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Oxygen Reduction Kinetics of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ Electrodes for Solid Oxide Fuel Cells

Bo Guan

**Thesis submitted to
Benjamin M. Statler College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
In
Mechanical Engineering**

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Morgantown, West Virginia
2016**

**Keywords: Surface kinetics, $\text{LaNiO}_{4+\delta}$ cathode, electrochemical impedance
spectroscopy**

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Abstract

Oxygen Reduction Kinetics of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ Electrodes for Solid Oxide Fuel Cells

Bo Guan

In the development of intermediate temperature solid oxide fuel cell (IT-SOFC), mixed ionic-electronic conductors (MIEC) have drawn big interests due to their both ionic and electronic species transport which can enlarge the 3-dimension of the cathode network. This thesis presents an investigation of MIEC of Ruddlesden-popper (RP) phases like K_2NiF_4 type $\text{La}_2\text{NiO}_{4+\delta}$ (LNO)-based oxides which have interesting transport, catalytic properties and suitable thermal expansion coefficients. The motivation of this present work is to further understand the fundamental of the effect of Sr doing on the oxygen reduction reaction (ORR) kinetics of LNO cathode.

Porous symmetrical cells of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ($0 \leq x \leq 0.4$) were fabricated and characterized by electrochemical impedance spectroscopy (EIS) in different P_{O_2} from temperature range of 600~800°C. The spectra were analyzed based on the impedance model introduced by Adler et al. The rate determining steps (RDS) for ORR were proposed and the responsible reasons were discussed. The overall polarization resistances of doped samples increase with Sr level. Surface oxygen exchange and bulk ionic diffusion co-control the ORR kinetics. With high Sr content ($x=0.3, 0.4$), oxygen ion transfer resistance between nickelate/electrolyte is observed.

However for porous symmetrical cells it is hard to associate the resistance from EIS directly to each ORR elementary processes because of the difficulty in describing the microstructure of the porous electrode. The dense electrode configuration was adopted in this thesis. By using the dense electrode, the surface area, the thickness of electrode, the interface between electrode and electrolyte and lastly the 3PB are theoretically well-defined. Through this method, there is a good chance to distinguish the contribution of surface exchange from other processes. Dense and thin electrode layers in thickness of ~40 μm are fabricated by using a novel spray modified pressing method. Negligible bulk diffusion resistance is confirmed by parallel experiment and EIS analysis, resulting in exclusive focus on the surface process. It is ambiguously proved that Sr doping impairs the surface kinetics of lanthanum nickelates. The interstitial oxygen is suggested to be the key role when the oxygen incorporation is rat determining. For the first time, a physical model is proposed to illustrate how those interstitial species work to regulate the exchange rate of the incorporation reaction.

To achieve better surface exchange ability on LNO, Mn is chosen as the doping element substituted for Ni with different levels to improve the surface kinetics because Mn is much active both for adsorption process and for incorporation process due to the high state of Mn leading to the high amount of the interstitial oxygen. Mn is found to substantially promote the surface kinetics, showing highest surface exchange coefficient (k) of $1.57 \times 10^{-6} \text{cm/s}$ at 700°C on composition of $\text{La}_{1.8}\text{Sr}_{0.2}\text{Ni}_{0.9}\text{Mn}_{0.1}\text{O}_{4+\delta}$. Such value is ~80% larger than that of the undoped sample, and is one of the highest k among the currently available R-P phase intermediate temperature (IT) cathode

Acknowledgments

I would like to express my sincere appreciation to my supervisor Dr. Xingbo Liu, for providing me with the opportunity to pursue my Master studying. I am truly grateful for his guidance, understanding, patience, and most importantly, his encouragement during my research. Through him, my mind was opened to wider fields and I become a qualified candidate who can handle critical comments with careful respect.

I would also like to thank the rest of my thesis committee, Dr. Xueyan Song and Dr. Hui Zhang for their mentoring and assistance in experimental and discussions.

I also thank all my group members, Dr. Greg Collins, Meng Yao, Xinxin Zhang, Jianhua Yan, Shanshan Hu, Nan Zhang, He Qi and Jiang Chang, for their assistance in experimental and discussion. I also want to thank Tao Yang for his generous and knowledgeable suggestions. I appreciate that I can get help from all of them and I am very happy we can have a memorable happy time.

Specially thank my husband Wen Yuan Li for his support, care, and encouragement during my graduate study and daily life. Thank my parents for their unconditional love.

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List of Abbreviation

3PB	Three-phase boundary
2PB	Two-phase boundary
ECR	Electrical conductivity relaxation
EIS	Electrochemical impedance spectroscopy
GDC	$\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$
LSM	$(\text{LaSr})\text{MnO}_{3\pm\delta}$
LSGM	$(\text{LaSr})(\text{GaMg})\text{O}_{3-\delta}$
LSCF	$(\text{LaSr})(\text{CoFe})\text{O}_3$
LNO	$\text{LaNiO}_{4+\delta}$
LSNO	$\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$
MIEC	Mixed ion and electron conductor
ORR	Oxygen reduction reaction
RDS	Rate determining step
IT-SOFC	Intermediate temperature solid oxide fuel cell
TEC	Thermal expansion coefficient
YSZ	Yttrium stabilized zirconia
C	Capacitance
c	Concentration
D	Chemical diffusion coefficient
e	Electron change
E_a	Activation energy
f_0	Characteristic frequency
F	Faraday constant
k	Surface exchange coefficient
k_B	Boltzmann constant
n	Reaction order
O_i''	Interstitial oxygen
P_{O_2}	Oxygen partial pressure
R	Reaction rate
R_p	Polarization resistance
$V_O^{\bullet\bullet}$	Oxygen vacancy
σ	Conductivity

Chapter 1: Introduction and Research Objectives

As electrochemical devices converting chemical energy of fuel directly into electrical energy, solid oxide fuel cell (SOFC) has been drawing increasing interest because its high energy conversion efficiency. During operation, in the cathode side oxygen from air is flowed as an oxidant and in the anode side hydrogen or hydrocarbons are used as fuel and the solid electrolyte transports O^{2-} ions from the cathode to anode side. However, the high operating temperature $\sim 1000^\circ\text{C}$ leads to undesired reaction and harms the long-term stability. These difficulties lead researchers changing their interests to intermediate temperature (500~800°C) SOFC (IT-SOFC), and lowering the operation temperature has become one of the main SOFC research goals.[1-3] Nevertheless the lower operating temperature leads to poor oxygen reduction reaction kinetics with the conventional cathode materials, e.g. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM). In this regard, mixed ionic and electronic conducting (MIEC) materials which have high catalytic activity at lower temperature become potential candidate as cathode electrodes for IT-SOFCs. MIEC are not only active catalysts for surface ORR but also allow substantial interstitial oxygen or vacancy in their bulk which can enlarge the 3-dimension of the cathode network. Recently, one kind of MIEC materials in Ruddlesden-popper (RP) phases [4-6] like K_2NiF_4 type $\text{La}_2\text{NiO}_{4+x}$ (LNO)-based oxides with higher oxygen ionic conductivity than conventional LaCoO_3 based perovskite such as $(\text{LaSr})(\text{CoFe})\text{O}_{3-x}$ (LSCF), have also been proposed as possible candidates and are chosen as research subject for this thesis.

1.1 SOFCs cathode

For the SOFC with ionic conductive electrolyte, oxygen reduction reaction occurs by accepting electrons from the external circuit at the cathode side, and then the fuel is catalytically oxidized at anode by the oxygen transported through electrolyte. The overall reaction can be written by Kroger-Vink notation as:

For SOFC cathode materials, some requirement can be written as following:[7-9]

- (1) Catalytic activity is high enough for oxygen reduction reaction.

- (2) Chemical stability and no interaction with electrolyte.
- (3) Sufficient conductivity both for electronic transport and ionic.
- (4) Thermal expansion coefficient (TEC) matching with other cell components

Platinum and some other noble metals were used in the early days. Then the perovskites type $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ has been studied as a traditional cathode materials for SOFC because of its good compatibility with conventional electrolyte yttrium-stabilized zirconia ($\text{Y}_{0.16}\text{Zr}_{0.92}\text{O}_{2.08}$, YSZ) and the considerable electronic conductivity.[10, 11] These kinds of materials can be written as ABO_3 and shown in Fig. 1.1. Although for ideal perovskite the relation of the radius between different ions should satisfy Goldschmidt factor $t = r_A + r_O / \sqrt{2}(r_B + r_O)$, the real structures of materials are easily distorted and deviate from the ideal model. LSM has very satisfactory oxygen surface exchange coefficient (k) but poor oxygen diffusion coefficient (D) because its poor ionic conductivity which leads to the oxygen reduction reaction in LSM mainly occurs at triple phase boundary (TPB) area and this would result in sluggish oxygen diffusion rate. Although LSM shows good electronic conductivity, the poor oxygen ionic conductivity and the necessity of high operation temperature because Mn^{4+} is too stable to create oxygen vacancies in the lattice at intermediate temperature determine it out of fashion for IT-SOFCs.

Fig. 1.1 schematic ABO_3 perovskite structure.

MIEC is more popularly because the oxygen diffusion of MIEC is enhanced due to the high ionic conductivity and the large amount of oxygen vacancies compare to LSM.[12, 13] The perovskite structure $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-x}$ (LSC) is earliest found as the MIEC material which has considerable high oxygen diffusivity because of the large amount of oxygen

vacancies. The LSC cathode has poor chemical stability with YSZ because it reacts with YSZ to create an insulation phase, for example, $\text{La}_2\text{Zr}_2\text{O}_7$ or SrZrO_3 at high temperatures. Fortunately new electrolyte materials can be used between YSZ and LSC as the barrier layer like Ceria-based electrolyte (Gadolinia-doped ceria, $\text{Ga}_{0.1}\text{Ce}_{0.9}\text{O}_{2-x}$, GDC) and LaGaO₃-based electrolyte ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-x}$, LSGM). However the thermal expansion coefficient (TEC) of LSC ($\sim 22 \times 10^{-6} \text{K}^{-1}$) is too high to match the electrolytes YSZ ($\sim 11 \times 10^{-6} \text{K}^{-1}$) or GDC ($\sim 14 \times 10^{-6} \text{K}^{-1}$) which would lead to the big crack at the interface between LSCF and YSZ when sintering them together at high temperature even though LSC has good chemical stability with GDC. Partial substitution of Fe for Co to form LSCF perovskite cathode lowers the TEC of LSC down to 14 to $16 \times 10^{-6} \text{K}^{-1}$. Meanwhile, the chemical stability of LSCF is enhanced by the substitution compare to LSC[14].

