This article can be cited before page numbers have been issued, to do this please use: L. Zhang, A. Cheruvathur, C. Biz, M. Fianchini and J. Gracia, Phys. Chem. Chem. Phys., 2019, DOI: 10.1039/C8CP07832G.

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Introduction

Water oxidation enables conversion of electricity into storable hydrogen, needed for clean energy and a sustainable economy. In water electrolysis, the oxygen evolution reaction (OER) is the rate limiting step of the overall process. Therefore much attention has devoted to understand the rationale behind triplet state O₂ evolution in order to develop active, stable and abundant catalysts that accelerate it. In 1980 Matsumoto and co-workers examined the OER activity of the La₁₋ₓSrₓFe₁₋ₓCoₓO₃₋δ (0 ≤ x ≤ 1) family of perovskites in alkaline solution; even though the group could not synthesise the (Co⁺⁺⁺) SrCoO₃₋δ composition, they predicted that it will show the lower overpotentials. The La₀.₇Sr₀.₃Fe₂O₅₊₀.₅ structure was obtained by Matsumoto as an excellent and stable electrocatalyst for OER; similar compositions and oxidation states typically lead to good catalysts. In the smaller LaₓSrCoO₃₋δ group, SrCoO₃₋δ shows the optimum OER kinetic and is, in fact, one of the best catalysts.

In 1984 Bockris and Otagawa described the electrocatalytic activity of perovskite oxides in terms of molecular orbital theory; they showed that the antibonding (AB) 3d-metal orbitals directed towards the ligands (O) overlap with the lobes of the reactants forming AB σ*-type orbitals, ε₂g₂-2p shells in octahedral coordination. The authors explained that the catalysts having occupied ε₂g₂-2p levels achieve high rates of oxygen evolution due to mild bonding between the catalyst and the intermediates. Separately, Goodenough has established the foundations of the theoretical understanding of the electronic and magnetic transitions in metal oxides. These works have been key to derive the significant influence of quantum spin exchange interactions (QSEI) in the orbital chemistry of magnetic catalysts, also known as spintron-catalysis. Due to the impact of QSEI in compositions with open-shell configurations, conventional electronic analysis in heterogenous catalysis like the d-band centre model / band theory is insufficient to describe the highly-correlated electrons; and then lead to rough approximations for the catalytic activity of materials based-on Earth-abundant magnetic elements. As in spintronics, the spins of many electrons can act together, affect the magnetic and electronic properties of a material, and influence significantly its catalytic behaviour.

QSEI reduce the electronic repulsions and are key for charge mobility in magnetic systems. A ferromagnetic (FM) conduction band indicates that the physics of the itinerant electrons is significantly influenced by Fermi holes, a fundamental requirement for optimal electrocatalysts based on 3d-metals. By looking carefully, we can see examples where magnetic structures associate overall with active heterogeneous catalysts. FM oxides show better activity than Pt in the oxidation of nitrous oxide (NO has doublet ground state), NF, NO nitrides improve ammonia synthesis, or Co doping in MoS₂ induces FM and enhances the activity in various reactions. In addition of particular interest for electrocatalysis, inter-atomic FM orderings leads to favourable spin-charge transport, avoiding antiferromagnetic (AFM) electronic localization. Fully AFM insulators like LaCrO₃ or LaFeO₃ are poor oxygen catalysts. Spin selection in polarized density of states facilitates the oxidation/reduction of triplet state O₂. Nature has evolved excellent magnetic catalysts from abundant 3d-metals, e.g. during photosynthesis, via engineering QSEI.

In a broad context, the rationalisation of the orbital physics in magnetic structures is important in theoretical heterogenous catalysis, because it will allow to study activities across the whole periodic table based on the interplay between chemical composition, and electronic configuration. Successful catalytic design based on orbital occupation may proceed from the rigorous analysis of the quantum chemistry, in the LaₓSrₓCoO₃₋δ family two ends for the OER activity can be defined: LaCoO₃ as the less active and SrCoO₃₋δ as the most efficient. The orbital physics behind the intrinsic activity of SrCoO₃₋δ is unknown, as well as the effect of the iron ions in compositions like LaₓSrₓFe₁₋ₓCoₓO₃₋δ. Also, the specific orbital configuration of LaCoO₃ at room temperature is controversial, because three spin states representing the 3d-2p AB-orbitals in octahedral coordination, t₁₂gₐ₀ (low-spin, LS), t₁₂gₐ₂ (high-spin, HS) and t₃₂gₐ₂ (intermediate spin, IS), are accessible for the Co³⁺⁻O bonds. LaCoO₃ presents the following, not fully understood, electronic transitions as a function of temperature:

- 0 K < T < 35 K: bulk cobalt cations are preferentially in the Low-Spin (LS) t₃₂gₐ₂⁰⁰ magnetic state.
- 35 K < T < 110 K: cobalt cations coexist in intermediate-spin (IS) t₃₂gₐ₂⁴ and high-spin (HS) t₃₂gₐ₂ configurations with a ratio of LS(HS) > 0.5.

