Electro- and Thermal-Catalysis by Layered, First Series Ruddlesden – Popper Oxides

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Abstract

First series Ruddlesden-Popper oxides (referred herein as R-P-1, with a formula $A_{n+1}B_nO_{3n+1}$ where $n = 1$) have been used in a number of electrochemical and thermochemical reactions. In this review, we examine in detail the effect of the synthesis methods and the composition of the A and B sites on their electrocatalytic/catalytic activity. Effects on important activity parameters, such as surface exchange coefficient (k), oxygen diffusion coefficient (D), hyperstoichiometry (δ), and electronic conductivity are discussed. We find that synthesis plays an important role in their final structure and hyperstoichiometric oxygen content, which significantly impact their activity. In addition, we show that the composition of the A and B sites has an effect on the catalytic/electrocatalytic activity parameters, such as D , k , δ , and electrical conductivity. The use of these oxides for thermal-catalysis is also discussed. We find that while R-P-1 oxides have been widely implemented for high temperature electrocatalysis, their potential for thermal-catalysis has not been fully explored. Limited reports on thermal-catalysis suggest that the redox properties of the B-site transition metal in these oxides, as well as the oxide's ability to accept and release oxygen under reaction conditions play an important role in their catalytic activity. A perspective on catalysis by R-P-1 oxides is provided at the end of the review.

Keywords: Nickelate Oxides; Thermal-Catalysis; Surface Oxygen Exchange Coefficient; Oxygen Diffusion Coefficient; Electronic Conductivity; Oxygen Hyperstoichiometry.

1. Introduction

Metal oxides play an important role in many technologically relevant chemical and electrochemical conversion processes. Mixed ionic and electronic conducting (MIEC) oxides have attracted significant attention especially in electrochemical energy conversion and storage, [1-8] gas sensors [9-11] and oxygen transport membranes [12-17]. Particular attention has been brought to oxides belonging to the Ruddlesden-Popper (R-P) phases, $A_{n+1}B_nO_{3n+1}$ ($n = 1, 2, 3 \dots$), which are characterized by alternating perovskite, $(ABO_3)^-$, and rock-salt $(AO)^+$, layers (Figure 1). In these oxide structures, “A” is an alkali, alkaline earth or a rare earth metal, while “B” is a transition metal. These phases were first studied in 1958 by Ruddlesden and Popper, who discovered the homologous series of titanates, $Sr_{n+1}Ti_nO_{3n+1}$. [18] The discovery of subsequent series of oxides with this structure has revealed their diverse and unique structural, [19-21] transport, [5] and magnetic properties [22-24]. In particular, these materials exhibit high ionic and electronic conductivities, as well as high thermal and mechanical stabilities, which have important implications in a number of catalytic and electrocatalytic processes. [2, 5, 25-29] The R-P phases of the first series ($n = 1$) with the general formula $A_2BO_{4+\delta}$ are among the most studied for high temperature electrocatalytic/catalytic reactions, due to their stability and highly mobile nature of the hyperstoichiometric oxygen (δ) in their structure. [30-34] The hyperstoichiometric oxygen is accommodated by the oxygen interstitial sites in between adjacent rock-salt layers [21, 35-37] and charge compensated by the B-site transition metal, which exists in a mixed valence state [25, 38-40].

A key property of these layered metal oxides that makes them promising for catalytic applications is their ability to effectively catalyze, on their surface, the activation of molecular oxygen and the subsequent exchange of gas-phase oxygen with the oxygen atoms in the lattice; a process known as surface oxygen exchange. [14, 21] Recently, a detailed combined theoretical/experimental investigation of the mechanism that governs the surface oxygen exchange process on $La_2NiO_{4+\delta}$ has been reported. [41] The mechanism (summarized in Figure 2) involves the formation of surface oxygen vacancies through migration of surface oxygen to an interstitial site, and the dissociative adsorption and desorption of gas-phase O_2 . [38, 42, 43] It was shown that an ideal R-P-1 oxide catalyst with fast oxygen exchange properties should exhibit an optimal compromise between the energetics associated with oxygen vacancy formation and dissociative adsorption of gas-phase O_2 .

Figure 1. Stoichiometric crystal structure of A_2BO_4 -type oxides, where A is lanthanum (green atoms) and B is nickel (gray atoms).

Figure 2: The surface oxygen exchange mechanism: (1) A surface oxygen atom in the lattice migrates to a vacant interstitial site in the bulk, leaving behind a surface vacancy. (2) Gas phase molecular oxygen is activated on the surface, healing the surface vacancy and leaving an adsorbed oxygen atom on the adjacent B-site atom. The reverse process involves the formation of the surface vacancy via oxygen desorption to the gas phase (3), followed by surface vacancy healing via an interstitial bulk oxygen atom (4).

Experimentally, the surface exchange coefficient (k) is the kinetic parameter that describes the rates of the surface oxygen exchange (the oxygen flux through the oxide surface). On the other hand, the oxygen diffusion coefficient (D) is used to describe the oxygen transport in the bulk of these oxides and is a measure of the bulk oxygen diffusion rates and ionic conductivity. [21] These parameters are mainly obtained from ^{18}O IEDP (Isotope Exchange Depth Profiling) coupled with SIMS (Secondary Ion Mass Spectrometry) and ECR (Electrical Conductivity Relaxation) experiments. [44] A detailed discussion is beyond the scope of this review, but a basic overview of these techniques is provided here. The IEDP technique consists of annealing the sample (usually a dense ceramic pellet or a single crystal) in an ^{18}O isotopically enriched environment for a given period of time followed by depth profiling (usually using SIMS) to determine the permeation of the isotopic label into the sample. [45] Fitting the experimental data to mathematical models yields the values for D and k . [46] Among other parameters, appropriate sample preparation to obtain dense pellets is critical for the accuracy of the experimental results. ECR involves monitoring the transient change in electrical conductivity of a MIEC sample due to a stimulus of instantaneous change in partial pressure of oxygen ($p(\text{O}_2)$) at a constant temperature. [47] Another method used is isothermal isotope switching [48] where the oxide is loaded in a flow reactor, followed by heating and exposure to isotopically enriched ^{16}O under isothermal conditions. The feed is quickly switched to isotopically enriched ^{18}O at the same flow rate, temperature and pressure, while simultaneously monitoring the rate of formation of the scrambled product $^{18}\text{O}^{16}\text{O}$. [48]

D and k can be tuned by partial or complete substitution of the A (with lanthanide or alkaline earth metals) and/or the B (with transition or main group metals) sites in these oxides, as reviewed in detail below. Due to the size difference between the substituted and the original ions in the lattice, the volume of the interstitial space changes, leading to changes in the migration energetics of the oxygen ions in the La_2O_2 rock salt layers. [49] This

consequently affects the magnitude of D and k . Surface termination [41, 50, 51], electrochemical activation [52], and application of mechanical stress [53] are among other approaches also exploited to tune D and k in these oxides. For example, in the case of using surface termination to tune k , it was shown that the surface termination of $\text{La}_2\text{NiO}_{4+\delta}$ (lanthanum nickelate oxide) plays an important role in the kinetics of the oxygen surface exchange, with (001) NiO surface terminated $\text{La}_2\text{NiO}_{4+\delta}$ electrocatalysts exhibiting the highest rates for oxygen exchange. [41] As such, oxygen exchange rates (k) could be enhanced by synthesizing R-P-1 oxide nanoparticles highly terminated by (001) transition metal oxide surface facets.

The oxygen hyperstoichiometry, δ , is another parameter linked to the catalytic activity of R-P-1 oxides, since it affects D , k and the oxidation state of the B-site transition metal. [39] δ also affects the crystal structure of the oxides, since the interstitial oxygen plays an important role in stabilizing the R-P-1 structure. Experimentally, δ is estimated using thermogravimetric analysis (TGA) [21, 54], coulometric titration [55], iodometric titration [56], and powder neutron diffraction [57, 58] studies. δ is reported to depend on the temperature, $p(\text{O}_2)$, nature of the A and B site [36], as well as substitutions of the A or B site in the oxide [30, 59-61].

