Interplay between Electronic Structure and Catalytic Activity in Transition Metal Oxide Model System

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ABSTRACT

The efficiency of many energy storage and conversion technologies, such as hydrogen fuel cells, rechargeable metal-air batteries, and hydrogen production from water splitting, is limited by the slow kinetics of the oxygen electrochemical reactions. Transition-metal oxides can exhibit high catalytic activity for oxygen electrochemical reactions, which can be used to improve efficiency and cost of these devices. Identifying a catalyst “design principle” that links material properties to the catalytic activity can accelerate the development of highly active, abundant transition metal oxide catalysts for more efficient, cost-effective energy storage and conversion system. In this thesis, we demonstrate that the oxygen electrocatalytic activity for perovskite transition metal oxide catalysts primarily correlates to the $\sigma^*$ orbital ("$e_g$") occupation. We further find that the extent of B-site transition metal-oxygen covalency can serve as a secondary activity descriptor. We hypothesize that this correlation reflects the critical influences of the $\sigma^*$ orbital and transition metal-oxygen covalency on the ability of the surface to displace and stabilize oxygen-species on surface transition metals. We further propose that this ability to stabilize oxygen-species reflect as the rate-limiting steps of the oxygen electrochemical
reactions on the perovskite oxide surfaces, and thus highlight the importance of electronic structure in controlling the oxide catalytic activity.

Thesis Supervisor: Yang Shao-Horn

Title: Gale E. Kendall Professor of Mechanical Engineering and Materials Science
To my parents, Vorathai and Chungcharoen, my brother, Jate, and my teachers
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Table 4.2. Characterizations of the oxides studied in this chapter. The number averaged diameter, $d_{\text{number}}$, the volume-area averaged diameter, $d_{v/a}$, and the specific surface area, $A_s$, were obtained from particle size distribution measurements. Methodology for calculating each variable is given elsewhere (Ref. 14).

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Table 5.1. The number averaged diameter, $d_{\text{number}}$, the volume-area averaged diameter, $d_{v/a}$, and the specific surface area, $A_s$, were obtained from particle size distribution measurements as described in the previous chapter. Note that we also measured the BET area for BSCF, which were found to be within a factor of 2 of the specific area determined from SEM.

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Chapter 1 – Oxygen Electrocatalysis

1.1 Motivation

Driven by growing concerns about global warming and the depletion of petroleum resources, developing renewable energy production and storage technologies represents one of the major scientific challenges of the 21st century. A critical element in pursuit of this quest is the discovery of efficient and cost-effective catalysts for energy storage and conversion processes. Prominent examples of reactions requiring catalysts are the hydrogen evolution and the oxygen evolution reaction (OER) in solar-driven water-splitting concepts and in the temporary storage of renewable energy by electrolytic hydrogen, the hydrogen oxidation and the oxygen reduction reaction (ORR) in hydrogen fuel cells, and the ORR and OER in metal-air batteries. Over the past decade, substantial efforts have been devoted to discovering catalytic surfaces with high activities to facilitate these reactions. However, even with the state-of-the-art catalysts, the electrocatalytic performance is insufficient – the slow reaction kinetics and the high price of required precious metal catalyst impart significant inefficiency and cost to the system. The goal of this thesis aims to assist as parts of the effort to help design novel, highly active, low-cost materials that can effectively help reduce the cost and the inefficiency of specifically the oxygen electrochemical reactions (ORR and OER) by building a structure-property relation capable of identifying suitable activity descriptor for a model series of catalytic materials – in this case, a class of transition metal oxides known as the “perovskites”.

1.2 Introduction to Oxygen Electrocatalysis

Oxygen electrochemical reactions are a class of electrochemical reactions (“redox”) in which a chemical transformation of oxygen is coupled to electron transfer. The ubiquitous nature of oxygen makes mastery of its electrochemistry an essential building block for a variety of energy and environmental technologies. For example, in fuel cells, where chemical fuels are converted to electricity, oxygen electrochemistry is an integral
component of the cathode, where oxygen is reduced to form either water (in proton-exchanged membrane fuel cells, PEMFCs, \( O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \))\(^7\) or hydroxide (in alkaline fuel cells, AFCs, anion-exchanged membrane fuel cells, AMFCs, and metal-air batteries, \( O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \))\(^12\). Similarly, in storage devices, where electrical energy is stored in form of chemical bonds, the OER is an enabling chemistry for the anode in proton-exchanged membrane (PEM, \( 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \)), alkaline, anion-exchanged membrane electrolyzer and metal-air batteries (\( 4OH^- \rightarrow O_2 + 2H_2O + 4e^- \)). Figure 1.1 and 1.2 demonstrate cartoon drawings of the oxygen electrode (where the ORR and the OER occur) in both proton-exchanged and anion-exchanged membrane devices.

Research efforts have been devoted to mastering and accelerating the kinetics of the oxygen electrochemical reactions as, from the technology standpoint, the prohibitively sluggish kinetics of the oxygen electrochemical reactions is one of the largest sources of inefficiencies and cost in the electrochemical energy storage and conversion devices\(^7\)\(^,\)\(^14\). At present, platinum nanoparticles supported on carbon blacks ("Pt/C") are used as electrocatalyst to catalyze the ORR for both PEMFCs\(^7\)\(^,\)\(^11\) and AMFCs\(^14\). The utilization of platinum catalyst for the ORR is however far from ideal: more than 0.3 V of overpotential is still required before any appreciable kinetics current can be obtained\(^7\)\(^,\)\(^11\), and the majority fraction of the price of PEMFC is attributed to the platinum cost\(^15\). The kinetics limitation of the oxygen electrochemical reaction also occurs in the case of the OER. A PEM electrolyzer generally uses either iridium oxide or oxide electrocatalyst, either option requires non-negligible overpotential (generally more than 0.3 V) and also adds significant material cost to the system\(^16\)\(^,\)\(^17\).
To address the need for a superior oxygen electrocatalyst, significant efforts have been focused toward discovering new or more active form of ORR/OER catalytic surfaces. However, over many decades, the development of new catalysts for ORR and OER has been largely empirical. Although Sabatier’s principle provides a qualitative argument for tuning catalytic activity by varying the bond strength between the catalyst surface and the reactant/product (neither too strong nor too weak, leading to maximum activity at moderate bond strength, Figure 1.3), it has no predictive power to find catalysts with enhanced activity. The ability to predict new catalyst has been only recently enabled by fundamental ORR surface science research\textsuperscript{18} aided by ab-initio modeling\textsuperscript{19}, a combination of which have identified a unique descriptor for the surface electronic properties of platinum-based catalysts, viz., the d-band center relative to the Fermi level. Specifically, the d-band center has been shown to govern the metal-oxygen bond strength by controlling the degree of antibonding population of the surface-oxygen interaction and
thus exhibit a volcano relationship with the ORR activity\textsuperscript{20,22}, reflecting the fact that the maximum catalytic activity is attained at a moderate metal-oxygen bond strength (neither too strong nor too weak). Controlling this descriptor has led to the discovery of promising new Pt-based catalysts\textsuperscript{18,21}.

**Figure 1.2.** Illustration of the oxygen electrode in AMFC ("conversion") and anion-exchanged membrane electrolyzer ("storage"). Image was adapted from the initial drawing of Dr. Eva Mutoro.
Figure 1.3. Illustration of the Sabatier Principle – “Volcano plot”, where varying the bond strength between the catalyst surface and the reactant/product to moderate bond strength (neither too strong nor too weak) can lead to maximum kinetics activity.

While advanced platinum-based catalysts might enable fuel cell commercialization, abundant, non-precious-metal-containing catalytic surfaces such as transition metal oxides, graphitic carbons, and enzyme-mimicking supramolecular complex might offer an alternative, more economical option to energy storage and conversion devices. However, a suitable descriptor for the oxygen electrocatalytic activity of these non-precious-materials has not been identified, thereby hampering the development of more active oxygen electrocatalysts. The objective of thesis seeks to address this open question by developing design principles for non-precious-metal-containing catalytic materials. Motivated by the success of the d-band center theory, this work will focus on transferring the concept of the activity descriptor in the case of platinum metals to the non-precious-metal-containing catalytic materials, specifically, transition metal oxides. To accomplish the identification of the activity descriptor, transition metal oxides with perovskite structure, which has a formula of $A_{1-x}A'B_xB'_1\ldots$, where $A$ or $A'$ is a rare-earth or alkaline-earth metal, and $B$ or $B'$ is a transition-metal, are chosen as
model series of catalytic compounds because of its flexibility in both physical-chemical and catalytic properties. The ORR and the OER catalytic activities of the model oxo-perovskite compounds are then measured in alkaline environment to take advantage of the oxide stability in high pH environment, which allows wide array of perovskite chemistries to be investigated systematically. In combination with the electrocatalytic measurement, spectroscopic tools such as X-ray absorption spectroscopy will be conducted to study the electronic structure of these oxide materials, from which, the design principles will be developed from.

![Diagram](image)

**Figure 1.4.** Illustration of the perovskite structure, where the blue atom represents the transition metal position (B-site), the red atom represents the oxygen, and the yellow atom represents rare earth, alkaline earth, or mix therefore (A-site).

### 1.3 Scope of the thesis

This thesis will cover the methodology of the electrocatalytic measurement, the electronic structure model used for establishing the activity descriptor, and the resulting design principles of transition metal oxide catalyst materials.

Chapter 2 is devoted to the molecular orbital model for electronic structure of perovskite transition metal oxide that will be used in this work as a guideline toward rationalizing
the activity descriptor. This chapter will also include a method to estimate the mixing between the cationic and the anionic states ("covalency"), which is one of the key features (vide infra) for understanding and developing the electronic structure descriptor for the transition metal oxide catalysts.

Chapter 3 provides the basis for the experimental approach for quantifying the electrocatalytic performance of the oxide materials. The technique, known as the thin-film rotating disk electrode technique, takes advantage of the convective transport, which can eliminate the contribution from the diffusion and allow electro-kinetics extraction, will be applied to assess a variety of transition metal oxide catalysts. Comparison and projection to the actual electrochemical device performance will be discussed.

Chapter 4 focuses on the electrocatalytic trend for the ORR on the perovskite transition metal oxide model catalysts. Trend as derived using the rotating disk electrode technique described in Chapter 3, will be evaluated using the electronic structure model described in Chapter 2. The hypothesis on the activity descriptor and the ORR mechanism on perovskite oxide surfaces will be presented.

Chapter 5 is devoted to the application of the activity descriptor found for the ORR to the descriptor for the OER. We also present the hypothesis of the OER mechanism given the information on the ORR side, and demonstrate the use of a design principle to help search for a new compound for the OER, from which comparison to state-of-the-art oxide materials will be given.

Chapter 6 presents the results to support the proposed mechanisms for ORR and OER by examining the role of the cation in the alkaline electrolyte. Mechanism based on recent finding of non-covalent interaction between surface oxygen and the cation species, and its effect on the electro-kinetics will be present.

Chapter 7 provides an outlook for future work in the area of oxygen electrocatalysis with particular attention paid to integration with the photoelectrochemistry setup, which may allow development of future design principles for integrated catalyst-semiconductor structure for solar-driven water-splitting.
Chapter 2 – Molecular Orbital Approach to Perovskite Oxides

2.1 Simplified Molecular Orbital Model for Perovskite Oxide

The electronic structure complexity of perovskite transition metal oxides underpin many phenomena such as superconductivity\textsuperscript{28,29}, ferroelectricity\textsuperscript{30,31}, magnetoresistance\textsuperscript{32,33}, and metal-insulator transition\textsuperscript{34}. In the scope of this thesis, we focus on the simplest treatment of the transition metal oxide electronic using the linear combination of atomic orbital approach from the molecular orbital theory. For oxo-perovskites, this wavefunction is constructed from the interaction between the 3d (and 4s/4p) states of the B transition metal and the 2p states of the oxygen in octahedral geometry, where crystal field removes the degeneracy of the B 3d manifold. The general result of the BO\textsubscript{6} molecular orbital model can be crudely summarized as the formation of the bonding (predominantly of O character) and the antibonding (predominantly of B character) level (see Figure 2.1). Notably, the B 3d state is now split into \( e_\text{g} \) and \( t_{2g} \) states (the drawing of the \( e_\text{g} \) and \( t_{2g} \) states in BO\textsubscript{6} octahedra is shown in Figure 2.2.)

We note that this model is overly simplistic. We have not taken into account effects such as bandwidth, spin-orbit coupling, electron-electron interaction, and etc. Nonetheless, the model serves as a starting point for oxygen electrocatalysis model, which focuses mainly on the interaction between B transition metal and adsorbed oxygen-like species. On the zero-order approximation, the surface BO\textsubscript{5} with an adsorbed oxygen-like species resembles BO\textsubscript{6} locally although, strictly speaking, the symmetry changes from \( O_\text{h} \) to \( C_{4v} \). In this work, we have assumed that the splitting is small due to the similarity in the electronegativity between the O\textsuperscript{2−} and the oxygen adsorbate species. In this assumption, the \( e_\text{g} \) and \( t_{2g} \) states are assigned the antibonding, which is generally used as a determinant of the B-O strength ("bond order"). This hypothesis has been discussed\textsuperscript{35,36} and is similar to the concept of the d-band center in precious metal surfaces\textsuperscript{19,37,38}, where the position of the d-band center is postulated to correlate to the degree of the antibonding occupancy of
the adsorbed state. This will be further discussed in Chapter 3. For the remaining of this chapter, we will focus on the nature of the $e_g$ and $t_{2g}$ states, which generally is not the same as the crystal field state due to hybridization with the O 2p states ("covalency").

![Molecular orbital diagram for BO$_6$ geometry. The drawing is adapted from a well-known textbook by Ballhausen and Gray\textsuperscript{39}. The antibonding level is denoted with an asterisk.](image)

**Figure 2.1.** Molecular orbital diagram for BO$_6$ geometry. The drawing is adapted from a well-known textbook by Ballhausen and Gray\textsuperscript{39}. The antibonding level is denoted with an asterisk.

![Drawing of the $e_g$ and $t_{2g}$ states. The oxygen axis shows the direction of the B-O bond. Notably, the $e_g$ state points directly toward O, whereas the $t_{2g}$ points away.](image)

**Figure 2.2.** Drawing of the $e_g$ and $t_{2g}$ states. The oxygen axis shows the direction of the B-O bond. Notably, the $e_g$ state points directly toward O, whereas the $t_{2g}$ points away.
2.2 Transition metal - oxygen covalency in perovskite oxide

Covalency or hybridization has received substantial attention as an underpinning parameter for various transition metal oxides behaviors including localized-to-itinerant transition\textsuperscript{40}, intercalation potential\textsuperscript{41,42}, optical\textsuperscript{43}, magnetic\textsuperscript{44,45}, and other unique physical properties at oxide interfaces\textsuperscript{46,47}. This effect has been discussed in a range of transition metal oxides including perovskite\textsuperscript{40,44,45}, spinel\textsuperscript{49}, pyrochlore\textsuperscript{50}, and layered structures\textsuperscript{42}, and has been proposed to be key to many functionalities including intercalation potential\textsuperscript{41,42} and oxygen electrocatalytic activities\textsuperscript{51,52}. Several experimental methods have been applied to estimate the degree of covalency, ranging from X-ray Photoemission Spectroscopy (XPS)\textsuperscript{53,54}, Electron Energy Loss Spectroscopy (EELS)\textsuperscript{55,56}, X-ray Absorption Spectroscopy (XAS)\textsuperscript{57}, and neutron diffraction\textsuperscript{58}. However, to date, there has not been a study to systematically compare perovskite oxides with different transition metals and cation substitution. The lack of such study is partially due to the fact that there is currently no simple method for systematically comparing covalency of different transition metal compositions. An approach that has been reported in literature relies on an extraction of the p-d transfer integral of the cluster-type charge-transfer calculation of the photoemission spectra\textsuperscript{59}. In this chapter, we report a simpler method as part of efforts to quantify the transition metal oxide covalency. We focus on a structurally similar system of perovskites (formula: AA'BB'O\textsubscript{3}, where A and A' are rare-earth and/or alkaline earth metals, B and B' are 3d transition metals, and O is oxygen) as model compounds using the O K-edge XAS, which takes advantage of the first-order transition from O 1s to O 2p state to selectively measure the unoccupied state with dominant O 2p symmetry ("O 2p hole") and consequently probe covalency\textsuperscript{57}. This selective excitation is as a result of the dominating dipole transition matrix and can therefore be indicative of the electron sharing between O 2p and B 3d states. De Groot et al., has previously examined O K-edge XAS in a series of model oxides in the context of the localized e\textsubscript{g} and t\textsubscript{2g} states\textsuperscript{57}. Their work has indirectly revealed evidence for B 3d - O 2p state mixing but has not lead to a conclusive finding about how the mixing evolves with 3d electron. Abbate and co-workers also have systematically studied O K-edge XAS on La\textsubscript{1-x}Sr\textsubscript{x}FeO\textsubscript{3} and La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3}, where they found that the hole doping induced
by Sr substitution lies in a heavily mixed O 2p and B 3d states\textsuperscript{60}. Their study however does not lead to a conclusive mean of quantifying covalency between different transition metals. In this contribution, we demonstrate a method to extract the degree of O 2p – B 3d covalency from O K-edge XAS in perovskite oxides using Golden Rule and molecular-orbital assumptions. We apply our method to study how the degree of covalency evolves in in La\textsubscript{1-x}Ca\textsubscript{x}BO\textsubscript{3} (where B = 3d transition metals) perovskite, and the La\textsubscript{1+x}NiO\textsubscript{3+x} Ruddlesden-Popper oxides. From which, we explain the trend on the basis of an electronegativity model.

