COMMUNICATION

Protonation states in a cobalt-oxide catalyst for water oxidation: fine comparison of *ab initio* molecular dynamics and X-ray absorption spectroscopy results†

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Ab initio **molecular dynamics simulations of a recently proposed cobalt-based catalyst for water oxidation provide insight into the properties of protons at the water/oxide interface. Calculations and X-ray absorption spectroscopy data indicate a cubane-like structure of the catalyst, support the occurrence of protonated μ_2-O atoms, suggest deprotonated μ_3-O atoms and the presence of sites promoting low-barrier hydrogen bonds.**

Photosynthetic processes occurring in biological systems are designed to capture sunlight very efficiently and convert it into chemical energy, that is organic molecules.[1,2] Inspired by such natural processes, the goal of artificial photosynthesis is to create technologically relevant photo-electrolytic cells to generate chemical fuels (*e.g.*, hydrogen) directly from sunlight, efficiently and at low cost. A recently proposed inorganic cobalt-based catalyst film (CoCat) may turn out to be a promising candidate to solve the problem in a crucial step of the cycle: the splitting of water into molecular oxygen, electrons (reducing equivalents) and protons.[3] The CoCat has attracted much interest because it is efficient at neutral pH and very stable (self-repair) under working conditions, operates close to the Nernstian potentials for the H_2O/O_2 half-cell reaction, and is self-assembled from low-cost materials.[3] Recent X-ray Absorption Spectroscopy (XAS) measurements[4,5] revealed that active CoCat films share some common structural features with the biological systems involved in water splitting, that is, the pentanuclear Mn_4Ca complex of photosystem II (PSII).[6] Both systems are characterised by a compact metal-oxo core with several μ-oxo bridges between the transition metal ions. However, a full understanding of the structural properties of these complexes has not been attained. In particular, XAS analyses suggest that: (i) the CoCat likely consists of blocks of Co ions interconnected by di-$\mu_{2,3}$-O/OH (see Fig. 1 and 2). The presence of other species (Cl^-, PO_4^{3-}, K^+, Ca^+ ions, depending upon the composition of the starting solution) does not affect significantly the CoCat structure and properties.[7] (ii) The Co atoms are found to be (mainly) in the 3+ oxidation
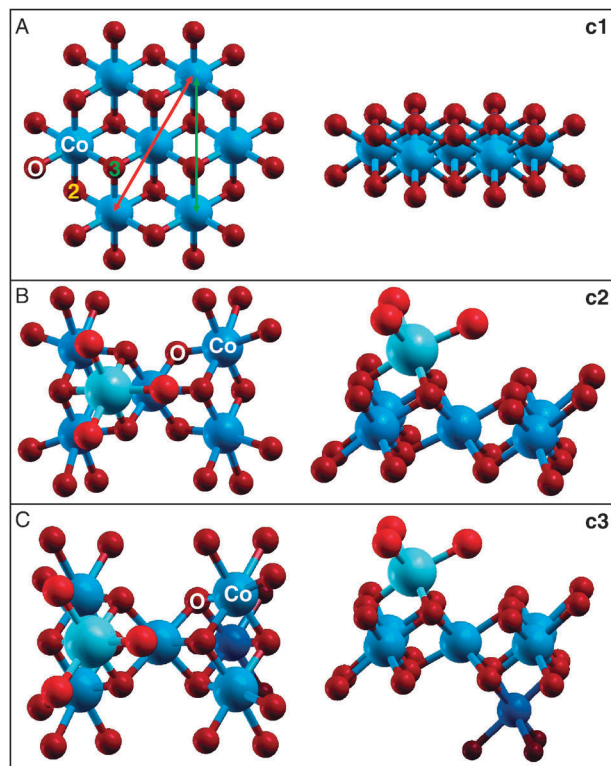

Fig. 1 Top and side views of: (A) Co_7O_{24} c1 cluster; (B) Co_6O_{23} c2 cluster; (C) Co_7O_{26} c3 cluster. Larger spheres and brighter colours indicate atoms belonging to topmost layers. "2" and "3" labels indicate examples of μ_2-O and μ_3-O sites. The red and green lines in the upper panel identify three collinearly arranged Co atoms (Co–Co 3 distance in Table 1) and two Co atoms separated by oxo bridges (Co–Co 2 distance in Table 1), respectively.

