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Electrode Reaction Pathway in Oxide Anode for Solid Oxide Fuel Cells

Wenyuan Li

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Electrode Reaction Pathway in Oxide Anode for Solid Oxide Fuel Cells

Wenyuan Li

**Dissertation 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**

**Doctor of Philosophy
In
Mechanical Engineering**

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Morgantown, West Virginia
2015**

**Keywords: solid oxide fuel cells, oxide anode, H₂ oxidation mechanism, catalytic activity,
overpotential**

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ABSTRACT

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Wenyuan Li

Oxide anodes for solid oxide fuel cells (SOFC) with the advantage of fuel flexibility, resistance to coarsening, small chemical expansion and etc. have been attracting increasing interest. Good performance has been reported with a few of perovskite structure anodes, such as (LaSr)(CrMn)O₃. However, more improvements need to be made before meeting the application requirement. Understanding the oxidation mechanism is crucial for a directed optimization, but it is still on the early stage of investigation. In this study, reaction mechanism of oxide anodes is investigated on doped YCrO₃ with H₂ fuel, in terms of the origin of electrochemical activity, rate-determining steps (RDS), extension of reactive zone, and the impact from overpotential under service condition to those properties.

H₂ oxidation on the YCs anodes is found to be limited by charge transfer and H surface diffusion. A model is presented to describe the elementary steps in H₂ oxidation. From the reaction order results, it is suggested that any models without taking H into the charge transfer step are invalid. The nature of B site element determines the H₂ oxidation kinetics primarily. Ni displays better adsorption ability than Co. However, H adsorption ability of such oxide anode is inferior to that of Ni metal anode. In addition, the charge transfer step is directly associated with the activity of electrons in the anode; therefore it can be significantly promoted by enhancement of the electron activity. It is found that A site Ca doping improves the polarization resistance about 10 times, by increasing the activity of electrons to promote the charge transfer process.

For the active area in the oxide anode, besides the traditional three-phase boundary (3PB), the internal anode surface as two-phase boundary (2PB) is proven to be capable of catalytically oxidizing the H₂ fuel also when the bulk lattice is activated depending on the B site elements. The contribution from each part is estimated by switching the electrolyte to change 3PB kinetics. Compared to Ni, Co doping activates the bulk oxygen more significantly, promoting the reaction at 2PB. The active surface reaction zone is found to be enlarged by the electrolyte with high oxygen activity (SSZ vs. YSZ) when charge transfer is one of the RDS. Due to the larger exchange current for charge transfer in 3PB with SSZ electrolyte, the adsorption gradient zone is broadened, leading to enhanced surface reaction kinetics. The potential application of such finding is demonstrated on SSZ/YSZ/SSZ sandwich, showing largely improved electrode performance, opening a wide door for the utilization of electrolytes that are too expensive, fragile or instable to be used before.

The bulk path way in 2PB reaction can be affected by overpotential in terms of local vacancy concentration, built-in electrical field and stability. It is proven that an uneven distribution of lattice oxygen is established under operation conditions with overpotential by both qualitative analysis and analytic solution. An electrostatic field force is present besides the

concentration gradient in the anode lattice to control the motion of oxygen ions. Compared to the usual estimation based on chemical diffusion mechanism, the real deviation of ionic defects concentration under polarization from the equilibrium state near electrode/electrolyte interface is smaller with the built-in electrical field. The overpotential is demonstrated to be able to open up or shut down the bulk pathway depending on the ionic defects of electrodes. The analysis on the bulk pathway in terms of local charged species and various potentials provides new insight in anion diffusion and electrode stability.

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List of Symbols and Notations

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	$(\text{LaSr})(\text{CoFe})\text{O}_3$
LSCM	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$
MPD	Maximum power density
MIEC	Mixed ion and electron conductor
ORR	Oxygen reduction reaction
RDS	Rate determining step
SOFC	Solid oxide fuel cell
SSZ	Scandium stabilized zirconia
TEC	Thermal expansion coefficient
YCC	$\text{YCr}_{0.8}\text{Co}_{0.2}\text{O}_3$
YCCC	$\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Co}_{0.2}\text{O}_3$
YCCN	$\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$
YSZ	Yttrium stabilized zirconia
B-V	Bulter-Volmer
V-I	Voltage-current
C	Capacitance
c	Concentration
D	Chemical diffusion coefficient
e	Electron change
$\vec{E}$	Electrical field
E_a	Activation energy
E_N	Nernst potential
f_0	Characteristic frequency
F	Faraday constant

I	Current
J	Current density
k	Surface exchange coefficient
k_B	Boltzmann constant
n	Reaction order
P_{H_2}	Hydrogen partial pressure
P_{O_2}	Oxygen partial pressure
R	Reaction rate
R_p	Polarization resistance
z	Formal charge

α	Symmetry factor
ϵ	Relative permittivity
ϵ_0	Vacuum permittivity
η	Electrode overpotential
θ	Surface coverage
μ	Electrochemical potential
ρ	Local charge density
σ	Conductivity
ϕ	Galvanic potential

Subscripts

0	Steady state
ct	Charge transfer
e	Electron
i	Oxygen ion
h	Electron hole
v	Oxygen vacancy

Chapter 1

INTRODUCTION

Industrial development improves people's lives at the expense of increasing consumption of energy and severe environmental consequences. Of various solutions to promote energy utilization efficiency, SOFCs have attracted intensive attention due to their intrinsic high efficiency in chemical-electrical energy conversion.

Besides the most commonly used Ni/YSZ (yttrium stabilized zirconia) anode, an array of oxide materials have been investigated as anode candidates for SOFCs in consideration of the advantage in fuel flexibility, structure stability during redox process and long-term reliability. As most effort has been focused on the output performance of those materials, the main aspect missed out so far is the understanding of the operating mechanism.

Through nearly four decades, the anode reaction mechanism is being studied on Ni/YSZ and other noble metal anode, such as Pt and Ag. But the results on those metal anodes cannot be interpreted into oxide anodes directly. First of all, oxygen as the oxidant is supplied by the electrolyte only in those metal anodes because none of them is confirmed with significant oxygen ion conductivity, even though Pt is found to conduct oxygen slightly through grain boundary at relative low temperature. In contrast, the conduction of oxygen in oxide anodes are highly possible through lattice oxygen vacancy or interstitial oxygen or grain boundary hyperstoichiometry oxygen. Secondly, surface adsorption process in metal anode simply involves H, and lots of simulation work has been done in order to illustrate the correlation

between the adsorption ability and the chemical bonding. However, those results would be different on oxide anode provided that oxygen in principle could escape from lattice, becoming an adsorbed atom on the surface, which reacts with adsorbed H. In addition, the adsorption ability of metal element in the oxide anodes could be heavily dependent on its oxidation state, leading to different trends from the pure metal anodes. In addition, a long distance diffusion process in Ni/YSZ is not common as the primary reaction area is confined to 3PB. In contrast, the ionic conductivity in oxide anode could enable a broadened reactive zone where a significant bulk diffusion process occurs. Based on the knowledge from cathode investigation, such broadened area influences the performance greatly in electrode with good ionic conductivity. Similarly, it will influence the anode performance also when particular conditions are met. Judged by the experimental and simulation studies for cathode where a larger body of data set is available on this topic, such pathway can be activated by the overpotential applied to the electrode under steady state. Therefore, a new bulk pathway in the anode which varies under different flowing current is newly present in oxide anode, and no such information can be lent from traditional metal anode.

In the present study, Cr-based perovskite is chosen as the oxide anode. The oxidation mechanism including surface process, activity of bulk oxygen, dominant reactive zone, variation of bulk pathway and the new insight on stability under the influence of overpotential and etc. are investigated experimentally and analytically.

LITERATURE REVIEW

2.1 SOFCs anode materials

Fig. 2.1 Schematic diagram of SOFC.[1]

Solid oxide fuel cells converting chemical energy directly to electrical power offers advantages over other techniques in the intrinsically high conversion efficiency and minimal environmental impact. The state-of-the-art SOFCs consist of YSZ electrolyte, Ni/YSZ anode and lanthanum strontium manganite (LSM) cathode. Fig. 2.1 shows the operation principle of SOFC with oxygen conductive electrolyte. Fuel is catalytically oxidized at anode by the oxygen transported through electrolyte. Taking H_2 fuel oxidation as an example, the anode reaction can be written as

As illustrated by this simple equation, the following features with anode materials can be drawn:

- Tolerant to reducing atmosphere, e.g. up to around 10^{-24} for H_2 .
- Electronic conductive to lead away accumulated electrons.
- Catalytic activity in terms of adsorbing and dissociating fuel like H_2 .
- Possible catalytic activity that comes from activating oxygen.

Considering the structure of fuel cell, the followings are also required:

- Chemical stability with other components.
- Thermal expansion matching with other parts.

2.1.1 Conventional Ni anode

The Ni/YSZ cermet is the most commonly used anode in SOFC with H_2 fed as fuel. Such cermet more than merely meets most of the requirements mentioned above, but even exhibits lots of compelling properties as an excellent anode. For example, Ni/YSZ can be prepared with a simple and efficient dry-pressing method in both lab and industrial scales. Fig. 2.2 shows a typical porous structure of Ni/YSZ anode. Ni/YSZ shows very good chemical compatibility. They are neither reactive nor immiscible with each other in a wide range of temperature, enabling cost-efficient co-sintering fabrication method and long-term stability. Ni also shows closely matched thermal expansion coefficient (TEC) with YSZ, therefore avoiding damaging

stress to build up in the interface which may lead to cracking or delamination eventually. Most importantly, besides those merits, Ni shows excellent catalytic activity towards H_2 oxidation. Because of such excellence, when operating Ni/YSZ anode at high temperature (800-1000°C), the resistance associated with anode is very small, and the major part of the resistance comes from the ohmic resistance of electrolyte and polarization resistance of cathode.

Fig. 2.2 SEM pictures of the surface and cross section of Ni/YSZ cermet anode, surface (a) and cross-section (b).[2]

However, Ni/YSZ anode degrades in hydrocarbon and impurity containing syngas quickly due to coking and poisoning by contaminants such as S as shown in Fig. 2.3 and 2.4. To operate this anode on CH_4 , CH_4 needs to be reformed externally or internally with high vapor content in the feeding gas. Fuel containing a few ppm H_2S which is common in the natural gases, can also kill Ni by physical and/or chemical adsorption of H_2S on the surface and the sulfidation of Ni.[3] Various strategies have been developed to eliminate those detrimental effects when using Ni in hydrocarbon fuels, including coating Ni with CeO_2 -based material, replacing Ni with

Cu or other oxide materials and etc.[4] Those approaches are effective in certain extent but also suffer from particular drawbacks. For example, CeO_2 -based deposits protect the activity of Ni by adsorption and reaction with sulfur. The consumption of CeO_2 hints it is not a solution once and for all. Cu displays much better coking-resistance than Ni, which probably originates from the inert nature of Cu in catalyzing the C-H bond. In that case, it is not surprising to find low catalytic activity of Cu in boosting the oxidation reaction of hydrocarbon. Cu-based anode always requires extra catalyst to be added in to promote the kinetics, which by itself will be another major investigation interest in SOFC. Another drawback associated with Cu metal anode is the degradation at high temperature owing to the propensity of Cu coarsening, usually leading to damage in the electronic conducting network and then increasing in anode ohmic resistance. Therefore, exploration of novel alternative materials to overcome these barriers of the conventional Ni-YSZ anode is of significance in furthering the progress of SOFC application.