2.3 Experimental Procedure

The perovskites samples used in this study were synthesized with a co-precipitation method. Briefly, rare- and/or alkaline-earth nitrate, and transition-metal nitrate (both 99.98\% Alfa Aesar) in a 1:1 mole ratio were mixed in Milli-Q water (18 M\(\Omega\) cm) at 0.2 M metal concentration. The solution containing rare and alkaline earth, and transition metals was titrated to 1.2 M tetramethylammonium hydroxide (100\% Alfa Aesar). The precipitate was filtered, collected, and dried. The powder samples were subjected to heat treatment at 1000\(^\circ\)C under Ar atmosphere for the La\textsubscript{1-x}Ca\textsubscript{x}MnO\textsubscript{3} (x = 0, 0.5) and La\textsubscript{0.5}Ca\textsubscript{0.5}CrO\textsubscript{3} samples, at 1000\(^\circ\)C under dried air atmosphere for LaCrO\textsubscript{3}, La\textsubscript{1-x}Ca\textsubscript{x}FeO\textsubscript{3} (x = 0, 0.25, 0.5), La\textsubscript{1-x}Ca\textsubscript{x}CoO\textsubscript{3} (x = 0, 0.5), La\textsubscript{3}Ni\textsubscript{2}O\textsubscript{7}, La\textsubscript{4}Ni\textsubscript{3}O\textsubscript{10} samples, and at 800\(^\circ\)C under O\textsubscript{2} atmosphere for the LaNiO\textsubscript{3} sample. LaMnO\textsubscript{3} was prepared from an 800\(^\circ\)C heat treatment of LaMnO\textsubscript{3} in air. La\textsubscript{2}NiO\textsubscript{4} was synthesized in 2 steps: 1000\(^\circ\)C under Air atmosphere and then heated at 800\(^\circ\)C under Ar atmosphere. All gases had ultra-high-grade purity (Airgas). All samples were characterized by X-ray diffraction to determine phase purity with a Rigaku High-Power Rotating Anode X-ray Powder Diffractometer at a scan rate of 0.8 degree /min. All X-ray diffraction data and refined lattice parameters had single-phase purity, except LaNiO\textsubscript{3}, where <2\% of NiO was present. O K-edge X-ray Absorption spectra were collected at Saga-LS (BL-12), Japan. All measurements were collected in electron-yield mode at 10\textsuperscript{7} Pa pressure (corresponding to 10 nm penetration depth\textsuperscript{61}). All spectra were normalized to the oxygen absorption background at \(\sim\)550 eV.
2.4 Covalency Trend in Model Series of Perovskite Oxides

The results of the O K-edge spectra of LaBO₃ (where B = Cr, Mn, Fe, Co, Ni) are shown in Figure 2.1. Our results have similar features to the spectra that have been reported in literature, where the first peak (~ 530 eV) corresponds to the excitation from the O 1s state to the hybridized O 2p – B 3d state as a result of the covalency between the two levels, and the second peak (~ 535 eV) and third peak (~ 543 eV) correspond to the excitations of O 1s to O 2p – La 5d, and O 2p – B 4sp respectively⁶⁰. The second and third features remain largely unchanged throughout 3d transition metal substitution, in contrast to the first feature, which undergoes significant transformation in both shape and energy in going from Cr to Ni. This observation is expected as the second feature corresponds to the La 5d state, which is chemically identical to all the LaBO₃ samples, and the third feature corresponds to the 4sp state, which generally has a wider bandwidth and therefore is largely similar across different B transition metals. The first peak of the O K-edge spectra, which contains information on the covalency, or the hybridization of the O 2p and B 3d system, however, changes drastically across different 3d transition metal substitution. As Figure 2.1 shows, this feature varies significantly in both energy and line shape. We hypothesize that this is a result of a dissimilar covalency and number of hole across different LaBO₃ compounds.

To isolate the covalency contribution to the hybridized O 2p and B 3d excitation in the O K-edge spectra from the contribution from the varying number of hole with different 3d transition metal and consequently enable a quantitative comparison of the O 2p – B 3d excitation lines, we assume the simplest form of the molecular orbital construct, where covalency arises from the mixing between O 2p with transition metal (“B”) 3d states. Driven by the proximity of the electronegativities, the O 2p and B 3d states overlap and induce formation of hole in the nominally O 2p level. This has a direct consequence of a charge transfer (“redox”) from oxygen to the transition metal. In the case of perovskite oxides, B 3d states undergo field splitting to the $e_g$ and $t_{2g}$ symmetry. By assuming that these are the two essential energy levels in the perovskite oxides, we can write a hybridized O 2p – B 3d state construct as the following:
\[
\Psi_{\text{unoccupied}} = C \left( e_{g}^{n_{e}} t_{2g}^{n_{t2g}} + n_{e0}^{1/2} T_{\sigma} \left( e_{g}^{n_{e}+1} t_{2g}^{n_{t2g}+1} L \right) + n_{t0}^{1/2} T_{\pi} \left( e_{g}^{n_{e}} t_{2g}^{n_{t2g}+1} L \right) \right)
\]

Here, \( C \left( = (n_{e0}(1 - |T_{\sigma}|^2) + n_{t0}(1 - |T_{\pi}|^2))^{1/2} \right) \) is a normalization coefficient, \( L \) denotes the ligand hole, \( n_{e0} \) and \( n_{t0} \) are the nominal hole numbers in the \( e_{g} \) and \( t_{2g} \) symmetry, and \( T_{\sigma} \) and \( T_{\pi} \) represent the matrix element in orbital mixing for the \( e_{g} \) and \( t_{2g} \) symmetry respectively. From this simple molecular model, a systematic comparison of \( |T_{\sigma}|^2 \) and \( |T_{\pi}|^2 \) can describe the degree of covalency between different perovskite oxides, from which the trend will be estimated from the O K-edge spectra. To enable such comparison, we examine the O K-edge spectral feature, which is a culmination of various many-body effects that generally requires multi-scattering-type calculations. In this work, we assume that the spectra can be estimated based on the simple dipole selection rule, which restricts the O 1s transition to the O 2p hole state (state with ligand hole) only. Thus:

\[
I \propto n_{e0}|T_{\sigma}|^2 + n_{t0}|T_{\pi}|^2
\]

In this construct, \( I \) corresponds to the intensity of the B 3d – O 2p peak, which we use linear background between local minima to correct for the background absorption\(^{51}\). Then, using \( T_{\pi} \approx T_{\sigma}/2 \), this equation simplifies to\(^{62}\):

\[
|T_{\sigma}|^2 \propto \frac{I}{n_{e0} + n_{t0}/4}
\]

The covalency parameters \((|T_{\sigma}|^2)\) of the model LaBO\(_3\) compounds as extracted from the O K-edge data (Figure 2.1) are plotted against the number of d-electron in Figure 2.2. Our analysis shows that, as the d-electron number increases, the covalency increases in a monotonic fashion. This finding is in agreement with the previous trend reported derived from p-d transfer integral extraction in the case of binary oxides and sulfides by Bocquet and co-workers but not ternary oxides\(^{59}\). As the extraction of the p-d transfer integral is a highly convoluted process, we caution that a sensitivity analysis would be essential to understand this difference. Nonetheless, to explain our experimental trend, we use the following argument: the 3d electron trend follows that of the electronegativity for LaBO\(_3\) system, and thus the degree of hybridization increases with it\(^{63,64}\). In the context of
molecular orbital theory, the transition metal moves to the right of the periodic table as the 3d electron increases, and, as a result, the electronegativity of 3d transition metal becomes closer to that of oxygen, which results in an overlap in their energy levels that consequently lead to stronger hybridization. The agreement between our results and intuitive concept such as electronegativity gives us confidence in further applying this model to examine a more complicated scenario such as in the case of the cation substitution.

**Figure 2.1.** O K-edge X-ray Absorption Spectroscopy of LaBO$_3$ ($B =$ Cr, Mn, Fe, Co, Ni). The shaded region centered at $-530$ eV represents the feature assigned to B 3d – O 2p hybridization. Spectra were collected in electron yield mode at room temperature.
Figure 2.2. Evolution of LaBO$_3$ covalency paremeter (Abs./($\text{hole}_{eg} + 1/4 \text{hole}_{t_{2g}}$)) for B = Cr, Mn, Fe, Co, Ni with respect to d-electron count. The absorbance was taken to the shade region shown in Figure 2.1 (corresponding to the unoccupied state with the O 2p symmetry,) corrected with linear background. The dashed gray line serves only as guide to the trend.

In this section, we apply this covalency model to understand the role of B-site substitution on covalency in LaNi$_{0.5}$Mn$_{0.5}$O$_3$ and LaCu$_{0.5}$Mn$_{0.5}$O$_3$ compounds. The O K-edge spectra are shown in Figure 2.3 (Top), where LaMnO$_3$ is shown in a light gray dashed line as reference. By assuming that mixing of Ni-Mn and Cu-Mn results in an averaged d-electron transition metal, the covalency trend is in good agreement with that obtained from the LaBO$_3$ case as shown in Figure 2.3 (Bottom). This finding is believed to be as a result of the fact that the electronegativity, and consequently the covalency of LaNi$_{0.5}$Mn$_{0.5}$O$_3$ and LaCu$_{0.5}$Mn$_{0.5}$O$_3$ compounds can be approximated by an average of the two transition metal cations. We caution however that these findings may be coincidental and further experiments with regarding to cation ordering (consequently valency, vide infra) would be essential to understand the impact of B-site substitution on covalency.
Figure 2.3. O K-edge X-ray Absorption Spectroscopy LaBB'O₃ (BB' = Cu₀.₅Mn₀.₅ and Ni₀.₅Mn₀.₅). (Top) Raw spectra. The dashed grey lines show a LaMnO₃ O K-edge reference. (Bottom) LaBB'O₃ covalency parameter v.s. d-electron count, with LaBO₃ data as references. The dashed gray line serves only as guide to the trend.

We then examine the role of Ca-substitution for La in the series of La₁₋ₓCaₓBO₃ (where B = Cr, Mn, Fe, Co). The raw O K-edge spectra are shown in Figure 2.4A-C, where the unsubstituted LaBO₃ spectra of the same B transition metal are also displayed in dashed grey lines as reference. With Ca-substitution, all three features of the spectra change.
significantly, in agreement with the previous literature report with the similar case of divalent Sr-substitution\textsuperscript{60,65,66}. This is as a result of the fact that Ca-substitution modifies the electronic structure of excitations to both the A-site and the B-site. As our interest is in the B 3d – O 2p hybridization, we again focus on the first feature which corresponds to the excitation of the hybridized state. Figure 2.5 demonstrates how the Ca-substitution influences the covalency parameter. Here, by normalizing the covalency parameter of the compounds with aliovalent substitution to the parent LaBO\textsubscript{3} compounds, we found that the oxidation of B transition metal from the initial, un-substituted 3+ state to oxidized (>3+) state, generally results in an increase in covalency. This finding is consistent with the fact that oxidation of B metal leads to a reduced electron-electron interaction, which consequently lowers the 3d electron energy level, bringing the 3d level closer to the O 2p energy state\textsuperscript{67}. We note that interestingly the covalency parameters of La\textsubscript{0.5}Ca\textsubscript{0.5}CoO\textsubscript{3-δ} and LaCoO\textsubscript{3} are quite similar, which is likely a result of the oxygen-vacancy-mediated charge neutralization, leaving Co valence unchanged and thereby does not affect the Co-O covalency.

To further explore the opposite of this oxidation effect, where the B metal is reduced, we use La\textsubscript{1+x}NiO\textsubscript{3+x} as model compounds. The O K-edge spectra for La\textsubscript{4}Ni\textsubscript{3}O\textsubscript{10} and La\textsubscript{2}NiO\textsubscript{4} are shown in Figure 2.4D, where LaNiO\textsubscript{3} O K-edge spectra is also shown in grey line as baseline for comparison. We then conduct the covalency analysis for the Ruddlesden-Popper phases, which serve as model compounds for reduced B transition metal in Figure 2.5. In this system, the reduced Ni-containing Ruddlesden-Popper phases are found to have lowered covalency parameter. In the context of electron-electron interaction mentioned in the case of La\textsubscript{1-x}Ca\textsubscript{x}BO\textsubscript{3}, this finding is in an excellent agreement. We therefore propose that in the limit of the oxo-perovskites, the factor that dominates the covalency of the compound is the choice of the B transition metal and its oxidation state.
Figure 2.4. O K-edge X-ray Absorption Spectroscopy $\text{La}_x\text{Ca}_{1-x}\text{BO}_3$ and $\text{La}_{1+x}\text{NiO}_3$. (A) $\text{La}_{0.5}\text{Ca}_{0.5}\text{CrO}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$. $\text{LaCrO}_3$ and $\text{LaCoO}_3$ are shown in dashed grey lines as references. (B) $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{LaMnO}_3$. $\text{LaMnO}_3$ are shown in dashed grey lines. (C) $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$ and $\text{La}_{0.75}\text{Ca}_{0.25}\text{FeO}_3$. $\text{LaFeO}_3$ are shown in dashed grey lines. (D) $\text{La}_4\text{Ni}_3\text{O}_{10}$ and $\text{La}_2\text{NiO}_4$. $\text{LaNiO}_3$ are shown in dashed grey lines.
2.4 Chapter 2 Conclusion

This chapter describes a simplified picture of the transition metal oxide electronic structure using linear combination of atomic orbitals. This approach focuses on the interaction between transition metal 3d and oxygen 2p states. We place emphasis on the antibonding levels of this interaction, which has two symmetry states: triply degenerated $t_{2g}$ and doubly degenerated $e_g$. To better understand the nature of the antibonding states, we deconstruct them to the original transition metal 3d and oxygen 2p states and extract the extent of hybridization between the twos from the O K-edge XAS Spectra. This procedure relies on the molecular orbital and Golden Rule assumptions, which, albeit is arguably too simplistic, results in a covalency trend that is sensible from both chemical and physical intuition viewpoints. We found that the covalency increases with d-electron number for LaBO$_3$ ($B = \text{Cr, Mn, Fe, Co, Ni}$) compounds, which we attribute to the increasing electronegativity as d-electron number increases. The d-electron vs. covalency
trend persists even in the case of B-site substitution, which we demonstrate for LaCu$_{0.5}$Mn$_{0.5}$O$_3$ and LaNi$_{0.5}$Mn$_{0.5}$O$_3$ cases. We further report that covalency is highly sensitive to the oxidation state of B transition metal, where from combined studies on Ca-substitution and Ruddelsden-Popper phases, we found that increasing oxidation state can further increase covalency. We assign this observation to the sensitivity of the electronegativity on the electron-electron interaction.
Chapter 3 – Thin-film Rotating Disk Electrode

3.1 Thin-film Rotating Disk Electrode Methodology

One of the largest cost and efficiency limitations of electrochemical energy conversion devices which have an air electrode, such as PEMFCs, AFCs, AMFCs, electrolyzers, and metal-air batteries, lies in the slow kinetics of the ORR at the cathode (air electrode), which must be facilitated by an electrocatalyst. For example, viable large-scale commercialization of PEMFCs requires either to substitute the current carbon-supported platinum ORR catalyst (Pt/C) with non-precious metal catalysts or to improve the intrinsic activity of platinum. Therefore, a large number of novel catalysts have been developed by industrial and academic laboratories, and are typically screened for their ORR activity using the thin-film rotating disk electrode (RDE) method, where a catalyst suspension is drop-cast as a thin-film onto a glassy carbon rotating disk electrode, using small amounts of Nafion as binder. The measured ORR currents are then corrected for O₂ mass transport resistances using the Levich equation to obtain the ORR activity of the catalyst. Compared to ORR activity measurements in fuel cells, which require time-consuming optimization of membrane electrode assemblies (MEAs) for each catalyst, the thin-film RDE method is a fast screening tool to obtain ORR activities which are consistent with those obtained in MEAs, and it has led to the discovery of highly active novel ORR catalysts.

While noble metal catalysts with significantly enhanced activity compared to conventionally used Pt/C may enable commercialization of PEMFCs, AMFCs and metal/air batteries offer an alternative route toward low cost, noble metal-free fuel cells. Here, oxide-based ORR catalysts are possible substitutes for platinum. In the case of oxide-based ORR catalysts for either alkaline fuel cells or metal/air batteries, the ORR activity is most frequently tested in PTFE-bonded gas diffusion electrodes, where elimination of O₂ mass transport resistances is difficult. Therefore, despite the fact that many different oxide materials have been examined in these studies, it is not possible
to extract absolute ORR activities referenced to either oxide surface area (i.e., *specific activity*) or mass (i.e., *mass activity*). A more systematic evaluation of the ORR activities of a wide range of perovskites was conducted by Bockris and Otagawa\textsuperscript{35, 82}, using immersed porous pellets, whose very high internal surface area however introduces significant $O_2$ mass transport resistances within the pellets so that meaningful ORR kinetics can only be obtained at very low current densities (on the order of $\leq 0.1 \, \mu A \, cm^{-2}_{oxide}$). The same restrictions apply to the RDE method using a recessed porous pellet as electrode (*recessed RDE*)\textsuperscript{83, 84}, since the thickness of these porous disk electrodes (on the order of 100 $\mu m$) is much larger than the RDE diffusion boundary layer thickness (on the order of 10 $\mu m$\textsuperscript{85}). One method to avoid undefined $O_2$ mass transport resistances when measuring the ORR activity of oxide catalysts is the adoption of the thin-film RDE method, where a very thin film (on the order of 1 $\mu m$) of oxide particles is attached to a glassy carbon disk electrode using an ionomeric binder, analogous to the method used in acid electrolytes described above\textsuperscript{70}. This method was adopted recently in studying the ORR activity of La$_{1-x}$Sr$_x$MnO$_3$ perovskites\textsuperscript{86, 87}, but the use of highly acidic Nafion\textsuperscript{®} ionomer poses the risk that the oxide catalyst might be partially dissolved in the acid environment during film casting. This can be avoided either by using an alkaline ionomeric binder (i.e, anion-exchange ionomers\textsuperscript{88}), or by the neturalization of the protons in Nafion\textsuperscript{®} solution with alkali hydroxides, producing alkali metal exchanged Nafion\textsuperscript{®} binder.

In the following, we will introduce the latter approach, viz., the thin-film RDE characterization of the ORR activity of several perovskite catalysts using sodium ion exchanged Nafion\textsuperscript{®} solutions as binder. We demonstrate that absolute specific and mass activities can be obtained, which enables a more rigorous and relatively rapid activity comparison of well-characterized model oxide ORR catalysts. Furthermore, we will compare the ORR activity of these model oxides with that of conventional Pt/C and provide an estimate of the kinetically limited ORR activity in an optimized alkaline fuel cell cathode.
3.2 Experimental Procedure

Synthesis and characterization. The perovskite transition metal oxides studied in this chapter (La$_{0.75}$Ca$_{0.25}$FeO$_3$, LaCu$_{0.5}$Mn$_{0.5}$O$_3$, and LaNiO$_3$) represent the full ORR activity range obtained for various oxides measured in our laboratory, which were synthesized using a co-precipitation method described elsewhere. Briefly, rare earth and alkali earth nitrates and transition metal nitrates (all 99.98% purity, Alfa Aesar) at the respective stoichiometric ratio were mixed in Milli-Q water (18 MΩ cm) at metal concentrations on the order of 0.1 M. This solution was then titrated with 1.2 M tetramethylammonium hydroxide (Alfa Aesar) until a solid precipitate was formed. The precipitate was filtered, collected, and dried at 200°C for 12 hours, and then subjected to heat-treatment at 1000°C in dry air (ultra-high purity grade, Airgas) for 12 hours for La$_{0.75}$Ca$_{0.25}$FeO$_3$ and LaCu$_{0.5}$Mn$_{0.5}$O$_3$. To ensure the oxygen stoichiometry of LaNiO$_3$, this sample was synthesized at 800°C in pure O$_2$ (ultra-high purity grade, Airgas) for 8 hours and thermogravimetric analysis (TGA, Perkin Elmer) was used to confirm that its oxygen content was approximately 98% of the nominal value. X-ray Diffraction (Rigaku) revealed these materials to be single-phase, as shown in Figure 3.1. Particle sizes and surface areas were quantified via Philips XL30 FEG Environmental SEM (FEI-Philips), determining mass specific surface areas, $A_s$, by approximating spherical geometry:

$$A_s \approx (\Sigma 4\pi r^3)/(\Sigma (4/3)\pi r^3) = 6/\rho [(\Sigma d^3)/2] = 6/(d_{va}/\rho)$$

where $\rho$ is the oxide bulk density, $d$ is the diameter of individual particles determined by SEM, and $d_{va}$ is the volume/area averaged diameter. While the value of $A_s$ for non-supported oxide catalysts can also be determined from nitrogen BET area (Brunauer, Emmett, and Teller) measurements, we did not have sufficient material for most of our samples to conduct meaningful BET analysis. Sufficient material for BET analysis was only available for LaNiO$_3$, and the measured BET area of ~5.6 m$^2$ g$^{-1}$ (Micromeritics ASAP2020) is reasonably consistent with the SEM-based value of ~3.5 m$^2$ g$^{-1}$. Therefore, we believe that a comparison of the specific ORR activity of the various oxides using the SEM-based $A_s$-values listed in table 3.1 is reasonably accurate.
Table 3.1. SEM characterization of the oxides studied in this chapter. The number averaged diameter, $d_{\text{number}}$, with standard deviation (in parentheses), the volume-area averaged diameter, $d_{v/a}$, and the specific surface area of the oxide (see equation 1), $A_s$, were obtained from particle size distribution measurements.