Another class MIEC materials which present double perovskite structure having the general formula $\text{AA}'\text{B}_2\text{O}_{5+x}$ as shown in Fig. 1.2 has been proposed and used as cathode electrode, where A is the rare earth metal and A' is alkaline metal, Co and Mn transition metals are on the B site. These two elements occupy the A site in order due to the big difference between the rare earth metal radius and alkaline metal radius, along c axis layout in $[\text{BO}_2]\text{-}[\text{A}'\text{O}]\text{-}[\text{BO}_2]\text{-}[\text{AO}_x]$ orders.[15, 16] This kind of materials have very excellent oxygen diffusion coefficients at intermediate temperature, and are well-known catalysts with high activity where the activation of oxygen by dissociation into reactive species is a key part of the catalyst function.[17, 18] However the stability of these materials are not satisfied because at 503°C the structure has ordered to disordered transition.[19] Fortunately some rare earth like Niobium substitution has been used effectively to improve stability of the highly oxygen permeable cubic perovskite structure.[20] Deng reported the evaluation of the cubic B site cation-ordered composition $\text{Ba}_2\text{CoMo}_{0.5}\text{Nb}_{0.5}\text{O}_{6-\delta}$ with a mixed Co charge state stabilized by a combination of Mo and Nb doping as a new mixed conductor.[21]

Fig. 1.2 schematic $AA'B_2O_{5+x}$ double perovskite phase structure [15]

1.2 Ruddlesden-Popper phase cathode

In recent years besides the perovskite and double perovskite type MIEC, the Ruddlesden-Popper phase (R-P) structure lanthanum nickelates family has been brought forth as new cathode alternatives due to their high ionic conductivity and surface reaction kinetics[22-25] to promote the relatively sluggish ORR kinetics after lowering operating temperature from 800~1000°C to IT region (600~800°C). The lattice structure of LNO is composed of perovskite layers alternating with La_2O_2 rock salt layers. Oxygen hyperstoichiometry is observed and associated to the incorporation of oxygen into the interstitial sites of La_2O_2 layers, whose amount depends on the composition, structure, heat treatment history and etc.[30-33]. Such materials exist over a broad range of oxygen nonstoichiometry and that its structural, electric, and magnetic properties are very sensitive to the amount of oxygen contents. Oxygen hyperstoichiometry is confirmed and associated to the incorporation of oxygen atoms into the interstitial sites of LaO layers. La and/or Ni site element substitution have been used to tailor the materials in attempt to improving certain physical parameters, such as the surface exchange, bulk diffusion coefficients and electrical conductivity. The mobility of oxygen in oxides with LNO structure has been studied using a number of theoretical theorems.

Fig. 1.3 schematic A_2BO_{4+x} RP phase structure

Compared to the popular Co-based perovskite $(LaSr)(CoFe)O_{3-\delta}$ (LSCF), nickelates display smaller thermal expansion coefficient and lower volatility so as to offers the advantages in structure compatibility with current IT electrolytes, such as $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) and $(LaSr)(GaMg)O_{3-\delta}$ (LSGM), and chemical stability during long-term operation.^[14-16] Such layered structure is able to accommodate a wide range of oxygen stoichiometry from significant excess to deficient. This feature provides a broad freedom to engineer those compounds in terms of chemical diffusion (D), surface oxygen exchange coefficients (k), electrical conductivity and so on to meet application requirement.^[17-19] As a result of the major progress in R-P phase cathode development, encouraging performances have been achieved in several groups with various compositions, such as $Nd_2NiO_{4+\delta}$, $(LaPr)_2NiO_{4+\delta}$, $La_2(NiCo)O_{4+\delta}$, and etc.^[20-24] Owing to the good balance between catalytic activity and chemical stability, $La_2NiO_{4+\delta}$ (LNO) stands out as a promising candidate to fulfill the near future application most possibly.^[19, 21] Considering the relatively high electronic and ionic conductivities, good electro-catalytic properties and compatible thermal expansion coefficient with commonly used electrolytes, Lanthanum nickelates with R-P structure has been chosen as cathode materials for this thesis.

1.3 Dense electrode EIS

Porous electrode symmetrical cells are usually characterized by electrochemical impedance spectroscopy. Different impedance arc presents different ORR process. However, it is hard to distinguish each process accurately for porous electrode cells from

EIS directly due to the complex nature of the polarization resistance which includes influence from material composition, bulk diffusion, surface exchange as well as microstructure. Thus the dense electrode/electrolyte/dense electrode sandwich configuration was adopted in this thesis even though in practice porous electrode is chosen over the dense electrode.

In the ideal condition for dense electrode is that the resistance from surface exchange is the same for electrodes with different thickness, the contribution from bulk diffusion and surface exchange can be distinguished by plotting the polarization resistance with the thickness. The intercept with y-axis will be the contributions from surface and interface exchange, and the slope of the straight line characterizes the ionic bulk diffusion resistance. Besides, by using the specific EIS fitting circuit, the ionic conductivity and chemical capacitance can be derived from the spectra, which can lend us credit after comparing those values with known parameters reported in the literature. On the other hand, a porous LNO layer was added onto the surface of some dense electrode cells to decrease the surface exchange resistance. Through this method, the validity of the attribution we did based on dense electrode alone can be double checked. And any newly present EIS spectra will be analyzed based on the known macro-parameters.

By using the dense electrode, the surface area, the thickness of electrode, the interface between electrode and electrolyte and lastly the 3PB are theoretically well-defined. Through this method, there is a good chance to distinguish the contribution from surface exchange, ionic and electronic bulk transport and ion interface exchange.

1.4 Objectives of this work

Oxygen reduction at the cathode is considered as the main rate limiting factor in the performance of the whole operating system. Fundamental studies of the ORR mechanisms are important and necessary. The motivation of this thesis is to further understand the fundamental of the ORR kinetics of LNO cathode.

- (1) The overall ORR and main rate determining steps of LSNO needs to be determined by EIS testing.
- (2) Due to the surface process is more complicated compared to bulk characterization; the surface kinetics investigation of LSNO on symmetric cells with simple geometry will be studied.
- (3) With the fundamental understanding of surface kinetics, the performance improvement will be attempted by the active element substituted.

Chapter 2: Experimental methods

2.1 Fabrication cathode materials by Sol-Gel synthesis

The investigated powders were synthesized by EDTA-citric Sol-Gel method. Stoichiometric nitrates (Alfa Aesar or Acros Organics) together with citric acid (Alfa Aesar) were dissolved into distilled water separately. EDTA powders (Fisher Scientific) as complexant was dissolved into diluted ammonia water (the mole ratio of metal cation: citric acid: EDTA = 1:1.5:1). The solutions above were mixed together followed by adjusting PH to 8, then held at $\sim 80^{\circ}\text{C}$ and stirred until gelation. The gel was heated to 600°C to decompose nitrates and organic residual. The resultant powders were sintered in air at 1000°C for 4h and examined by X-ray diffraction (XRD, PANalytical X'pert PRO, Cu K α radiation) to check phase purity.

2.2 Fabrication dense double layers by modified spray -pressed

The resultant powders along with polyvinyl butyral (PVB) and fish oil at the weight ratio of 100:2:1.5 was added into ethanol (5 g powders to 30mL ethanol), then ball-milled for 24 h to produce suspension which was air-brushed onto both sides of electrolyte to fabricate thin layer. In brief, the electrolyte in 1.5g was dry pressed under 50MPa in a 16.5 mm die. The suspension was evenly sprayed to electrolyte surface, followed by an intermediate pressing of 200MPa. The sample was taken out and inserted back to the die with the uncoated surface facing outside this time. The spray process was repeated, followed by a final pressing at 300MPa. Electrode/electrolyte/electrode sandwiches were sintered to 1300°C 4 h for densification. In order to avoid any possible element-enrichment in the surface, the sintered pellets were polished manually using grind paper then 2 μm polishing cloth. The removed thickness for each sample could not be precisely controlled, but was estimated in the range of 30~70 μm after inspection by scanning electron microscopy (SEM, Hitachi S-4700F), depending on individual samples.

2.3 Fabrication symmetrical cells

To make the cathode slurry, the as-prepared powders were blended with an ink vehicle (Fuel Cell Materials Co.) at the weight ratio of powders:vehicle=10:11, then ground in a mortar until homogeneous slurry was formed. Gadolinia-doped ceria ($\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$, GDC, from Fuel Cell Materials Co.) slurry was produced in the same method and screen-printed to both sides of the sintered yttria-stabilized zirconia ($\text{Y}_{0.16}\text{Zr}_{0.92}\text{O}_{2.08}$, YSZ, from NextechCo.) pellets as buffer layer, followed by sintering at 1350°C for 3h. Afterward, the cathode slurry was screen-printed symmetrically onto the GDC layer with an area of 0.7cm^2 , followed by sintering at 1050°C for 2h. Pt mesh was attached onto the cathode by Pt paste as the current collector.

2.4 Characterization

The X-ray diffraction (XRD, PANalyticalX'pert PRO and Bruker AXS, Cu K α radiation) test is conducted to examine purity of phase. To analyze XRD spectra commercial software Jade 5 is used.

The conductivity testing is tested by Van der pauw or 4-probe DC methods. Electrolyte or anode pellets for conductivity tested were dry pressed using dies with different diameters followed by sintering at different temperatures. Four silver wires were bonded to the surface of samples using silver paste symmetrically, followed by heating to 850 °C. The measurement was carried out in a temperature-programed tube furnace. The gas composition was controlled by mass flow controller. The electrical conductivity data was collected using Keithley, with sourcing current of 10 mA and monitoring the voltage.

The electrochemical performance is characterized by electrochemical impedance spectroscopy (EIS) through solartron 1286&1260 or Autolab Model. EIS characterization was conducted on those symmetric cells in 4 different P_{O_2} ($\log(P_{\text{O}_2}/\text{atm})=-0.678, -1, -1.5, -2$) atmospheres by Solartron 1287 electrochemical interface and 1260 impedance analyzer at open circuit condition (OCV) over the frequency range from 0.1 Hz to 1 MHz. The

designed P_{O_2} was produced by mixing air with N_2 controlled via mass flow meters (Alicat Scientific). An AC perturbation signal of 20 mV was applied in each measurement. The resulting spectra were deconvoluted using Z-view software.