Fig. 2.3 Deposited carbon on Ni-YSZ cermet: (a) carbon fiber, (b) Ni-YSZ cermet.[5]

Fig. 2.4 Increasing of polarization resistance of Ni/YSZ anode at 1000°C with different concentration of H₂S added into 79% H₂+21% H₂O fuel.[6]

2.1.2 Perovskite oxide anodes

Fig. 2.5 Schematic diagram of ABO₃ perovskite structure.

Due to the flexible choices at A and B sites with respect to not only wide size variety but also different valence combination, perovskite oxides are largely adjustable in terms of the

electronic, ionic conductivities, TEC, catalytic properties, chemical stability and etc.[7] The schematic representation of the lattice structure of perovskite is shown in Fig. 2.5. The A site is usually rare earth elements with bigger radii, B site element transition metals with small radii. The big tolerance of oxygen vacancy in the lattice entitles such structure with interesting transport property. The stability of perovskite towards P_{O_2} mainly depends on the B site elements as rare and alkaline earth elements are relatively more stable. To accommodate the stability requirement of the anode site, Ti, V and Cr are the most suitable choices for the B site. At 1000°C, the decomposing P_{O_2} is 10^{-15} , 10^{-17} , 10^{-7} and 10^{-1} for Mn, Fe, Co and Ni respectively,[8-9] which are too high to be used at anode in large amount. But LnTiO_3 and LnCrO_3 keep unchanged in the testing P_{O_2} range down to 10^{-22} .[8]

Titanates---Titanates show intrinsic n-type conductivity which increases with decreasing P_{O_2} . Generally oxide materials fall far back compared to metal in terms of electronic conductivity even at SOFC operation temperature. Titanate conducts electron by the redox of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in small-polaron hopping mechanism. SrTiO_3 possesses marginal electronic conductivity due to the lack of intrinsic electron carriers; therefore it serves as parent material for modification. La is the most popular Sr-site dopant due to the similar atom size and yields apparent improvement. Although $(\text{LaSr})\text{TiO}_3$ system exhibits 1~4 S/cm when sintered in air, it increases to the order of 1000 S/cm when sintered in H_2 .[10] The summary of electrical conductivities of titanate with different dopant choices and levels are presented in Table 2.1.

Table 2.1 Electrical conductivities of titanate-based perovskites.

Sample composition	Electrical conductivities (S/cm)		Ref.
	Reducing	oxidizing	
La _{0.1} Sr _{0.9} TiO ₃	3(1000°C)	1(1000°C)	[11]
La _{0.1} Sr _{0.9} TiO ₃ (R)	80(1000°C)	0.004(1000°C)	[11]
La _{0.2} Sr _{0.8} TiO ₃	3(1000°C)	1(1000°C)	[11]
La _{0.2} Sr _{0.8} TiO ₃ (R)	200(1000°C)	0.03(1000°C)	[11]
La _{0.3} Sr _{0.7} TiO ₃	4(1000°C)	1.3(1000°C)	[11]
La _{0.3} Sr _{0.7} TiO ₃ (R)	200(1000°C)	0.01(1000°C)	[11]
La _{0.4} Sr _{0.6} TiO ₃	16(1000°C)	0.004(1000°C)	[11]
La _{0.4} Sr _{0.6} TiO ₃ (R)	360(1000°C)	0.03(1000°C)	[11]
SrTi _{0.99} Nb _{0.01} O ₃	0.4(800°C)	0.06(800°C)	[12]
SrTi _{1.09} Nb _{0.01} O ₃	0.16(800°C)	0.16(800°C)	[12]
La _{0.4} Sr _{0.6} TiO ₃	1(800°C)	2×10 ⁻⁵ (800°C)	[13]
La _{0.4} Sr _{0.6} Ti _{0.8} Mn _{0.2} O ₃	0.1(800°C)	2×10 ⁻² (800°C)	[13]
La _{0.4} Sr _{0.6} Ti _{0.6} Mn _{0.4} O ₃	0.1(800°C)	2(800°C)	[13]
La _{0.4} Sr _{0.6} Ti _{0.4} Mn _{0.6} O ₃	2(800°C)	20(800°C)	[13]
Y _{0.08} Sr _{0.92} Fe _{0.2} Ti _{0.8} O ₃	0.08(700°C)	0.14(700°C)	[14]
Y _{0.08} Sr _{0.92} Fe _{0.4} Ti _{0.6} O ₃	0.11(700°C)	0.03(700°C)	[14]
Sr _{0.85} Y _{0.15} Ti _{0.95} Ca _{0.05} O ₃	37(800°C)	-	[15]
Sr _{0.85} Y _{0.15} Ti _{0.95} Co _{0.05} O ₃	45(800°C)	-	[15]
Sr _{0.85} Y _{0.15} Ti _{0.95} Zn _{0.05} O ₃	13(800°C)	-	[15]
Sr _{0.85} Y _{0.15} Ti _{0.95} Mn _{0.05} O ₃	6(800°C)	-	[15]
Sr _{0.88} Y _{0.08} TiO ₃	64(800°C)	-	[15]
La ₄ Sr ₈ Ti ₁₁ MnO _{38-δ}	7.8(900°C)	-	[16]
La ₄ Sr ₈ Ti ₁₁ Mn _{0.25} Ga _{0.75} O _{38-δ}	7(900°C)	-	[16]
La ₄ Sr ₈ Ti ₁₁ Mn _{0.5} Ga _{0.5} O _{38-δ}	0.9(900°C)	0.001(900°C)	[17]
La ₄ Sr ₈ Ti ₁₁ Mn _{0.75} Ga _{0.25} O _{38-δ}	7.7(900°C)	-	[16]
La ₄ Sr ₈ Ti ₁₁ GaO _{38-δ}	6.8(900°C)	-	[16]
La _{0.33} Sr _{0.67} Ti _{0.92} Mn _{0.08} O ₃	5.1(870°C)	-	[18]
La _{0.33} Sr _{0.67} Ti _{0.92} Mn _{0.08} O ₃	0.3(870°C)	-	[18]
La _{0.33} Sr _{0.67} Ti _{0.92} Mn _{0.08} O ₃	0.6(870°C)	-	[18]
La _{0.33} Sr _{0.67} Ti _{0.92} Mn _{0.08} O ₃	2(870°C)	-	[18]
La _{0.33} Sr _{0.67} Ti _{0.92} Mn _{0.08} O ₃	7.3(870°C)	-	[18]
La _{0.33} Sr _{0.67} Ti _{0.92} Mn _{0.08} O ₃	1.8(870°C)	-	[18]
La _{0.33} Sr _{0.67} Ti _{0.92} Mn _{0.08} O ₃	6.8(870°C)	-	[18]

Note: (R) sample prepared in reducing atmospheres.

Although titanate usually shows fair electrical conductivity, the catalytic activity is limited. The maximum power density (MPD) for a $\text{La}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ anode with YSZ electrolyte reaches only 25 mW/cm^2 at 900°C in H_2 . [10] Due to the stability of Ti, very few oxygen vacancies are present in the lattice, which limits the role of LST to a pure electron conducting phase without much catalytic activity. On the other hand, Ti-site substitution can be adopted to improve such drawback in some extent. Multiple elements have been tried in $(\text{LaSr})\text{TiMO}_3$ ($\text{M}=\text{Al, Fe, Ga, Mg, Mn}$ and Sc). [18] In the blanket study of B-site dopants, it was verified that the anode kinetics is heavily affected, with Sc-doped LST compound yielding the best performance. Table 2.2 summarizes the performance of titanate anodes operated in H_2 and CH_4 . Even though advances are progressively made as can be seen, more optimization on the performance still need to be carried out before those compounds can be used.

Table 2.2 Electrode performance from titanates in H_2 and CH_4 .

Sample composition	Polarization resistance (Ωcm^2)		Ref.
	H_2	CH_4	
$\text{La}_{0.4}\text{Sr}_{0.6}\text{Ti}_{0.6}\text{Mn}_{0.4}\text{O}_3(\text{C})$	0.35(855°C)	0.8(855°C)	[13]
$\text{La}_2\text{Sr}_4\text{Ti}_6\text{O}_{18}$	2.97(900°C)	8.93(900°C)	[19]
$\text{La}_4\text{Sr}_8\text{Ti}_{11}\text{MnO}_{38-\delta}(\text{C})$	0.3(950°C)	0.7(950°C)	[20]
$\text{La}_4\text{Sr}_8\text{Ti}_{11}\text{Mn}_{0.5}\text{Ga}_{0.5}\text{O}_{38-\delta}(\text{C})$	0.2(900°C)	0.57(900°C)	[17]
$\text{La}_2\text{Sr}_4\text{Ti}_{5.7}\text{Sc}_{0.3}\text{O}_{19-\delta}(\text{R})$	0.5(900°C)	1.2(900°C)	[21]
$\text{La}_2\text{Sr}_4\text{Ti}_{5.5}\text{Sc}_{0.5}\text{O}_{19-\delta}(\text{R})$	1.4(900°C)	4.1(900°C)	[21]
$\text{La}_{0.1}\text{Sr}_{0.9}\text{TiO}_3(\text{R})$	510(800°C)	-	[22]
$\text{La}_{0.2}\text{Sr}_{0.8}\text{TiO}_3(\text{R})$	350(800°C)	-	[22]
$\text{SrTi}_{0.97}\text{Nb}_{0.03}\text{O}_3$	700(800°C)	-	[22]

$\text{Sr}_{0.94}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3(\text{C})$	52(850°C)	-	[23]
$\text{Sr}_{0.88}\text{Y}_{0.08}\text{TiO}_3(\text{C})$	2.9(800°C)	-	[24]
$\text{Sr}_{0.9}\text{Ti}_{0.8-x}\text{Ga}_x\text{Nb}_{0.2}\text{O}_3(\text{R})$	1.3(800°C)	-	[25]
$\text{La}_{0.33}\text{Sr}_{0.67}\text{TiO}_3(\text{C})$	1.4(850°C)	-	[18]
$\text{La}_{0.33}\text{Sr}_{0.67}\text{Ti}_{0.92}\text{Mn}_{0.08}\text{O}_3(\text{C})$	5.5(850°C)	-	[18]
$\text{La}_{0.33}\text{Sr}_{0.67}\text{Ti}_{0.92}\text{Fe}_{0.08}\text{O}_3(\text{C})$	4.8(850°C)	-	[18]
$\text{La}_{0.33}\text{Sr}_{0.67}\text{Ti}_{0.92}\text{Al}_{0.08}\text{O}_3(\text{C})$	3.7(850°C)	-	[18]
$\text{La}_{0.33}\text{Sr}_{0.67}\text{Ti}_{0.92}\text{Mg}_{0.08}\text{O}_3(\text{C})$	26(850°C)	-	[18]
$\text{La}_{0.33}\text{Sr}_{0.67}\text{Ti}_{0.92}\text{Ga}_{0.08}\text{O}_3(\text{C})$	2.9(850°C)	-	[18]
$\text{La}_{0.33}\text{Sr}_{0.67}\text{Ti}_{0.92}\text{Sc}_{0.08}\text{O}_3(\text{C})$	2.9(850°C)	-	[18]

Note: (R) sample prepared in reducing atmospheres, (C) composite anode used.