**Ion-exchanged Nafion® solution preparation.** Because perovskite samples in this work have on the order of hundreds of nanometer in size, oxide coatings on a glassy carbon disk for thin-film RDE measurements with these relatively large and heavy catalyst particles require an immobilizing binder that at the same time facilitates the transport of dissolved O₂ to the catalyst surface. To avoid possible corrosion of the oxide due to the strong acidity of commercially available Nafion® solution (DE520, Ion Power, USA), we ion-exchanged the solution with sodium hydroxide which, similar to an earlier report on lithiated Nafion®, was made by adding a defined aliquot of 0.1 M NaOH to the Nafion® solution: for an equivalent weight of 1050 g$_{\text{polymer/molH}^+}$ of the 5%wt. Nafion® solution, corresponding to a $\sim$0.05 M proton concentration, replacement of H$^+$ with Na$^+$ requires a $\sim$2/1 volume ratio of Nafion® solution and 0.1 M NaOH. The thus obtained Na$^+$-exchanged Nafion® solution had a pH of $\sim$11, indicating a slight molar excess of NaOH (ca. 1 mM). This solution was then used to prepare oxide coatings for thin-film RDE measurements.
Figure 3.1. X-ray diffraction spectra of the oxides studied in this chapter.

Oxide electrode preparation. While all of the here examined samples had reasonably high electronic conductivities (~0.1 S cm\(^{-1}\) \(^{92}\), ~0.5 S cm\(^{-1}\) \(^{93}\), and ~1500 S cm\(^{-1}\) \(^{94}\) for La\(_{0.75}\)Ca\(_{0.25}\)FeO\(_3\), LaCu\(_{0.5}\)Mn\(_{0.5}\)O\(_3\), and LaNiO\(_3\), respectively), the perovskite oxides were mixed with acetylene black (AB) carbon at a 5/1 mass ratio of oxide/carbon in order to eliminate any concerns regarding electronic conductivity limitations within the thin electrodes. The AB (Chevron) was treated in nitric acid overnight at 80°C, then filtered and finally dried at 100°C overnight. Catalyst inks were prepared by horn sonication (Branson 3510, Branson) of perovskite oxides, AB, and an appropriate amount of the Na\(^+\)-exchanged Nafton\(^\text{®}\) solution with tetrahydrofuran (THF, 99.9+% Sigma-Aldrich), yielding inks with final concentrations of 5 mg\(_{\text{oxide}}\) ml\(^{-1}\) ink, 1 mg\(_{\text{AB}}\) ml\(^{-1}\) ink, and 1 mg\(_{\text{Nafion}}\) ml\(^{-1}\) ink. Next, 10 μl of catalyst ink were drop-cast onto a glassy carbon (GC) electrode (0.196 cm\(^2\) area, Pine, USA) polished to a mirror finish with 0.05 μm alumina slurry (Buehler). The catalyst layer on the GC substrate was dried overnight in a sealed glass jar which had been pre-saturated with THF vapor, enabling slow ink drying rates which were found to be required for homogenous thin-film coatings on the GC disk electrode. The electrode had a final composition of 250 μg\(_{\text{oxide}}\) cm\(^{-2}\) disk, 50 μg\(_{\text{AB}}\) cm\(^{-2}\) disk, and 50 μg\(_{\text{Nafion}}\) cm\(^{-2}\) disk at an estimated film thickness of ~2 μm. Based on the density of water-immersed recast Nafton\(^\text{®}\) of ~1.4 g cm\(^{-3}\) \(^{95}\), the Nafton film thickness based on the
geometric area of the disk would correspond to ~0.4 μm, sufficiently thin so that the O₂ transport resistance within the ionomer phase is negligible. Assuming uniform Nafion® coverage on the oxide and carbon particles in the electrodes, the actual Nafion® film thickness is more than one order of magnitude lower, due to the high electrode roughness factors of the oxide and the carbon of ~2.5 cm²oxide cm⁻²disk (at 250 μgoxide cm⁻²disk and ~1 m² g⁻¹oxide) and ~25 cm²oxide cm⁻²disk (at 50 μgAB cm⁻²disk and ~50 m² g⁻¹AB), respectively.

**Platinum electrode preparation.** Glassy carbon disk electrodes coated with a thin film of Pt/C catalyst (46 %wt. Pt on high-surface area carbon, TKK, Japan) were prepared as described elsewhere. Briefly, 15 μl of an aqueous Pt/C ink of a composition of 0.15 mgcatalyst ml⁻¹ and 0.04 mgNafion ml⁻¹ was drop-cast onto a GC disk electrode and allowed to dry overnight, yielding a Pt loading of 5 μgPt cm⁻²disk and 3 μgNafion cm⁻²disk. The Pt/C surface area was estimated from the electrochemical H₂ underpotential deposition as described elsewhere and yielded a Pt specific surface area of 48 m² g⁻¹Pt⁻¹.

**Electrochemical characterization.** All electrochemical measurements were conducted in a three-electrode glass cell (Pine Instrument) and using a rotator (Pine) to which the thin-film RDE working electrodes were attached; the potential was controlled using a VoltaLab PST050 potentiostat. The 0.1 M KOH electrolyte was prepared from Milli-Q water (18 MΩ cm) and KOH pellets (99.99% purity, Sigma-Aldrich). All measurements were conducted at 10 mV s⁻¹ in either N₂ or O₂ (ultra-high purity grade, Airgas) at room temperature. A saturated calomel electrode (SCE) reference electrode (Pine Instrument) was used and was calibrated in the same electrolyte by measuring hydrogen oxidation/evolution currents on a Pt-RDE and defining the potential of zero current as the reversible hydrogen electrode potential (RHE); 0 V vs. RHE in this case corresponds to 0.998±0.005 V vs. RHE. All the potentials in this study were referenced to the RHE potential scale and correspond to the applied potentials, Eapplied, unless they are stated to be iR-corrected potentials, EiR-corrected, calculated by the following equation:

\[ E_{iR-corrected} = E_{applied} - iR \]

where \( i \) is the current and \( R \) is the uncompensated ohmic electrolyte resistance (≈45 Ω)
measured via high-frequency AC impedance in O₂-saturated 0.1 M KOH. ORR activities reported in the work were obtained from the negative-going scans in pure O₂ at 1600 rpm and were corrected for capacitive currents in pure N₂. Error bars represent standard deviations from at least three independent repeat measurements, whereby the change in activity over subsequent potential cycles is less than 3%. To achieve this steady-state response, the potential range was kept within 0.7 to 1 V vs. RHE in order to prevent degradation of the oxide catalysts by oxidation/reduction, with the exception of LaCu₀.₅Mn₀.₅O₃, which displayed remarkable stability down to 0.4 V vs. RHE. The mass transport correction was performed using the well-known RDE correction (Levich equation):

\[ i_{\text{measured}} + i_D = i_k + i_D \]

where \( i_{\text{measured}} \) is the measured O₂ reduction current density, \( i_k \) is the mass-transport corrected kinetic ORR current density, and \( i_D \) represents the limiting current density which was obtained experimentally for LaNiO₃ and LaCu₀.₅Mn₀.₅O₃ electrodes (vide infra).

To avoid impurities from the corrosion of the glass cell, all experiments were collected within 2 hours of the initial exposure of KOH to the glass cell. The absence of contamination effects from the glass cell under these conditions is demonstrated by the fact that the ORR mass activity at 0.9 V vs. RHE of Pt/C obtained in our measurements (0.15 A mg⁻¹Pt, see Figure 3.7) is essentially identical to that reported for a Teflon cell (0.12 A mg⁻¹Pt).¹⁰⁰

**3.3 Results from Thin-film Rotating Disk Electrode**

LaNiO₃ has been known as highly active ORR catalyst for some time and was recently applied as cathode catalyst in a sodium-borohydride/air fuel cell. Figure 3.2 shows the cyclic voltammogram of a thin-film LaNiO₃ electrode in N₂ saturated 0.1 M KOH at 10 mV s⁻¹, indicating the absence of any noticeable oxidation/reduction feature in the range of 0.7 to 1.0 V RHE, consistent with previous reports. It should be noted that most ORR activity studies in the past use a Hg/HgO reference scale, whereby 0 V RHE corresponds to approximately -0.92 V Hg/HgO. In O₂ saturated 0.1 M KOH, the onset
of ORR currents is observed below ~0.95 V vs. RHE (see Figure 3.2), confirming the high ORR activity of LaNiO$_3$. Figure 3.3 compares the ORR activity of the three different perovskites examined in this work, showing the capacity-corrected net ORR current densities of the negative-going scan at a rotation rate of 1600 rpm. The ORR activity of the glassy carbon substrate and of the acetylene black (AB) added to the oxide electrodes is also shown in Figure 3.3, indicating that background contributions from the AB and the GC disk are negligible above ~0.7 V vs. RHE. Therefore, even for the oxide with the lowest measured ORR activity (La$_{0.75}$Ca$_{0.25}$FeO$_3$), the background contribution from the carbon materials is negligible and the measured ORR activity is that of the oxide itself. The more than 0.22 V lower ORR activity of La$_{0.75}$Ca$_{0.25}$FeO$_3$ compared to LaNiO$_3$ (Figure 3.3) is somewhat surprising, since similar exchange current densities were reported previously for LaNiO$_3$, La$_{0.7}$Sr$_{0.3}$FeO$_3$, and La$_{0.5}$Sr$_{0.5}$FeO$_3$ and since one would not expect that the exchange of A-site atoms of different sizes (i.e., Sr for Ca) would produce such a large shift in ORR activity (e.g., the ORR activity of AMnO$_3$ compounds is within 50 mV for A=La, Pr, Nd, Sm, Gd, Dy, or Y). This discrepancy may be related to the strong O$_2$ mass transport limitations in thick high-porosity pellet electrodes used previously, rendering the quantification of the ORR activity ambiguous, if not impossible, and highlighting the need for a simple ORR activity measurement method with well-controlled O$_2$ mass transport properties.
Figure 3.2. Cyclic voltammograms of LaNiO$_3$ at 10 mV s$^{-1}$ in 0.1 M KOH at room temperature in N$_2$-saturated electrolyte at 0 rpm (blue) or in O$_2$-saturated electrolyte at 1600 rpm. Sweep directions are shown by the arrow.

Figure 3.3. ORR current densities (capacity-corrected negative-going scans) of GC-supported and Nafion*-bonded (Na$^+$ ion exchanged) thin-film LaNiO$_3$, LaCu$_{0.5}$Mn$_{0.5}$O$_3$, La$_{0.75}$Ca$_{0.25}$FeO$_3$ electrodes at 1600 rpm in O$_2$-saturated 0.1 M KOH at 10 mV s$^{-1}$. The
background ORR activity deriving from either the GC substrate or a thin-film Nafion®-bonded acetylene black (AB) thin-film electrode is shown for reference.

Figure 3.4 compares the ORR activity of LaCu$_{0.5}$Mn$_{0.5}$O$_3$ with that of Pt/C at 1600 rpm and 10 mV s$^{-1}$, showing that the same diffusion limited current density of $\sim$5.7 mA cm$^{-2}$ was obtained for both catalysts. This value is consistent with the 4-electron limiting current for O$_2$ reduction to water which has been reported previously for platinum single- and poly-crystalline electrodes in 0.1 M KOH at room temperature$^{98,102,103}$. Therefore, one can conclude that O$_2$ is reduced to water in an overall 4-electron process on the thin-film LaCu$_{0.5}$Mn$_{0.5}$O$_3$ electrode, which was also confirmed by the Koutecky-Levich analysis shown in Figure 3.5, where the slope of the lines is related to the number of electrons, $n$, exchanged in the overall O$_2$ reduction reaction:

$$slope = (0.62nFD_O^{2/3}v^{-1/6}C_O)^{-1}$$

where $F$ is the Faraday’s constant, $D_O$ is the diffusivity of the O$_2$ molecule in the electrolyte, $\omega$ is the rotation speed, $v$ is the kinematic viscosity, and $C_O$ is the concentration of O$_2$ in the electrolyte. The fact that the same slope is obtained for both LaCu$_{0.5}$Mn$_{0.5}$O$_3$ and Pt/C confirms the complete 4-electron reduction of O$_2$ to water. Figure 3.5 also shows the Koutecky-Levich analysis for LaNiO$_3$ and the essentially identical slope demonstrates the 4-electron reduction to water on LaNiO$_3$, in agreement with previously reported rotating ring disk electrode (RRDE) measurements on LaNiO$_3$.$^{83}$ Unfortunately, owing to its low ORR activity ($\sim$0.2 mA cm$^{-2}_{disk}$ at 0.7 V, see Figure 3.3), no Koutechky-Levich analysis could be conducted with the La$_{0.75}$Ca$_{0.25}$FeO$_3$ sample. Even though in general the final product of the reduction (i.e. number of electron transferred) must be known to quantify the kinetic ORR current (see equation 3), the transport correction term is negligible ($\sim$10%) if the measured current is less than 10% of the minimum limiting ORR current (i.e., that for assuming a 2-electron reduction), which is the case for the La$_{0.75}$Ca$_{0.25}$FeO$_3$ electrode, so that sufficiently precise kinetic ORR current densities can be obtained even in this case where the final reaction product (H$_2$O$_2$ or H$_2$O) is unknown.
Figure 3.4. Polarization curves of GC supported thin-film LaCu$_{0.5}$Mn$_{0.5}$O$_3$ and Pt/C electrodes using a Na$^+$ ion-exchanged Nafion$^\circledR$ binder: 1600 rpm in O$_2$-saturated 0.1 M KOH at 10 mV s$^{-1}$.

A cautionary note on the interpretation of the above described Koutechky-Levich analysis or of RRDE measurements is suggested here as it was shown that the apparent number of electron transferred in the ORR deduced from (R)RDE measurements can depend on electrode thickness$^{72,104,105}$. For example, Fe-N-C based catalysts were shown to quantitatively reduce O$_2$ to H$_2$O$_2$ (2-electron process), but owing to the facile non-electrochemical H$_2$O$_2$ decomposition (H$_2$O$_2$ $\rightarrow$ H$_2$O + 0.5O$_2$), RRDE measurements on thick electrodes (>5 μm based on the known packing density of high-surface area carbons$^{106}$) indicated an apparent mostly 4-electron reduction process on these catalysts$^{72}$. Since our electrode thickness is only ~2 μm, we would not expect this artifact and believe that LaCu$_{0.5}$Mn$_{0.5}$O$_3$ and LaNiO$_3$ indeed reduce O$_2$ in a 4-electron process to water. Nevertheless, to unambiguously identify the ORR product (H$_2$O vs. H$_2$O$_2$), detailed RRDE measurements of electrodes with varying thickness would be necessary.
Figure 3.5. Koutecky-Levich analyses for GC-supported thin-film LaCu$_{0.5}$Mn$_{0.5}$O$_3$, LaNiO$_3$, and Pt/C electrodes (O$_2$ saturated 0.1 M KOH at 10 mV s$^{-1}$).

To extract the actual ORR kinetics of these oxides and of Pt/C, ohmic drop and mass transport corrections were applied to the ORR measurement using the Levich equation for the convective transport in an RDE configuration (see experimental section). The resulting kinetic ORR activities were then normalized by the measured specific surface areas of the oxides (Table 3.1) or of Pt/C (see experimental section) to obtain the specific ORR activity, $i_s$, plotted in Figure 3.6. In terms of specific activity, LaNiO$_3$ is the most active of the three studied oxide materials, with a value of $\sim$40 $\mu$A cm$^{-2}$ oxide compared to $\sim$320 $\mu$A cm$^{-2}$ Pt for Pt/C at the typical benchmark condition of 0.9V vs. RHE (Figure 3.6). Despite the fact that there are many previous articles on the use of LaNiO$_3$ as ORR catalyst, specific activities can only be extracted from the study of Bockris and Otagawa$^{82}$ with a value of $\sim$0.1 $\mu$A cm$^{-2}$ oxide ($\sim$100 $\mu$A cm$^{-2}$ electrode at a reported roughness factor $\sim$1000 cm$^2$ oxide cm$^{-2}$ electrode). The difference between this previously reported low specific activity for LaNiO$_3$ and our measurement can be attributed to undefined O$_2$ mass transport overpotentials in the thick and porous pellet electrodes used$^{82}$, whereby this artifact could be avoided in our thin-film RDE measurements. The Tafel slopes of the three different oxides and of Pt/C (Figure 3.6) are all within $\sim$60±10 mV decade$^{-1}$. While this is consistent with the Tafel slope reported for poly-crystalline Pt at the same
conditions, reported Tafel slopes for LaNiO$_3$ scatter over a wide range (45 mV decade$^{-1}$, 60 mV decade$^{-1}$, 82, 120 mV decade$^{-1}$), which again is most likely related to the poorly controlled O$_2$ mass transport in these measurements based on thick porous pellets or gas diffusion electrodes.

**Figure 3.6.** ORR specific activities, $i_s$, of of LaNiO$_3$, LaCu$_{0.5}$Mn$_{0.5}$O$_3$, La$_{0.75}$Ca$_{0.25}$FeO$_3$ (using specific surface areas listed in table 3.1) and of Pt/C versus potential, obtained after iR and O$_2$ mass-transport correction (from capacity-corrected negative-going scans at 10 mV s$^{-1}$ in 0.1 M KOH for oxides, from positive-going scans at 10 mV s$^{-1}$ in 0.1M KOH for Pt/C). Error bars represent standard deviations from at least three independent repeat measurements.

Figure 3.7 shows the ORR activity mass activity, $i_m$, of the various perovskites and Pt/C. At the typical benchmark voltage of 0.9 V vs. RHE, the measured mass activity of Pt/C (0.15 A mg$_{Pt}^{-1}$) is in good agreement with the literature (0.12 A mg$_{Pt}^{-1}$). Unfortunately, most studies on the ORR activity of LaNiO$_3$ provide no information on catalyst mass in the electrodes or lack detailed experimental conditions. Only two studies allow the evaluation of defined LaNiO$_3$ mass activities (pure O$_2$, room temperature, 0.9 V vs. RHE corresponding to -0.02 V vs. Hg/HgO), with values of ~2 A g$_{oxide}^{-1}$ (6 M KOH) and ~0.7 A g$_{oxide}^{-1}$ (5 M KOH), which are reasonably consistent with the value of
~1.6 A g\text{oxide}^{-1} (0.1 M KOH) obtained from Figure 3.7. The mass activities of LaCu_{0.5}Mn_{0.5}O_3 and La_{0.75}Ca_{0.25}FeO_3 are significantly lower than LaNiO_3 and no comparison data are available in the literature.