Scanning electron microscopy (SEM, JEOL JSM-7600F) is used to observe the microstructure of samples.

Chapter 3: Investigation of Sr-doped LNO on porous symmetrical cells

In this chapter, porous symmetrical cells of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ($0 \leq x \leq 0.4$) (LSNO) were fabricated by sol-gel method. To further clarify the effect of Sr doping on the electrode performance of LNO cathode, or more specifically, how it affects the bulk diffusion and surface exchange kinetics in the cathode ORR, LSNO cathode are characterized by EIS in different P_{O_2} in temperature range of 600~800°C. The spectra were analyzed based on the impedance model introduced by Adler et al. The rate limiting steps for ORR were proposed and the responsible reasons were discussed.

3.1 Characterization of basic physic properties of different candidates

Fig. 3.1 XRD patterns for $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ($x=0, 0.1, 0.2, 0.3, 0.4$) samples.

Fig. 3.1 shows the XRD spectra from the powder samples of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ($x=0, 0.1, 0.2, 0.3, 0.4$). Each pattern matches the K_2NiF_4 structure, indicating pure R-P phase is obtained for all nickelate samples in this study.

Fig. 2 shows the electrical conductivities of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$. Sr doping enhanced the conductivity regardless of the doping level. The highest one is achieved with Sr10. But

with heavier doping, the conductivity decreases gradually, which is different from the results reported by Nakamura[37] that the conductivity increased with Sr content. Although sintered at 1450°C, the pellets are still not completely dense. The relative density is determined by Archimedes method: 95.7% for LNO, 94.2% for Sr10, 93.6% for Sr20, 92.7% for Sr30, 91.9% for Sr40. Therefore, the difference shown in this work should be partially from the relative density. From 600 to 800°C, the conductivity decreases with temperature, which is more significant for LNO, Sr10 and Sr20 compared to Sr30 and Sr40. It primarily results from the reduction of electron hole density, accompanying by the decrease of δ as temperature increases.[37-40]

Fig. 3.2 Electrical conductivities for $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ tested in air.

Fig. 3a shows the cross-section of the LNO electrode. GDC is inserted between cathode and YSZ electrolyte to promote the performance. The typical thickness of the cathode layer is ~20 μm . Shown in Fig. 2b-f are the interfaces of GDC/nickelates. The bond between GDC and nickelate is good in each sample. The average particle size is round 0.4 μm for LNO, and roughly 0.7, 0.7, 0.5, 0.4 μm for Sr10, 20, 30 and 40, respectively.

Fig. 3.3 Cross-section view of Sr10 electrode (a), and the nickelates/GDC interface: LNO (b), Sr10 (c), Sr20 (d), Sr30 (e) and Sr40 (f).

3.2 Decreased performance upon Sr doping and the co-limited electrode process

Fig. 3.4 shows the EIS profiles for those samples measured in air at 700°C. The spectra were analyzed based on the impedance model introduced by Adler et al.[41, 42]. The ohmic resistances have been subtracted. The spectrum for LNO features half tear shape, showing a 45° straight line at high frequency (HF) and a semi-circle in the low frequency

(LF) domain. Straight line at HF limit as such is a prominent indicator of diffusion limitation. And the half tear-shaped spectrum is usually assigned to the Gerischer impedance depicting a situation controlled by a chemical reaction and the subsequent mass diffusion.[43, 44]

Fig. 3.4 EIS spectra for different nickelates at 700°C in various P_{O_2} .

Rooting in this Gerischer element, Adler et al.[41] built a model (referred as ALS model) to describe the impedance response of a porous MIEC electrode with an extended active zone with details including polarization resistance, chemical capacity, characteristic length and etc. Judged by the reported high D and k values for LNO and the spectrum feature observed here,[27, 45] it is suggested that the electrode process could be co-limited by surface exchange and diffusion in LNO cathode. LNO spectrum is then fitted by the ALS model. Likewise, for Sr doped samples similar half tear-shaped profiles can be seen in Fig. 3.4, but with the slope of the HF straight line decreased and the LF part arc more

suppressed. It is noted that for Sr30 and Sr40, an additional small arc appears and overlaps with the straight line at the HF limit, which can be found more easily in the corresponding Bode plot in Fig. 4a, with two peaks occurring at $\sim 10^4$ Hz and between 10~100 Hz.

Fig. 3.5 Bode plot for Sr30 (a), and ALS fitting for LNO (b) and Sr30 (c).

Eqs.3-1 and 3-2 express the impedance and capacitance of the co-limited chemical processes in the ALS model, inclusive of the surface and bulk diffusion contributions.

$$Z(\omega) = \frac{R_{\text{chem}}}{\sqrt{1+(j\omega t_{\text{chem}})^{\alpha}}} \quad (3-1)$$

$$C_{\text{chem}} = \frac{t_{\text{chem}}}{R_{\text{chem}}} \quad (3-2)$$

R_{chem} is the resistance of chemical contribution to the cell impedance, t_{chem} the characteristic relaxation time related to the solid state diffusion and oxygen surface exchange, C_{chem} the capacitance associated with the change of oxygen stoichiometry in the MIEC. A parameter, α , is adopted here to account for the non-ideal behavior as shown in Sr doped samples. Such practice has been found more applicable for accurate fitting and the concept has been addressed by Boukamp et al.[43, 46-48] Besides, for Sr30 and Sr40 at

600~700°C, a RC element is added in series to the ALS impedance to represent the HF arc response at shown in Fig. 4a. At higher temperature where the HF arc disappears most probably due to the large thermal-activated improvement in interface exchange rate, satisfactory fitting can be obtained using the ALS element alone. As examples, the fitting spectra of LNO, Sr30 in air at 700 °C and the related equivalent circuits are shown in Fig. 4b and c, respectively.

Table 3-1 Summary of resistances, capacitances, characteristic frequencies from ALS fitting.

T=700°C	Total R (Ωcm^2)	O ²⁻ transfer nickelates/GDC			chem process		
		$R_{\text{IT}}(\Omega\text{cm}^2)$	C (mF/cm ²)	(Hz)	$R_{\text{chem}}(\Omega\text{cm}^2)$	$C_{\text{chem}}(\text{mF/cm}^2)$	α
LNO	0.41	-	-	-	0.41	14.1	0.96
Sr10	0.61	-	-	-	0.61	15.9	0.90
Sr20	1.74	-	-	-	1.74	2.1	0.80
Sr30	8.1	0.83	0.011	13000	7.3	0.20	0.90
Sr40	14.4	1.92	0.091	5400	12.5	0.15	0.88

The measured polarization resistances (R_p) and fitting results for all samples at 700°C are tabulated in Table 3-1. The best performance is obtained with the undoped LNO sample, which reads 0.41 Ωcm^2 and is a competitive output for the intermediate temperature cathodes at 700 °C.[44, 49] The polarization resistance increases with doping level. Those results are consistent with the ones reported by Aguadero et al.[50] According to the fitting results, the small capacitances and the large characteristic frequencies for the HF arcs of Sr30 and Sr40 indicate that those arcs can be reasonably associated to a charge transfer process.[51-53] The incorporation of oxygen into cathode lattice has been taken into account in the ALS element. Meanwhile, the electron transfer from current collector to the cathode must not be the case because Sr30 and Sr40 possess higher electrical conductivities than LNO.[37] In fact, a similar situation has been found on the LSCF electrode: a small HF arc was observed when replacing GDC with the less conductive electrolyte YSZ, and attributed to the slowed oxygen exchange rate between LSCF and

YSZ.[54] Such arcs herein are therefore assigned to the oxygen ion transfer process between lanthanum nickelates/GDC. The occurrence of such arcs should be determined by the transfer rate in the interface and attributed to the decrease of oxygen diffusivity of the Sr doped cathodes, since GDC barrier layer is the same in each sample from LNO to Sr40.

The chemical capacitance in Table 3-1 stems from the change of oxygen content in the oxide cathode when experiencing potential vibration during EIS testing. Because oxidation/reduction of those nickelates is accompanied by the increase/decrease of compensating holes, the variation of oxygen stoichiometry, without violating the electro-neutrality, can be significant, thereby leading to considerable capacitance.[55] More specifically in the porous electrodes, it is literally determined by the microstructure, a thermodynamic factor (f) representing how facile the stoichiometry changes with P_{O_2} and a characteristic length ($l_\delta \propto \frac{D}{k}$) describing how far the active reaction zone stretches away from the cathode/GDC interface ($C_{chem} \propto \frac{l_\delta}{f}$). [55] This capacitance can be used as an indicator, showing whether the electrode bulk is active or not. The evolution of such capacitance under P_{O_2} change is shown in Fig. 5. For each single sample, the capacitance increases with decreasing P_{O_2} , 57mF/cm² for LNO at 1% O₂. It is found in a variety of composition and transport studies of lanthanum nickelates that the ionic conductivity or D displays a dependence of $\sim 1/6$ to P_{O_2} , [25, 40, 56] whereas the surface reaction processes in general exhibit greater dependency on P_{O_2} , such as a reaction order of 1 for the adsorption process. In this case, lowering P_{O_2} could diminish surface kinetics more substantially than the diffusion process, resulting in a bigger l_δ . Meanwhile, Vashook et al. [38] found that the oxygen stoichiometry of La_{2-x}Sr_xNiO₄ varies more facilely with reducing P_{O_2} , leading to a reduced f at lowered P_{O_2} . The same was also confirmed by Kim et al. through the impedance studies of thin film LNO. [57] Consequently, the resultant C_{chem} is expected to enlarge with decreasing P_{O_2} , which is consistent with the results shown in Fig. 5. The different values for C_{chem} between those doped samples hinge on the influence of Sr doping on the amount of interstitial oxygen. The change of oxygen stoichiometry with P_{O_2} (or the equivalent P_{O_2} from applied potential in EIS) in lanthanum nickelates is reported to turn harder rapidly with reducing δ after Sr doping, and almost keeps unchanged in Sr40 sample

which possesses little excess oxygen ($\delta=0\sim0.05$) when measured in the similar conditions as in this work.[58] Such tendency would lead to diminished C_{chem} . However, it is noteworthy that the measured C_{chem} could otherwise come from the surface adsorbents when the bulk stoichiometry change turns hard, as will be discussed below.

Table 3-2. Estimated characteristic lengths in the bulk.

