor Pt\textsuperscript{2+} species. The presence of metallic Pt can therefore be identified by both Pt 4f and C 1s spectra. The appearance of metallic Pt features in the Pt 4f spectra is concomitant with the appearance of a C 1s feature (F) corresponding to CO in the on-top configuration.

4. Reactivity of supported single atom catalysts towards H\textsubscript{2}

4.1. Supported single metal atoms in the absence of metal particles

Dissociation of molecular hydrogen is the major function of the anode catalyst in hydrogen powered PEMFCs. It was reported that surface cationic Pt species promote dissociation of H\textsubscript{2} and facilitate hydrogen spillover on Pt-doped CeO\textsubscript{2} powders prepared by the solution combustion method.\textsuperscript{114} The origins of this reactivity, however, remained obscure. One of the reasons is that the role of atomically dispersed Pt\textsuperscript{2+} on CeO\textsubscript{2} had not been studied individually, i.e. in the absence of other active species such as Pt\textsuperscript{4+}, Pt\textsuperscript{0}, and oxygen vacancies.\textsuperscript{114-116} Using well-defined model catalysts, atomically dispersed Pt\textsuperscript{2+} species can be prepared and studied individually.\textsuperscript{21,99} The corresponding approach involves the preparation of Pt–CeO\textsubscript{2} films with low Pt loading at low temperature followed by brief annealing to 700 K.\textsuperscript{21} The same procedure allows the preparation of atomically dispersed Pd\textsuperscript{2+} and Ni\textsuperscript{2+} species on nanostructured ceria.\textsuperscript{98} Thus, the reactivity of atomically dispersed Pt\textsuperscript{2+}, Pd\textsuperscript{2+}, and Ni\textsuperscript{2+} species can be investigated under identical experimental conditions.

Changes in the oxidation states of Pt\textsuperscript{2+}, Pd\textsuperscript{2+}, and Ni\textsuperscript{2+} species upon reaction with H\textsubscript{2} were investigated by means of SRPES with high surface sensitivity under UHV conditions (see Fig. 19). Additionally, the oxidation state of Ce cations was monitored by means of resonant photoemission spectroscopy (RPES). The resonant enhancement ratio (RER) scales with the Ce\textsuperscript{3+}/Ce\textsuperscript{4+} concentration ratio.\textsuperscript{117}

Based on the analysis of the corresponding Pt 4f, Pd 3d, and Ni 2p core level spectra and the RER in Fig. 19, it was concluded that isolated Pt\textsuperscript{2+}, Pd\textsuperscript{2+}, and Ni\textsuperscript{2+} species do not facilitate dissociation of molecular hydrogen under the
experimental conditions employed, since reduction of neither these metal cations nor Ce$^{4+}$ ones by H$_2$ has been detected.$^{98,99}$ This experimental finding was corroborated by DFT calculations for the case of ceria supported Pt$^{2+}$ species.$^{99}$ The reaction pathways and the energetics for H$_2$ dissociation on the Pt$–\text{CeO}_2$ system and the CeO$_2$ (111) surface are compared in Fig. 20. The Pt$–\text{CeO}_2$ system was modeled as a low-energy vicinal surface exposing CeO$_2$ (111) terraces and step edges along the [110] direction accommodating Pt$^{2+}$ ions. These calculations showed that the barrier for H$_2$ dissociation at the Pt$^{2+}$ sites (1.2 eV) is even larger than the barrier for dissociation on the pristine CeO$_2$(111) surface (1.0 eV).$^{99}$ The rather high H$_2$ activation energy is consistent with a very high thermodynamic stability of the Pt$^{2+}$ species.$^{21}$ This implies that the low barrier desorption of weakly adsorbed H$_2$ is strongly favored over dissociation, in accordance with the experimental findings.$^{99}$

In contrast to isolated Pt$^{2+}$ species, DFT simulations show that sub-nanometer Pt clusters supported on ceria are highly active for H$_2$ dissociation. For instance, the calculated activation energy of only $\sim$0.3 eV (Fig. 20, green line) for Pt$_6$ on CeO$_2$(111) could be easily overcome even at room temperature.$^{99}$

4.2. Supported single atom catalysts with traces of metallic clusters

Higher levels of metal loading in Pt–CeO$_2$ and Pd–CeO$_2$ films yield metallic particles upon annealing$^{98}$ (Fig. 21a and d). In contrast, no metallic Ni was detected in Ni–CeO$_2$ films despite the high metal loading (Fig. 21g).