One of the most exploited catalytic applications of R-P-1 oxides is high temperature electrocatalysis, due to their fast oxygen transport rates and mixed ionic and electronic conductivity at elevated temperatures. [2] Significant attention has been given to investigating their use as cathode electrocatalysts in solid oxide fuel cells (SOFC), which are high temperature electrochemical devices that generate electrical energy from the electro-oxidation of fuels (i.e., H_2 , CO, hydrocarbons). [30, 62, 63] The cathode of the SOFC facilitates the oxygen reduction reaction (ORR) and is traditionally comprised of a perovskite-type electrocatalyst. Characteristics of an optimal cathode electrocatalyst for SOFCs include, high oxygen ion conductivity, high electronic conductivity ($\sim 100 \text{ S cm}^{-1}$ at operating temperatures) [56], comparable thermal expansion coefficient (TEC) to the other cell components, as well as long-term stability under operating temperatures. R-P-1 oxides show promise as SOFC cathode electrocatalysts, since many of them exhibit high oxygen exchange/reduction and diffusion rates, good electronic conductivity (for e.g. $60\text{-}80 \text{ S cm}^{-1}$ at 700°C for $\text{La}_2\text{NiO}_{4+\delta}$ [64]) and TECs comparable to commonly used SOFC electrolytes, such as yttria-stabilized zirconia (YSZ) or gadolina-doped ceria (GDC) [65].

R-P-1 oxides have also been successfully used to catalyze a number of thermochemical reactions, such as hydrocarbon oxidation [1, 66-68] and NO reduction [69-71]. The redox properties of the B-site transition metal in these oxides, as well as the oxide's ability to accept and release oxygen under reaction conditions, play a role in their catalytic activity for these processes. While promising, the limited literature reports indicate that their potential for thermo-catalytic processes has been far less explored when compared to high temperature electrocatalysis.

In the next few sections, a comprehensive review of the methods used to synthesize R-P-1 oxides and the effect of the A and B site compositions on the catalytic/electrocatalytic properties of these materials is provided. We find inconsistencies in the literature reported values for the critical activity parameters, k and D , for a given R-P-1 oxide. As will be alluded to several times in the text, these discrepancies mainly stem from the sample preparation techniques that do not allow adequate control over their structure, lack of appropriate surface characterization and the fact that techniques to measure D and k often yield values that are in the mixed diffusion-controlled and surface exchange-controlled regimes. Thus there is a need for standardization of the experimental procedures to yield

consistent and reproducible catalytic performance data for a given catalyst. Another issue that needs to be addressed is the characterization of the structure of these oxides as a function of δ and the composition. Several unusual observations are attributed to changes in the structure of these oxides, as discussed below. In the case of thermal-catalysis, a major challenge is characterization of the catalyst post reaction and identification of the catalytically active sites. In absence of such data a fair comparison between catalysts is often challenging.

2. Synthesis of R-P-1 Oxides

Synthesis of R-P-1 oxides provides an opportunity for optimizing their catalytic activity by allowing control over the amount of interstitial oxygen, particle size and active surface area. [1, 33, 72, 73] Currently, the most common synthesis methods reported in the literature include, the citrate-nitrate method (modified Pechini method), [74] sol-gel method, [75] solid-state route, [75] and the glycine-nitrate method [76]. Less commonly used methods are zone melting [31] and “soft” methods [77]. The citrate-nitrate method (also known as modified Pechini method) [78-80] involves the use of citric acid as a way to trap the metal ions in a gelified citric acid network leading to the formation of the oxide. However, there have been no reports on the characterization of the metal-citrato complex formed *in-situ* during synthesis, [81] providing limited understanding of ways to control the shape and size of R-P-1 oxide particles using this synthesis approach. In the sol-gel method [75] directing agents (i.e., ethanolamine) are used to facilitate the arrangement of the desired metal ions in aqueous solution. This leads to the formation of a gel, which is further calcined at high temperatures (i.e., ~ 1000 °C) to obtain the oxide. Limited understanding of the factors that govern the formation of the R-P-1 oxide particles using this method exists. The solid-state synthesis [75] is another commonly used method to synthesize oxide ceramic particles. In this method, the metal precursors (i.e., the respective acetates) are subjected to ball milling using zirconia beads, followed by calcination. As in the previous methods, limited control over the nanostructure of the resulting oxide particles is possible with this approach. In the case of the glycine-nitrate synthesis method (GNP) [76, 82], a self-sustained exothermic reaction between an oxidizer (e.g. a metal nitrate) and a “fuel” (e.g. amino-acetic acid - glycine) is used to form the oxide. Various parameters have shown to play a role in the crystallinity and specific surface area of the final product, such as the fuel type, fuel to oxidizer ratio, water content in the precursor mixture, and ignition temperature.

While the synthesis methods described above are often used to synthesize R-P-1 oxides, characterization of the surface and nanostructure of the oxides after synthesis and as a function of different synthesis parameters is limited. Most of the literature reports discussed above rely mainly on powder XRD (X-Ray Diffraction) and low resolution scanning electron microscopy (SEM) to characterize the oxide particles after synthesis. As also discussed in a review by Schaak and Mallouk, the synthesis of R-P phase materials thus far has been mainly dominated by serendipity, as opposed to rational design. [77] Since synthesis plays a key role in the final structure of these oxides, and consequently affects their catalytic/electrocatalytic properties, development of synthesis techniques that allow for control over the final structure of R-P-1 oxides is critical in systematically understanding these complex materials.

Recently, it has been shown that the nanostructure of R-P-1 oxides can be controlled via the use of reverse micro-emulsion systems. [83] In this process, two separate micro-emulsions (one containing metal cations and the other precipitating anions) are mixed and the metals are allowed to react inside of the “microreactor”. [84] Different

synthesis parameters, such as surfactant/co-surfactant choice and concentration, and the ratio of water to surfactant (w_0) in the micro-emulsion suspensions, have been shown to facilitate control over the size and shape of the reverse micelles, and thus of the final product. [85] It was demonstrated that an optimum w_0 is essential for the formation of $\text{La}_2\text{NiO}_{4+\delta}$ nanorod structures that are highly surface terminated by (001) transition metal oxide (i.e., NiO) facets as corroborated by (Figure 3) scanning transmission electron microscopy (STEM) using high angle dark field (HAADF), and electron energy loss microscopy (EELS). The surface oxygen exchange properties of $\text{La}_2\text{NiO}_{4+\delta}$ synthesized using this method have been investigated and shown to be dependent on the geometry and distribution of the surface facets of the particles. [83] This synthesis method provides an opportunity for improving the catalytic activity of R-P-1 oxides by allowing for optimization of the size and morphology of the nanoparticles.

Figure 3. (a) BF-TEM (Bright Field-Transmission Electron Microscopy) image and the corresponding SAED (Selected Area Diffraction) pattern (inset) of a $\text{La}_2\text{NiO}_{4+\delta}$ nanorod recorded along the [001] zone axis. (b) HRTEM (High Resolution-TEM) images recorded from the red-boxed area marked in (a). The bottom inset illustrates a [001] projected model of the nanorod. (c) TEM images and the corresponding SAED pattern (bottom inset) of a $\text{La}_2\text{NiO}_{4+\delta}$ polyhedron recorded along [121] zone axis. The dark field (DF) TEM image (top inset) of the polyhedron. (d) HRTEM images recorded from the red-boxed area marked in (c). The bottom inset illustrates a [121] projected model of the polyhedron. From reference [83]; Reproduced with permission from Royal Society of Chemistry.

3. Effect of A- and B-site Compositions on the Electrocatalytic Properties of R-P-1 Oxides.

The effects of the A and/or B site composition of the R-P-1 oxides on their surface oxygen exchange and diffusion properties have been explored by many. [21, 75, 86-90] As we discuss below, the primary motivations for varying the composition and doping (substitution) of the A and/or B site in these oxides include obtaining improved electrocatalytic properties in terms of better oxygen exchange properties, and enhancement of oxygen hyperstoichiometry, as well as enhancing stability of the catalyst at operating conditions. For example, substitutions of the A and/or B sites in the oxide significantly affect the oxygen hyperstoichiometry, δ , which, to maintain charge neutrality, result in the modification of the oxidation state of the B-site metal, and hence the B-O bond length. In some cases this change in oxidation state results in a change in the spin state [91] of the transition metal (which may result in different tendencies to promote Jahn-Teller distortions) in the structure, affecting the oxygen exchange properties. In this section, we summarize the literature findings on the impact of A and B site substitutions in these oxides on critical electrochemical activity parameters, such as k , D , electronic conductivity and δ .