Vanadate---vanadate stands out by the even better electrical conductivity. SrVO_3 shows metallic conductivity behavior and reaches $\sim 1000\text{S/cm}$ at peak value. La partially substituted strontium vanadate ($\text{La}_{1-x}\text{Sr}_x\text{VO}_3$, LSV) display electrical conductivities in the range of $100\sim 10000\text{ S/cm}$ in the fuel cell operation temperature. The electrical conductivities of various V-based perovskites are summarized in Table 2.3. Such excellent property guarantees wide investigation on those compounds aiming for anode candidate. Due to the multivalent of vanadium cations from +2 to +5, several compositions exists for vanadate depending on the synthesis conditions. When synthesized in air, AV_2O_7 is the most common product.[26-27] Orthovanadate is usually formed in the modestly oxidizing atmosphere.[28-29] For the viable structure that can be used in SOFC, AVO_3 perovskite needs to be synthesized under reducing gases. In our previous experimental study on LSV, it was formed in 5% H_2 balanced by argon gas at 1250°C . The composition $\text{La}_{0.8}\text{Sr}_{0.2}\text{VO}_3$ possesses an electrical conductivity of $\sim 800\text{ S/cm}$

at peak value. Nevertheless, such perovskite structure as prepared is highly susceptible to oxidizing atmosphere, and can be easily oxidized back to the original oxides with V being +5 at the operation temperature. This process is irreversible at the same temperature even with H₂ fed to the anode. The propensity of vanadate to stay in higher oxidation state places strict requirement in the synthesis, cell assembling and operation process in terms of P_{O_2} control.

LSV produces proper anode performance in H₂ and CH₄. R_p of 9 Ωcm^2 is obtained on the LSV anode at 900°C.[30] Interesting enough about such compound is the tendency shown by LSV towards the catalytic oxidation of H₂S. It was reported that the performance of full cell with H₂ can be increased from ~50 to ~200 mW/cm² by mixing 5% H₂S to it. The selectivity of LSV on H₂S and the corresponding constructive performance results make ABO₃ vanadate promising sulfur-tolerant anode nominees or electrocatalyst decoration for the traditional anode. In the end, compared to the performance concerns, perhaps the more severe problem associated with vanadate is the high susceptibility to oxidizing atmospheres.

Table 2.3 Electrical conductivities of vanadate-based perovskites.

Sample composition	Electrical conductivities (S/cm)		_ Ref.
	Reducing	oxidizing	
La _{0.7} Sr _{0.3} VO ₃	120(800°C)	300(25°C)	[31]
La _{0.8} Sr _{0.2} VO ₃	45(800°C)	120(25°C)	[31]
La _{0.9} VO ₃	2.9(800°C)	3.3(25°C)	[31]
CaV _{0.5} Mo _{0.5} O ₃	500-1800(25-800°C)	10 ⁻⁵ -10 ⁻⁴ (800-900°C)	[32]
SrV _{0.5} Mo _{0.5} O ₃	280-450(25-900°C)	10 ⁻⁹ -10 ⁻⁵ (500-950°C)	[33]

$\text{Ce}_{1-x}\text{Ca}_x\text{VO}_3$ ($x=0.1, 0.2,$	$2-13(700^\circ\text{C})$	$10^{-3} (700^\circ\text{C})$	[34]
$0.3, 0.4)$			
$\text{Ce}_{0.85}\text{Sr}_{0.15}\text{VO}_3$	$2.7(700^\circ\text{C})$	$15(700^\circ\text{C})$	[35]
CeVO_3	$0.09(600^\circ\text{C})$	-	[35]
$\text{Ce}_{0.9}\text{Sr}_{0.1}\text{V}_{0.5}\text{Cr}_{0.5}\text{O}_3$	$6.5(850^\circ\text{C})$	-	[36]
SrVO_3	$800(800^\circ\text{C})$	-	[37]
$\text{La}_{0.3}\text{Sr}_{0.7}\text{VO}_3$	$770(800^\circ\text{C})$	-	[37]
$\text{La}_{0.5}\text{Sr}_{0.5}\text{VO}_3$	$300(800^\circ\text{C})$	-	[37]
$\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$	$150(800^\circ\text{C})$	-	[37]
LaVO_3	$5.5(800^\circ\text{C})$	-	[37]
$\text{Ce}_{0.9}\text{Sr}_{0.1}\text{VO}_3$	$0.4(700^\circ\text{C})$	-	[38]

Chromites---Due to the strong preference of 6-coordination in the octahedron, chromites display an extremely good stability towards a wide range of P_{O_2} , enabling the possibility of being used as oxide anode candidate. Doped lanthanum chromites [39-42] have been investigated extensively as interconnect in the first place due to the high electronic conductivity at both oxidizing and reducing atmospheres. However, poor catalytic activity was found on those electronic conductors if no further modification is made. For instance, a polarization resistance of $\sim 90 \Omega\text{cm}^2$ was obtained on LaCaCrO_3 at 850°C in H_2 . [43] Decoration with transition metal at B site is necessary from a viewpoint of practical application. $\text{La}(\text{CrM})\text{O}_3$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) have been prepared and examined for the catalytic activity on hydrocarbon fuels. [44] Most of the compound display good coking resistance, except for Fe. Carbon deposition was found on the surface of electrode grains under SEM when running LaSrCrFeO_3 in CH_4 -containing gases at temperature over 900°C . Of those dopants, Ni showed best results towards CH_4 oxidation. However, one concern associated with B site doping is the exsolution of dopant element under reducing atmosphere. It has been documented by Arai et al. [45] in the perovskite catalyzing CO

oxidation studies that the activity of perovskite in the oxidation of CO, CH₄ was less influenced by the nature of the fuels, but mainly hinged on the redox ability of the B site element, which was essentially correlated to the reducibility as long as another critical criteria are met. In this sense, high catalytic activity generally coincides with the less stability in the operation conditions. Indeed, it has been reported that Co and Fe exsolution were observed when treated in reducing conditions for a prolonged period of time. The reducibility of those dopants ranges in order Ni<Co<Fe<Mn.[8] Due to such phenomenon, the amount of substitutes is highly limited as far as the long-term operation is concerned. Of those choices, Mn shows a wider level substitution without giving rise to immediate stability concern. But small amount of Mn has not promoted such material to a new level with high performance. The polarization resistance of La_{0.8}Sr_{0.2}Cr_{0.8}Mn_{0.2}O₃ in wet H₂ turns out to be ~50 Ωcm² at 850°C.[46] However, the turning point appears when increasing Mn level to 50% percent. La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM) as specific recipe has been proposed by Tao et al,[39] and shown a relatively encouraging performance among those oxide anodes. R_p of 0.5 and 0.8 Ωcm² was achieved in wet H₂ and CH₄ at 900°C respectively. It also shows good stability towards both wet H₂ and CH₄ atmospheres. Though comparatively good electrode performances were obtained with YSZ/LSGM electrolytes on methane, the output without any addition of noble metal or CeO₂ is still far from the acceptable level for practical application. Another weakness of such material is the intrinsic p-type conductivity, which means lower electrical conductivity will be yielded at reducing condition compared to the oxidizing atmosphere owing to the consumption of holes by the formation of oxygen vacancy. It is reported to be ~30 S/cm for air but reduces to ~1 S/cm in H₂. Low conductivity as such basically deprives it of being used as anode-supported cell. Table 2.4 summarizes the electrical conductivity of Cr-based perovskites. To overcome such difficulty, Cu

is brought forth as additive to enhance the conductivity. A maximum output of 520 mW/cm² in CH₄ was achieved in the Cu-LSCM anode.[47] Other strategies to make use of the merit of LSCM include impregnation to the Ni/YSZ anode backbone, or co-impregnation of Ni, LSCM to achieve resistance towards coking but meanwhile retain the requested electrode performance.[48-49] Table 2.5 displays the performance of Cr perovskites in H₂ and CH₄.

Table 2.4 Electrical conductivities of chromite-based perovskites.

Sample composition	Electrical conductivities (S/cm)		____ Ref.
	Reducing	oxidizing	
LaCrO ₃	-	0.34(700°C)	[50]
La _{0.7} Mg _{0.3} CrO ₃	0.17(800°C)	3.4(800°C)	[51]
La _{0.75} Sr _{0.25} CrO ₃	7.1(800°C)	59(800°C)	[51]
La _{0.7} Ca _{0.3} CrO ₃	1.6(800°C)	50(800°C)	[51]
La _{0.7} Ba _{0.3} CrO ₃	-	2.7(800°C)	[51]
La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃	0.22(800°C)	28.8(800°C)	[51]
La _{0.8} Sr _{0.2} Cr _{0.5} Mn _{0.5} O ₃	1.3(900°C)	38(900°C)	[41]
La _{0.7} Sr _{0.3} Cr _{0.5} Ti _{0.5} O ₃	0.02(800°C)	-	[52]
La _{0.95} Ca _{0.05} Cr _{0.5} Co _{0.5} O ₃	-	2.3(700°C)	[53]
La _{0.95} Ca _{0.05} Cr _{0.8} Ni _{0.2} O ₃	-	63(700°C)	[50]
La _{0.8} Ca _{0.2} Cr _{0.8} Fe _{0.2} O ₃	-	9.2(700°C)	[54]
La _{0.8} Ca _{0.2} Cr _{0.5} Fe _{0.5} O ₃	-	6.8(700°C)	[54]
La _{0.8} Ca _{0.2} Cr _{0.2} Fe _{0.8} O ₃	-	12(700°C)	[54]
La _{0.85} Ca _{0.15} Cr _{0.8} Co _{0.2} O ₃	-	25(700°C)	[55]
La _{0.85} Ca _{0.15} Cr _{0.5} Co _{0.5} O ₃	-	130(700°C)	[55]
La _{0.85} Ca _{0.15} Cr _{0.2} Co _{0.8} O ₃	-	400(700°C)	[55]
LaCr _{0.8} Ni _{0.2} O ₃	-	8.2(700°C)	[56]
LaCr _{0.6} Ni _{0.4} O ₃	-	26(700°C)	[56]
LaCr _{0.4} Ni _{0.6} O ₃	-	83(700°C)	[56]

Table 2.5 Electrode performance for chromites in H₂ and CH₄.

