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Oxygen transport kinetics of surface Pt & Ag-modified perovskite oxide La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF)

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Abstract

 $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) perovskite oxide is considered as a promising candidate for intermediate temperature solid oxide fuel cell (IT-SOFC) cathode material, due to its excellent mixed ionic and electronic conductivity, high oxygen reduction activity and high stability. Recent research shows that with catalytic metals coated on the surface, the surface exchange performance of LSCF can be further enhanced^[1], while the mechanism needs to be further investigated.

In this study, dense perovskite La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3.6} membranes were fabricated using commercial powders. The prepared membranes were polished and thermo-treated to achieve a smooth surface. Platinum and silver nanoparticles were homogenously deposited on the membrane surface by sputtering to modify the membrane surface. The influence of metal deposition on the surface oxygen reduction reaction (ORR) was investigated. The kinetic parameters of oxygen transport, the oxygen diffusion coefficient (D_{chem}) and the surface exchange coefficient (k_{chem}) were characterized by electrical conductivity relaxation (ECR). The ECR measurements were conducted in the range of 600 °C to 900 °C with an oxygen partial pressure (P_{O2}) step change from 0.215 atm to 0.464 atm and vice versa. The results reveal that the oxygen diffusion in LSCF is independent to the platinum deposition but greatly affected by the silver deposition. For bare LSCF, the surface exchange coefficient is of a factor of 10 higher than the literature values at 800 °C, and is not further promoted by either of these catalytic particles.

Keywords: Surface exchange reaction; Perovskite-type oxide; Oxygen transport membrane; Surface modification; Electrical conductivity relaxation; Metal NPs sputtering

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1. Introduction

As a worldwide demand for an effectively clean energy strategy to replace the coal power stations, solid oxide fuel cells (SOFCs), as a promising solution, have been widely investigated in the last 20 years. A typical schematic diagram of an SOFC is shown in Figure 1.1, it consumes various fuels to generate electricity through electrochemical reactions. The cell consists of three main parts, a cathode, an electrolyte and an anode. The oxygen molecules transport from the gas phase into the solid phase through the oxygen reduction reaction on the cathode, oxygen ions are conducted by the electrolyte and react with the fuels on the anode. In the meantime, electrical energy is collected through an outer circuit.



Figure 1.1 Schematic diagram of a commercial solid oxide fuel cell (Convion Ltd.)^[2]

The oxygen reduction process is considered as the main rate limiting factor to the performance of the SOFC system^[3], and it is highly limited by the cathode kinetics at intermediate working temperature (600 °C~800 °C). Therefore, the development of SOFC cathode materials with high stability and oxygen reduction reaction activity is demanded.

electronic conductive (MIEC) perovskite oxide The mixed ionic and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) is considered as a state-of-art cathode material for the intermediate temperature solid oxide fuel cell (IT-SOFC) application, owing to its proper chemical stability, high ORR electrocatalytic activity, high electronic and ionic conductivities, and adequate compatibility with other cell components^[4-8]. The oxygen transport mechanism of LSCF goes via the dissociation and reduction of oxygen molecules to oxygen ions on the membrane surface, followed by the incorporation of the oxygen ions into the perovskite lattice. The chemical surface exchange coefficient (k_{chem}) and oxygen diffusion coefficient (D_{chem}) are the kinetic parameters used to describe the oxygen transport process^[9]. Usually, the bulk diffusion is determined by the intrinsic properties of the material, e.g. oxygen mobility, oxygen stoichiometry, lattice parameters^[10]. The surface exchange is influenced by both ionic and electronic conductivity, surface oxygen vacancy concentration, oxygen adsorption and dissociation reaction and surface morphology^[9, 11, 12].

Surface modification through noble catalytic metal coating on the LSCF membrane surface allows the surface reaction rate to be further enhanced by promoting the ORR route. Jun *et al.*^[13] used plasma deposition method to homogeneously coat Ag nanoparticles on the La_{0.6}Sr_{0.4}Co_{0.3}Fe_{0.7}O_{3–δ} surface. The results showed that the Ag particles were well attached, both physical adsorption and chemical bonds existed between Ag and LSCF. The single cell peak power density at 650 °C increased from 0.083 W/cm² to 0.113 W/cm² after 0.46 wt.% Ag coating. Liu *et al.*^[14] reported a novel infiltration method to in situ incorporate Ag into an La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} based cathode. The durability measurement at 500 °C for 168 h showed that there was no obvious degradation of the cell. Yang *et al.*^[15] conducted a combination study of first-principles calculation and experiment towards O₂ reduction on Pt-modified La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} cathode. It was found that adsorption and dissociation of oxygen on the perfect LSCF (100) surface can barely happen due to its low catalytic activity. With the additional Pt to the LSCF surface, adsorption and dissociation of O₂ were greatly enhanced. The surface exchange coefficient measured at 775 °C by ECR was

six times higher after Pt coating. These findings implicate that the LSCF cathode performance and surface exchange rate can be theoretically and experimentally improved through surface Ag and Pt coating. In this thesis, the functions of Ag and Pt coating on LSCF surface are studied in detail.

Objective of the thesis

The aim of this research is to study the oxygen transport kinetics of LSCF, mainly the surface exchange properties, after coating dense samples with Ag and Pt nanoparticles. A controllable and repeatable method to fabricate polished membranes with similar material properties between sample to sample is decided. A proper coating and annealing method for various metals is established. Material crystal structure, surface morphology and membrane performance are characterized before and after surface modification.

This study directly looks into the LSCF surface exchange rate with different metal modifications and will further call for the investigation of other catalytic metal coatings in order to obtain a clear picture of the inner mechanism of the surface oxygen reduction reaction and push the limit of the cathode material application.

2. Theoretical background

2.1 Defect chemistry

In a perfect crystal, atoms or ions are well ordered by the intrinsic nature of the constituent particles to form symmetric patterns that repeat along the three-dimensional space. The smallest group of particles in the material that constitutes the repeating pattern is called the unit cell. The unit cell defines the symmetry and structure of the entire lattice. But in real materials at temperatures above 0 K, defects or deviation from the ideal arrangements occur; these defects significantly influence the electrical and chemical properties of real materials. The defects are generally classified into electronic defects and structural defects. Electronic defects are caused by the excitation of electrons from valence to conduction bands. Structural defects in the crystal can be subdivided into point defects, line defects and surface defects^[16]. Although many types of defects may occur, the crystal structure is usually dominated by only one or two kinds of defects.

2.1.1 Point defects in oxides

Point defects are where an atom is missing or is in an irregular place in the lattice structure, including self-interstitial atoms, interstitial impurity atoms, substitutional atoms and vacancies, some examples are displayed in Fig 2.1. In oxides, common point defects are vacancies on the cation and anion sites, substitutional cations, and electronic defects.



Fig 2.1 Point defects in crystal structures: interstitial and substitutional atom, vacancy, Frenkel defect (open source work by Dani Feri)^[17]

These point defects are normally described by Kröger-Vink (K-V) notation. Table 2.1 lists some of the possible defects in La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃₋₈. Co and Fe are both multivalent atoms, when the oxygen partial pressure in the atmosphere is changed, some cations are partially oxidized or reduced, the oxygen vacancy concentration and electron holes change accordingly to maintain the charge neutrality in the crystal. The P_{O2} dependency of the point defects is quantitatively described in Brouwer diagrams^[18].