3.1 Effect of A-site substitution on R-P-1 oxides.

La-based R-P-1 oxides Substitution of La^{3+} with a larger cation, such as Sr^{2+} , leads to variations in oxygen stoichiometry that consequently affects the oxygen transport and exchange properties. [92] In multiple reports this has been demonstrated to result in a decrease of δ , D and k in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ oxides as compared to undoped $\text{La}_2\text{NiO}_{4+\delta}$ oxide. [21, 30, 92, 93] However, another report [40] on $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ oxides has shown that the value of k does not change significantly with the amount of Sr substitution. Moreover, for $x > 0.6$, an increase in D with Sr doping has been observed. [40] This behavior was attributed to the variations in ion-mobility and δ as a function of composition.

Figure 4: (a) Arrhenius plots of $\log k$ vs. $1/T$ for $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ($x=0, 0.1, 0.2$). Data extracted from references: [21, 25, 30, 31, 40, 93]. (b) Calculated values for activation energies for the surface diffusion coefficients (k) for $\text{La}_2\text{NiO}_{4+\delta}$ (A: ab plane, B: c axis, C: Ceramic) [31], D [21], E [25], F [30], G [56], H [54], I [93], $\text{La}_{1.9}\text{Sr}_{0.1}\text{NiO}_{4+\delta}$ (I: [93], D: [21]), and $\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$ (J: [40], I: [93]).

Figure 4a shows some representative Arrhenius plots constructed from the literature data for the rates of surface oxygen exchange (k) as a function of temperature for undoped and Sr-doped lanthanum nickelate oxides. [21, 25, 30, 31, 40, 54, 56, 93] To visually compare the data obtained at different temperatures, trendlines as opposed to individual data points are plotted. Figure 4b summarizes the activation energies for the surface oxygen exchange obtained from the Arrhenius plots for the different oxides. Figure 4b shows significant variations in the magnitude of the activation energies for surface oxygen exchange on $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$ oxides reported in the literature. This indicates potential mechanistic variations in the oxides analyzed by different groups. The large variations in k for the same oxide could also be attributed to the lack of non-standardized synthetic, surface characterization and measurement techniques. [44] Regarding the measurement techniques, for example, due to the sample thickness, the k values using both SIMS and ECR are typically measured in diffusion limited or mixed regimes rather than strictly surface controlled regime, introducing errors in the measurements. Isotope exchange studies on powder samples have been used to overcome this challenge. [44] Figure 4 also indicates that the synthesis methods play a role in the surface oxygen exchange process on these oxides, by potentially affecting their surface structure and oxygen hyperstoichiometry. If points A (ab plane, single crystal), B (c axis, single crystal) and C

(dense ceramics) in Figure 4b (for $\text{La}_2\text{NiO}_{4+\delta}$ obtained from the same report) are compared, [31] the values for the activation energies for the former two are close to one another, while the latter is significantly lower. The main difference between these systems is the synthesis method. We find large variations in the reported activation energies for the surface oxygen exchange on $\text{La}_2\text{NiO}_{4+\delta}$ limiting our ability to conclude on a general trend for the effect of Sr doping of $\text{La}_2\text{NiO}_{4+\delta}$ on the surface oxygen exchange

Comparison of the rates of diffusion (D) for undoped and Sr-doped lanthanum nickelate oxides obtained at the same temperature, from different literature reports [21, 25, 31, 40, 93] indicates that the magnitude of D is influenced by composition, crystal morphology, synthetic techniques and anisotropy in these oxides. A general trend of a decrease in the value of D upon increasing Sr doping is observed due to the reasons discussed earlier. As in the case of k, synthesis methods might also play a role in the magnitude of D as the values obtained from single crystals [31] are substantially different from those obtained from ceramic samples.

An effect on the electronic conductivity of $\text{La}_2\text{NiO}_{4+\delta}$ with Sr doping is also observed. The electronic conductivity of $\text{La}_2\text{NiO}_{4+\delta}$ increases with an increase in Sr substitution ($\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$). [86, 94, 95] These materials were reported to exhibit semiconductor-like behavior at low temperatures ($< 600^\circ\text{C}$), that is transformed into metallic-like behavior at elevated temperatures. [96] Sr substitution in lanthanum nickelates also leads to Sr segregation to the outermost surface affecting the surface catalytic activity. [97]

There are different viewpoints in the literature regarding as to what is responsible for compensating the charge imbalance upon substituting a trivalent A-site cation, such as La^{3+} , with a divalent cation, such as Sr^{2+} . [40] It is argued that the valency of the B-site metal predominantly contributes to balance the charge at higher amounts of A substitution. [40] However, in another report, [98] where XANES (X-ray absorption near edge structure) experiments were used to investigate $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ ($x=0, 0.05, 0.15, 0.25$ and 0.35) oxides, it was inferred that in the case of high Sr doping, the valency of Cu did not increase accordingly, and the oxygen vacancies were attributed to the balancing of the charge in the structure.

Sm, Pr and Nd based R-P-1 oxides: As we go across the lanthanides in the periodic table, the size of the atoms decreases due to lanthanide contraction. In principle, A-site cations with a smaller size than La^{3+} should allow for higher amount of non-stoichiometric oxygen in the lattice, and faster oxygen transport properties. [33, 61] The challenge, however, is the thermodynamic stability of these structures. To predict whether a stable A_2BO_4 type crystal structure with a given stoichiometry of the A and B metals is energetically feasible, a parameter, known as the tolerance factor, t , whose value depends on the A-O and B-O bond lengths, is used. [99] Due to the smaller size of Sm^{3+} as compared to Pr^{3+} and Nd^{3+} , Sm based R-P-1 structure ($\text{Sm}_2\text{NiO}_{4+\delta}$) in principle should exhibit the highest oxygen diffusion rates among the three oxides. Practically, however, the ionic radius of Sm is too small for it to form a stable R-P-1 structure. It has been shown that doping the A-site with a larger cation, such as Sr^{2+} ($\text{Sm}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$), can lead to improved structural stability of samarium nickelates [87], and stable $\text{Sm}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ oxides have been synthesized for $x \geq 0.5$. Compositions with $x = 0.5, 0.6, 0.8, 1.0$ have been tested in SOFCs with CGO ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$) electrolyte and shown to be stable up to a temperature of 1000°C . [87] Among these, SmSrNiO_4 and $\text{Sm}_{1.4}\text{Sr}_{0.6}\text{NiO}_{4+\delta}$ exhibited the best electrochemical performance in terms of low area specific resistance (ASR – cell resistance per electrode surface area induced by the inefficiency of the electrocatalysts to facilitate the

electrochemical reactions), overpotential, reactivity with YSZ and TEC. [87] Other studies on Sm-doped lanthanum nickelates ($\text{La}_{2-x}\text{Sm}_x\text{NiO}_{4+\delta}$; $0 \leq x \leq 1.1$) showed a significant improvement in electronic conductivity upon doping that peaked at 130 S cm^{-1} ($T \sim 500^\circ\text{C}$, $x = 0.5$). [100] It has been reported that the value of ASR decreased with increasing Sm content (x), while there was no clear dependence of Sm doping on δ . [100] The reports discussed above suggest that structurally stable, Sm-doped nickelate oxides, in general, exhibit good electronic conductivity and low ASRs, making these materials promising electrocatalysts for SOFCs.

Praseodymium and neodymium nickelates ($\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$, respectively) have been reported to exhibit faster oxygen transport properties than $\text{La}_2\text{NiO}_{4+\delta}$. [33, 61] Boehm et. al., [33] showed that $\text{Pr}_2\text{NiO}_{4+\delta}$ had the highest D as compared to $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$, while the highest k was observed for $\text{La}_2\text{NiO}_{4+\delta}$. The values of D and k were compared to the ones reported by Skinner and co-workers, [21, 93] obtained using the same sample preparation and data collection techniques. The values of D were identical, while the values of k were similar only at high temperatures. Boehm et al., argued that the variations in k were due to the difference in the morphology of the particles they used as compared to ones in the report by Skinner and co-workers. Based on this analysis, it was concluded that while D was not dependent on the particle morphology, k was, reinforcing the fact that particle surface morphology plays an important role in the surface oxygen exchange process. [33] Bassat and co-workers, [101] while studying anisotropic oxygen diffusion in $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$ single crystals, observed that D and k in these systems were higher along the a - b plane than along the c -axis. The D and k values for $\text{Pr}_2\text{NiO}_{4+\delta}$ were higher than for $\text{Nd}_2\text{NiO}_{4+\delta}$, which was attributed to the difference in the activation energies for the respective processes between these systems. $\text{Pr}_2\text{NiO}_{4+\delta}$ also exhibited the highest electronic conductivity ($\sim 167 \text{ S cm}^{-1}$ at 500 - 600°C), when compared to Nd and La nickelates. [6, 102] Among $\text{La}_{2-x}\text{Pr}_x\text{NiO}_{4+\delta}$ oxides ($x = 0, 0.6, 1.0, 1.4, 2.0$), $\text{Pr}_2\text{NiO}_{4+\delta}$ demonstrated the highest electronic conductivity, lowest polarization resistance, and the highest power generation in SOFCs. [103] While these properties would make $\text{Pr}_2\text{NiO}_{4+\delta}$ a very promising electrocatalyst, $\text{Pr}_2\text{NiO}_{4+\delta}$ lacks stability at temperatures of $\sim 800^\circ\text{C}$ under oxidizing atmospheres. [104, 105] Its chemical stability though can be improved by doping the A-site with Nd [106], Sr [107] or La [108].

