Spin Polarization in Dual Catalysts for The Oxygen Evolution and Reduction Reactions

Jose Gracia,[a],* Mauro Fianchini,[a] Chiara Biz,[a,b] Victor Polo,[c] Roberto Gómez[d]

a) MagnetoCat SL, General Polavieja 9 3I, 03012 Alicante, Spain.

b) Universitat Jaume I, Av. Vicente Sos Baynat s/n, E-12071 Castellón de la Plana, Spain.

c) Departamento de Química Física and Instituto de Biocomputación y Física de Sistemas

Complejos (BIFI), Universidad de Zaragoza, Zaragoza, Spain.

d) Departament de Química Física i Institut Universitari d'Electroquímica, Universitat d'Alacant, Ap. 99, E-03080 Alicante, Spain

** Email: jose.gracia@magnetocat.com*

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Abstract. The orbital physics relevant in electrocatalytic activity present subtle differencies between oxygen evolution (OER) and reduction reactions (ORR). Achieving maximum efficiency in (electro)catalysis requires a detailed understanding on the electronic interactions. Quantum correlations and, in particular, spin-exchange interactions are decisive to understand the necessary underlying physics. Besides adsorption energies of reaction intermediates, there are other critical factors to characterize electrocatalysts such as charge, spin and flow sense of the electron transport. A revolution is going on right now in the understanding of oxygen electrochemistry, meant to close the gap with the novel research in strongly correlated materials or spintronics and to re-establish general fundaments of catalysis. We present a concise review taking as central example the dual catalyst $LaNi_{0.8}Fe_{0.2}O_3$.

Introduction. The slowdown of global warming critically depends on the development of more efficient OER and ORR catalysts based on abundant and cheap metals.[1] Goodenough in 2015 showed the excellent dual catalytic activity of the magnetic oxide $LaNi_{0.8}Fe_{0.2}O_3$[2], an electrocatalyst more active in alkaline media than $LaNiO_3$, also proven an admirable dual catalyst.[3],[4] It is uncommon to simultaneously enhance both OER and ORR, therefore $LaNi_{0.8}Fe_{0.2}O_3$ is a case worth to analyse in detail. Actually, outstanding works, also authored by Goodenough, show that typically a good catalyst for OER is not ideal for ORR, even though they are opposite reactions.[3],[4] If optimum oxides for OER have a certain partial occupation of the anti-bonding frontier orbitals ($3d$-e_g electrons for metals in an octahedral MO_6 coordination), the corresponding efficient ORR catalysts have a higher degree of occupation of the valence band.

Complex oxides (as well as nitrides and sulphides) display several interesting activity peculiarities. Their catalytic activity versus the number of antibonding electrons shows at least a double-volcano plot ,[5] but popular non-correlated theoretical approximations, generally recognized as reasonably reliable for 4d and 5d metals, faultily predict single-volcano plots.[6],[7] Likewise, the finest experimental works prove that the number of anti-bonding d-electrons are key for activity. However, massive computational efforts still describe as active materials even alloys without d-electrons, like $SrSbO_3$ or $MgBaO_3$, erroneously projected as more active than $LaNiO_3$.[8] These discrepancies show that only by including properly electronic correlations one can learn why complex magnetic compositions like $LaNi_{0.8}Fe_{0.2}O_3$ can be such good dual catalysts.
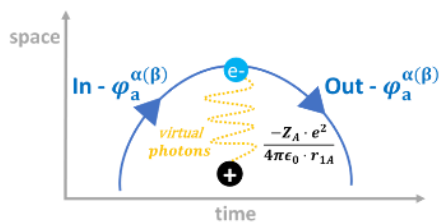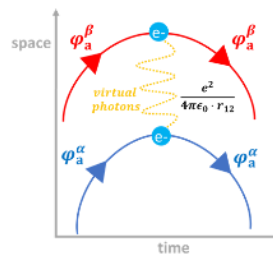
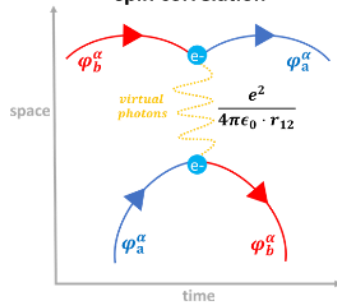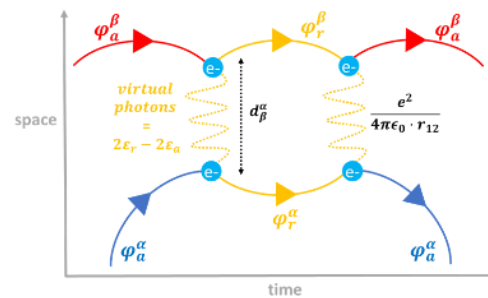**Figure 1**. *Feynman diagrams describing the electronic interactions in atomic orbitals. The time variable is in the X axis, while the space one is in the Y axis. The curved lines depict the space-time evolution of the electrons e.g. in the orbitals φ_a^α and φ_b^α . The lines are curved to represent the attractive quantized Coulomb potentials from nucleus. The arrows just indicate the direction of the space-time development.*