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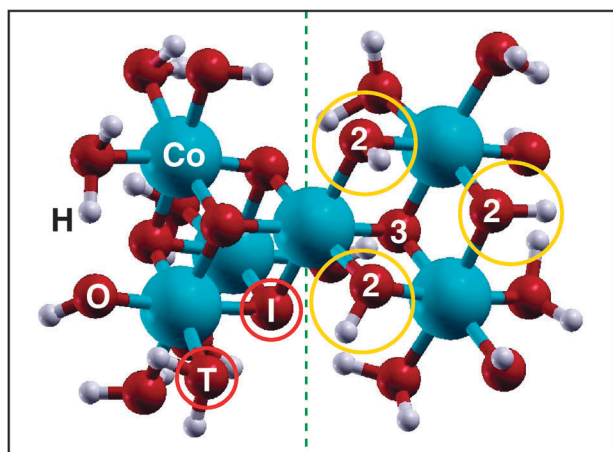
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Fig. 2 Equilibrium geometry of the H saturated $Co_6O_{23}H_{28}$ c2 structure. The "2" label indicates protonated μ_2-O sites, which are also enclosed by yellow circles. The "3" label indicates one of the non-protonated μ_3-O sites. The "I" and "T" labels indicate inner (that is, belonging to cubane structures) and terminal (that is, not interconnecting Co atoms and carrying saturating H atoms) O atoms, respectively, also enclosed by red circles. A dashed green line divides a complete cubane unit (left side of the figure) from a defective one (right side of the figure).

state for the "resting conditions" used in the XAS analyses.[4] (iii) The CoCat shows a short-range ordered structure, formed by Co(III)O$_6$ octahedra, but lacks long-range ordering.

Different models of the CoCat structure have been proposed on the ground of such results.[4–6] All the models are built by interconnecting in different ways two simple blocks, that is, complete and defective "cubane-like" Co–O units (see Fig. 1 and 2). Here, we report the results of an *ab initio* theoretical

investigation which: (i) support the experimental findings; (ii) provide an accurate description, at the atomistic scale, of the structural and dynamical properties of the CoCat; (iii) suggest the occurrence of protonated μ_2-O atoms in the CoCat samples; (iv) provide a solid ground for further investigations regarding the water splitting mechanism.

The structural, dynamical and electronic properties of CoCat models have been investigated by using *ab initio* molecular dynamics (AIMD) simulations,[8] both in the gas phase and in solution, together with static geometry optimisations based on Density Functional Theory, as developed in the Quantum-ESPRESSO package.[9] Co–O clusters containing complete and defective "cubane-like" units have been modelled and saturated by a number of H atoms suitable for enforcing a +3 valence state for the Co atoms, suggested by XAS measurements.[4,5] Most of the calculations have been performed at the GGA (Generalised Gradient Approximation) level of the theory,[10] but accurate tests have been performed by using an Hubbard U correction,[11,12] which has been proven to be successful in order to improve the GGA electron correlation description in transition metal oxides and related compounds.[13,14] Further details on theoretical methods can be found in the ESI.†

We are aiming at a comparison of characteristic inter-atomic distances obtained by *ab initio* calculations and by XAS measurements at the K-edge of cobalt. To assess the capability of our calculations to predict Co–O and Co–Co distances at sufficient precision, we have investigated a crystallographically characterized (by X-ray diffraction, XRD) Co-oxo compound with close structural similarity to the CoCat, namely LiCoO$_2$. This material consists of Co–O sheets of interconnected defective cubane units (layers of edge-sharing Co(III)O$_6$ octahedra) separated by intercalated Li$^+$ ions. Table 1 provides a comparison of distances