Table 2.1 List of possible defects in LSCF (lattice oxygen site is not a defect, but also listed in the table because it is involved in the exchange reaction)

	č /
V _O	Oxygen vacancy
0 ^x ₀	Lattice oxygen site
Sr' _{La}	Strontium on Lanthanum site
Co _{Fe}	Cobalt on Iron site
h [.]	Electron hole

2.1.2 Mixed ionic and electronic conductivity

As a mixed ionic and electronic conductor, the oxygen transport properties of perovskite-type oxide are determined by various electrical charge carriers, such as oxygen ions, and electronic species. If the formation of oxygen vacancies in the conductor is complemented by the formation of electrons, the conductor is generally called an n-type conductor. The other type of conductor creates electron holes (h^{\cdot}) to complement the formation of metal vacancies (or interstitial oxygen ions). This type of conductor is denoted as a p-type conductor^[19]. The ionic conductivity (σ_i) results from the transport of the ionic charge carriers, as given in Eq. (2.1), c_i is the ion concentration in mole fractions, q_i is the charge per ion, and μ_i is the mobility of the species. Similarly, the electronic conductivity (σ_e) results from the transport of conductors.

$$\sigma_{\rm i} = \sum c_i q_i \mu_i \tag{2.1}$$

$$\sigma_{\rm e} = nq_{\rm e}\mu_{\rm e} + hq_{\rm h}\mu_{\rm h} \tag{2.2}$$

In addition to Eq. (2.2), another contribution to the electronic conductivity can be caused by the presence of multivalent cations in mixed oxides. The electrons hop between cations with different valence states and it is commonly called the 'hopping conductivity contribution'^[20]. This effect is not taken into account in order to simplify the process.

The total conductivity is given by the sum of the ionic and electronic conductivity, as shown in Eq. (2.3).

$$\sigma_{\text{total}} = \sigma_{\text{e}} + \sigma_{\text{i}} \tag{2.3}$$

Commonly, the mobility values of electrons and electron holes are about two or three orders of magnitude greater than that of ions. In other words, the ionic conduction will be dominant only in the case when the concentration of ionic defects is at least 100~1000 times higher than the concentration of electronic defects^[19]. In the thesis, the LSCF is recognized as a p-type MIEC conductor, and we focus on the total conductivity change while tuning the oxygen vacancy equilibrium.

2.2 LSCF properties

The La_{1-x}Sr_xCo_{1-y}Fe_yO_{3- δ} family is a state-of-art mixed ionic and electronic conductive cathode material owing to the high electrical and ionic conductivity, the chemical and physical stability and the proper working temperature that matches the commonly used YSZ electrolyte. For the different compositions, different electrochemical properties are achieved, La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} is considered as one of the most promising compositions for SOFCs application.

2.2.1 Crystal structure and chemical composition

Most LSCFs do not have ideal cubic perovskite structure, phase transformations happen temperatures depending on composition. For example, various the at $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF6428) has a rhombohedral phase at room temperature^[21], and transits to cubic perovskite at approximately 773 K^[21]. Apart from the temperature, the composition also influences the crystal structure of the LSCF family. According to the Goldschmidt factor, at high Fe and/or low Sr contents, the orthorhombic structure is preferable, while at high Sr content, cubic perovskite phase dominates^[22]. Additional A-site deficiency also influences the structure and material properties. For LSCF6428, with a proper Sr deficiency (<0.025), the oxygen ion conductivity is enhanced but the electronic conductivity decreases due to the reducing of the electronic hole concentration^[23]. By introducing La deficiency (0.05 and 0.02), the sintering behavior and electrical performance are promoted, while the long-term stability is sacrificed^[5].

2.2.2 Sintering behavior

Sintering is the thermal process that fuses the perovskite powders into a solid disk with a certain density and shape. Most of perovskite materials are sintered at high temperature in air. Since the sintering temperature is associated with the crystal phase transformation, thermal expansion, and density, the sintering temperature has significant effects on the material properties. Möbius *et al.*^[24] studied the sintering behavior of LSCF6428 at 1050 °C, 1150 °C and 1250 °C for different amounts of time. It was found that with higher sintering temperature and longer sintering time, a higher material density was reached, but in the meantime caused the impurity phase like cobalt oxide to be present on the surface. Zeng *et al.*^[25] compared the ionic conductivity of LSCF6428 sintered from 1000 °C to 1300 °C and found a positive correlation between sintering temperature and ionic conductivity. In a recent paper, Hashim *et al.*^[26] claimed that for LSCF6428, the shrinkage and porosity were completely determined by the sintering temperature, while the sintering time, heating rate as well as sintering temperature jointly contributed to the density.

2.2.3 Electrical conductivity

The electrical conductivity of La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3- δ} (x=0.1-0.4) was studied by Tai *et al.*^[27] in a wide temperature range. As shown in Fig 2.2, with different A-site compositions, the maximum electrical conductivities range from 200-330 S·cm⁻¹. The maximum conductivity temperature shifts reciprocally with the Sr content. The composition LSCF6428 has the highest electrical conductivity with the peak value of 330 S·cm⁻¹ at 550 °C, indicating that it is a promising composition as a conductor. A possible explanation is that the Sr substitution is compensated by both electron holes and oxygen vacancies, which leads to a higher concentration of the charge carries.



Fig 2.2 Electrical conductivity of $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-\delta}$ as a function of temperature and Sr content (mol fraction) in air^[27].



Fig 2.3 Linear thermal expansion, oxygen content, electrical conductivity, and Seebeck coefficient of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ as function of temperature in air^[27].

It is recognized that the oxygen vacancy concentration correlates to the electrical conductivity. As shown in Fig 2.3, when the material reaches the so-called characteristic temperature, the oxygen content starts decreasing, as well as the electrical conductivity. From the charge neutrality point of view, the increasing oxygen vacancy concentration causes a decrease in electron hole concentration, then the electrical conductivity reduces. Another mechanism that would decrease electrical conductivity is that the oxygen vacancies may act as scattering centers or random traps for electrons, reducing the mobility of electron holes^[28].

2.2.4 Ionic conductivity

The ionic conductivity of LSCF results from the directional movement of the ionic charge carriers, in this case, oxygen ions. Under a given oxygen potential gradient between the two side of the cathode material, the oxygen ions can hop to neighboring vacancy sites in the crystal lattice, causing an oxygen flux to the low oxygen potential side, whereas the transport of any other species is excluded. Teraoka *et al.*^[29] reported that the LSCF materials are good mixed conductors with ionic transport number 10⁻²-10⁻⁴. At 1073 K, for instance, ionic conductivity ranged in the order of 1-10⁻² S·cm⁻¹ while electronic conductivity was around 10² S·cm⁻¹. It was also suggested that the increase of Sr and Co dopant enhanced the ionic conductivity while Sr content was more influential.

$$\{Sr'_{La}\} + n = 2\{V'_0\} + p \tag{2.5}$$

The charge neutrality in the LSCF can be written as Eq. (2.5). The increase of Sr dopant leads to a higher oxygen vacancy concentration which explains the enhancement of the conductivity.

2.3 Surface exchange

There are mainly two oxygen transport regimes, the diffusion in the bulk and gas-tosolid exchange on the surface. The surface exchange is a complex process consists of several steps, including the adsorption from the gas phase, charge transfer reaction between the adsorbed species and the bulk^[30], oxygen surface diffusion and incorporation of ionized oxygen into oxygen vacancies. The surface exchange coefficient (k_{chem}) is a kinetic parameter used to described the overall surface reaction rate.