		600 °C	650 °C	700 °C	750 °C	800 °C
$l_{\delta}(\mu\text{m})$	LNO	7.8	5.7	3.3	3.2	2.1
at 0.21 atm	Sr10	6.8	4.9	3.8	2.6	1.9
$l_{\delta}(\mu\text{m})$	LNO	11.2	9.1	7	5.2	3.8
at 0.01 atm	Sr10	10	7.5	5.7	4.3	3.2
$f(0.21 \text{ atm})$		900	788	675	563	450
$f(0.01 \text{ atm})$		500	425	350	275	200

f is averaged over the values from Ref. 37 and 41.

Based on C_{chem} in this work, and estimated f values from those for LNO reported by Kim and Jeon,[25, 57] the characteristic lengths can be calculated using Eq. 3,[55] (note: f from Adler's work has a different form from those in Ref [25, 57]. Simple mathematical conversion yields $f(\text{Adler})=0.5f(\text{Kim})$ for R-P phase lanthanum nickelates)

$$l_{\delta} = \frac{RT}{4F} \frac{C_{\text{chem}} V_m f}{(1-\varepsilon)} \quad (3-3)$$

Where V_m is the mole volume of the nickelate and ε is the porosity of electrode (roughly estimated as 0.3 from the SEM pictures), R , F and T remain the usual physical meanings.

l_{δ} for LNO under P_{O_2} 0.21 and 0.01atm are summarized in Table 3-2. f values used in the calculation are listed as well (f in the table is $\frac{1}{2}$ of its original value in Kim and Jeon's work). The characteristic length at 700 °C is 1.7 μm in air, comparable to the typical MIEC cathode (LaSr)CoO₃ with $l_{\delta}= 2 \mu\text{m}$ at the similar condition.[41] Lowering P_{O_2} increases l_{δ} , just as analyzed above on the basis of the different dependencies for D and k to

P_{O_2} . f for the doped nickelates is not available in the literature so far. In addition, related stoichiometry measurements by different authors scatter to some extent,[38, 58] making approximation of f from stoichiometry data and the resultant l_δ unreliable. As a rough estimation, l_δ for Sr10 are directly computed using the same f from LNO. The accurate lengths for this sample should be larger than the calculated ones listed in Table II, given that f for Sr10 are actually bigger than those for LNO. Those significant bulk active lengths in Table II work to justify our earlier supposition on the reaction & diffusion co-limiting nature and the use of ALS model for EIS fitting. Since the difference of such thermodynamic factor between doped samples and LNO baseline becomes progressively larger with increasing doping level, it is not instructive to use the same f on the heavier doped samples. l_δ for Sr20-40 are left out in the table.

Figure 3.6 The evolution of chemical capacitance with P_{O_2} at 700°C.

Generally speaking, the magnitude of C_{chem} for the end members Sr30 and Sr40 in Fig. 3.6 are not necessarily greater than those measured from TPB-controlling cathodes. However, as reported by Lu et al.[59] in the continuation work on the original ALS model, those ALS spectra for Sr30 and Sr40 can also be fulfilled by considering the parallel surface transport path when the cathode materials display relatively poor bulk transport coefficients. In this case, C_{chem} originated from the surface adsorbents can be orders of magnitude lower compared to the bulk-related ones.

Given Sr doping decreases D value, the occurrence of the extended active bulk in LNO and Sr10, which is essentially determined by the ratio of D/k , implies that k is also reduced upon 5% A site Sr doping. But for the heavier doping levels, without any specific f values or other relevant information, the magnitude of l_δ and the change of it towards Sr cannot be presented quantitatively. Nevertheless, a speculation based on limited wisdom on EIS profiles from independent results in literature may be made to illustrate the change of surface kinetics qualitatively on those materials. For Sr20-40 samples, the spectra all consist of a straight line in the high frequency limit. As stated before and from a variety of EIS studies on cathodes, such straight line almost always coincides with a diffusion limitation in a significant diffusion length,[42, 43, 60, 61] and sometimes is even referred to as the high frequency Warburg response directly. More specifically, in the theoretical treatment of the Gerischer-type impedance on porous electrodes, Nielsen et al.[44] showed that the appearance of such impedance requires the co-existence of the surface oxygen reaction and diffusion processes in the thick porous cathode model, or in other words a decent l_δ . When those two contributions are off-balanced and one process is vastly superior to the other, e.g. the bulk diffusion process being much faster, the whole electrode is active and the spectrum will deviate from the half tear shape and reduce to a single arc in the limiting case. On the other hand, if we assume the surface reaction is greatly better, l_δ would shrink substantially. This would turn the electrolyte/electrode interface into the primary reaction area where the spillover mechanism near 3PB takes place and shortcuts the significant bulk/surface diffusion pathway. On this occasion, the suppressed arc instead of the half-tear shaped spectrum will also be expected, which has usually been confirmed in most 3PB limited electrodes like LSM.[51] In view of those implications of the Gerischer behavior, it seems that D and k are most possibly well balanced also in those Sr20-40 specimens. k is progressively reduced by Sr doping as D is. In this sense, for all Sr doping samples, the relative importance of surface exchange and bulk/surface diffusion to the overall performance may be essentially similar to each other by adjusting l_δ . It is thus suggested that sacrificing D to improve k through Sr doping, even if one could, may not effectively enhance the performance because neither of them is the sole determining factor.

3.3 Reaction order and surface limiting steps

The RLS in surface exchange is investigated through the P_{O_2} -dependent polarization resistance. The reaction orders (n) in the relationship of $1/R \propto P_{O_2}^n$ for the electrode process fall into 1/3 to 1/2 for all cathodes as shown in Fig. 3.7a-c.

Figure 3.7: Reaction orders from the overall polarization resistances for nickelates: LNO (a), Sr10 (b), Sr20 (c), Sr30 (d) and Sr40 (e).

Due to the polarization resistances consists of surface and bulk contributions, the related n is influenced by both of them. The P_{O_2} dependency for the diffusion contribution is determined by the variation of D (or δ) towards the change of P_{O_2} . As stated before, D (or δ) is reported to depend on P_{O_2} by a factor around or less than 1/6.[56, 62] Therefore, oxygen dependency from the surface exchange reaction part needs to be over 1/2 to yield the measured values of 1/3~1/2.

The surface exchange process is carried out in several sequent steps as shown above. The reaction orders are calculated using the routine reported elsewhere by Heuveln et al.[51, 63, 64] and listed after each elementary reaction. Burriel et al.[65] observed that the surface exchange reaction was 2 orders of magnitude faster in a-b plane than along c-axis in the (001)-oriented epitaxial LNO thin film. As a result, for those specimens with apparent excessive oxygen such as LNO and Sr10, interstitial vacancy in LaO layer instead of oxygen vacancy in ABO_3 layer is taken as the primary active species, as shown in step 3. Since the amount of excessive oxygen decreases with Sr doping, for the end members with little oxygen hyper-stoichiometry like Sr40, oxygen vacancies in perovskite layer might also come to play as active sites. Therefore, besides through interstitial insertion, the incorporation step can proceed via the lattice oxygen vacancies as shown in step 3' as well.

It needs to be mentioned that in the reaction order derivation, the activity of interstitial oxygen in step 3 is taken to be independent to P_{O_2} for simplicity, which in fact changes more or less with P_{O_2} in those lanthanum nickelates. However, how to formulate this effect into the reaction order equations has not been addressed in literature so far. We tentatively believe that one solution could be using the O_2 -dependent form of the activity for O_i'' , and meanwhile separating the total overpotential into different parts consumed by

surface exchange (ΔE_1), bulk diffusion (ΔE_2) and interface exchange (ΔE_3) respectively, in order to meet the Nernst equation $E = E_0 + \frac{RT}{4F} \ln P_{O_2}$ for the overall reaction. As $\Delta E_1 \leq \Delta E$ in magnitude, the dependency on P_{O_2} from potential activation effect is actually less than 1/8. After adding the 1/6 O_2 -dependency for O_i'' into it in step 3, the net reaction order, 7/24 in maximum, is still much less than 1/2. As for step 3', since the activity of $O_o^\times$ shows a negative dependence on P_{O_2} , the reaction order is actually less than 1/8. It is thus clear that among those four steps the surface dissociative adsorption is the main contribution in the surface exchange process.

Oxygen adsorption in perovskites is generally believed to be facilitated by the interaction between oxygen molecule and the transition metal at B site.[66] The importance of the transition metal would also largely retain in the K_2NiF_4 structure given the nearest surrounding of such element is the same as that in perovskite. For example, the surface exchange rate of LNO is found to increase about 1 order of magnitude after 10% Co substitution of Ni, accompanied by a largely decreased activation energy,[67] suggesting the dissociative adsorption ability of the $A_2BO_{4+\delta}$ structure heavily depends on the nature of B site element. For lanthanum nickelates, the charge compensation for Sr doping is realized by loss of interstitial oxygen and oxidation of Ni^{2+} . [27, 37] Increased oxidation state from Ni^{2+} to Ni^{3+} as well as the resultant increased oxygen adsorption energy as Sr doping is reported recently by Lee et al. in the thin film $(LaSr)_2NiO_{4+\delta}$ study.[68] The surface exchange rate is found to decrease with Sr. It hence can be concluded that Sr doping diminishes the surface dissociative adsorption activity by increase the oxidation state of Ni.

The fact that dissociative adsorption process is the main contribution to the surface exchange resistance cannot preclude the possibility of influence from other elementary step. Anisotropic kinetics is observed on surface exchange for such materials in a few of studies as mentioned above. However, among those elementary steps, the incorporation process could be most different along a-axis (100) compared to c-axis (001), since adsorption is processed by the same Ni ions in both cases. It implies that although the incorporation process in a-b plane is truly much faster than that proceeding along c-axis, it could be no faster than other elementary steps in some cases; otherwise the rate for the overall reaction cannot be substantially altered by changing surface orientation. Such incorporation in a-b

plane displayed in step 3 is related directly to the activity of O_i'' which in turn is largely determined by Sr doping. As a result, Sr doping would likely affect the incorporation process also. As we can see, the reaction orders in Fig. 6a and b increase with temperature for LNO and Sr10. Because the interstitial oxygen is more sensitive to P_{O_2} at higher temperature,[38, 40] these trends can probably imply the involvement of resistance from incorporation process in the overall polarization resistance. On the other hand, reaction order for Sr30 in Fig. 6d shows small changes, or even decreases in Fig. 6e for Sr40 with increasing temperature, possibly meaning the $O_o^\times$ starts to work in such process.