In the case of $\text{Nd}_2\text{NiO}_{4+\delta}$, [61] although it exhibits high oxygen exchange rates at 700°C , the rates drop significantly with a decrease in temperature due to the high activation energy for this process. [53] The activity of $\text{Nd}_2\text{NiO}_{4+\delta}$ and its stability with common electrolytes was determined to be reasonable for SOFCs operating at temperatures in the range 700 - 900°C . [6, 109] The interfacial electrode-electrolyte resistance was shown to be the most important contribution to the total impedance, indicating that optimization of this interface, potentially by morphological modification using controlled synthetic procedures would increase the performance of SOFCs containing $\text{Nd}_2\text{NiO}_{4+\delta}$ -based cathodes. [109] Doping the A-site of $\text{Nd}_2\text{NiO}_{4+\delta}$ with Sr^{2+} was shown to enhance the stability and oxygen exchange properties of $\text{Nd}_2\text{NiO}_{4+\delta}$. [76]

Figure 5: (a) Arrhenius plots of $\log k$ vs. $1/T$ for $\text{Nd}_2\text{NiO}_{4+\delta}$ and $\text{Pr}_2\text{NiO}_{4+\delta}$. Data extracted from references: [33, 53, 61, 101]. (b) Calculated values of the activation energies for surface oxygen exchange (k) for $\text{Nd}_2\text{NiO}_{4+\delta}$ and $\text{Pr}_2\text{NiO}_{4+\delta}$ from the following references: $\text{Nd}_2\text{NiO}_{4+\delta}$ A: [33], B: [101], C: [53], D: [61], and $\text{Pr}_2\text{NiO}_{4+\delta}$ A: [33], B: [101].

Figure 5a shows the Arrhenius plots for the rates of surface oxygen exchange as a function of temperature extracted from different literature reports for Nd and Pr nickelate oxides. [33, 53, 61, 101] The rates of the surface oxygen exchange process as well as the slopes of the Arrhenius plots for the same oxide differ from different literature sources. Figure 5b shows the activation energies for surface oxygen exchange calculated from Figure 5a. While in general Figure 5b suggests that the activation energies for the surface oxygen exchange on Pr nickelates are lower than on Nd nickelates, these trends are reversed (Point B) when using single crystal systems. [101] This suggests once again that the preparation methods play an important role in the kinetics of surface oxygen exchange.

Lanthanum cobaltates, cuprites, and manganites: Co, Cu and Mn-based R-P-1 oxides known as cobaltates, cuprites, and manganites, respectively, have also been explored by many for electrocatalysis. [99, 110-117] In Sr-doped rare-earth cobaltates ($\text{Ln}_{2-x}\text{Sr}_x\text{CoO}_{4+\delta}$, where $\text{Ln} = \text{La} - \text{Dy}$ and $x = 0.75 - 1.5$) the average Co oxidation state increases with Sr doping varying from +2.96 to +3.72. [99] In Sr-doped neodymium cobaltates ($\text{Nd}_{2-x}\text{Sr}_x\text{CoO}_{4+\delta}$ with $x = 0.8, 1.0$ and 1.2), it has been reported that the electrochemical performance improved with increasing Sr^{3+} content [110] and the best candidate for electrochemical applications was shown to be $\text{Nd}_{0.8}\text{Sr}_{1.2}\text{CoO}_4$, as it exhibited the highest chemical stability, the lowest polarization resistance, the lowest cathodic overpotential, and the highest conductivity of 212 S cm^{-1} at 800°C in air. [110]

Sr substitution in lanthanum cuprites ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$) leads to significant changes in the oxygen nonstoichiometry, thus effecting diffusion energetics in these oxides. [111-115] δ was found to dependent on the oxygen partial pressure and Sr doping. Thermogravimetric and coulometric titration studies showed that increasing Sr content in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ from $x = 0$ to $x = 0.3$ changed the nonstoichiometry from oxygen excess to oxygen deficient, effecting the nature of defects in the system, and hence the diffusion energetics. [111] Molecular dynamic simulations of the oxygen mobility in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ concluded that there was a different mobility behavior of the oxygen species in the Cu_2O layers and the $(\text{LaSr})\text{O}$ layers, with the former being energetically more favorable. [112]

The calculated oxygen diffusivities (from molecular dynamic simulations) for $\text{La}_{1.64}\text{Sr}_{0.37}\text{CuO}_{3.81}$ and $\text{LaSrCuO}_{3.5}$, [112] were an order of magnitude higher than the experimental observed ones [113, 118]. In the case of the oxygen activation characteristics of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, kinetic studies at 650 °C on $\text{La}_{1.7}\text{Sr}_{0.3}\text{CuO}_4$ showed a complex dependence on both the partial pressure of oxygen ($p(\text{O}_2)$) and temperature [114], which was attributed to the variations in δ with oxygen pressure and temperature. Among Sr-doped lanthanum cuprites ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$, $x = 0.1, 0.3, 0.5$) investigated for SOFC applications, $\text{La}_{1.7}\text{Sr}_{0.3}\text{CuO}_4$ exhibited the lowest ASR and overpotential, while the highest electronic conductivity reported was for $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ (148 S cm^{-1} at 700 °C). [114] It was found that further increase in the Sr doping ($x > 0.1$) led to a decrease in the electronic conductivity, which was attributed to a change from p-type to n-type conductivity in these oxides. With regard to the chemical compatibility of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with the SOFC electrolytes, the performance of the oxide with $x = 0.3$ was the most promising. [114, 115]

In the case of lanthanum manganite R-P-1 oxides, the electrocatalytic activity is limited by structural instability due to phase changes that occur at a relatively low temperature of 470 °C. [119] Furthermore, achieving reasonable electronic conductivity for electrochemical applications is also challenging with these oxides. [116] Although it has been reported that their electronic conductivities can be improved by doping the A-site with Sr, these conductivities are still too low for applications where both high ionic and electronic conductivities are needed. [116, 117] Among $\text{La}_{2-x}\text{Sr}_x\text{MnO}_{4+\delta}$ with $0 \leq x \leq 1.4$ the maximum electronic conductivity was found to be 5.7 S cm^{-1} for $\text{La}_{0.6}\text{Sr}_{1.4}\text{MnO}_{4+\delta}$ at 800 °C. [116, 117]

3.6. Effect of B-site Composition on Electrocatalytic Properties of R-P-1 Oxides

A number of literature reports [64, 88, 100, 120, 121] have investigated the effect of B-site modifications on the catalytic properties of R-P-1 oxides. Results of modeling studies [37] have shown that doping of the B-site in lanthanum nickelate oxides with alkaline earth metals having a 3^+ oxidation state (i.e., Fe, Cu, and Co) leads to a higher ionic charge carrier concentration. However, these computational studies also suggested that this would lead to a decrease in the oxygen anion mobility. [37] These findings were corroborated by experimental studies on $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ ($0 \leq x \leq 1$), using IEDP-SIMS and conductivity relaxation methods. [56]

Doping the B-site of lanthanum nickelates with Cu ($\text{La}_2\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_{4+\delta}$) has a significant effect in oxygen exchange rates (k). [56] Figure 6a shows the Arrhenius plots for the rates of surface oxygen exchange on $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ extracted from literature. Figure 6b shows the calculated activation energies for surface exchange process on $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ as a function of Cu doping (x). Figure 6b shows that an increase in Cu doping (up to ~ 75%) leads to an increase in the activation energy for surface oxygen exchange, suggesting that Cu doping decreases the catalytic activity of R-P-1 oxides for the surface oxygen exchange. However, for the pure lanthanum cuprite (La_2CuO_4), the activation energy drops and becomes lower than that for the 25 mol% Cu doped R-P-1 oxide, suggesting potential change in the mechanism for surface oxygen exchange on this oxide. Additional composition dependent mechanistic investigations are needed to fully understand this behavior.