![Graph showing ORR mass activities](image)

**Figure 3.7.** ORR mass activities, $i_m$, of LaNiO_3, LaCu_{0.5}Mn_{0.5}O_3, La_{0.75}Ca_{0.25}FeO_3 (using specific surface areas listed in table 1) and of Pt/C versus potential, obtained after iR and O_2 mass-transport correction ((from capacity-corrected negative-going scans at 10 mV s^{-1} in 0.1 M KOH for oxides, from positive-going scans at 10 mV s^{-1} in 0.1M KOH for Pt/C). Error bars represent standard deviations from at least three independent repeat measurements.

In the following, we seek to estimate the kinetically limited cathode performance of LaNiO_3 and Pt/C if used in a fuel cell based on mass activities shown in Figure 3.7. A recent report compared the cathode performance of La_{0.8}Sr_{0.2}MnO_{3.15} with that of Pt/C at equal loading (1 mg\text{oxide} or 1 mg\text{Pt} per cm\text{^2 cathode}), showing an only ~0.1 V lower performance for the perovskite catalyst\textsuperscript{86}. Another study showed essentially identical performance of La_{0.6}Sr_{0.4}Mn_{0.8}Fe_{0.2}O_3 with that of a Pt/C cathode of, however, undefined Pt loading\textsuperscript{81}. In general, it is not straightforward to compare the potential cathode activity of “cheap” oxide catalysts with that of expensive precious metal catalysts, since the cathode loading of non-precious metal oxide catalysts is limited only by electrode
thickness constraints, while the loading of a Pt catalyst is constrained by cost considerations. Here we assume that the maximum electrode thickness for a “cheap” oxide-based cathode electrode is on the order of 100 μm as suggested previously and will compare it to the conventionally used Pt loading of 0.4 mgPt cm⁻². We emphasize this projection is based on an idealized scenario in the oxide electrode, where full utilization of the catalyst with minimum mass transport loss is assumed. Given the density of 7.2 g oxide cm⁻³ of LaNiO₃ and assuming 50% porosity in the catalyst layer, the maximum LaNiO₃ cathode loading would be ~36 mg oxide cm⁻² (obtained by multiplying cathode thickness, density, and porosity). The kinetically limited cathode performance of a LaNiO₃ catalyst can then be estimated by multiplying the maximum LaNiO₃ loading with its mass activity values shown in Figure 3.7, which then can be compared to the cathode performance of a Pt/C catalyst obtained by multiplying its mass activity data in figure 7 with a typical loading of 0.4 mgPt cm⁻². This is shown in Figure 3.8, indicating that essentially identical cathode performance for Pt/C and LaNiO₃ would be projected under these assumptions. Another strategy to match the activity of the LaNiO₃-based cathode to the Pt-based without constructing 100 μm electrode is to synthesize smaller particles to reduce particle size from 200 nm to 40 nm to allow for 5 times larger surface area per mass. Many synthesis routes have been reported to prepare oxide particles in the range of 30-100 nm. At this particle size, the oxide-based electrode performance can be as competitive as that of Pt-based at ~7 mg oxide cm⁻² (with an estimated electrode thickness of ~20 μm.) At this loading, the assumption of full utilization with minimum mass transport loss is likely more realistic.

From this analysis, the oxide-based cathode performance could indeed be competitive with that of Pt/C but, at the same time, it is clear that oxides with higher ORR activity than LaNiO₃ are desired with, most importantly, long-term stability over a wider potential range. The establishment of a reliable and fast ORR activity screening method as presented in this work can accelerate the development of oxide-based ORR catalysts with enhanced activity and durability. Identifying more active and more durable oxide-based ORR electrocatalysts is subject of the next chapter, where we will examine the ORR activity of a large number of model perovskites using the thin-film RDE technique with
alkali ion exchanged Nafion® binder presented here, seeking to develop fundamental ORR activity descriptors which would allow to more effectively search the large parameter space of partially substituted AA'BB'O₃ perovskites, analogous to what was developed for noble metal catalysts²¹.

Figure 3.8. Projected kinetically limited cathode performance under an idealized scenario of full utilization of the catalyst with minimum mass transport loss for electrodes with different ORR catalysts and catalyst loadings: LaNiO₃ at 36 mg oxide cm⁻² electrode or commercial Pt/C at 0.4 mg Pt cm⁻² electrode. Projections are based on the mass activity data in figure 7 (100 kPaabs O₂ at room temperature).

3.4 Chapter 3 Conclusion

We report a methodology using the thin-film RDE technique to quantify the mass and specific ORR activities of sub-micron-sized oxide catalysts, as poor mass transport in traditional porous electrodes leads to ambiguity in comparing the intrinsic ORR activity of different oxides. Using this method, we show that La₀.₇₅Ca₀.₂₅FeO₃ has the lowest mass and the specific activities, followed by LaCu₀.₅Mn₀.₅O₃, and by LaNiO₃, which is the most active. The Koutecky-Levich analysis indicates that, for LaNiO₃ and LaCu₀.₅Mn₀.₅O₃, the reaction proceeds through the 4-electron reduction where water is
the final product. Compared to state-of-the-art platinum nanoparticle catalysts, LaNiO$_3$ has only about an order of magnitude lower specific activity. The performance projection of LaNiO$_3$ catalysts in actual fuel cell cathodes, where the catalyst loading of noble-metal free catalysts is limited by electrode thickness constraints, suggests comparable performance to platinum nanoparticles supported on carbon, where catalyst loading is constrained by cost instead. This chapter establishes a fast, reliable technique to screen sub-micron-sized catalysts, which can aid in the development of highly active and low-cost ORR catalysts.
Chapter 4 – Activity Descriptor for ORR

4.1 Introduction

Transition metal oxides have shown reasonably high activity for the ORR in fuel cells\textsuperscript{23,13} and the OER in water electrolysis\textsuperscript{5,35} and direct solar water splitting\textsuperscript{108} at neutral and high pH. However, lack of fundamental understanding of the ORR mechanism and the material properties that govern the catalytic activity hampers the development of highly active oxide catalysts. In this chapter, we report a volcano relationship between a material property that serves as the activity descriptor and the intrinsic ORR activity of perovskite-based oxides. Such information has predictive power and provides insights into the design of new catalysts with enhanced ORR activity similar to those reported for platinum-based metals\textsuperscript{18,19,21}.

We examine the perovskite family, where A sites with rare-earth metal ions, and B sites with transition metal ions can allow partial substitution to form AA'BB'O\textsubscript{3} to experimentally examine a large number of oxides (fifteen total) in order to establish a catalytic descriptor for ORR. Matsumoto et al.,\textsuperscript{24,109,110} and Bockris and Otagawa\textsuperscript{82} have reported the geometric currents of perovskites in thick, porous electrodes as a function of potential but the intrinsic specific ORR activity (kinetic current densities normalized to catalyst surface area) necessary for ORR mechanistic discussion is not available. In the last chapter, we describe a methodology using a thin-film rotating-disk electrode with well-defined oxygen transport\textsuperscript{13} to allow a precise comparison of the ORR activity of different transition metal oxides. This method yields a more accurate determination of the intrinsic ORR activity than that estimated from the data reported by Bockris and Otagawa\textsuperscript{13} as oxygen mass transport resistances in thin-film electrodes are much better compensated than thick electrodes with very high internal surface area. In this work, we apply this methodology to assess the ORR activity on fifteen perovskite-based oxides with various A-site (La\textsubscript{1-x}Ca\textsubscript{x}BO\textsubscript{3}, La\textsubscript{1+\textit{x}}BO\textsubscript{3+\textit{x}}) and B-site (LaB\textsubscript{1-x}B'\textsubscript{x}O\textsubscript{3}) substitutions, which is used to identify material properties (descriptors) that govern the intrinsic ORR activity. Here we utilize the molecular orbital approach to identify descriptors for the
ORR activity of oxides, in contrast to the hypothesis proposed previously by Matsumoto et al.,\textsuperscript{24,109,110} which is based on the conjecture that the ORR activity of oxide electrodes can be greatly influenced by the formation and filling of a $\sigma^*$ band between the $e_g$ orbital of bulk transition metal ions and a molecular orbital of surface oxygen. The use of the molecular orbital approach to these perovskites is supported by a large number of reports that the surface of transition metal oxides favors electron localization over the bulk-itinerant electron state\textsuperscript{29,111,112}. Herein, we show that the primary descriptor that governs the ORR activity of the fifteen perovskites examined in this work is the extent of $\sigma^*$ antibonding (“$e_g$”) orbital filling of surface transition metal ions. This hypothesis is further supported by an increasing ORR activity with more hybridization of the B-O (B-site-metal and oxygen) bond as revealed by O K-edge X-ray absorption spectroscopy (XAS) analysis.

4.2 Experimental Procedure

Material synthesis. The perovskites samples used in this study were synthesized with a co-precipitation method. Rare and alkaline earth nitrate and transition metal nitrate (both 99.98\% Alfa Aesar) in a 1:1 mole ratio were mixed in Milli-Q water (18 MΩ-cm) at 0.2 M metal concentration. The solution containing rare and alkaline earth, and transition metals was titrated to 1.2 M tetramethylammonium hydroxide (100\% Alfa Aesar). The precipitate was filtered, collected, and dried. The powder samples were subjected to heat treatment at 1000°C under Ar atmosphere for the La$_{1-x}$Ca$_x$MnO$_3$ ($x = 0, 0.5$) and La$_{0.5}$Ca$_{0.5}$CrO$_3$, LaNi$_{0.5}$Mn$_{0.5}$O$_3$ and LaCu$_{0.5}$Mn$_{0.5}$O$_3$ samples, at 1000°C under dry air atmosphere for LaCrO$_3$, La$_{1-x}$Ca$_x$FeO$_3$ ($x = 0, 0.25, 0.5$), La$_{1-x}$Ca$_x$CoO$_3$ ($x = 0, 0.5$), La$_3$Ni$_2$O$_7$, La$_4$Ni$_3$O$_{10}$ samples, and at 800°C under O$_2$ atmosphere for the LaNiO$_3$ sample. LaMnO$_{3+\delta}$ was prepared from an 800°C heat treatment of LaMnO$_3$ in air. La$_2$NiO$_4$ was synthesized in 2 steps: 1000°C under Air atmosphere and then heated at 800°C under Ar atmosphere. All gases had ultra-high-grade purity (Airgas). All samples were characterized by X-ray diffraction to determine phase purity with a Rigaku high-power rotating anode X-ray powder diffractometer at a scan rate of 0.8 degree/min. All X-ray diffraction data and refined lattice parameters are shown in Table 4.1 respectively. All
the oxides used in this study had a single phase except LaNiO$_3$, where <2\% of NiO was present. Average particle sizes with standard deviations and estimated surface area values were quantified via Philips XL30 FEG ESEM (FEI-Philips), which are listed in Table 4.2.

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<td>La$<em>{0.5}$Ca$</em>{0.5}$MnO$_{3-δ}$</td>
<td>Pnma</td>
<td>5.42</td>
<td>7.65</td>
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<td>La$<em>{0.5}$Ca$</em>{0.5}$FeO$_{3-δ}$</td>
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<td>La$<em>{0.75}$Ca$</em>{0.25}$FeO$_{3-δ}$</td>
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<td>5.52</td>
<td>7.80</td>
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<td>La$<em>{0.5}$Ca$</em>{0.5}$CoO$_{3-δ}$</td>
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<td>7.59</td>
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<tr>
<td>LaMnO$_{3+δ}$</td>
<td>R-3c</td>
<td>5.52</td>
<td>5.52</td>
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</tbody>
</table>

Table 4.1. The derived lattice parameters of the oxide model compounds in this work
<table>
<thead>
<tr>
<th>Compound</th>
<th>$d_{\text{number}}$ ($\mu$m)</th>
<th>$d_{\text{via}}$ ($\mu$m)</th>
<th>$A_s$ ($\text{m}^2 \text{g}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO$_3$</td>
<td>0.64 ($\pm 0.25$)</td>
<td>0.83</td>
<td>1.1</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>1.05 ($\pm 0.52$)</td>
<td>1.51</td>
<td>0.6</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>0.71 ($\pm 0.34$)</td>
<td>1.01</td>
<td>0.9</td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>0.78 ($\pm 0.40$)</td>
<td>1.10</td>
<td>0.7</td>
</tr>
<tr>
<td>LaNiO$_3$</td>
<td>0.20 ($\pm 0.06$)</td>
<td>0.24</td>
<td>3.5</td>
</tr>
<tr>
<td>La$_2$NiO$_4$</td>
<td>0.49 ($\pm 0.25$)</td>
<td>0.70</td>
<td>1.2</td>
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<tr>
<td>La$_4$Ni$<em>5$O$</em>{10}$</td>
<td>0.45 ($\pm 0.15$)</td>
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<td>LaNi$<em>{0.5}$Mn$</em>{0.5}$O$_3$</td>
<td>0.34 ($\pm 0.11$)</td>
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<tr>
<td>LaCu$<em>{0.5}$Mn$</em>{0.5}$O$_3$</td>
<td>0.58 ($\pm 0.28$)</td>
<td>0.80</td>
<td>1.1</td>
</tr>
<tr>
<td>La$<em>{0.5}$Ca$</em>{0.5}$CrO$_{3-\delta}$</td>
<td>0.19 ($\pm 0.06$)</td>
<td>0.22</td>
<td>4.9</td>
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<td>La$<em>{0.5}$Ca$</em>{0.5}$MnO$_{3-\delta}$</td>
<td>0.92 ($\pm 0.44$)</td>
<td>0.62</td>
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<tr>
<td>La$<em>{0.5}$Ca$</em>{0.5}$FeO$_{3-\delta}$</td>
<td>0.62 ($\pm 0.31$)</td>
<td>0.89</td>
<td>1.1</td>
</tr>
<tr>
<td>La$<em>{0.75}$Ca$</em>{0.25}$FeO$_{3-\delta}$</td>
<td>0.36 ($\pm 0.22$)</td>
<td>0.59</td>
<td>1.8</td>
</tr>
<tr>
<td>La$<em>{0.5}$Ca$</em>{0.5}$CoO$_{3-\delta}$</td>
<td>0.43 ($\pm 0.23$)</td>
<td>0.63</td>
<td>1.6</td>
</tr>
<tr>
<td>LaMnO$_{3+\delta}$</td>
<td>1.39 ($\pm 0.58$)</td>
<td>1.81</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 4.2. Characterizations of the oxides studied in this chapter. The number averaged diameter, $d_{\text{number}}$, the volume-area averaged diameter, $d_{\text{via}}$, and the specific surface area, $A_s$, were obtained from particle size distribution measurements. Methodology for calculating each variable is given elsewhere.$^{13}$
**Electrode preparation.** Glassy-carbon electrodes (5 mm in diameter, Pine Instrument) were polished with 0.05 μm Alumina slurry (Buehler) to obtain a mirror finish. Perovskite oxides were mixed with acid-treated acetylene black (Chevron) at a mass ratio of 5:1. Catalyst ink was prepared by mixing perovskite oxides and acetylene black with tetrahydrofuran (THF, 99.94% Sigma-Aldrich) and an appropriate amount of neutralized Nafion (5% weight, Ion power) as described elsewhere. The electrode had a final composition of 250 μg_{oxide} cm^{-2}_{disk}, 50 μg_{AB} cm^{-2}_{disk}, and 50 μg_{Nafion} cm^{-2}_{disk}.

**Electrochemical characterization.** Electrochemical measurements were conducted with a rotating-disk electrode (Pine Instrument). All measurements were collected in a 100 mL solution of 0.1 M KOH, prepared from Milli-Q water (18 MΩ·cm) and KOH pellets (99.99% weight, Sigma-Aldrich) electrolyte, with a VoltaLab PST050 potentiostat. In this work, error bars represent standard deviations from at least three independent repeat measurements. The analysis of ORR kinetic currents were outlined in our previous work, and the specific ORR activity was obtained from normalizing the kinetic current by the surface area of each oxide estimated from SEM images (Table 4.2). Because the errors associated with the surface area estimation (Table 4.2) are smaller than the experimental uncertainty in the intrinsic ORR activity of oxides from our RDE measurements (~30 mV standard deviation, translating to a change of ~3.2 times in the ORR current density normalized to oxide surface considering a Tafel slope of 60 mV/decade), the ORR trend are not affected significantly by the errors in the oxide surface area. In addition, BET measurements of the surface area of select oxides showed reasonable agreements with those estimated from SEM images (e.g. LaNiO₃, 5.6 m²/g from BET measurements vs. 3.5 m²/g estimated from SEM images). Moreover, it should be noted that the specific ORR current densities for LaCrO₃ and LaFeO₃ were comparable to the ORR activity of acetylene black (background ORR activity) considering experimental uncertainty and therefore, the ORR activity values reported here can only present as upper limits for these two oxides. Furthermore, the ORR activity results obtained from the thin-film RDE measurement can be well translated to the actual performance of the air electrode in fuel cells and metal-air batteries as shown previously for PEMFCs. Lastly, it should be mentioned that preliminary stability testing of the
most active oxide, LaMnO$_{3.6}$, showed very small ORR activity changes (smaller than the experimental uncertainty in the RDE measurements) during 3.5 hours of continuous cycling between 0.7 and 1.0 V vs. RHE, which suggests that oxide materials can serve as reasonably stable ORR catalysts in fuel cells and metal-air batteries.

**Hard X-ray Absorption characterization.** Hard X-ray Absorption Spectroscopy (XAS) was collected at beamline X11A of the National Synchrotron Light Source at the Brookhaven National Laboratory with the electron storage ring of 2.8 GeV and a current in the range of 150-300 mA. The Mn, Ni, Co, and Fe K-edge electron yield modes were collected from oxide powders mounted on carbon conductive tape with a Lytle detector at room temperature using Si(111) double-crystal monochromator detuned to ~70% of the maximum intensity. The spectra were calibrated to the reference metal foils by setting the maximum inflection points (E$_0$) to their respective reference energies. X-ray absorption near edge structure (XANES) was extracted from the absorbance with the IFEFFIT package by subtracting from the pre-edge region with a linear fit and normalizing to a per atomic basis with the average of the absorption cross section over the post-edge region$^{113}$.

**Determination of $e_g$ filling of non-stoichiometric LaMnO$_{3.6}$.** Based on the published thermodynamics, subjecting LaMnO$_3$ to a heat treatment in air at 800°C will result in a phase transformation to an oxygen over-stoichiometric LaMnO$_{3.6}$ compound with δ ≈ 0.11 (±0.05)$^{114}$. To ensure that the synthesis of LaMnO$_{3.6}$ was successful, XRD was collected to confirm the rhombohedral phase of LaMnO$_{3.6}$ (Table 4.1). From the published δ ≈ 0.11, LaMnO$_{3.6}$ has a high spin $t_{2g}^3e_g^{0.79}$ configuration and $e_g$ filling of 0.79 (±0.05) ≈ 0.8$^{115}$.