2.3.1 Surface exchange reaction

Step by step, the surface exchange reaction can be written as follows:

$$O_{2(g)} \leftrightarrow O_{2(ad)} \tag{2.6}$$

$$O_{2(ad)} + e \leftrightarrow O'_{2(ad)} \tag{2.7}$$

$$O_{2(ad)}' + e \leftrightarrow 2O_{(ad)}' \tag{2.8}$$

$$O'_{(ad)} + e \leftrightarrow O''_{(ad)} \tag{2.9}$$

$$O_{(ad)}'' + V_0^{"} \leftrightarrow O_0^X \tag{2.10}$$

Eq. (2.6) is the adsorption of the oxygen molecule from the gas phase. Following the Langmuir isotherm adsorption model, the surface coverage depends on the oxygen partial pressure and the temperature. Eq. (2.7) to (2.9) cover the oxygen dissociation: the adsorbed oxygen molecule gets electrons from the solid surface and is ionized. After the ionized oxygen diffuses to the right position, it can react with the surface oxygen vacancy site and incorporate into the lattice, described as Eq. (2.10). By lumping all the intermediate steps together, the overall surface reaction is written as Eq. (2.11).

$$\frac{1}{2}O_{2(g)} + V_0^{"} + 2e \leftrightarrow O_0^X \tag{2.11}$$

Since both oxygen vacancy and electron are presented as the reactants, the mixed ionic and electronic conductivity is crucial for the surface exchange ability of a perovskite material. Comparing the pure electronic conductors with little ionic conductivity (LMO, LSM, and LFO) with the MIEC conductors (LSF, LCO, LSC, LSCF), it was found that there was a significant contribution of ionic conductivity to the surface exchange coefficient^[31]. For example, at 900 °C the exchange coefficient k_{chem} of LaFeO₃ is $4 \times 10^{-8} \text{ cm} \cdot \text{s}^{-1[32]}$, while of La_{0.8}Sr_{0.2}CoO_{3- $\delta}$} is $2 \times 10^{-5} \text{ cm} \cdot \text{s}^{-1[33]}$, of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} is $2 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1[34]}$.

2.3.2 Surface modification

Noble metal nanoparticles are well known as catalyst to promote the oxygen reduction reaction. The metal particles deposited on the LSCF surface provide active dissociativeadsorption sites as well as electrons to enhance the oxygen splitting. In addition, the gas-metal-perovskite triple-phase boundary is considered as active ORR site by combining the advantages of both noble metals and perovskite materials. There are a few studies about the surface exchange coefficient after the surface modification. Yang et al.^[15] studied the Pt-modified LSCF surface by both first principles calculation and experiment. It was found that the Pt cluster coating on the LSCF (100) surface can remarkably enhance its catalytic activity, and the surface exchange coefficient increased from 6.05 \times 10⁻⁵ cm·s⁻¹ of the bare LSCF cathode to 4.04 \times 10⁻⁴ cm·s⁻¹ of the Ptmodified LSCF cathode at 775 °C. Zhu et al.[35] reported the exchange coefficient of Ag decorated $Sr_{0.95}Ag_{0.05}Nb_{0.1}Co_{0.9}O_{3-\delta}$ (SANC) can be enhanced by ~6.6 times relative to the bare SANC at 500 °C, but the enhancement decreases drastically at higher temperature. However, the mechanism of the metal promotion on the perovskite is not exactly known, and whether the physical model to calculate the exchange coefficient from the electrical conductivity relaxation measurement can be directly applied on the

modified surface remains a question.

2.4 Bulk Diffusion

Diffusion is a mass transport process in gas, liquid, or solid as a consequence of random motion. The diffusive species move toward an equilibrium where all the species in the mixture are uniformly dispersed. Fick's second law predicts how diffusion causes the concentration to change with time. The diffusion coefficient D is the kinetic parameter to describe the flux at unit concentration gradient. In a perovskite oxide, the diffusion substance is the oxygen ion, it jumps to a nearby oxygen vacancy site in the presence of an oxygen potential gradient. The oxygen diffusivity of the perovskite material strongly determines the electrochemical properties.

2.4.1 Fick's law

Fick's law is based on the hypothesis that the rate of diffusion through a unit area in a section is proportional to the concentration gradient. In a perovskite oxide, assuming an isotropic environment, at steady state where there is no net flux, the one-dimensional diffusion in the bulk is given as:

$$J_{02} = -D\frac{\partial c}{\partial x} \tag{2.12}$$

Where J_{02} is the oxygen flux in mol·m⁻²·s⁻¹, *D* is the diffusion coefficient in m⁻²·s⁻¹, *c* is the oxygen concentration and *x* is the diffusion direction. At non-steady state, if the diffusion coefficient is a constant, the time dependent one-dimensional differential equation is given as:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{2.13}$$

Eq. (2.12) and (2.13) are referred as Fick's first law and Fick's second law. The perovskite membrane surface is the interface of surface exchange and bulk diffusion, as described by J. Crank^[36], the boundary condition is:

$$-D\frac{\partial c}{\partial x} = k(c_{\rm s} - c_{\infty}) \tag{2.14}$$

Where k is the surface exchange coefficient, c_s is the actual concentration just within the surface and c_{∞} is the concentration required to maintain equilibrium with the surrounding atmosphere. Eq. (2.13) and (2.14) are used in the system modelling of electrical conductivity relaxation (ECR) measurement in this thesis.

2.5 Mathematica solution to diffusion equation

Eq. (2.13) is a linear partial differential equation, the solution requires one initial condition and two boundary conditions. Considering a flat sheet with the thickness of 2*l*, initially the sheet is in equilibrium with the surrounding atmosphere. At t=0, the oxygen concentration in the sheet is c_0 everywhere, and after a sudden change of P_{O2} , at $t=\infty$, a new equilibrium state with the oxygen concentration c_{∞} is established. The boundary conditions are given by^[37]:

$$J(l) = -D \frac{\partial c}{\partial x}\Big|_{x=l} = K_{\rm tr}(c_l - c_{\infty})$$
(2.15)

$$J(-l) = -D \frac{\partial c}{\partial x}\Big|_{x=-l} = -K_{\rm tr}(c_{-l} - c_{\infty})$$
(2.16)

Where J is the oxygen flux, K_{tr} is the exchange rate, and c_l , c_{-l} are the oxygen concentration at the surface. The schematic diagram of the concentration change with time in the sheet is shown in Fig 2.4.



Fig 2.4 Concentration profile in the sheet. Note the discontinuity at the surface, caused by the surface transfer process^[38].

There are several methods to solve Eq. (2.13), such as Laplace transform and eigenfunction expansion. The method used in this thesis is in detail described by M.W. den Otter^[38]. Worth to mention, for the calculated D_{chem} and k_{chem} , the characteristic length L_c is defined as:

$$L_c = \frac{D_{\rm chem}}{k_{\rm chem}} \tag{2.17}$$

$$L_{\alpha} = \frac{l}{L_c} \tag{2.18}$$

 L_{α} is the ratio of the half thickness to the characteristic length. For $L_{\alpha} < 0.03$, the surface transfer is rate limiting, and the equilibrium towards the new nonstoichiometric oxygen concentration is entirely governed by the surface reactions. While for $L_{\alpha} > 30$, diffusion is rate limiting and the equilibrium is not affected by surface exchange^[39]. One way to tune L_{α} in the range of 0.03-30 is to control the sample thickness, but usually the thickness is limited by the fabrication technique.

2.6 Electrical conductivity relaxation (ECR)

During the ECR measurement, the conductivity of a bar-shaped sample relaxes following a perturbation that alters its oxygen stoichiometry. In this case, an instantaneous change of the oxygen partial pressure in the surrounding atmosphere is introduced. The oxygen transport until reaching a new equilibrium is monitored by continuously measuring the conductivity as a function of time, as shown in Fig 2.5. The numerical values of oxygen surface exchange coefficient (k_{chem}) and diffusion coefficient (D_{chem}) can be obtained by fitting conductivity data to the solution of Fick's second law.