Table 1 *Upper table*: structural properties extracted by gas-phase AIMD simulations of c1, c2 and c3 clusters, shown in Fig. 1, as well as GGA and GGA + U simulations for the LiCoO$_2$ crystal. The Co–O column is related only to Co–O bonds belonging to the cubane structures. The Co–Co 1 label denotes the distance between nearest neigbours separated by a μ-oxo bridge; Co–Co 2 is the shortest distance between two Co atoms which are not directly connected by a μ-oxo bridge, and Co–Co 3 is the distance between the far atoms in three collinearly arranged Co atoms. *Lower table*: structural properties of the most stable solvated c2 cluster, shown in Fig. 2. The Co–O column is related to all the Co–O bonds belonging to the cubane structures. The Co–O (μ_3) column is related to Co–O bonds involving di-μ_3-O atoms. The Co–O (μ_2) column is related to Co–O bonds involving μ_2-O atoms. Co–Co 1, 2 and 3 columns are analogous with the upper table ones. The (com) and (def) labels indicate Co–Co nearest neighbour distances within the complete and the defective cubane structures, respectively. In the case of static GGA and GGA + U simulations, data have been averaged on different bonds of the same type, whereas they have been averaged on different bonds of the same type and along the trajectory in the case of 10 ps AIMD simulations at 300 K (12 ps at 300 K in the case of the c2 + 58H$_2$O (AIMD)). A more complete version of this table, as well as further details on XAS data, can be found in the ESI† and in ref. 4 and 16. LiCoO$_2$ XRD data are taken from ref. 17

Cluster (method)	Bond distance/Å [Co coordination number]			
	Co–O	Co–Co1	Co–Co2	Co–Co3
c1 (AIMD)	1.91 ± 0.05 [6.0]	2.81 ± 0.06 [3.4]	4.86 ± 0.07 [1.7]	5.61 ± 0.07 [0.9]
c2 (AIMD)	1.90 ± 0.07 [6.0]	2.81 ± 0.08 [3.0]	4.85 ± 0.20 [1.3]	5.63 ± 0.11 [0.7]
c3 (AIMD)	1.89 ± 0.06 [6.0]	2.79 ± 0.06 [3.4]	4.82 ± 0.11 [1.7]	5.56 ± 0.08 [0.9]
Co Cat XAS data	1.89 [5.8]	2.81 [3.7]	4.86 [0.5–0.7]	5.62 [0.9]
LiCoO$_2$ (GGA)	1.936	2.854	4.944	5.709
LiCoO$_2$ (GGA + U)	1.926	2.828	4.898	5.656
LiCoO2 XAS data	1.91	2.81	4.94	5.61
LiCoO2 XRD data	1.92	2.816	4.878	5.633

Cluster (method)	Bond distance/Å							
	Co–O	Co–O (μ_3)	Co–O (μ_2)	Co–Co1	Co–Co1 (com)	Co–Co1 (def)	Co–Co2	Co–Co3
c2 (AIMD)	1.90 ± 0.07	1.88 ± 0.05	1.97 ± 0.06	2.81 ± 0.08	2.79 ± 0.07	2.86 ± 0.07	4.85 ± 0.20	5.63 ± 0.11
c2 + 58H$_2$O (AIMD)	1.91 ± 0.05	1.90 ± 0.05	1.95 ± 0.06	2.84 ± 0.06	2.83 ± 0.06	2.86 ± 0.06	4.77 ± 0.16	5.65 ± 0.08
c2 + 58H$_2$O (GGA)	1.91 ± 0.03	1.89 ± 0.03	1.97 ± 0.02	2.83 ± 0.02	2.83 ± 0.02	2.83 ± 0.03	4.75 ± 0.13	5.59–5.64
c2 + 58H$_2$O (GGA + U)	1.91 ± 0.02	1.89 ± 0.03	1.96 ± 0.02	2.84 ± 0.03	2.83 ± 0.03	2.84 ± 0.02	4.75 ± 0.17	5.60–5.66
CoCat XAS	1.89	—	—	2.81	—	—	4.86	5.62