The definition of the interplay between chemical composition, electro-magnetic configuration and catalytic activity requires a rational study of the orbital physics behind active materials. Apart from Coulomb forces, quantum spin exchange interactions (QSEI) are part of the potentials that differentiate the activity of magnetic oxides in electron transfer reactions, strongly correlated electrocatalysts. Ferromagnetic (FM) cobalt oxides can show low overpotentials for the oxygen evolution reaction (OER); and the LaₓSrₓCoO₃₋δ family of perovskites is a good ground to gain understanding of the electronic interactions in strongly correlated catalysts. In this case, Sr-doping raises the OER activity, the conductivity and increasing FM spin moments. The efficiency of electrocatalysts based on Earth-abundant 3d-transition metals correlate with the interrelated factors: mild-boding energies, the reduction of the electronic repulsions because of the QSEI in the open-shells, and with enhanced spin delocalization in FM orderings. The epitome of the outstanding OER activity of SrCoO₃₋δ is the accumulation of FM holes in the 3d-2p bonds, including the ligand orbitals, thus facilitating spin-selected charge transport and production of triplet O₂ moieties, from the oxidation of diamagnetic precursors. Spin-polarized oxygen atoms in the lattice can participate in O-O coupling and extrusion of O₂ in a Mars-Van Krevelen mechanistic fashion. We show that the stabilizing FM QSEI decrease the adsorption and activation energies during oxygen evolution; and spin-dependent potentials are part of the factors that govern the catalytic activity of magnetic compositions: spintron-catalysis.
Theoretical methods

We have performed periodic Density Functional Theory (DFT) calculations using VASP (Vienna Ab-initio Simulation Package), a program that combines ab-initio energy calculations with plane-wave basis sets. The electron-ion interactions for the atoms are described by the projector augmented wave method developed byBloechl. The exchange-correlation energy has been calculated within the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof functional revised for solids. We used a cut-off energy of 400 eV for the expansion of the wave function into plane waves. The Monkhorst-Pack scheme has been chosen for the integration in the reciprocal space. We have used the so-called DFT+U approach for the corrections accounting for the strong correlation among the electrons at the Co and Fe atoms. The Hubbard +U correction is desirable in 3d-metals to consider explicitly non-local interactions between localized electrons. The value of U is a constant, thus, in order to get accurate results, a structure-dependent parametrization of U is necessary. An initial calibration of GGA +U method was performed in order to match the electronic configurations of the LaCoO₃ and SrCoO₂.6 catalysts. The lattice parameters for monoclinic I2/a LaCoO₃ were optimized using a single unit cell, 4 La, 4 Co and 12 oxygen atoms, versus U. Optimizations indicate that for U 2.0 - 2.5 the Hubbard correction is suitable to both experimental Jahn-Teller distortions and theoretical calculations. In our calculations, the LaCoO₃ ground-state has all the Co⁺⁺⁺ configurations in LS + HS states configuration. The t₂g₉e_g⁰ structure presents no JT distortion and the predicted Co-O distance is about 1.893 Å. The density of states (DOS), Fig. 1a, shows that LS LaCoO₃ is an insulator with a band gap of about 0.5 eV. The second most stable phase is the ½ LS + ¼ HS configuration, Fig. 1b; the inter-atomic exchange interactions are favourably ferromagnetic, because the e_g band is overall more empty than occupied.

Results and discussion

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Table 1. Calculated and experimental LaCoO₃-Co-O distances (Å) and relative energies per Cobalt atom (meV/Co³⁺) for the most stable configurations.

| State  | Co-O (Å) | ΔE (meV) |
|--------|----------|----------|
| DIA 90 K | 1.918  | 1.924  | 1.934  |
| FM 298 K | 1.874  | 1.925  | 1.993  |

Both ½ LS + ¼ HS and ½ LS + ¼ HS structures present JT distortions on the cobalt atoms with localized magnetic moments, see Tab. 1. The DOS for ½ LS + ½ HS LaCoO₃ also has a band gap of ~0.5 eV, while ¼ LS + ¼ IS is a half-metal. This last configuration, less stable, is not detected experimentally. At room temperature LaCoO₃ possesses a narrow optical gap < 1.0 eV; and our calculations predict a band gap of ~0.5 eV (Fig. 1a and 2). The LS t₉g₉e_g⁰ configuration has a band gap because of the energy difference between the fully occupied t₉g⁰ and the empty e_g⁰ levels; effect due to the splitting of 3d-shells in the crystal-field. A similar thing occurs between the fully occupied valence band in the HS t₉g₉e_g⁰ and the conduction band. However, for IS t₉g₉e_g⁰ configurations, the degenerate and semi-occupied 3d-shells form metallic bands.

