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A perspective on the relationship between the acidity of perovskite oxides and their oxygen surface exchange kinetics

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Abstract

The oxygen exchange reaction kinetics of a large number of ternary mixed ionic and electronic conducting oxides were analyzed with respect to their calculated surface acidity factors derived from the Smith acidity factors of the corresponding binary oxides from which the ternary oxides are composed. The analysis suggests that the surface exchange kinetics have a direct link to the acidity of the mixed conducting oxide. The possible interplay between acidity and transport properties is discussed. The analysis is also applied to OER electrocatalysts but does not show a link between OER overpotentials and acidity, suggesting that the link is more relevant for gas/oxide interactions at high temperatures. The observations suggest that acidity impacts most directly the oxygen adsorption process while impacting the electron charge transfer only indirectly.

1 Introduction

The reduction of molecular oxygen at the surface of oxide materials is a key reaction in many energy storage, sensor, and memory applications¹⁻⁵. In a previous article, we have shown that it is possible to tune the surface exchange kinetics of a given mixed conducting oxide, *i.e.* praseodymium substituted ceria ($\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$), by many orders of magnitude by infiltrating single valence binary oxides with different acidities⁶, as defined in an acidity scale initially proposed by Smith *et al.*⁷. In our previous work, the activation energy of the oxygen surface exchange coefficient of $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ remained unchanged for the different surface infiltrated binary oxides, and only the pre-exponential factor changed, showing a linear dependence of the log of the pre-exponential factor on the Smith acidity factor. Based on work function and electrical conductivity trends, we explained this phenomenon by arguing that the infiltrated oxides act as electron donors or acceptors depending on whether the surface additive was more basic or acidic than $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$, and thereby be able to tune the surface electron concentration in $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ by up to many orders of magnitude either in accumulation or depletion. This pointed to the acidity of the infiltrated oxide *relative* to the host, *i.e.* $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$, as the key

relevant parameter to consider in manipulating the oxygen surface exchange kinetics. Here, we examine if 1) the relationship between acidity and oxygen surface exchange kinetics can be extended to a broader range of oxides, and 2) if the absolute value of acidity, rather than relative acidity in a two phase system, has importance for oxygen exchange kinetics. To perform this analysis, we propose a calculation of an acidity factor for perovskites, based on the Smith acidity for binary oxides, that allows ranking perovskite oxides on an acidity scale, from the most basic to the most acidic. Then, we use a selection of literature data for oxygen surface exchange kinetics, measured primarily by electrochemical impedance spectroscopy and O¹⁸ tracer diffusion experiments, for a wide variety of mixed conducting oxides, and analyze the relationship between their respective acidity and their catalytic activity.

2 Methods

2.1 Calculation of the Smith acidity factor for complex oxides

To be able to study the influence of acidity of ternary and quaternary compounds such as perovskites and double perovskites, commonly considered as efficient catalysts for the oxygen exchange reaction, their acidity must first be calculated. The method for determining acidity values of various binary oxides proposed by Smith relies on the availability of thermochemical data for those oxides⁷. The calculation involves knowledge of the enthalpy of formation of a variety of salts for each oxide, which are not necessarily available for more complex oxides. An alternate approach was therefore developed to calculate an effective acidity of these more complex oxides based on available data. Here we chose to use a linear extrapolation of perovskite acidity based on the Smith acidity of the binary oxides that make up given perovskite compositions of nominal composition ABO₃. This extrapolation is reasonable considering that the original calculation by Smith for binary compounds is also based on a linear mean value extracted from various reaction enthalpies⁷. The Smith factor for a given binary oxide is normalized with the cation stoichiometry, for example, $\alpha(\text{La}_2\text{O}_3)$ is divided by a factor of 2 to be used in perovskite of general composition LaMO₃. As a perovskite has two moles of cations per unit formula, we choose to divide the sum of α by the overall number of cations.