To more clearly unveil the mechanism on surface exchange, cathode with simpler microstructure is preferred. In the present porous structure, the bulk contribution in the co-limiting situation is comparative to surface process, and variation of P_{O_2} will not only change the activity of adsorbents but also the actual active reaction zone. Those factors will more or less affect the accuracy of reaction order judgment. A dense and thin cathode deposited on electrolyte will be able to bypass those issues, since the contribution from bulk is literally controlled by the cathode thickness and the surface exchange area is unchangeable with P_{O_2} and temperature. The experimental study on the dense cathode is undergoing currently in our group and will be presented in the near future.

3.4 Summary

In this chapter, the effect of Sr doping on electrode performance and ORR kinetics of LNO R-P phase has been investigated. The best performance was obtained with the undoped material, and Sr doping increased the polarization resistance. The surface exchange and bulk/surface diffusion co-controlling situation is observed. Significant bulk active lengths are confirmed through the chemical capacitance, 3.9 and 3.4 μm for LNO and Sr10 at 600°C, respectively, indicating the importance of bulk diffusion contribution in determining the electrode performance. On the other hand, for the surface exchange reaction, oxygen dissociative adsorption is suggested to be the primary elementary step mediating the exchange kinetics. The impaired adsorption ability after Sr doping is associated to the increased oxidation state of Ni.

Chapter 4: Investigation of surface exchange kinetics on dense symmetrical cells

From our previous EIS results regarding porous Sr-doped LNO cathode, it is hard to associate the resistance from EIS directly to each ORR elementary processes because of the difficulty in describing the microstructure of the porous electrode. The dense electrode configuration was adopted in this chapter even though in practice porous electrode is chosen over the dense electrode. By using the dense electrode, the surface area, the thickness of electrode, the interface between electrode and electrolyte and lastly the 3PB are theoretically well-defined. Through this method, there is a good chance to distinguish the contribution from surface exchange, ionic and electronic bulk transport and ion interface exchange.

As bulk characterization has been documented by co-workers with less controversy compared to the surface process, this chapter is devoted to the surface kinetics investigation of LSNO on symmetric cells with simple geometry. Dense electrode layers in thickness of $\sim 40\text{ }\mu\text{m}$ are fabricated successfully using a novel spray-modified pressing method. Negligible bulk diffusion resistance is confirmed by both parallel experiment and EIS analysis, resulting in exclusive focus on the surface process. The performance characterization is carried out in various P_{O_2} atmospheres. It is ambiguously proved that Sr doping impairs the surface kinetics of lanthanum nickelates. The corresponding rate determining step is discussed base on the reaction orders. The interstitial oxygen is suggested to be the key role when the oxygen incorporation is rat determining. For the first time, a physical model is proposed to illustrate how those interstitial species work to regulate the exchange rate of the incorporation reaction. It is noteworthy that through the present study the spray-modified pressing route exhibits its handiness and reliability, then the potential capability in the surface kinetics investigations of electrode materials.

4.1 Chemical stability with LSGM and microstructure of LSNO thin layers

Fig.4 .1 XRD for LSNO/LSGM mixtures heated at 1300°C.

Since the air-sprayed LSNO layers were co-sintered with LSGM at 1300°C, the chemical compatibility is examined first. Fig. 4.1 shows the XRD of LSNO/LSGM mixture after heated to 1300°C. XRD for LNO sharing the same pattern with Sr doped samples is provided as baseline. No foreign peaks are observed in those spectra for all mixtures.

Fig. 4.2 Cross-sectional SEM for LSNO thin layers.

Fig. 4.2 displays the morphology of the LSNO thin layers. The cross section of post-test samples was polished and thermally etched at 1200°C for 4 h before SEM observation. All thin layers are successfully densified and the adhesion between LSGM and LSNO is very good in each sample. With close inspection, no impurity at the interface is found, consistent with the XRD results and proving good chemical stability between LSNO and LSGM.

4.2 Surface-dominant situation on the well-defined R-P cathodes

In our experiment, it was found that polarization resistances from dense electrode samples in the same batch using silver paste as current collector varies 2~5 times in magnitude, because silver paste on the dense electrode specimens may partially block the surface or work as extra catalyst. Bare LSNO surface is actually the most desirable configuration to credibly characterize the ORR kinetics if the sheet resistance allows. For the bare surface samples in this study, the sheet resistance is calculated to be 0.07 Ω , assuming $\sigma_e=100$ S/cm, layer thickness of 50 μm . Such value is marginal even compared with the smallest R_p (absolute value of 3.7 Ω as will be shown below), therefore allowing no current collector being applied in the EIS measurement.

Table 4-1. Summary of R_{surf} from different cells measured in air at various temperatures and the related relative standard deviation (RSD).

T (°C)	LNO				Sr20				Sr40			
	Cell-1 (38 μm)	Cell-2 (20 μm)	Cell-3 (8 μm)		Cell-1 (19 μm)	Cell-2 (38 μm)	Cell-3 (49 μm)		Cell-1 (30 μm)	Cell-2 (40 μm)	Cell-3 (18 μm)	
	R_p (Ωcm^2)			%RSD	R_p (Ωcm^2)			%RSD	R_p (Ωcm^2)			%RSD
600	41	33.6	52.1	22	116	135	122.6	7.7	--	--	--	--
650	16.2	15	18.3	10.1	39.9	47.6	49.2	10.9	103.2	99.4	112.7	6.5
700	7.9	7.1	8.2	7.4	21	23.1	24.8	8.3	34.6	36.4	39.9	7.3
750	4.4	4.2	5.3	12.6	11.9	12.9	13.6	6.7	17.4	19.6	21.2	9.8
800	2.6	2.7	3.0	7.5	6.9	7.8	8.1	8.2	9.5	10.4	10.8	6.5

The reproducibility of so-called spray-modified pressing method is examined to ensure genuine evaluation on those candidates. Three cells of each kind were made and

measured, each with a different electrode thickness. R_p and the relative standard deviation (RSD) are summarized in Table 4-1. RSD as such are generally much smaller than those from the porous electrodes. The statistical error around 10% is well acceptable provided that performance discrepancy is ~200% between LNO and Sr20, ~60% between Sr20 and Sr40, confirming the reliability of this sample fabrication procedure and the following measurement. In addition, from this table, no systematic correlation between R_p and the layer thickness can be drawn, indicating negligible contribution from bulk diffusion. Also, the important speculation in our prior study that Sr doping brings detrimental effect to the surface kinetics is unambiguously proven in this table.

Fig. 4.3 (a) The equivalent circuit for LSNO dense electrode with electronic rail blocked by the LSGM, derived from Ref....The electronic resistance is omitted due to its far higher conductivity than ionic rail. R_{ion} and C_{chem} refer to the overall values from the dense layer, and both are weighted by $1/n$ with n being the number of units in the transmission model. (b) EIS profiles simulated by Z-view using the circuit in (a) with R_{LSGM} and R_{intf} short-circuited in view of brevity, $C_{\text{chem}}=1000C_{\text{dl,surf}}$. Three scenarios are carried out under a

fixed total resistance with different portions from the bulk and surface: $R_{\text{blk}}=10R_{\text{surf}}$,

$R_{\text{blk}}=R_{\text{surf}}$, $R_{\text{blk}}=0.1R_{\text{surf}}$. (c) The simplified circuit for the surface-dominant case.

The EIS features are interpreted to verify the designed surface-control situation from another aspect. The resistive/capacitive behavior of surface reaction, bulk diffusion as well as interface exchange in those LSNO samples can be mapped into an equivalent circuit as shown in Fig. 4.3a on the basis of the theoretical impedance treatment of MIEC materials by Jamnik et al.[69, 70] In this model, two rails conduct different charge carriers throughout the dense layer. The electronic rail is finally blocked by LSGM at the interface. R_{ion} and C_{chem} refer to the total ionic resistance and chemical capacitance of the thin layer, respectively. Being proportional with the volume of LSNO, C_{chem} can be considerably larger than the double layer capacity in interfaces. For the sake of directness, the relative importance of bulk diffusion and surface reaction is simulated by Z-view under three representative scenarios: bulk dominant as $R_{\text{blk}}=10R_{\text{surf}}$, equal contribution as $R_{\text{blk}}=R_{\text{surf}}$, surface dominant as $R_{\text{blk}}=0.1R_{\text{surf}}$. C_{chem} of 400~800 F/cm³ for LSNO (shown later in Fig. 4.6) yields 1~2F/cm² in area specific values for dense electrodes 20~50μm in thickness. In this regard, C_{chem} is set 1000 times $C_{\text{dl, surf}}$ in the simulation, $C_{\text{dl, surf}}$ being the surface double layer capacitance with a typical value of ~1mF/cm². The results are displayed in Fig. 4.3b (R_{LSGM} and R_{intf} are omitted for brevity). In fact, it is found that those spectra profiles are largely valid as long as $10C_{\text{dl, surf}} < C_{\text{chem}}$, a wide condition readily met in most MIEC electrode materials. As shown in Fig. 4.3b, in the bulk dominant case the spectrum features a distinguished near straight line response at the high frequency(HF) region, which is perfectly consistent with the bulk O²⁻ diffusion limit modeled by Adler for MIEC electrodes. In the equal contribution case, such HF feature is still distinct though less prominent. In the surface dominant situation, the spectrum is mostly controlled by a semicircle due to the surface reaction. For the last case, the equivalent circuit can be simplified as Fig. 4.3c given R_{ion} and $C_{\text{dl, surf}}$ are much smaller than R_{surf} and C_{chem} , respectively. In this simplified circuit, a two-arc EIS profile can be anticipated when the characteristic frequencies differ.

Fig. 4.4 (a) Measured and fitted surface-dominant spectrum of LNO, and (b) comparison of EIS profiles for LNO, Sr20 and Sr40 at 700°C in air.

Fig. 4.4a shows the impedance for LNO measured in air at 650°C. Two arcs can be clearly observed after zooming in the HF arc in the insert. Such spectrum coincides with the last case only in Fig. 4.3b, confirming the surface-control judgment. This result is quite rational, considering that the critical length of LNO marking comparable contributions from surface and bulk is 500~1000 μm , much bigger than the LNO thin layer here. As such, the spectrum is fitted into the simplified circuit in Fig. 4.3c. A very satisfactory fitting is displayed in Fig. 4.4a.