Fig 2.5 Schematic diagram of ECR principle

2.6.1 Apparatus

Fig 2.6 depicts the configuration of the ECR set up. The sample is placed in the alumina chamber enclosed in the furnace, tied by four gold wire electrodes that connect the outer circuit. The working gas stream flows through the electrochemical cell and goes to the ventilator, the switch gas stream directly flows through the oxygen sensor. A rapid switch of the two premixed gas streams is obtained by switching two pneumatic-controlled four-way valves simultaneously. A Keithley SourceMeter® provides a stable

current through the whole sample, and the voltage between the two inner electrodes is measured. The conductivity signal is continuously recorded by the computer and presented in the LabVIEW program.



Fig 2.6 Schematic representation of the electrical conductivity relaxation set-up. The sample is placed in the electrochemical cell, enclosed in a furnace.

2.6.2 Data processing

The conductivity data is processed based on the assumption that if a small step perturbation in P_{O2} is applied to the surrounding atmosphere and the step change is nearly ideal, *i.e.* instantaneous, the response of conductivity (σ) to perturbations in P_{O2} and the corresponding oxygen non-stoichiometry (δ) is linear^[40]. Then the relationship between conductivity and oxygen non-stoichiometry of the sample can be written as:

$$\frac{\sigma_t - \sigma_0}{\sigma_\infty - \sigma_0} = \frac{\delta_t - \delta_0}{\delta_\infty - \delta_0} \tag{2.19}$$

 σ_0 , σ_∞ , σ_t represent initial, equilibrium and time-related conductivity, respectively, similarly to oxygen non-stoichiometry. Replacing the oxygen non-stoichiometry by bulk oxygen concentration, we have:

$$\frac{c_t - c_0}{c_\infty - c_0} = \frac{\sigma_t - \sigma_0}{\sigma_\infty - \sigma_0} \tag{2.20}$$

And normalized conductivity g(t):

$$g(t) = \frac{c_t - c_0}{c_\infty - c_0}$$
(2.21)

Combine with the solution of Fick's second law from eigenfunction expansion method, we have:

$$g(t) = 1 - \sum_{n=1}^{\infty} \frac{2L_{\alpha}^{2}}{\alpha_{n}^{2}(\alpha_{n}^{2} + L_{\alpha}^{2} + L_{\alpha})} \exp(-\frac{t}{\tau_{n}})$$
(2.22)

 α_n are the eigenvalues solved from:

$$\alpha_n \tan \alpha_n = L_\alpha \tag{2.23}$$

And the time constants τ_n are given by:

$$\tau_n = \frac{l^2}{D\alpha_n^2} \tag{2.24}$$

The detailed data fitting process is described by M.W. den Otter^[41], including the iteration method, error control, and the correction of flushing time.

3. Experimental

3.1 Preparation of samples

The La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} powders used in this study were obtained from Forschungszentrum Jülich, Germany. The powders were ball-milled in ethanol for 72 h using 2 mm diameter zirconia milling balls. After milling and drying, the powders were ground in a mortar and sieved to collect the particles below 38 µm. Then the powders were uniaxially pressed at 100 kPa in a 4.0 cm×2.2 cm (*l*×*w*) rectangular mold. The green body pellets were sintered at 1200 °C for 10 h in air with heating and cooling rates of 3 °C/min. The density of the pellets was measured using the Archimedes method. The pellets that were in excess of 95% theoretical density were cut into roughly 10 mm×6 mm (*l*×*w*) bars, and then ground and polished on both side using SAPHIR 360 manual grinder to achieve a mirror surface with a sample thickness of 0.5±0.1 mm. The as-polished LSCF bars were re-sintered at 1200 °C for 1 h in air in order to renovate the surface that might be damaged by the rough polishing procedure. After that, the LSCF bars were ultrasonically cleaned in acetone and ethanol 1:1 mixture for 10 min to remove the contaminants from the surface.

3.2 Metal modification on sample surface

Pt metal particles were deposited on both surfaces of LSCF using a sputter coater (Jeol JFC-1300). The equipped sputtering target was platinum with a purity of 99.999%. The deposition chamber was first pumped to a base pressure of 3 Pa. After flushing the chamber by Ar (99.999%) for three times, the pressure was controlled at 6 Pa by a leak valve, a current of 10 mA was applied to generate an Ar plasma. The target-to-substrate distance was kept at 5.0 cm and the deposition was done at room temperature. These conditions were kept unchanged for all the sputtering experiments. Prior to metal deposition, the deposition rate of the sputter coater at experimental condition was

measured. An 18.75 mm×8.76 mm ($l \times w$) silica wafer was Pt-sputtered for 15, 15, 30, and 30 seconds subsequently. After each sputtering process, the total mass of the substrate was weighted in a TGA balance (NETZSCH STA499 F3) at 50 °C. The deposition mass as a function of sputtering time was calculated based on the mass difference method. The LSCF samples were Pt-sputtered for 20, 40, 60, 120 seconds on each surface (abbreviated as LSCF@Pt20, 40, 60 and 120), then annealed at 600 °C for 1 h. After Pt sputtering, the deposition chamber was carefully cleaned and the target was replaced by silver (99.999%), continued with the same sputtering time and annealing process for Ag-sputtered LSCF samples (abbreviated as LSCF@Pt20, 40, 60 and 120). Apart from metal deposition, Ar plasma might also influence the LSCF surface to some extent. Therefore, the net plasma treatment without metal deposition was conducted by sheltering the LSCF samples from metal beam using a watch glass, while the sample was still surrounded by Ar atmosphere. The plasma treated samples were abbreviated as LSCF@Plasma20, 40, 60 and 120.

3.3 ECR measurement

The electrical conductivity relaxation measurement was conducted using a homemade set up, shown in Fig 2.6. Electrodes were painted onto the LSCF bars using gold paste (MaTeck, Germany), gold wires of 0.25 mm diameter (Alfa Aesar, 99.999%) were attached to establish electrical connections to two Keithley 2400 SourceMeter® devices. The bars were placed in an alumina tube reactor of which the inlet was narrowed such that the flush time of gas stream in the step change was minimized. The total gas flow was 280 ml/min, by mixing N₂ and O₂ gas. The mixed gas streams were fed to the tube reactor via a 4-way valve, so that a nearly instantaneous switch of P_{O2} was performed. The P_{O2} step change from 0.215 atm to 0.464 atm was the so-called oxidation run, and the backwards change was the reduction run. The measurement temperature varied between 600 °C and 900 °C, with intervals of 25 °C or 50 °C and ramp rate of 5 °C/min. At the increasing temperature stage, ten relaxation measurements were performed at each temperature point: five oxidation runs, and five reduction runs. And at the reducing temperature stage, three oxidation runs, and three reduction runs were performed in the same way. The conductivity data was fitted numerically by a MATLAB program.

3.4 Characterizations of samples

3.4.1 X-Ray Diffraction (XRD)

The crystal structures of both raw LSCF powders and sintered membranes were determined by X-ray diffraction (Bruker D2 powder XRD) using Cu-K α radiation. The diffraction patterns were measured at room temperature, with X-ray scanning angles 20° $\leq 2\theta \leq 80^{\circ}$. All samples were placed on a low-background plastic sample holder. For metal coated samples, the XRD tests were conducted after the ECR measurement, without removing the gold paste.

3.4.2 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

SEM (JEOL JSM-6010LA) was used to characterize the microstructure and surface morphology of LSCF samples. EDS was attached in the same equipment, which allowed point analysis and surface element mapping to study the surface composition. Before measurement, ethanol cleaned samples were pasted on cylinder holders using carbon tape. Since the carbon tape could remove particles or layers from the surface, SEM tests were performed on samples after ECR measurements. For SEM, secondary electron beam with a voltage of 5 kV was used under 10 mm working distance, for EDS, the voltage was raised to 15 kV.