The general expression of α for perovskite oxides of general formula $A_xA'_{1-x}B_yB'_{1-y}O_3$ is as follow:

$$\alpha_{A_xA'_{1-x}B_yB'_{1-y}O_3} = \frac{x\alpha_{AO} + (1-x)\alpha_{A'O} + y\alpha_{BO} + (1-y)\alpha_{B'O}}{2} \quad (1)$$

The same approach is used for double perovskites, but because their unit formula is twice that of perovskite, the sum is divided by 4 instead of 2, which allows for comparison between the two different structures.

The main issue arising when attempting this calculation comes from the transition metal on the B site. For the A site, the cations are primarily single-valent, and there is only one stable oxide from which

we can use a Smith acidity factor. For transition metals such as Fe or Co, several stable oxides exist, sometimes with mixed valence (Co_3O_4 for example), which makes the selection of a relevant Smith factor less obvious. It is tempting to consider that the transition metal in most perovskites is primarily in the 3+ valence state, and therefore one would choose the acidity factor of the M_2O_3 oxide to better match the oxidation state in the perovskites. However, this strategy is less convenient because the acidity of the corresponding M_2O_3 oxide is not available for all transition metals considered in this study. This is because the Smith factor for a given oxide is determined from the formation of oxoacid salts that are, for transition metals, primarily in the 2+ oxidation state. As there are more thermochemical data available for oxoacid salts with the 2+ oxidation state, the Smith acidity value for BO oxides is also more reliable because it is calculated from an average of more reaction enthalpies. Therefore, for comparison purposes, we chose to use the Smith acidity for the 2+ oxide of each transition metal oxide (when possible). Nevertheless, one should keep in mind that the Smith factor can change greatly with the oxidation state of a given cation. For example, $\alpha(\text{MnO})$ is -4.8 whereas $\alpha(\text{Mn}_2\text{O}_7)$ is 9.6, which illustrates the challenge in comparing a large number of different compositions with this analysis. Additionally, one should keep in mind that different levels of A site doping of rare earth 3+ cations with alkaline earth like Sr^{2+} can have two opposite effects: decreasing A site acidity because alkaline earth oxides are more basic, and increasing B cation oxidation state which would increase its acidity. On the other hand, oxygen deficiency in perovskites can also induce a lower oxidation state of the B cation. In summary, seeking more accuracy in the determination of the acidity factor for perovskites will inevitably make it lose its simplicity, which defeats the purpose of this analysis.

2.2 Selection of surface exchange kinetic data from the literature

To apply our analysis, we chose to use data for surface exchange coefficient k^* (measured by isotopic exchange) and surface polarization resistance R_p (measured by impedance) that were already gathered and averaged in the work of Lee *et al.*⁸ on a large number of perovskites and double perovskites.

Measuring oxygen exchange kinetics at high temperature can often induce surface modification of the perovskite, such as cation segregation or contamination from the measurement setup. These effects can degrade the surface exchange kinetics and complicate our analysis. To minimize this issue, we included the work from Baumann *et al.*⁹ in this analysis, because it compares the surface polarization resistance R_p of a range of perovskites, measured on thin films, prepared under the same conditions. This study therefore serves to reduce the uncertainties arising from the collection of data from a large number of laboratories with a variety of different sample preparation and measurement conditions.

This analysis was also extended to the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) in alkaline solutions, often considered a rate limiting step for electrochemical water splitting. In this case, measurements of ORR activity by Suntivich *et al.*¹⁰ for a large number of oxide

catalysts were extracted and plotted against their respective Smith acidity. In alkaline solution, the stability of the surface of the oxide catalyst can also be an issue that would complicate our analysis. For example some materials such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ are known to amorphize during operation¹¹. To avoid those issues and complete our analysis, the theoretical OER activity data from Man *et al.*¹² for a large number of perovskites was also extracted and analyzed with respect to their calculated Smith acidity.