The space-time representation of the electronic interactions in atomic systems, see Fig. 1, are on top of the actual new developments.[9] To ultimately comprehend catalysis, we must essentially answer Robert S. Mulliken: "What are the Electrons Really Doing in Molecules?": quantum correlations are stabilizing mechanisms that reduce the electronic Coulomb repulsions.[9] They can be divided into two general kinds, spin-exchange (QSEI) and multiconfigurational-excitation interactions (QEXI). Both can be described as space-time mechanisms to avoid electrons being too close in their movement in orbitals, thus moderating their repulsion. Since quantum mechanics escapes from the classical intuition, it is difficult to imagine or have an awareness of electronic interactions. Space-time diagrams greatly help to understand correlation interactions. Two electrons with the same spin have the possibility of exchanging their respective orbitals *via* QSEI, thus avoiding each other. QEXI is then available for electrons with different spin, and it is based on the temporary excitation of the electrons to larger empty orbitals, thus again impeding them to be too close.
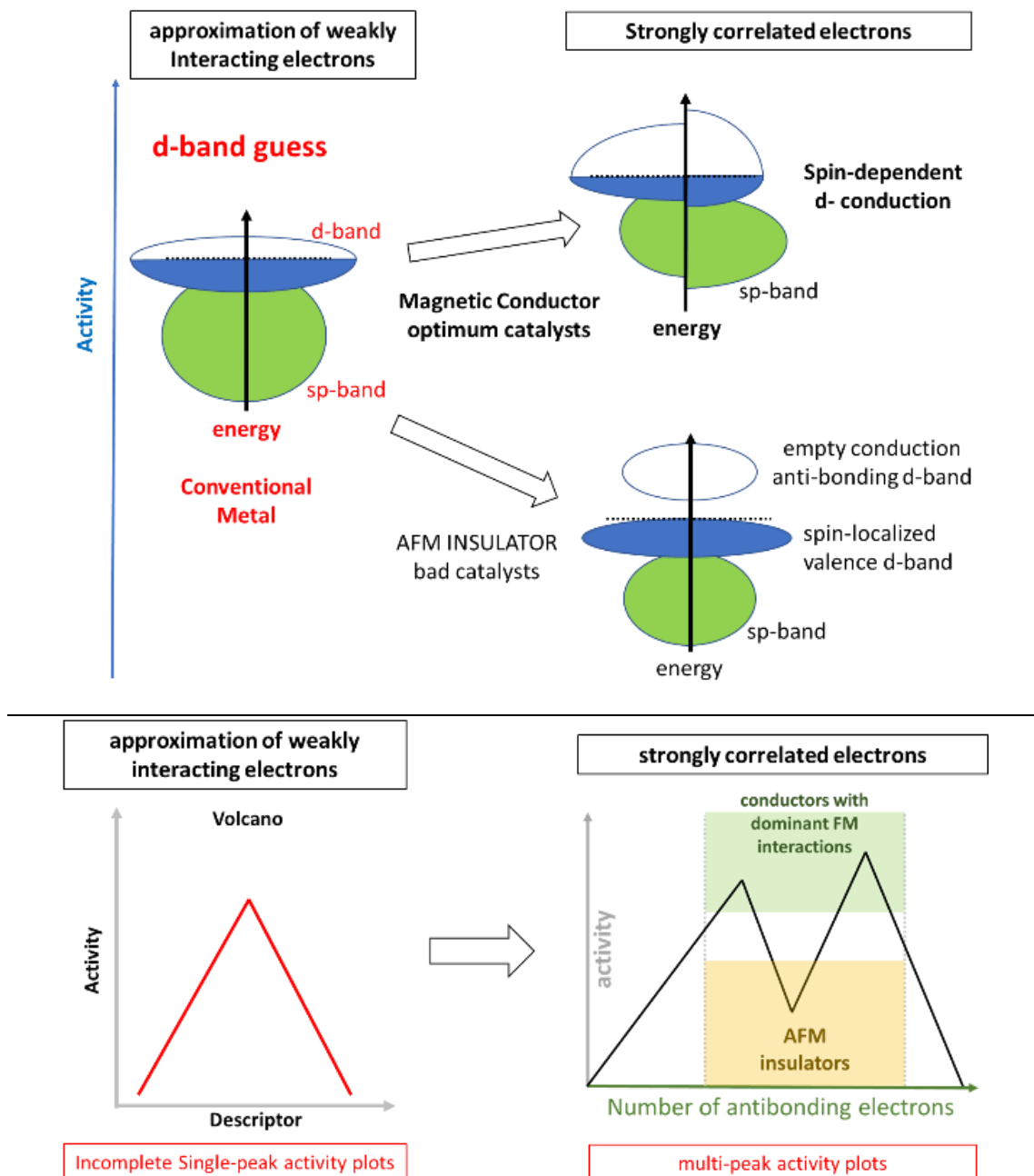
Figure 2. *Comparison of the d-band model versus a correlated model in catalysis. Top) Types of density of states useful to understand changes in the overall electronic structure. Bottom) Possibility of multipeak activity plots due to abrupt oscillation of the properties with the orbital occupation for strongly correlated catalysts*.

