Perovskite oxides as an opportunity to systematically study the Electrooxidation of alcohols and Polyols on materials based on abundant elements: Learning from the experience using pure metals and metallic oxides in (Electro-)catalysis.

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ABSTRACT: The cost-effective production of green hydrogen is one of the most important challenges for a sustainable energy transition. To decrease the cost in the production of hydrogen through electrolysis, there are several obstacles that must be overcome. For instance, more active and stable anodes made of abundant and cheap materials will contribute to lowering the capital and operational expenditure of the process. It is well-known that the oxidation of water requires high overpotentials, which is the main limitation for the performance of the device. In this context, we believe that substituting the oxidation of water (OER) at the anode of electrolyzers by the oxidation of biomass-derived substances could contribute to the overall process by decreasing the power input of the devices and, in some cases, by producing value-added chemicals.

Herein, we re-visited some of the most important fundamental aspects of the (electro-)oxidation of alcohols and polyols on metal-based catalysts, focusing on reaction descriptors. Then, we moved to the (electro-)oxidation of these molecules on metal oxides, re-visiting some of the literature about their application in heterogeneous catalysis and for OER, to get insights about the relation of the structure of the materials and their activity.

Due to the lack of fundamental knowledge about the electro-oxidation of alcohols and polyols on metallic oxides and to the vast literature about the use of perovskite oxides for OER, we propose to start systematic studies using perovskite oxides for the electrooxidation of alcohols and polyols. We believe that fundamental studies in this topic would permit the establishment of reaction descriptors, speeding up the searching for suitable materials for this reaction and paving the way for a most cost-effective production of green hydrogen.

KEYWORDS: (Electro-)oxidation reaction, CO, Alcohols, Polyols, Reaction descriptors, Perovskite oxides

1. INTRODUCTION

Pollution, global warming, and their consequences for the society are increasing the opportunities for bio-based economies[1]. Thus, there are several abundant and cheap biomass-derived resources such as glycerol[2], ethanol[3], furfural[4], glucose[5] and several valuable bio-based acids like levulinic acid, succinic acid, and acrylic acid[6] that can be used to produce fine chemicals for different industries[7,8]. In this context, electrochemistry emerges as an attractive alternative to produce chemicals derived from the electrochemical oxidation of these resources. Besides, concomitantly to this oxidation, energy (in fuel cells)[9,10] or high purity hydrogen (in electrolyzers)[11,12,13,14] can be obtained. Hydrogen will probably become the most important energy carrier of this century in several developed countries, pushed up by the exponential growth of the hydrogen fuel cells (H_2FC) market[1,15,16] and the increasing demand of this molecule to produce important industrial chemicals like ammonia[17]. Thus, electrolysis is expected to become a central player in a hydrogen-based economy, as it is the most suitable method to produce high purity hydrogen, required in several applications, such as in PEM (Proton Exchange Membrane) fuel cells. Besides, with the rapid expansion of the solar energy in several countries and the concerns about global warming, this would be a promising alternative to the conventional hydrogen production through natural gas reforming[18].

1.1 BIOMASS-DERIVED RESOURCES IN ELECTROLYZERS

In an electrolyzer, both the anode and the cathode are fed with an alkaline or acid solution and receive an input of energy to drive the oxygen evolution reaction (OER: $2H_2O \longrightarrow 4e^- + 4H^+ + O_2$) at the anode and the hydrogen evolution reaction (HER: $2H^+ + 2e^- \rightarrow H_2$) at the cathode[19]. The standard potential for the hydrogen reduction/oxidation reaction is 0 V and the standard potential for the OER of water is 1.23 V. Thus, the minimum potential necessary to run an electrolyzer is 1.23 V (figure 1). The overpotentials applied depends on the kind of technology and on the application[20], for instance, 1.8–2.4 V are applied in alkaline electrolyzers to attain currents of 0.2-0.4 Acm^{-2} and of 1.7 V in PEM electrolyzers to attain currents of 1 Acm^{-2}. Unfortunately, all the catalyst requires extra-energy input for the OER[20], which highly increases the production cost of the hydrogen and impacts the stability of some components of the device[21].

An interesting alternative to overcome this problem is to substitute the water by solutions of several organic molecules derived from biomass, since the standard potentials for the complete electrooxidation of these molecules are much lower [11,22]. For example, substituting the oxidation of water by the oxidation of glycerol (a polyol, $C_3H_8O_3$) can reduce the minimum potential input to run the electrolyzer by approximately 1 V (Figure 1), which would be a substantial energy saving.

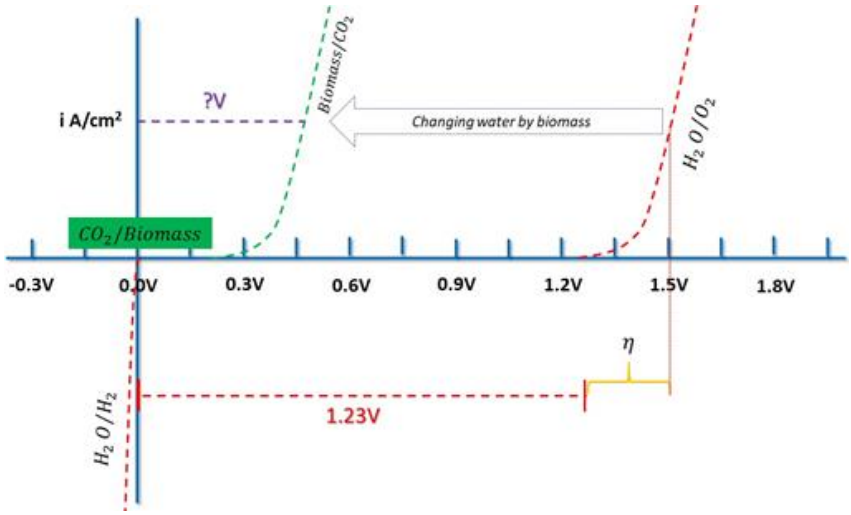


Figure 1. Important reactions and electrochemical parameters for low temperature electrolyzers. All the electrochemical potentials are referenced to the RHE. In this scheme, the oxidation of water starts at 1.23 V (curve in red) and the current follows the Butler-Volmer relation between current density and potential. To run the device at a current of "i A/cm^2" the potential at the anode must be equal to 1.23V + η. The hydrogen reaction can be driven relatively close to the reversible potential, but requires an expensive catalyst such as Pt. The green rectangle shows a range of standard potentials for the complete oxidation of several small organic molecules. We have also inserted an arbitrary current-potential curve for the oxidation of an organic molecule (in green). An arrow shows how the potential input required to run the electrolyzer could hypothetically decrease by ~1 V by changing the electrooxidation of water by the electrooxidation of a biomass-derived molecule.

This idea has been successfully tested using several small organic molecules and biomass-derivatives (methanol, ethanol, glucose, oligomers, etc.)[23] using noble metal-based nanomaterials, which are expensive and scarce[24]. In this context, several earth-abundant and cheaper materials have been investigated as a substitute for the noble metals, unfortunately with still limited success due to several factors, namely: poor catalyst stability[25], relatively high overpotential[26,27,28] and lack of selectivity towards the desired product[26,29].

Perovskite oxides are versatile materials that can be synthesized through several techniques[30], using earth-abundant elements[30], with control of particle size and shape in the nanoscale regime[31]. These materials have been extensively used to catalyze OER, from water oxidation, in basic solution[32] and SOFC (solid oxide fuel cell) applications (at temperatures higher than 600°C)[33]. However, as we will show in this article, there are just a few contributions exploring these materials for the oxidation of organic molecules at low temperatures (lower than 100°C) and most of them are related to the MEOR (methanol electrooxidation reaction). Herein, we review the most important mechanistic aspects and results of the (electro)oxidation of CO, alcohols and polyols on metals and metallic oxides surfaces. When possible, we discuss the results in terms of activity descriptors, and hypothesize about the key mechanistic aspects (and descriptors) of the electrooxidation of alcohols and polyols on perovskite oxides. Therefore, the aim of this article, instead of being a revision about the electrooxidation of alcohols/polyols on perovskite oxides, is to encourage our colleagues to start developing systematic studies in this topic and put together some valuable information to facilitate this process, avoiding a complete random process of searching for active, selective, and durable materials for the application.

1.2 THERMODYNAMICS OF KEY PROCESS

Figure 1 illustrates the significant diminution of the standard open circuit potential for an electrolyzer when the oxidation of water is substituted by the oxidation of a small organic molecule. The complete oxidation of any alkyl alcohol (containing only one -OH group) to CO_2 can be generalized as shown in equation 1.

$$C_nH_{2n+1}OH \text{ (liq)} + (2n-1)\, H_2O \text{ (liq)} = nCO_2 \text{ (gas)} + 3n\, H_2 \text{ (gas)} \qquad [1]$$

The standard Gibbs free energy (ΔG_r°) and the corresponding standard potential (E_r°) of the reaction can be calculated by equations 2 and 3:

$$\Delta G_r^\circ = n\, \Delta G_f^{CO_2} + 3n\, \Delta G_f^{H_2} - (2n-1)\, \Delta G_f^{H_2O} - \Delta G_f^{C_nH_{2n+1}OH} \qquad [2]$$

$$E_r^\circ = \frac{\Delta G_r^\circ}{nF} \qquad [3]$$

where F is the Faraday constant. Table 1 shows values of the standard potential for the complete oxidation of methanol and ethanol calculated using equations 1 to 3. We have also calculated E_r° for the partial oxidation of the alcohols and for the partial and complete oxidation of glycerol. All the reactions, equations and calculations can be found in the supporting information (SI).

Table 1: Standard potential for the partial and complete oxidation of alcohols and polyols and number of electrons involved. Most standard Gibbs free energies of formation can be found elsewhere[34].

Alcohol	Product	E^0 (V)	n
Methanol (H_3COH)	CO_2	0.016	6
Methanol (H_3COH)	Formic acid (HCOOH)	0.109	4
Methanol (H_3COH)	Formaldehyde (H_2CO)	0.332	2
Ethanol (H_3CH_2COH)	CO_2	0.084	12
Ethanol (H_3CH_2COH)	Acetic acid (H_3CCOOH)	0.057	4
Ethanol (H_3CH_2COH)	Acetaldehyde (H_3CHCO)	0.245	2
Ethanol (H_3CH_2COH)	Oxalic acid (COOHCOOH)	0.195	10
Glycerol ($C_3H_8O_3$)	CO_2	0.004	14
Glycerol ($C_3H_8O_3$)	Formic acid (HCOOH)	0.135	8
Glycerol ($C_3H_8O_3$)	Glyceraldehyde[35] ($C_3H_6O_3$)	0.401	2
Glycerol ($C_3H_8O_3$)	Glyceric acid ($C_3H_6O_4$)	0.086	4

For all the reactions, the values of E_r° are much lower for methanol, ethanol and glycerol oxidation compared to water (Table 1). However, it is important to notice that, except when the oxidation of the alcohol leads to the corresponding aldehyde, the electrooxidation of alcohols and polyols requires the transference of several electrons, involving many reaction intermediates. The existence of several reaction intermediates, some of them binding to the catalysts in similar ways to the alcohol/polyol, impose severe thermodynamic restrictions to these reactions due to the so-called scaling relationships[36–38]. For example, materials that have strong affinity for the alcohols and catalyze their de-hydrogenation steps, also bind CO (and other partially de-hydrogenated species) too strongly (Pt, Rh, etc.), being surfaces that ends suffering from poisoning. Therefore, the main output of this discussion is that even though it is relevant to know the standard potential of the reactions, to optimize a catalyst for the (electro)chemical oxidation of alcohols and polyols in a rational way, it is important to consider the "intrinsic" overpotential generated by the sometimes-unavoidable scaling relationships. Finally, it is worth to know that while we can calculate the equilibrium electrochemical potential only by knowing the reactant and product, the overpotentials can be estimated only if we know the reaction mechanisms and the catalyst structure, i.e., if we have information about the key reaction intermediates on the surface of interest.

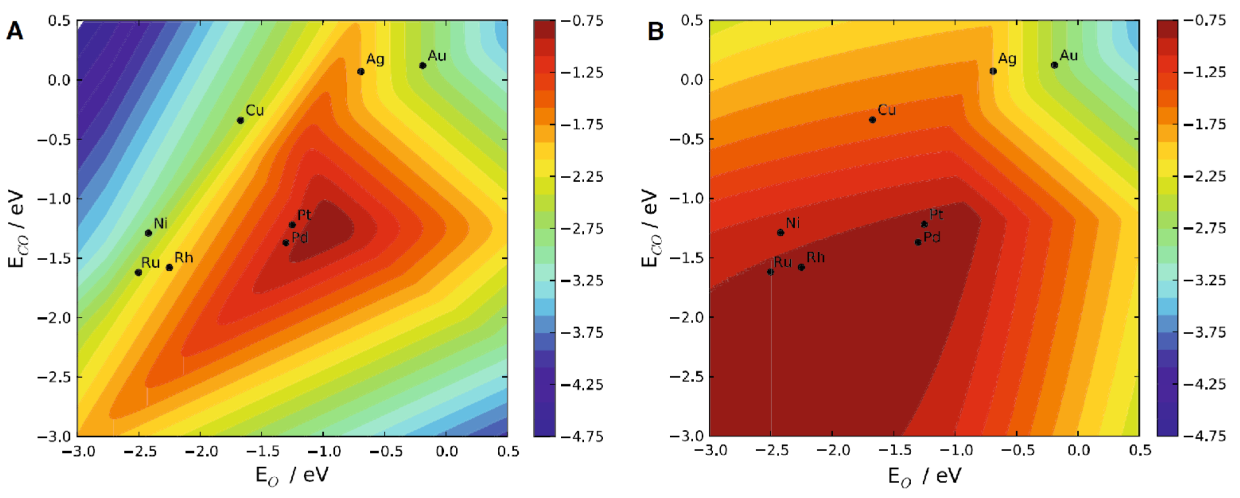
2. (ELECTRO)OXIDATION OF ALCOHOLS AND POLYOLS ON METALS

Although CO is not a candidate to feed anodes of electrolyzers, it is present as a poisoning intermediate in the oxidation of most of the organic molecules[39,40]. We will see soon that the electrooxidation of small organic molecules can proceed through a direct or an indirect pathway, i.e., with or without the participation of CO as intermediate, respectively[41,42]. This distinction between direct and indirect pathways arises as this intermediate is highly poisoning for some metals, and it is important to tune the materials properties to enhance the CO oxidation rate or to hinder this pathway. The fundamentals of the (electro)oxidation of CO on metals is by far the most studied system in the literature, permitting us to discuss important aspects of the effect of intermediates/poisoning species in a (electro-)chemical reaction and introduce important mechanistic concepts. Besides, it is important to note that in some experimental conditions (high enough O_2 pressures and temperatures or high enough electrochemical potentials, if we are discussing results in the field of heterogeneous catalysis or electrochemistry, respectively) the metals are completely covered by the corresponding metal oxide[43]. Therefore, we believe that the concepts/results discussed here will be useful to properly interpret/discuss systematic results obtained with perovskite oxides used for the electrooxidation of alcohols/polyols.