The activation of molecular hydrogen becomes strongly favored in the presence of metallic Pt and Pd particles on Pt–CeO$_2$ and Pd–CeO$_2$ films. The process is accompanied by the reduction of Pt$^{2+}$ and Pd$^{2+}$ species coupled with the reduction
capping layer. Such encapsulation processes of the metallic Ni lar reactivity towards H2. Therefore, the mechanisms of hy-

bility of the Ni2+ state preventing formation of metallic Ni.98 In less of the Ni loading. The reason is the particularly high sta-

bility of the Pt2+ species depends on the proximity of the oxygen vacancies, their number, the Pt2+ concentration, and the distribution of Ce3+ ions.99 Reduction of Pt2+ species is expected once the adsorption energy of atomic Pt falls be-

low the bulk cohesive energy of Pt (−5.85 eV (ref. 120)).

The formation of a single oxygen vacancy outside the PtO4 moiety (Fig. 22a) is not sufficient to initiate the reduction of a Pt2+ cation. In contrast, removal of one oxygen atom di-
rectly from the PtO4 moiety lowers the adsorption energy Pt2+ species strongly and triggers the reduction, followed by re-
lease of Pt from the resulting Pt–O–Pt moiety. However, the vac-
ancy formation is strongly disfavored at the pocket sites in the presence of Pt2+ species, rendering such a process rather unlikely.99 This suggests that oxygen vacancies are preferen-
tially formed outside the Pt–O–Pt moiety. If two such oxygen va-
cancies are created per Pt2+ ion, the Pt2+ adsorption energy falls well below the cohesive energy (Fig. 22b). Thus, density functional calculations indicate that the onset of Pt2+ reduc-
tion occurs when approximately two oxygen vacancies are cre-
ated per Pt2+ site.

A rough estimation of the ratio between the concentration of oxygen vacancies and the Pt2+ cations at the onset of Pt2+
For the Pt–CeO$_2$ film, the corresponding ratio for reduction of Pt$^{2+}$ to Pt with hydrogen was determined to be about 1.5 O vacancies per Pt$^{2+}$ cation. The direct involvement of metallic Pt particles in the reduction of Pt$^{2+}$ species can be ruled out by using methanol as a reducing agent.$^{121}$ The decomposition of methanol on CeO$_2$ films involves the formation of formaldehyde, CO, and oxygen vacancies.$^{122-124}$ Therefore, the reduction of Pt$^{2+}$ species is observed as a consequence of the formation of oxygen vacancies regardless of the Pt loading (see Fig. 23). The estimation of the number of oxygen vacancies at the onset of Pt$^{2+}$ reduction suggested that the formation of two oxygen vacancies is required for reduction of one Pt$^{2+}$ species.$^{121}$ This agrees with results of density functional calculations.$^{99}$ Also, a good correspondence of the ratio between the number of O vacancies and the number of reduced Pt$^{2+}$ species determined in the presence and in the absence of metallic Pt particles rules out a direct involvement of Pt particles in the destabilization of Pt$^{2+}$.

Notably, the reduction of Pt$^{2+}$ species on the Pt–CeO$_2$ film yields two types of metallic Pt, labeled as Pt$^0$ and Pt$^*$ (see Fig. 23). The different binding energies are associated with differences in particle sizes. Based on the value of the binding energy in the Pt 4f spectra, the particle size for the Pt$^*$ components falls into the sub-nanometer range (less than 25 Pt atoms per particle) while the Pt$^0$ signal corresponds to "regular" nanoparticles with a size above 2 nm.$^{117}$

As one would expect, the formation of sub-nanometer Pt$^*$ particles precedes the formation of larger Pt$^0$ particles. The stability of the sub-nanometer Pt$^*$ particles strongly depends on the Pt loading in the Pt–CeO$_2$ films. In the presence of Pt$^0$ particles, Pt$^*$ particles are rapidly lost by sintering and coalescence with Pt$^0$ particles.
In the absence of Pt particles, however, the sub-nanometer Pt\textsuperscript{*} particles show remarkable stability upon annealing even under strongly reducing conditions (see Fig. 23a).

Due to the high binding energy of the Pt\textsuperscript{*} contribution in the Pt 4f spectra (72.0 eV), the metallic nature of sub-nanometer Pt\textsuperscript{*} particles is difficult to prove.\textsuperscript{98,99} For example, the presence of a PtO phase or the adsorption of CO on Pt\textsuperscript{*} gives rise to spectral contributions at similar binding energies.\textsuperscript{112,125} Therefore, it is instructive to compare the trends in the formation of oxygen vacancies on Pt–CeO\textsubscript{2} films with different Pt loadings with respect to the Pt-free CeO\textsubscript{2} film during reaction with methanol (see Fig. 24). The nearly linear increase of the RER on the Pt-free CeO\textsubscript{2} film indicates the formation of oxygen vacancies resulting from desorption of formaldehyde, CO, and water that involves partial removal of lattice oxygen from ceria.\textsuperscript{122–124} In the presence of metallic Pt particles, however, a second channel opens that involves reverse hydrogen spillover followed by desorption of molecular hydrogen.\textsuperscript{118}