The HF axis intercept is 3.6 Ωcm^2 , in reason able agreement with the resistance predicted on LSGM electrolyte 1.4 mm in thickness at 650°C (3.3 Ωcm^2 after normalized). Such value will be affected if chemical reaction in LSGM/LSNO interface occurs. The HF small arc of 0.18 Ωcm^2 at 3000 Hz is assigned to the oxygen transfer resistance in the light of observations from similar thin film electrode investigations.[54] Such resistance is reported to depend on the ionic conductivities of the components at interface, and consequently would be sensitive to the interfacial impurity here. Therefore, in addition to XRD and SEM results, the absence of anomalous resistances in the spectra corroborates the chemical stability between LSGM/LSNO as well. Fig. 4.4b shows the EIS profiles including Sr20 and Sr40. All specimens display similar semicircle-dominant feature, meaning that the surface-control situation is valid in all samples.

4.3 Surface exchange kinetics of LSNO

The specimens with intermediate resistance in each kind are chosen to study the underlying mechanism of Sr doping. The equivalent k values can be derived from the impedance according to Eq. 4-1,[71, 72]

$$k^q = \frac{RT}{4F^2 R_{\text{surf}} c_o} \quad (4-1)$$

Where F is the Faraday's constant, c_o the oxygen concentration of LSNO, R and T remain the usual physical meanings. Displayed in Fig. 4.5 are k^q calculated from the impedance. k^q is 1.63×10^{-7} cm/s for LNO at 600°C, in reasonable agreement with $\sim 2 \times 10^{-7}$ cm/s for polycrystalline thin film LNO at 587°C reported by Kim et al. At the intermediate temperature 700°C, k^q is 8.59×10^{-7} cm/s for LNO and decreases to 2.65×10^{-7} , 1.68×10^{-7} cm/s for Sr20 and Sr40, respectively. The activation energies are fitted from those Arrhenius curves. E_a in 1~1.3 eV have been assigned to the surface exchange process of lanthanum nickelates in the studies by skinner et al, consistent with the present surface reaction dominant situation. For each sample, E_a decreases with increasing temperature. Such trend can be expected, assuming two or more processes with different E_a are involved in the overall reaction, because the process with higher E_a will naturally be outweighed by the one with lower value as temperature increases.

Fig. 4.5 Temperature-dependency of k^q and E_a .

Fig. 4.6 shows the volume specific capacitances derived from the semicircles. C_{chem} is reduced upon Sr doping. In addition, when lowering P_{O_2} it decreases in LNO, but almost remains the same for the doped samples. The same phenomena are reported in our previous porous LSNO study. As C_{chem} is related to the concentration of interstitial oxygen (O_i'' in Kröger–Vink notation), it was once used to determine the relevance between the catalytic activity and the amount of O_i'' . However, no uniform correlation between C_{chem} and the electrode performance (as shown in Fig. 4.5 and Fig. 4.7) can be established herein so as to explain the effect of Sr doping and the influence of P_{O_2} change at the same time. The lack of certain connection challenges the prior supposition in literature, but is not difficult for one to agree to after checking the meaning of C_{chem} carefully. In the electrode with well-defined geometry, C_{chem} is solely determined by the thermodynamic factor (f),[55]

$$C_{\text{chem}} = \frac{16F^2}{RTV_{\text{m}}f} \quad (4-2)$$

$$f = \frac{1}{2} \frac{\partial \ln P_{\text{O}_2}}{\partial \ln(4+\delta)} \quad (4-3)$$

where V_{m} is the molar volume of LSNO ($\sim 113 \text{ cm}^3/\text{mol}$), δ the oxygen hyperstoichiometry.

Fig. 4.6 Variation of C_{chem} and f towards P_{O_2} at 700°C.

As formulated by Eq. 4-2 and 4-3, although C_{chem} is related to O_i'' , what it describes directly is the willingness of change in oxygen stoichiometry, instead of the amount of O_i'' . Truly, only the variation of O_i'' can be derived from C_{chem} through f . Rearranging Eq. 3 gives,

$$f = \frac{1}{2} \frac{\partial \ln P_{O_2}}{\partial \ln(4+\delta)} = \frac{4+\delta}{2\delta} \frac{\partial \ln P_{O_2}}{\partial \ln \delta} \quad (4-4)$$

Integrating Eq. 4 yields,

$$\delta = \delta_0 P_{O_2}^{\frac{4+\delta}{2\delta f}}, \text{ or } \delta \propto P_{O_2}^{\frac{4+\delta}{2\delta f}} \quad (4-5)$$

The P_{O_2} dependency of δ is then estimated as $\delta \propto P_{O_2}^{\frac{1}{22}}$ at P_{O_2} near air, assuming $\delta \approx 0.15$. For the doped samples, it becomes complicated. At heavier doping level O_i'' could be depleted where as the oxygen vacancy in the perovskite layers is created. Such fact seems to dispute the validity of Eq. 4-3 in which O_i'' is formally assumed as the primary defect, because the capacity effect also comes from the change of $V_o^{\bullet\bullet}$ content. However, the capacity behavior originates from the accumulation/depletion of negative charges in form of oxygen ions in the materials (accompanied by the compensating change of electronic defects). All oxygen ions equally add to C_{chem} regardless whether in the form of interstitial or lattice oxygen. As a result, Eq. 4-3 is complete in expressing the correlation between C_{chem} and oxygen content since the total nonstoichiometric oxygen is rightfully represented by δ . If assuming $\delta \approx 0.07$ for Sr20 and 0.05 for Sr40 according to Vashook et al, P_{O_2} dependency can be determined as $\delta \propto P_{O_2}^{\frac{1}{13}}$ for the former and $\delta \propto P_{O_2}^{\frac{1}{11}}$ for the latter based on those C_{chem} . It can be seen at last that no simple linear conversion between C_{chem} and O_i'' exists, therefore one cannot rule out the role of O_i'' in electrode performance based on C_{chem} .

The reaction orders (n) of R_{surf} towards P_{O_2} in the form of $1/R \propto P_{O_2}^n$ are displayed in Fig. 4.7. After eliminating bulk influence, the reaction orders in Fig. 4.7 are more strictly representative of ORR. n for all specimens are nearly 0.5, suggesting the same limiting

step(s) for all samples regardless of Sr doping. In comparison to the previous results, it is reasonable to find that those reaction orders for dense layer samples are generally larger than obtained from the surface/bulk co-control porous samples since bulk resistance usually yields smaller P_{O_2} dependency. The elementary steps in ORR are listed as below. One single step cannot account for the results in Fig. 4.7. The involvement of multiple processes is implied by the changing E_a presented in Fig. 4.5 as well. The assignment of RDS to the oxygen dissociative adsorption and ion incorporation was proposed in the last work based on the detailed analysis regarding n values and basic findings in literature, and is corroborated here by those newly obtained reaction orders.

Fig. 4.7 P_{O_2} -dependent resistances for LNO (a), Sr20 (b) and Sr40 (c).

While reaction order to identify RDS has been prevalent in EIS studies, several remarks concerning the limitation of such approach might be noteworthy. In the original deviation founded on the mass action law, several assumptions are taken to simplify the complexity of the real case or make it physically achievable. For instance, a) low surface coverage in Langmuir isothermal adsorption is assumed to yield a linear relationship between adsorbents and P_{O_2} , like in step 1; b) the inventory of oxygen defects in the electrode is assumed constant, like in step 3 and 3'; c) the activity of electronic defects is assumed to be subject only to the electrochemical potential difference in the form of $\exp(\frac{\pm F}{2RT}\Delta E)$ (if taking reaction symmetry factor as 1/2) between two phases, such as surface/electrode, or electrode/electrolyte. While those assumptions are largely justifiable for noble metal electrode, like Pt, or oxides stable in a wide P_{O_2} range, like LSM, some of them may not be sound in some extent for materials with variable stoichiometry, such as LNO at the present case. Firstly, for assumption b), as estimated from C_{chem} in Fig. 4.6, the oxygen hyperstoichiometry in LSNO shows dependency on P_{O_2} . Although not big, it adds complexity to the accurate judgment. In principle, what's more important is how to take account of this influence theoretically into the equations is not clear so far. A possible solution mentioned in our last work is to divide the total overpotential into small parts associated with individual reactions, in order to reconcile the contradiction in the Nernst relationship between electrode potential E and P_{O_2} (leaving the form of E the same but replacing the constant activity of O_i'' with $\delta \propto P_{O_2}^{\frac{1}{22}}$ yields a contradictory result $E = E_0 + \frac{11RT}{48F} \ln P_{O_2}$). Division of the overpotential based on the specific surroundings for each reaction such as two-phase boundary (2PB), or three-phase boundary (3PB) reactions (ΔE_{2PB} , ΔE_{3PB}) will of course add more sense to the physical picture of the reality, but seems still inadequate, considering at last a material-specific property will be expressed by an universal formula applicable to anything. Secondly, for the activity of electrons in assumption c), from the viewpoint of free energy change, the electrode potential E indeed correctly describes the energy status of this species in the forward/backward reaction, and also embrace the concentration effect of available electrons with Boltzmann distribution (changing the energy level other than the total amount), but it has nothing to do with the inventory change of electrons triggered by P_{O_2} (changing the total amount). Leaving out

such P_{O_2} dependence of concentration in the rate equation is virtually equivalent as taking the concentration as constant over the P_{O_2} range studied, which is acceptable for metal electrode but not valid for oxides experiencing remarkable fluctuation in the electron population upon P_{O_2} variation. For instance, through managing Fe amount in $Sr(TiFe)O_3$ to adjust the Fermi level and the resultant concentration of active electrons, Jung et al. concluded that the reaction rate is governed by the density of electrons in the conduction band,[73] corroborating the importance of the quantity of electron in the reaction kinetics. Back to the present case, upon P_{O_2} change the amount of electronic defects in LSNO is found to alter in a large extent as can be seen from the average valence of Ni or from the Seebeck coefficient results, casting extra contribution to the overall P_{O_2} dependence for the charge transfer steps. In view of those concerns, it might be wise of one to use the reaction orders in Eq. (4-6)-(4-9) as a loose guide, and meanwhile seek further evidence from other physical phenomena, such as, the similar decreasing trend of k and D on Sr doping, the changing E_a towards varying temperature in Fig. 4.5 and the anisotropic properties of LNO witnessed in literature and etc. As an example, considering the common trend between D and k , it is rational to view the amount of O_i'' in LSNO as a key role, which in turn favors step 3 being rate-determining. This speculation has already been addressed briefly in the prior study. But specifically how such species works to mediate the surface kinetics is technically missing thus is presented in more details in below.