Fig. 2 shows a comparative summary of the most characteristic effects introduced by quantum correlations in heterogenous catalysis. Three basic electronic structures (among others) for catalysts are those of a conventional metal or insulator, an antiferromagnetic (AFM) insulator and a spin-polarized metal. The huge possible oscillations in the electronic properties, reflected in the density of states, is actually

the origin of multipeak activity versus orbital occupation plots for strongly correlated catalysts.[7] These effects will be analysed for $LaNi_{1-x}Fe_xO_3$ (x = 0, 0.2, 1) materials in order to clarify their dual catalytic activity.
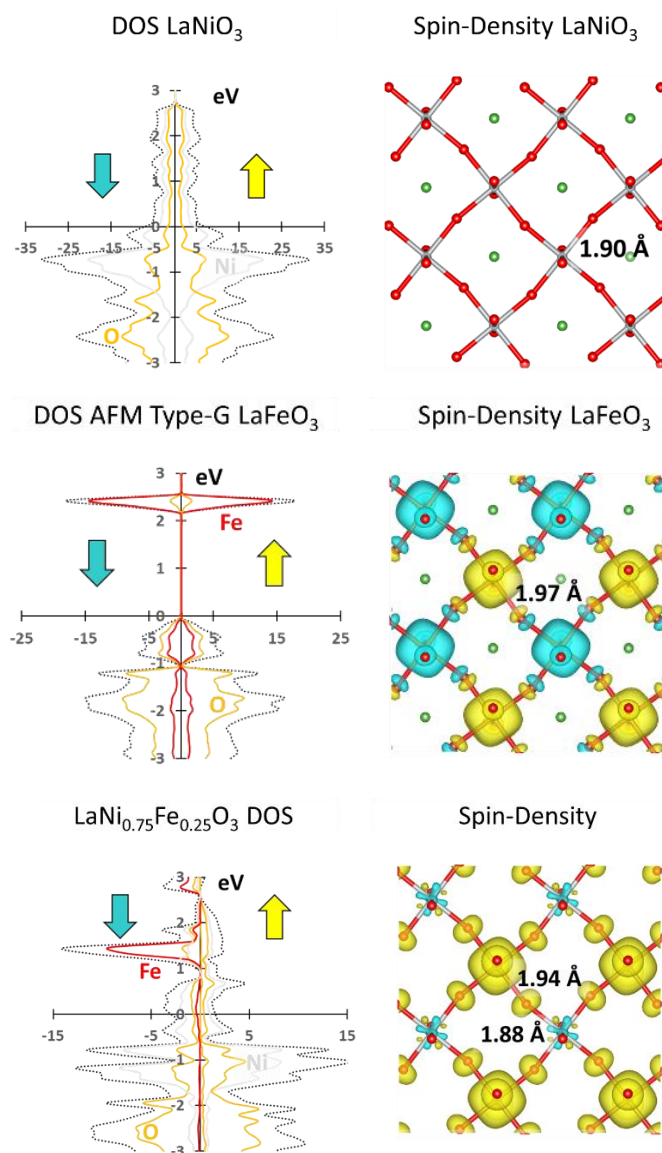
Figure 3. *Left)* Density of states (DOS) and *Right)* spin-density for the most stable electronic state for *Top)* LaNiO₃, *Middle)* LaFeO₃ and *Bottom)* LaNi₀.₇₅Fe₀.₂₅O₃.