Figure 6: (a) Arrhenius plots of $\log k$ vs. $1/T$ for $La_2Ni_{1-x}Cu_xO_{4+\delta}$ ($x=0.25, 0.5, 0.75, 1.0$). Data extracted from [56]. (b) Calculated values for activation energies for the surface exchange coefficients for $La_2Ni_{1-x}Cu_xO_{4+\delta}$ [56].

Electronic conductivities for Cu-doped lanthanum nickelates ($La_2Ni_{1-x}Cu_xO_{4+\delta}$, $0 \leq x \leq 1$) are reported to be in the range of $\sim 15\text{-}50 \text{ S cm}^{-1}$, with $La_2NiO_{4+\delta}$ exhibiting the highest conductivity, which decreases with an increase in Cu doping. [56, 120] However, it was shown that for low Cu doping ($< 10 \text{ mol\%}$) of lanthanum nickelates an increase in electronic conductivity and decrease in the ASR occur as the Cu doping is increased. [121] These results suggest a change in behavior as a function of Cu doping: low Cu doping ($< 10 \text{ mol\%}$) improves the electronic conductivity of lanthanum nickelates, while higher Cu doping ($> 10 \text{ mol\%}$) leads to a decrease in the electronic conductivity of these oxides. This unusual behavior of the electronic conductivity upon Cu doping is not well understood. In addition, it has been reported that, in general, $La_2Ni_{1-x}Cu_xO_{4+\delta}$ ($0 \leq x \leq 1$) oxides exhibited stable TECs ($\sim 13 \times 10^{-6} \text{ K}^{-1}$) at different temperatures that were comparable to that of YSZ [56], making these materials suitable for use in SOFCs. $La_2Ni_{0.8}Cu_{0.2}O_{4+\delta}$ oxide was reported to have a TEC of $13.3 \times 10^{-6} \text{ K}^{-1}$, as well as good stability with the LSGM ($(La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3-\delta}$) electrolyte. [88]

Doping the B-site of $La_2NiO_{4+\delta}$ with 10% mole Fe [93] has been shown to lead to no significant improvements in D or k as compared to $La_2NiO_{4+\delta}$. In contrary to these experimental findings, theoretical studies [35] have however predicted improved catalytic activity upon Fe substitution in lanthanum nickelates. The difference between the experimental results and theoretical predictions could stem from the difference in the model system used in the computational studies as compared to experiments.

In Al-doped lanthanum nickelates ($La_2Ni_{0.95}Al_{0.05}O_{4+\delta}$) [122], k was found to be greater than D . Under oxidizing conditions, the activation energy for the diffusion process was found to be slightly higher than that for the surface oxygen exchange, suggesting that oxygen ion diffusion is the limiting process in these oxides. While these oxides were limited by oxygen ion diffusion, the activation energies for oxygen diffusion were much lower than the perovskite-type mixed conductors. This was attributed to the interstitial mechanism governing oxygen diffusion in the former, as opposed to vacancy mechanism in the latter. Furthermore, it was found that the ionic conductivity of $La_2Ni_{0.95}Al_{0.05}O_{4+\delta}$ was higher than that of the undoped lanthanum nickelates, and the value of TEC was found to be $\sim 13.77 \times 10^{-6} \text{ K}^{-1}$, close to that of YSZ, making it a promising SOFC electrocatalyst.

In low Co substituted lanthanum nickelates ($\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_{4+\delta}$ where $0 < x < 0.5$) oxygen diffusion has been shown to increase only slightly with an increase in Co content. [54] Unlike D , the surface exchange coefficient (k) was reported to be strongly dependent on the degree of Co doping with the difference in surface exchange properties becoming more prominent at lower temperatures. [54] For example, k for $\text{La}_2\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_{4+\delta}$ was shown to be > 2 orders of magnitude higher than $\text{La}_2\text{NiO}_{4+\delta}$ at 400°C . There was a decrease in the enthalpy of activation for the surface exchange process to a very low value of ~ 20 kJ/mol in $\text{La}_2\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_{4+\delta}$ as compared to ~ 60 kJ/mol in $\text{La}_2\text{NiO}_{4+\delta}$. [54] The significant effect of Co doping on k , as compared to the minimal effect on D , was hypothesized to be due to changes in the surface properties of the R-P-1 oxides with an increase in Co doping. However, an unidentified secondary phase was also observed for the composition of $\text{La}_2\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_{4+\delta}$, which might have also been a factor in the observed behavior. Higher Co-substitutions of lanthanum nickelates ($\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_{4+\delta}$ with Co doping of 30, 50, 80 and 100%) have also been investigated. [123] It was found that oxygen diffusion and surface exchange coefficients were almost double than those for $\text{La}_2\text{NiO}_{4+\delta}$ in the case of higher Co loadings. In agreement with the findings for low Co-doped lanthanum nickelates [54], k improved significantly with an increase in Co doping and there was negligible effect on D (up to a Co doping of 30 mol%). It was also shown that in $\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_{4+\delta}$, the temperature dependence of oxygen diffusivity exhibited a significant variation with the amount of Co doping. [123] At low Co doping, the diffusion coefficients were significantly dependent on temperature and had high activation energies (80-100 kJ/mol). An increase in Co doping led to a decrease in activation energies to 10-20 kJ/mol. [100] Furthermore, the normal linear temperature dependence of oxygen diffusivity was not obeyed in the case when $x = 0.5$ and 0.8 . [100, 123] It was found that an unusual trend in the activation energies for the diffusion process was observed for these samples at high and low temperature regimes. [123] Amow and Skinner [100] in a follow-up report attributed this phenomenon to structural changes, however neutron diffraction studies could not unequivocally verify this hypothesis. The only inference from the neutron diffraction data was that at 600°C , where some trends indicating structural changes were seen on the apical transition metal-oxygen bond. [100]

Figure 7a summarizes the Arrhenius plots for the rates of surface oxygen exchange as a function of temperature for Co-doped lanthanum nickelates ($\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_{4+\delta}$) obtained from literature. Figure 7b shows the activation energies for the surface oxygen exchange as a function of Co doping (x) in $\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_{4+\delta}$ calculated from the Arrhenius relationships in Figure 7a. Figure 7b shows that the activation energies for the surface oxygen exchange from the two sources for $\text{La}_2\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_{4+\delta}$ vary significantly, although the trends seem to be similar at low Co substitutions.

Figure 7: (a) Arrhenius plots of $\log k$ vs. $1/T$ for $La_2Ni_{1-x}Co_xO_{4+\delta}$ ($x=0.1, 0.2, 0.3, 0.5, 0.8, 1.0$). Data extracted from [54] and [123]. (b) Calculated values for the activation energies for the surface oxygen exchange coefficients for $La_2Ni_{1-x}Co_xO_{4+\delta}$. Data calculated from reference [54] are shown with squares, while from [123] are shown with diamonds.

Electronic conductivity of Co substituted lanthanum nickelates ($La_2Ni_{1-x}Co_xO_{4+\delta}$, $0 \leq x \leq 1$) has been reviewed in detail by Amow and co-workers. [100] It was shown that undoped $La_2NiO_{4+\delta}$ exhibited a broad metal-insulating transition behavior at $\sim 327^\circ C$. However, at this temperature, with a progressive increase in Co doping up to $x \sim 0.7$ in $La_2Ni_{1-x}Co_xO_{4+\delta}$, this behavior changed to insulating. Further increase in Co doping led to an increase in electronic conductivity. [100] This was explained by the fact that the electronic conductivity in the R-P systems was dominated by B-oxygen-B interactions in the basal plane of the perovskite layer. As Co doping was increased, the Ni(Co)-O bond length was increased, leading to a more covalent character of the bond, which in turn led to a decrease in electronic conductivity. The increase in electronic conductivity for $x > \sim 0.7$ was attributed to structural changes resulting from the deviation of the Ni(Co)-O-Ni(Co) bond from 180° in tetragonal to orthorhombic symmetry, a proposition supported by neutron diffraction data. [100] It was also reported that δ increased with increased Co doping in $La_2NiO_{4+\delta}$ ($La_2Ni_{1-x}Co_xO_{4+\delta}$) until $x = 0.3$, followed by drastic decrease with additional increase in Co doping. [124] This phenomenon was attributed to the difference in the synthesis method used for the oxides with Co doping (x) in the range of $0 \leq x \leq 0.2$ and $x > 0.2$. [80] The former oxides were prepared in air, which intrinsically led to higher oxygen incorporation in the lattice. On the other hand, the latter oxides were prepared in a reducing Ar atmosphere due to the inherent instability of these oxides in air, resulting in lower δ . [100]

The above literature reports suggest that Co-doped lanthanum nickelates lead to improved oxygen transport properties and catalytic activity for surface oxygen exchange as compared to pure lanthanum nickelate, which makes these oxides promising electrocatalysts for SOFC. However, Co-doped lanthanum nickelates (even at low Co doping ($La_2Ni_{1.9}Co_{0.1}O_{4+\delta}$)) exhibit poor long-term stability at high temperatures ($> 900^\circ C$) when in contact with SOFC electrolytes, such as LSGM and CGO. [80] In addition, these oxides are very reactive in oxygen, which makes their synthesis, long-term storage and operation challenging.