2.1 CARBON MONOXIDE (ELECTRO)OXIDATION ON METALS

The oxidation of CO has been extensively studied in Pt surfaces, due to the application of this metal in electrolyzers and fuel cells[44–47]. CO is also an important poison for H_2FC, since H_2 is mainly obtained from syngas, produced by catalytic reforming of natural gas[48], and contains CO traces that can seriously compromise the performance of the device.

In noble metal-based electrodes, the oxidation of CO is believed to occur through a Langmuir-Hinshelwood mechanism (L-H)[45,46]. DFT (density functional theory) experiments have contributed to the understanding of this reaction from a thermodynamic perspective. Nørskov *et al.*[49] used DTF to study CO oxidation at high temperatures on transition metals surfaces (Figure 2A and B). They found volcano-type relationships for the reaction rate as a function of the O and CO binding energies (Figure 2A). Interestingly, they found that the interaction between the adsorbates influences the activity of the catalysts, which is rarely considered in computational experiments due to the higher complexity and computational cost (Figure 2B). The complex, non-linear behavior, discussed by the authors on Pt(111) is a consequence of the interaction between the adsorbates and the different adsorption sites of the model surface. A rule of thumb is that the less coordinated the atom is, stronger the binding with the adsorbate[50]. The calculations showed that metals that bind adsorbates too strongly, such as Ni, Ru, Rh become more active when the interactions between adsorbates are considered, and this increases the complexity of the real problem since adsorbate coverages are affected by several parameters, such as particle size, temperature, concentrations, among others. As these materials bind the adsorbates too strongly, the repulsion between the adsorbed species decreases their stability, making the desorption easier.



Langmuir-Hinshelwood mechanism

It is a model for a bimolecular chemical reaction. Two reactants adsorb on a catalyst forming two adsorbed intermediates. Then the adsorbates react at the catalyst surface leading to product formation[51].

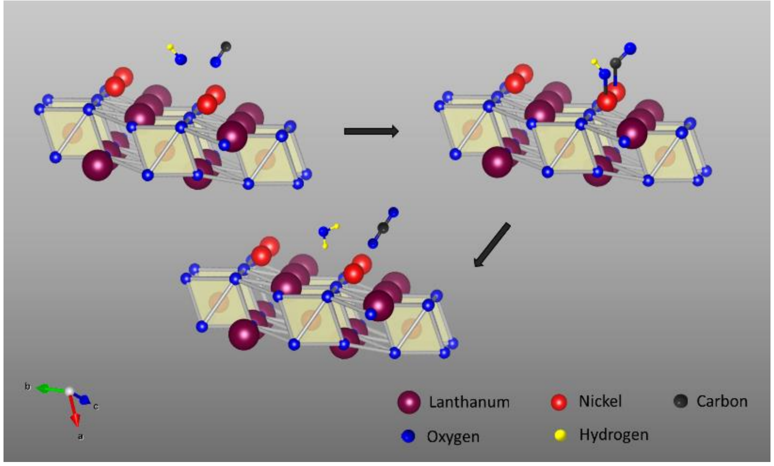


Figure 2. Contour plots of the CO oxidation activity under high-temperature conditions (T = 600 K, PO_2= 0:33 bar; P_{CO} = 0.67 bar, PCO_2=1 bar) as a function of the binding energies of O and CO with(A) adsorption energies independent of coverage and B) considering a coverage dependent binding energy. It is worth noticing how Ni, Ru and Rh have considerably moved closer to the volcano top. The figures were adapted from *Nørskov et al. for (111) fcc metals surfaces*[42]. (C) Proposition of a scheme for a hypothetical L-H mechanism for the oxidation of CO on a $LaNiO_3$ perovskite oxide. In the first step, CO and OH bind to neighboring Ni sites. Then, these species react to form CO_2. Finally, H from the OH species reacts in alkaline media forming H_2O.

The electrooxidation of CO in an electrochemical ambient is far more complicated due to the presence of water, different electrolytes, and the electric field, which increase the degrees of freedom of the problem, making it more difficult for the models to capture the main aspects of the reactions. Despite the reaction complexity, several details are well-known for CO electrooxidation on Pt surfaces. Using Pt single-crystal electrodes, Farias *et al*. made valuable contributions to the understanding of the complex dynamics of the electrooxidation of CO in acid[52] and alkaline media[53]. The authors also extended the results to shape controlled Pt nanoparticles (~8 nm)[52,53]. They found that the oxidation of CO depends on the CO coverage of the electrode[54], on the symmetry of the sites[55,56] (crystalline plane), on the pH (acid[57] or alkaline[58]) and, on the presence (or absence) of CO traces in the electrolyte[57]. More details about this reaction can be found in the contributions of Lebedeva et al.[57] and Calle Vallejo et al.[59,60]. For instance, by performing electrochemical and computational experiments, Calle Vallejo et al.[59,60] found quantitative coordination–activity relations[60], paving the way for the smart preparation of catalysts for this reaction by tunning the relative quantity of different sites on the material. They found that the steps are the active sites for CO oxidation and that the reaction is likely limited by the formation of OH species. Further support comes from a kinetic study of the CO stripping on stepped Pt surfaces, showing that the steps are indeed the active sites for the reaction[59].

Electrochemical results qualitatively agree with the findings in Figure 2, i.e., CO stripping experiments with Rh[61,62], Pd[63,64,65], Ru[66] and Ni[67] showed qualitatively similar behavior to Pt (note that they have similar adsorption energies). On the other hand, as CO does not absorb on Ag, Au, and Cu, stripping experiments are not performed on these surfaces, but the molecule can be oxidized by scanning the electrochemical potential in a solution saturated with CO (Figure 3). Figure 2A shows that Ag, Au, and Cu bind CO much weaker than Rh, Pd, Pt, Ru and

Ni. Besides, it is worth noticing that the main reactivity findings for the CO_2RR studies (CO_2 reduction reaction), one of the most studied reactions nowadays, agree with the trends for the CO oxidation in electrochemical ambient and with the computational results showed in Figure 2[22,49]. The results discussed before qualitatively explain why, during the CO_2RR: i) Pt, Pd and Ni are strongly poisoned by CO, ii) Au and Ag produce mainly CO (the interaction is too weak with this intermediate), and iii) Cu shows an intermediate behavior. These results are also valuable in the context of electrooxidation of alcohols and polyols; however, Cu and Ni cannot be evaluated in these conditions as Cu dissolves in acid and alkaline media and Ni dissolves in acid media at typical potentials for the electrooxidation of CO.

Studies with Au[68,69], Ag[70] and Ni[67,71,72] demonstrated a strong dependence of their activity with the pH, showing higher activity in alkaline media. It is interesting to note that the activity/interaction of Ag and Au increases in alkaline media due to the presence of hydroxide and/or the formation of oxides at their surfaces[68,70], which was not considered in the computational experiments described before. For example, Orozco *et al*.[70] showed that CO adsorb on Ag in both acid and alkaline media. However, while CO remained on the Ag surface after N_2 bubbling in alkaline solution, it was removed in acid media. Similarly, Au was less active in acid media[68], but it showed a surprisingly excellent activity in alkaline media. By using *in situ* Raman experiments with cyclic voltammetry (CV), Angelucci *et al*.[73] showed that the presence of CO promoted the formation of oxygenated species at low overpotentials (Figure 3B), enabling the CO oxidation through the Langmuir-Hinshelwood mechanism at unexpectedly low potentials (Figure 3A). These synergistic effects generated by the favorable interaction between CO and the oxygenated species were not predicted by the computational models discussed above. Therefore, it is important to notice, that even if computational modeling has been extremely valuable to explain the most important aspects of the (electro)oxidation of CO on metals, permitting to understand the problem in terms of adsorption energies of key intermediates, the complexity of some systems make the approach quite limited.

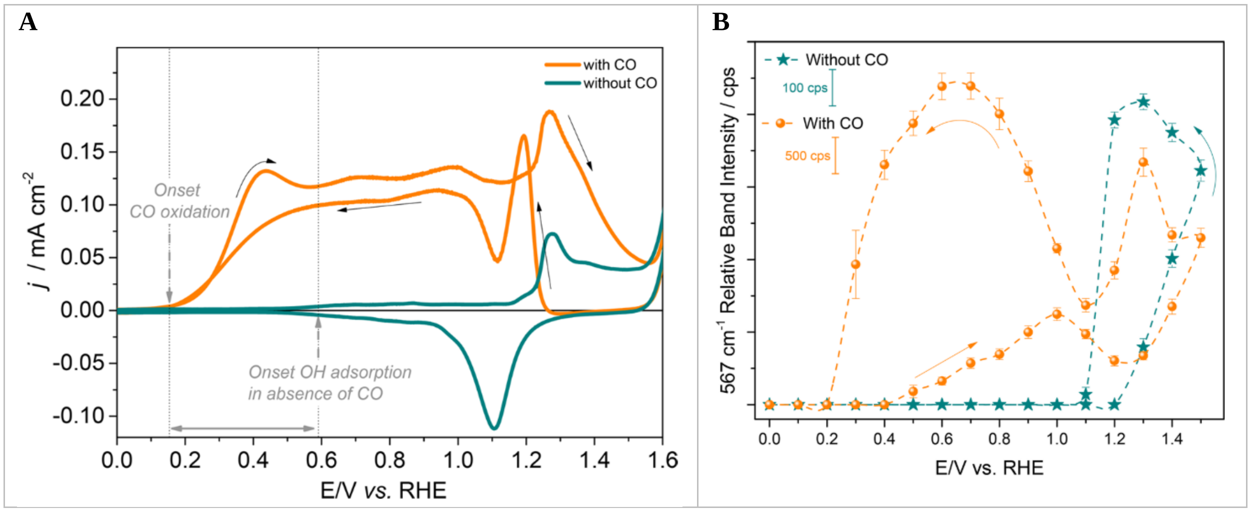


Figure 3: (a) Cyclic voltammetry of a polycrystalline gold electrode in 0.1 M KOH in the presence and absence of CO at $50 mVs^{-1}$. (b) Relative band intensity measured by RAMAN during cyclic voltammetry on gold electrode in the presence and absence of CO. Image adapted from Angelucci *et al*.[73]

To end with this section, we want to mention some findings and concepts that will be important in the following sections. We mentioned that Pt is one of the elements that adsorb CO too strongly and that the electrooxidation of CO on Pt is limited by the formation of OH species. Thus, the most used approach to increase the activity of Pt for this reaction (or increase the tolerance to CO poisoning) is to combine Pt with other transition elements (typically Ru and Sn), forming an alloy, or depositing them as adatoms, etc. In principle, this "Pt modification" have at least two effects, namely: i) the well-known electronic effects due to the modification of the electronic structure of the metal, changing the adsorption energy of all the adsorbates[74] and ii) via a bifunctional mechanism[74,75]. The reaction [4] help illustrating this last effect. This reaction can be easily translated to the L-H mechanism drawn in figure 2 for the oxidation of CO on a $LaNiO_3$ perovskite. In this case, CO is adsorbed on a Pt site (in figure 3 we adsorb CO on a Ni ion), while a water molecule (or a hydroxyl ion, depending on the pH of the media) reacts with a Ru site to form OH specie (in figure 2 we also adsorb OH on a Ni ion). Then, both adsorbates combine forming CO_2 and replenish the reaction sites to continue the reaction. Of course, it is a very simplified view of a complex problem[75], but this picture is useful as a starting point for the discussions involving more complex materials like perovskite oxides.

$$Pt - CO + Ru - OH \rightarrow CO_2 + H^+ + e^- + Pt + Ru \qquad [4]$$

2.2 METHANOL (ELECTRO)OXIDATION ON METALS

The electrooxidation of alcohols and polyols occurs through a complex mechanism that includes dehydrogenation, dehydration, oxidation and/or C-C bond-breaking steps. The simplest organic alcohol, methanol, although not an abundant biomass-derived product that can be used to obtain value-added molecules, but has been studied in detail[76] due to: i) the interest in using this molecule in direct methanol fuel cells (DMFC)[77] and ii) the importance of formic acid/formate for several industries[78] and also to be used in direct formate fuel cells[79]. Its molecular structure, containing C-H, C-O and O-H bonds, makes it an excellent model to understand the oxidation of other more complex alcohols and polyols, which are abundant in the biomass and can be used as precursors of many value-added molecules.