4.4 The role of O_i'' in the incorporation reaction of R-P phase

A similar trend between D and k in perovskites has been reported. After collecting a number of results from independent sources, Kilner et al. derived an expression for k in terms of bulk atomistic parameters.[74] Conceptually, the surface exchange reaction includes all subsequent steps until the mass transfer finishes in the gas/solid interface, which is different from the bulk transport that occurs in a single phase. The sole factor involved into both processes is V_o'' . Therefore by assuming V_o'' to act a major role in the surface exchange process, the relationship between D and k was established in perovskites.[74-77] Likewise, it appears rightful for one to explain the D & k correlation in LSNO by similarly stressing O_i'' . But comparing the defects in perovskites and R-P phase,

an immediate question coming up is how two opposite species, $V_O^{\bullet}$ and O_i'' , can play similar roles in the incorporation process, because only vacancies regardless in lattice or in interstice are the active sites in such reaction. In the following, a relationship between k and O_i'' is proposed, by which the seemingly contrary roles of $V_O^{\bullet}$ in perovskite and O_i'' in R-P structure could be harmonized in principle.

Within the law of mass action, the reaction rate for step 3 is,

$$r_3 = k_3[O_{ads}^-][V_i^{\times}] \exp\left(-\frac{\Delta E_{2PB}F}{2RT}\right) - k_3^-[O_i''] \exp\left(\frac{\Delta E_{2PB}F}{2RT}\right) \quad (4-10)$$

where k_i and k_i^- are the rate constants for the forward and backward reaction, $[X]$ the activity of X species.

Assuming step 3 as the RDS, at equilibrium, there is no net oxygen flux across the surface/electrode and the 2PB overpotential is zero. The exchange oxygen ion flux density of step 3, j_3^0 , is

$$j_3^0 = k_3[O_{ads}^-][V_i^{\times}] = k_3^-[O_i''] \quad (4-11)$$

At this moment, a false proportional dependency between j_3^0 and $[O_i'']$ is about to be drawn if focusing on $k_3^-[O_i'']$ only, because the opposite can be arrived if instead considering the second term $k_3[O_{ads}^-][V_i^{\times}]$. The cause of such discrepancy lies in the unique feature of this reaction: site conservation.

Interstitial site conservation in R-P phase gives

$$[O_i''] + [V_i^{\times}] = C \quad (4-12)$$

where C is a constant.

Inserting Eq. 4-12 into Eq. 4-11 gives

$$K_3 = \frac{k_3}{k_3^-} = \frac{1}{[O_{\text{ads}}^-] \left(\frac{C}{[O_i'']} - 1 \right)} \quad (4-13)$$

Where K_3 is the equilibrium constant of step 3. It is found that K_3 will increase with $[O_i'']$ provided $[O_{\text{ads}}^-]$ is not directly dependent on $[O_i'']$, meaning k_3 may increase and/or k_3^- may decrease as $[O_i'']$ rises.

Combining Eq. 4-11 and 4-12 to eliminate $[O_i'']$ and $[V_i^\times]$, one obtains

$$j_3^0 = \frac{C}{\frac{1}{k_3 [O_{\text{ads}}^-]} + \frac{1}{k_3^-}} \quad (4-14)$$

By appropriately setting the evolution of k_3 and k_3^- towards $[O_i'']$, a non-monotonic relationship between $[O_i'']$ and j_3^0 can be established. A possible scenario is qualitatively illustrated in Fig. 4.8. In this diagram, k_3 increases and k_3^- decreases with $[O_i'']$ according to the dependency of K_3 on $[O_i'']$ in Eq. 4-13. Within $[O_i'']$ poor region, k_3 is set to change more drastically than k_3^- ; in the $[V_i^\times]$ poor region, the opposite is valid. Due to the different gradients for k_3 and k_3^- vs. $[O_i'']$, j_3^0 reaches its maximum at a certain $[O_i'']$ value according to Eq. 4-14. Over that point, going forward to increase $[O_i'']$ or backward to increase $[V_i^\times]$ will lead to decrease in j_3^0 .

It seems that the constant C in Eq. 4-12 should be determined under the charge neutrality corresponding to Ni oxidation status ($C=0.25$ at Ni^{3+}). However, as the interstitial vacancies in La_2O_2 layer are equivalent in the incorporation reaction and each site has the same chance to accommodate an adsorbed oxygen ion, it makes more sense to take C as the maximum interstitial sites in the rock salt layer, that is, 2 per unit cell. The reported δ values for LSNO in cathode condition are about 0.15 and turn fewer after Sr doping, [38, 40, 78] which belongs to the $[O_i'']$ poor region. In this case, increasing $[O_i'']$ results in enlarged j_3^0 . Likewise, a similar diagram can be built for perovskites, except C being 3 per unit cell. The reported $[V_O^\bullet]$ for the perovskites seldom exceeds 0.5, which probably belongs to $[V_O^\bullet]$ poor region. As a result, increasing $[V_O^\bullet]$ will increase the exchange rate of incorporation

reaction in perovskites. By this fashion, the contradiction mentioned before could be resolved.

Fig. 4.8 Evolution of k_3 and k_3^- , and the resultant j_3^0 with $[O_i'']$.

Fig. 4.9 Equivalent circuit for LSNO with two subsequent surface processes.

Some analysis can be conducted to check the possibility of the scenario in Fig. 4.9. The feasibility of building such parabolic profile for j_3^0 relies on the variability of K_3 , then k_3 and k_3^- . For normal chemical reactions where the initial concentrations of reactants/products are independent of each other, the equilibrium constants can really be constant, and certainly the reaction rate constants are related to E_a , temperature ($k_i \propto \exp(\frac{-E_a}{RT})$) only, other than to the concentrations of reactants/products. But because of the site conservation in defect chemistry which puts an extra restriction on step 3, the

development of equilibrium is hence partially influenced by Eq.4-11 which, when combined with Eq.4-10, leads to Eq.4-12, indicating that K_3 could alter with $[O_i'']$. This observation has been favored by the changeable E_a for $[O_i'']$ formation depending on the oxygen stoichiometry of the R-P phase materials.[58]

As reported, the uptake of O_i'' is an exothermic process, $E_{a,forward} < E_{a,backward}$, [56, 58] which consequently lead to a judgment that $E_{a,forward}$ decreases, and $E_{a,backward}$ increases with $[O_i'']$ if the trends of k_3 and k_3^- vs. $[O_i'']$ in Fig. 4.9 is valid. It in turn gives rise to the prediction that the formation enthalpy for $[O_i'']$ decreases (more negative) with increasing $[O_i'']$, and vice versa. The supportive evidences about this prediction can actually be found. Firstly, an increased enthalpy with Sr doping is implied by the phenomenon that $[O_i'']$ in LSNO decreases as Sr, [38, 40] which corresponds to a weakened driving force for the formation of O_i'' as Sr doping. Secondly, the partial molar enthalpy of O_i'' formation in LSNO have been calculated by Nakamura et al, [58] and such value is found to enlarge with increasing Sr (less O_i'') in the whole oxygen hyperstoichiometry region, enabling the possibility that at a fixed P_{O_2} the formation enthalpy increases with Sr doping. Nevertheless, it is particularly notable that the enthalpy tendency towards $[O_i'']$ triggered by Sr doping in LSNO might be not applicable to the change induced by P_{O_2} variation, because $[O_{ads}^-]$ in Eq. 13 is assumed to be constant upon $[O_i'']$ change, which in fact is explicitly dependent on P_{O_2} .

In above deviation, the activity of electron is left out assuming it is sufficient in all LSNO samples. $[O_{ads}^-]$ is taken as a fixed value which probably varies more or less at different Sr contents. In addition, the deviation is mathematically qualitative. However, in spite of all these assumptions, such model is a meaningful try to exploit the role of O_i'' in surface exchange kinetics for the R-P phase structure materials.

4.5 Summary

In this chapter, ORR kinetics for surface for the R-P phase structure is investigated with LSNO dense cathodes by EIS in this study. With the well-defined geometry, accurate

surface reaction resistances are obtained. The results clearly prove that Sr slows down the ORR kinetics. LNO yields a surface exchange coefficient of 8.59×10^{-7} cm/s at 700°C. Sr doping decreases such value to 2.65×10^{-7} cm/s for Sr20, 1.68×10^{-7} cm/s for Sr40. RDS are identified based on the reaction order. Even though those n values from ORR on dense cathodes show consistency with the judgment on RDS in our prior study, it is clearly addressed here that the practice of using reaction order to determine RDS should be conducted with caution due to the limitation associated with the basic assumptions in the deviation of reaction orders, especially on materials with readily changeable oxygen stoichiometry. Dissociative adsorption and ion incorporation are presented as the limiting factors for ORR on LSNO in combined consideration of the EIS results and independent observations reported in literature. In the incorporation process, O_i'' in rock salt layers is suggested to mediate the exchange rate of such elementary step, therefore show substantial influence on the final performance. A model is proposed, for the first time, to illustrate the possible way O_i'' works to realize its positive effect on the incorporation rate of such unique R-P phase structure.

Chapter 5: Improvement of surface kinetics by Mn&Sr doping

From previous work we already knew, for R-P phase materials, the interstitial oxygen are more active than vacancy in ABO₃ layer in terms of incorporation, and Ni is the main active site for oxygen adsorption process. Combining these two key results we choose Mn substitution Ni into the lattice of R-P phase to enhance the surface kinetics. Mn has strong ability of adsorbing oxygen which is already verified from the good k in LSM. On the other hand, Mn presents high state in R-P phase, which will be expected to produce the big amount of the interstitial oxygen.

Mn is found to substantially promote the surface kinetics, showing highest k of 1.57×10^{-6} cm/s at 700°C on La_{1.8}Sr_{0.2}Ni_{0.9}Mn_{0.1}O_{4+δ}. Such value is ~80% larger than that of the undoped sample, and is one of the highest k among the currently available R-P phase intermediate temperature cathode.

5.1 XRD and electrical conductivity of Mn&Sr doped LNO

Fig. 5.1 a) XRD of LSMN samples synthesized at different temperatures and mixture of Sr60Mn30 and LSGM calcined at 1300°C, b) electrical conductivities of LSMN in air from 100-800°C.