This process is accompanied by re-oxidation of ceria. As a result, the amount of the oxygen vacancies formed in the presence of Pt particles is lowered. The limited density of oxygen vacancies in the presence of the Pt particles is reflected by the RER which shows saturation with increasing temperature. Notably, the formation of vacancies is limited on both Pt–CeO\textsubscript{2} films regardless of the Pt loadings. This suggests the
presence of metallic Pt on all Pt–CeO$_2$ films and corroborates the assignment of the Pt$^*$ component to sub-nanometer Pt particles. It can be concluded that the formation of stable sub-nanometer Pt particles is possible via preparation of stable atomically dispersed Pt$^{2+}$ species followed by their reduction. A similar preparation strategy was employed to obtain finely dispersed Pt particles via Pt segregation from Pt-doped ceria.\cite{126}

5.2. Redox coupling with the reducing agent

The relationship between the formation of oxygen vacancies and stability of the Pt$^{2+}$ species\cite{99,121} enables new methods to prepare thermally stable sub-nanometer Pt particles.\cite{127} Since the formation of oxygen vacancies in ceria-based materials leads to reduction of Ce$^{4+}$ to Ce$^{3+}$, one could speculate that reduction of Pt$^{2+}$ could be controlled via the formation of Ce$^{3+}$ centers.

Following this idea, the reduction of Pt$^{2+}$ species in Pt–CeO$_2$ materials might be triggered by addition of reducing agents which do not involve the removal of oxygen. For instance, the adsorption of Sn on CeO$_2$ films results in the formation of Sn$^{2+}$ cations accompanied by the reduction of Ce$^{4+}$ cations and formation of Ce$^{3+}$ centers.\cite{130,131,132} Thus, the adsorption of Sn on Pt–CeO$_2$ could trigger the conversion of Pt$^{2+}$ to sub-nanometer Pt particles. The process could occur at low temperature and without the formation of oxygen vacancies.

Indeed, stepwise Sn deposition onto the Pt–CeO$_2$ film at 300 K in UHV initiated the reduction of Pt$^{2+}$ species yielding sub-nanometer Pt particles (see Fig. 25). Comparing the trends in the formation of Pt particles under different Sn deposition conditions, it was possible to correlate the onset of Pt$^{2+}$ reduction with the concentration of the Ce$^{3+}$ centers determined by the RER.\cite{127} Estimating the number of Ce$^{3+}$ centers formed by Sn deposition on the Pt–CeO$_2$ film it was concluded that approximately 6 Ce$^{3+}$ cations are required per Pt$^{2+}$ species to induce the reduction of Pt$^{2+}$. This number corresponds to 3 Sn$^{2+}$ cations deposited per Pt$^{2+}$ species. This finding is in good agreement with density functional modeling data.\cite{127}

![Fig. 25](image-url)

Sn 4d (a) and Pt 4f (b) spectra obtained from a 10% Pt–CeO$_2$ film during stepwise Sn deposition at 300 K in UHV. The Sn 4d and Pt 4f spectra were obtained with photon energies of 60 and 180 eV, respectively. The spectra are grouped (i)-(iv) according to the Pt and Sn oxidation states in the film. In the corresponding ball-and-stick models (i)-(iv), red, yellow, blue, and dark grey balls represent oxygen, cerium, platinum, and tin, respectively. Reproduced from ref. 127 with permission from the Royal Society of Chemistry.
6. Properties of supported sub-nanometer metal particles

6.1. Metal–support interaction as a function of particle size

Metal particles supported on reducible ceria-based materials retain a number of unique properties arising from electronic metal–support interactions (EMSI). These include, for instance, higher reactivity and selectivity, structural flexibility, and self-cleaning capacity. Depending on the strength of the EMSI, there is a substantial charge transfer between the supported metal particle and the supporting oxide. Combining synchrotron-radiation photoelectron spectroscopy and scanning tunneling microscopy it was possible to “count” the number of electrons transferred across the metal/oxide interface as a function of particle size (Fig. 26). The maximum charge transferred per Pt atom was detected at particle sizes between 1 and 1.5 nm corresponding to a number of 30 and 70 Pt atoms per particle (see Fig. 26a). At higher Pt coverage the overall number of transferred electrons approaches a limit (Fig. 26b). Consequently, the average charge per Pt atom decreases as a function of size for particles containing more than 70 Pt atoms (Fig. 26a). At these particle sizes, the metal–support interaction is mostly associated with the restructuring of the particle shape and Pt/ceria interface which is rather insensitive to the charge transfer. Density functional modeling rationalized the magnitude of the charge transfer, mainly depending on three parameters, i.e. the size of the Pt particles, their density, and the presence of oxygen vacancies (Fig. 27). In particular, the limits of charge transfer were attributed to the electrostatic destabilization at a high surface concentration of Ce$^{3+}$ centers. In this respect, the degree of nanostructuring, i.e. the size of ceria nanoparticles or the roughness of the ceria support, becomes an additional parameter that has a direct impact on the magnitude of the charge transfer. The charge transfer would thus increase with increasing density of low-coordinated Ce$^{4+}$ cations which are capable of accepting electrons from Pt particles and still avoid electrostatic destabilization.