DMFC has a much lower performance than H_2FC due to the relatively high overpotential necessary to completely oxidize the reaction intermediates[80] to generate formaldehyde, formic acid, or CO_2 (Figure 4). Ferrin *et al*.[41] studied the oxidation of methanol on close packed metals (Figure 4A) and showed that the alcohol can be completely oxidized to CO_2 through a direct (black lines) or indirect pathway (green lines), i.e., with or without having CO as intermediate, respectively[41]. The authors found that, apart from the coinage metals (Cu, Ag and Au), several transition and precious metals successfully activate (dehydrogenate) methanol, but as shown in the previous section, they also bind CO too strongly suffering from poisoning from it and other related intermediates[41] (Figure 4B). On the other hand, the coinage metals were not poisoned by CO, but they were not able to activate the methanol molecule. This study concluded that there was not a pure metal able to efficiently catalyze the oxidation of methanol, as none of the studied materials was able to fulfill the following three fundamental requirements to run the reaction as close as possible to the thermodynamic potential, namely: 1) activation of the methanol (dehydrogenation of the -CH_3 or -OH group), 2) activation of the water molecule (to form oxygenated species on the metal) and 3) hinder the surface poisoning by adsorbed CO, or other intermediates adsorbed through the C or O atoms. Nevertheless, this study paved the way for the computational screening of new materials, showing that all the thermodynamic barriers for the electrooxidation of methanol in metals can be considered as a function of two descriptors, namely, the adsorption free energies of OH and CO[41].

This lack of success to find a single metal able to fulfill the requirements of a successful electrocatalyst, motivated researchers to synthesize and test a myriad of different combinations of metals for the oxidation of methanol[81]. There is a consensus that PtRu-based alloys are the best candidates for DMFC, which can be explained by the adsorption free energies of OH and CO. Pt is in a region of the plot where the PDS (potential determining step) is the oxidation of CO due to the unfavorable activation of water. Ru also binds CO favorably, but it is affected by the formation of oxides on its surface under the experimental conditions. Interestingly, PtRu alloys adsorb CO like Pt and Ru, but the activation energy of water is midway between the two atoms[82]. Unfortunately, both Pt and Ru are expensive and scarce metals. However, Rossmeisl *et al*.[83] performed a computational screening using the same descriptors (i.e., adsorption energy of OH and CO) and identified PtCu alloys as good candidates for this reaction[84]. All the computational results discussed in this section qualitatively explain those obtained in electrochemical ambient. However, it is important to note that the favorable interaction between OH species and electrolyte were not considered in this work, and they will likely move the lines of the graphic in Figure 4B downward, i.e., decrease the energy of all OH species absorbed on the metals.

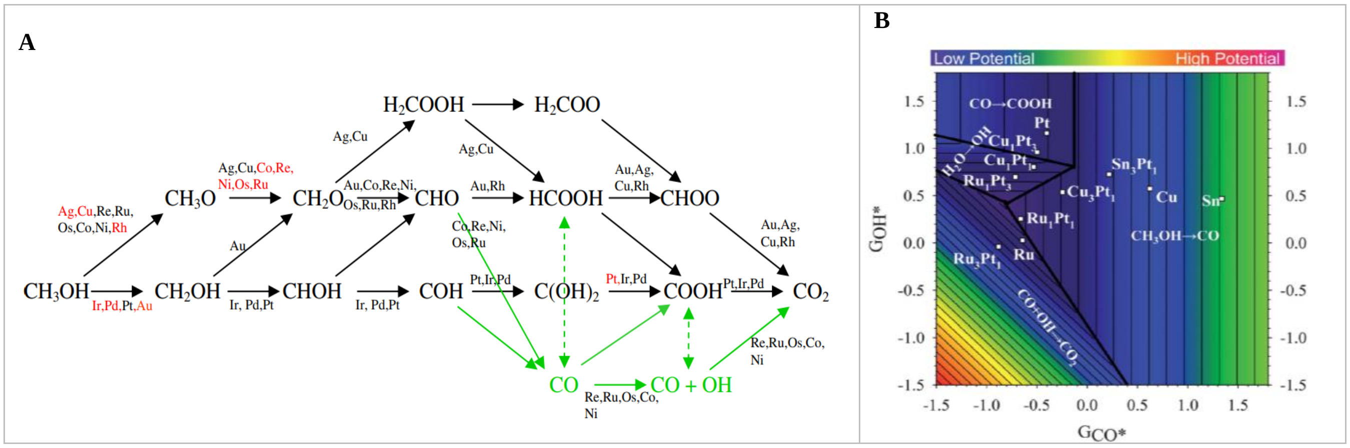


Figure 4: (a) Pathways for the MEOR on different metals and (b) volcano plot pointing the best catalyst candidates considering G_{OH} and G_{CO} as descriptors and the indirect mechanism found for Pt(111) surface . The green lines in (a) correspond to the indirect pathway, involving the formation of CO as intermediate. Images adapted from Ferrin *et al*.[38] and Rossmeisl *et al*.[69]

2.3 (ELECTRO)OXIDATION OF BIGGER MOLECULES ON METALS

The electrochemical oxidation of small organic molecules has been intensively studied on noble metal electrodes[85] and despite the ongoing debate, details about the electrooxidation of methanol[42,86] and formic acid[87] are relatively well-understood. The results described for the (electro)oxidation of CO and methanol aid us to understand the main features of bigger alcohols and polyols. Regardless of the organic molecule, its complete electrooxidation involve many steps, namely: dehydrogenation, C-C bond breaking and C-O bond formation[88,89]. Thus, catalysts that bind CO too strongly like Pt, Pd, etc., will be poisoned by this intermediate in the oxidation of virtually any alcohol or polyol. Besides, the CO adsorption energy scales linearly with other intermediates bounded to the surface through their C. Thus, this catalyst will also bind other species strongly, having several poisoning intermediates[90]. Studies performed with other alcohols and polyols like ethanol and glycerol showed similar trends to methanol[91,92]. In an electrochemical ambient, the reactions were studied mainly on Pt based electrocatalysts. The results have shown that: the activities were higher in alkaline media[93,94], the catalyst suffered from poisoning[95,96,97,98], CO was not the only poisoning species[99,100] and the modification of Pt by species that block the formation of strongly poisoning intermediates increased the electrocatalytic activity[101]. Therefore, considering the experimental and computational experiments performed and discussed for methanol for decades where: i) the adsorption energy of OH and CO were relatively good descriptors for the reaction, and ii) the similarities described here between the findings for the oxidation of methanol and bigger polyols; we hypothesize that the adsorption energies of OH and CO can be also used as guidelines to find materials suitable for the (electro)oxidation of these more complex molecules.

Studies about the electrooxidation of ethylene glycol[102,103], ethanol[104,105,106], glycerol[101,107,108] and glucose[109,110] have mainly focused on the determination of reaction products and intermediates by combining several electrochemical and analytical tools. Some works have used electrochemical, analytical, and computational tools to arrive to a more general understanding, from the atomic point of view, of the first steps that occur in the electrooxidation of polyols[99,111]. In these works, researchers have focused on compounds with low oxygenation degree, which generate several value-added chemicals. On the other hand, the pathways involving C-C bond breaking, which are more favorable at higher potentials (in general, hundreds of millivolts after the onset potential), are in principle less desirable because they drive the reaction through a myriad of intermediates, generating high overpotentials and electrode poisoning as previously discussed[112,101,113,114].

Figure 5 summarizes the main findings about the selectivity of the oxidation of polyols in the primary and a secondary carbon on Pt at early stages of oxidations, i.e., at those potentials where value-added compounds are generated. By using Pt single crystals, Garcia *et al*.[99] showed that double-dehydrogenated intermediates for the electrooxidation of glycerol determined if the primary or secondary carbon of the polyol would be oxidized in acid medium. Then, using the same idea, Soffiati *et al*.[111] extended the results for the electrooxidation of polyols (figure 5). Using Pt(111), Pt(100) and Pt(110), the authors showed that more compact surfaces (Pt (111) > Pt (100) > Pt (110)) increases the tendency to form enediol-like intermediates, which are the precursors of ketones.

The electrooxidation of alcohols and polyols is faster in alkaline media, thus many works have been performed under this condition[115,116,117]. Even though the study of the reaction is more complicated in alkaline media due to the instability of several aldehydes and ketones, which are generated electrochemically but are then quickly oxidized in solution[118,119], the higher activity (important for the concomitant H_2 production) encouraged researchers to work in high pHs[101,112].

Apart from Pt, metals such as Pd[102,103], Au[93], Ni[26,29,120] and Ag[107,112,121] have been used for the electrooxidation of small organic molecules due to the lower cost and/or higher abundance. Unfortunately, the reactions occur at much higher potentials matching the formation of oxygenated species at the electrocatalyst surface, suggesting again the key role of these species. Thus, to avoid or highly reduce the use of Pt, Pd and Au, it is important to search for suitable catalyst non-based on these materials or containing very low quantities[112,122]. For more mechanistic details and discussions about the electrooxidation of glycerol (probably applied to other similar molecules), we refer the reader to the work of Li and Harrington[123]. It is important to note that for all metals, the oxidation degree of the products and extent of the C-C bond breaking increase with the potential of the electrode, which could help rationalize the results on oxides discussed below.

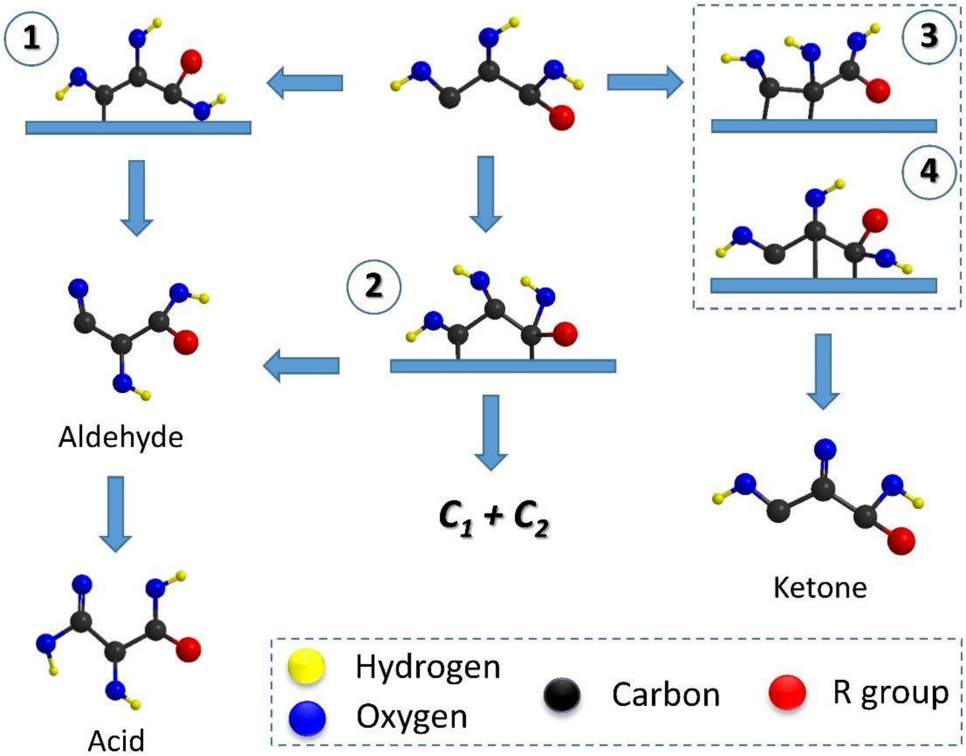


Figure 5: The figure shows a generic intermediate containing 3 -COH groups and a residue “R”. Three double-dehydrogenated intermediates are shown: Intermediate 1 is double bonded through its primary carbon and carried to the oxidation of the adsorbed carbon. The relative stability of intermediate 1 decrease in the order Pt(110)>Pt(100)>Pt(111). Intermediate 2 is the most stable in all the surfaces and it was proposed to intermediate the oxidation of the primary carbon and the C-C bond breaking. Next, 3 and 4 are enediol-like intermediates that produce the ketone. This kind of intermediates is particularly stable in Pt(111). Besides, they become even more stable in the presence of positively charged atoms on the electrode surface. Finally, the selectivity to C1 and C2 products increase with the electrochemical potential.

3. (ELECTRO)OXIDATION OF CO, ALCOHOLS AND POLYOLS ON METAL OXIDE

Like the previous sections devoted to metals, we will focus now on the (electro-)chemical behavior of metallic oxides for the (electro)oxidation of CO and alcohols. Metallic oxides can be easily prepared in a broad range of compositions and structures, offering in consequence, a myriad of possibilities to be explored. As described previously, the reaction mechanism on metals from a microscopic point of view consists of calculating the binding energy of key intermediates, which usually scales linearly with the activation energy. These simple energetic relations between a reaction step and the corresponding activation energy, which highly simplified the analysis of multistep reactions, are the so-called Brønsted–Evans–Polanyi relations[124,125]. In the case of metals, the adsorption energies of CO and OH were reasonable descriptors for several reactions within the scope of this article. In principle, the same approach can be used in case of oxides; however, the higher difficulty to perform systematic experiments with metal oxides single crystals (instead of complex heterogeneous structures) increases the challenge to correlate experimental results and computational calculation and find general descriptors.

Despite these limitations, if the structure/property of the oxides is changed in a systematic way, we will see in the following sections that there are several successful examples in correlating material properties (usually bulk properties) with its catalytic activity. Thus, before going to the section about the (electro)catalytic behavior of metallic oxides, we will briefly describe the structure of a particular class of oxides, the perovskites oxides, and their properties, to show how these properties can be rationally tuned to change the activity and selectivity in a catalytic reaction.