3.4.3 Low-Energy Ion Scattering (LEIS)

The surface composition of bare LSCF and net plasma treated LSCF after ECR measurements were analyzed by low-energy ion scattering (LEIS). Prior to the LEIS analysis, the sample surfaces were treated by oxygen plasma in the sample preparation chamber attached to the instrument at room temperature, to remove any hydrocarbon contaminants from exposure to the atmosphere. Once the cleaning was completed, a fresh area of the sample surface was selected for scattering measurement using a 5 keV ²⁰Ne⁺ beam. The LEIS signal in the range of scattering energy 0.8~3.5 keV was collected and further categorized.

4. Results

4.1 Sputter coater calibration

The calibration curve of the sputter coater using Pt target is shown in Fig 4.1. The error scatter is mainly caused by the instability of the TGA balance when weighting the mass of samples. The deposition rate of Pt is $1.8 \cdot 10^{-4}$ mg/s·cm², as derived from the slope and sample area.



Fig 4.1 The Pt deposition mass as a function of sputtering time.

The deposition rate varies for different metal targets. Suggested by MTI $Corp^{TM[42]}$, it can be described by the equation:

$$L_d = K I T \tag{4.1}$$

Where L_d is the deposited film thickness (Å), K is the material constant, for Au in Ar gas, $K \sim 0.17$, and for Pt, $K \sim 0.9$, I is the sputtering current (mA), which is adjusted by Ar gas partial pressure and T is the sputtering time (s). Since K for the Ag target is unknown in this case, the absolute Ag deposition rate cannot be calculated. But when the sputtering current, Ar partial pressure and the sample-to-substrate distance are fixed, the Ag deposition mass should be linearly proportional to the sputtering time, according to Eq. (4.1). This corresponds to the data presented in Fig 4.1.

4.2 Crystal structure

4.2.1 Bare LSCF



Fig 4.2 XRD patterns of (a) LSCF powders; (b) LSCF membrane after sintering; (c) LSCF membrane after ECR

Fig 4.2 shows the XRD patterns of LSCF powders, sintered LSCF membrane and LSCF membrane after ECR measurement. In the XRD pattern of LSCF powers (Fig 4.2a), LSCF peaks are sharply present, while the impurity peaks at 25.5°, 37.9° and 56.0° are referred to be Co₂O₃ phase (JCPDS no.022-0770). Through pattern refinement, the LSCF powder is confirmed to be rhombohedral perovskite structure, with the lattice parameter a=b=5.525 Å, c=13.455 Å. The XRD peaks of sintered LSCF membrane (Fig 4.2b) split at high angles, indicating the distortion of the oxygen octahedrons in LSCF perovskite structure. In the sintering process, Co₂O₃ reacted with LSCF and incorporated into the perovskite lattice, which may explain the vanishing of Co₂O₃ peaks in Fig 4.2b. The gold peaks (JCPDS no.04-0784) in Fig 4.2c results from the use of gold paste in the ECR measurement, apart from this, no obvious lattice distortion or phase transition is observed. Additionally, Co₃O₄ peak (JCPDS no.009-0418) shows up after the ECR measurement. Liu *et al.*^[43] studied the Raman spectrum of LSCF after a long-term test and found the existence of Co₃O₄ on the surface, which is consistent with our result.

4.2.2 Pt-sputtered LSCF



Fig 4.3 XRD patterns of Pt-modified LSCF membranes after ECR: (a) LSCF@Pt20;(b) LSCF@Pt40; (c) LSCF@Pt60; (d) LSCF@Pt120

Fig 4.3 shows XRD patterns of Pt-modified LSCF membranes after ECR measurements. The standard XRD patterns of fcc Pt (JCPDS no.04-0802) and fcc Au (JCPDS no.04-0784) are very similar. The overlap of the peaks appeared at some angles, when Au and Pt are present on the LSCF surface simultaneously. In the magnified pattern, an increase of Pt peak intensity at two-theta angle 39.5° is observed with higher Pt deposition, which is an evidence of the existence of Pt crystals. In all patterns, PtO₂ phase is not found, means the deposited Pt particles are stable in the oxidation atmosphere. At two-theta angle 36.2° , the Co₃O₄ impurity peak remains, which is also confirmed by the SEM micrographs latter.

4.2.3 Ag-sputtered LSCF



Fig 4.4 XRD patterns of Ag-modified LSCF membranes after ECR: (a) LSCF@Ag20; (b) LSCF@Ag40; (c) LSCF@Ag60; (d) LSCF@Ag120

Fig 4.4 is the XRD patterns of Ag-modified LSCF membranes after ECR measurements. The standard Au (JCPDS no.04-0784) and Ag (JCPDS no.04-0783) patterns completely overlap. Therefore, the Ag peaks can't be distinguished under the interference of Au, the same situation occurs for Ag₂O. In order to analyze the oxidation state of Ag deposition after oxidation treatment, X-ray photoelectron spectroscopy (XPS) needs to be applied. Except for LSCF@Ag60, there is a shift of the XRD patterns to the low angle with increasing Ag deposition, which may be indicating an increase in the lattice parameters. It is suggested that the introduction of A-site deficiency into the perovskite structure produces additional oxygen vacancies and increases the lattice parameters^[23]. But in the magnified XRD patterns, Au/Ag peak shows the same shift behavior. Since the metal lattice is not affected by the oxygen vacancies, it is more likely that the peak shift is merely caused by the instrumental error of XRD. The Co₃O₄ impurity peak again exists in the Ag-modified LSCF samples.



4.2.4 Plasma-treated LSCF

Fig 4.5 XRD patterns of plasma-treated LSCF membranes after ECR: (a) LSCF@plasma20; (b) LSCF@plasma40; (c) LSCF@plasma120

Fig 4.5 shows the XRD patterns of net plasma-treated LSCF membranes after ECR measurements. Except for the presence of gold peaks and a very weak Co₃O₄ peak, there is no evidence of other impurities on the surface or phase transitions of LSCF. Though it is suspected that the Ar plasma is able to remove metal ions from the top surface, or the low oxygen partial pressure in the plasma chamber provides a reducing environment for LSCF, the possible changes on the surface cannot be detected by normal XRD due to the relatively large penetration depth of X-ray.

4.3 Surface morphology

4.3.1 Effect of sintering and polishing

Fig 4.6 shows the SEM images of the LSCF surfaces sintered at different conditions that have been reported, (a) 1200 °C for 10 h; (b) 1250 °C for 5 h; and (c) 1350 °C for 2 h. For all samples, the grains are closely breasted and the grain size grows larger at higher sintering temperature. The dark areas in Fig 4.6c are suspected to be non-conductive phases, possibly results from the decomposition of LSCF at 1350 °C. Fig 4.6a and b both show a typical LSCF surface morphology, and the measured densities are in excess of 96% of the theoretical density. In practice, the bar-shape sample sintered at 1250 °C often showed extensive cracks while the sample sintered at 1200 °C retained a completely intact rectangular appearance. From the perspective of yield, 1200 °C was chosen as the sintering temperature in this study.



Fig 4.6 SEM micrographs of the LSCF surface directly after sintering at (a) 1200 °C for 10 h; (b) 1250 °C for 5 h; (c) 1350 °C for 2 h

It was found that the surface roughness can seriously affect the surface exchange reaction^[11], therefore, a well-polished smooth sample surface is necessary in determining the surface exchange rate. After sintering, the LSCF samples were ground to reach an appropriate thickness. As shown in Fig 4.7a, pores and large particles are widely spread on the surface after grinding. The polishing process partly removes particles and pores, but introduces scratches to the surface, shown in Fig 4.7b. Therefore, polished samples were re-sintered at 1200 °C for 1 h to renovate the surface damage thermodynamically. As can be seen in Fig 4.7c and d, a relatively smooth surface is achieved for the latter experiments.