**Determination of $e_g$ filling of Ca-substituted La$_{0.5}$Ca$_{0.5}$MnO$_3$.** Previous studies using X-ray emission spectroscopy$^{115}$, thermogravimetric analysis (TGA)$^{116}$, X-ray absorption near-edge spectroscopy (XANES)$^{117}$, and magnetic measurement$^{118}$ have shown that charge compensation following Ca-substitution in LaMnO$_3$ occurs via Mn$^{4+}$ formation. We, therefore, assume that our La$_{0.5}$Ca$_{0.5}$MnO$_3$ compound charge-compenses by forming Mn$^{4+}$. As a result, La$_{0.5}$Ca$_{0.5}$MnO$_3$ has an average Mn oxidation state of 3.5+ and therefore an electron configuration of $t_{2g}^3e_g^{0.5}$. We had conducted Mn K-edge XANES to
confirm that the Mn in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ shifts to higher oxidation state in relative to $\text{LaMnO}_3$ (Figure 4.1).

**Figure 4.1.** X-ray Absorption Spectra $\text{LaMnO}_3$ vs. $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

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Determination of $e_g$ filling of Ca-substituted $\text{La}_{0.75}\text{Ca}_{0.25}\text{FeO}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$. The charge compensation following Ca-substitution in $\text{LaFeO}_3$ is assumed to occur via $\text{Fe}^{4+}$

**Figure 4.2.** X-ray Absorption Spectra $\text{LaFeO}_3$ vs. $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$
formation in high spin configuration. This is in agreement with the observation of Fe$^{4+}$ formation in Ca-substituted LaFeO$_3$ using Mossbauer spectroscopy$^{119,120}$. Our own Fe K-edge XANES also confirms that the Fe oxidation shifts to higher oxidation state with increasing Ca content (Figure 4.2).

![Figure 4.3. X-ray Absorption Spectra LaCoO$_3$ vs. La$_{0.5}$Ca$_{0.5}$CoO$_{3-\delta}$.](image)

**Determination of $e_g$ filling of Ca-substituted La$_{0.5}$Ca$_{0.5}$CoO$_{3-\delta}$.** Because the exact spin-state of La$_{0.5}$Ca$_{0.5}$CoO$_{3-\delta}$ has not been determined yet in the literature, partly due to the fact that the majority of Co remains $3^+$ despite the substitution of La$^{3+}$ by Ca$^{2+}$ ion$^{121}$, we approximate the spin state of this compound as a mixture of LaCoO$_3$ and SrCoO$_{2.5}$. Using a mixture of intermediate spin LaCoO$_3$ ($t_{2g}^5 e_g$)$^{112}$ and high spin SrCoO$_{2.5}$ ($t_{2g}^4 e_g^2$)$^{122}$, we arrive at an approximation of $e_g \approx 1.5$ for La$_{0.5}$Ca$_{0.5}$CoO$_{3-\delta}$. The concept of high-spin Co stabilization with Ca-substitution has been proposed in the literature$^{121,123,124}$, so we believe our approximation is within reason, especially for the surface Co. We had also conducted TGA to confirm the formation of oxygen vacancy ($\delta_{TGA} = 0.21 \pm 0.01$) that had been reported in the literature following Ca-substitution. Our Co K-edge XANES additionally demonstrated that the Co edge remained unchanged following
Ca-substitution, which provides further evidence for the stabilization of Co$^{3+}$ in La$_{0.5}$Ca$_{0.5}$CoO$_{3.6}$ (Figure 4.3).

**Determination of e$_g$ filling of LaNi$_{0.5}$Mn$_{0.5}$O$_3$ and LaCu$_{0.5}$Mn$_{0.5}$O$_3$.** The e$_g$ filling for the mixed B-site compounds (LaNi$_{0.5}$Mn$_{0.5}$O$_3$ and LaCu$_{0.5}$Mn$_{0.5}$O$_3$) is complicated by the presence of two inequivalent B atoms and thus two different e$_g$ fillings. It is also widely known that a charge-ordered Mn/Ni undergoes charge-disproportionation into Mn$^{4+}$ and Ni$^{2+}$ in LaNi$_x$Mn$_{1-x}$O$_3$\(^\text{125}\). Thus, to determine properly the e$_g$ filling for the mixed compounds, the oxidation state of both B atoms was measured with XANES. Using a known-relationship where $E_0$ (maximum inflection point of the absorption edge) scales with oxidation state\(^\text{126}\), we estimate the valence state of Mn in both LaNi$_{0.5}$Mn$_{0.5}$O$_3$ and LaCu$_{0.5}$Mn$_{0.5}$O$_3$ to be 3.7 (high spin configuration, Figure 4.4). A high-spin configuration of Mn leads to an e$_g$ filling of 0.3 for the Mn site. Similar analysis was applied to Ni in LaNi$_{0.5}$Mn$_{0.5}$O$_3$, and the oxidation state of 2.3 was found (Figure 4.4). Based on this information, the e$_g$ filling for Ni is thus determined to be 1.7 (low-spin configuration).

While we did not perform this analysis on Cu in LaCu$_{0.5}$Mn$_{0.5}$O$_3$, we believe the Cu oxidation state should be close to that of Ni if not lower due to the higher electronegativity of Cu atom. Furthermore, the similarity in the Mn oxidation state between LaNi$_{0.5}$Mn$_{0.5}$O$_3$ and LaCu$_{0.5}$Mn$_{0.5}$O$_3$ also indicates that the Cu and the Ni oxidation state should be very close to each other ($\approx$2.3$^+\text{.}$). Thereby, we conclude that the e$_g$ filling for Cu is 2.7 or higher. When we apply the e$_g$ filling from either Mn or Ni (Cu) to the volcano plot, we have found that the use of e$_g$ filling from Mn is most consistent with the observed activity trend (vide infra). Had we used the e$_g$ filling of average B atoms, or Ni or Cu, the e$_g$ would have resulted in an underestimation of the ORR activity. The consistency of selecting Mn e$_g$ filling with our volcano plot also leads us to propose that the active site on the mixed compounds is the Mn atom, where both Ni and Cu atoms had too many e$_g$ electrons, rendering their catalytic properties inactive. The proposed Mn active site is consistent with our observation with the Ruddlesden-Popper compounds that Ni(+2) and Ni(+2.5) were not active for the ORR. Hence it is unlikely that Ni(2.3$^+$), which was observed in LaNi$_{0.5}$Mn$_{0.5}$O$_3$, would be the active site.
Figure 4.4. Determination of B-site oxidation state of LaNi$_{0.5}$Mn$_{0.5}$O$_3$ and LaCu$_{0.5}$Mn$_{0.5}$O$_3$. (Top) Mn oxidation state for LaNi$_{0.5}$Mn$_{0.5}$O$_3$ (red circle) and LaCu$_{0.5}$Mn$_{0.5}$O$_3$ (blue triangle) is estimated to be $\approx$3.7+. (Bottom) Ni oxidation state in LaNi$_{0.5}$Mn$_{0.5}$O$_3$ (red circle) is estimated to be $\approx$2.3+.

4.3 Method for ORR Activity Comparison

The ORR currents of a LaCu$_{0.5}$Mn$_{0.5}$O$_3$ thin-film electrode at various rotation speeds are shown in Figure 4.5 as an example. The onset of the ORR occurs at ca. 0.8 V vs. RHE (reversible hydrogen electrode), and an oxygen-transport-limited current appears at
potentials below ca. 0.5 V vs. RHE. The slope of the Koutecky-Levich plot in the mass-transport-limited region (0.4 V vs. RHE, Figure 4.5 inset) has a value of \( \approx 1 \) (mA cm\(^{-2}\) disk\(^{-1}\)), which indicates 4-e\(^{-}\) reduction of oxygen to water\(^{13,127}\). The mass-transport correction to the oxygen diffusion overpotential was applied to all measurements to obtain the ORR kinetic currents as outlined in our previous work\(^{13}\). The surface-area-normalized kinetic current densities of four representative oxides, referred to as specific activity \((i_s)\),\(^{13}\) are plotted as a function of voltage in Figure 4.6. Because all fifteen oxide catalysts had comparable Tafel slopes around 60 mV per decade (Figure 4.7), the dashed line in Figure 4 shows the intrinsic activity for each catalyst can be assessed by the potential to achieve a given specific ORR current (25 µA/cm\(^2\)). For LaCu\(_{0.5}\)Mn\(_{0.5}\)O\(_3\), LaMnO\(_3\), LaCoO\(_3\), and LaNiO\(_3\), this specific activity current can be reached at potentials of 781(±15), 834(±24), 847(±3), and 908(±8) mV vs. RHE, respectively. Higher potential indicates higher electrocatalytic activity for a given oxide. It is interesting to note that oxides such as LaMnO\(_{3+δ}\) and LaNiO\(_3\) have intrinsic ORR activity comparable to the state-of-the-art Pt/C (Figure 4.8).

**Figure 4.5.** Oxygen reduction activity of LaCu\(_{0.5}\)Mn\(_{0.5}\)O\(_3\) electrode in O\(_2\)-saturated 0.1 M KOH at 10 mV/s scan rate at rotation rates of 100, 400, 900, and 1600 rpm.
respectively. The Koutecky-Levich analysis (inset) of the limiting currents (0.4 V) indicates a $4e^-$ transfer reaction.

**Figure 4.6.** Specific activities of $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$, $\text{LaMnO}_3$, $\text{LaCoO}_3$, and $\text{LaNiO}_3$. The potential at 25 $\mu$A/cm$^2_{\text{ox}}$ is used as a benchmark for comparison (shown as the intersection between the activity and a horizontal gray dashed line).
Figure 4.7. Tafel plot of the ORR specific activity of oxides studied in this chapter using thin film RDE.
Figure 4.8. Tafel plot of the ORR specific activity of LaMnO$_{3+\delta}$ vs. Pt/C from the thin film RDE experiments. These two catalysts have very similar ORR activities (~50 mV shift, corresponding to less than an order of activity difference). Error bars represent standard deviations of at least three independent measurements.

4.4 ORR activity descriptor identification

To identify an ORR activity descriptor, we begin by examining the relationship between the 3d-electron number of B-site ions and the ORR activity with the hypothesis that the 3d-electron number, which represents the antibonding electron occupation of the B-O bond, can influence the B-O$_2$ interaction strength$^{35}$ (see Scheme 4.1). This hypothesis is supported by the recent observation that the adsorption energy trend of B-O$_2$ can be approximated by that of B-O$^{128}$. Interestingly, the comparison between the ORR activity of the perovskites and the d-electron number per B cation (Figure 4.9) reveals an M-shaped relationship with the maximum activity attained near $d^4$ and $d^7$, which resembles the trend reported for oxidation activity of gas-phase CO and hydrocarbon on perovskites$^{36,129}$. 
**Scheme 4.1. Molecular orbital of BO\(_6\) interaction.** The energy levels of the d-electrons in free B ion, octahedral BO\(_6\), and surface BO\(_6\) configurations. The initial d manifold degeneracy is split into the antibonding e\(_g\) and t\(_{2g}\) levels. Mn\(^{3+}\) (\(d^4\)) in high spin configuration is shown as an example of a cation with an antibonding e\(_g\)-orbital degeneracy with a single e\(_g\) electron. At a surface cation, the degeneracy is removed by a tetragonal site symmetry (C\(_{4v}\)) in which the occupied e\(_g\) electron occupying a z\(^2\) orbital directed toward a surface OH\(^-\) is lowered in energy relatively to the e\(_g\) electron occupying the x\(^2\)-y\(^2\) orbital.

We further show that the intrinsic ORR activity of all the oxides exhibits a volcano shape as a function of the e\(_g\)-filling of B ions. Assuming that the O\(_2\) molecule likely adsorbs on the surface B sites end-on, the e\(_g\) orbital directed toward an O\(_2\) molecule overlaps the O-2p\(_o\) orbital more strongly than the overlap between the t\(_{2g}\) and the O-2p\(_n\) orbitals, and therefore suggests that the filling of e\(_g\) rather than t\(_{2g}\) of the B-ion should more accurately determine both the energy gained by adsorption/desorption of oxygen on B ions and the ORR activity if such an adsorption/desorption process was involved in the rate-limiting step of the ORR. This conjecture is supported by the correlation between increasing e\(_g\) filling and decreasing onset temperature of oxygen release measured via O\(_2\) temperature-programmed desorption in the order of LaCrO\(_3\) (e\(_g\) = 0) > LaMnO\(_3\) (e\(_g\) = 1) ~ LaCoO\(_3\) (e\(_g\) ~ 1) ~ LaNiO\(_3\) (e\(_g\) ~ 1) > LaFeO\(_3\) (e\(_g\) = 2)\(^{130}\), which is indicative of the strength of bonding.
between B-site cations and oxygen. We have taken into account whether partial substitution on the A or B sites undergoes charge compensation via oxygen vacancy or changing of B ion valency in the $e_g$ calculation of the surface B ions, which was determined from a combination of literature data, thermogravimetry and XAS (see Table 4.3). Plotting ORR activity as a function of the $e_g$ filling produces a definitive volcano plot (Figure 4.10) with a voltage span of 0.25 V corresponds to ~ 4 orders of magnitude in the intrinsic ORR activity (using ~60 mV/decade Tafel slope.)

![Figure 4.9](image)

**Figure 4.9.** The potentials at 25 $\mu A/cm^2$ of the perovskite oxides have M-shaped relationship with the d-electron number. The data symbols vary with the type of B ions (square red for Cr, orange circle for Mn, beige upside up triangle for Fe, green upside down triangle for Co, blue diamond for Ni, and purple left triangle for mixed compounds), where $x = 0$ and 0.5 for Cr, and 0, 0.25, and 0.5 for Fe. Error bars represents standard deviations of at least 3 measurements.
Figure 4.10. The potentials at 25 μA/cm² as a function of e₉-orbital in perovskite-based oxides. The data symbols vary with the type of B ions (square red for Cr, orange circle for Mn, beige upside up triangle for Fe, green upside down triangle for Co, blue diamond for Ni, and purple left triangle for mixed compounds), where x = 0 and 0.5 for Cr, and 0, 0.25, and 0.5 for Fe. Error bar represents standard deviations of at least 3 measurements.
<table>
<thead>
<tr>
<th>Valence Spin state Assignment</th>
<th>Example of reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO$<em>3$ Cr$^{3+}$ n/a $t</em>{2g}^3$</td>
<td>LS and HS identical</td>
</tr>
<tr>
<td>LaMnO$<em>3$ Mn$^{3+}$ H.S. $t</em>{2g}^3 e_g^1$</td>
<td>Magnetization$^{118}$</td>
</tr>
<tr>
<td>LaFeO$<em>3$ Fe$^{3+}$ H.S. $t</em>{2g}^3 e_g^2$</td>
<td>Mossbauer spectroscopy$^{120}$</td>
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<tr>
<td>LaCoO$<em>3$ Co$^{3+}$ I.S. $t</em>{2g}^5 e_g^1$</td>
<td>Magnetization$^{131}$</td>
</tr>
<tr>
<td>LaNiO$<em>3$ Ni$^{3+}$ L.S. $t</em>{2g}^6 e_g^1$</td>
<td>Extrapolation from RNiO$_3$ magnetization$^{132}$</td>
</tr>
<tr>
<td>La$_2$NiO$<em>4$ Ni$^{2+}$ n/a $t</em>{2g}^6 e_g^2$</td>
<td>LS and HS identical</td>
</tr>
<tr>
<td>La$<em>2$Ni$<em>5$O$</em>{10}$ Ni$^{2.7+}$ L.S. $t</em>{2g}^6 e_g^{1.3}$</td>
<td>Extrapolation from LaNiO$_3$ and La$_2$NiO$_4$</td>
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<tr>
<td>LaNi$<em>{0.5}$Mn$</em>{0.5}$O$<em>3$ Mn$^{3.7+}$ H.S. (Mn) $t</em>{2g}^3 e_g^{0.3}$ (Mn)</td>
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</tr>
<tr>
<td>Ni$^{2.3+}$ L.S. (Ni) $t_{2g}^6 e_g^{1.7}$ (Ni)</td>
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</tr>
<tr>
<td>Mn$^{3.7+}$ H.S. (Mn) $t_{2g}^3 e_g^{0.3}$ (Mn)</td>
<td>See Supplementary Method</td>
</tr>
<tr>
<td>Cu$^{2.3+}$ L.S. (Cu) $t_{2g}^6 e_g^{2.7}$ (Cu)</td>
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<tr>
<td>La$<em>{0.75}$Ca$</em>{0.25}$CrO$<em>{3+\delta}$ (Assume $\delta = 0$) Cr$^{2.5+}$ n/a $t</em>{2g}^{2.5}$</td>
<td>LS and HS identical</td>
</tr>
<tr>
<td>La$<em>{0.5}$Ca$</em>{0.5}$MnO$<em>{3+\delta}$ (Assume $\delta = 0$) Mn$^{3.5+}$ H.S. $t</em>{2g}^3 e_g^{0.5}$</td>
<td>Magnetization$^{118}$, X-ray Emission$^{115}$ Mossbauer spectroscopy$^{119,120}$</td>
</tr>
<tr>
<td>La$<em>{0.5}$Ca$</em>{0.5}$FeO$<em>{3+\delta}$ (Assume $\delta = 0$) Fe$^{3.5+}$ H.S. $t</em>{2g}^3 e_g^{1.5}$</td>
<td>Mossbauer spectroscopy$^{119,120}$ La$_{1-x}$Ca$<em>x$CoO$</em>{3+\delta}$ extrapolation$^{121}$ X-ray Emission</td>
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<tr>
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<td></td>
</tr>
<tr>
<td>LaMnO$<em>{3+\delta}$ Mn$^{3.2+}$ H.S. $t</em>{2g}^3 e_g^{0.8}$</td>
<td>Spectroscopy$^{115}$</td>
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Table 4.3. Summary of literature information on the spin state of the perovskite oxides
4.5 Proposed ORR mechanism

We explain the volcano trend of oxide ORR activity with the following. Too little of \( e_g \) filling in \( \text{La}_{1-x}\text{Ca}_x\text{CrO}_3 \) (\( t_{2g}^3e_g^0 \) for \( x = 0 \), \( t_{2g}^{2.5}e_g^0 \) for \( x = 0.5 \)) can result in too strong B-O\(_2^2^-\) bonding while too much \( e_g \) filling in \( \text{La}_{1-x}\text{Ca}_x\text{FeO}_3 \) (\( t_{2g}^3e_g^2 \) for \( x = 0 \), \( t_{2g}^3e_g^{1.75} \) for \( x = 0.25 \), \( t_{2g}^3e_g^{1.5} \) for \( x = 0.5 \)) and \( \text{La}_{1-x}\text{NiO}_3 \) having (1-x) \( t_{2g}^6e_g^1 + x t_{2g}^6e_g^2 \) can lead to too weak O\(_2^2^-\) interaction, neither of which are optimum for the ORR activity. On the other hand, a moderate amount of \( e_g \)-filling (~1) in \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) (\( t_{2g}^3e_g^1 \) for \( x = 0 \), \( t_{2g}^3e_g^{0.5} \) for \( x = 0.5 \)), \( \text{LaCoO}_3 \) (\( t_{2g}^5e_g^1 \)), and \( \text{LaNiO}_3 \) (\( t_{2g}^6e_g^1 \)), yields the highest activity. The striking correlation between the \( e_g \) filling and 4 orders of magnitude of the ORR activity suggests that the \( e_g \) filling represents a unifying and primary descriptor for the ORR activity of these oxides. The importance of \( e_g \) filling also explains the origin of the peaks at high-spin \( d^4 \) and low-spin \( d^5 \) in the M plot of ORR activity versus the number of d electrons (Figure 1d): both possess \( e_g \) filling of ~1. The M shape thus arises from the spin-state transition on the B ions from high spin (\( d < 6 \)) to low spin (\( d > 6 \)).