Fig. 5.1a shows the phase purity of synthesized powders. In the Mn-based R-P phase studies, Munnings et al.[81] found that the single phase range for La_{2-x}Sr_xMnO_{4+δ} is

$0.6 \leq x \leq 2.0$. Later on, Sun et al.[82] reported that such range is $1.4 \leq x \leq 1.6$ when preparing in air. Although the exact Sr limit in the solid solution varies in above studies, both indicate that single phase is more favorable in the Sr-rich composition. It is indeed confirmed in the present work that La_2O_3 secondary phase appears in the composition $\text{La}_2\text{Ni}_{0.9}\text{Mn}_{0.1}\text{O}_{4+\delta}$. Therefore Sr was doped into LNO simultaneously with Mn to ensure the phase purity. The synthesis temperature for different doping levels varies and is marked in Fig. 5.1a. The final XRD patterns for all samples correspond to pure phase R-P structure (PDF 11-0557). As the dense symmetrical samples were prepared with LSGM electrolyte at high temperature, the chemical compatibility between LSNM and LSGM is examined through Sr60Mn30 and LSGM mixture sintered at 1300°C for 4h. As can be seen in Fig. 5.1a, no observable reaction is found.

Fig. 5.1b exhibits the electrical conductivity of LSNM. Mn doping decreases the conductivity gradually. Poor conductivity has been reported for $(\text{LaSr})_2\text{MnO}_{4+\delta}$ with the maximum less than 10 S/cm when measured under 900°C . It has been published that the electrical conductivity for pure LNO is thermally activated at low temperature as semi-conductor, but turns oppositely to thermally deactivated like metal when temperature is higher than $\sim 600\text{K}$. [83] LSNM with $\text{Mn} \leq 10$ resemble the pure LNO behavior, but follow the semi-conducting trend of $(\text{LaSr})_2\text{MnO}_{4+\delta}$ at higher Mn levels. The ohmic resistance estimated from the electrical conductivities of Sr15Mn5, Sr15Mn7 and Sr20Mn10 with a typical electrode structure (porous electrode in thickness of $50\mu\text{m}$, 1/10 of the conductivity of dense bulk) is less than $0.0025 \Omega\text{cm}^2$ in $600\text{-}800^\circ\text{C}$, which in most cases is negligible compared to the cathode polarization resistances in the IT region.

Fig.5. 2 Cross-section of (a) Sr15Mn7, (b) Sr20Mn10 and (c) Sr40Mn20-LSGM bilayers.

Fig. 5.2 shows the microstructure of Sr15Mn5/LSGM sample. Dense structure except for few of closed pin holes was obtained after 1300°C sintering. Good adhesion between Sr15Mn5 and LSGM is confirmed. No chemical reaction can be observed in the interface area, which is consistent with the XRD results. The small thickness of LSNM renders that the resistance from bulk diffusion in EIS characterization is marginal compared to the surface exchange process, given the characteristic length for LNO is 500~1000 μm . [35]

5.2 Surface improvement by Mn doping

Fig. 5.3 shows the EIS arcs measured from LSNM symmetrical cells. To accurately assess the surface kinetics of cathode materials, dense thin layer has been widely adopted in literature in order to avoid bulk diffusion influence and complex microstructure in the standard porous electrode. An equivalent circuit for the dense electrode under surface exchange dominant situation has been derived elsewhere and is presented in Fig. 3. The combination of the C_{chem} originated from oxygen stoichiometry change upon potential perturbation and the R_{surf} is responsible for the main arc. Sr15Mn5 was fitted by this EC satisfactorily. The rest samples share the similar profile due to the same surface-dominant situation and were fitted into this EC also to yield R_{surf} .

Fig.5.3 EIS of LSMN symmetrical cells at 700°C in air

The equivalent surface exchange coefficient can be calculated from R_{surf} through Eq. 5-1,[71, 72]

$$k = \frac{RT}{4F^2 R_{\text{surf}} c_0} \quad (5-1)$$

where F is the Faraday's constant, c_0 the oxygen concentration in LSMN, R and T keep the usual physical meanings.

Fig. 5.4 displays the k values for LSMN. The exchange rate ranks as $\text{Sr20Mn10} > \text{LNO} > \text{Sr15Mn7} > \text{Sr15Mn5} > \text{Sr40Mn20} > \text{Sr60Mn30}$. k for Sr20Mn10 is about twice bigger than that of the pristine LNO. The highest value is achieved by this modestly doped sample; increasing or decreasing Mn content further will lower the surface kinetics. To assess the real effect of Mn on this trend, both Sr and Mn need to be taken into account in such evolution of k . As stated before, although Mn is the designed substitute for Ni, Sr has to be used to obtain single phase structure. It has been demonstrated in previous studies that Sr doping impairs the surface kinetics of LNO by increasing the oxidation state of Ni

and reducing interstitial oxygen population[68, 84]. Thus, the improvement from Mn doping could be partially offset by Sr.

Fig. 5.4 Equivalent k for LSMN calculated from R_{surf} .

Due to this very concern, Sr15Mn5 sample was prepared. Comparing Sr15Mn5 and Sr15Mn7, with fixed Sr level, k is increased from 3.7×10^{-7} to 6.9×10^{-7} cm/s at 700°C by the extra 2.5% Mn content, which ambiguously proves the advantageous effect of Mn. On the other hand, Daroukh et al.[85] found that full Mn B site $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ tends to keep the exact stoichiometry in a wide range of P_{O_2} with strong reluctance to either accommodate interstitial oxygen or lose lattice oxygen to form vacancy. As the interstitial oxygen is crucial to the ion incorporation, high Mn content will probably lead to decreased exchange rate when limited by the incorporation process. As a result, the optimum Mn content should be the one balancing the rate limits from surface adsorption and ionic incorporation. The apparent activation energy is derived based on this Arrhenius plot. It is reduced gradually in those $\text{Mn} \geq 10$ samples compared to LNO, indicating an energetically more favorable surface process with Mn presence.

Table 5-1 summarizes some of the most commonly used R-P phase cathodes. Sr20Mn10 from this work displays one of the best k values, 1.57×10^{-6} cm/s at 700°C, which

is much better than its Co or Fe doped counterpart, demonstrating the substantial advantage of Mn over other dopants. At last, since the Sr/Mn=2 ratio was empirically chosen, higher surface performance can be reasonably expected through systematical study on the Sr content in the future.

Table 5-1 Comparison of k for common R-P phase cathodes at 700°C

	k (cm/s)	E_a (eV)	Ref.
Sr20Mn10	1.57×10^{-6}	0.91~1.07	This work
$\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_{4+\delta}$	1.41×10^{-6}	0.6	[67]
$\text{Pr}_2\text{NiO}_{4+\delta}$	1.0×10^{-6}	0.77	[45]
LNO	8.6×10^{-7}	0.97~1.21	This work
$\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_{4+\delta}$	4.0×10^{-7}	1.39	[86]
$\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$	2.7×10^{-7}	1.06~1.37	Our work
$\text{Nd}_{1.8}\text{Ca}_{0.2}\text{NiO}_{4+\delta}$	1.5×10^{-7}	1.35	[45]

5.3 Summary

Mn doped $(\text{LaSr})_2\text{Ni}_{1-x}\text{Mn}_x\text{O}$ ($0.05 \leq \text{Mn} \leq 0.3$) are investigated as IT cathode candidates for enhanced surface exchange kinetics. Pure phase was obtained at Mn&Sr doped into LNO simultaneously. The surface exchange resistance was evaluated by EIS on the dense thin layer structure. The best performance was obtained from Sr20Mn10. k for such composition is 1.57×10^{-6} cm/s at 700°C in air, approximately twice bigger than that for the pristine LNO. Of the often used R-P phase cathode materials, Sr20Mn10 displays one of the greatest k values, proving Mn doping is successful and more effective than Co and Fe in terms of surface kinetics. With optimization of Sr content, further improvement in k can be reasonably anticipated.

Chapter6: Conclusion

In this thesis, investigation of Sr doped MIEC cathode in Ruddles-Popper phase $\text{La}_2\text{NiO}_{4+x}$ oxides has been conducted. ORR kinetics of LNO is discussed though the effect of Sr doping on electrode performance. The best performance was obtained with the undoped material, and Sr doping increased the polarization resistance. The surface exchange and bulk/surface diffusion co-controlling situation is observed. Significant bulk active lengths are confirmed through the chemical capacitance, 3.9 and 3.4 μm for LNO and Sr10 at 600 °C, respectively, indicating the importance of bulk diffusion contribution in determining the electrode performance. On the other hand, for the surface exchange reaction, oxygen dissociative adsorption is suggested to be the primary elementary step meditating the exchange kinetics. The impaired adsorption ability after Sr doping is associated to the increased oxidation state of Ni.

Surface exchange kinetics was further discussed in a well-defined dense electrode configuration. Dense cathode cells were made by using a novel spray-modified pressing method. With the simple geometry, accurate surface reaction resistances are obtained in dense cathode. Dissociative adsorption and ion incorporation are presented as the limiting factors for surface reaction on LSNO in combined consideration of the EIS results and independent observations reported in literature. In the incorporation process, O_i'' in rock salt layers is suggested to mediate the exchange rate of such elementary step, therefore show substantial influence on the final performance. A model is proposed to illustrate the possible way O_i'' works to realize its positive effect on the incorporation rate of such unique R-P phase structure. It is found that the amount of O_i'' affects its formation energy in the site conserved lattice structure, which in turn changes the activation energy of forward/backward reaction rate.

Mn is chosen as B site dopant in $(\text{LaSr})_2\text{Ni}_{1-x}\text{Mn}_x\text{O}$ ($0.05 \leq \text{Mn} \leq 0.3$) in order to enhance the surface exchange kinetics. Pure phase was obtained at Mn&Sr doped into LNO simultaneously. The surface exchange resistance was evaluated by EIS on the dense thin layer structure. The best performance was obtained from Sr20Mn10. k for such

composition is 1.57×10^{-6} cm/s at 700°C in air, approximately twice bigger than that for the pristine LNO. Of the often used R-P phase cathode materials, Sr₂₀Mn₁₀ displays one of the greatest k values, proving Mn doping is successful and more effective than Co and Fe in terms of surface kinetics. With optimization of Sr content, further improvement in k can be reasonably anticipated.

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