The most remarkable behavior was observed in the regime of sub-nanometer sized Pt particles (Fig. 26a). There, the charge transfer per Pt atom was found to decrease compared to what was predicted by DFT calculations for Pt particles on surfaces of stoichiometric ceria. Indeed, calculated models also showed that vacancies reduce the net charge transfer from Pt to ceria (Fig. 27). In consequence, the net charge transfer is a function of the degree of reduction of the ceria support. Depending on the specific system, metal particles can bear a positive charge on highly oxidized ceria supported and a negative charge on highly reduced supports.

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**Fig. 26** (a) The number of electrons transferred per Pt particle to the ceria support increases with increasing particle size (green squares). The partial charge per Pt atom reaches a maximum for particles with 30 to 70 atoms (yellow circles). Here, the EMSI is largest. (b) At higher Pt coverage the total amount of transferred charge approaches a limit which we denote as the “charge transfer limit” (red squares). The atomic models show schematically the average particle sizes in the different regions. Reproduced with permission from ref. 117, Copyright 2016, Nature Publishing Group.

**Fig. 27** Summarized results of density functional calculations of Pt$/_$/CeO$_2$(111) models. The particle size, the particle density, and the oxygen vacancy density on the support are important factors that control the charge transfer across the metal–oxide interface. Reproduced with permission from ref. 117, Copyright 2016, Nature Publishing Group.
6.2. Charge transfer in aqueous environments

On ceria-based catalysts, water molecules readily dissociate via proton transfer to surface O atoms, resulting in partial surface hydroxylation. DFT calculations were employed to investigate water dissociation at the ceria (111) surface and at the ceria/liquid interface as well as to elucidate the charge transfers between Pt particles and the ceria support resulting from water dissociation. The influence of the aqueous environment on the reaction mechanism, thermodynamics and kinetics was investigated by means of ab initio molecular dynamics (MD) simulations.

At equilibrium, these MD simulations revealed the existence of a fast proton dynamics at the water/ceria interface involving surface hydroxyl groups, solvated hydroxide ions, and water molecules coordinated to the surface Ce4+ cations at the water/ceria interface. Under these conditions, the dissociation of water molecules in the first surface solvation layer becomes a reversible dynamic process, which is governed by solvent-induced short-ranged transfers of protons between the adsorbed water molecules and the surface oxygen sites, or, in the reverse process, between surface hydroxyl groups and solvated hydroxide ions. The local increase of concentration of hydroxide ions on ceria surface, which results from water dissociation, activates a water-mediated Groththus-like mechanism that gives rise to fast long-ranged proton diffusion along the water/ceria interface. It involves concerted transfer of protons along the chains formed by solvent water molecules bridging between surface hydroxide and surface water molecules (Fig. 28a and b).

The catalytic importance of this dynamic process was demonstrated for water dissociation in the presence of supported sub-nanometer-sized Pt nanoparticles where the solvent accelerates the spillover of ad-species between oxide and metal sites. The mechanism of this process, calculated in the presence of a Pt6 cluster on a stoichiometric ceria (111) slab, is demonstrated in Fig. 28c-e. In the first step, a water molecule of the solvation layer dissociates at the periphery of the supported Pt particle into a hydroxide ion and a proton. This activates the dissociation of a neighboring solvent water molecule (see ovals in Fig. 28c and d), which mediates the proton transfer at the oxide/water interface. The proton is effectively transferred to an oxide surface site away from the nanoparticle, forming a surface hydroxyl (Fig. 28e). The resulting OH− species readily binds to a Pt site of the supported cluster inducing substantial charge transfer across the metal/oxide interface.

Upon electron reorganization in the Pt/CeO2 system one electron from the hydroxide species and another one from the Pt cluster are transferred to the oxide substrate through the metal/oxide interface, thus indicating that the cluster/solvent and metal/oxide interfaces are strongly coupled. This demonstrates that, with respect to UHV conditions, the number of electrons transferred from a supported Pt cluster in an aqueous environment to the ceria support is larger by up to a factor of two. Given the concerted reaction mechanism, the transfer of protons away from the Pt cluster cannot be distinguished from the transfer of the hydroxide ion towards the Pt cluster. In any case, however, the supported Pt clusters act as a basin attracting hydroxide species, which consequently accumulate at the cluster sites.