Sample composition	Polarization resistance (Ωcm^2)		Ref.
	H ₂	CH ₄	
La _{0.75} Ca _{0.25} Cr _{0.9} Mg _{0.1} O ₃	21(850°C)	-	[43]
La _{0.7} Ca _{0.32} CrO ₃	86(850°C)	-	[43]
La _{0.8} Sr _{0.2} Cr _{0.97} V _{0.03} O ₃	5(850°C)	30(850°C)	[43]
La _{0.8} Sr _{0.2} Cr _{0.97} V _{0.03} O ₃	-	28(850°C)	[57]
La _{0.8} Sr _{0.2} Cr _{0.97} Fe _{0.03} O ₃	1.15(850°C)	1.79(850°C)	[58]
La _{0.75} Sr _{0.25} Cr _{0.95} Ru _{0.05} O ₃	68(860°C)	170(855°C)	[59]
La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃	1.4(800°C)	2.3(800°C)	[60]
La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃	2.5(800°C)	11(800°C)	[61]
La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃	-	2.62(900°C)	[62]
La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃	1.1(800°C)	8.1(800°C)	[63]
La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O ₃	0.18(900°C)	-	[64]
La _{0.7} Sr _{0.3} Cr _{0.8} Ti _{0.2} O ₃	40(857°C)	-	[52]
La _{0.8} Sr _{0.2} CrO ₃	256(850°C)	-	[46]
La _{0.8} Sr _{0.2} Cr _{0.8} Mn _{0.2} O ₃	51(850°C)	-	[46]
La _{0.75} Sr _{0.25} Cr _{0.5} Fe _{0.5} O ₃	1.15(850°C)	-	[58]

In the particular kind, YCrO₃ perovskite has been examined as possible interconnect material as they display advantages over the LaCrO₃-based materials in terms of the chemical expansion and compatibility with YSZ electrolyte.[65-71] In addition of working as interconnect, YCrO₃ based materials have been evaluated as potential anode after multiple doping at A and B sites: an anode made from Ca and Co doped YCrO₃ lately has demonstrated an encouraging performance in H₂, and more importantly, displayed good tolerance towards 20 ppm H₂S.[72] Such preliminary information suggests that YCrO₃-based perovskite could be a promising parent

material for anode aiming at H_2S containing fuel. However, compared to the Ni/YSZ anode, those oxide anodes are inferior in terms of certain critical factors, such as electrical conductivity and output performance which is usually 10 times smaller than Ni anode. Even though the unique advantages of oxide anode over Ni anode are the coking resistance and sulfur poison tolerance, the performance is inevitably a key role that determines the possibility of application and need to be enhanced further to meet the requirement. Understanding the oxidation mechanism on those oxide anodes will be crucial to point out limiting factors and the possible direction to improve them. However to the best of our knowledge, besides the electrode performance research, no investigation regarding the anode reaction mechanism on those oxide materials has been reported. Before plunging into this topic, it is worth digressing for a moment on the mechanism research of Ni/YSZ anode accumulated over several decades in hope of building guidelines for oxide anode study later.

2.2 H_2 oxidation pathway in traditional Ni/YSZ anode

To identify the reactive zone on Ni/YSZ anode, Gauckler et al. fabricated the Ni pattern anode on YSZ electrolyte as shown in Fig. 2.6, and found that the polarization resistance is inversely proportional to the 3PB length as displayed in Fig. 2.7.[73] From that study along with a series of other Ni electrode investigations,[74-77] it is clear that for the Ni metal anode catalytic reaction takes place only at the 3PB area. Considering that Ni is electronic conductive and YSZ ionic conductive, this result is consistently reasonable.

But still, nothing can occur literally at one dimension. This begs the question that of YSZ and Ni, which surface is or whether both surfaces are active near the 3PB. In fact, models favor

each of them can be found readily in literature. Morgensen et al.[78] summarized them as in Fig. 2.8. The first scenario as shown in Fig. 2.8a was argued by Morgensen and many others as the main mechanism for the H_2 oxidation reaction considering the general knowledge of the active interaction between Ni and H.[78] The second scenario was introduced by Mizusaki et al.[79] based on the findings that a compact Ni/YSZ anode also showed reaction rate much bigger than 0, which in fact showed every limited 3PB length that could only come from the imperfection of the Ni film covering YSZ substrate. Citing the tremendous difference of exposed YSZ surface between the compact Ni/YSZ and Ni pattern anode, they concluded that the RDS of H_2 oxidation was controlled by the surface process on Ni as illustrated in Fig. 2.9.[79] The last scenario in Fig. 2.8c was proposed by Minh et al. as a possibility but without a body of experimental evidence.[80] In particular, on the Ni side, by varying the thickness of the Ni strips in the pattern electrodes, it was found that the reaction rate increased with the thickness until several microns. [81] It was thus concluded that the active length on Ni could be on the order of submicron to micron.

Fig. 2.6 Schematic of Ni pattern sample on single crystal YSZ (a), and SEM image of Ni on YSZ (b).[73]

Fig. 2.7 Polarization resistance vs. 3PB length on the Ni pattern sample deposited on single crystal YSZ [73]

Figure 2.8 Schematics of possible reaction paths of Ni/YSZ discussed in the literature, (a) H_2 adsorption on the Ni results in the formation of H^+ ions, then migrate to the site along the surfaces or through bulk Ni and bulk YSZ to form H_2O in the surface of YSZ. (b) O^{2-} or OH^- migrates from YSZ to Ni along surfaces and finally form H_2O on Ni surface. (c) H_2 is adsorbed on YSZ surface then reacts with lattice oxygen to form H_2O at YSZ surface, electron transport to the Ni through the surface bulk of YSZ.[78]

Fig. 2.9 Ni surface limiting reaction mechanism of H_2 oxidation on Ni/YSZ anode.[79]

Secondly, what are the elementary steps? Bieberle et al.[82] proposed a complete reaction model as shown in Fig. 2.10 combining the results from H_2 and H_2O interaction with Ni solid surfaces and the previous modeling on Pt, H_2 - H_2O system.[83-86] The simulation was compared with several set of experimental data. As concluded in the end, though good consistency was found with some data sets, a rather extensive collection of data was required to unambiguously interpret the kinetics of this system. In particular, the activity of the electrolyte surface needed to

be considered with quantitative data concerning the adsorption and removal of H and OH as its effect on the kinetic had been speculated in several references.[76, 87-88] Further, Vogler et al.[89] proposed a reaction pathway in their reaction-diffusion models based on Bieberle's study as shown in Fig. 2.11. Such model features 7 different scenarios of charge transfer in form of spillover of adsorbates between Ni and YSZ surfaces at 3PB, which are illustrated in Fig. 2.12. It was found that only one mechanism involving H spillover mechanism from Ni to YSZ to react with O or OH yielded good agreement with the complete set of experimental data. Such observation had been confirmed later by Bessler in their combined experimental and theoretical model anode study for the H₂ oxidation mechanism. Four steps were proposed as RDS at high temperature in this electrochemical process: hydrogen spillover to oxygen, water association on YSZ, water desorption from YSZ and surface diffusion of adsorbed OH ions on YSZ surface. And they would reduce to H spillover as the single RDS at low temperature (T<=500°C). Those studies, though not embraced all the views of H₂ oxidation on Ni/YSZ, outlined the major part of results in the reaction mechanism investigations.

Fig. 2.10 H₂ oxidation model in Ni/YSZ system by Bieberle et al. (a) schematic, (b) corresponding elementary steps.[82]

YSZ surface reactions

Ni surface reactions

Charge-transfer reactions

Fig. 2.11 Elementary reaction steps for H₂ oxidation by Vogler et al.[89]

Fig. 2.12 Different scenarios of charge transfer on H₂/YSZ 3PB by Vogler et al.[89] (a) spillover of hydrogen from Ni surface to an oxygen ion or hydroxyl ion on YSZ surface, (b) charge transfer reactions with and without spillover of oxygen ions from YSZ surface to Ni surface, (c) hydroxyl spillover from YSZ surface to Ni surface, (d) charge transfer by an interstitial proton, (e) charge transfer and chemical reactions on the electrolyte surface only.

2.3 Broadened reaction zone in oxide anodes

While the active site for oxidation reaction in Ni metal anode is limited to the 3PB vicinity, the oxide anode might be able to extend such area to a broader area due to the oxygen conductivity of the anode. It is proven that mixing ionic conductive electrolyte with metal anode will extend the 3PB from anode/electrolyte interface to a 3-dimension network in the anode. Similarly, by using a MIEC anode the active site centering at the 3PB line could be broadened to several micrometers away which could be a substantial expansion considering the width of 3PB active area is usually believed to be less than 100 nanometers. It has been reported that tremendous improvement is achieved with MIEC cathode materials, like (SmSr)CoO₃ or (LaSr)(CoFe)O₃. With the significant ionic conductivity, the broadened active area on those cathode is estimated to be several to tens of microns. For the oxide anode, with appropriate doping choices, oxygen ion conductivity can be expected from those materials by creating oxygen vacancy in the lattice. Therefore, besides diffusion of H towards 3PB by the surface, oxygen from electrolyte can also be transported by the anode bulk pathway to areas away from 3PB, making those sites active for H₂ oxidation. In the present time, theoretical modelling or experiment verification on such properties of anode materials are still sparse, therefore is one of the principal investigation interest of this study.

2.4 Influence on performance of overpotential

Because of the simplicity in thermodynamic, a large portion of the electrode research was conducted under equilibrium conditions.[72, 90-91] Through those studies, general principles about the anode properties, such as the catalytic difference between various materials, possible reaction mechanisms and etc. have been pointed out. However, with applied overpotential, the

local electrical status, surface adsorption and even local chemical composition will be altered, which in turn may impact the reaction kinetics, the activation or deactivation of broadened active zone according to the intrinsic correlation to the overpotential, and durability of electrode in long-term operation.

To more clearly evaluate this topic, we can first geometrically divide the reaction pathway into surface process, including hydrogen (dissociative) adsorption, ionization and association between H, O and OH, bulk process---the transport of oxygen species toward 2PB, and interface process---ion transfer from electrolyte to anode. Among these three subsequent processes, as pointed out in several polarization studies, ion transfer at the MIEC/electrolyte interface is dependent on the oxygen activity of interface composition. Fast transfer process can be obtained by using appropriate electrolytes, like GDC or LSGM,[92] therefore is less critical and complex. As for the surface process, tremendous effort has been devoted to understanding the very nature of it in order to promote the output of electrode with overpotential, or to further guide novel composition and structure designs. Major advances in terms of identifying the correlation between the reaction kinetics and surface local composition/electrical conditions, influence of the oxygen defects in electrode bulk and etc. have been elucidated by different groups.