4. Thermal-Catalysis by R-P-1 oxides

R-P-1 oxides have been investigated as catalysts in a number of redox reactions, including oxidation of hydrocarbons [1, 66-68] and NO reduction [69-71]. Oxygen vacancies in the crystal structure, as well as the oxidation state of transition metal of these oxides, have been shown to play an important role in their catalytic activity. [125] It has also been suggested that the catalytic activity of these oxides can be effected by the oxygen mobility [126] and the crystal structure of the oxide [127]. In addition, modifications of the A and/or B site have been shown to impact their catalytic properties, as these effect δ , the oxidation state of the transition metal, concentration of the oxygen vacancies, oxygen mobility and the crystal structure, as in the case of electrocatalytic reactions. In the next paragraphs, we discuss in detail the literature findings on the catalytic activity of R-P-1 oxides for different thermochemical reactions. Table 1 summarizes some of the relevant reactions using R-P-1 oxide catalysts that will be discussed.

4.1 Oxidation Reactions

$\text{La}_2\text{NiO}_{4+\delta}$ [66], $\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_{4+\delta}$ [1], and $\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_{4+\delta}$ [67] have been investigated as catalysts for partial oxidation of methane in membrane reactors due to their high oxygen permeability, ionic conductivity, and moderate thermal- and chemical-induced expansions. For example, $\text{La}_2\text{NiO}_{4+\delta}$ tubular membranes (relative density 92%, length 2.0 cm, inner diameter 0.73 cm and wall thickness 0.12 cm) have been used to separate oxygen from air, by simultaneously catalyzing the partial oxidation of methane on the other side of the membrane (temperature $\sim 900^\circ\text{C}$ with methane and air fed to the two opposite sides of the membrane at a 2:1 ratio). [66] Methane conversion of 89%, and CO selectivity of 96% were reported. In absence of the methane flow, it was reported that the activation energy for oxygen (on the air-rich side) diffusion through the membrane was ~ 43 kJ/mol, which dropped to ~ 28.9 kJ/mol in presence of the fuel. This was attributed to the reaction of oxygen with adsorbed methane on the fuel side of the membrane. The active catalyst for methane oxidation using the $\text{La}_2\text{NiO}_{4+\delta}$ tubular membranes was suggested to be Ni formed from the decomposition of the R-P-1 oxide membrane on the fuel side. This was supported by parallel experiments using $\text{La}_2\text{NiO}_{4+\delta}$ powder catalysts (instead of a membrane) in a fixed bed catalytic reactor, where Ni was observed by XRD on the spent catalyst. The membrane on the permeate (air-rich) side of the reactor did not decompose.

Doping the B-site of $\text{La}_2\text{NiO}_{4+\delta}$ with Fe ($\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_{4+\delta}$) led to high CO selectivity (as high as 90-95% at a temperature of 827°C and feed flow of 1:10 $\text{CH}_4:\text{He}$) during partial oxidation of methane by lattice oxygen. [67] The experiments were carried out using thermogravimetric measurements on dense pellets (to model membranes) that had been exposed to oxygen for 1 hour at 500°C . As in the case of $\text{La}_2\text{NiO}_{4+\delta}$, decomposition to metallic Ni was found to be responsible for the catalytic activity. This was supported by the observation of metallic Ni and LaO using XRD. At high temperatures (950°C) under low oxygen pressures ($5 \times 10^{-3}\text{atm}$), δ was found to fall below the minimum hyperstoichiometry (0.011-0.012) required to maintain the integrity of the R-P crystal structure, and thus led to decomposition. This phenomenon coincided with a sharp increase in the catalytic activity, indicating that the species produced upon decomposition were the active catalysts for the reaction. In light of the decomposition of $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_{4+\delta}$, which resulted in the formation of metallic Ni, a potential active catalyst for methane oxidation, the catalytic activity of these R-P-1 oxides could not be fully assessed for this process. In the case of doping the B-site of $\text{La}_2\text{NiO}_{4+\delta}$ with Co ($\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_{4+\delta}$), it was found that the oxide was stable up to an

operating temperature of 900 °C during methane oxidation, but methane conversion was only about 20% with CO selectivity of 17%, when methane and air were fed to the two opposite sides of the membrane at a 1:1 ratio. [1] The main conclusion drawn from these studies is that Co-doping improves the stability of $\text{La}_2\text{NiO}_{4+\delta}$ during methane oxidation in membrane reactors.

$\text{La}_{1.9}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$ have shown good activity toward propane oxidation at temperatures as low as 300 °C but no effect of Sr-doping on the activity was observed. [126] In these studies, the catalysts were treated in an oxygen atmosphere at 500 °C for 1h, cooled to 100 °C, followed by exposure to the fuel (propane) at 1.8 liters/hr. The catalysts were then heated to 500 °C at 15 °C/min and the relevant reaction products were monitored by mass spectroscopy. At 500 °C, $\text{La}_{1.9}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$ exhibited propane conversions of 50% and 32% and CO_2 selectivities of 80% and 57%, respectively. If normalized per reported surface areas (2.5 m²/g and 1.5 m²/g for $\text{La}_{1.9}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$, respectively) the catalytic activity of these oxides is similar. Using temperature programmed desorption, it was concluded that not all the lattice oxygen released upon heating actually reacted with propane, as this was limited by the number of active catalytic sites available to activate propane. Experiments conducted without gaseous oxygen also resulted in propane oxidation, as this was facilitated by the interstitial oxygen in the R-P-1 oxide structure. No indication of the decomposition of the R-P-1 oxides during reaction was observed, suggesting that $\text{La}_{1.9}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$ were the active catalysts for the reaction.

As discussed above synthesis can have a significant effect in the activity of these oxides. It was shown that for methane combustion, a catalyst prepared by using polymethyl methacrylate (PMMA) templated $\text{La}_2\text{CuO}_{4+\delta}$ [128] performed better than the one synthesized by the traditional citrate-nitrate method. A 90 % methane conversion at 672 °C was observed in a feed mixture of CH_4/O_2 at a ratio of 1 to 10. This was attributed to the higher porosity of the former, which potentially led to a higher active surface area. No decomposition of $\text{La}_2\text{CuO}_{4+\delta}$ was reported. The structural Cu ions were reported to be the catalytically active sites for the reaction.

Doping the A-site of lanthanum cuprates with Eu ($\text{La}_{2-x}\text{Eu}_x\text{CuO}_{4+\delta}$ where $0 < x < 1.33$) has shown to lead to improved stability during phenol oxidation. [127] It was also observed that oxides with higher Eu concentration were more resistant to structural changes induced by oxygen deficiencies in the structure that occurred during phenol oxidation. It was suggested that $\text{La}_{2-x}\text{Eu}_x\text{CuO}_{4+\delta}$ oxides with greater oxygen content favored the formation of more oxidized product, *p*-benzoquinone, as compared to hydroquinone and catechol. However details regarding the reaction conditions, product yields and selectivity were limited. XRD analysis indicated no changes in the R-P structure of the spent $\text{La}_{2-x}\text{Eu}_x\text{CuO}_{4+\delta}$ oxide catalysts.

Doping the A-site of lanthanum cuprates with Rb ($\text{La}_{2-x}\text{Rb}_x\text{CuO}_{4\pm\delta}$, $x = 0.1, 0.2, 0.3, 0.4, 0.5$) was shown to improve the activity for oxidation of diesel soot to CO_2 . [129] An increase in catalytic activity of these oxides was observed with an increase in Rb doping. The best performance was obtained for $\text{La}_{1.6}\text{Rb}_{0.4}\text{CuO}_{4-\delta}$. Increasing the degree of Rb substitution led to an increase in the degree of hyperstoichiometric oxygen and amount of Cu^{3+} , both of which had a positive impact on the catalytic activity. Formation of a tetragonal T* phase from the orthorhombic phase for $\text{La}_2\text{CuO}_{4+\delta}$, was observed upon increased Rb substitution (formed for $x > 0.3$). It was suggested that this tetragonal phase in $\text{La}_{1.6}\text{Rb}_{0.4}\text{CuO}_{4-\delta}$ might also contribute to the enhanced activity. No decomposition of the R-P structure of these oxides during reaction was reported.