Figure 1. Top: density of states (DOS) versus energy in eV. Bottom: Spin density isosurfaces (0.03 e/Å³) have been realized using VESTA.
The FM ½ LS + ½ HS ordering is slightly more stable than the AFM configuration, and above 120 K entropy disorders the spins. These structures accessible at 300 K present cooperative Jahn-Teller type distortions with ~5% of maximum deviation between the average experimental distances and the calculated ones. Both LS and HS Co\(^{3+}\) atoms show localization of spin density within the 3d-metal and 2p-oxygen orbitals. This suggests the presence of a mixed valence occupations and enhanced 3d-2p hybridization with the increment of on-site magnetism. Overall, the electrocatalytic activity of LaCoO\(_3\) observed at room temperature is at least initially restricted by the limited charge conductivity.

The participation of the AB-orbitals. The on-site QSEI observed at room temperature is at least initially restricted by the limited charge conductivity. 

SRCoO\(_{3.5}\) is a FM conductor (\(T_C = 305\) K) with a total magnetization of ~2.5\(\mu_B\) per octahedral shell\(^{44}\) and a percentage of oxygen vacancies typical of Co\(^{4+}\) oxides\(^5\). Calculations on the SrCoO\(_2\) and SrCoO\(_{2.75}\) stoichiometries result in FM metallic ground states with a total spin of ~2.5\(\mu_B\) within Co-O bonds, in perfect agreement with experimental data. Fig. 3 shows the conduction band constituted by the frontier \(t_2g\)-2p and \(e_g\)-2p orbitals, for the majority and minority of spin. The on-site QSEI in the open-shells are crucial to investigate the correct electron paring and the partial population of the AB-orbitals. The alternate orientation pattern in the adjacent orthogonal atomic 3d-orbitals reduces the electronic repulsions, without JT elongations and instead with some short Co-O bonds of 1.83 Å. A hypothetical AFM configuration, about 0.8 eV higher in energy from the FM configuration, recovers the JT distortions, with an elongation of some Co-O bonds to about 1.93 Å.

The admirable agreement between the GGA+U calculations and the experimental structural, electronic and magnetic properties for the two oxidation extremes, LaCoO\(_3\) and SrCoO\(_{3.5}\), indicates a high degree of confidence in the comparison with the following stoichiometries: La\(_{0.8}\)Sr\(_{0.2}\)CoO\(_3\); La\(_{0.5}\)Sr\(_{0.5}\)CoO\(_3\), La\(_{0.25}\)Sr\(_{0.75}\)CoO\(_{3.5}\) and La\(_{0.25}\)Sr\(_{0.75}\)CoO\(_{3.5}\)Fe\(_{0.25}\)O\(_{3.5}\).

All the compositions in the La\(_{1-x}\)Sr\(_{x}\)CoO\(_{3.5}\) family are extended FM gapless conductors apart from LaCoO\(_{3.5}\), p-type semi-conductor. In their ground-states, the AB-eigenvectors show a concomitant increment of the 3d-2p hybridization with the magnetization, which is maximum in SrCoO\(_3\) (Fig. 3 and 4). The participation of the 2p-orbitals of the ligands in the AB-shell at the conduction band increases with the number of Fermi holes. The relative number of t\(_{2g}\)-2p electrons with minority spin decreases with the increasing oxidation states, and the magnetic density in the Co-O bonds growths, favoured by the QSEI.

FIG. 2. Top: density of states (DOS) versus energy in eV. Bottom: spin density for the Co\(^{3+}\) atoms in the two ½ LS + ½ HS accessible configurations of LaCoO\(_3\) at 110 K < T < 350 K; a) FM ½ LS + ½ HS, b) AFM ½ LS + ½ HS. Different colours for the spin density on the cobalt atoms indicate a relative change in the orientation of the spins.