The importance of a single \( e_g \) electron for ORR catalysis can be molecularly explained by the previously proposed competition between the O\(_2^2^-\)/OH\(^-\) displacement (Step 1) and OH\(^-\) regeneration (Step 4) on the surface of the transition metal ions as rate-limiting for ORR in an alkaline solution\(^{134} \) (see Figure 4.11). In this scheme, B is a transition metal cation with an \( e_g \) electron ordered into an orbital directed toward the surface OH\(^-\) ion. As a first order of approximation, the kinetics of the O\(_2^2^-\)/OH\(^-\) exchange can be rationalized in terms of the energy gained by breaking the B-OH\(^-\) bond to form B-O\(_2^2^-\). The presence of a single \( e_g \) represents a \( \sigma^* \) electron that can serve to destabilize the B-OH\(^-\) bond and promote the O\(_2^2^-\)/OH\(^-\) exchange reaction. The displacement of the OH\(^-\) ion that experiences a \( \sigma^* \) electron in the B-OH bond by the O\(_2^2^-\) (or O\(_2\text{ads}^-\)) species removes the highly energetic \( \sigma^* \) electron from the B-OH bond to give a more stable B-O\(_2^2^-\) configuration. If the \( e_g \) electron is more than 1 (the right branch in Figure 4.10), the O\(_2^2^-\)/OH\(^-\) exchange does not gain sufficient energy during the displacement and the ORR kinetics can be limited by the rate of the O\(_2\)/OH exchange (Step 1). On the other hand, if there is less than one \( e_g \) electron on the B cation (the left branch in Figure 4.10), the B-O\(_2^2^-\)
is not sufficiently de-stabilized and the ORR kinetics can be instead limited by the rate of surface OH\textsuperscript{-} regeneration (Step 4).

![ORR Mechanism Diagram]

**Figure 4.11.** Proposed ORR mechanism on perovskite oxide catalysts\textsuperscript{134}. The ORR proceeds via 4 steps: 1 surface hydroxide displacement, 2 surface peroxide formation, 3 surface oxide formation, and 4 surface hydroxide regeneration.

While our observation on the importance of $\sigma^*$ electron transfer to O\textsubscript{2} in ORR activity is in qualitative agreement with the previous hypothesis of Matsumoto et al.\textsuperscript{24,109,110}, our work offers a quantitative correlation between the $e_g$ filling of surface transition metal ions and intrinsic ORR activity up to 4 orders of magnitude and predicts $e_g \sim 1$ to be a key criterion for developing the highest activity. In addition, an important distinction of our analysis is the assumption of a localized $e_g$ electron in an orbital directed toward an O\textsubscript{2} molecule from the surface B cations instead of the traditional band theory\textsuperscript{24,109,110}. We here discuss many works that have provided evidence to this assumption to date. In the case of LaNiO\textsubscript{3}, which has itinerant bulk $\sigma^*$ electrons, the site symmetry of the bulk rhombohedral structure in LaNiO\textsubscript{3} does not permit a localization of an $e_g$ electron in the bulk; but the symmetry of a surface B site changes to tetragonal, which allows ordering of a localized $e_g$ electron directed toward the surface anion species. This phenomenon is also displayed in low-temperature LaCoO\textsubscript{3}, where $e_g$ localization gives rise to the
ferromagnetic surface intermediate-spin Co(III):t_2g^5e_g^1 despite the low-spin Co(III):t_2g^6e_g^0 bulk phase^{112}. A similar argument applies to the metallic system La_{1-x}Sr_xMnO_3, which exhibits a transition with increasing x from localized e_g electrons to a narrow \( \sigma^* \) band on the high-spin Mn atoms in the bulk^{29}. Here, the localization of the surface e_g electrons is stabilized by a reduction of the number of Mn near neighbors as well as by site symmetry.

4.6 Influence of B-O covalency on ORR activity

To further support that the e_g filling of surface B ions governs the ORR activity, we examine the influence of the covalency of the B-O bond of the perovskites on the ORR activity. Stronger covalency of the B-O bond should increase the driving force and thereby facilitate the \( \text{O}_2/\text{OH}^- \) exchange on the surface B ions, which can be considered as the rate-limiting step of ORR for oxides (Figure 4.11). To quantify the B-O bond covalency of the perovskites, we performed the O K-edge XAS, which revealed excitations from the O 1s orbital to the unoccupied states above the Fermi level from regions within \( \sim 10 \) nm from the surface (50% of the signal comes from top 1 nm^{61}). The O K-edge spectra collected from perovskites consist of two major excitations: O 1s \( \rightarrow \) B 3d - O 2p band from 527 - 533 eV, and O 1s \( \rightarrow \) La 5d - O 2p band from 533 - 537 eV^{60}. As discussed in earlier chapter, the specificity of 1s \( \rightarrow \) 2p excitation in the former permits the quantification of the covalency or hybridization effect of the perovskites in this study. To probe the effect of hybridization on the ORR activity without interference from the e_g filling effect, we plot the influence of the hybridization parameter on the ORR activity of perovskites at constant e_g filling in Figure 4.12. Increasing hybridization positively affects the ORR activity (Figure 4.12), which is in agreement with the molecular picture of the proposed ORR mechanism.
Figure 4.12. The role of B-O covalency on the ORR activity of perovskite oxides. The potentials at 25 μA/cm² as a function of the B-O covalency at e₉ filling = 1. Error bars represents standard deviations of at least 3 measurements.

4.7 Chapter 4 Conclusion

This chapter shows that the design principle for enhancing the ORR activity of transition metal oxide perovskites is an e₉ filling having a value of ~1 for maximum activity, which can be further improved by increasing the covalency between the metal 3d and oxygen 2p orbitals. Our findings can be explained by a competition between a rate-limiting O₂²⁻/OH⁻ exchange (Step 1 in Figure 4.11) and the regeneration of OH⁻ on the surface (Step 4 in Figure 4.11). This exchange depends on an energy gained by transferring a single σ*-antibonding e₉ electron of the B-OH⁻ bond to the O₂²⁻ adsorbates, thereby stabilizing the displacement. The greater the covalent contribution to the B-O₂²⁻ bond, the greater the energy realized by the exchange to stabilize the adsorbate and therefore the faster ORR kinetics. This work shows that tuning surface electronic structure features such as transition metal e₉ filling and covalency is a promising strategy to develop highly active non-precious-metal-containing oxide catalysts for oxygen reduction in electrochemical conversion and storage devices. Considering the synergism between the OER and the
ORR expected from the pioneering *ab initio* works of Rossmeisl et al.\textsuperscript{135}, these descriptors could also influence the OER activity of oxides, and such a study would test the validity of the proposed influence of $e_g$ filling of transition metal ions on $O_2$ electrocatalysis.
Chapter 5 – Activity Descriptor for OER

5.1 Introduction

The ability to design cost-effective, highly active catalysts for energy storage applications is a critical element in the pursuit of sustainable energy. The OER in particular is an enabling process for many energy storage options such as direct-solar, electricity-driven water splitting ($\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$), and rechargeable metal-air batteries ($\text{M}_x\text{O}_2 \rightarrow \text{M}_x + \text{O}_2$). The OER kinetics is sluggish, however, even when facilitated by the state-of-the-art, precious-metal-containing catalysts. This limitation imposes a significant overpotential requirement, similar to the case of the ORR for fuel cell applications. First-row transition-metal oxides such as NiCo$_2$O$_4$ and LaNiO$_3$ are cost-effective alternatives, but they underperform relative to IrO$_2$, which is considered to be state-of-the-art. To assist the discovery of highly active catalysts based on abundant elements, substantial effort has been devoted to understanding the mechanism and parameters that govern the OER activity (namely activity descriptor). Pioneering works of Trasatti, Bockris and Otagawa, and Rossmeisl et al. have reported the enthalpy of a lower to higher oxide transition, the $3d$ electron number of bulk transition metal ions, or the surface oxygen binding energy as an OER activity descriptor, respectively. However, it is not straightforward to predict new transition-metal oxides with high OER activity with these proposed descriptors. In this chapter, we develop an OER activity design principle, where a near-unity occupancy of the $e_g$ orbital of surface transition-metal ions and high covalency with oxygen can enhance the intrinsic OER activity of perovskite transition-metal oxides in alkaline solution ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$). We further show that this design principle has predictive power, from which an oxide catalyst with much higher activity than the state-of-the-art IrO$_2$ catalyst was found.

5.2 Experimental Procedure

Material synthesis. The perovskite oxides were synthesized with a co-precipitation method as described in the previous chapter with the exception of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3.5}$. 

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(BSCF), which was synthesized with a nitrate combustion method. In the BSCF synthesis, alkaline earth and transition-metal nitrates (all 99.998+% Sigma-Aldrich) were prepared at 0.2 M concentration, to which glycine (>99% Sigma-Aldrich) was added at 0.1 M concentration. The mixture was heated until vigorously evaporating, at which point, sparks are emitted as a result of combustion; it was then calcined at 1100°C under air atmosphere for 24 hours. Figure 5.1 shows the diffraction pattern of the as-synthesized BSCF, where the crystal was found to be single phase (P m 3 m) with lattice parameter of 3.99 Å. The particle size distributions and estimated surface areas of BSCF are listed in Table 5.1.

Electrochemical characterization. The oxide electrode consisted of perovskite oxides, acetylene black (Chevron), and neutralized Nafion® (Ion power); they were prepared at a loading of 0.25 mg_{ox} cm^{-2}_{disk}, 0.05 mg_{AB} cm^{-2}_{disk}, and 0.05 mg_{Nafion} cm^{-2}_{disk}, similar to the case of the ORR. Electrochemical measurements were conducted with a rotating-disk electrode (Pine) using a VoltaLab PST050 potentiostat. The electrolyte was prepared from Milli-Q water (18 MΩ•cm) and KOH pellets (99.99% weight, Sigma-Aldrich). All measurements were collected under O₂ saturation (ultra-high-grade purity, Airgas) to ensure the O₂/H₂O equilibrium at 1.23V vs. RHE at a rotation rate of 1600 rpm where no mass transport limitation was observed. The analysis of OER kinetic currents was capacitance-corrected by taking the average between positive and negative-going scans, and then iR-corrected (Figure 5.2). The specific OER activity was obtained from normalizing the kinetic current by the surface area of each oxide estimated from particle size distribution. All the potentials are iR-corrected potentials unless stated as applied potentials. The rotating ring disk electrode (Pine) with Pt-ring was calibrated with a potassium ferricyanide couple as described elsewhere. Generated O₂ was collected at a ring potential of 0.4 V vs. RHE.
Table 5.1. The number averaged diameter, $d_{\text{number}}$, the volume-area averaged diameter, $d_{\text{via}}$, and the specific surface area, $A_s$, were obtained from particle size distribution measurements as described in the previous chapter. Note that we also measured the BET area for BSCF, which were found to be within a factor of 2 of the specific area determined from SEM.

<table>
<thead>
<tr>
<th></th>
<th>$d_{\text{number}}$ (μm)</th>
<th>$d_{\text{via}}$ (μm)</th>
<th>$A_s$ (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.8}$Fe$</em>{0.2}$O$_{3.5}$</td>
<td>0.84 (±1.27)</td>
<td>7.01</td>
<td>0.2</td>
</tr>
<tr>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.8}$Fe$</em>{0.2}$O$_{3.5}$ (ball-milled)</td>
<td>0.23 (±0.09)</td>
<td>0.30</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Figure 5.1. X-ray Diffraction Pattern of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3.5}$. The experiment was conducted at room temperature using Cr source. The pattern revealed a space group of Pm $\bar{3}$ m (simple cubic) with a lattice parameter of 3.99 Å.
Synthesis of rutile IrO$_2$ nanoparticle. IrO$_2$ were synthesized in a 2-step reaction as described elsewhere$^{17}$. Briefly, a solution of either IrCl$_4$·xH$_2$O in tetralin and oleylamine was prepared at room temperature and then heated to 60 °C under Ar atmosphere for 20 minutes, followed by an injection of tetrabutylammonium borohydride in chloroform. The reaction mixture was heated up to 200 °C for 19 hours. Afterward, the nanoparticles were precipitated by ethanol addition and collected by centrifugation at room temperature before re-dispersing in hexane, which was followed by a 500 °C heat-treatment for 20 hrs under O$_2$ atmosphere. Both electron and X-ray diffraction reveal the rutile crystal structure (P4$_2$/mmn). Catalyst inks were prepared by horn sonication of oxides in 70 wt% 2-propanol (99.9+% Sigma-Aldrich) as solvent. 10 µL of catalyst ink was drop-cast onto a glassy carbon electrode (0.196 cm$^2$ area, Pine Instrument) polished to a mirror finish with 0.05 µm alumina slurry (Buehler). The catalyst thin-film was dried at ambient conditions overnight. We find that the OER specific activity of rutile IrO$_2$ was insensitive to the loading, which suggests full utilization of the catalyst layer in our electrode.

Figure 5.2. Ohmic and capacitive corrections of the as-measured OER activity of example perovskite oxide catalyst. The as-measured OER activity of the La$_{0.5}$Ca$_{0.5}$CoO$_3$.5 thin-film composite catalyst (“raw”, solid red line) is capacity-corrected by taking an average of forward and backward (positive and negative-going) scans. The capacity-corrected OER current (short-dash blue line) is then ohmically corrected with
the measured ionic resistance (≈45 Ω) to yield the final electrode OER activity (long-dash green line).

**Determination of e\textsubscript{g} filling of LaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} and LaCu\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3}**. The e\textsubscript{g} fillings of LaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} and LaCu\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} are complicated by the fact that these compounds undergo charge-disproportionation between Mn and Ni/Cu atoms. To estimate the e\textsubscript{g} filling, we use the strategy from previous chapter, which relies on tracking the oxidation states of each metal with X-ray Absorption Spectroscopy (XANES). From a known-relationship where E\textsubscript{O} (maximum inflection point of the absorption edge) scales with oxidation state\textsuperscript{126}, we estimate the Mn electronic configuration to be t\textsubscript{2g} 3 e\textsubscript{g} 0.3 for both LaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} and LaCu\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3}, and Ni to be t\textsubscript{2g} 0 e\textsubscript{g} 1/2 for LaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} and Cu to be t\textsubscript{2g} 2 e\textsubscript{g} 2.7 for LaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3}. When we apply the e\textsubscript{g} filling from each B atom to the OER volcano plot, we have found that the use of e\textsubscript{g} filling from Ni is most consistent with the observed activity for LaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} and Mn for LaCu\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3}. Had we used the e\textsubscript{g} filling of average B atoms, or Mn for LaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} or Cu for LaCu\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3}, the e\textsubscript{g} would have resulted in an underestimation of the OER activity. The consistency e\textsubscript{g} filling selection with our volcano plot also leads us to propose that the active site for the OER is the Ni atom for LaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} and the Mn atom for LaCu\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3}, where the Mn atom in LaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} has too little e\textsubscript{g} electron filling and Cu atoms in LaCu\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} has too many e\textsubscript{g} electrons, rendering their catalytic properties inactive.

**Determination of e\textsubscript{g} filling of Ba\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3-δ} compound**. The e\textsubscript{g} filling for the mixed A-site and B-site BSCF is highly complicated by the presence of four distinct cations and a large concentration of oxygen vacancies inside the host structure. We measure the oxygen vacancy concentration with thermogravimetry (TGA), where we found δ\textsubscript{TGA} to be ~0.4. While this δ\textsubscript{TGA} is in agreement with the literature value\textsuperscript{141}, it alone still cannot determine the oxidation state of Co and Fe atoms. Therefore we resort to the use of XANES to estimate the Co oxidation state. Using CoO (Sigma-Aldrich) and LaCoO\textsubscript{3} as model compounds, we estimate the oxidation state of the Co to be ~2.8+ (Figure 5.3). Considering the previous works of Harvey et al.\textsuperscript{142,143} and Arnold et al.\textsuperscript{144}, whose XANES and X-ray Photoemission Spectroscopy studies have shown that the Co oxidation state in BSCF is partially reduced below 3+ and that the Fe oxidation state is
partially oxidized above 3+, our estimated oxidation state is therefore not unexpected. Taking into account that the surface Co state in BSCF has been reported to be in an intermediate spin state$^{144}$, similar to the case of LaCoO$_3$, the electronic configuration of the Co in BSCF is likely $t_2^6e_g^{-1.2}$.

Figure 5.3. Co K-edge XANES of CoO, LaCoO$_3$, and BSCF. (A) The Co K-edge spectra. (B) The edge position ($E_0$, defined to be the energy at the highest first derivative of the absorbance) of BSCF fits right in between CoO and LaCoO$_3$. By using the known metal oxidation vs. $E_0$ relationship, we estimate the Co oxidation state to be $\sim$2.8+. 
Ball-milling of \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} \) compound. The as-synthesized BSCF powder was ball-milled with a Fritsch pulverisette 6 planetary mill. A 5:2 mass ratio of 1 mm zirconia milling beads to BSCF was prepared with 10 mL of N-methyl-2-pyrrolidinone (NMP) solvent. The materials were milled in a zirconia crucible at 500 rpm for 8 hours, with a 30-minute rest period every one-hour. The BSCF-NMP mixture was then dried in a furnace at 195 °C in air, and then at 240 °C in vacuum overnight to evaporate off any remaining solvent. The powder was then finely ground by a mortar and pestle before electrochemical characterization. We caution, however, that this ball-milling method does not result in a sufficient miniaturization of the BSCF particle; a strategy based on nanoscale oxide synthesis will likely produce more uniform, high-surface-area oxides. We studied the ball-milling sample at both 0.25 mg_{ox} cm^{-2} disk, and 0.05 mg_{ox} cm^{-2} disk to ensure that there is no transport limitation in our measurement. The mass and specific activities were found to be the same regardless of the loading.