1200 °C

4.3.2 Surface impurities

Segregated micron-sized particles were observed on LSCF surface after sintering. Energy dispersive spectroscopy (EDS) point analysis was performed to study the composition of these particles. As shown in the SEM micrograph in Fig 4.8 and corresponding composition listed in Table 4.1, point (001) and (002) are Fe-rich particles, while point (003) is a stoichiometric LSCF grain. Limited by the resolution and penetration depth of the EDS point analysis, the precise composition of the Fe-rich particles cannot be obtained.



Fig 4.8 SEM micrograph and EDS point analysis of the LSCF sample sintered at 1200 °C

	La	Sr	Со	Fe
001	0.32	0.35	0.22	1.11
002	0.32	0.35	0.25	1.08
003	0.62	0.38	0.17	0.83

Table 4.1 Contents of elements calculated from EDS point analysis of Fig 4.8

For the sample sintered at 1250 °C, different impurity phases were found, *e.g.* Co-rich and Co-free particles, shown in Fig 4.9 and Table 4.2. The Co-rich particles form at LSCF grain boundaries, which may result from the migration of segregated cobalt

species on the surface. Combined with the XRD analysis of the samples after ECR measurements, the Co-rich particles are very likely to be Co₃O₄, an effective catalyst for oxygen reduction reaction^[44, 45]. In our study, these Co-rich particles are found on all samples after ECR measurements, which may be an unignorable factor in determining the surface exchange rate.



Fig 4.9 SEM micrograph and EDS point analysis of the LSCF sample sintered at 1250 °C

Table 4.2 Stoichiometry of elements calculated from EDS point analysis of Fig 4.9

	La	Sr	Со	Fe
001	0.03	0.02	1.57	0.38
002	0.62	0.39	0.15	0.84
003	0.68	0.46	nd	0.86
004	0.03	0.02	1.62	0.32

4.3.3 Pt-modified LSCF surface

Fig 4.10 shows the SEM micrograph of Pt-modified LSCF membranes after ECR. Both for 10s and 120s sputtering, the platinum particles are homogeneously distributed on the surface and concentrated on the grain boundaries. Comparing with 10s sputtered

LSCF, the 120s sputtered sample has a higher platinum surface coverage together with a larger average particle size, indicating that the agglomeration happened during heat treatment, but the platinum particles did not form a complete layer. After ECR measurement, the LSCF grain morphology remains. In the red circle are the Co-rich particles, they appear at LSCF grain boundaries and have comparable size to LSCF grain. The regular shape of these particles indicates they are crystalline.



Fig 4.10 SEM micrograph of Pt-modified LSCF surface after ECR, (a) LSCF@Pt10,(b) LSCF@Pt120. In the red circles are the Co-rich particles.

4.3.4 Ag-modified LSCF surface

Unlike platinum, silver particles are more mobile, thus the distribution is less homogeneous. In the magnified micrograph of LSCF@Ag20 (Fig 4.11b), silver particles are deposited on the top of the grain surface and boundaries with a clear contour, while in Fig 4.11d, the silver particles are partly sunken into the LSCF grains. In Fig 4.11f, LSCF grains beneath the silver particles show holes, whereas the impurity particles with silver on top remain their shapes, indicating that the LSCF surface is etched by silver particles but that of impurities is not. In Fig 4.11e, the area that was etched by silver turns black under electron beam, meaning that a non-conductive phase is generated after silver reacted with LSCF. In Fig 4.11g and h, the corrosion is completed, nano-size holes are present on the LSCF surface instead of silver particles, and the black area disappears. From Fig 4.11a to 4.11h, the only variable is the sputtering time of silver, therefore, the level of Ag incorporation depends on the Ag concentration. After ECR measurements in the same temperature range, oxygen partial pressure, and working circles, the surface morphologies of Ag-modified LSCF are completely different. The incorporated silver forms a conductive phase and a nonconductive phase, depending on the amount of silver.





Fig 4.11 SEM micrograph of Ag-modified LSCF surface after ECR, (a, b) LSCF@Ag20, (c, d) LSCF@Ag40, (e, f) LSCF@Ag60, (g, h) LSCF@Ag120

4.3.5 Plasma treated LSCF surface

Fig 4.12 shows the surface of plasma-treated LSCF after ECR measurement. Except for the Co-rich particles, some relatively small particles appeared, of which the EDS signals couldn't be related to any metal. Compared to the metal-modified LSCF, the surfaces of plasma-treated sample have a large variation of grain size from 0.2-2 μ m. It is possible that the Ar plasma introduces metal deficiencies and further results in phase

transitions on the LSCF surface. Mass transports from grains to particles, causing a poor grain size distribution.



Fig 4.12 SEM micrograph of 60s plasma-treated LSCF surface after ECR

4.4 LEIS



Fig 4.13 LEIS spectra of LSCF membranes after ECR (a) bare membrane, (b) 120s plasma-treated LSCF. Spectra are shown for the outmost surface, after 15 min O_2 plasma cleaning.

Fig 4.13 shows the LEIS spectra of the outmost surface of bare LSCF and 120s plasmatreated LSCF after ECR measurements. The spectra were acquired using a 5 keV 20 Ne⁺ beam. The Ne beam gives a good separation for heavy ions, which are the strontium, lanthanum and bismuth/lead peaks in Fig 4.13, while cobalt and iron signals are difficult to analyze. In both spectra, clear impurity peaks that are assigned to bismuth or lead are observed. Druce *et al.*^[46] also found this lead contamination on LNO and suggested the source is the segregation of lead impurity from the bulk to the outer surface of the pellet during the high temperature annealing, while cross-contamination by volatile lead species from the annealing equipment cannot be excluded.

By coincidence, on one sample, on the area between the gold electrodes, bismuth/lead contained particles were observed, shown in the SEM micrograph Fig 4.14. These particles form a nearly continuous layer on the LSCF surface, the bismuth/lead signal in the EDS spectra shown in Fig 4.15 confirms the existence of these elements. Since these particles were never observed on the LSCF bulk area, there are two possible

sources of the bismuth/lead contaminations: the gold paste or the ECR chamber. Since the contamination particles are only found on one SEM sample, it is reasonable to suspect that the electrode of this particular sample touched the inner wall of the ECR chamber, and was directly contaminated by the chamber. For the other ECR samples, under high temperature, the LSCF surfaces were exposed to the bismuth/lead vapor, a small amount of bismuth/lead agglutinated on the LSCF surface, and cannot be revealed by XRD or EDS.



Fig 4.14 SEM micrograph of bismuth/lead containing particles on the electrode area



Fig 4.15 EDS spectrum corresponding to Fig 4.14

4.5 ECR

4.5.1 Normalized conductivity

In the electrical conductivity relaxation measurement, at each temperature, four kinds of data points were achieved, which were the oxidation P_{O2} step at heating, the reduction P_{O2} step at heating, the oxidation P_{O2} step at cooling, and the reduction P_{O2} step at cooling. If the surface exchange reaction ideally follows Eq. (2.11), the oxygen partial pressure in atmosphere switches instantaneously and no side reaction or decomposition happens in the working temperature range, the normalized conductivity as a function of time should be the same for the four situations.



Fig 4.16 Experimental data of normalized conductivity as a function of time, 800 °C, P_{O2} (0.215-0.464 atm), bare LSCF.