FIG. 3. Frontier orbitals in the ground state of SrCoO\(_2\). a) t\(_{2g}\)-2p (yellow), b) e\(_g\)-2p (blue) and c) density of states, DOS.

FIG. 4. Experimental and predicted, obtained using Eq. 1, relative OER intrinsic activity for the \(La_1SrCoO_{3.5}\) family with respect to LaCoO\(_3\), in alkaline media. It indicates that increasing FM in the G.S. seems inherent to the OER activity in cobalt-based oxides.

Fig. 4 shows the trend of the accumulated FM spin-moment in Co-O bonds (in the ground state) versus the experimental relative intrinsic OER activity\(^6\); we could have also used only the spin-density on the oxygen atoms (\(\mu_{FM}^{O})\). The electronic structure of La\(_{0.25}\)Sr\(_{0.75}\)Co\(_{0.75}\)Fe\(_{0.25}\)O\(_{3.5}\) shows that this material possesses the same overall average magnetization as SrCoO\(_{3.5}\). The presence of Fe ions increases the magnetism due to their own t\(_{2g}\)-2e\(_{g}\) shells, while the spin-polarization overall decreases on the Co-O AB-orbitals. Overall La\(_{0.25}\)Sr\(_{0.75}\)Co\(_{0.75}\)Fe\(_{0.25}\)O\(_{3.5}\) has less FM ligand holes, this explains that iron atoms serve to increase the stability of the Co\(^{4+}\) oxides, but not the intrinsic OER activity. The trend shown in Fig. 4 is mathematically expressed by Eq. 1, that is derived from Eq. 3 by assuming that \(\Delta H_{act,1}^{(O)} \approx \Delta H_{act,2}^{(O)}\). For the \(La_1SrCoO_{3.5}\) family, \(\Delta \mu_{cat}^{OER, QSEI}\) gives almost a quantitative prediction of the relative OER activity. The composition with the highest OER activity has a maximum \(\mu_{cat}^{OER}\) value. The validity of this derivation should

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serve to compare the relative intrinsic OER activity of different structures and 3d-metals by using $\mu_{0}^{\text{FM}}$.

$$\text{Eq. 1} \quad k_{\text{Relative.OER}}^{\text{QSEI}} = e^{\frac{\Delta H_{\text{cat}}^{\text{QSEI}}}{k_{\text{B}}T}} \cdot \mu_{0}^{\text{FM}}.$$  

The enthalpy of any chemical event mainly depends upon three kinds of energy terms, Eq. 2. In magnetic catalysts, the additional non-classical QSEI$_{\text{open-shell}}$, $\Delta \text{Exc}_{\text{e}}^{\text{QSEI.open-shells}}$, $\Delta J_{\text{QSEI}}$, are part of the stabilizing potentials, and relatively as higher is their value smaller are the Coulomb terms.

$$\text{Eq. 2} \quad \Delta H_{\text{cat}} = \Delta H_{\text{kinetic}}^{\text{FM}} + \Delta \text{J}_{\text{QSEI}} + \Delta \text{Exc}_{\text{open-shells}}^{\text{QSEI}}.$$  

Cooperative QSEI$_{\text{open-shell}}$ are indispensable to understand magnetic catalysts, since spin-potentials are responsible of the electronic conductivity and important in the orbital interactions, but how much? Limiting our study to the formation triplet $O_2$. Fig. 5 shows the thermodynamic steps of two possible mechanisms over a SrCoO$_{3-\delta}$ (001) surface for oxygen evolution. We compare between hypothetical close-shell (non-spin-polarized) calculations (Fig. 5 top) and the open-shell spin-polarized mechanisms (Fig. 5 bottom). OSEI reduce the energy of open-shells by a contribution of around 3±0.5 eV; this is not a trivial value. The kinetic is also significantly improved in the spin-polarized calculations, the activation barriers and the adsorption energies decrease considerably between 15% and 35% in comparison with the fictitious close-shell system. The initial surface formation of an O-O bond has an activation energy of $\approx$0.75 eV in the non-spin-polarized calculations. Fig. 5 is in agreement with the specialized GGA+U literature. Moreover, calculations reveal structural discrepancies between close-shell and open shells calculations, for instance M-O bond distances vary by $\pm$0.1 Å.

We considered two possible pathways for O-O coupling (centre-to-left and centre-to-right): calculations of a classical surface mechanism go from the centre to the right; and a sub-surface pathway is from the centre to the left. The surface mechanism is more favourable mainly due to the restricted mobility of sub-surface O-O* units. Our observations are in line with the work of Mefford and co-workers: the group noticed the presence of bulk oxygen mobility in OER on SrCoO$_{3-\delta}$ catalysts. It is also consistent with the role of lattice oxygen in the computational work of Yoo and co-workers.