5.3 OER Activity Descriptor Identification

As discussed in the previous chapter, our approach is based on a concept of molecular orbital bonding. As the \( e_g \)-orbital of surface transition-metal ions \( \sigma \)-bonds with a surface-anion adsorbate\cite{145, 146}, its occupancy can greatly influence the binding of oxygen-related intermediate species on B sites and thus the OER activity. We selected the perovskite structure, \( \text{A}_{1-x}\text{A'}_x\text{B}_y\text{B'}_{1-y}\text{O}_3 \), where \( \text{A} \) or \( \text{A'} \) is a rare-earth or alkaline-earth metal, and \( \text{B} \) or \( \text{B'} \) is a transition-metal as model system to verify this hypothesis. Representative OER currents of oxides collected in this study are shown in Figure 5.4, which were obtained by using a methodology based on thin-film rotating-disk electrodes with well-defined oxygen transport\cite{13}. The background contributions for OER from a carbon additive (acetylene black, AB) and Nafion\textsuperscript{®} in the oxide films and glassy carbon electrode (GCE) are negligible below \(~1.65 \text{ V vs. Reversible Hydrogen Electrode (RHE)}\), as shown in Figure 1a. To separate the surface area effect from the intrinsic catalytic activity, we analyzed the surface-area-normalized kinetic current density (referred to as specific activity, \( i_s \)) as a function of voltage vs. RHE to assess the intrinsic OER activities of the perovskite oxides. Our measurements consistently yield a comparable or higher specific OER activity of oxides than those found in previous reports\cite{35, 147-150} (Table 5.2).
This can be attributed to a higher catalyst utilization in thin-films (<10 cm$^2_{\text{ov}}$/cm$^2_{\text{disk}}$) on GCE 13, 96 than traditional porous electrodes having a very high internal surface area (~10$^4$ cm$^2_{\text{ov}}$/cm$^2_{\text{disk}}$) used in earlier work, thus yielding more accurate determination of the specific activity of powder oxide catalysts.

Figure 5.4. Example OER currents of La$_{1-x}$Ca$_x$CoO$_3$ and LaCoO$_3$ thin-films on GCE in O$_2$-saturated 0.1 M KOH at 10 mV s$^{-1}$ scan rate at 1600 r.p.m, which were capacitance-corrected by taking an average of the positive and negative scans. The contributions from AB and binder (Nafion®) and GCE are shown for comparison.
<table>
<thead>
<tr>
<th>Compounds (reference)</th>
<th>Electrode (i) (mA cm(^{-2}) disk)</th>
<th>Loading (mg cm(^{-2}) disk)</th>
<th>Mass (i) (A g(^{-1}))</th>
<th>Specific (i) (μA cm(^{-2}) ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNiO(_3) (Bockris &amp; Otagawa(^{82}))</td>
<td>~20-2,000 (extrapolated)</td>
<td>n.a.</td>
<td>n.a.</td>
<td>30-360 (extrapolated)</td>
</tr>
<tr>
<td>La(_{1-x})Sr(_x)CoO(_3) (Bockris &amp; Otagawa(^{82}))</td>
<td>~2-40</td>
<td>n.a</td>
<td>n.a</td>
<td>~13-50</td>
</tr>
<tr>
<td>La(_{1-x})Sr(_x)FeO(_3) (Bockris &amp; Otagawa(^{82}))</td>
<td>~2-10</td>
<td>n.a</td>
<td>n.a</td>
<td>3-30</td>
</tr>
<tr>
<td>La(_{1-x})Sr(_x)MnO(_3) (Bockris &amp; Otagawa(^{82}))</td>
<td>~0.1-1</td>
<td>n.a</td>
<td>n.a</td>
<td>0.2-1</td>
</tr>
<tr>
<td>La(_{1-x})Sr(_x)CoO(_3) (Matsumoto et al.(^{148}))</td>
<td>~3-10</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a.</td>
</tr>
<tr>
<td>La(_{1-x})Sr(_x)FeO(_3) (Wattiaux et al.(^{150}))</td>
<td>~0.1-2.5</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a.</td>
</tr>
<tr>
<td>La(_{1-x})Sr(_x)MnO(_3) (Matsumoto &amp; Sato(^{151}))</td>
<td>~0.2-0.6</td>
<td>n.a</td>
<td>n.a</td>
<td>n.a.</td>
</tr>
<tr>
<td>LaNiO(_3) (this work)</td>
<td>~3.5</td>
<td>0.25</td>
<td>~14</td>
<td>~370</td>
</tr>
<tr>
<td>La(_{1-x})Ca(_x)CoO(_3) (this work)</td>
<td>~0.5-3</td>
<td>0.25</td>
<td>~2-15</td>
<td>~250-800</td>
</tr>
<tr>
<td>La(_{1-x})Ca(_x)FeO(_3) (this work)</td>
<td>~0.2-4</td>
<td>0.25</td>
<td>~0.8-16</td>
<td>~90-1,500</td>
</tr>
<tr>
<td>La(_{1-x})Ca(_x)MnO(_3) (this work)</td>
<td>~0.03-0.4</td>
<td>0.25</td>
<td>~0.12-1.6</td>
<td>~20-100</td>
</tr>
</tbody>
</table>

**Table 5.2.** Benchmark OER activities of various state-of-the-art perovskite oxide catalysts. All the OER activities were ohmic-corrected and normalized to the actual surface area at 0.4 V overpotential in basic electrolyte (>13 pH).
Our result shows that the specific OER activities of the perovskite oxides exhibit a volcano shape as a function of the $e_g$-filling of surface B cations (Figure 5.5), where the activities are compared in terms of the overpotential required to provide a specific current of 50 $\mu$A/cm$^2_{\text{ox}}$. In this analysis, the $e_g$ filling of B ions was estimated from a combination of literature data, thermogravimetry and X-ray adsorption results$^{152}$; partial substitution on the A or B sites resulting in oxygen vacancy or B-ion valency changes were taken into consideration. The assignment of the $e_g$-orbital occupancy for oxides with two different B ions such as LaMn$_{0.5}$Cu$_{0.5}$O$_3$ was based on the more active surface transition-metal cation under an assumption that the less active cation contributes negligibly. Using a Tafel slope of ca. 60 mV/decade, the $e_g$ occupancy correlates with the specific OER activities of oxides across four orders of magnitude, over a voltage span of 0.3 V, an observation that allows identification of $e_g$-filling of surface transition-metal ions as a universal activity descriptor for these oxides. It should be noted that the $e_g$-filling descriptor proposed in this study is fundamentally different from the number of 3d-electrons (both $e_g$ and $t_{2g}$ electrons) of bulk B cation proposed by Otagawa and Bockris$^{35}$ or the conduction band described by Matsumoto$^{148}$. The filling of the surface transition-metal antibonding states of $e_g$-symmetry parentage proposed by us is more appropriate for catalysis since the $\alpha$-bonding $e_g$ orbital has a stronger overlap with the oxygen-related adsorbate than the $\pi$-bonding $t_{2g}$ orbital and thus can more directly promote electron transfer between surface cation and adsorbed reaction intermediates. Moreover, lowering of the site symmetry at the surface can induce orbital localization and modify the surface electronic state to differ from that of the bulk$^{112}$, and the usage of the surface $e_g$ filling as opposed to the bulk value is crucial to prescribe accurately the catalytic trend for ORR on oxides$^{51}$. 
1.4 LaNiO$_3$, La$_2$CoO$_4$, La$_2$O$_9$Ca$_{0.4}$Co$_{0.6}$O$_3$

1.5 LaMnO$_3$, LaMn$_{0.5}$Ni$_{0.5}$O$_3$

1.6 LaMn$_{0.5}$Cu$_{0.5}$O$_5$; La-SCaxFeO$_3$

1.7 LaCrOs

Figure 5.5. The relation between the OER catalytic activity, defined by the overpotentials at 50 $\mu$A cm$^{-2}$ of OER current, and the occupancy of the $e_g$-symmetry electron of surface B transition metal. Data symbols vary with type of B ions (Cr, red; Mn, orange; Fe, beige; Co, green; Ni, blue; mixed compounds, purple), where $x = 0$, 0.25, and 0.5 for Fe. Error bars represent standard deviations of at least three independent measurements. The dash volcano lines are shown for guidance only.

5.4 Proposed OER mechanism

We explain the OER activity trend in Figure 5.5 as follows. Considering the *ab initio* finding of Rossmeisl *et al.*$^{135}$, whose work suggests a universal dependence of the OER activity on the oxygen binding strength, we propose that the $e_g$ filling of surface transition-metal cations can greatly influence the binding of OER intermediates to the oxide surface and thus the OER activity. For the right branch of the volcano, the rate-determining step (RDS) is the formation of the O-O bond in OOH adsorbate on B ions ($B^{(m+1)+}$-$O^{2-}$ + OH$^-$ $\rightarrow$ $B^{(m)+}$-OOH$^-$ + e$^-$) while for the left branch of the volcano, the deprotonation of the oxy-hydroxide group to form peroxide ions ($B^{(m+1)+}$-OOH$^-$ + OH$^-$ $\rightarrow$ $B^{(m+1)+}$-O$_2^{2-}$ + H$_2$O + e$^-$) is rate-limiting (Scheme 5.1)$^{135}$. Having $e_g$ close to unity can allow the oxide catalyst to facilitate these RDSs efficiently and thus lead to the highest OER activity. Our molecular orbital model is further supported by the observation that
the OER activity can be enhanced with increasing covalent mixing between B and O atoms of oxides at a constant $e_g$ filling (Figure 5.6). Greater B-O covalency, where the active redox couple of B ions is becoming pinned at the top of the O-2p level, promotes the charge transfer between surface cations and adsorbates such as $O_2^{2-}$ and $O^{2-}$ in the RDSs of OER, which can result in higher OER activity.

![Graph showing the role of B-O covalency on the OER activity of perovskite oxides.](image)

**Figure 5.6.** The role of B-O covalency on the OER activity of perovskite oxides. The potentials at 50 $\mu$A/cm$^2$ as a function of the B-O covalency, which is estimated by the normalized soft X-ray absorbance at $e_g$ filling = 1. Error bars represent standard deviations of at least 3 measurements. The B-O covalency data was from chapter 2.
Scheme 5.1. Proposed OER mechanism on perovskite transition-metal oxide catalysts. Both (top) the OER and (bottom) the ORR proceeds via 4 electron transfer steps. In the OER case, the RDS are the O-O bond formation (2 in OER) and the proton extraction of the oxy-hydroxide group (3 in OER). For the ORR, the RDS are either the surface hydroxide displacement (4 in OER) or the surface hydroxide regeneration (1 in OER).
5.5 Application of the Activity Descriptor

The OER design principle shown in Figure 5.5 was applied to obtain a highly active OER catalyst, BSCF, which was best known for its high performance as cathode in solid oxide fuel cells\textsuperscript{153} and oxygen permeation membranes. Because the surface Co cations of BSCF are in the intermediate spin state\textsuperscript{142,143}, the electronic configuration of Co cation (estimated oxidation state of \(~2.8\), see Section 5.2, Experimental Procedure) in BSCF can be assigned as $t_{2g}^5e_g^{-12}$. We found that the BSCF had the highest OER activity among all oxides studied as predicted by the $e_g$ activity descriptor (Figure 5.5). To ensure that the observed oxidation current is from oxygen evolution, we applied a rotating-ring-disk electrode measurement to detect O$_2$ gas generated from the catalyst by electrochemically reducing the generated gas at the Pt ring electrode that was held at the ORR potential of 0.4 V vs. RHE (Figure 5.7). The reduction current detected on the ring electrode suggests that the oxidation current from BSCF can be accounted for fully by the OER. In comparison to the state-of-the-art catalyst, the intrinsic OER activity of BSCF is two orders of magnitude higher than that of IrO$_2$ nanoparticles ($d_{\text{avg}} \sim 6$ nm) in Figure 5.8. The exceptional OER activity of BSCF was further confirmed by galvanostatic measurements, where no degradation in the OER activity of BSCF was observed in this study (Figure 5.9). Once the sizes of BSCF particles were reduced to sub-micron range via ball-milling, the mass activity of ball-milled BSCF (BM-BSCF) was found to compare favorably with IrO$_2$, and the overpotential of BM-BSCF was shown to be nearly identical to that of IrO$_2$ at a mass activity of 10 A g$^{-1}_{\text{ox}}$ (Figure 5.9). 

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Figure 5.7. Evidence of O$_2$ generated from BSCF using rotating ring disk electrode measurements. The O$_2$ gas generated from BSCF on GCE disk (OER current given as $i_{\text{disk}}$) is reduced at the Pt ring at a constant potential of 0.4 V vs. RHE.

Figure 5.8. The OER specific activity of BSCF (square) and IrO$_2$ (circle) as extracted from the polarization. Error bars represent standard deviations of at least three independent measurements.
Figure 5.9. Galvanostatic (constant current) measurement of mass activities of BSCF, ball-milled BSCF (BM-BSCF), and IrO$_2$.

5.6 Chapter 5 Conclusion

This work reports a model for the OER electrocatalytic activity of oxides in alkaline solution using the catalytic trend observed in the case of the ORR. The principle was used to discover an oxide OER catalyst that is competitive against state-of-the-art precious-metal containing electrocatalyst. Considering the OER volcano trend of oxides (peak at $e_g \sim 1.2$) with that of ORR (peak at $e_g \sim 0.8$) reported previously $^{51}$, and the fact that the ORR activity of BSCF is not among the highest$^{52}$, we arrive at an important implication that no simple oxide can be optimal for both the ORR and the OER. Our work suggests the importance of developing a transition-metal oxide having a surface-cation $e_g$ occupancy close to unity and high B-O covalence as a promising strategy to create bi-functional oxide catalysts and electrodes for the development of efficient, rechargeable metal-air batteries, regenerative fuel cells, and other rechargeable air-based energy storage devices.
Chapter 6 – Influence of Cation Species

6.1 Introduction

Understanding electrochemical splitting and forming of oxygen bond via the ORR and the OER is central to many sustainable energy storage and conversion technologies. Occurring at the solid-liquid interface, both ORR and OER are multi-electron transfer reactions that have been intensively studied as model prototypical multi-intermediate electrochemical reactions. In the past decade, fundamental works by Rossmeisl and Norskov have applied ab initio calculations, in combination with Bronsted-Evans-Polanyi Relations to describe the ORR and the OER mechanisms. Using this strategy, they have developed the activity descriptor approach, which has led to discoveries of novel catalytic surfaces for the ORR. This Rossmeisl-Norskov model, however, assumes that the ions in the electrolyte do not specifically influence the electrocatalytic behavior of the ORR/OER surfaces. In this chapter, we seek to understand the effect of Li+ ion on the ORR/OER electrocatalysis, especially on transition metal oxide surfaces, which we have previously reported as promising candidates for alkaline ORR and OER electrocatalysts. As the presence of the cationic species such as Li+ is unavoidable in aqueous Li-air and other metal-air batteries, understanding the role of the cation on the ORR/OER electrokinetics on transition metal oxides is critical to developing a more efficient, cost-effective aqueous metal-air devices.

The model for ion-surface interaction originates from the early works on the ORR electrokinetics of Pt(111) in strongly absorbing anion-containing electrolytes. In H2SO4, for example, the sulfate anion was found to interact strongly with Pt(111) surface, consequently poisoning and rendering the surface ineffective for catalyzing the ORR. This effect has been observed for phosphate anion, which also interacts with Pt(111)
surface in a similar fashion\textsuperscript{161}. Consequently, the ORR of Pt(111) in weakly absorbing electrolyte such as HClO\textsubscript{4} displays faster kinetics than strongly absorbing H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{3}PO\textsubscript{4} due to less surface poisoning and thus more available active site\textsuperscript{162}. The perspective on the cation-surface interaction, on the other hand, has received substantially less attention. Due to the deep energetic levels of the cationic species, the cation's role in electrocatalysis is believed to serve primarily as ions to neutralize surface in the double layer space charge region. However, recent report has shown that the effect of these interface cations on electrocatalysis are non-negligible and can significantly influence the catalytic rate by more than an order of magnitude for Pt surfaces\textsuperscript{157}. The explanation thus far concluded the stronger non-covalent interaction between surface Pt oxide and smaller Li\textsuperscript{+} than bigger K\textsuperscript{+} to be the main factor behind the activity difference. Strmcnik and co-workers thereby proposed that smaller Li\textsuperscript{+} can interact more strongly with the Pt oxide and consequently has a longer resident time at the surface than larger K\textsuperscript{+}. While there, Li\textsuperscript{+} also has a more "rigid" hydration layer than larger K\textsuperscript{+} and thus, in combination with its long surface resident time, can interfere with the availability of the nearby active site. Recently, the cation effect has shown to prevail on Au surfaces, where the presence of the oxide species on Au was proposed to underpin the observed cation influence on the ORR\textsuperscript{158,163}.

While previous studies of cation influences on Pt and Au are the first demonstrations of the role of the cation on the ORR electrokinetics, the proposed mechanism of cation-oxide influences is convoluted by the presence of both metallic and oxide surfaces at the ORR turnover condition. Consequently the mechanistic investigation of cation's influence on Pt and Au can be challenging to interpret, as the possibility of the selective cation interaction with either phase cannot be excluded. In this aspect, transition metal oxide catalyst offers an all-inclusive oxide-phase surface to build the understanding of the cation effect from. To further demonstrate the nature of the cation influence and its interaction with the oxide species, we examine the mechanism of the cation influence on the ORR kinetics of LaMnO\textsubscript{3+\delta} and the OER kinetics of rutile IrO\textsubscript{2} (r-IrO\textsubscript{2}) and and Ba\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3-\delta} (BSCF) catalysts. These compounds were selected as they were recently reported to be among the most active ORR/OER electrocatalytic compounds among the class of transition metal oxide materials; LaMnO\textsubscript{3+\delta} was found to be one of the
most active ORR compounds\textsuperscript{51,164,165}, while r-IrO\textsubscript{2} has long enjoyed its long reputation as the OER benchmark catalyst\textsuperscript{135,140}. BSCF was recently reported to have an intrinsic OER activity even higher than r-IrO\textsubscript{2}\textsuperscript{52}. In this work, we examine the influence of the cation on these compounds' kinetics behaviors, from which the mechanism for cation effect will be postulated.

6.2 Experimental Procedure

\textit{Transition metal oxide synthesis}. The Perovskites, LaMnO\textsubscript{3}+\textsubscript{δ} and BSCF, and the rutile r-IrO\textsubscript{2} were synthesized as reported elsewhere \textsuperscript{52,159,166}. In the LaMnO\textsubscript{3}+\textsubscript{δ} synthesis, rare earth nitrate and manganese nitrate (99.98\% Alfa Aesar) at the respective stoichiometric ratio were mixed in Milli-Q water (18 MΩ cm) at metal concentrations on the order of 0.1 M. This solution was then titrated with 1.2 M tetramethylammonium hydroxide (Alfa Aesar) until a solid precipitate was formed. The precipitate was filtered, collected, and dried at 200 °C for 12 hours, and then subjected to heat-treatment at 1000 °C under argon (Airgas 99.999\%) for 12 hours. The oxide was subsequently heat-treated at 800 °C under dry air (Airgas) to obtain oxygen over-stoichiometric phase. In the BSCF synthesis, alkaline earth and transition-metal nitrates (99.998+\% Sigma-Aldrich) were prepared at 0.2 M concentration in Milli-Q water, to which glycine (>99\% Sigma-Aldrich) was added at 0.1 M concentration. The mixture was heated until vigorously evaporating, at which point, sparks are emitted as a result of combustion; it was then calcined at 1100°C under air atmosphere for 24 hours. In the r-IrO\textsubscript{2} synthesis, a solution of 0.6 mmol of IrCl\textsubscript{4}·xH\textsubscript{2}O, 10 mL of tetralin and 10 mL of oleylamine was prepared at room temperature (20 °C) in a four-neck flask. The mixture was heated to 60 °C under Ar atmosphere (Airgas 99.999\%) and kept at that temperature for 20 min to dissolve the precursor homogeneously into the solution with continuous stirring. 2.4 mmol of TBABH in 2 mL of chloroform was quickly injected into the above solution and left for 20 min. The reaction mixture was further heated up to 200 °C and kept at that temperature for 19 hrs. The solution was cooled down, and Ir NPs were precipitated by ethanol addition and collected by centrifugation. The product was re-dispersed in hexane and then annealed in 500 °C for 20 hrs in pure O\textsubscript{2} (Airgas 99.999\%). X-ray Diffraction revealed all the studied oxide materials to be single-phase.
Oxide electrode preparation. The procedure for preparing oxide ORR/OER electrode is described in details in previous chapter. Briefly, the perovskites were mixed with acetylene black carbon (AB) at a 5/1 mass ratio of oxide/carbon. Catalyst inks were prepared by horn sonication (Bransonic 3510, Branson) of the oxide, AB, and an appropriate amount of the Na⁺-exchanged Nafion® solution with tetrahydrofuran (THF, 99.9+ % Sigma-Aldrich), yielding inks with final concentrations of 5 mg oxide ml⁻¹, 1 mg AB ml⁻¹, and 1 mg Nafion ml⁻¹. Next, 10 μl of catalyst ink were drop-cast onto a glassy carbon (GC) electrode (0.196 cm² area, Pine, USA) polished to a mirror finish with 0.05 mm alumina slurry (Buehler). The perovskite electrode had a final composition of 250 μg oxide cm⁻² disk, 50 μg AB cm⁻² disk, and 50 μg Nafion cm⁻² disk. For the r-IrO₂, the electrode was prepared from an ink containing r-IrO₂ solubilized in 70% 2-propanol (Sigma, 99.9+% Sigma-Aldrich). The rutile electrode had a final composition of 50 μg oxide cm⁻² disk.