3.1 THE STRUCTURAL VERSATILITY OF PEROVSKITES

Perovskites are typically ABX_3-type compounds with A being a lanthanide, alkaline or alkaline earth cation such as La, Nd, Sr, Ba, or Ce, B a transition metal such as Mn, Co, Fe, Ni, Cr, or Ti, and X a halogen, such as F, Cl, Br, and I, or a chalcogen, such as O (in perovskites oxides). The ideal crystal structure of a perovskite oxide is based on a cubic unit cell formed by A ions located at the corners, the B cation at the center and the O at the center of the facets (Figure 6a). This results in a cubic lattice of 6-fold corner shared BO_6 octahedrons and 12-fold O coordinated A-site cations in the center of a cube formed by the BO_6 octahedron[126]. However, deviations from the ideal structure are well-known for perovskites due to the large variation of sizes of the various multivalent ions and structural defects arising from cationic and anionic vacancies in the lattice. These lead to the formation of rhombohedral, tetrahedral, orthorhombic, monoclinic, brownmillerite, and hexagonal crystal structures based on the tilt and distortion of the BO_6 octahedrons[126].The Goldschmidt factor (equation 4) is used to predict the formability and geometric distortion of the crystal structure.

$$t = \frac{r_A + r_O}{\sqrt{2}(r_O + r_B)} \qquad [4]$$

where r_i is the radii of the ion "i". A Goldschmidt factor of $t = 1$ leads to the ideal cubic crystal structure, while $t > 1$ gives hexagonal structure and t between 0.75-1 leads to tetragonal and rhombohedral crystal structures[127]. More recently, a more comprehensive factor has been introduced that includes the oxidation state of the A cation (n_A) in the tolerance factor expression using equation 5[128],

$$\tau = \frac{r_O}{r_B} - n_A \left(n_A - \frac{\frac{r_A}{r_B}}{\ln\frac{r_A}{r_B}} \right) \qquad [5]$$

While the Goldschmidt factor had only 74% successful prediction rate, this new factor provides a predictability of 92% for perovskite formability. However, such simple prediction models do not consider the multi-valent ion substitution that is possible at each of the three ion sites, which lead to wide variety of double[129], triple[130], and quadruple[131] perovskites materials that have been used to study the OER, ORR and in SOFC applications. To predict the stability of such complex crystal structures with multivalent substitution, DFT-based convex hull analysis combined with machine learning algorithms have also been used[132].

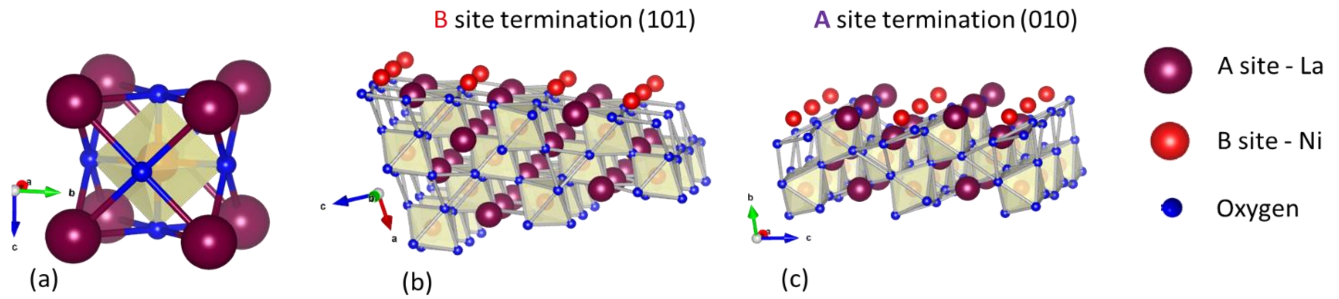


Figure 6. (a) Unit cell of a perovskite oxide crystalline structure (cubic). The site A is occupied by a large cation such as La^{+3}, or an alkaline metal or earth alkaline metal. The site B is occupied by a small cation, commonly a transition metal, such as a Ni ion. The B site is the Lewis acid center of the structure and the oxygen site the basic center. (b) 3D structure of a perovskite oxide´s cluster with B site termination and (c) A site termination at the top. These 3D structures highlight the importance of the atoms exposed at the surface of the material which will determine its (electro-)catalytic behavior.

While the transition metal cation at the *B* site is the main Lewis acid center of the structure, the oxygen sites are the Lewis basic centers. The Miller indices determines the site termination (A, B, or both) affecting the surface properties (figures 6B and 6C). Furthermore, both the A-site and B-site and partial substitutions, along with the defect chemistry can be explored to tune the electronic structure of perovskites, directly affecting their performance in electrooxidation reactions. A simplified diagram of DOS (density of states) is shown in Figure 7a. The octahedral symmetry of the transition metal cations leads to the split in t_{2g} and e_g d-states. The main valence bands are formed by the hybridization of the O-*2p* bands and the transition metal t_{2g} antibonding states, whereas the conduction band close to the Fermi energy corresponds to the transition metal e_g antibonding states[133]. The main bands of the A metal are usually much lower/higher in energy. The positions of the t_{2g} and e_g d-band centers and the Fermi energy related to the O-2p band determines the extension of metal-oxygen covalency. Both A and B metals determine bands alignment and substituting the B-site by a more electronegative transition metal or by favoring a higher oxidation state of the B-site oxidation state (by changing the A-site for example), decreases the Fermi energy related to the O-2p band center (Figure 7b). The position of the Fermi energy related to the O 2p-band center also impacts in the energetics of oxygen vacancy formation, oxygen storage capacity and oxygen mobility[134]. Lee *et al.* showed the existence of an inverse linear correlation between these two parameters within the $LaBO_3$ series; from the less to the more electronegative transition metal, i.e., Mn to Ni, the O 2p-band center gets closer to the Fermi energy making less expensive to create oxygen vacancies[135]. Other works have shown that the substitution in the B-site with traces of the noble metals improved their reducibility (oxidizing ability)[136], generating higher activities than the bare material.

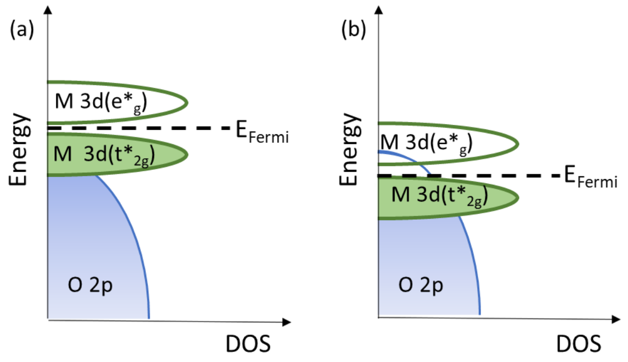


Figure 7 (a) A simplified DOS diagram for a ABO_3 perovskite, in which B is a transition metal of the 3rd period (b) the modification of the bands position and Fermi energy depending on the A and B metals that increases the metal-oxygen covalency. Figure adapted from reference[137]

While the d-band center model[138], which correlates the adsorptions energies of intermediates with the metal d-band center, works well for metallic surfaces, several other descriptors such as e_g filling[139,140], O-2p band center relative to the Fermi level[139], metal-oxygen covalency charge transfer energy[139,141] and, more recently, a frontier band orbital descriptor[139,142] have been proposed for metal oxides. These descriptors have been correlated to activity metrics for OER[139,141], ORR[143], CO oxidation[142,144], NO oxidation[142,145] and have been summarized in previous reviews[134,146–148]. Below, we briefly describe the main aspects of the most accepted descriptors that will certainly be useful to rationalize the electro(oxidation) reactions of alcohols and polyols, , i.e., after performing some systematic fundamental studies on this topic.

3.2 REACTION DESCRIPTORS

As discussed before, the identification of structural/electronic descriptors of the electrocatalyst that can be correlated to the performance is highly desired. Due to the local octahedral symmetry of the B site in perovskites, the d levels of the transition metal in the molecular orbital bonding framework are split in e_g and t_{2g}, with the former corresponding to the d orbitals pointing directly to the O neighbors as well as outward the surface, participating in the σ-bonding with the adsorbates. Although the metal-adsorbate interaction can be further enhanced through π-back donation involving t_{2g} states, it has been shown that the e_g filling of the transition metal B-site captures better the binding strength between the surface and the adsorbates and can be used as descriptor in several reactions[140].

Hong *et al*.[149] pointed out, however, that while the e_g filling and adsorption energies of oxygenates intermediates work as good descriptors for some perovskites oxides in OER, such as $LaCoO_3$, not all of them follow this relationship, such as $La_{1-x}Sr_xCoO_{3-\delta}$ in which the lattice oxygen participates in the reaction mechanism through the Mars−van Krevelen (MvK), see section 3.3. Based on a statistic analysis of the literature, the authors identified that both the d band electron filling and metal-oxygen covalency should be considered as good descriptors. These parameters are well captured by the charge-transfer energy, which describes the difference in energy between the unoccupied d transition metal band and O-*2p* band center and was able to explain the changes in the rate-determining step for the OER reaction (Figure 8A). High charge-transfer energy values correspond to high electron transfer barrier. On the other hand, at low charge-transfer energies, this barrier become negligible, and the oxygen binding energy becomes the rate-determining step.

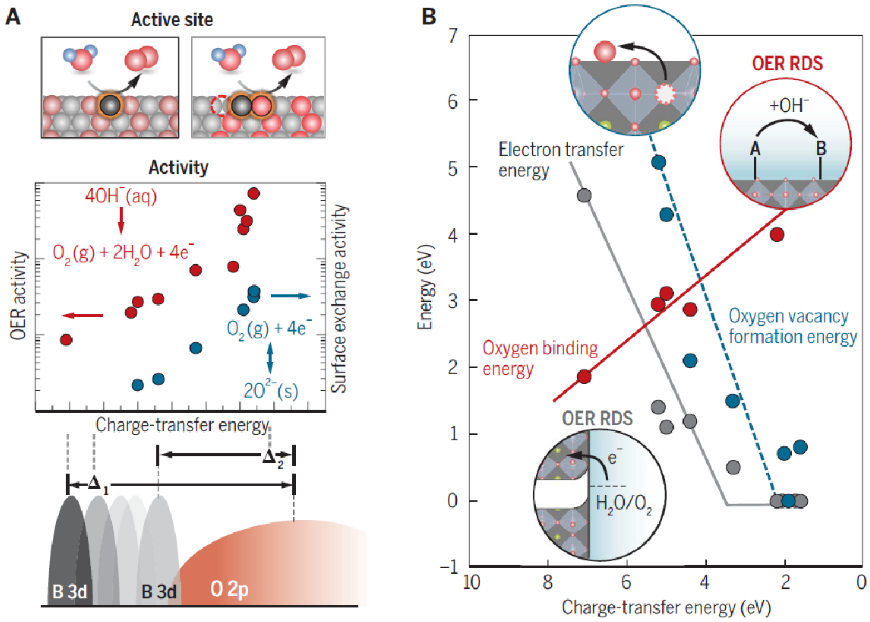


Figure 8: (A) A simplified view of the dependence of two rate-determining steps in OER, i.e, oxygen binding energy and oxygen vacancy formation as a function of the charge-transfer energy. (B) Trends in the oxygen vacancy formation, electron transfer energy, and oxygen binding energy as a function of charge-transfer energy. Adapted from ref.[150]

In other reactions, such as ORR in alkaline solution ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$), it was proposed that the metal-oxygen bond covalency or the bulk O 2p-center represent better descriptors, depending on the conditions[151,152]. When oxygen vacancy formation and bulk oxygen transport are involved in the rate determinant step, such as in SOFCs that operates at high temperatures, the bulk O 2p-center is the best choice.

Despite the complexity of the systems, improvements in the field of the computational and experimental sides are continuous. Thus, recently, Xu et al.[142] developed a frontier band orbital descriptor, which is defined as the energy difference between the highest occupied band orbital and the lowest unoccupied band orbital. The authors successfully tested the descriptor for the oxidation of CO and NO.

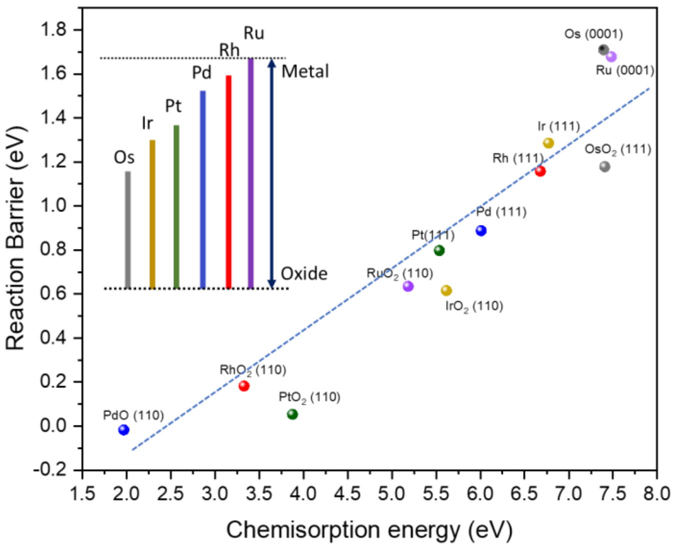
It is worth noticing that most of the descriptor discussed in the literature are bulk descriptors, even if it is well-known that most of the catalytic reactions occurs at the surface of the materials. This fact is due to the key role of the computational experiments on this field, to the difficulties to perform in situ characterization of the surface and to the even higher limitations to carry out experiments using model surfaces of metal oxides. When a perovskite oxide (or other material) is modelled, also some facets of the crystals take part of the model. If instead of calculating bulk properties, we want to get information about the surface, we should choose one or more crystal planes to work with. Besides, this election would be based on computational stability studies (which highly increase the computational cost) and/or experimental evidence about the main facets presents on the catalyst (an information really complex to get). Despite these limitations, it should be remembered that at the end of the day our aim is to get descriptors with predictive power, which is much more important than if the measured/calculated parameter is directly connected with the energetic of the reaction or not. For example, Giordano et al. have recently discussed the predictive power of the energy of the oxygen 2p states[134]. The authors pointed many cases of success in using this descriptor to predict the activity of perovskite oxides on catalysis and electrocatalysis. Besides, they clearly stated that even if it is not a property directly related with the adsorption energy of the adsorbates (or another parameter directly involved in the reaction), this descriptor has several times a linear correlation with a directly involved parameter, for instance, the M-O binding energy. Finally, they claimed that sometimes the bulk descriptors do not linearly correlate with the directly involved parameter (for instance, M-O adsorption on a given crystalline plane) losing its predictive power.