3 Results

To analyze the possible relationship between acidity and surface exchange kinetics, values of polarization resistances R_p and surface exchange coefficient k^* taken from Lee *et al.*⁸ were plotted against the calculated Smith acidity for a series of perovskites : LaMnO_3 , $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, LaCoO_3 , $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, and double perovskites: $\text{PrBaCo}_2\text{O}_{5+\delta}$, and $\text{GdBaCo}_2\text{O}_{5+\delta}$. Figure 1a shows the evolution of $\log R_p$ as a function of the Smith acidity of these materials, and demonstrates that there is a clear linear relationship between surface exchange kinetics and acidity for most of the considered materials. However, the trend does not hold for the two manganites considered, *i.e.* LaMnO_3 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, which have significantly higher R_p values than their cobalt and iron-based counterparts. The same trend is observed in Figure 1b comparing $\log k^*$ values as a function of the corresponding materials acidity, with the exception that for this set of data, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ is also significantly lower than the linear trend observed with the other materials. Although this trend is remarkable for such a wide variety of materials, it is necessary to discuss the possible reasons that some materials clearly fall outside of it. For manganites, there are two hypotheses that can explain why their surface exchange rate is not correlated directly to their acidity. First, the manganites are not oxygen deficient at high pO_2 ¹³. This is a problem since the oxygen vacancy concentration is key to the oxygen exchange reaction, as oxygen vacancies are needed at the surface to incorporate freshly reduced oxygen ions generated at the surface into the bulk. They are also key for insuring sufficient oxide ion conduction, allowing for adsorbed oxygen to rapidly find incorporation sites and diffuse from the surface sites and become incorporated into the bulk of the oxide¹⁴. The acidity of the oxide material thus only becomes a highly relevant parameter if the oxide also possesses a sufficiently high oxygen vacancy concentration. Second, manganese in perovskites can be significantly more oxidized than its nominal 3+ state, especially at the surface. Wu *et al.*¹⁵ measured the average oxidation state of Mn in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ at the surface by photoelectron spectroscopy to be +3.5. Although this might have implications for its catalytic activity toward the oxygen reduction reaction, it also means that using the acidity of MnO for calculating the Smith acidity of Mn based perovskites can significantly underestimate the overall acidity of the perovskite.

For $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, the inconsistency between the k^* and R_p data raises the question of the reliability of surface exchange data in the literature. Especially in the case of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$,

stability issues and reactivity problems are well known to exist due to the formation of surface carbonates that could negatively impact the analysis. Another feature that renders the analysis of surface exchange kinetics with acidity more difficult than in our previous work, is that the activation energy for k^* (or R_p) can change significantly between materials, especially when the 3d cation, believed to be the redox center, changes.