Platinum electrode preparation. Glassy carbon disk electrodes coated with a thin film of high surface area carbon-supported platinum nanoparticle (“Pt/C”) catalyst (46 %wt. Pt, Tanaka Kinzoku, Japan) were prepared as described elsewhere. Briefly, 15 μl of an aqueous Pt/C ink of a composition of 0.3 mg catalyst ml⁻¹ and 0.08 mg Nafion ml⁻¹ was drop-cast onto a GC disk electrode and allowed to dry overnight, yielding a Pt loading of 54 μg Pt cm⁻² disk, and 3 μg Nafion cm⁻² disk. The Pt/C surface area was estimated from the electrochemical H₂ underpotential deposition and found to be consistent with the electrochemical surface area reported elsewhere.

Electrochemical characterization. All electrochemical measurements were conducted in a three-electrode glass cell (Pine Instrument) and using a rotator (Pine) to which working electrode in a thin-film rotating disk electrode (RDE) configuration was attached; the potential was controlled using a VoltaLab PST050 potentiostat. The 0.1 M concentration of alkaline electrolyte was prepared from Milli-Q water (18 MW cm) and either LiOH, NaOH, or KOH pellets (99.99% purity, Sigma-Aldrich). All measurements were conducted at 10 mV s⁻¹ in either N₂ or O₂ (ultra-high purity grade, Airgas) at room temperature. A saturated calomel electrode (Pine Instrument) was used as a reference. Error bars represent standard deviations from at least three independent repeat
measurements. The mass transport correction was performed for the ORR using the well-known RDE correction (Levich equation). The OER activity was analyzed without mass-transport correction.

6.3 The Influence of Li⁺ Cation on the ORR

A typical ORR result of Pt/C RDE in 0.1 M KOH, NaOH, and LiOH at various rotation rates is shown in Figure 6.1. The electrocatalytic activity of Pt/C was highest in K⁺ cation containing electrolyte, followed by Na⁺, and Li⁺, respectively, in agreement with the previous work. Interestingly, the relative difference between the specific activities in each electrolyte we observed (~1 order of magnitude) was not as high as the difference reported by Strmcnik et al (~2 order of magnitude). We attribute this observation to the size difference between the two Pt/C studied with our smaller 2 nm (vs. 5 nm) size having less sensitivity to the cation effect, which should be expected as different Pt planes have different sensitivities to the cation and that smaller particle forms more under-coordinated facets. We note that the presence of Nafion⁻⁻ ionomic binder in our samples also influenced the catalytic difference as a result of an additional interaction of the sulfone group with the cation on the platinum surface (Figure 6.2). The ionomer influence, however, is at a smaller factor and is not enough explain the difference between our result and the literature value.

To measure the cation influence on the transition metal oxide surfaces, we utilize the thin-film RDE technique to quantify the ORR activity of model transition metal oxide surface. Figure 6.3 show exemplary ORR currents of LaMnO₃₋₅ in 0.1 M LiOH, 0.1 M NaOH, 0.1 M KOH. These ORR currents have been background-corrected and are shown at a scan rate of 10 mV/s as examples. The onset for the ORR activity in the K⁺ electrolyte was found near 1 V vs. RHE with lower potentials found for smaller cations such as Na⁺ and Li⁺. The trend that the ORR activity decreases with decreasing cation size (Li⁺ < Na⁺ < K⁺) is similar to the case found for the ORR kinetic activities of Pt/C in the same set of electrolytes (Figure 6.1) and is also similar to the earlier report of the ORR trend for Pt(111), poly-Pt, and Pt/C. The fact that both perovskite and Pt/C carry the same cation trend is peculiar when considering that the non-covalent cation effect
mechanism proposed by Strmcnik et al. is based on having the hydration layer of the cation that is non-covalently bound on the surface oxide species blocking nearby open, active metal sites (Scheme 6.1). This mechanism presents a great deal of difficult to understand the ORR trend in the context of the perovskite oxide catalyst, where the surface is uniformly terminated with either a hydroxide or an oxide species as active sites\textsuperscript{35, 82, 170}, and therefore does not have any open “metal” site to be blocked. Furthermore, when considering the fact that the earlier cation mechanism predicts a strong non-covalent cation “poisoning” of the surface oxide/hydroxide species, the fact that the ORR current on an oxide-terminated surface can be observed in strongly absorbing cation electrolyte such as LiOH forces us to re-consider how the cation influences the ORR electrokinetics on the oxide surfaces.

![Figure 6.1. The ORR activity of thin-film Pt/C RDE in the positive potential-going scan direction at 10 mV/s in various alkaline electrolytes at 900 r.p.m.](image)

\textbf{Figure 6.1.} The ORR activity of thin-film Pt/C RDE in the positive potential-going scan direction at 10 mV/s in various alkaline electrolytes at 900 r.p.m.
Figure 6.2. The influence of Nafion® on the ORR specific activity of thin-film Pt/C RDE in KOH and LiOH.

6.3 The Influence of Li⁺ Cation on the OER

To better understand how the cation influences the surface oxide species during the turnover condition for oxygen electrocatalysis, we conduct the OER measurement of two benchmark OER oxide catalysts in the same set of alkaline electrolytes as the ORR. Figure 4 shows typical findings for the OER kinetic currents of r-IrO₂ and BSCF in the same set of electrolytes (i.e. 0.1 M LiOH, 0.1 M NaOH, and 0.1 M KOH). Both the r-IrO₂ and BSCF have onset potentials of the OER activities at about 1.4 V vs. RHE, with higher onset potentials with smaller cations. Interestingly, the same cation trend, where the OER activity decreases with decreasing cation size (Li⁺ < Na⁺ < K⁺) for both rutile and perovskite surfaces is observed, which indicates that the trends for the cation on oxygen electrocatalysis are the same for both r-IrO₂ and BSCF surfaces. Because the rate-limiting species on the transition metal oxide surfaces during the OER turnover are likely a hydroxo/oxyhydroxo/oxo species, the fact that both surfaces have the same trend in the cation effect is not surprising. However, when considering that the non-covalent cation effect should poison all of the oxide surfaces and block them from being active, it is interesting to observe that, like in the case of the ORR, the OER current in LiOH can be observed at all (in fact, very close to that measured in KOH).
Figure 6.3. The ORR activity of thin-film LaMnO$_{3+δ}$ (supported on acetylene black and neutralized Nafion®) RDE in the negative potential-going scan direction at 10 mV/s in various alkaline electrolytes at 1600 r.p.m.
Scheme 6.1. Graphic illustration of Strmcnik and co-workers’ model for cation’s non-covalent interaction, at which the cation species interacts with OH_ads group to interfere the open active Pt site by “blocking” mechanism^{157,172}.

6.4 Proposed Cation Mechanism

To explain the observed cation effect on the transition metal oxide surfaces, we take hints from the observation that the difference between the ORR kinetic currents is about an order of magnitude, whereas the difference between the OER kinetic currents is significantly less. This observation reveals the cation effect to be potential-dependent; there is less cation on the surface at the OER potential than the ORR potential. Combining this with the fact that the cation did not effectively “poison” the whole transition metal oxide surfaces completely (as there is still measurable ORR/OER activity), we propose that the cation influences the ORR/OER by ways of modifying the hydration of the reaction intermediates (Scheme 6.2). As we have previously proposed the competition between $\text{O}_2^{2-}/\text{OH}^-$ species, and $\text{O}^{2-}/\text{OOH}^-$ as rate-limiting for the ORR and the OER, these negatively charged species draw in cation during the ORR/OER turnover at the alkaline pH. The potential-dependent factor supports this fact as it has been observed previously that the absorbing anion on the surface can be de-protonated at higher potential (equivalent to a cation removal)\textsuperscript{173}. This is likely a result of the charge transfer between surface and the adsorbing species, which helps reducing the net charge on the adsorbate. Our proposed mechanism is similar to that proposed earlier by Strmcnik et al., with one exception: the cation does not virtually “block” the ORR/OER
active site, but rather modify their hydration energetics and effectively the reaction kinetics. We point out here that we cannot differentiate whether the perturbation of the ORR/OER intermediates from the cation is a result of the cation-direct interaction (Scheme 6.2 Top) or cation-hydration-mediated interaction (Scheme 6.2 Bottom). Further spectroscopic studies using for example, sum frequency generation would be essential to evaluate this proposed mechanism.

**Figure 6.4.** The OER specific activity of thin-film rutile IrO$_2$ and BSCF (the latter is supported on acetylene black and neutralized Nafion®) RDEs.
**Scheme 6.2**: Proposed cation effect on the ORR/OER on transition metal oxide surfaces. (Top) cation or (Bottom) its hydration interacts with the hydroxo/superoxo/peroxo species and its energies during the turnover condition. The kinetics is affected by the intermediate energy modifications. The B label represents active transition metal atom, which we previously proposed as the active site for oxygen electrocatalysis on transition metal oxide surfaces.

### 6.5 Chapter 6 Conclusion

The influences of cationic species on oxygen electrocatalytic activities on oxide surfaces are studied in this chapter. We found that both the ORR and the OER activities increases with increasing cation size ($K^+ > Na^+ > Li^+$), following the Hofmeister series, with the effect of the cation more pronounced in the ORR than the OER. We rationalize this observation by proposing that the cation serves to modify the solvation energetics of reaction intermediate, which in turns, affect the catalytic activities. At higher potential (OER turnover condition), the electrode draws more negative charge away from the
adsorbate, which effectively reduces the need for hydration and hence less pronounced effect in the OER activity. Our proposed mechanism is congruent with the proposed competition between $O_2^{2-}/OH^-$ species, and $O^2-/OOH^-$ as rate-limiting for the ORR and the OER on transition metal oxides. The complexity of the solid-liquid layer however will need further experimentation to resolve. Our finding demonstrates the importance and the opportunity to tailor the electrified interface for catalysis and energy conversion applications.
Chapter 7 – Summary and Outlook

7.1 Thesis Summary

We present a model to understand the catalytic trend of transition metal oxide catalysts for oxygen electrochemical reactions. To develop the model, we conducted a systematic examination of the electrocatalytic activity of model oxide compounds using thin-film oxide rotating disk electrode methodology, which de-convolutes the oxygen electro-kinetics from the transport and the ohmic losses, and thereby allow quantitative comparison between different oxide catalysts. We found that the oxygen electrocatalytic activities (both ORR and OER) for perovskite transition metal oxide catalysts correlate to the $e^*$ orbital (“eg”) occupation. We propose that this correlation is a consequence of the importance of the eg-symmetry parentage electron on the oxygen binding strength. From our finding, we hypothesize that the rate-limiting step of the oxygen electrochemical reactions, is the competition between $O_2$/$OH^-$ displacement and OH$^-$ regeneration for the ORR, and for the OER, is the competition between the formation of the O-O bond and the deprotonation of the oxy-hydroxide species. This hypothesis is in qualitative agreement with the model previously proposed for precious metal and precious metal oxide surfaces – that both the ORR and the OER can be described by the same activity descriptor despite following different rate-limiting steps$^{135,136}$. We also demonstrate that transition metal-oxygen covalency carries a significant influence on the oxygen electrocatalytic activity, which can serve as a secondary activity descriptor. To explain this observation, we postulate that transition metal-oxygen covalency promotes charge transferability between transition metal and oxygen, which allows the surface to perform redox on the adsorbed oxygen. We further discuss how covalency evolves in the perovskite oxide using molecular orbital theory, which hints at us to further design next-generation perovskite oxide with stronger extent of transition metal-oxygen covalency. Lastly, we demonstrate the application of our catalytic trend by finding a novel OER catalyst, which has catalytic activity that rivals state-of-the-art, precious-metal-containing catalyst.
7.2 Outlook

This thesis shows that it is possible to develop a descriptor framework to understand oxygen electrocatalysis on non-precious-metal surfaces. Our proposed “e_g” mechanism relies heavily on (1) ex-situ characterization of transition metal oxide catalysts, (2) the ability to distinguish surface state from bulk, and (3) assumption of the octahedral geometry during turnover condition. These are big assumptions. Therefore, the ability to do in situ spectroscopic capabilities to evaluate the mode of surface-oxygen interaction during the turnover condition, from which the role of e_g-symmetry parentage electron can be assessed in a more accurate manner, will substantially improve this work, and also our understanding of the fundamental mechanism of the oxygen electrochemical reactions.

Infrared and Raman Spectroscopy on well-defined single crystal of transition metal oxides in operando may be able to address this need. Raman Spectroscopy, a technique highly sensitive to local symmetry of the vibrational mode, may help reveal, for example, if BSCF undergoes change from cubic (first-order forbidding Raman) to tetragonal during turnover condition, although differentiating surface from bulk contribution is not straightforward. Similarly Infrared Spectroscopy, which probes molecule’s vibrational behavior, may be able to resolve O-O bond during O-O bond formation, where the interaction with surface causes O-O bond to develop a non-zero dipole. Information from these experiments will prove decisive at determining the validity of many electrocatalysis models, including ours.

An interesting question for the proposed e_g model is whether such a correlation would extend to a molecular transition metal complex catalysis system. It has long been known that enzymes are made of transition metal ions coordinated to various ligand chemistries\textsuperscript{174}. In theory, the molecular orbital assumption of the perovskite oxide system should directly translate to these molecular catalysts. However, to our knowledge, such correlation has not been done yet.

The proposed e_g model also opens question about whether such a descriptor can be appropriately applied to design a direct-solar water-splitting system. One approach can be to directly apply BSCF coating on buried p-n junction, where photo-generated carrier
within the buried junction develops a photovoltage to assist with water splitting (Figure 7.1). Another approach would be to integrate the \( e_g \) catalytic functionality directly in an oxide semiconductor electrode (Figure 7.2). This approach, albeit more simple, has many open questions. For example, what should the role of \( e_g \) be? Two possibilities are the use of \( e_g \) band as a Fermi level pinner, where upon illumination of the bulk oxide semiconductor, the photo-generated hole can be swept to the surface \( e_g \) state (Figure 7.2, Top), and the use of \( e_g \) band as a photo-absorbing band itself (Figure 7.2, Bottom). Future work in this area will plant the seed for the next-generation design of a device that can directly capture solar energy and store it in term of chemical fuels.

**Figure 7.1.** Schematic drawing of an integrated catalyst-p-n junction for photoelectrochemical water splitting.
Figure 6.2. Schematic drawings of a proposed catalytically active oxide semiconductor-liquid junction for photoelectrochemical water splitting. The catalytically active $e_g$ state can either be integrated as a Fermi-level pinner at the surface (Top), or as a valence band, where hole can be generated upon excitation (Bottom).
Reference


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76. Bursell, M.; Pirjamali, M.; Kiros, Y., La$_{0.6}$Ca$_{0.4}$CoO$_3$, La$_{0.1}$Ca$_{0.9}$MnO$_3$ and LaNiO$_3$ as bifunctional oxygen electrodes. *Electrochim. Acta* **2002**, *47*, 1651-1660.


89. Breger, J.; Meng, Y. S.; Hinuma, Y.; Kumar, S.; Kang, K.; Shao-Horn, Y.; Ceder, G.; Grey, C. P., Effect of high voltage on the structure and electrochemistry of LiNi_{0.5}Mn_{0.5}O_2: A joint experimental and theoretical study. Chem. Mat. 2006, 18, 4768-4781.


116. Rormark, L.; Wiik, K.; Stolen, S.; Grande, T., Oxygen stoichiometry and structural properties of La$_{1-x}$A$_x$MnO$_{3+\delta}$ (A = Ca or Sr and $0 \leq x \leq 1$). *J. Mater. Chem.* **2002**, *12*, 1058-1067.


119. Li, J., Investigation of orthorhombic perovskite La$_{1-x}$Ca$_x$FeO$_{3-y}$ ($0 \leq x \leq 0.5$). *Phys. Scr.* **1992**, *45*, 62-64.


121. Mastin, J.; Einarsrud, M. A.; Grande, T., Crystal structure and thermal properties of La$_{1-x}$Ca$_x$CoO$_{3-\delta}$ ($0 \leq x \leq 0.4$). *Chem. Mat.* **2006**, *18*, 1680-1687.


123. Samoilov, A. V.; Beach, G.; Fu, C. C.; Yeh, N. C.; Vasquez, R. P., Giant spontaneous Hall effect and magnetoresistance in La$_{1-x}$Ca$_x$CoO$_3$ ($0.1 \leq x \leq 0.5$). *J. Appl. Phys.* **1998**, *83*, 6998-7000.

124. Samoilov, A. V.; Beach, G.; Fu, C. C.; Yeh, N. C.; Vasquez, R. P., Magnetic percolation and giant spontaneous Hall effect in La$_{1-x}$Ca$_x$CoO$_3$ ($0.2 \leq x \leq 0.5$). *Phys. Rev. B* **1998**, *57*, 14032-14035.


141. Jung, J.; Misture, S. T.; Edwards, D. D., Oxygen stoichiometry, electrical conductivity, and thermopower measurements of BSCF (Ba$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Fe$_x$O$_{3-δ}$, $0 \leq x \leq 0.8$) in air. *Solid State Ionics* **2010**, *181*, 1287-1293.


143. Harvey, A. S.; Litterst, F. J.; Yang, Z.; Rupp, J. L. M.; Infortuna, A.; Gauckler, L. J., Oxidation states of Co and Fe in Ba$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-δ}$ ($x$, $y=0.2$-0.8) and oxygen desorption in the temperature range 300-1273 K. *Phys. Chem. Chem. Phys.* **2009**, *11*, 3090-3098.


152. Materials and Methods are available as supporting materials on Science online.


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