Fig. 2.13 The linear (a) and logarithm (b) plots of V-I relationship for charge transfer reaction in MIEC electrode calculated from different surface coverage (θ) and surface local overpotential (χ) by Fleig et al.[93]

First, for the surface process, the overpotential is capable of influencing any charged species on the surface directly. Since such intrinsic correlations between the element reaction steps and overpotential are built with basic electrostatics, they are largely valid regardless of the specific electrode materials after modifying the specific boundary conditions. In specific, the charge transfer rate for example in the traditional solid/liquid interface is formulated by B-V equation. Converting it to adapt the unique surface adsorption in SOFC MIEC electrode system, Fleig et al.[93] built a model to account for the relationship between surface coverage and the surface overpotential in cathode, which in turn mediate the charge transfer rate at the gas/solid interface showing a voltage-current (V-I) relationship different from the traditional B-V equation. The new V-I relationship for high surface adsorption case is much steeper than B-V, the symmetrical coefficients can be 2 to 4 times bigger than 0.5 since the surface overpotential can be even larger than the externally applied one as shown in Fig. 2.13. It therefore shows stronger effect on the surface reaction rate than the usual B-V relationship.

Fig. 2.14 Polarization resistance of LSM cathode under cathodic and anodic treatments by Wang et al: (a) initially treated a fresh cathode with 200 mA/cm² cathodic current with different duration, (b) followed by treated at 200 mA/cm² anodic current with different duration, (c) followed again by treated at 200 mA/cm² cathodic current with different duration.

Next, it is also well-known that in lots of cases overpotential is able to change the local chemical composition of electrode. Citing from large body of data on the most commonly studied LSM cathode, overpotential tends to dissolve the surface enriched element into the lattice structure, like Sr, to remove the inert layer towards adsorption as demonstrated by Wang et al.[94] in Fig. 2.14, or even is believed to bring some element from lattice to surface, like La, to activate the surface exchange process. By changing the chemical stoichiometry of the surface,

overpotential has obviously enhanced or impaired the electrode performance significant compared to equilibrium condition. However, until so far, similar studies in anode side are missing.

At last, for the bulk process, even less information is available in literature on either oxide anode or cathode. The chemical stoichiometry and electrical environment of electrode materials can be influenced by applied overpotential, which in turn trigger the change in diffusion kinetics. According to the drift-diffusion equation, concentration gradient and electrical field forces are two driving forces for charged species diffusion in the homogeneous phase. The contribution from concentration gradient is determined by Fick's law and the electrical field contribution is governed by Ohm's law. As already been stressed in the MIEC electrode research, concentration gradient is believed as the only factor determining transport kinetics in bulk diffusion. Due to the local neutrality assumption, internal electrostatic potential gradient is usually neglected, and then the corresponding electrical driving force is left out. However, as we will see in detail later in the main section, such neutrality assumption, even though seems intuitively right, has oversimplified the essence of theoretical treatment on the diffusion process. Theoretical exploration of transport behavior in MIEC material can date back to Wagner's classic work in 1930s.[95-97] The framework built since then by Wagner and many others has been used to develop various models to determine the transport properties based mostly on Ag_2S media. More recently, transport in MIEC related to oxygen transport membrane (OTM) application has been studied by Liu et al.[98] Liu examined the physical treatment of those transport equations and obtained analytical solutions for charge carrier distributions in MIEC subject to definite boundary conditions on both sides of the sample. Jamnik and Maier mapped

the electrochemical kinetics for MIEC bulk into equivalent circuit based on the transport equations for electronic and ionic defects.[99-100] Afterwards, Lai et al. derived the AC impedance response of MIEC exemplified by ceria-based oxides under chemical potential gradient using the same fundamental transport equation system. Liu later on indeed presented the electrochemical study on porous MIEC electrode for SOFC application, with taking account of the ion transport resistance, for an equivalent circuit approximation.[98]

Actually, despite of all the significant progress made in above works, the interest in oxygen transport behavior in MIEC electrodes either in anode or cathode conditions with detailed distribution profiles has not been investigated yet. Under steady state, the ionic flow inside the MIEC electrode is constant but in principle the electronic one is eventually blocked at the MIEC/electrolyte interface. The blocking of electronic species in fact can simplify the electron-ion coupled transport process drastically and makes the analytical solution possible under reasonable assumptions, which renders clear assessment of the driving forces and the corresponding prediction on the material stability at boundaries.

Considering the void of overpotential influence study on the oxide electrode and its potentially great impact on the bulk pathway, the oxygen transport is investigated by interpreting the general transport equation into the specific case with electron-blocking electrolyte combined with experimental study in Chapter 7, the defects distributions in MIEC and the impact of those results on the understanding of electrode stability under polarization are derived and discussed with a one dimensional model.

RESEARCH OBJECTIVES

Through the literature review, it is found that though certain oxide anodes, such as LSCM ($1.1 \Omega\text{cm}^2$ at 800°C H_2), yield relatively good performances, most of the rest show polarization resistances much bigger than the application requirement ($\sim 0.5 \Omega\text{cm}^2$). Because of this barrier of energy loss in electrode reaction, lots of merits from those oxide materials cannot be utilized in SOFC anode, e.g. the high H_2S tolerance of V-based materials at the present stage. Understanding the reaction mechanism and therefore the limiting factors can provide right direction for optimization in the future, making performance improvement highly possible and widening the choices in anode candidates with particular merits. Because that the mechanism exploration for those oxide anodes is scarce in literature, this study is devoted to this subject and investigate H_2 oxidation pathway on oxide anode in both the fundamental of electrochemical reaction and evolution of geometry active area with chemical composition and overpotential. In specific, the following objectives are investigated:

- ❖ Characterize the electrochemical performance of doped chromite oxide anode with chosen dopants to point out the vital factors controlling the performance.
- ❖ In the reaction kinetics, propose a complete reaction chain with the elementary steps for H_2 oxidation and identify the rate-determining step for those oxide anodes;

- ❖ In the reactive microstructure, identify the primary reactive area and certify the possible broadened active site away from 3PB;

- ❖ In service condition with overpotential, investigate the influence of overpotential on the chemical and electrical profiles of oxide electrode; discuss the related consequence on the bulk reaction pathway and stability of oxide anode.

EXPERIMENTAL METHODS

4.1 Synthesis of materials

The chromites powders were synthesized by EDTA-citric Sol-Gel method as illustrated in Fig. 4.1. Standard nitrates (from Alfa Aesar or Acros Organics) in stoichiometric percentage together with citric acid (Alfa Aesar) were dissolved into distilled water. EDTA powders (Fisher Scientific) as complexant along with ammonia water (Alfa Aesar) was dissolved into the other set of distilled water. The above solutions were blended together followed by adjusting pH to 8 through ammonia water, then held at $\sim 80^{\circ}\text{C}$ and stirred until gelation. The gel was heated to 400°C to decompose nitrates and organic residual. Resultant powders were calcined at different temperatures for several cycles with or without intermediate ground to crystallize.

Fig. 4.1 Diagram of powder synthesis with Sol-gel method

4.2 Fabrication of cells

Doped YCrO₃ symmetrical porous cells---to make anode slurry, those anode powders were ground in ink vehicle (Fuel Cell Materials Co.) with the weight ratio of anode powders: vehicle 10:11. Anode slurry was screen printed onto both sides of YSZ electrolyte symmetrically. The electrolyte discs were made by pressing powders into pellets (1mm in thickness, 31 mm in diameter), followed by sintering at 1400°C for 4 h. The number of screen printing cycles depended on the designed electrode thickness. Typically, a single printing resulted in 5 µm in thickness after sintering. The effective electrode area was 0.7 cm² at each side. The as-made symmetric cells were sintered at 1000°C for 2 h in air. Pt mesh was bonded to both electrodes as current collector using Pt paste, followed by heating at 700°C for 2 h.

Dense LSCF(thick)/GDC(thin) half cells---GDC powders (Fuel Cell Materials Co.) was evenly mixed with 1 cat.% Co(NO₃)₃ as sintering aid and heated to 400°C in order to decompose Co(NO₃)₃ into Co₂O₃ and achieve initial firm bond with GDC particles. The resultant mixture 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 30 mL ethanol), then ball-milled for 24 h to produce suspension which was air-brushed onto one side of electrode to fabricate thin layer electrolyte. In brief, LSCF (Fuel Cell Materials Co.) in 1.5 g were dry pressed under 50 MPa in a 16.5 mm die. The suspension was evenly sprayed to LSCF surface, followed by pressing at 300 MPa. The thickness of GDC layers can be controlled by the volume of suspension served to the gun and was set to ~50 µm for all samples. LSCF/GDC sandwiches were sintered to 1300°C 4 h for densification. Pt paste was applied to GDC surface as counter electrode and heated to 700°C for 2 h. Silver wires were attached to both surfaces using silver paste as lead wires heated to 600°C for 2 h.

4.3 Electrical and electrochemical characterizations

DC conductivity measurement---the electrical conductivity was measured using Van der Pauw 4 probe method as shown in Fig. 4.2.[101] Powders in 0.7 g were dry pressed into pellet with a 16.5 mm die, followed by sintering at 1300°C for 4 h. Four silver contact points were located at on one side symmetrically. The testing was conducted from 600 to 850°C in both air and 5% H₂ balanced with N₂ using Keithley 2400 SourceMeter. Current I_0 flows from I_1 to I_2 probe, voltage between V_1 and V_2 probes is measured with the configurations of Fig. 4a and b. The resistance is calculated using Eq. 4.1.

Fig. 4.2 Configuration of Van der Pauw measurement.

$$\rho_e = \frac{d}{\ln 2} \frac{R_1 + R_2}{2} f\left(\frac{R_1}{R_2}\right) \quad (4.1)$$

where ρ_e is the resistivity, d sample thickness, R_1 , R_2 measured resistance from configuration a and b respectively. $f(R_1/R_2)$ is the function of the ratio R_1/R_2 in the range (0, 1).

The DC resistance of LSCF/GDC half cell was measured by standard 4-probe method with constant current flows in the range of 0.01-10 mA by Keithley 2400 SourceMeter and 2182A Nanovoltmeter at 700°C.

Electrochemical performance---EIS testing was carried out on these symmetric cells in various H₂-containing and O₂-containing atmospheres by Solartron 1287 and 1260 at open circuit condition over frequency range from 0.1 Hz to 99 MHz. The AC signal applied was 20 mV. H₂ or O₂ content in H₂/N₂ or O₂/N₂ mixture was adjusted by mass flow controller (Alicat Scientific). H₂-containing gases were all moisturized by passing through a water bubbler at room temperature before feeding to samples and the vapor partial pressure is approximately 3%.