6.3. Formation of oxygen vacancies and reverse oxygen spillover

In the context of metal–support interaction, the supported metal particles may have a significant influence on the reactivity of ceria and, particularly, on its oxygen storage capacity. For bare ceria, the formation of oxygen vacancies in ceria nanostructures is strongly favored with respect to bulk samples. DFT calculations suggest that the oxygen vacancy formation energy decreases from 2.25 eV on the CeO2(111) slab to 0.8 eV on ceria nanoparticles such as Ce60O140 (see Fig. 29). The deposition of a Pt particle appears to have only little effect on the energy of vacancy formation, both on extended ceria and on ceria nanoparticles (Fig. 29). However, the formation of an oxygen vacancy results in a variation of the initial charge of the supported Pt6 particle as a function of the size of the ceria nanoparticle, i.e. the degree of ceria nanostructuring. This effect reflects the flexibility of the electronic structure of nanostructured ceria-based systems.
In the presence of supported Pt particles, oxygen vacancies can also be created by migration of atomic oxygen from the support onto Pt particles. The corresponding process is denoted as reverse oxygen spillover. Considering the energy of oxygen vacancy formation on CeO$_2$(111) (2.25 eV) and the adsorption energy of oxygen on Pt(111) (0.60–1.55 eV), such a reverse spillover process seems to be energetically unfavorable. At this point, the degree of the nanostructuring of ceria plays a critical role. In particular, the low energy for oxygen vacancy formation on nanostructured ceria favors reverse oxygen spillover and makes the process exothermic by 0.51 eV (Fig. 29). The reaction is accompanied by the formation of two new Ce$^{3+}$ centers. These estimations strongly suggest that the occurrence of oxygen reverse spillover intrinsically requires the presence of a nanostructured ceria support.

The above described processes associated with charge transfer and reverse oxygen spillover were investigated experimentally (see Fig. 30). In particular, the initial increase in Ce$^{3+}$ concentration indicates the charge transfer from the Pt particles to the ceria film. In contrast to the charge transfer, reverse oxygen spillover is associated with a substantial activation barrier and does not occur spontaneously at low temperature. However, a rapid increase of the Ce$^{3+}$ concentration was observed upon annealing above 500 K which is associated with the onset of reverse oxygen spillover (Fig. 30).
6.4. Structural flexibility of sub-nanometer metal particles

The structural flexibility of metal particles facilitates a chemical reaction by reducing the activation barrier.\textsuperscript{137,148–153} In the regime of sub-nanometer size this property should become increasingly important. For instance, for a Pt\textsubscript{6} cluster supported on a regular CeO\textsubscript{2}(111) surface the structural flexibility of the former turns the energetic balance of oxygen reverse spillover from endothermic, when structural changes are neglected, to weakly exothermic, when structural changes are taken into account (see Fig. 31).\textsuperscript{137} In other words, the binding energy of an oxygen atom to the Pt\textsubscript{6} cluster becomes comparable to the binding energy of oxygen in the ceria lattice if structural rearrangements in the Pt cluster are considered. Interestingly, this effect suggests that oxygen transfer to supported Pt clusters does not necessarily require nanostructured ceria particles, but may become slightly exothermic for very small Pt clusters even on extended ceria surfaces.\textsuperscript{137,145}

Notably, the initial and final stages of this process identified with global structural optimization indicate a transition from a 3D to 2D morphology of the supported Pt\textsubscript{6} cluster (Fig. 31).

6.5. Interconversion between atomically dispersed Pt\textsuperscript{2+} and sub-nanometer sized Pt particles

Because of the strong correlation between the oxidation state of Pt and the degree of reduction of the ceria support, it is expected that the Pt–CeO\textsubscript{2} catalyst can switch between two stable states, one associated with atomically dispersed Pt\textsuperscript{2+} species anchored at \{100\} sites and a second one with the Pt from sub-nanometer-sized Pt aggregates. The interconversion between the two states will occur in response to changes of the reactive environment. The latter may be associated with changes in the gas composition or, in the case of the fuel cell catalysts, in response to changes of the electrode potential.

Reversible changes in the oxidation state of Pt particles supported on nanostructured ceria have previously been monitored by Hatanaka et al.\textsuperscript{154} The presence of oxidized Pt species was explained by the formation of Pt–O–Ce bonds in an oxidative atmosphere at high temperature. It was proposed that the formation of such bonds drives the re-dispersion of Pt particles into smaller clusters.\textsuperscript{155} These studies\textsuperscript{154,155} suggested the formation of a monolayer of oxidized Pt on the surface of a ceria-based material after treatment in an oxygen atmosphere. Based on the binding energy of the corresponding species in Pt 4f spectra, we speculate that the species described in that work are similar to Pt\textsuperscript{2+} species anchored at \{100\} facets described above.