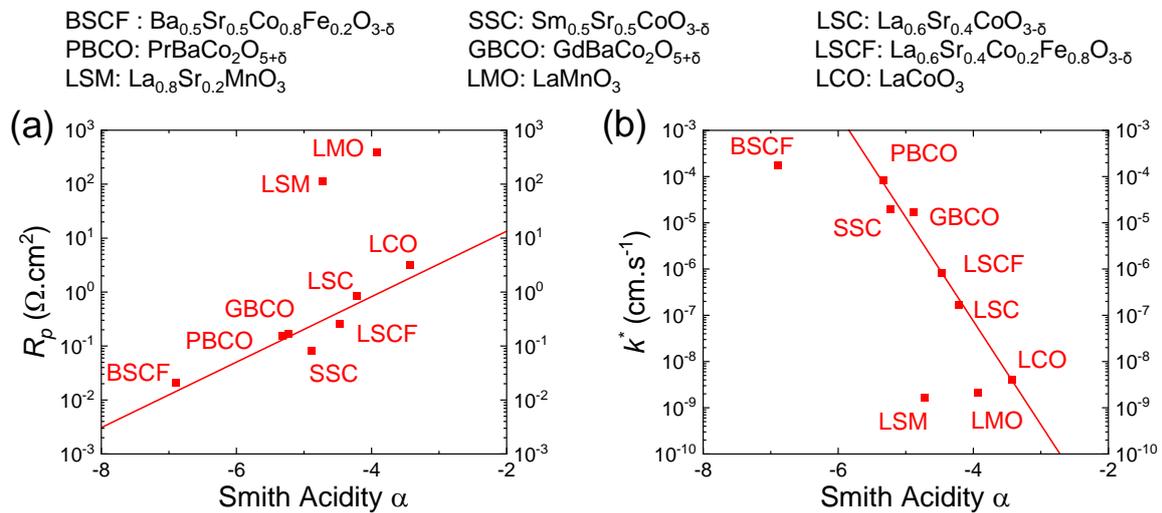


Figure 1 : Polarization Resistance (a) and surface exchange coefficient k^* (b) as a function of Smith acidity for materials measured at 1000 K. Data copied from⁸, initially collected from refs¹⁶⁻⁴³.

To overcome potential data inconsistencies collected from different research groups who utilized different measurement techniques, we found it useful to apply our analysis to results obtained in studies that examined different materials, but under the same conditions of preparation and measurement. Baumann *et al.* studied the surface exchange kinetics of different Co-Fe based perovskites, prepared by Pulsed Laser Deposition by impedance spectroscopy utilizing microelectrodes under near identical conditions⁹. Figure 2a compares the polarization resistance associated with the surface exchange kinetics (R_p) of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ with respect to their Smith acidity. Similar to what is observed in Fig.1, the polarization resistance R_p shows a strong correlation and dependence on the calculated Smith acidity. To assess whether this correlation is perhaps caused by third parameter that could be linked to both Acidity and surface exchange kinetics, it is necessary to study the evolution of other keys parameters with the Smith acidity. Previous studies of parameters affecting surface exchange kinetics have shown that fast kinetics can stem from high oxide ion conductivity⁴⁴, or high electronic conductivity⁴⁵ (regardless of n or p type character). Therefore, the oxide ion diffusion coefficient and the electronic conductivity of the materials considered in the Baumann study were also plotted as a function of the calculated Smith acidity. In Figure 2b, the tracer diffusion coefficient D^* measured at 600 °C by various authors^{17,23,46-48} is shown to decrease with increasing Smith acidity for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, but that correlation does not hold for the most acidic material of the series, namely $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$, which

shows a higher D^* than $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$. On the other hand, the electronic conductivity, also extracted from various studies^{49–53} (Figure 2c) also decreases when the Smith acidity increases, but the correlation does not hold for the most basic materials of the series, namely $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, which shows the lowest conductivity. These observations suggest that the surface exchange kinetics correlate better with the Smith acidity than they do with electronic and ionic transport properties. To look further into possible side correlations between Smith acidity and relevant properties for surface exchange kinetics, the oxygen vacancy concentrations were also compared with respect to the Smith acidity. Indeed, oxygen vacancies were previously shown to be involved in nearly all relevant rate determining steps in most of the relevant mixed conducting oxides¹⁴. Figure 2d shows the chemical capacitance of each materials as a function of the Smith acidity, extracted from the impedance measurements of Baumann *et al.*⁹ at 750 °C. In the case of thin films in which oxygen chemical potential is homogenous and controlled by the oxygen exchange reaction, the chemical capacitance is a good measure of the vacancy concentration⁵⁴. Again, although it scales nicely with the Smith acidity for $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$, the correlation does not hold for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$.