4.4 aterial structure characterization

Crystal structure---the power phase purity or mixture powders compatibility was examined through X-ray diffraction (XRD, PANalytical *X'pert* PRO and Bruker AXS, Cu K α radiation) Commercial software Jade 5 was used to analyze XRD spectra.

Microstructure---structure of the electrode and morphology of materials were inspected via scanning electron microscopy (SEM, JEOL JSM-7600F, Hitachi S-4700).

FACTORS CONTROLLING H₂ OXIDATION ON DOPED YCrO₃

Due to the excellent catalytic activity of Ni for H₂ oxidation, the anodic polarization resistance is relatively small in the overall internal resistance of SOFC, which reasonably shifts the research effort to the cathode part in most cases. However, when it comes to the alternative oxide anode materials, the presently available materials will account for a major part of the overall resistance as shown in Table 2.2 and 2.5, therefore, justifying extensive and systematic studies on anode performance to gain insight on how to understand and optimize electrode activity in the future. Unfortunately, most studies regarding oxide anodes are focused on the overall performance evaluation instead of the reaction mechanisms. To this end, this chapter is devoted to illustrate the possible factors controlling fuel oxidation on those oxide anodes using H₂ as an example. The designed samples with compositions as

- 1) YCrO₃,
- 2) Y_{0.8}Ca_{0.2}CrO₃,
- 3) YCr_{0.8}Co_{0.2}O₃ (YCC),
- 4) Y_{0.8}Ca_{0.2}Cr_{0.8}Co_{0.2}O₃ (YCCC)
- 5) Y_{0.8}Ca_{0.2}Cr_{0.9}Ni_{0.1}O₃ (YCCN)

were synthesized by sol-gel method as stated before. Different element dopants were adopted at A and/or B site in order to separate the possible roles of those relevant parameters in the catalytic activity, in terms of electrical conductivity, lattice oxygen activity, reducibility and etc. The

phase purity and electrical conductivities were first measured and the influence on electrode performance was evaluated with EIS. The model of H_2 oxidation was finally proposed.

5.1 Phase purity, compatibility and electrical conductivities

Fig. 5.1 XRD patterns for different YCs samples.

Fig. 5.1 shows the XRD spectra from the powder samples of pristine and doped $YCrO_3$. Because the co-existence of Ca and Co in YCCC was found to make hard to obtain pure phase, it is worth a while to discuss such phenomenon in more detail. For YCCC treated at 1100°C , a foreign peak marked with a triangle at around 24.6° was detected and identified as the main peak of $Ca_2Cr_2O_5$ (PDF#48-0791) by Jade 5.0. It has been reported by K. J. Yoon etc. that pure phase

Ca&Co co-doped YCrO_3 was obtained by glycine-nitrate method at 1200°C . [72] And they also confirmed good chemical stability of such material in oxidizing and reducing atmosphere and good compatibility with YSZ. But in our study, it was observed that diffusion between YCCC pellet and YSZ felt holder occurred when sintered above 1200°C . The investigation of sintering behavior of Ca-Cr system has been conducted in lots of literature. [102-103] It was shown in those studies through the $\text{CaO-Cr}_2\text{O}_3$ phase system, liquid phase would appear in $\text{CaO-Cr}_2\text{O}_3$ when heating up to $\sim 1022^\circ\text{C}$. [104] Therefore, doping Ca into Cr-based perovskite as a strategy was even employed to improve the sinterability because the transient liquid phase. CaCrO_4 , $\text{Ca}_3(\text{CrO}_4)_2$, $\text{Ca}_5(\text{CrO}_4)_3$, etc, appear at different sintering phrases, and will eventually dissolve into the lattice when elevated temperature along with prolonged sintering time is used. What's more, Co is found to be able to complicate the transition of transient liquid phase further. Doping Co into $(\text{LaCa})(\text{CrCo})\text{O}_3$ facilitates the formation of liquid phase, resulting in an above 94% sinterability at 1300°C . [105] Indeed, it also was confirmed herein that YCCC sample experienced a liquid sintering phrase in the middle of sintering process. Some area on the surface of YCCC pellet sintered at 1100°C was coated by a glass-like phase, which can be seen by bare eye and also observed by SEM as shown in Fig. 5.2(a).

Fig. 5.2 Morphology of YCCC sintered at 1100°C (a), 1200°C (b), $Y_{0.8}Ca_{0.2}CrO_3$ (c) and YCCN (d) sintered at 1200°C.

Such phenomenon has not been observed on YCC or YCCN. The shrinkage simply calculated from the sizes of sample before and after sintering at 1400°C, is 17% for YCCC, compared to 15% for YCC and 12% for YCCN. Based on the facts above, it is clear that Co doping facilitates the formation of Ca-Cr liquid phase, further improving the sinterability of yttrium chromites, even though Co itself somehow has not been significantly embraced into this phase. EDS was carried out and the results are shown in Fig. 5.3 and Table 2.1. This dense bulk phase shows the ratio of Y:Ca:Cr:Co as 0.1:1:1.1:0.03, in which the Ca:Cr ratio is consistent with the secondary phase $Ca_2Cr_2O_5$ identified by XRD at 1100°C.

Fig. 5.3 EDS on impurity in YCCC.

Table 5.1 Composition of the impurity at spectrum 1 in YCCC.

Element	Weight%	Atomic%	Relative ratio
O K	35.05	62.15	3.6
Y L	5.73	1.83	0.1
Ca K	23.37	16.54	1
Cr K	34.78	18.97	1.1
Co K	1.06	0.51	0.03

Such phase in YCCC disappeared as shown in Fig. 5.2 (b) when calcined at 1200°C. Accordingly, only a tiny peak at 24.6° (the highest peak for $\text{Ca}_2\text{Cr}_2\text{O}_5$) was detected by the XRD for 1200°C calcined YCCC powder. Another consequence of Co facilitating sintering is that the particle size of YCCC is larger than those of YCC and YCCN sintered at the same temperature. As can be seen in Fig. 5.2, the grain size is 0.2~0.5 μm for YCC, 1~1.5 μm for YCCC and 0.2~0.5 μm for YCCN respectively. At last, by sintering YCCC to 1250°C with 2 cycles of intermediate grinding, pure phase was obtained as shown by XRD in Fig. 5.1. For all other

compounds under the marked calcined temperature, all patterns correspond to the orthorhombic perovskite structure (PDF#48-0474), pure phase are at last obtained.

Fig. 5.4 Electrical conductivities for doped YCrO_3 in air.

Fig. 5.5 Electrical conductivities for doped YCrO_3 in 5% H_2 - N_2 .

Fig. 5.4 shows the electrical conductivities of YCs in air. YCrO_3 , YCaCrO_3 , YCC, YCCC and YCCN pellets were all sintered in air at 1300°C , except for YCCC at 1200°C , resulting in 81%, 92%, 93%, 98%, and 86% relative density. The data have been calibrated in terms of the porosity impact in a sphere sample.[106] Due to the very small concentration of intrinsic hole defects, YCrO_3 exhibits electrical conductivity at 10^{-2} S/cm order of magnitude. Doping regardless at A or B site as shown in Fig. 5.4 improves such value substantial by increase the hole concentration. Comparing YCCC and YCCN, the increase was much more pronounced for the former. The conductivity value reads 0.027, 6.7, 25, 44 and 28 Scm^{-1} for YCrO_3 , $\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$, YCC, YCCC and YCCN at 850°C respectively. The value of YCCC is comparable with published results, while for YCC, it almost doubles.[67] In reducing atmosphere as shown in Fig. 5.5, all the conductivities reduce tremendously because of the formation of vacancy and the resultant loss of holes because of the p-type nature of those semi-conductors, which can be described in Kroger-Vink citation as:

The conductivity reads 0.009, 12, 0.58, 3.5 and 3.7 for YCrO_3 , $\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$, YCC, YCCC and YCCN at 850°C respectively. Surprisingly, the highest value is from YCC. And even with further doping at B site, like YCCC and YCCN, the conductivity is not enhanced but instead reduced. Similar phenomenon has been reported on Mn doped $(\text{LaSr})\text{CrO}_3$ by Raffaele et al.[107] At doping level $<10\%$ of Mn at Cr site, the conductivity reached its minimum. Such trend was explained by that the Mn site which possess lower energy level than Cr acts as hole trap that did not share the hole with its surrounding Cr sites once catching one, resulting in low hole concentration in the lattice. As Mn content increased, the chance of those trapped holes hopping between Mn sites rose, starting to building a conductive network again. In this sense,

similar reason probably works here to mediate the conductivity. However, further experiment is needed to completely confirm this speculation.

Usually, the electrical conductivity of electrode materials is aimed at ~ 100 S/cm. As in the traditional Ni/YSZ anode such conductivity has never been a problem, this criterion is only enforced upon the newly explored cathode materials. However, since the conductivities for those chromites are far below of 100 S/cm, its influence on electrode performance needs to be evaluated first. Even though 100 S/cm is desirable, in more than few cases the newly developed materials cannot meet such standard which on the other hand still display modest to outstanding performance. Literally, electrical conductivity describes the easiness of transporting electronic charges (most of the time the ionic conductivity is much lower in the electrode materials) in the same medium. Therefore, it can be calculated how much the ohmic resistance is from the electrode part. Assuming the apparent conductivity of the practical porous electrode is $\sim 1/10$ of the dense bulk sample. For electrolyte-supported cell with electrode thickness of 50 μm , the ohmic resistance for YCrO_3 , $\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$, YCC, YCCC and YCCN anode at 850°C will be 5.5, 0.004, 0.086, 0.014 and $0.014 \Omega\text{cm}^2$, respectively. Compared to the allotment of $\sim 0.15 \Omega\text{cm}^2$ for anode,[108] except for YCrO_3 and YCC, the others exhibit marginal ohmic resistance. If anode-supported configuration is used with a 300 μm anode, those values increase up 6 times to 33, 0.024, 0.516, 0.084 and $0.084 \Omega\text{cm}^2$. It renders only YCCC and YCCN suitable for this application. However, except the ohmic resistance, the role of electrical conductivity has to be considered in the catalytic activity as will be shown below.

5.2 Factors determining catalytic activity in H_2 oxidation

The electrochemical performance evaluation was carried out on symmetrical cells. Before that, the compatibility between those chromites and YSZ electrolyte was checked by XRD. Fig. 5.6 displays the phase compatibility between doped $YCrO_3$ and YSZ at fabrication and testing conditions. No chemical reaction is observed in the limit of XRD, showing good compatibility between those compounds.

Fig. 5.6 XRD patterns for compatibility between YSZ and chromites in the electrode preparation condition and electrochemical testing condition.