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obtained experimentally (by XRD and XAS) and calculated by various *ab initio* approaches. Experimentally determined and calculated distances agree reassuringly well. Using the GGA + U approach, the deviations are around 0.02 Å; slightly more pronounced deviations were observed in the GGA simulation. In conclusion, both the XAS and *ab initio* calculations have reproduced sufficiently well the atom–atom distances of the first (Co–O) and second (Co–Co) coordination spheres of $LiCoO_2$ (further details are provided in the ESI†). We can confidently address therefore the CoCat properties by performing a comparison of XAS and *ab initio* results.

We exploit the structural similarities between CoCat and $LiCoO_2$ by focusing on three different CoCat models, which have been built by interconnecting defective and complete cubane blocks. In detail, a Co_7O_{24} cluster (c1), shown in Fig. 1A, has been cut out from a Co–O sheet of $LiCoO_2$. Then, one or two Co atoms, together with a number of O atoms suitable to ensure the correct $Co(III)O_6$ coordination for every Co, have been swapped above or below the Co–O plane to model a Co_6O_{23} cluster (c2) and a Co_7O_{26} cluster (c3) (see Fig. 1B and C, respectively). Two main reasons suggest such a choice: (i) the CoCat is likely formed by cubane units interconnected to form still unknown patterns, as proposed on the ground of XAS measurements.[4–6] We consider the c1, c2 and c3 clusters in order to compare their structural properties with previous experimental findings, *e.g.*, Co–Co and Co–O distances. Our models contain indeed both the proposed complete and defective cubane blocks and permit to span a complete set of clusters, ranging from defective cubane units only (c1) to complete cubane units only (c3), passing through a mixed solution (c2). (ii) By using this set of different models, we can modulate the number of μ_2-O and μ_3-O atoms, that is, O atoms interconnecting Co atoms within the complete and defective cubane-like structures. Differences between such sites can be acknowledged by looking at the "2" and "3" labels in Fig. 1 and 2. Such μ-oxo sites are supposed to play a key role in the water splitting reactions, possibly promoting proton assisted electron transfer processes.[6,15] An in-depth investigation of their properties may provide a sound starting point to clarify the water splitting mechanism promoted by the cobalt catalyst.

As a first major achievement, we have found a remarkable agreement between present theoretical simulations and previous XAS results concerning the structural properties of the CoCat (see Table 1). All the investigated models show calculated Co–O and Co–Co distances quite similar to the XAS ones. They are also close to the Co–O and Co–Co distances calculated and measured for the $LiCoO_2$ crystal, and this fact justifies the assumption that the local structures of $LiCoO_2$ and CoCat are closely related. An accurate comparison of distances between the investigated clusters may suggest that the c1 and c2 models, that is, the ones containing defective cubane units, fit slightly better the XAS data. In the case of the c3 model, a short Co–Co 1 distance of 2.79 Å is calculated which may be in conflict with the measured distance, given also the fact that Co–Co distances are rather slightly overestimated than underestimated by the present theoretical simulations. It has to be stressed that differences between clusters are mainly related to the presence of defective or complete cubane units. The above cited similarities between the CoCat and $LiCoO_2$ structures suggest the occurrence of defective cubane units in the CoCat structure, whereas complete units could act as bridges between Co–O sheets formed by defective units. Very similar results have been obtained in the case of both static and AIMD simulations (a more complete version of Table 1 can be found in the ESI†), suggesting once more that a reliable model of the CoCat can be built by interconnecting defective and complete cubane units.