From these comparisons, it becomes possible to evaluate what appears to be the most relevant parameters relating to oxygen surface exchange in mixed conducting perovskites. First, although there is broad consensus that adequate ionic and electronic transport properties are mandatory for an oxide to be a good catalyst for oxygen exchange, those parameters, in and of themselves, are not sufficient to predict how fast the oxygen exchange kinetics will be. For example, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ has a much lower electronic conductivity compared to some of the other transition metal perovskites, but still exhibits some of the fastest oxygen surface exchange kinetics. One can argue that oxide ion diffusivity is the most relevant property to describe oxygen exchange kinetics and the correlation between D^* and k^* demonstrated by Kilner *et al.*⁴⁴ shows that. This still holds true here, except between $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ for which the difference of D^* is not significant enough to clearly invalidate the trend. Then, an important question is whether the acidity/ k relationship is just a correlation, not a causation. However, even if this question remains open, we believe that because this link exists, it is interesting to analyse it in terms of the possible effects that acidity can have on the surface reaction, in an attempt to enrich the discussions on the matter. From this standpoint, the Smith acidity seems to exhibit a more direct relationship with oxygen exchange kinetics than the transport properties. This observation implies that the interaction of molecular oxygen with a more basic oxide surface is always favorable for fast kinetics. This statement naturally draws attention to adsorption-related steps involved in the overall reaction. If molecular oxygen was actually adsorbing preferentially on surface oxygen vacancies, one would expect a linear trend between the chemical capacitance (vacancy concentration), the Smith acidity and the surface exchange kinetics. Again, the chemical capacitance fails to explain the very fast kinetics observed with $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, while

the Smith acidity does. This observation suggests that high oxygen vacancy concentration at the surface does not necessarily mean fast kinetics. This is consistent with the previous findings of Tsvetkov *et al.*⁵⁵ which aimed at lowering surface vacancy concentration to limit Sr segregation in $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$. In that work, the authors proved that high enthalpies of vacancy formation at the surface do not decrease surface exchange properties. It also corroborates our previous observation⁶ that infiltrating non redox active oxides on a mixed conducting oxide can induces dramatic changes in the surface exchange kinetics. Indeed, those oxides are not expected to modify the vacancy concentration at the surface because of their close shell electronic structure.