Fig. 5.7 morphology of YCCC (a), YCCN (b) and the microstructure of YCCC/YSZ (c), YCCN/YSZ (d) electrodes

Fig. 5.7 shows the morphology of YCCC (a) and YCCN (b) particles, and the microstructure of different electrodes (c for YCCC-YSZ, d for YCCN-YSZ). The particle size is 0.5~1 μm for YCCC and 0.3~0.5 μm for YCCN, separately. All electrodes have the similar thickness, ~20 μm. No diffusion or reaction can be seen in the electrode/electrolyte interface, which is in agreement with the XRD results. The surface of electrolyte pellets was roughened during the dry-pressing process to improve the electrode/electrolyte bond, which can be seen clearly in c and d.

To illustrate the importance of electrical conductivity, two extremes, $\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ with the biggest and YCC with the smallest conductivity, were measured by EIS in wet H_2 at different temperatures. Fig. 5.8a shows the performance for $\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$. Even though the performance is thermally activated, it is around $240\ \Omega\text{cm}^2$ at 850°C , too big to have any practical use in anode. In comparison, the performance for YCC in Fig. 5.8b at the same conditions is much better, which reads $8\ \Omega\text{cm}^2$ at 850°C . This simple comparison unambiguously indicates that the electrical conductivity (mainly electronic conductivity for those chromites) is not the determining factor of performance, but the nature of B site element affects it substantially.

Fig. 5.8 EIS of (a) $\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ and (b) YCC in wet H_2 at different temperatures.

Fig. 5.9 Performance for YCCC and YCCN on YSZ electrolyte in wet H_2 .

Fig. 5.9 shows the performance for the rest samples, YCCC and YCCN. Good performance is obtained with YCCC anode. The polarization resistance $0.96 \Omega\text{cm}^2$ is among the best ones available from literature. It means materials with good electrical conductivity and active B site elements give rise to good performance. However, as stated above, electrical conductivity can only cast a negligible influence on the ohmic resistance. Therefore, the correlation between electrical conductivity with polarization resistance is important. After doping Ca at A site to make YCC into YCCC, the performance is ~ 10 times better than before. Given the B site composition is totally the same, the difference should stem from the electron part. So, it is more appropriate to refer to the influence from electron part as electron activity instead of electrical conductivity. In all the element steps, charge transfer step is directly affected by the electron Fermi level in the anode materials. Therefore, charge transfer step could be a rate-limiting step in YCC and is improved in YCCC, which we will discuss in detail below.

5.3 Rate-limiting steps on doped YCrO_3 anodes

Fig. 5.10 P_{H_2} -dependent polarization resistances of YCCC (a) and YCCN (b) in 750°C on YSZ.

The electrochemical behaviors of YCCC and YCCN under different P_{H_2} are characterized. The high frequency intercept for the ohmic loss has been subtracted from the Cole-Cole plots. All spectra feature two-arc profile, as shown in Fig. 5.10.

Fig. 5.11 Reaction orders of the overall polarization resistances for YCCC (a) and YCCN (b).

The corresponding reaction orders (n) in the relationship of $1/R \propto P_{H_2}^n$ are plotted in Fig.

5.11. The overall polarization resistances demonstrate reaction orders of 0.2-0.45 and 0.15-0.2

for YCCC and YCCN at different temperatures, respectively. In the Ni-YSZ system, results on partial pressure dependence have been extensively reported in literature [77, 88, 109-112]. Jiang et al. reported the HF arc for Ni/YSZ electrode decreased when H_2 content in H_2-N_2 (with constant 2% H_2O) mixture decreased from 98% to 10% [110]. It is suggested more O-Ni bond or sub-oxide at Ni surface stemmed from higher P_{O_2} facilitated dissociative adsorption and diffusion of H from electrode to YSZ surface near 3PB, which in turn elevated the rate of charge transfer at 3PB. M. Brown et al. found resistances for high frequency arc were complicatedly dependent with P_{H_2} [111, 113]. In their study reaction order of this arc towards P_{H_2} varied from -1.15 to 0.15 at constant H_2O content when different configurations of Ni/YSZ anode were used. In addition, for the Ni film anodes used by N. Nakagawa [112] HF arc exhibited no H_2 dependence in the P_{H_2} range from 10^{-2} to 1 with constant 2% H_2O . However, none of the observations in Ni-YSZ system can be easily applied to interpret the kinetic behavior of ceramic anodes and there have been very few studies on H_2 oxidation mechanism in ceramic anodes in SOFC. In the studies of catalytic activity of anode material by J. Rossmeisl and T. setoguchi [114-115], it was concluded that for a desirable anode catalyst, the strength of oxygen-metal bond should be strong enough to get oxygen transported from electrolyte and weak enough to avoid poisoning the catalyst surface. Of all the metal elements investigated, Ni showed medium bind energy with O, resulting in the highest catalytic activity. From this point of view, the intermediate binding energy between Ni and O might be the key for the O-Ni species to work out. In contrast, doped $YCrO_3$ with mostly Cr at B site display poor O adsorption according to kinetics of O_2 adsorption and non-stoichiometric surface behavior studies [116-117]. Therefore it is difficult for YCs to hold O stably on the surface especially in an extremely reducing

atmosphere. In addition, relatively high surface H coverage is demanded in spillover effect. Otherwise the supply of H would be mitigated by lowering P_{H_2} .

Because of the two-arc profiles exhibited by YCCC and YCCN, all spectra were fitted using the equivalent circuit as shown in Fig. 5.12, where L_1 represents the overall inductance from the test-stand, R_0 the total ohmic resistance composed of contributions from electrolyte, electrodes and lead wires, R_1 and R_2 represents the polarization resistance in HF and LF. The constant phase element (CPE) is adopted due to the frequency dispersion phenomenon in electrode processes.

Fig. 5.12 Equivalent circuit used to fit the EIS of YCCC and YCCN anodes.

Table 5.2 R , C and f_0 for HF and LF arcs after fitting YCCC and YCCN anodes tested in at 850°C , and the corresponding E_a as well as reaction order (n) in the temperature and P_{H_2} ranges used in the work.

In wet H_2 at 850°C		R (Ωcm^2)	C (F/cm^2)	f_0 (Hz)	E_a (eV)	n
HF arc	YCCC	0.65	5.2×10^{-5}	3500	1.0	0.25~0.33
	YCCN	5.2	5.3×10^{-5}	530	1.6	0.10~0.16
LF arc	YCCC	0.33	6.9×10^{-3}	70	0.8	0.34~0.50
	YCCN	3.2	1.1×10^{-3}	45	0.6	0.18~0.37

Table 5.2 summarizes the fitting results of the resistance (R), capacitance (C) and characteristic frequency (f_0) for HF and LF arcs of two electrodes tested in the case of wet H_2

(without N₂) at 850°C, as well as reaction order (n) in the relationship of $1/R$ $P_{H_2}^n$ and

apparent activation energy (E_a) obtained in the testing temperature (650~850°C) and P_{H_2} (0.01~1 atm) ranges. The overall H₂ oxidation reaction in anode can be represented in Eq. 5.2,

Several sub-steps must occur before H₂ is thoroughly oxidized as above. A model for the reaction path on YCs anodes can be presented in Table 5.3 as following:

Table 5.3 A model for H₂ oxidation reaction at YCs anode.

	H ₂ oxidation model	n in $P_{H_2}^n$
Step 1	$H_2 \rightleftharpoons 2H_{ads, YCs}$	1
Step 2	$H_{ads, YCs} \rightleftharpoons H_{ads, 3PB}$	1/2
Step 3	$H_{ads, 3PB} + OH_{ads, 3PB} \rightleftharpoons H_2O + e$	1/4
Step 4	$H_{ads, 3PB} + O_O^X \rightleftharpoons V_O^{\square\square} + OH_{ads, 3PB} + e$	1/4
Split step 4:		
Step 4'	$O_O^X \rightleftharpoons V_O^{\square\square} + O_{ads, 3PB} + e$	-1/4
Step 4''	$H_{ads, 3PB} + O_{ads, 3PB} \rightleftharpoons OH_{ads, 3PB}$	0

Four basic assumptions are taken:

- 1) these reactions are microscopic reversible;
- 2) the adsorption of any species is governed by Langmuir type isotherm;

3) the surface coverage for all adsorbed species is low;

4) the stoichiometric change of oxygen in anode materials is neglected

to simplify the derivation. The corresponding reaction rate for step 1~4 can be written as:

$$r_1 = k_1 P_{H_2} \quad k_1 a_{H,YCs}^2 \quad (5.3)$$

$$r_2 = k_2 a_{H,YCs} \quad k_2 a_{H,3PB} \quad (5.4)$$

$$r_3 = k_3 a_{H,3PB} a_{OH^-,3PB} \exp(\beta_1 fE) \quad k_3 P_{H_2O} \exp(-\alpha_1 fE) \quad (5.5)$$

$$r_4 = k_4 a_{H,3PB} \exp(\beta_2 fE) \quad k_4 a_{OH^-,3PB} \exp(-\alpha fE) \quad (5.6)$$

where k_i and k_i are the rate constants for the corresponding anodic and cathodic reaction; $f=F/RT$ (F , R and T have their usual physical meaning) and E the electrode potential. α_i and β_i are symmetric coefficients, $\alpha_i+\beta_i=1$. If first assuming step 4 the RDS other steps are in near equilibrium state. It follows:

$$a_{H,YCs} = \sqrt{\frac{k_1 P_{H_2}}{k_1}} \quad (5.7)$$

$$a_{H,3PB} = \frac{k_2 a_{H,YCs}}{k_2} = \frac{k_2}{k_2} \sqrt{\frac{k_1}{k_1}} P_{H_2} \quad (5.8)$$

$$a_{OH^-,3PB} = \frac{k_3 P_{H_2O}}{k_3 a_{H,3PB}} \exp(-fE) = \sqrt{\frac{k_1}{k_1}} \frac{k_2 k_3}{k_2 k_3} \sqrt{\frac{P_{H_2O}^2}{P_{H_2}}} \exp(-fE) \quad (5.9)$$

Inserting Eq. 5.7~9 into 5.6 gives

$$r_4 = \sqrt{\frac{k_1 P_{H_2}}{k_2}} \frac{k_2}{k_1} \exp(-\alpha_2 fE) \sqrt{\frac{k_1}{k_2}} \frac{k_2 k_3 k_4}{k_1 P_{H_2}} P_{H_2O} \exp[(1+\alpha_2) fE] \quad (5.10)$$

Eq. 5.10 represents the reaction rate of step 4 at the steady state, and the corresponding current density is $i = nFr$. In equilibrium conditions, no net current flows through the anode, i.e., $r_4=0$, which yields the Nernst potential

$$E = \text{const} + \frac{RT}{2F} \ln \frac{P_{H_2O}}{P_{H_2}} \quad (5.11)$$

Inserting Eq. 5.11 back into 5.10 we obtain the relationship $i_{o,4} = P_{H_2}^{1/4}$ (take $\alpha_2=\beta_2=0.5$), $i_{o,4}$ the exchange current density for step 4 in equilibrium. In the same way, all remaining reaction orders tabulated in the Table 5.3 above can be derived.