In practice, the measured conductivity for the reduction process reaches a faster equilibrium than the oxidation process. Fig 4.16 shows the curve of the normalized conductivity as a function of time for four data sets and the table lists the calculated k and D values, and Fig 4.17 gives the magnified graph in the initial time range. As can be seen, for both surface exchange and bulk diffusion, the reduction runs have better

performances. This behavior may indicate that the gas phase adsorption influence the surface exchange reaction as well as the conductivity euqilibrium, and can cause a huge variation in the calculated k_{chem} and D_{chem} parameters. Since there is not a preference to use a specific oxidation/reduction or heating/cooling data set, the measured reduction/cooling data are analyzed in this thesis.



Fig 4.17 Magnified graph of Fig 4.16, in the time range of 0-30 s, the flat line in the front section is casued by the flush time of the stream.

4.5.2 Bare LSCF



Fig 4.18 Measured oxygen transport kinetic parameters of the presented bare LSCF sample and the reported values plotted as a function of inverse temperature (and temperature) (a) oxygen bulk diffusion coefficient; (b) surface exchange coefficient

The oxygen diffusion coefficient and surface exchange coefficient results of bare LSCF sample from this work and reported values measured by electrical conductivity relaxation are shown in Fig 4.18 a and b^[37, 47, 48]. For the diffusion coefficient D_{chem} , the presented values are consistent with the reported values, means there is no significant

difference in the bulk structure and diffusion properties. For the surface exchange coefficient k_{chem} , the presented results are of one order of magnitude higher than the reported values at 800 °C, which very likely means the surface exchange reaction is catalyzed. In SOECs applications, a high surface exchange rate is pursued, but in this thesis, if the bare sample possesses an abnormal high exchange rate, the surface modification of catalyst particles would have limited promotion effect.

In chapter 2.5, the characteristic length L_c and the parameter L_a are introduced, L_a needs to be in the range of 0.03-30 to ensure the assumed kinetic oxygen transport model is meaningful. At 700 °C, the characteristic length L_c of bare LSCF is 8 µm. In practice, the sample thickness was 0.565 mm. The calculated L_a =35.3, which is higher than the maximum limit, meaning that the oxygen transport through the sample is dominated by bulk diffusion. Under this circumstance, the oxygen surface exchange has a minor influence on the relaxation kinetics. Thereby, the calculated exchange coefficient is less accurate, and, furthermore, the influence of metal deposition is not significant. It is found that at lower temperature, the L_a value decreases to the reasonable interval, *e.g.* at 600 °C, the L_a value for bare LSCF is 22.2. Another solution to lower the L_a value is to prepare a thinner sample. However, low temperature ECR measurements cost unaffordable time for this thesis, and the manufacturing technique used in the experiment reaches a minimum sample thickness of 0.4 mm. So, the high L_a value remains to be a drawback of this study.

4.5.3 Pt-modified LSCF



Fig 4.19 Measured oxygen transport kinetic parameters (a) bulk diffusion coefficient (b) surface exchange coefficient of the Pt-modified LSCF samples. The black dash line is the bare LSCF reference, the purple line is the $log_{10}(k_{chem}) \sim 1/T$ curve when L_{α} =30.

Fig 4.19 a and b show the k_{chem} and D_{chem} results of the platinum coated LSCF samples deducted from the reduction/cooling runs of ECR measurements. The diffusion coefficients of LSCF samples with different platinum loading amount and the bare LSCF do not have a distinct variation. It corresponds to the assumption that the ionic

transport properties within the bulk of LSCF are not affected by the surface deposition. In Fig 4.19b, the Arrhenius plot of surface exchage is presented. The black dashed line is the surface exchange rate of the bare LSCF sample, and the purple dash line is the effective maximum surface exchange rate when L_{α} equals 30. The exchange rates under the purple line are considered well-described by the model while the data points over the purple line are less accurate. The surface exchange coefficients of the LSCF samples decrease over the full temperature range when raising the platinum deposition amount. This means that the surface exchange reaction on the LSCF surface was not promoted by the coated platinum particles, and the excessive platinum coverage blocked surface active reaction sites, leading to the drop of surface exchange activity. At 600 to 700 °C, the 20 s and 40 s sputtered LSCF samples show a higher surface exchange rate than the bare LSCF, but these data points are above the effective interval, therefore, whether platinum promotes the surface exchange reaction at low temperature is uncertain.



4.5.4 Ag-modified LSCF



Fig 4.20 Measured oxygen transport kinetic parameters (a) bulk diffusion coefficient (b) surface exchange coefficient of the Ag-modified LSCF samples. The black dash line is the bare LSCF reference

As shown in Fig 4.20, the silver-modified LSCF samples have different behavior compared to the platinum-modified LSCF. In Fig 4.20a, the D_{chem} of LSCF@20Ag at 800 °C is $3.9 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, 50% lower than the bare LSCF, $7.9 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$. The drop of D_{chem} becomes larger as temperature decreases. For LSCF samples with higher amounts of silver deposition, the diffusion coefficients gradually increase, and the diffusion coefficient for LSCF@Ag120 is slightly higher than bare LSCF. Fig 4.21 shows the relation between D_{chem} and the silver sputtering time. With increasing amount of silver deposition, the diffusion coefficient of LSCF increases proportionally, at all selected temperatures. Since the oxygen bulk diffusion properties of LSCF are commonly not affected by the surface modification, it is possible that in this case, the silver atoms incorporated into the LSCF lattice and changed the oxygen mobility forms strontium oxide. The initial silver dopant has negative effects to the oxygen diffusion, however, when the silver concentration increased, the oxygen diffusion is promoted.



Fig 4.21 Bulk diffusion coefficient D_{chem} as a function of silver sputtering time, at 700 °C, 750 °C, 800 °C, and 850 °C

Fig 4.20b shows the k_{chem} of silver-modified LSCF. The k_{chem} values reduce to 2% ~ 15% compared to the bare LSCF. The surface exchange rate needs to be analyzed together with the surface morphology. In Fig 4.11f and h, silver particles seem to have completely incorporated into the LSCF lattice, providing surface oxygen vacancies, leaving surface pores as extra surface area, which may explain why the LSCF@Ag120 and LSCF@Ag60 samples have higher k_{chem} values than LSCF@Ag20 and LSCF@Ag40. In the surface exchange reaction, both electrons and oxygen vacancies are reactants. In principle, the non-conductive area on the LSCF@Ag60 surface shown in Fig 4.11e would cause a negative effect, but the k_{chem} value of LSCF@Ag60 does not show obvious decay, possibly means the reaction is ionically controlled. The surface of silver-modified LSCF is very complicated, factors like the silver concentration, silver incorporation, surface conductivity and surface microstructure can all have an influence on the surface exchange reaction. Therefore, based on the SEM and ECR analyses, it is not clear which factors are more decisive.

4.5.5 Plasma-treated LSCF



Fig 4.22 Measured oxygen transport kinetic parameters (a) bulk diffusion coefficient (b) surface exchange coefficient of the plasma-treated LSCF samples. The black dash line is the bare LSCF reference, the purple line is the $log_{10}(k_{chem}) \sim 1/T$ curve when $L_{\alpha}=30$.