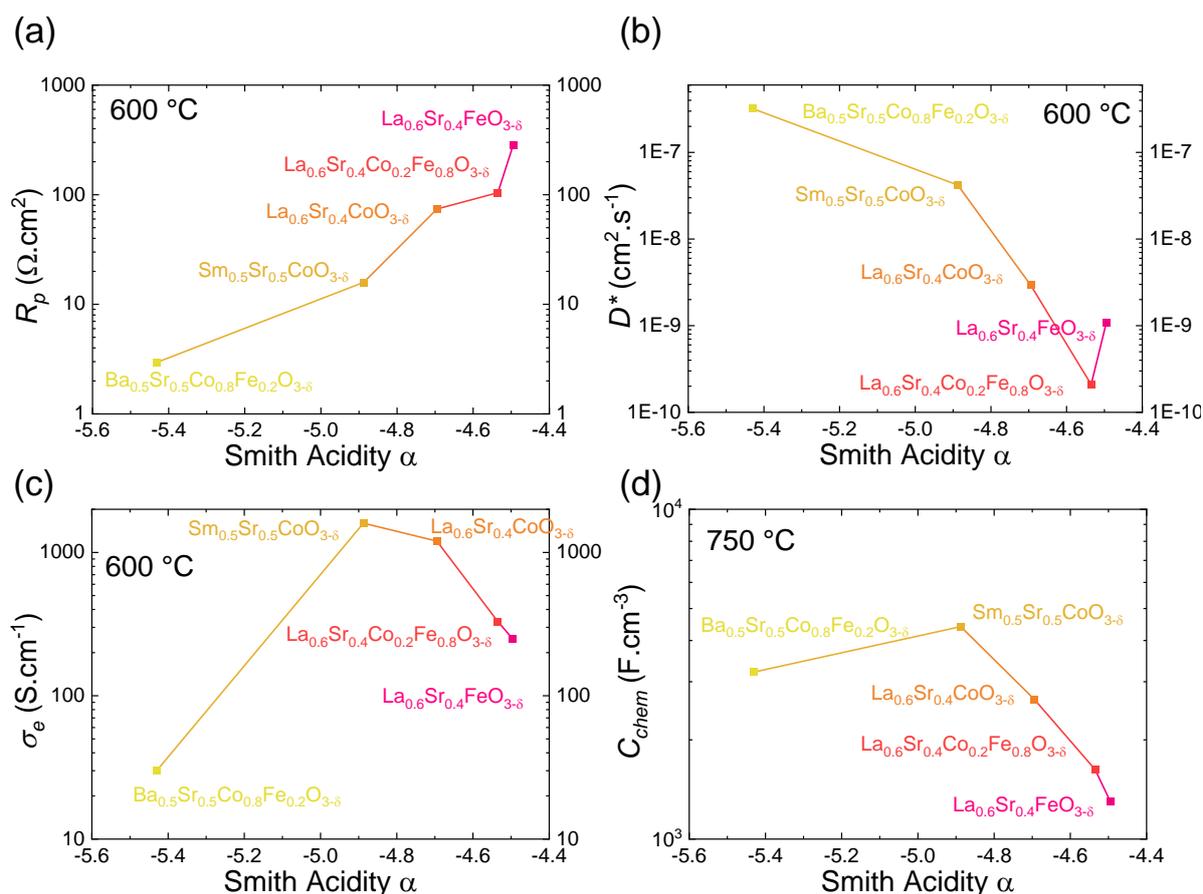


Figure 2: Dependence on Smith acidity of surface exchange kinetics and transport properties. (a) Area specific resistance associated with oxygen exchange kinetics, R_p , of thin films of various perovskites measured at 600 °C reproduced from Baumann *et al.*⁹. (b) Oxygen diffusion coefficient D^* measured at 600 °C reproduced from various authors^{17,23,46-48}. (c) Electronic conductivity measured at 600 °C reproduced from various authors⁴⁹⁻⁵³. (d) Chemical capacitance measured by impedance spectroscopy at 750 °C by Baumann *et al.*⁹. All parameters are plotted against the calculated Smith Acidity for each composition.

Although the link between an oxide's acidity and the associated oxygen surface exchange kinetics appears to be established, the main question remains: what reaction mechanism is so tightly bound to acidity, and in what way does changing acidity change the overall exchange kinetics?

In our previous work, we discussed the connection between acidity and surface electron concentration at the surface, although this change alone could not be responsible for the change of kinetics experienced on Pr-doped ceria. Here, the problem is different because we are no longer considering interfacial effects between two materials. It is interesting to discuss possible reactions steps that can be influenced by acidity.

For the majority of commonly used mixed conducting oxides, *i.e.* those with fast oxide ion conductivities, the rate limiting step of the oxygen surface exchange reaction is either a step related to adsorption of molecular oxygen, or to the charge transfer step, corresponding to the reduction of neutral oxygen species with electrons provided by the mixed conductor. Hence, we choose to limit the discussion to these two steps. We begin by considering the following: if the acidity of an oxide is affecting the charge transfer reaction of oxygen reduction, similar trends could be expected for electrocatalysts studied for the oxygen evolution reaction in water electrolysis at room temperature. To assess if this is the case, the calculation of the Smith acidity using Eq. (1) was repeated for a number of *oxygen evolution reaction* (OER) electrocatalysts. Then, their activity as an oxygen electrode is plotted as a function of the calculated Smith acidity and discussed. The ~~overpotential~~ first set of data is extracted from the theoretical work of Man *et al.*¹², in which they calculate an electrode overpotential based on the free energy of the rate limiting step. Although their approach can be considered over simplified as previously discussed⁵⁶, their work has the advantage of gathering a large number of perovskites, which is convenient for looking at a potential trend with our analysis. To complete this analysis, experimental data of oxygen reduction reaction activity (ORR) was extracted from the work of Suntivich *et al.*¹⁰. Figure 3a shows the theoretical OER overpotential of various perovskites as a function of their acidity, and Figure 3b shows the ORR potential at 25 $\mu\text{A}\cdot\text{cm}^{-2}$ of various perovskites, also as a function of their calculated Smith acidity. It becomes clear from this analysis that in the case of OER catalysts, no clear trend between their performance and the Smith acidity is evidenced. This independence between the two metrics strongly suggests that the acidity of the oxide does not have a direct link with the charge transfer step of the oxygen evolution reaction. It also points to a different behavior of materials between high temperature gas phase reactions and low temperature water reactions. There are a number of hypotheses that could explain this difference. First, at low temperature, oxygen vacancies in perovskites are not mobile which can have a direct effect on reaction rates. Second, electronic transport is also much different at low temperature. Most of these oxides being semi-conductors, the availability of electron at the surface is much lower than at high temperature (for gas phase reactions). On the other hand, the reactant molecule is different and their adsorption onto the active site is also fundamentally different (gas vs liquid phase).