On single-crystal-based Pt–CeO\textsubscript{2} model films containing traces of metallic Pt, annealing in a H\textsubscript{2} atmosphere was shown to trigger reduction of Pt\textsuperscript{2+} and formation of metallic Pt, both in the form of sub-nanometer sized aggregates and larger Pt particles.\textsuperscript{98,99} The corresponding situation is shown in Fig. 32a.

Remarkably, the subsequent annealing of the Pt–CeO\textsubscript{2} film in oxygen triggers partial re-dispersion of metallic Pt particles. We observe a partial recovery of the characteristic signal associated with the Pt\textsuperscript{2+} species anchored at the \{100\} sites (Fig. 32a). Similar and partially reversible changes were also observed between Pd\textsuperscript{2+} species and metallic Pd particles (Fig. 32b). The degree of reversibility between two oxidation states likely depends on the conditions of the redox treatment, e.g. the temperature and the pressure of hydrogen and oxygen. Additionally, the degree of sintering can be controlled by the metal loading in a ceria-based catalyst.\textsuperscript{156} In this respect the ideal Pt loading should allow full recovery of the atomically dispersed state.\textsuperscript{104} It is likely that the degree of stabilization and the strong dependence of the catalytic activity (power density) on Pt loading observed for the Pt–CeO\textsubscript{2}

![Fig. 31 Thermodynamics of reverse oxygen spillover between a supported Pt\textsubscript{6} cluster and a CeO\textsubscript{2}(111) surface. Initial state (a) Pt\textsubscript{6} cluster deposited on a stoichiometric CeO\textsubscript{2}(111) slab and final states (b–f), partially oxidized Pt\textsubscript{6}O cluster on the slab with an oxygen vacancy beneath the cluster, resulting from a usual structural relaxation towards the local minimum (b) and from a basin hopping structure optimization (c–f) that allows the global minimum to be reached in the configurational space. Pt atoms are in gray, oxygen from the first (second) layer in red (violet), Ce\textsuperscript{4+} in yellow, and Ce\textsuperscript{3+} in orange. The oxygen vacancy site is indicated by blue squares. Reproduced with permission from ref. 137, Copyright 2014, American Chemical Society.](image1)

![Fig. 32 The development of Pt 4f (a) and Pd 3d (b) spectra obtained from Pt–CeO\textsubscript{2} and Pd–CeO\textsubscript{2} films, respectively, following the annealing in UHV (top), under H\textsubscript{2} (middle), and O\textsubscript{2} (bottom) atmosphere.](image2)
anode fuel cell catalysts are associated with the degree of reversibility that can be achieved in the catalyst film.41

7. Active state of Pt–CeO$_2$ thin film catalysts under electrochemical conditions

The active state of the Pt–CeO$_2$ catalyst films under electrochemical conditions can be examined by means of spectro-electrochemical methods. In line with the above discussion, changes of the electrode potential give rise to dynamic changes in the oxidation state of ceria and, in response, also of the supported Pt species. The stability of Pt–CeO$_2$ catalyst films was investigated as a function of Pt loading by means of electrochemical infrared spectroscopy.109 In these experiments CO formed during electro-oxidation of methanol was employed as a probe molecule. The corresponding IR spectra obtained from Pt–CeO$_2$ films are presented in Fig. 33. Reference spectra obtained from Pt(111) under identical conditions are also shown for comparison.

Typically, CO adsorption on Pt(111) gives rise to two bands associated with adsorption in on-top (CO$_t$) and bridging (CO$_b$) configurations (see Fig. 33a). Clearly, the emergence of CO$_t$ stretching bands on Pt–CeO$_2$ films indicates that a fraction of the atomically dispersed Pt$^{2+}$ species was converted into metallic Pt particles already in the first potential cycle. The red shift and broadening of the CO$_t$ band along with the absence of the CO$_b$ on Pt–CeO$_2$ films suggests the formation of small Pt aggregates with less developed (111) facets.157 In particular, the contributions from the low-coordinated sites and from (111) facet are well resolved on Pt–CeO$_2$ films with high Pt loading (see dark and light grey areas and arrows in Fig. 33a). In the limit of low Pt loadings, the CO$_t$ band is dominated by the contributions from CO adsorbed at low-coordinated sites. This situation is consistent with the formation of sub-nanometer-sized Pt particles that do not expose any measurable fraction of regular (111) facets.