LaNiO₃. LaNiO₃ is a non-magnetic OER and ORR dual catalyst, with a density of states (DOS) typical of conventional metals, Fig. 3 top. All the electrons are paired in the $t_{2g}^6 e_g^1 \uparrow\downarrow -O-\uparrow\downarrow e_g^1 t_{2g}^6$ Ni-O-Ni bonds. The full population of the t_{2g}^6 orbitals plus one electron in the e_g^1 anti-bonding orbital moderates the adsorption energies of reactants

and creates a metallic conduction band.[10] The Ni-O = 1.90 Å bonds are neither too short nor too long.[11] Outcome overall dual activity, however, still results suboptimal.

LaFeO₃. LaFeO₃ is a poor OER and ORR catalyst;[12],[13] because of the High-Spin (HS) $Fe^{3+}: t_{2g}^3 e_g^2$ configuration with all the 3d-like orbitals half-filled. The intra-atomically spin-aligned interactions dictate at the same time inter-atomic omnidirectional antiferromagnetic (AFM) Fe-O-Fe super-exchange interactions.[14] As far as we know, all the $A^{3+}Fe^{3+}O_3$ perovskites are Type-G antiferromagnetic insulators (Fig. 2), immediately labelled as bad-electrocatalysts: why? because charge transport , relevant in electrocatalysis[15], it is also spin transport.[16] Related with previous factors, the long Fe-O bond lengths (1.97 Å) indicate significant electronic repulsions, because of the strongly localized Fermi heaps associated with the dominant AFM couplings.[17]

LaNi₀.₈Fe₀.₂O₃. The finest OER and ORR catalysts are strongly correlated electronic materials with partially populated antibonding 3d orbitals, like LaNi₀.₈Fe₀.₂O₃, but also keeping excellent spin-conductivity, or delocalised Fermi holes.[18] Fig. 2 shows the spin-density of LaNi₀.₈Fe₀.₂O₃: FM QSEI stabilize the electrons in the catalysts leading to a situation of "magnetic nobility". Essentially Fermi holes combined with mobile spin-polarized electrons, stabilized by dominant inter-atomic FM QSEI, enhance the activity, in excellent agreement with the spin-rules in catalysis.[10]

Structural alterations[19] are the consequence, rather than the origin of the activity. Two types of active sites appear in LaNi₀.₈Fe₀.₂O₃, immersed in the spin conductive crystal field. Longer Fe-O bond lengths (1.94 Å) are prone to ORR,[11] associated with electron-rich high-spin configuration $Fe^{3.\delta+}(t_{2g}^3 e_g^{1.\delta})$ further indication of ORR selectivity.[10] On the other hand, the shorter Ni-O bond lengths (1.88 Å) are prone to OER, [11] associated with spin-polarized oxygen atoms and $Ni^{2.\delta+}(t_{2g}^6 e_g^{1.\delta})$, configuration richer in holes in the highest occupied valence band and further indication of OER selectivity.[10]