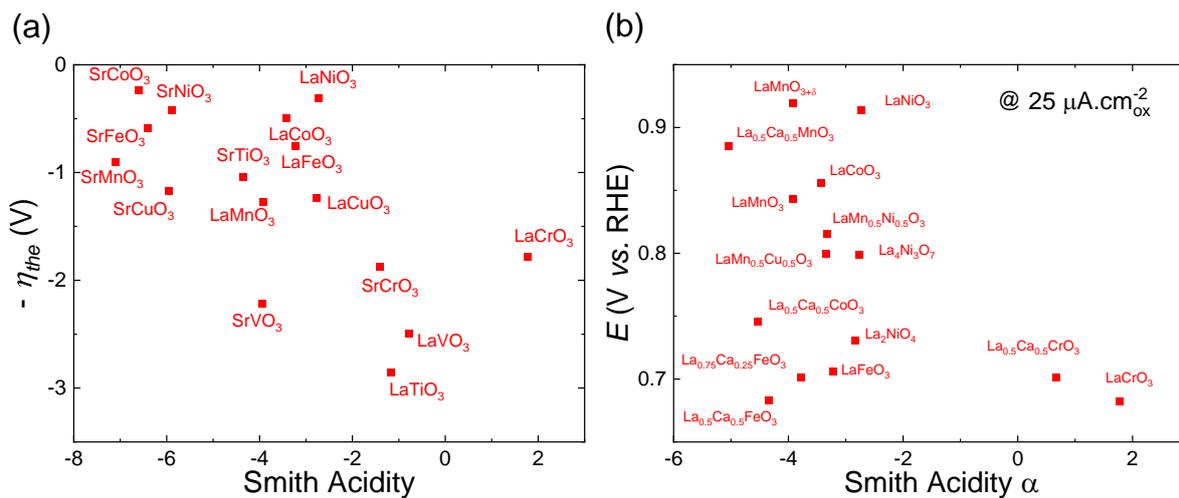


Figure 3: OER and ORR activity as a function of Smith acidity for various oxides at room temperature. (a) Calculated overpotential from Man et al.¹² and (b) ORR potential measured at $25 \mu\text{A}\cdot\text{cm}^{-2}$ from Suntivich et al.¹⁰

4 Discussion

Assuming charge transfer is not affected by the acidity of the oxide (at least not directly), then the adsorption of molecular oxygen from the gas phase takes over as the most likely mechanism. In the case of alkaline electrolysis, the adsorption of reactants on active sites have fundamentally different energetics than for a gas phase at high temperature, being in the liquid phase and at room temperature. For example, physisorption of gas molecules on a solid is not believed to maintain to high temperatures, so that only chemisorbed molecules can remain. That, in principle, sets aside the possibility of multilayer adsorption, adsorbate interactions, etc. The high temperatures at which solid oxide cells operate also decreases the surface coverage of adsorbates dramatically; so that it is often concluded that the adsorption sites are nearly empty (coverage $\rightarrow 0$)^{57,58}. Considering a strong relationship between oxide acidity and adsorption kinetics is reasonable and is already well established in other fields of research. For example, CO₂ capture from the gas by solid sorbents relies on highly basic compounds such as alkaline oxides⁵⁹.