The peculiar property of the highly oxidised mixed-valence SrCoO$_{3-\delta}$ composition is the ability to insert nucleophilic lattice oxygen towards the formation of O$_2^*$, which after desorption, leaves concomitant oxygen vacancies. These mobile vacancies can be rapidly occupied by oxygen atoms through the diffusion of bulk atoms and by gas phase intermediates, alike. This phenomenon creates a high turnover in the numbers of the active centres at the surface. Then excellent OER activities seem associated with an overall Mars-van Krevelen type mechanism that is characteristic of total oxidations.

We already knew that coupled mixed-valence spin orbiters (or donors), showing preferential FM interactions in the partially occupied $AB e_g$-$2p$ orbitals, are good conductors and excellent oxygen spintro-catalysts. Furthermore, prototypical oxides for OER are those structures with metals in a high oxidation state, and then sufficiently electronegative. Eq. 3 correlates the overall activation energy of FM catalysts with the specific influence of QSEI$_{\text{open-shell}}$, added via a Heisenberg type exchange term.
Eq. 3 means that $3d-2p$ hybridization and magnetization of the AB-eigenvectors, $\mu_{\text{cat.}} = P_{3d} + P_{2p}$, is an important design factor in every technology involving oxygen production and evolution. Eq. 3 also explains that the trends for $3d$-metals do not follow the simple parabolic behaviours postulated by band theory. For instance, Mott insulators governed by antiferromagnetic (AFM) superexchange interactions are less active oxygen electro-catalysts indicating $\Delta_{\text{act. st}} F_{\text{M.E.C.}} \cdot P_{\text{AFM}} > 0$. Magnetism is not a simple catalytic descriptor, on the contrary, it reflects multiple interrelated electronic properties. These factors are spin-dependent charge conductivity, oxidation state, ligand holes, intermediate bonding, reduction of the electronic repulsions. Since the nature of the magnetic coupling (whether AFM or FM) is related to electrostatic potentials, covalency and electron occupancy, spin-potentials strongly influence OER activity, and provide a physical sense to the statistical evaluation of descriptors done in the group of Shao-Horn. In comparison with other theoretical descriptors in oxygen electrocatalysis, the recent calculations by Tripkovic and co-workers on the series LaMO$_3$ ($M = Cr, Mn, Fe, Co, Ni$) show the ineffectiveness of trying to differentiate the electrocatalytic activities of magnetic systems simply from the binding energies of species like $O^*$ and $OH^*$. We report the suitability of the GGA+U method in the description of the electronic structure of La$_{1-x}$Sr$_x$Fe$_3$O$_{2.5}$ compositions; what it is not a surprise since GGA+U is a well-established approach to try to capture the physics of strongly correlated catalysts. Computational studies on correlated oxides without Hubbard corrections are more in error when calculating reactions. In addition, if spin polarization is not even included on magnetic oxides the reported values are too inaccurate, which lead to multiple errors like the overestimation of the activity of insulating materials.

Conclusions

Are quantum spin exchange interactions a fundamental electronic factor in the catalytic activity of magnetic oxides? Yes, they are. We have seen that the inter-atomic magnetic moment accumulated in the bonds of Co-based perovskites relates with charge conductivity, Fermi holes in the ligands, spin-selection and moderate binding energies. Consequently, $QSE_{\text{open}}$-shells are indispensable to understand the behaviour of magnetic materials, and for determining their electrocatalytic activity and selectivity. Expected conclusion considering that are materials of interest in spintrons.

The increment of oxidation state for Co from LaCo$_{0.95}$O$_{2.5}$ to SrCoO$_{2.5}$ induces an improvement of O$_2$ release, in addition to good spin-conductivity, consequently an enhancement of the OER activity indicated by maximum $\mu_{\text{cat.}} ^{\text{FM}}$ and $P_{\text{FM}}$. In the highly active SrCoO$_{2.5}$, the initial formation of the O-O bond is governed by spin-transfer from the ligands to the electronegative metal atoms (Co), in a mechanism guided by $QSE_{\text{open}}$-shells.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

Syngaschem BV and MagnetoCat SL gratefully acknowledge significant funding from Synfuels China Technology, Co, Ltd, Beijing-Huairou. CB and JG acknowledge and thank the Servei D’Informatica and the University Jaume I for the provision of the computational resources and Prof. Armando Beltrán Flors of the Quimica Teorica y Computacional group for the useful training.

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