Despite its relevance for understanding the catalytic mechanism, the protonation states of μ-oxo bridges have not been investigated so far. A 12 ps AIMD simulation of the c2 cluster solvated with water molecules gave us insights on the properties of protons at the CoCat/water interface. The simulation reveals that μ_2-O sites between Co atoms, which can be found only in defective cubane units, are stably protonated, irrespective of the initial position of H atoms in the simulation. In contrast, μ_3-O atoms do not tend to capture protons during the simulations, even though they form quite strong H bonds with saturating and surrounding water molecules. Noticeably, terminal O atoms, labelled "T" in Fig. 2, tend to exchange protons amongst them (either by means of direct exchange, or of double proton exchange involving a nearby water molecule) quite frequently. In particular, Co–Co nearest-neighbours carrying pairs of parallel Co–O bonds (an example is shown in Fig. 3) are expected to be present in all of the CoCat models proposed in ref. 4–6. The occurrence of such Co–Co pairs allows the formation of stable O–H···O structures characterised by low-barrier H bonds. The fast proton exchange between O atoms can be clearly acknowledged by looking at the lower panel of Fig. 3, where the evolution of the
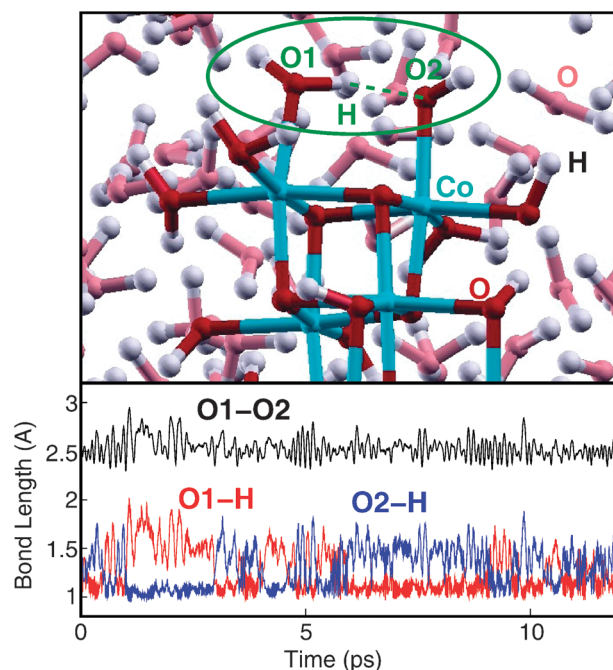

Fig. 3 Upper panel: snapshot from the AIMD simulation of the c2 model in water solution. The green ellipse identifies a pair of terminal O atoms which undergoes a fast proton exchange along the AIMD simulation. O atoms belonging to surrounding water molecules have been displayed in a lighter red colour for the sake of clarity. Lower panel: evolution of atomic distances related to the O–H···O structure along the AIMD simulation.

atomic distances related to the O–H⋯O structure along the AIMD simulation is reported. The special properties of such a structure at the CoCat/water interface (analogous to similar structures reported for different metal-oxide and metal-complexes based catalysts, see ref. 6 and references therein) are closely related to the Co–Co nearest-neighbour distance of about 2.8 Å, optimal for promoting strong H bonds.

The properties of protonated μ_2-O sites have been investigated by performing a detailed analysis of results concerning the c2 cluster, the one containing a complete and a defective cubane unit, both in the gas phase and in water solution (see Fig. 2 and the lower part of Table 1). In particular, Co–O distances have been divided into Co–O bonds involving (non-protonated) μ_3-O atoms and (protonated) μ_2-O ones (μ_3 and μ_2 labels in Table 1, respectively). Such an analysis shows that a stable protonation of μ_2-O sites affects the length of Co–O bonds in which they are involved: the Co–OH bonds are about 4% longer than the μ_3-O Co–O bonds. The protonation of μ_2-O sites (which are present only in defective cubane units) affects at the same time the Co–Co nearest-neighbour distances, which have been therefore split into two columns related to the complete unit and to the defective unit of the c2 cluster ("com" and "def" labels in Table 1, respectively). These Co–Co distances, slightly longer in the case of incomplete cubane units, are less affected by protonated μ_2-O sites to an extent which seems to depend more upon solvation. All in all, solvation effects do not seem to affect significantly the structural properties of the CoCat model; the same holds for electronic correlation effects, which might, in principle, affect the strength of Co–O bonds (compare static GGA and GGA + U results).