Therefore, despite some success using bulk predictors, it is clear the necessity of the use of predictors based on parameters that directly determine the reaction kinetics. In this sense, we would like to highlight two contributions in the field of DFT calculations: i) Vojvodic et al.[124] found Brønsted-Evans-Polanyi relations for the dissociation of several adsorbates (N_2, O_2, NO, CO, N_2 and NO) on metal oxides and perovskites oxides and ii) Su et al.[153] showed that the formation of vacancies on MO_2 (being M a transition metal) is an excellent descriptor for the dissociation of several molecules (N_2O, CH_3OH,NH_2OH and CO_2) as the energy of the formation of the vacancies has a linear relationship with the dissociation energies of the molecules on the studied oxides. This last contribution, from the group of Calle-Vallejo, is extremely important because it links a bulk property (most of the descriptors in the field are connected to bulk properties) with the energy of the reaction (and adsorption energies of intermediates), i.e., a property that is directly connected with the thermodynamic/kinetic of the reaction. We believe that this kind of approach, despite the difficulties commented before, show that it possible to perform similar studied to those carried out with metals for decades, which have permitted to understand many details about microscopic events in the field of (electro-)catalysis.

3.3 CARBON MONOXIDE (ELECTRO)OXIDATION ON METAL OXIDES

It has been experimentally observed in heterogeneous catalysis that several metal oxides are generally more active than their metallic counterparts in C-O bond activation[154,155,156]. Through DFT calculations, Gong *et al.*[156] found that the energetic barriers for the oxidation of CO are lower for the oxides as showed in Figure 9,top. In addition, the authors showed that there is also a geometric effect influencing this general result. In metallic surfaces, the reaction occurs through a L-H mechanism where the adsorbed oxygen initially sits in a hollow site and then, must move to a bridge site to react with the adsorbed CO. These finding were recently confirmed using an elegant approach involving chip-based electrochemistry mass spectrometry by Scott et al.[45,46]. The authors showed that the electrochemical oxidation of CO does occurs through a L-H mechanism between CO and $H^{18}O$ species formed by the electrochemical reduction of isotopically labelled $Pt^{18}O_x$. On the other hand, the reaction on the transition metal oxides is believed to usually occur preferentially through the MvK mechanism (Figure 9-down[157–161]), where the O from the oxide lattice directly reacts with the CO adsorbed on the adjacent metal site. Gong *et al.*[156] compared the reactivity of the metals with the corresponding oxides and showed that the change in the binding mode of the O atom in the metal creates an extra energy cost compared to oxides, which together with the different adsorption energies explain the observed trends showed in figure 9-top.

An insightful work by Goulas *et al.*[162], showed that metal oxides can also be more active and selective than metals for C-O bond activation in C_{2+} molecules even in the presence of moderate H_2 pressures and temperatures (conditions required for hydrodeoxygenation reaction, for example). They found that the Gibbs free energy of M-O bond formation was a good reaction descriptor, suggesting a MvK mechanism. Besides, they showed that if the energy for the formation of an oxygen vacancy is low enough, it led to the reduction of the oxides, explaining the metal-like behavior of some metal oxides.



Mars−van Krevelen mechanism

In this reaction model, a reactant adsorbs on the catalyst surface and then one or more reaction products leave the surface of the solid catalyst with elements from catalyst lattice[163].

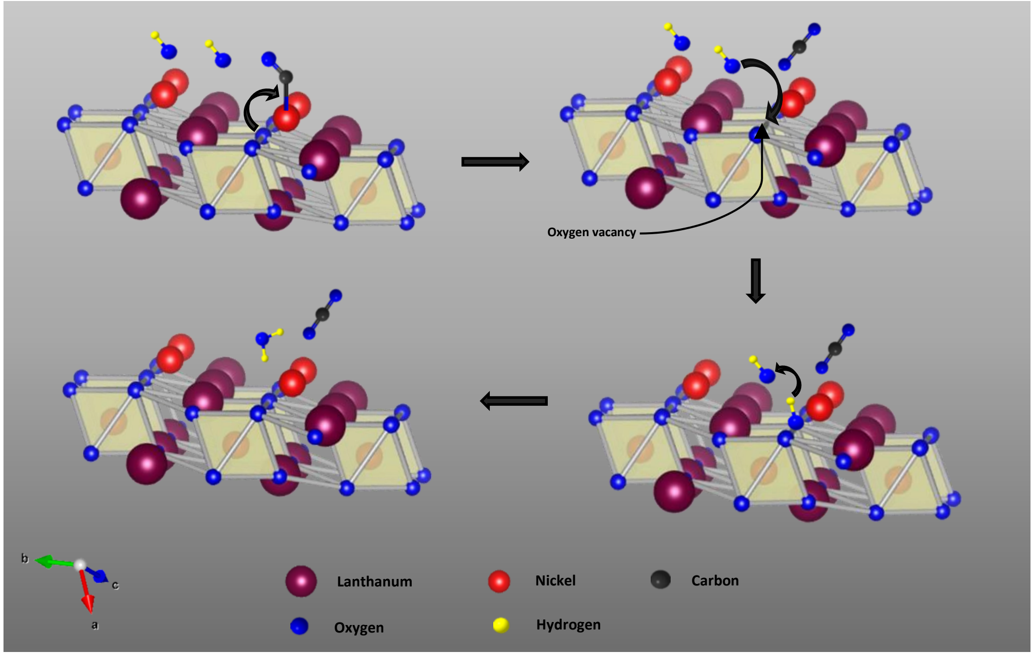


Figure 9: (Top) Reaction barrier as a function of the total chemisorption energy (CO and O) for 4d and 5d metals and their corresponding oxides. The color bars show the relative difference between the reaction barriers for the metals and their corresponding oxides. Image adapted from Gong *et al.*[156]. (Down) Scheme of the Mars−van Krevelen mechanism. The mechanism looks similar to what was shown in figure 2 for the L-H mechanism. We propose that the reaction starts with the adsorption of CO on the B-site. Subsequently, the adsorbed CO reacts with the lattice oxygen forming CO_2 and leaving a vacancy in the lattice. Further, the hydroxyl ions from the electrolyte attack the oxygen vacancy, retaining the surface structure of perovskite.

Voorhoeve *et al.*[164] studied the CO oxidation activity for $LaBO_3$, $La_{0.85}Sr_{0.15}CoO_3$ and $La_{0.7}Pb_{0.3}MnO_3$, with B = Cr, Mn, Fe, Co and Ni. The catalytic activity of the perovskite oxides depends on the reaction conditions. For a mixture of 2:1 ratio of $CO:O_2$ at atmospheric pressure and relatively low temperatures (100° to 300°C) they found a volcano plot relationship between the activity and the e_g filling with maximum activity for $e_g \approx 1$ (Figure 10C). The success of this descriptor guided researchers to tune the composition of perovskites oxides to improve the performance for the CO oxidation. Using this strategy, Chan *et al.*[165] tuned the e_g filling of $LaMnO_3$ and $LaCoO_3$ by partially substituting the La^{3+} at the A site by Sr^{2+}. They found an increase in the materials' activity for $La_xSr_{1-x}MnO_3$ and $La_xSr_{1-x}CoO_3$ by augmenting the e_g filling from 0.2 to 0.8. The authors claimed that the results correlate with the oxygen mobility in the materials.

The filling of the e_g orbitals have shown some predictive power for several reactions on perovskite oxides[143]. It was found that both the CO and O binding energy depends on the e_g filling (figure 10A). The oxidation of CO, ORR and oxidation of hydrocarbons showed that the optimal catalysts bind the reactant to the BO_5 site with the optimal energy when the $e_g \approx 1$[166] (strictly speaking, the BO_5 site corresponds to C_{4v} point group and the two-fold degenerate e_g level splits in a_1 (d_{z^2}) and b_1 ($d_{x^2-y^2}$) energy levels whereas the three-fold degenerate t_{2g} level splits in b_2 (d_{xy}) and b_1 (d_{xz}, d_{yz}) energy levels (figure 10B).

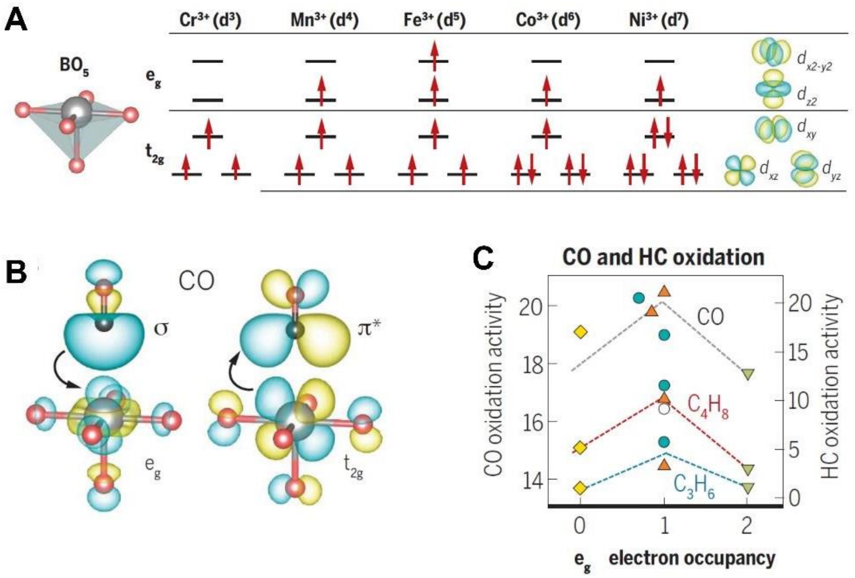


Figure 10: (A) Electronic configuration and d-orbitals for metallic cations of first-row transition metals in a BO_5 configuration. (B) CO σ orbital in the top left. In the right, the π* orbital of CO receives electrons from the occupied perovskite t_{2g} orbital. (C) Correlation of perovskite e_g occupation with catalytic activity for CO, propene (C_3H_6), and isobutylene (C_4H_8) oxidation [164,167 ,168]. Image adapted from Hwang *et al.*[143].

Due to the participation of the lattice oxygen in the oxidation of CO, the M-O binding energy has proven to be an excellent descriptor for some oxides. For example, Elias *et al.*[169] studied trends for the oxidation of CO on $M_{0.1}Ce_{0.9}O_{2-\delta}$, M = Mn, Fe, Co, Ni and Cu. The authors showed that the reaction rate scales linearly with the oxygen vacancy energy (E_{vac}) (Figure 11, left). The E_{vac} measures the energy necessary to break the Ce-O bond of the crystal lattice. They rationalize it by considering a MvK mechanism (Figure 9 and Figure11, right) where the reaction occurs through a downhill binding of CO to M^{3+} site, having the Ce-O bond breaking as the rate-limiting step. As the activity (expressed as TOF, turnover frequency = number of molecules converted per second per active site) increases monotonically as the Ce-O binding energy decreases, it was concluded that all these materials are in the branch of the 2D volcano plots where the Ce bind the oxygen too strongly. Thus, an optimal catalyst for the reaction should have $E_{vac} < 0.85$ eV. The authors also demonstrate the robustness of the descriptor by tuning the activity of $Cu_{0.1}Ce_{0.9}O_{2-\delta}$ by partially substituting Ce by Ln = La, Pr, Sm, Dy, Er. If the reaction occurs through the MvK mechanism and the formation of lattice oxygen vacancy is the rate-determining step, the E_{vac} would certainly be an excellent descriptor not only for the oxidation of CO but for any oxidation reaction.

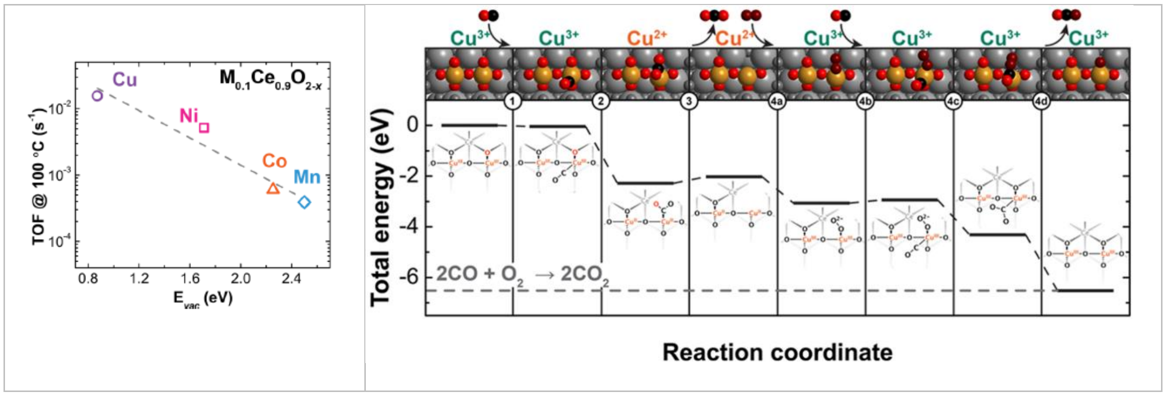


Figure 11. (Left) Correlations between computed E_{vac} and the intrinsic CO oxidation activity on $M_{0.1}Ce_{0.9}O_{2-x}$ and (right) DFT computed reaction mechanism of CO oxidation on {111}-terminated copper substituted ceria. The total energy of the system is the sum of the energies for the slab, gas molecules and adsorbates. Image extracted from Elias *et al.*[170].

Perovskite oxides can be synthesized containing different amounts of oxygen vacancies. For instance, Falcón *et al*.[171] studied the oxidation of CO on $LaCuO_{3-\delta}$ ($\delta = 0.05-0.45$) perovskites. The structural instability of the material and its activity increases monotonically with δ. In line with the article of Elias *et al*.[169] the authors claimed that the lattice oxygen participates in the reaction mechanism and that the creation of oxygen vacancies was the rate-determining step.