Fig 4.22a is the oxygen bulk diffusion coefficient plot as a function of reciprocal temperature. The curve precisely matches the bare LSCF reference, and shows that the plasma treatment does not introduce changes to the oxygen bulk diffusion rate. As well

as Fig 4.19b, Fig 4.22b shows the surface exchange coefficient together with the bare LSCF reference and the effective maximum surface exchange rate limited by L_{α} . If only considering the trend of the Arrhenius plot of the plasma-treated samples, longer plasma treatment leads to an increase of the surface exchange rate without changing the bulk properties. The exchange coefficient of LSCF@Plasma120 at 700 °C is $1.4 \cdot 10^{-4} \text{ m} \cdot \text{s}^{-1}$, ~4.5 times higher than the bare LSCF. Compare with the bare LSCF, the plasma-treated samples have a lower activation energy, owing to a cleaning effect of argon plasma, or the removal of large ions that creates active surface reaction sites. When the surface composition changes after plasma treatment, the crystal stoichiometry changes accordingly, and the heat treatment during ECR measurement accelerates the generation of new phases, which can explain the small particles found in Fig 4.12.

5. Discussions

The LSCF raw powders were obtained from Forschungszentrum Jülich, which in term commercially obtained it from a large-scale production process. The powder XRD measurement shows the existence of Co_2O_3 phase in the raw powders. After ECR measurement, the excess cobalt transported to the surface and generated Co_3O_4 . As an ORR catalyst, Co_3O_4 particles on the grain boundaries can promote the oxygen surface exchange reaction and interfere with the ECR measurement. It is one reason to explain the high surface exchange coefficient achieved in this study. In future research, substrate or base materials should be prepared in the laboratory, to achieve a higher purity. Another reason for the high exchange rate could be the bismuth or lead contaminations on the surface. The sources of these elements in this study could be the bismuth/lead layer on the electrode area was captured, the contaminations are more likely from the ECR chamber or gold paste. The ECR set up needs to be dismantled and

the elements of the remainders on the inner wall of ECR chamber need to be characterized. LEIS measurement needs to be conducted on a silicon substrate with gold paste on the surface. If the source of the bismuth or lead contamination is determined, a new ECR protocol needs to be established. The functions of Co_3O_4 and bismuth/lead coating on perovskite surface are also new research topics. For the clean LSCF surface, the surface exchange rate should be comparable with the literature values. After proper surface modification, the promoted surface exchange rate should still stay in the effective range defined by L_{α} , hopefully leading to results that can be considered more dependable.

Platinum and silver particles show different behavior on the LSCF surface after ECR measurement. It was reported by Gong et al.^[50] that platinum is a better current collector for EIS measurements than silver at temperatures higher than 650 °C. Silver undergoes a deep penetration and abundant distribution into the cathode/electrolyte interface region and greatly affects the polarization ASR. In the present study, platinum particles on the LSCF surface were stable in the experimental temperature and atmosphere, while silver etched the LSCF surface and incorporated into the lattice, and thereby seriously changed the oxygen transport properties of LSCF. Shown in Fig 4.11, the level of silver incorporation depends on the deposition amount: the more particles sputtered on the surface, the more serious corrosion was observed. It is difficult to explain this phenomenon with the current knowledge. The incorporated silver could be located as interstitial ions or substitute the metal sites. Since the Shannon radii of six coordinated Ag^{2+} (1.15 Å) is closed to Sr^{2+} (1.18 Å)^[49], it is likely that silver substitutes the lattice strontium ions. The positive interstitial ions lead to a reduction of the oxygen vacancy concentration, and the silver substituted strontium sites are compensated by extra oxygen vacancies. Since the diffusion coefficient increases with silver concentration, silver substitution is a more probable process in the lattice. The melting point of metal strontium is 777 °C, the exchanged strontium can spread on the surface, leaving surface pores. The Ag-modified LSCF samples possess lower diffusion and exchange rates than bare LSCF. The reason could be that with silver incorporation, the oxygen transport mechanism in a multi-phase material does not fully resemble the isotropic transport model. Another explanation is that the exchanged strontium is partly oxidized to generate SrO on the surface. It was found that the SrO surface precipitate is electrically insulating and can lead to a degradation of the surface catalytic activity of LSCF^[51]. For the platinum coated LSCF samples, the diffusion coefficients are unchanged. Since the LSCF substrate already has a high exchange activity, the oxygen transport is a diffusion controlled process, the catalytic effect of platinum on the surface is not prominent. In addition, the Co₃O₄ particles and the Bi/Pb impurities can also be catalysts that may provide reaction sites on the surface, the introduction of other catalytic particles may not have a distinct effect on the surface exchange reaction. The 120 seconds net plasma treated LSCF shows a remarkable enhancement on the exchange kinetics. The reason could be that the Ar plasma can clean the LSCF surface, dusts like silicon and hydrocarbons are removed, more active area is exposed to the atmosphere. Another possibility is that the large ions, in this case La³⁺, is removed from the surface lattice, ionic conducting phase, e.g. $SrCoO_{3-\delta}$, is generated thermodynamically. If the surface exchange reaction is ionically controlled, the formation of ionic conductive phase would significantly promote the reaction.

6. Conclusions

In this work, dense LSCF membranes with smooth surfaces were synthesized from commercial LSCF powders following a conventional protocol and extra heating. After thermal treatment, Co₂O₃ impurities in the raw powders immigrated to the surface and formed Co₃O₄ particles on the LSCF grain boundaries. The SEM results show that the Co₃O₄ phases are extensively available on all samples. The ECR results of bare LSCF show a reasonable diffusion coefficient and a remarkably high surface exchange coefficient compared to literature data. The possible reasons can be summarized as the catalytic effect of Co₃O₄ and bismuth/lead impurities, the inaccuracy of the fitting model limited by L_{α} , and the non-ideal behavior of heating/cooling oxidation/reduction data.

Controllable deposition of platinum and silver nanoparticles on the surface was achieved using sputtering. After long-term ECR measurements, platinum particles remained homogeneously dispersed on the LSCF surface with a particle size of 50-200 nm (600-800 °C), while after ECR measurement at slightly higher temperatures (700-900 °C) silver particles etched the surface and partly incorporated into the bulk phase. The ECR results show that platinum particles did not influence the bulk diffusion, while silver particles greatly changed the diffusion properties of LSCF, and the diffusion coefficient depended on the silver deposition amount. Both platinum and silver did not promote the surface exchange rate. For platinum, the reasons could be that the surface exchange rate for bare LSCF was catalyzed by impurities and already reached a high value, the deposited platinum particles could have played a hindrance role. For silver, the overall performance of surface exchange degraded with 2% to 15% of bare LSCF, factors like the surface microstructure, surface conductivity, and surface composition can be involved, the system is too complicated to be analyzed in this study. The 120 seconds net plasma treated LSCF has a distinct enhancement on the surface exchange

coefficient, possibly due to the cleaning effect of Ar plasma, or the formation of ionic conductive phase on the LSCF surface.

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List of symbols

 D_{chem} : the chemical bulk diffusion coefficient. k_{chem} : the chemical surface exchange coefficient. SOFC: solid oxide fuel cell. h⁻: electron hole in K-V notation. σ_i : ionic conductivity. c_i : ion concentration. q_i : the charge per ion. μ_i : mobility of charged species. $\sigma_{\rm e}$: electronic conductivity. σ_{total} : total conductivity. J₀₂: oxygen flux density. $c_{\rm s}$: oxygen concentration within the surface. c_{∞} : equilibrium oxygen concentration. $K_{\rm tr}$: the surface oxygen transport rate coefficient. L_c : the characteristic thickness. *l*: half thickness of the sample. σ_0 : initial conductivity. σ_{∞} : equilibrium conductivity. σ_t : time-related conductivity. δ_0 : initial oxygen non-stoichiometry value. δ_{∞} : equilibrium oxygen non-stoichiometry value. δ_t : time-related oxygen non-stoichiometry value. g(t): normalized time-dependent conductivity.

 L_d : the deposition thickness.

I: the sputtering current.

K: the sputtering material constant.