Nakayama and co-workers [130] investigated the effect of A-site composition of Ln_2CuO_4 ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}$) on the oxidation of carbon black. In these experiments, DSC (differential scanning calorimetry) and TG-DTA (thermogravimetric-differential thermal analysis) analysis were performed on 10 mg of a 19:1 mixture of commercial carbon black to catalyst. The sample was heated at $10^\circ\text{C}/\text{min}$ from room temperature to 700°C in a 20 ml/min flow of air. A decrease in combustion temperature (with minimum at $\sim 465^\circ\text{C}$) with an increase in ionic radius of Ln^{3+} was observed. Oxides with $\text{Ln} = \text{La}$ and Pr exhibited the highest catalytic activity in terms of lowering of the combustion temperature. Orthorhombic La_2CuO_4 and tetragonal Ln_2CuO_4 ($\text{Ln} = \text{Pr} - \text{Sm}$) prepared at 800°C showed higher carbon oxidation activity when compared to CuO treated at the same temperature. Characterization of the catalyst post-reaction was not reported. Thus, the nature of the active catalytic species and the stability of R-P-1 structures could not be assessed.

4.2 Reduction Reactions

R-P-1 oxides, including $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ and others discussed below, have been considered as NO reduction catalysts. It was shown that $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ had better conversion and selectivity towards N_2 than undoped $\text{La}_2\text{NiO}_{4+\delta}$ and perovskite $\text{LaNiO}_{3-\delta}$. [70] The active catalytic sites were reported to be a combination of Ni^{2+} and disordered oxygen vacancies. Furthermore, no structural changes were observed for the oxide catalysts tested.

Lanthanum cuprate oxide ($\text{La}_2\text{CuO}_{4+\delta}$) has been used to catalyze NO reduction using CO, but post reaction XRD and BET analysis indicated substantial degradation of the catalyst. [69] It was reported that the catalytically active species was metallic Cu, as post-reaction XRD characterization of the catalyst indicated the presence of $\text{La}(\text{OH})_3$, metallic Cu and La_2CuO_4 . In another study, it was found that A-site substitution of $\text{La}_2\text{CuO}_{4+\delta}$ with Th to form $\text{La}_{1.867}\text{Th}_{0.100}\text{CuO}_{4+\delta}$ led to an increase in conversion of NO to N_2 . [131] TGA and EPR studies on $\text{La}_{1.867}\text{Th}_{0.100}\text{CuO}_{4+\delta}$ indicated the presence of Cu^{2+} , Cu^+ and metallic Cu upon reducing the catalyst at 100°C , 300°C and 500°C , respectively. At 500°C , the R-P structure of the oxide decomposed due to the excessive loss of oxygen. However heating the catalyst at 800°C under an oxygen atmosphere resulted in the recovery of the structure (as corroborated by XRD). The best catalyst performance (65% NO conversion to N_2 , and 7% to N_2O) was observed for the catalyst calcined at 300°C . This performance was significantly better when compared to the undoped lanthanum cuprate, which resulted in 20% and 5% N_2 and N_2O conversion, respectively. It was suggested that the smaller particle size (via SEM) of the oxide catalyst calcined at 300°C might have contributed to the better performance. However, the nature of the active site and the role of Th were not accounted for. The active redox catalyst was suggested to be $\text{Cu}^+/\text{Cu}^{2+}$ in the structure of doped/undoped lanthanum cuprates.

Pd-doped lanthanum cuprates ($\text{La}_2\text{Cu}_{1-x}\text{Pd}_x\text{O}_{4+\delta}$ oxides where $x = 0.01, 0.05, 0.1, 0.2$) have been investigated as three-way catalysts for simultaneous $\text{CO}/\text{C}_3\text{H}_6$ oxidation and NO reduction. [132] For the latter reaction, the activities of the best performing catalysts in the series, $\text{La}_2\text{Cu}_{0.9}\text{Pd}_{0.1}\text{O}_{4+\delta}$ and $\text{La}_2\text{Cu}_{0.8}\text{Pd}_{0.2}\text{O}_{4+\delta}$, were comparable to $\text{Pt-Rh}/\text{CeO}_2/\text{Al}_2\text{O}_3$, while for the former two reactions the catalytic activity was better than $\text{Pt-Rh}/\text{CeO}_2/\text{Al}_2\text{O}_3$. The active catalytic species were proposed to be Pd^0 , Cu^+ and Cu^{2+} (characterized by XPS and FT-IR) formed from the decomposition of the R-P-1 structure and the formation of highly dispersed metallic phases. [132] The initial structure of the R-P-1 oxide was found to affect the nature of dispersion.

4.3 Other Thermochemical Reactions.

In addition to oxidation/reduction catalysis, R-P-1 oxides have also been used in liquid phase reactions, such as phenol hydroxylation [133] and alcohol dehydrogenation [134]. For phenol hydroxylation reactions using hydrogen peroxide, doping the A-site of lanthanum cuprates with Sr or Th ($\text{La}_{2-x}\text{A}_x\text{CuO}_{4+\delta}$ where A = Sr, Th) did not improve the catalytic activity of these oxides, but lowered the conversion because of the promotion of undesired side reactions, such as decomposition of hydrogen peroxide to molecular oxygen. [133, 135] In steam reforming of methanol to CO_2 and H_2 over $\text{La}_2\text{CuO}_{4+\delta}$ catalysts [136], it was found that $\text{La}_2\text{CuO}_{4+\delta}$ nanofibers that had been grown using single-wall carbon nanotube templates showed improved performance at lower temperatures. However it was observed that both the nanofibers and the powder samples were prone to form highly reduced metallic Cu. It is conceivable that the H_2 formed in the reaction would promote this reduction. Thus, it is highly probable that the structural integrity of the R-P-1 oxides was compromised under the reaction conditions and thus, a fair comparison might not be possible.

Table 1: Catalytic applications of selected R-P-1 oxide materials.

Compound	Reaction	Phase	Reactor Type	Reaction Temperature	Catalytically active species
$\text{La}_2\text{Cu}_{1-x}\text{Pd}_x\text{O}_{4+\delta}$ [132]	Reduction of NO	gas	plug flow	150 - 500 $^{\circ}\text{C}$	Pd^0 (dispersed) $\text{Cu}^+/\text{Cu}^{2+}$ in matrix
	Oxidation of CO				
	Oxidation of C_3H_6				
$\text{La}_{1.867}\text{Th}_{0.100}\text{CuO}_{4+\delta}$ [131]	Reduction of NO	gas	quartz microreactor	200-800 $^{\circ}\text{C}$	$\text{Cu}^+/\text{Cu}^{2+}$
$\text{La}_2\text{CuO}_{4+\delta}$ [69]	Oxidation of CO	gas	U shaped microreactor	150 - 650 $^{\circ}\text{C}$	Cu
	Reduction of NO				
$\text{LaSrCoO}_{4+\delta}$ [73]	Oxidation of CO	gas	flow reactor	60 – 600 $^{\circ}\text{C}$	$\text{Co}^{2+}/\text{Co}^{3+}$
	Oxidation of C_3H_8				
$\text{La}_{2-x}\text{Sr}_x\text{CoO}_{4+\delta}$ [137]	Oxidation of CO	gas	flow reactor	60 – 600 $^{\circ}\text{C}$	Co^{3+}
	Oxidation of C_3H_8				
$\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_{4+\delta}$ [1, 138]	Partial oxidation of CH_4	gas	Mixed-conducting membrane	800 - 900 $^{\circ}\text{C}$	-
$\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_{4+\delta}$ [67]	Partial oxidation of CH_4	gas	Mixed-conducting membrane	760 - 900 $^{\circ}\text{C}$	Ni
$\text{La}_2\text{NiO}_{4+\delta}$ [66]	Partial oxidation of CH_4	gas	Tubular fixed-bed membrane	900 $^{\circ}\text{C}$	Ni
$\text{La}_2\text{NiO}_{4+\delta}$ [70]	Decomposition of NO	gas	flow reactor	500 - 900 $^{\circ}\text{C}$	Ni^{2+}
$\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ [139]	Reduction of NO	gas	PFR	380 - 580 $^{\circ}\text{C}$	Ni^{2+}
$\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ [133]	Phenol hydroxylation	liquid	Stirred glass reactor	100 - 190 $^{\circ}\text{C}$	Cu^{2+}
$\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_4$ [68]	Oxidative coupling of CH_4	gas	Quartz flow	800 $^{\circ}\text{C}$	-
$\text{La}_{1.9}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$ or $\text{La}_2\text{NiO}_{4+\delta}$ [126]	Oxidation of propane	gas	Fixed bed flow	300 $^{\circ}\text{C}$	-
La_2CuO_4 [136]	Steam reforming of CH_3OH	liquid	Fixed bed flow	150 $^{\circ}\text{C}$	Cu
La_2CuO_4 [128]	CH_4 oxidation	gas	Fixed bed quartz	672-784 $^{\circ}\text{C}$	$\text{Cu}^{3+}/\text{Cu}^{2+}/\text{Cu}^+$