In order to provide experimental evidence for the occurrence of protonated μ_2-O sites in the CoCat samples, a new, more detailed analysis of previous XAS measurements[4] has been performed together with further, ancillary GGA calculations. Such calculations have regarded the gas-phase c2 cluster with different configurations of the saturating H atoms. Different (locally stable) equilibrium geometries have been found where some non-protonated μ_2-O bridges occur. An average Co–Co nearest-neighbour distance of 2.76 Å has been extracted by such structures, which represents a sizeably different estimate with respect to the 2.81 Å average value found in the case of Co–Co 1 distances for the c1 and c2 cluster models (see Table 1 for comparison). Then, the occurrence of Co–Co distances of 2.76 Å in the CoCat has been tested by the new analysis of XAS data. In this regard, Fig. 4 shows that assuming the total number of Co–Co vectors of 2.76 and 2.81 Å equal to 100%, the simulation deviates significantly from the measured XAS data for any appreciable contribution of 2.76 Å distances, in agreement with the above theoretical indications. Confidence levels and further details on the refined XAS analysis can be found in the ESI.†

In summary, the above theoretical results closely reproduce bond distances obtained by XAS data, supporting the idea that the CoCat structure is built by interconnecting defective and possibly complete cubane units. Moreover, they suggest that O atoms placed as μ_2-O bridges between Co(III) ions are likely to be protonated under working conditions of the CoCat, at variance with the μ_3-O bridges. Finally, they indicate that terminal O atoms, whose occurrence at the
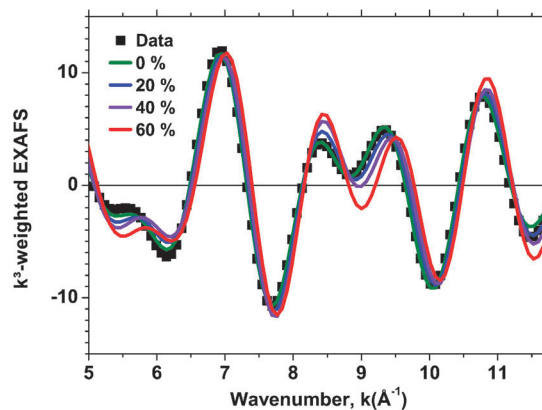

Fig. 4 Measured and hypothetical EXAFS spectra calculated for various contributions of Co–Co distances of 2.76 Å length. The EXAFS of the CoCat was measured and processed as described elsewhere.[4] The EXAFS data were calculated assuming various fractions (0%, 20%, 40%, and 60%) of Co–Co vectors of 2.76 Å length, which is the likely Co–Co distance for a Co-(μ_2-O)(μ_3-O)-Co motif. These simulations suggest that a contribution of short Co–Co distance of 20% or more would be incompatible with the experimental results. Both measured and calculated spectra were Fourier-filtered between 1.2 and 2.8 Å (reduced distance scale), only to clarify the graphical representation.

CoCat boundaries is expected for all of the catalyst models proposed so far,[4–6] are likely to form low-barrier H bonds. All these results may be regarded as valuable indications that provide a starting point for further investigations of the water oxidation reaction promoted by the CoCat.

The formation of Co(IV) ions, which has been recently reported in CoCat samples exposed to more positive electrode potentials,[7,18] followed by the release of a H$^+$ species from a neighbouring μ_2-O site could represent a first step of the water splitting reaction mechanism, followed by fast proton exchange processes involving terminal Co–OH sites. On the ground of present results, it can be speculated that an unprotonated μ_2-O bridge adjacent to a Co(IV) ion could be involved in proton-assisted electron transfer processes, as proposed for the Mn complex of photosynthetic water oxidation.[15] Such processes would restore the Co(III) state, saturate again the bridging O atoms coordinatively and drain electrons from water to the catalyst. Further experimental and theoretical investigations are needed for evaluation of the above hypotheses on structure–function relations in water oxidation by the CoCat. Our investigation may pave the way toward future understanding and design of these highly promising materials and their dynamical properties.

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