From this standpoint, we can speculate as to how the acidity of the mixed conducting oxide can change the overall rate of oxygen surface exchange. First, we can argue that the surface coverage increases with the basicity of the oxide, *i.e.* that the binding strength between molecular oxygen and the surface is increased on more basic oxides. That, on its own, does not appear to explain the orders of magnitude variations of k_{chem} as measured in our previous work on Pr doped ceria⁶, given that surface coverage can only vary by so much. Second, through the same modulation of binding strength between molecule and solid, the adsorption/desorption equilibrium is shifted towards more adsorption. This statement is essentially the same as increasing the surface coverage, in the sense that the latter is simply a consequence of the former according to the Langmuir theory of adsorption. Nevertheless, one can also interpret the equilibrium shift as a change of residence time for a molecule on the surface, *i.e.*

how long a molecule stays adsorbed before being desorbed. Expressing the adsorption as a residence time is essentially what originally led Langmuir to his pioneering expression of adsorption isotherms^{60,61}. We think it is a useful interpretation that can help one understand the acidity/surface exchange relationship. Indeed, assuming that an adsorbed molecule is either reduced and incorporated into the solid or desorbed, if a molecule stays longer on the surface, then the probability of it being reduced by electrons before being desorbed increases accordingly. This interpretation reflects the fact that a change in adsorption/desorption equilibrium will not simply change the surface coverage of adsorbed species, but will also modify the attempt frequency for the reduction reaction. This analysis can be particularly helpful if the surface coverage stays close to 0, *i.e.* at high temperatures, because it could differentiate slow and fast kinetics by simply modifying the attempt frequency for charge transfer. It would also explain our previous observation that the activation energy for the overall reaction is independent of the surface acidity⁶. This interpretation also resonates with what was previously discussed by Adler⁶², who concluded that for electron rich perovskites, the reaction can be limited by the availability of sites or intermediates, and that this does not change the activation barrier for the reaction.

5 Conclusion

The relative Smith acidity of binary oxides used to infiltrate mixed conducting SOFC cathode materials was previously demonstrated to serve as a key descriptor of the oxygen exchange kinetics at the cathode/oxygen atmosphere interface. The analysis proposed in this work was aimed at examining if the Smith acidity of ternary perovskite mixed conducting cathode candidate materials could likewise be used to predict oxygen exchange behavior. Towards this end, we proposed a readily calculable *acidity* parameter derived from knowledge of the acidity of the individual binary oxides, *i.e.*, AO & BO₂, that together make up the ABO₃ perovskite structure. This acidity parameter is then used to examine if trends in published oxygen exchange behavior can be correlated with this calculated Smith acidity factor. The main conclusion that can be drawn from this analysis is that there is a clear link between this calculated surface acidity and the oxygen exchange kinetics, and that this link seems to hold best when the mixed conducting properties of the examined oxides are already favorable, *i.e.* exhibiting both fast ionic and electronic transport. Because this correlation appears to apply only for high temperature gas/solid reactions, and not to the OER at reduced temperatures, we conclude that the impact of acidity lies more with the adsorption thermodynamics rather than the charge transfer reaction. Nevertheless, even though a link between acidity and surface exchange kinetics can be established, its implications at the mechanistic level appear rather complex and need further investigation. In particular, computation of accurate Smith acidity values for a large number of mixed conductors could provide a way to systematically predict the performance of mixed conductors utilized as the oxygen electrode in Solid Oxide Cells.

6 Supporting information

The datasets used in this manuscript are available as an excel spreadsheet in the supplementary information section.

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