Under electrochemical conditions, the blue shift of the CO$_t$ bands with increasing electrode potential is associated with the Stark effect.158 The relative offsets in the Stark plot between the Pt(111) and Pt–CeO$_2$ films (Fig. 33b) are related to the size of supported Pt particles. Density functional modeling reinforces the correlation between the stretching frequency and the particle size, on both unsupported and supported Pt particles.109,110 In particular, the offset of the CO vibrational frequencies by 26 cm$^{-1}$ with respect to Pt(111) indicates the formation of sub-nanometer-sized particles containing about 30 Pt atoms per particle.

The findings both in UHV and under electrochemical conditions suggest that the conversion of atomically dispersed Pt$^{2+}$ to sub-nanometer sized Pt particles transforms the Pt–CeO$_2$ film into an electrocatalytically active state. Notably, the stability of the sub-nanometer Pt particles under electrochemical conditions is a function of the Pt loading. A progressive blue shift of the CO$_t$ band on the Pt–CeO$_2$ film with high Pt loading during repetitive cycling is associated with sintering and growth of larger Pt particles with defined (111) facets (Fig. 34a). In sharp contrast, such changes are not seen for Pt–CeO$_2$ films with low Pt loading, even after repeated
potential cycling (Fig. 34b). This behavior is consistent with enhanced stability of the sub-nanometer Pt particles on Pt-CeO₂ films with low Pt loading in an electrochemical environment.

The enhanced stability of the sub-nanometer Pt particles is associated with the strong interaction between Pt particles and ceria support. The above findings suggest that Pt²⁺ species are formed under oxidizing conditions, which prevents the Pt particles from sintering during potential cycling. In this respect, the abundance of the {100} sites determines the maximum Pt loading in Pt-CeO₂ films up to which the stabilization mechanism will operate. At Pt loadings exceeding the density of these sites, the formation and growth of larger metallic Pt particles is no longer suppressed.

In summary, the Pt-CeO₂ catalyst with ideal Pt loading will be able to undergo reversible conversion between atomically dispersed Pt²⁺ species and sub-nanometer Pt particles as a function of the oxidation state and/or the electrode potential.

A consistent scenario would involve the presence of two stable states, denoted as the working state and the resting state (see Fig. 35). Accordingly, the resting state is associated with the formation of atomically dispersed Pt²⁺ anchored at {100} nanofacets. The conversion from the resting state into the working state is accompanied by the formation of sub-nanometer Pt particles triggered by the reduction under electrochemical conditions. Conversely, the resting state is recovered upon returning to oxidizing conditions. Note that such dynamic changes of the Pt oxidation state are typically associated with dissolution processes and sintering. In the presence of the ceria support, the release of Pt species may be prevented, leading to enhanced stability and constant activity.

Conclusions

A dynamic catalyst concept involving a single atom catalyst state has been applied to prepare anode fuel cell catalysts with high noble metal efficiency and enhanced stability. The approach involves the deposition of thin Pt-CeO₂ films on carbon substrates by means of radio frequency magnetron sputtering from separate CeO₂ and Pt targets in a non-reactive atmosphere. The deposition process is accompanied by the etching of carbon substrates yielding highly porous columnar structures coated with Pt–CeO₂ films. Atomically dispersed Pt was found to be present in these films in the form of Pt²⁺ and Pt⁴⁺ species at the surface and in the bulk, respectively. The ratio between the Pt²⁺ and Pt⁴⁺ species strongly depends on the degree of the nanostructuring of the Pt–CeO₂ films. Fuel cell tests demonstrated the direct link between the electrocatalytic performance of the Pt–CeO₂ films and the density of the surface Pt²⁺ species.

The local structure and reactivity of the Pt²⁺ species supported on nanostructured ceria films have been investigated by a variety of techniques including high-resolution TEM, SRPES, AR XPS, HAXPS, and STM in combination with density functional modeling. The appropriate model systems were developed to identify possible anchoring sites for the atomically dispersed Pt species. By means of density functional calculations and surface-science-based model catalysis the adsorption sites yielding strongly anchored Pt²⁺ were associated with {100} nanofacets on ceria particles. There, the Pt²⁺ species were found to be located in the center of a planar PtO₂ moiety forming a quadratic coordination environment. A similar structural element was found at the steps of CeO₂(111) films. CeO₂(100) nanofacets were also identified on real Pt-CeO₂ catalyst films by means of HRTEM.

The stability and the reactivity of the Pt²⁺ species were investigated as a function of Pt loading on the model Pt-CeO₂ films under ultra-high vacuum conditions. It was found that the capacity of the nanostructured ceria surface to form isolated Pt²⁺ is limited by the number of available {100} sites. If the Pt loading exceeds the density of anchoring sites available, the growth of Pt nanoparticles is observed.