Other aspects. From an experimental point of view, specific experiments need to be designed to pinpoint the influence of spin-dependent interactions in defining

electrocatalytic activity. Undoubtedly, working with families of oxides should allow both to detect stoichiometries leading to efficient OER and ORR electrocatalysis, and to contrast the results with computational insights (DFT). Another strategy that should be explored is that of working with ferrimagnetic electrocatalysts to which external magnetic fields are applied during film formation from pre-synthesized particles to achieve magnetization and spin orientation. The effects of magnetization should be apparent if spin electrochemistry is a central topic to be developed in coming years. Very recent results point in this direction.[20]

Conventional electrochemical experiments should be complemented by experiments performed in the presence of an external magnetic field. In such a case, the design of these experiments should allow to distinguish the actual enhancement of carrier transport and transfer from other effects induced by the magnetic field, comprising those linked to magnetohydrodynamics. The separate contribution of both aspects has been recently highlighted in a seminal work on the enhancement of the OER in the case of Co_3O_4 electrodes.[21] Therefore, the conditions of electrochemical reactions should be properly chosen to make sure that the process is not transport-limited and that the generation of gas bubbles is limited. In the case of the oxygen evolution reaction, the effects of spin correlation should be preferably observed as a diminution of the overpotentials needed at low current densities, because under these conditions the kinetics of the overall process is controlled by charge transfer.

It should be emphasized that the interpretation of the electrocatalytic activity for the ORR and OER processes on ternary oxides and hydroxydes (among others) often overlooks the possible contribution of spin-dependent interactions, even when they could become critical in the interpretation of the experimental results. For instance, one of us has been working on the enhancement that doping with phosphorus induces on nickel ferrite electrodes for the OER. In particular, it has been found that the effect of phosphorus strongly depends on the stoichiometry of the resulting oxide.[22] The interpretation of these results could be enriched by considering spin electrochemistry. Likewise, careful studies have been performed to understand the effect of the formation of Ni-O-Fe and Ni-O-Co units in layered metal hydroxides prepared with different procedures to achieve a good control the formation of these structures.[23]

The incorporation of the ideas delineated here in the understanding of the observed trends is expected to be central. More research along these lines is worthwhile and it is under way in our laboratories.

Finally, we believe that it is worth mentioning the influence of spin-dependent interactions and that of external magnetic fields on the photoelectrochemical water oxidation process (photogeneration of oxygen). These is a complex process for which a complete theoretical picture is not available yet. Besides all the aspects mentioned above, one should realize that electrons (actually, holes) are transferred to (from) a solid excited electronically through inter_band photon absorption. This opens the possibility of designing experiments with light and magnetic field management allowing for achieving spin polarization and analyzing its effect on photoelectrocatalysis. A few studies can be found in the literature showing a clear enhancement of the photoelectrochemical OER in the presence of an external magnetic field. Intriguingly such an effect has been found not only in magnetic materials such as $CoFe_2O_4$,[24] but also in other materials such as hematite or $BiVO_4$.[25] In this case, as the typical photocurrents are low, magnetohydrodynamical effects are likely absent.

Conclusions. As Dagotto perfectly explains, the collective state of strongly correlated catalysts cannot be understood based on the one-electron (or one-quasiparticle) approximation, even if fully quantum mechanical.[26],[27] We can already appreciate why the need for a theoretical electrocatalytic model that goes beyond the d-band approximation (and derived models). No other choice seems available, but incorporating properly quantum correlations, as we learned from the works in related fields like spintronics.[28],[29] Spin-rules in catalysis define the optimum compositions for the most important life-supporting reactions on Earth.[10]. It is critical to check whether these ideas may be extended to rationalize electrochemical processes, thus setting a firm basis for the establishment of spin electrochemistry. This subject indeed merits further perusal because of its fundamental new general principles and relevant applications.

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