Apart from E_{vac}, that can be calculated by performing computational experiments, a closely related parameter is the relative energy between the Fermi level and the band center of the O 2p states, which determine the metal-oxygen covalency and hybridization. As the Fermi level moves closer the O 2p states, the energy penalty to create O vacancy is reduced[134,135], which has direct implications in reactions where the oxygen vacancy formation determines the reaction rate or the material stability. So far, this concept has been applied to tune and understand the electrochemical behavior of perovskite oxides for the OER in alkaline media[137,172], in the study of the hydrogen evolution reaction[173], for the oxidation/reduction of NO_x[174]and for the oxidation of methane[175]. Even if this descriptor has not been applied for the (electro)oxidation reactions of interest of this work, the cases of success commented before and the fact that several times it linearly scales with potentially key properties for the (electro)oxidations of alcohols/polyols like E_{vac} and several binding energies (M-O and M-OH, etc.)[134], make us to believe that this descriptor can play a key role for the rational development and optimization of catalysts for the electrooxidation of biomass-derived resources.

To correlate the perovskite electronic structure with the binding energy of the species at its surface, a theory involving the band structure of the materials is more accurate. The band structure depends not only on the composition of the material, but also on the facet where the species adsorbs. As mentioned before, because of the difficulty to identify the real composition of the surface of any material under operation conditions and the fact that most of the studies using perovskite oxides are performed using complex polycrystalline materials, usually researchers calculate the electronic configuration of the bulk material. Fortunately, as mentioned before, sometimes this approach has proven useful to explain trends in (electro)catalysis[134] and to predict the stability of the materials. Calle-Vallejo *et al*.[176] have shown that the success of the bulk properties of perovskite oxides as a descriptor relies on the linear scaling relationship between bulk thermochemistry and surface adsorption energies.

3.4 (ELECTRO)OXIDATION OF ALCOHOLS AND POLYOLS ON METAL OXIDES

The number of works dealing in detail with the interaction of alcohols with oxides in electrochemical ambient are scarce compared to metals. Therefore, to understand the main aspects that govern the interaction between alcohols and oxides surfaces, we will examine the results obtained for the oxidation of methanol in heterogeneous catalysis. Despite the differences from an electrochemical ambient, as we will see, these results provide insightful information that can guide future studies about the electrooxidation of alcohols and polyols.

The methanol oxidation reaction is relatively well-understood from a microscopic point of view in the context of heterogeneous catalysis[177,178]. In fact, it has been also used as a probe reaction to identify redox, acid, and basic sites on oxides catalysts[177,178]. The most relevant products formed by this reaction in oxides are formaldehyde (CH_2O), dimethyl ether (CH_3OCH_3,), methyl formate ($HCOOCH_3$), dimethoxymethane ($(CH_3O)_2CH_2$) and CO/CO_2, and their distribution depends on the nature of the active sites. While formaldehyde, methyl formate and dimethoxymethane are products generated by redox sites, dimethyl ether is an acidic site product and CO/CO_2 are basic site products (Figure 12). These correlations can be rationalized by giving a closer look to the reaction mechanism (Figure 12).

The adsorption of methanol requires both acid and basic sites, i.e., M^{n+}-O on oxides. Methanol binds through the hydroxyl group, forming a methoxy group at the acid site (CH_3O-M^{n+}-O) and an M^{n+}-OH group at the basic site (Figure 12)[178]. Therefore, the first step of the reaction consists of the deprotonation and dissociative adsorption of methanol molecules on the dual acid-base site ($CH_3OH + 2M^{n+}\text{-O} \rightarrow CH_3O\text{-}M^{n+}\text{-O} + M^{n+}\text{-OH}$). If the material has a strong acid character (and low basicity), the adsorbed methoxy species will not be further dehydrogenated and eventually, two neighboring methoxy groups will follow a condensation pathway to form CH_3OCH_3. As the basic character is increased, the ability of the oxygen atoms to dehydrogenate the -CH_3 group increases, generating more oxidized products. At moderate-low acidities and low basicity CH_2O and $(CH_3O)_2CH_2$ are formed. A higher basicity leads to a fully dehydrogenation of the -CH_3 groups, which are oxidized forming CO and CO_2. It is worth noticing the dual role of the basic sites. The O atoms promotes the dehydrogenation of the adsorbates forming OH species, but also act as nucleophiles, binding to the C atoms of the adsorbate to form oxygenated products like CO and CO_2.

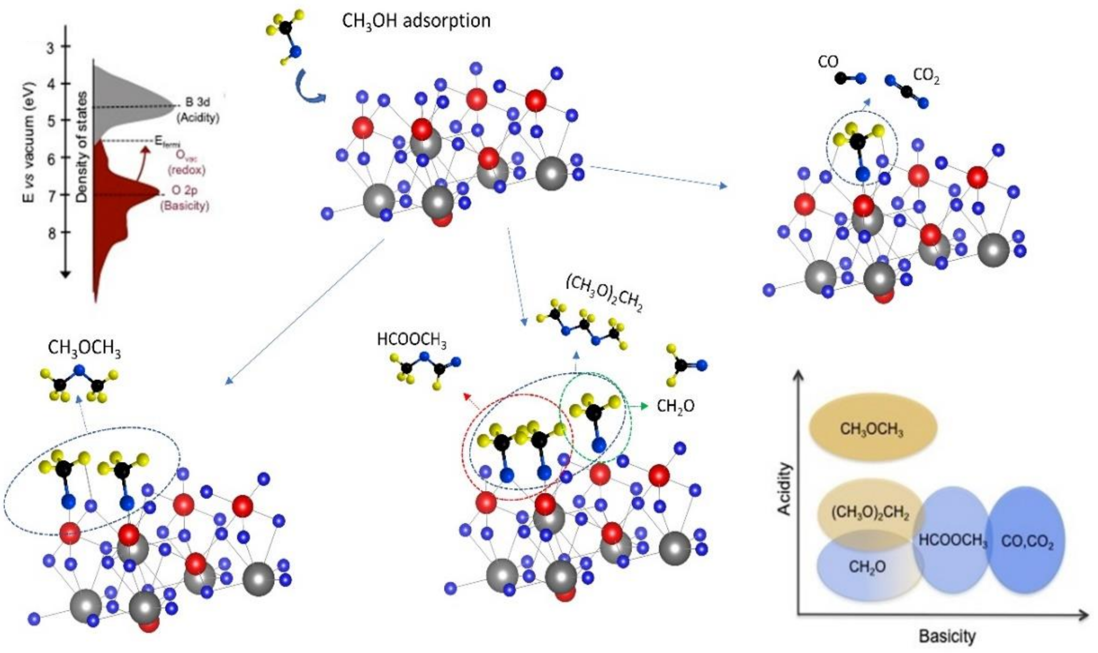


Figure 12: Schematic electronic structure of the perovskite oxide catalyst defining the basicity, acidity, and redox properties (Top-left). The figure shows the dissociative methanol adsorption on the BO_2-terminated perovskite oxide surface, stressing the dual acid-base (M^{n+}-O) site requirement for dehydrogenation of methanol in gas phase. A graph is included, showing the influence of the acidity and basicity of surface sites on the final products. While CO and CO_2 formation depends on the presence of strong basic sites, CH_3OCH_3 and $(CH_3O)_2CH_2$ are formed in the presence of strong-medium acid sites and CH_2O is favored in weak acid-base sites (Redrawn from Tatibouet[178])Badlani and Wachs[177] studied the oxidation of methanol on metal oxides (MgO, CaO, SrO, BaO, Y_2O_3, La_2O_3, CeO_2, TiO_2, ZrO_2, HfO_2, V_2O_5, Nb_2O_5, Ta_2O_5, Cr_2O_3, MoO_3, WO_3, Mn_2O_3, Fe_2O_3, Co_3O_4, Rh_2O_3, NiO, PdO, PtO, CuO, Ag_2O, Au_2O_3, ZnO, Al_2O_3, Ga_2O_3, In_2O_3, SiO_2, GeO_2, SnO_2, P_2O_5, Sb_2O_3, Bi_2O_3, SeO_2 and TeO_2) and found an inverse linear correlation between the TOF when considering the products formed on redox sites and the desorption temperature of the methoxy adsorbates (Figure 13a). These results clearly show that the adsorption energy of methoxy should be a good descriptor for the partial oxidation of methanol on metallic oxides. Besides, the inverse correlation of activity with the desorption temperature showed that all the catalysts were in the right branch of the volcano plot, where all the materials bound the methoxy groups too strongly.

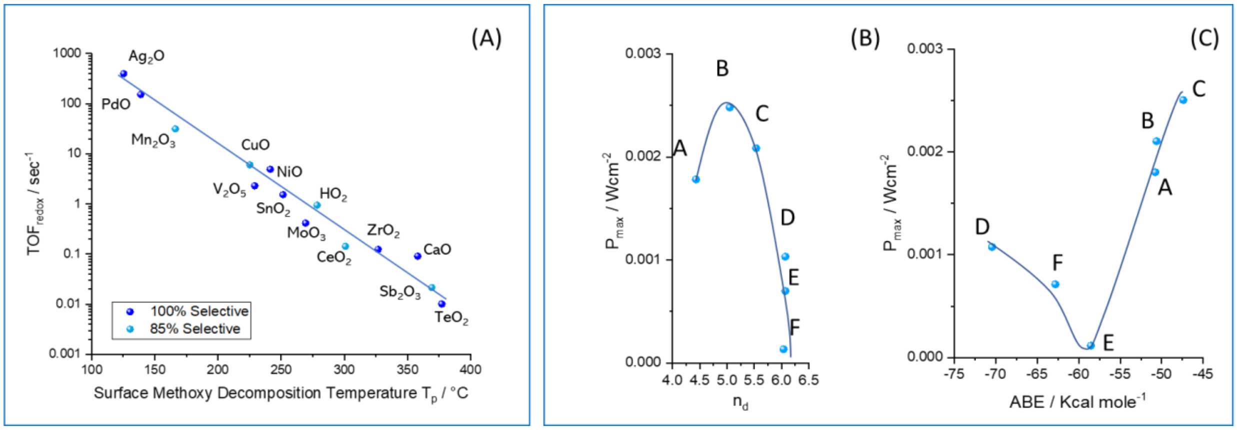


Figure 13: a) Semi-log plot of TOF_{redox} and surface methoxy decomposition temperature b) Optimum power density vs number of valence d-electrons for perovskites anode employed in DMFC c) Optimum power density vs average metal-oxygen binding energy (ABE) for perovskite anode employed in DMFC. Materials in b) and c): A- $SrRu_{0.8}Pt_{0.2}O_3$, B- $SrRu_{0.5}Pt_{0.5}O_3$, C- $SrCo_{0.25}Ru_{0.25}Pt_{0.5}O_3$, D-$SmCoO_3$, E-$SrPdO_3$ and F- $SrPd_{0.8}Pt_{0.2}O_3$. Two original points were disregarded in b) and c). One corresponded to Pt-C, which was out of our interest as it is not a perovskite oxide and the other corresponded to $PbRu_{0.5}Pt_{0.5}O_3$, which presented a behavior much different from the others. Images adapted from (a) Badlani *et al*.[89] and (b,c) adapted from White *et al*.[179].

The superior performance of oxides containing noble metals atoms have also been shown for $LaMnO_3$ and $LaMn_{0.95}B_{0.05}O_3$ (B = Pd, Pt, and Rh) perovskites[180]. To improve the activity further, $LaMnO_3$ was modified with different amounts of Pd. The authors identified Pd species in the lattice and in the perovskite surface, forming PdO. While the role of lattice Pd is not clear, the increase in PdO is proposed to promote the HCHO generation, CO conversion, and methanol combustion. It is important to note that the enhanced production of HCHO (a redox product) is in line with the results showed by Badlani and Wachs[177] (Figure 13a).

Perovskite oxides have been used as catalysts for the oxidation of methanol in electrochemical ambient. White and Sammells[179] selected the materials (see table S1) by performing CV experimentsin the presence and absence of methanol in 3M H_2SO_4 at 80°C. Several materials did not show activity and consequently were not used in the DMFC experiments. $SrRu_{0.5}Pt_{0.5}O_3$, $SrRu_{0.5}Pd_{0.5}O_3$, $SrPdO_3$, $SmCoO_3$, $SrRuO_3$, $La_{0.8}Ce_{0.2}CoO_3$, $SrCo_{0.5}Ti_{0.5}O_3$, and $La_{0.8}Sr_{0.2}CoO_3$, exhibited MEOR activity, with $SmCoO_3$ being the best catalyst among the precious metals-free oxides. Their results agree with the results for heterogeneous catalysis[177,180], i.e., we previously saw that pure noble-metal oxides were the most active for the oxidation of methanol, while in the last example, perovskites containing noble metals in the B-site outperformed the materials without noble metals for the electrooxidation of methanol. The electrochemical activity of noble metal oxides is not surprising. In the analysis made in section 2, we focused on the electrooxidation of molecules on metallic surfaces which, due to the presence of oxygen containing species plus the scanning of the electrochemical potential and/or the temperature, form OH species that react with the organic species likely through a L-H mechanism. This reaction has been studied in detail mainly on Pt surfaces. Briefly, the alcohol/polyol adsorbs on the metallic atoms and the oxidation to several products increases with the coverage of OH species. However, as we increase the quantity of OH, fewer sites are available for the adsorption of the organic molecules and the reaction rate eventually starts to decrease. However, in the electrochemical potential domain where bulk PtO_x is formed, the electrooxidation of the molecule start to increase again, likely due to a MvK mechanism[181–183]. The presence of Ru is also not completely surprising as the electrooxidation of methanol on pure Pt is improved by adding Ru. It is true that the Ru species present on the perovskite might be very different to those on a PtRu alloy. However, it is worth to note that the well-known improvement in the electrooxidation of methanol by partially substituting Pt by Ru atoms in a metallic catalyst is due to the facility of Ru to form OH species at lower potentials than pure Pt. Therefore, the Ru atoms that are indeed participating in the electrocatalytic process are not in the metallic state, but they keep a charge that depends mainly on the electrochemical potential. Thus, in the perovskite containing Pt and Ru (some of the most active in the work of White and Sammells[179]), the Pt ions are expected to bind methanol to form methoxy groups and Ru to react with water to form oxygenated species able to attack the C atom and increasing the oxidation degree of the adsorbate. Finally, it is important to emphasize the excellent activity of most of the perovskite oxides containing Pt (see table S1) outperforms the benchmarking Pt/C[179]. (Power/mg Pt). The authors also correlated the performances with parameters (Except for one of the materials), such as a volcano-type relation between the Power delivered by the fuel cell and the number of valence d-electrons (Figure 13b). The analysis suggest that the activity is optimized for materials with around 5 d-electrons. Interestingly, a minimum in the activity around -60 kcal/mol appeared when the authors plotted the Power density vs. the average M-O binding energy (Figure 13c). The activity increases for higher and lower binding energies likely due to a change in the rate-determining step of the reaction. Unfortunately, the authors did not measure the reaction selectivity to confirm this hypothesis.