					or Cu
$\text{La}_{2-x}\text{Rb}_x\text{CuO}_{4+\delta}$ [129]	Oxidation of NO, Oxidation of diesel soot	gas	fixed-bed quartz	200 - 700 $^{\circ}\text{C}$	Cu^{2+}

5. Conclusions and Prospective

This review summarizes important catalytic and electrocatalytic properties of first series ($n = 1$) R-P oxides with a formula of $\text{A}_2\text{BO}_{4+\delta}$. The reported effects of the nature of the A and B sites in these oxides on parameters governing key electrocatalytic properties, namely oxygen surface exchange (k), oxygen diffusion (D), oxygen hyperstoichiometry (δ), electrical and ionic conductivity, are discussed. Literature examples of thermochemical reactions using these oxides and the effect of their chemical composition on their catalytic activity are also reviewed. Literature reports suggest that the method of synthesis plays a key role in the final surface structure of these oxides, consequently affecting their electrocatalytic/catalytic activity. Therefore, development of synthesis techniques that provide control over the surface structure, nanostructure and oxygen hyperstoichiometry of these oxides is critical for tuning their electrocatalytic/catalytic activity.

The review shows that doping the A-site of Ni-based R-P-1 oxides with Sr decreased the oxygen diffusion rates (D); however, no discernible trends for its effect on the surface oxygen exchange rates (k) were found. The lack of trends in the case of k could be due to the inconsistencies in the methods used to synthesize these oxides, resulting in variations in the surface structure, which might have led to the inconsistencies in the surface oxygen exchange trends. On the other hand, electronic conductivity of lanthanum nickelate oxides was shown to improve upon Sr doping. Among other A-site modifications of nickelate oxides discussed, Sm-doped nickelates ($\text{Ln}_{2-x}\text{Sm}_x\text{NiO}_{4+\delta}$ ($\text{Ln} = \text{La}$ ($x=1$), Pr, Sm)), $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$ exhibited promising electrocatalytic properties, however they exhibited limited stability under high temperature SOFC operating conditions. The catalytic performance of Sr-doped lanthanum cobaltates and cuperites was found to be highly composition dependent, while in general lanthanum manganites exhibited poor electrocatalytic properties.

The effects of B-site substitution of R-P-1 oxides on the electrocatalytic activity were also reviewed in detail. Doping of the B-site of lanthanum nickelates with Cu resulted in decreased values of D and k . Doping with less than 10 mol% of Cu ($\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$) was found to enhance the electronic conductivity relative to the undoped oxide ($\text{La}_2\text{NiO}_{4+\delta}$). On the other hand, further increase in Cu doping (> 10 mol%) led to a decrease in electronic conductivity. Contrary to theoretical predictions, experimentally doping the B-site of nickelate oxides with Fe ($\text{La}_2\text{Ni}_{0.8}\text{Fe}_{0.2}\text{O}_{4+\delta}$) led to no significant improvements in oxygen exchange and diffusion rates (k and D , respectively) when compared to the undoped oxides. In the case of doping the B-site of lanthanum nickelates with Al, it was found that the oxygen diffusion process became rate limiting as opposed to the surface exchange. Doping the B-site of lanthanum nickelates with Co ($\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_{4+\delta}$) led to a slight increase in D increased with increased doping, while k was strongly dependent on the amount of doping. A significant variation in the temperature dependence of oxygen diffusivity was observed with variation in Co-content in these oxides. This was attributed to the composition-dependent structural features in $\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_{4+\delta}$ oxides.

R-P-1 oxides have been used to catalyze a number of thermochemical reactions such as oxidation of hydrocarbons, carbon (soot) and H_2S , as well as reduction of NO. It was found that $\text{La}_{1.9}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$ oxides exhibited reasonable activity toward propane oxidation, but the effect of Sr-doping on the catalytic activity of lanthanum nickelates could not be deduced from the limited reported studies. In the case of NO reduction, doping the A-site in $\text{La}_2\text{CuO}_{4+\delta}$ with Th ($\text{La}_{1.867}\text{Th}_{0.100}\text{CuO}_{4+\delta}$) was found to enhance the catalytic activity (conversion of NO to N_2). Catalytic activity of $\text{La}_2\text{CuO}_{4+\delta}$ was also shown to increase via doping the B-site with Rb ($\text{La}_{2-x}\text{Rb}_x\text{CuO}_{4\pm\delta}$) for oxidation of diesel soot. It was found that an increase in Rb doping led to a significant enhancement in the catalytic activity. Oxidation of carbon black using Ln_2CuO_4 ($\text{Ln} = \text{La, Pr, Nd, Sm, Gd}$) has also been studied and the catalytic activity was found to increase with an increase in ionic radius of Ln^{3+} . Several literature reports have suggested that decomposition of R-P-1 oxides can also occur under certain thermochemical reaction conditions. For example, partial decomposition of R-P-1 oxide membranes has been reported to occur and yield B-site metallic nanoparticles that act as the active catalyst for the reaction. This was the case for $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_{4+\delta}$ membrane reactors during methane oxidation, which led to the formation of Ni that acted as the active catalyst. Decomposition of the $\text{La}_2\text{NiO}_{4+\delta}$ membranes was minimized by doping the B-site of $\text{La}_2\text{NiO}_{4+\delta}$ with Co, forming $\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_{4+\delta}$ oxide.

While in this review we have discussed a number of thermochemical reactions where R-P-1 oxides have been used as catalysts, their potential has not been fully explored. Limited in-depth understanding of the impact of composition (A and/or B site) on catalytic performance of R-P-1 oxides exists. The primary focus of the current literature in the area has been to utilize the oxidation state of the B-site transition metal for redox catalysis and limited characterization of the surface structure has been provided. Given the complexity of these oxides, in order to fully explore the effect of the oxidation state of the B-site metal on the catalytic activity, thorough characterization of the surface structure as a function of composition is necessary. Furthermore, decomposition of the R-P-1 oxides under thermochemical conditions has been reported to occur leading to the generation of catalytically active nanostructures. Systematic studies that elucidate the factors that govern this phenomenon under thermochemical conditions are necessary to fully explore the potential of these oxides for thermal-catalytic applications.

Furthermore, while there are a number of studies on the effect of the A- and B-site composition on the catalytic/electrocatalytic properties of R-P-1 oxides, discrepancies among the reported data exist, making it difficult to draw conclusive composition/performance relationships for these oxides. Given the complexity of these oxides, combined experimental/theoretical approaches can be very useful in elucidating the mechanisms that govern their electrocatalytic/catalytic activity for different processes, and developing structure/performance relationships that can guide the design of optimal R-P-1 oxide catalysts and electrocatalysts. Another area that is fairly unexplored is the use of the nanostructure and surface structure of these oxides as a tool to tune their catalytic activity. With the advancements in synthesis techniques, it is now possible to control the nanostructure and surface structure of these oxides in order to enhance their electrocatalytic/catalytic activity. [140]

We would like to also note that in this review we mainly focus on the first series of R-P oxides, due to their wide use in catalytic applications. Higher order ($n > 1$) R-P phase oxides ($\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$), while fairly unexplored, might also be promising materials for catalysis. Although there have been few studies on the higher order R-P

oxides for electrocatalysis, initial results have shown great promise. [100, 141] For example $\text{La}_3\text{Ni}_2\text{O}_{6.95}$ and $\text{La}_4\text{Ni}_3\text{O}_{9.78}$ have been shown to be promising cathode electrocatalysts for intermediate temperature SOFCs. [97]

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