The activation of molecular hydrogen at single Pt²⁺ species is associated with a high activation barrier. In the presence of metallic Pt, the hydrogen activation is facile and eventually leads to reduction of all Pt²⁺ species. It was found that metallic Pt is not directly involved in the reduction of the Pt²⁺ species. Instead the reduction of Pt²⁺ is coupled to the reduction of Ce⁴⁺ to Ce³⁺, resulting from the formation of oxygen vacancies. Reaction with methanol also leads to reduction of the ceria support and triggers the formation of sub-nanometer Pt particles. Alternatively, the reduction of Pt²⁺ and the formation of Pt particles can also be mediated by co-adsorption of reducing agents such as Sn that lead to formation of Ce³⁺ without formation of oxygen vacancies. In an electrochemical environment, conversion of the Pt²⁺ species to sub-nanometer Pt particles is triggered by the electrode potential.

The sub-nanometer Pt particles exhibit remarkable thermal stability with respect to sintering under both UHV and electrochemical conditions. The chemical properties of the supported sub-nanometer-sized particles are modified by metal–support interactions associated with strong charge transfer, by their structural flexibility, and by spillover phenomena. Regarding
the electronic metal support interactions between Pt particles and ceria, the amount of charge accumulated on the Pt particle depends on the Pt particle, the particle density, the structure and the stoichiometry of the ceria support.

From the above results, a consistent picture emerges with respect to the operation of the Pt–CeO₂ catalyst films under electrochemical conditions. The stabilization mechanism involves reversible conversion between two chemical states, the atomically dispersed Pt²⁺ species and sub-nanometer-sized Pt particles in an electrochemical environment. This concept rationalizes the high stability of the Pt–CeO₂ catalyst films with low Pt loading under conditions of dynamically changing electrode potentials.

Regarding the transfer of the above described concepts to other less expensive metals, similar anchoring phenomena were predicted by density functional modeling for various metals from groups 8 to 11. The general trends in the energetics of the corresponding atomically dispersed metals have been established and could for some metals (Pd, Ni) be confirmed by experiments. However, characteristic differences are observed regarding the stability and segregation behavior, rendering the Pt–CeO₂ system unique in this comparison.

Outlook

At present, one challenge regarding the application of single-atom-based Pt–CeO₂ films in fuel cell catalysis is the limited density of the {100} sites, which also limits the total Pt loading and the resulting power density. Different strategies may be employed to tackle this challenge. The first strategy focuses on the improvement of the carbon supports. Along this line, GDLs coated with soot or nitrogen doped carbon films demonstrated great potential. The second strategy involves shaping the morphology of the Pt–CeO₂ film into high-surface area nanostructures with a large fraction of {100} facets, e.g. cubes or nanoscrews. This can be achieved, for instance, by innovative deposition techniques or a strain driven growth induced, for example, by doping. As a last strategy, we may consider to prepare the key structure, i.e. the square planar PtO₂ moiety, on a different support with a higher degree of nanostructuring.

Additional insight from theoretical modelling studies should also contribute to unravelling in greater detail the mechanism of reversible conversion between Pt²⁺ and the sub-nanometer Pt particles and their interaction with reactants. This will allow establishing a kinetic model of the catalyst under fuel-cell operating conditions, providing valuable understanding of the factors influencing the performance of catalytic materials with atomically dispersed metals.

List of abbreviations

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AR XPS</td>
<td>Angle-resolved X-ray photoelectron spectroscopy</td>
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<tr>
<td>CVD-CNTs</td>
<td>Chemical vapor deposited carbon nanotubes</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<tr>
<td>DWCNTs</td>
<td>Double-wall carbon nanotubes</td>
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<td>EMSI</td>
<td>Electronic metal–support interactions</td>
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<td>GDL</td>
<td>Gas diffusion layer</td>
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<tr>
<td>GLAD</td>
<td>Glancing angle deposition</td>
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<tr>
<td>HAXPS</td>
<td>Hard X-ray photoelectron spectroscopy</td>
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<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
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<tr>
<td>IRAS</td>
<td>Infrared absorption spectroscopy</td>
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<tr>
<td>MWCNTs</td>
<td>Multi-wall carbon nanotubes</td>
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<td>ND</td>
<td>Normal deposition</td>
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<td>PD</td>
<td>Power density</td>
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<td>PEMFC</td>
<td>Proton exchange membrane fuel cell</td>
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<td>RER</td>
<td>Resonant enhancement ratio</td>
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<td>RPES</td>
<td>Resonant photoemission spectroscopy</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SAC</td>
<td>Single atom catalyst</td>
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<td>SP</td>
<td>Specific power</td>
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<td>UHV</td>
<td>Ultrahigh vacuum</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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