Deshpande[122] *et al*. synthesized and tested an impressive number of perovskite oxides using a high throughput screening unit (with some similarities with a PEM fuel cell/electrolyzer), once again showing the importance of the presence of noble metals for the oxidation of the alcohol. The authors included binary oxides (e.g. Fe_2O_3, Fe_3O_4, RuO_2), perovskites (e.g. $LaFeO_3$, $SmCoO_3$, $SrRuO_3$, $La_{0.8}Sr_{02}Fe_{1-x}Ni_xO_3$, $La_{0.8}Sr_{0.2}CrO_3$) and cuprates (e.g. La_2CuO_4). Among the catalyst tested, $SrRuO_3$-based perovskites showed the best performance. It is important to note that none of the perovskites contained Pt or Pd, i.e., the materials whose oxides showed the best performances in the previous works revised in this section. Thus, to improve the material further, $SrRuO_3$ was modified with different loading of Pt. Figure 13 shows that for potentials below 0.4 V, $SrRuO_3$ is more active than the benchmarking PtRu. At higher potentials, Pt-Ru is more active than all the catalysts tested in this work. Even if the Pt loading is lower for the perovskites, the Ru content is much higher making the price of the materials comparable.

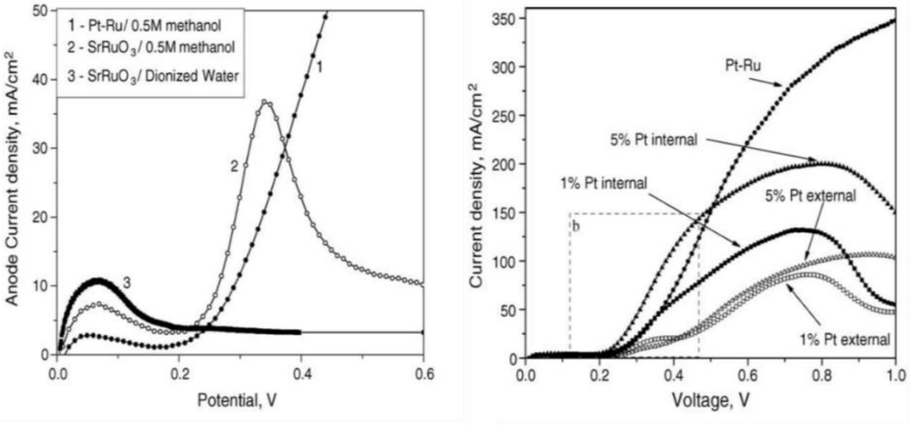


Figure 14: (Left) Linear voltammetry profile of Pt-Ru and of $SrRuO_3$ in presence of methanol (1,2) and SrRuO3 in methanol absence (3). (Right) Linear voltammetry profiles of SrRuO3 with different Pt loadings and its comparison to Pt-Ru profile. From Deshpande *et al*.[122]

Similar results were obtained by Lan and Mukasyan[184] using an analogous approach to that of Deshpande[122] *et al*.. They synthesized and tested (ABO_3; A = Ba, Ca, Sr, La; B = Fe, Ru) perovskite oxides and identified $SrRuO_3$ and $LaRuO_3$ as the most active materials. To improve its activity, these materials were modified by Pt attaining similar performances to PtRu but using less quantities of the noble metal.

It is well-known that the effect of the substitution of La by Sr in the A-site of perovskite oxides, which increases the surface basicity and the oxygen mobility by decreasing the M-O bond energy. Singh[185] *et al*. used this strategy to tune the activity of $La_{2-x}Sr_xNiO_4$ (x = 0, 0.25, 0.5) for the electrooxidation of methanol in 1 M KOH and found that the electrode activity increased with the Sr percentage. Like CO (electro)oxidation, the presence of highly oxidized transition metal cation increases the material activity. The CV profiles permitted to observe the reversible peaks due to the Ni^{+3}/Ni^{+2} redox couple in the perovskites and the potentials for the onset of the electrooxidation of methanol matched that of the redox couple. Thus, the results suggested that the presence of Ni^{+3} was a necessary condition for the oxidation of the alcohol. Besides, after reaching this condition, the rate of the reaction was limited by the M-O bond energy. The importance of the presence of Ni^{+3} has been observed for the electrooxidation of other organic molecules like ethanol[186,186] glycerol[187] and glucose[188,189]. There is consensus that when the nickel surface is in contact with the solution in alkaline media, it is covered by $Ni(OH)_2$[190]. At potentials higher than 1.3 V vs. RHE, the hydroxide is converted to an oxy-hydroxide NiOOH that can further oxidize the organic species[26,189]. The importance of high valence ions for the electrooxidation of methanol was also observed for Cu^{+3} by Raghuveer *et al*.[191,192]. The authors evaluated rare-earth cuprates of compositions $La_{2-x}M_xCu_{1-y}M'_yO_{4-\delta}$, where M = Sr, Ca and Ba and M' = Ru and Sb, with $0.0 < x < 0.4$ and $y = 0.1$. Similar to the results described for Ni-containing perovskites the onset for the electrooxidation of methanol matched the potential for the equilibrium Cu^{+2}/Cu^{+3}. B site substitution tunes the potential for the couple Cu^{+3}/Cu^{+2}, which also changed the onset for the oxidation of the alcohol, giving strong support to the idea that the presence of Cu^{+3} is a necessary condition for the oxidation of the organic. This result agrees with the findings of Elias *et al*.[169] for the heterogeneous oxidation of CO, where Cu^{+3} ions served as binding sites for the CO molecule.

It is important to be careful when we analyze the effect of the "addition" of noble metals in perovskite oxides. The characterization provided must clearly show if the atoms are part of the perovskite structure, if they are forming noble metal nanoparticles deposited on the perovskite surface or a combination of both species. An excellent example is the paper by Li and Lin[180]where the authors clearly state that the addition of Pd generated the substitution in the B-site of $LaMnO_3$, but also the formation of PdO at the surface, which seems to be the only responsible for the catalytic behavior of the material. Thus, in this case, the perovskite oxide seems to play more the role of support than of the active phase. In fact, the use of perovskites oxides as a support have been another approach that has shown some success. Results obtained with Ni nanoparticles deposited on $La_{2-x}Sr_xNiO_4$[193] and Pt nanoparticles on $La_{1-x}Sr_xCoO_3$ (x = 0, 0.2, 0.4 and 0.6) and $La_{1-x}Sr_xMnO_3$ (x=0.2)[194] show that the presence of the nanoparticles increases the electrocatalytic activity.

The revision of the (electro)chemical oxidation of methanol on metal oxides showed the importance of the presence of high valence ions at the catalyst surface in the B-site. Thus, one of the aims of the partial substitutions in the A and/or B-site should be to decrease the potential for the oxidation of the redox couple in this site. Considering the significance of this aspect, we would like to stress the importance of the blank voltammograms, which are not shown in most of the articles of the field revisited here and could give great insights to understand activity trends. Therefore, we suggest getting CV profiles in the base electrolyte using as working electrode the perovskite oxide deposited in an inert substrate (ex. Glassy carbon), without additives (ex. Nafion). The deposition of the perovskite oxide from an ultrapure water dispersion minimizes the presence of other signals coming from additives and/or contaminations that can cover the presence of redox couples. Finally, apart from the identification of the oxidation/reduction peaks, the blank voltammogram can render important information about the kind of the sites presents at the surface (ex. prevalence of any facet, termination, etc.) as well as information about the electroactive area[195,196,]. As mentioned before, the major drawback of several research papers in the field of electrocatalysis is the difficulty to determine the number of active sites and/or the Electrochemical Surface Area (ECSA). On top of that, it is sometimes wildering to dictate the contribution of this parameter to the observed differences in activities between the groups of catalysts. Thus, the lack in determining the areas or active sites make difficult to correlate fundamental properties of the materials (descriptors) and their activities. Fortunately, recent work of Morales and Risch[196], details a procedure for the correct determination of the capacitance of the electric double layer. Even if the procedure is inadequate to determine the number of active sites, this is an important contribution towards a fair comparison of the catalytic activities of other materials than pure Pt, Pd and Au, where the determination of the ECSA is well stablished.

As for the oxidation of CO, lattice oxygen plays an active role in the oxidation of the adsorbed methoxy group and other partially de-hydrogenated intermediates. Thus, it is important to tune the perovskite composition to generate O vacancies and increase the mobility of the O atoms, which, as discussed before will de-hydrogenate the organic molecule and/or bind to the C-atom of the intermediates. The heterogeneous catalysis and electrochemical ambient reactions would likely have some similarities; however, it is essential to consider some significant differences. First, the electrochemical experiments with perovskite oxides are usually performed in water and in alkaline media, as most of the good catalysts of this kind are unstable in acid media[197,198]. Thus, the alcohol and the groups at the surface of the electrocatalyst will participate in several acid-base equilibria in this condition. Besides, it is crucial to remember the major difference between these two fields, i.e., in electrochemistry, the energy of the electrons and ions in the electrode are controlled by the potentiostat, tuning the rate of the electrochemical reaction, the distribution of the species at the interface, the stability of the materials, among other many factors.

The literature about the electrooxidation of alcohols and polyols (different from methanol) on perovskite oxides is scarce, except for those related to SOFC, which are out of the scope of this review. Apart from the study performed by some of us using glycerol, there is one preliminary research about the electrooxidation of ethanol on $LaRuO_3$ and $SrRuO_3$[184] and another about the electrooxidation of glycerol and isopropanol on $LaFe_{1-x}Co_xO_3$ performed by Dulce Morales et al.[199]. Santiago *et al.*[200] studied the electrochemical oxidation of glycerol on $LaNiO_3$ and $LaCoO_3$ and identified the reaction pathway involving the formation of glycolic acid, oxalic acid and formic acid (Figure 15A and B respectively). Dulce Morales et al. (using $LaFe_{1-x}Co_xO_3$), in agreement with the results of Santiago *et al.*, showed clear benefits changing the water oxidation by the oxidation of the organics (for some materials), in terms of gains in energy and the production of value-added chemicals. The results of these contributions reinforce some of the conclusions drawn in the previous sections: i) CO does not adsorb in $LaNiO_3$ and $LaCoO_3$ in the conditions of the experiment (0.1M NaOH at room temperature), ii) $LaNiO_3$ and some compositions of $LaFe_{1-x}Co_xO_3$ are able to oxidize the organics faster than the water, iii) $LaNiO_3$ is more active that $LaCoO_3$ (in agreement with the results showed for glycerol steam reforming[201]), highly surpassing the activity (currents/mg Ni) measured with Ni/C[187], iv) it is extremely difficult to understand the trends observed for $LaFe_{1-x}Co_xO_3$ in terms of fundamental parameters of the materials due to their intrinsic complexity. Very interestingly, and agreeing with several results reviewed in this article, the oxidation of the organic starts only when Ni^{+2} oxidize to Ni^{+3} and Co^{+2} to Co^{3+} (inset Figure 15). Besides, it is remarkable to observe that none of the products observed by Santiago *et al.* where C_3 and the most important product observed by far in the work of Dulce Morales et al. was formate, i.e., all the products are generated after a C-C bond breaking. In noble metal electrodes, as stated before, as the electrochemical potential increases, promoting the oxide formation, the concentration of C_3 products decrease at expenses of an increase in the concentration of C_2 and C_1 products. Thus, we could ask ourselves if the C-C bond breaking is an intrinsic characteristic of metal oxides (the same phenomena have been recently observed for other materials[202,203]) or the C-C bond breaking occurs in oxides due to the relatively high potentials at which the oxidation reactions are driven (in comparison with the formation of C_3 products, for example on Pt[204]).

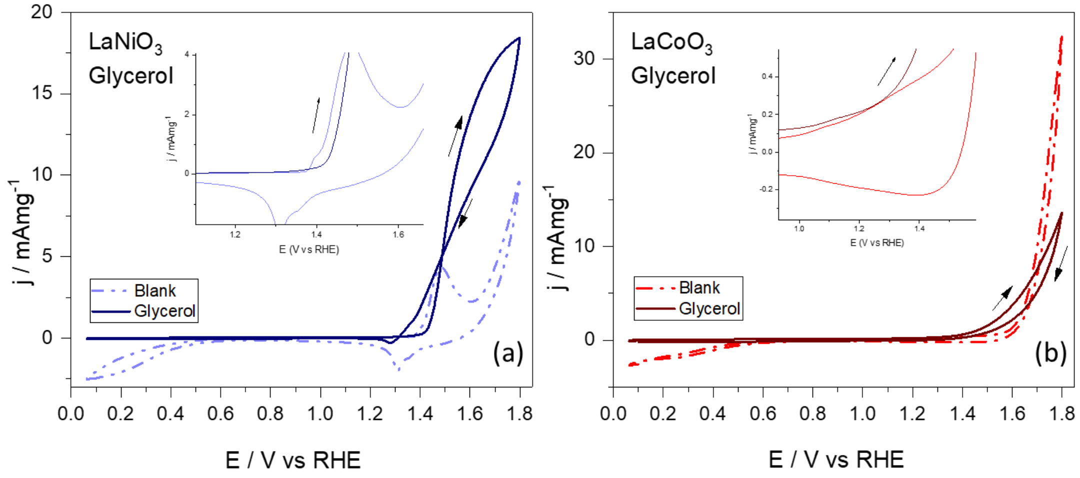


Figure 15: Cyclic voltammetry of (a) $LaNiO_3$ and (b) $LaCoO_3$ in the presence (solid lines) and absence (dash lines) of 0.1M glycerol in 0.1M NaOH. Inset: magnification of the region where both, the B-site and the organics oxidize[205].

Based on the fundamental knowledge about the electrooxidation of methanol on metal oxides, of polyols on metals, and the several products detected in the oxidation of alcohols with several carbons, we hypothesized several adsorption intermediates for the electrooxidation of polyols on metal oxides (Figure 16). According to the previous discussions, there is a consensus that the activation of the organic molecules on perovskite oxides occurs by binding the molecule to a high valence B-site cation. However, it is important to note that if the pHs is close to the molecule pKa, we have the presence of the alcohol and of the corresponding alkoxide in relevant quantities, the last binding very likely the acid site more strongly. At this point, it is also interesting to remember that the most reactive species on metals is the anion generated by the deprotonation of the -OH group in solution[93]. Thus, different from the proposal in figure 12 for methanol, we propose here that the reaction might start by the attack of the alkoxide to the B-site of the perovskite oxide (in this case, the anion is glycerolate). Then, this intermediate can directly form a product or form multiple-bonded intermediates through successive de-hydrogenations, which can drive the reaction to the formation of some of the multiple possible electrooxidation products.

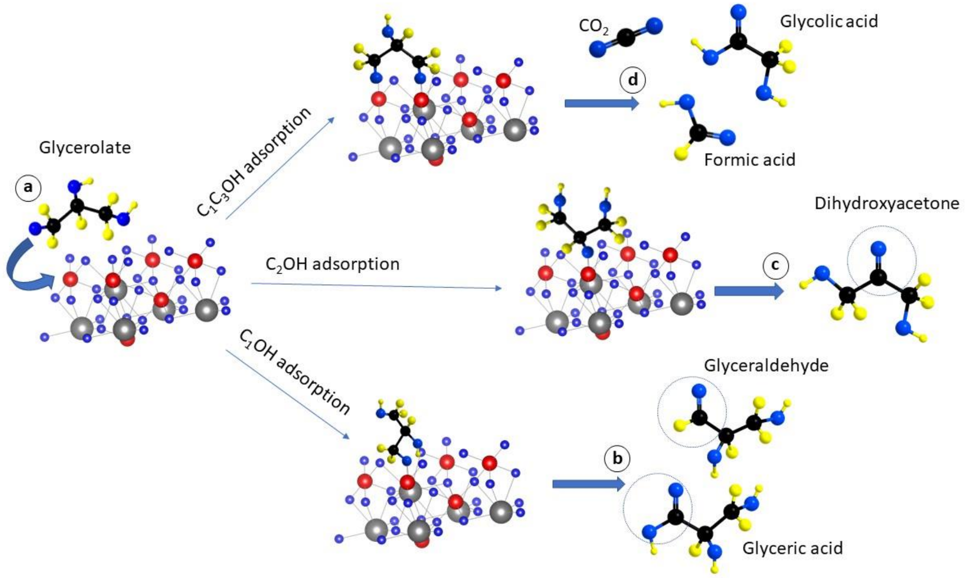


Figure 16: The scheme shows the attack of a polyol (in this specific example glycerolate) to the perovskite B-site (a) to form three of the several possible de-hydrogenated intermediates (b, c and d). It is important to notice that the glycerol molecule is completely hydrogenated in (a) but, depending on the pH of the solution the main reactant can be the de-hydrogenated specie (in this specific example the ion glycerolate). If the molecule adsorbs only through the -OH group of one of the primary carbons (b), depending on the site's properties, it will generate the corresponding aldehyde or acid (in this specific example glyceraldehyde and glyceric acid). If the molecule adsorbs only through the -OH group of one of the secondary carbons (c), it will generate a ketone (in this specific example only di-hydroxyacetone can be formed as glycerol has only one secondary carbon). Finally, if the molecule adsorbs from more than one -OH at the same time, it can promote the C-C bond breaking to generate C2 and C1 products. The extension of the oxidation will depend on the surface acid-basic and redox properties as discussed for the case of methanol.

As a final discussion of the most likely mechanism for the oxidation of alcohols and polyols, we would like to highlight two other contributions: i) another work of Dulce Morales et al. about the electrooxidation of ethanol and glycerol on Ni oxide[202]. Again, the authors showed the importance of the presence of Ni^{+3} species, the faster anodic reaction in the presence of the organics molecules and the high degree of oxidation, obtaining mainly C_1 and C_2 compounds; ii) Chen et al.[206] suggested that on Ni surfaces, during a positive going potential scan, Ni is converted to Ni(OH), to then form the reactive specie Ni(OH)O. The authors propose that the oxidation of the organic occurs through a chemical reaction between the organic molecule and Ni(OH)O. We think that it is a promising insight and that both, the adsorption energy of the intermediates proposed in figure 16 and the energy for the generation of M(OH)O species on metal oxides (including perovskite oxides) are candidates as a descriptor of the electrooxidation of organic molecules.

In our opinion, performing these reactions in electrochemical environment would potentially bring several benefits compared to heterogeneous catalysis experiments, where high temperatures are necessary to promote de dehydrogenation and further molecule oxidation. In electrochemical ambient we can modulate both, the oxygen mobility and/or the oxidation state of the atoms just by changing the electrochemical potential. Thus, the strategy to look for efficient perovskite oxides for the oxidation of alcohols/polyols would be to search for materials where the transition metals are stable in a high valence state at potentials as low as possible to bind the organics and/or to form M(OH)O species. Regarding the reaction selectivity, it seems tricky to avoid the C-C bond breaking and we should focus on obtaining mainly C_2 and C_1 products. In this sense, it seems that obtaining high selectivity to formate would be the less challenging goal[203].

In this context, perovskite oxides seem to be an excellent alternative for the electrochemical oxidation of organic molecules as their properties can be modulated by playing with the composition of both the A and B sites. Apart from the theoretical considerations about the relationship between structure-composition and properties, it is worth noticing that perovskite oxides have been prepared and used for several applications (e.g. capacitors[207], CO oxidation[208], hydrocarbon oxidation[209], and NOx reduction[210]) in the last 80 years. Thus, there are many available methods to prepare the materials not only playing with its composition but also with its size and shape, permitting to further optimize their properties[30]. Besides, many perovskite oxides have been computationally modelled, therefore, despite the limitations described before, there is a lot of information about the relation between the materials structure-composition and several properties (binding energies to different molecules, band gaps, work function, etc.)[134].

FINAL REMARKS, PERSPECTIVES AND CHALLENGES

The production of pure hydrogen through electrolysis is being boosted by the necessity of storing energy and the transition to a cleaner economy. To make the process more cost effective, researchers have searched for improved catalysts to increase the rate of the oxidation of water, i.e., the rate determining step. More recently, instead of searching for improved materials for water splitting, several researchers are proposing to oxidize different organic molecules instead of water at the anode. Therefore, we have analyzed in this work the oxidation of alcohols and polyols, because many biomass-derived molecules contain these organic groups, and they could be oxidized to obtain value-added chemicals.

Metals like Pt, Pd and Au stand out in alkaline media in terms of activity for the electrooxidation of organics. However, it is well-known that these are relatively scarce and expensive metals. In this context, earth abundant materials, mainly metal oxides, appeared as a suitable alternative to be tested[12,202,203], as several of these kinds of materials have been studied for years for water splitting[211,212]. Therefore, there is a vast literature about synthetic processes and characterizations of a myriad of materials containing non-noble metals, which could help accelerating the search for suitable catalysts for the electrooxidation of organic molecules, more specifically, for biomass-derived alcohols/polyols. Unfortunately, the attempts until now are scarce and not systematic enough to permit to correlate neither the activity nor the selectivity of the reactions with physicochemical parameters of the materials. Therefore, due to their extensive application for the OER and the knowledge about the synthetic processes, the characterization methods, and the properties; we believe that perovskite oxides arise as a promising starting point to perform experiments toward a fundamental understanding of the connection between structure/composition of the catalyst and activity/selectivity of the reaction. Thus, we hope that this contribution offers the readers a good background before starting this journey, by i) giving key information about reaction mechanism of some small organic molecules on metals and metals oxides, ii) showing the outstanding structural flexibility of perovskite oxides, and iii) critically discussing how some of their properties can be used as descriptors for several reactions. In this sense, we would like to stress again the importance of the quantification of the active sites (and/or the ECSA) or at least of the electrode capacitance, which is mandatory to make fairer activity comparisons. Besides, another important point, not discussed in this article, relates to the stability/dynamic of the surface of some perovskite oxides. While it is well-known the lack of stability of most of the metal oxides in acid media, there are several works being developed with the aim of finding active and stable catalyst in this media and/or to understand the descriptors that permit to mitigate this issue [197,198,213,214]. On the other hand, careful experiments in alkaline media have shown that long term experiments can generate changes in the activity of the materials due to, for instance, the incorporation of Fe (a usual contaminant in KOH and NaOH) in the perovskite oxides lattice[211]. This problem can be eliminated by i) purifying even high purity KOH and/or NaOH solutions or ii) restricting the experiments to a few voltametric cycles or iii) performing chronoamperometries only short times.

Briefly, we have shown here that several perovskite oxides can oxidize methanol, ethanol, etc. at lower potentials than water. This means that the appropriate choice of the biomass-derived molecule/catalyst pair will certainly enhance the performance of a conventional electrolyzer[202]. Besides, we highlighted that, if in place of methanol, other biomass-derived molecules as glycerol or glucose are oxidized, they could potentially improve the power of the device and be converted to value-added molecules. In this case, the catalyst selectivity, which has been considered poorly until now, will play an important role.

We have discussed some results from heterogeneous catalysis in which perovskite oxides were used as catalyst for CO and small organic alcohol oxidation. We believe that these findings can be used as starting point to guide us in the understanding of those reactions in electrochemical environment.

It is worth to note that even if some perovskite oxides generate higher currents in the presence of the organic molecules, the performance of the electrodes (or devices) are far from those based on noble metals[23]. In fact, the best results with perovskite oxides were obtained when the material was combined to noble metals. In any case, we think that it should not be considered as non-promising results, because, as stated before, just a few materials have been tested for these reactions and in a very limited range of experimental conditions (temperature, pH, etc.).

Another aspect that has not been studied yet is the stability of the perovskite oxides in the presence of the organics. Teles *et al.*[215] showed that Pt nanoparticles supported on graphene nanoribbons and on amorphous carbon have different stabilities and that the degradation rate depends on the alcohol that is oxidized. Considering that the electrochemical potential is a key parameter that determine the stability of perovskite oxides, the application of lower overpotentials in the presence of these molecules (compared to the OER) could potentially improve the anode durability.

Density Functional Theory + machine learning[216] experiments can screen materials suitable for these reactions expending much less time and laboratory resources than synthesizing and testing each material. However, to design computational experiments we need to know the reaction mechanism to look for possible descriptors, for instance, the binding energy of a key intermediate. To reach this level of knowledge, it is mandatory to focus on fundamental research. Thus, after choosing a target material to be tested, if the results are promising (as for instance those shown for $LaNiO_3$ for the electrooxidation of glycerol), the next step would be to prepare series of materials changing systematically their properties (by changing the composition and/or structure) and testing their activity and selectivity. This approach, in principle, would allow linking the performances with fundamental physicochemical parameters (as has been successfully done for the OER).

To get information about the intermediates and products of electrochemical reactions, FTIR *in situ* has stablished as the most reliable technique[217]. However, the main drawbacks are that it is not quantitative, and the superimposition of bands usually complicates the identification of the species generated in a reaction[101,114]. For molecules that produce several products as ethylene glycol, glycerol, etc., the combination of FTIR with HPLC analysis is mandatory to identify and quantify the products of the reactions[101,114]. There are others approaches, but the combination of these two techniques will certainly offer, in many cases, enough information about the most relevant products of the reactions. If it is still not enough, NMR (nuclear magnetic resonance) analysis can render useful information, but always combined with at least one of the techniques mentioned before[218]. Besides, if the reaction generates volatile products, DEMS (Differential electrochemical mass spectrometry) experiments can identify and quantify the products in real time[219,220]. At least to our knowledge, apart from the recent publication of some of us[221], there is not many articles studying the electrooxidation of organic molecules in perovskites oxides using *in situ* techniques to unravel the main reaction pathways of the reaction.

To model the structure of the perovskite oxide, it is not enough to fully characterize it after the synthesis. The contact with the electrolyte and mainly the electrochemical potential can modify the structure of the material and its electronic configuration on its surface[222]. Even if FTIR can give some insights, in our opinion, Raman spectroscopy is a well-stablished technique that can be performed *in situ* and has been comparatively unexplored in this field, due to its relatively low sensitivity. However, the use of pump-probe systems[223] and of shinners[224] opens new opportunities for the application of Raman spectroscopy in electrocatalysis[225].

Without doubts, techniques employing x-rays in synchrotrons can render the most valuable information about the structure and electronic configuration of these materials *in situ* condition[226,227]. For example, by performing XAFS measurements, we can follow the oxidation state of an element (among other properties) in function of the electrochemical potentials during the reaction[219], which has proven to be essential for the (electro)oxidation of organics on metal oxides.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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