5.4 H-must charge transfer reaction

In the above model, step 4 seems not to be an elementary one and therefore could be split into two steps, step 4' and 4''. By splitting step 4 into two simpler reactions, the reaction rates for step 4' and 4''

$$r_{4'} = k_{4'} \exp(\alpha_2 fE) = k_{4'} a_{O^-, 3PB} \exp(\alpha_2 fE) \quad (5.12)$$

$$r_{4''} = k_{4''} a_{H, 3PB} a_{O^-, 3PB} = k_{4''} a_{OH^-, 3PB} \quad (5.13)$$

Assuming step 4' the rate limiting step, step 1~3 yield the same relationship as in Eq.

5.7~9 and step 4'' gives:

$$a_{\text{O}^{\cdot-}, 3\text{PB}} = k_4'' a_{\text{OH}^{\cdot-}, 3\text{PB}} = \frac{k_1}{k_2} \left(\frac{k_2}{k_1} \right)^2 \frac{k_3 k_4'' P_{\text{H}_2\text{O}}}{k_3 k_4'' P_{\text{H}_2}} \exp(-fE) \quad (5.14)$$

Substituting those expressions in Eq. 5.7~8, 3.14 for terms in 5.12 gives

$$r_{4'} = k_{4'} \exp(-fE) \frac{k_1}{k_2} \left(\frac{k_2}{k_1} \right)^2 \frac{k_3 k_4'' P_{\text{H}_2\text{O}}}{k_3 k_4'' P_{\text{H}_2}} \exp[-(1+\alpha)fE] \quad (5.15)$$

Similarly, the Nernst potential can be derived in equilibrium and the relationship

$i_{0,4'} P_{\text{H}_2}^{1/4}$ can be readily obtained by inserting 5.11 back into 5.15.

The compelling consequence found is whether writing the oxygen ion transfer step explicitly, as in step 4', affects the final P_{H_2} dependence of the charge transfer step. Step 4' is exactly the same as that in the cathode reaction mechanism and the calculated P_{H_2} dependence is -1/4, consistent with the P_{O_2} dependence of 1/8 in the cathode. Judging by the positive charge transfer reaction orders listed in Table 5.2 for YCCC and YCCN electrodes, it means either step 4' is nonexistent in the present anode system or must be faster than any other steps in any conditions so that it won't be detected. The latter is obviously impossible given the extremely low P_{O_2} in the anode conditions.

Because the charge carrier in the electrolyte is O^{2-} , it might be fair for one to view the

change of P_{H_2} in reducing conditions solely as a way to adjust the O_2 content in these atmospheres. Indeed, the Nernst potential of a fuel cell can be written in the form of an O_2

concentration cell by merely taking P_{O_2} into account.[88, 118] This consequently leads to the idea that P_{O_2} is the major factor which affects the electrode performance even when tested in anode conditions. Although this assumption is valid when testing cathodes, it is not true for the anode measurement made in reducing atmospheres. Here the resistances decrease as P_{H_2} increases, or in other words, as P_{O_2} decreases as shown in Fig. 5.11. As a result, it seems H_2 not only works to lower P_{O_2} but also must participate in the reaction where charge transfer happens. This can explain that in the model in Table 5.3, the steps having electrons transferred but without involving H would give a negative reaction order. From this point of view, what matters is actually not how to rearrange the reaction step possibly but how to build the charge transfer step in anode appropriately. An available result that may be relevant to this idea is the modeling study on Ni/YSZ pattern anode by Vogler et al.[89]

To investigate the mechanism of charge transfer, five possible scenarios in the Ni-YSZ anode were proposed. The charge transfer steps they adopted for those oxygen spillover scenarios only included oxygen species on YSZ and Ni, whereas the hydrogen spillover ones included both oxygen and hydrogen species. The calculation results showed that only a double hydrogen spillover pathway could reproduce the experimental trends of the P_{H_2} dependent polarization resistance, and all oxygen spillover mechanisms led to the opposite trends. In this regard, the H_2 oxidation mechanisms proposed in literature can be divided into two categories according to how the charge transfer process is constructed: with H participating, and with only O involved. In reality, both cases have been used in the modeling work of Ni/YSZ anodes, but are sometimes classified as H [89, 119] and O [82] spillover mechanisms respectively. The positive P_{H_2} dependency has been used by Utz [120] as a rationale to choose the H instead of O

spillover mechanism for their patterned Ni anode. The calculated negative reaction order in step 4' then implies the proposal of charge transfer steps involving only O species in the H₂ oxidation models invalid in doped chromite anodes.

About such P_{H_2} dependency, besides YCCC and YCCN, the performance of other oxide anode materials was reported to apparently depend on it.[39, 121] CeO₂ anode showed a reaction order of 0.5 towards P_{H_2} . [122] The resistance of (LaSr)(CrFe)O₃ introduced by Tao increased 50% when reducing P_{H_2} from 0.4 to 0.1 atm.[58] It may seem no surprising to find that higher concentration of reactant (H₂) gives rise to larger exchange current and consequently smaller resistance. However, the adsorbed H species but not H₂ molecule in ambient atmosphere is involved directly into electrode reaction after adsorption. In fact, the generally stronger P_{H_2} dependence of oxide anodes relative to Ni-based anodes could be from the different electrode configurations, microstructure, lattice structures of components and etc. In particular, of all these relevant factors, the coverage (θ) of adsorbed H species on an electrode should be an important factor. The linear relationship between the square root of partial pressure and surface coverage is assumed in most cases, which makes it valid to establish a simple power law dependence between the reaction rate and the partial pressure of certain reactive species.[123-124] But such a linear relationship would not hold at the high surface coverage level as shown in Langmuir adsorption isotherm. As reported by M. Mogensen and S. Skaarup,[76] the H coverage on a Ni surface was estimated to be 0.23 for 1 atm H₂ pressure at 1000°C, indicating that the commonly used assumption $\theta \ll 1$ is not necessarily true in the anode. In fact, under high surface coverage conditions, the influence of the partial pressure of H₂ on the reaction rate of each elementary step will be damped because of the mitigated dependence of coverage on the partial pressure as

predicted by Langmuir adsorption isotherm. That may be responsible for the weak P_{H_2} dependent resistances in a number of Ni anode studies. In the same sense, it results that the H coverage on neither YCCC nor YCCN is sufficient to eclipse the influence from P_{H_2} changes. But comparatively, Ni is more effective in improving the H adsorption.

The reaction orders for those anodes listed in Table 5.2 are roughly 1/4 for the HF arcs and 1/2 for the LF arcs. Judging from these dependency results, in addition with C and f_0 values, the HF and LF can be accordingly assigned to charge transfer and H surface diffusion processes, respectively. The increased reaction order in YCCC electrodes with lowering P_{H_2} suggests that the eclipsing effect from surface coverage is reduced at low P_{H_2} . Given charge transfer is still a rate limiting step in YCCC, the enhanced electron activity in YCCC is most probably one of the reasons for the great improvement of YCCC over YCC.

It has to be admitted that the agreement found for interpretation of experimental observance with the modeled reaction scenario does not totally exclude other reaction mechanisms for YCs, especially for reaction taking place out of 3PB. Doped YCs possess some level of ionic conductivity at very low P_{H_2} condition. They turn MIEC when working as anodes, and the charge transfer process (step 3 and 4) not only take place at 3PB area but also occur at 2PB area as O ions can be transported through the bulk of YCCs. The activity of oxygen vacancy in step 3 for 2PB reaction is no longer constant, but dependent to P_{H_2} . Considering this fact, the reaction path in anode should be more than those equations above proposed for 3PB that in this model.

5.5 Summary

In this chapter, the anode oxidation reaction process has been investigated on YCrO_3 -based perovskites materials as newly emerged oxide anodes. Sr, Co and Ni were doped into YCrO_3 to enable a systematic variation in terms of B site element, electrical conductivity and catalytic activity. The characterization was conducted by EIS at different P_{O_2} in temperature range from 650~850°C. The rate-determining factors, difference and similarity between oxide anode and Ni metal anode and the possible H_2 oxidation model have been discussed based on those results.

Good performance was yielded from YCCC, $0.9 \Omega\text{cm}^2$ at 850°C which is among the best performance presently available from oxide anodes. According to the reaction order, charge transfer at the high frequency and hydrogen surface adsorption/diffusion at low frequency were identified as limiting factors in those doped YCrO_3 anode. Similar to the perovskite used as cathode, B site element worked as a decisive role in determining catalytic activity. Such activity was proven to be H-related, e.g. H surface adsorption/coverage was dependent to those B site elements. Compared to metal Ni, the oxides displayed worse H adsorption ability judging by the apparent P_{H_2} dependent resistance. YCCN showed better adsorption ability than YCCC even with less dopant content at B site. A possible model was presented to describe the elementary steps in H_2 oxidation. It was suggested that particularly for the charge transfer step, any hypothesis models presented without taking H into account were invalid. It was also found that high electrical conductivity ($>100 \text{ S/cm}$), though usually cited as a prerequisite, was not necessary in those chromites to obtain a good electrode performance. High performance came from combination of high electrical conductivity and B site active element. As among all the

element steps, charge transfer step was directly affected by the electron activity in the anode materials.

EXTENDED ACTIVE AREA DUE TO LATTICE VACANCY AND ACTIVE ELECTROLYTE

In the Chapter 5, the nature of H_2 oxidation reaction on chromites has been investigated. The catalytic property of B site element has been partially associated to H surface adsorption ability. On the other hand, oxygen as the other reactant, whose activity could also be able to affect the reaction kinetics and even the available active area, will be discussed in this chapter. As mentioned in the Introduction, the activity of lattice oxygen could be viewed as one of the major virtues of those oxide anodes when it can give rise to a different pathway in H_2 oxidation. It will be seen in this chapter that B site elements also work as the key roles in activate lattice oxygen. Due to the B site doping elements in those $YCrO_3$, 2PB reaction is enabled, resulting in faster H_2 oxidation kinetics. YSZ and SSZ electrolyte are employed to unveil the contribution from 2PB enabled by bulk diffusion, based on the fact that 2PB reaction is usually associated with a big chemical capacitance and not directly affected by the nature of electrolyte. The influence of electrolyte on extended surface adsorption/diffusion area for 3PB reaction due to enhanced oxygen activity in electrolyte is also discussed. Although such observation is not new in literature, no devoted study has been conducted to explain this phenomenon yet. To this end, a thorough polarization resistance analysis is made and a mechanism is proposed to unveil the real cause for this electrolyte effect. The potential of this advantage in electrolyte design to enable smaller R_p is briefly demonstrated on the SSZ/YSZ/SSZ sandwich structure, promising a new future for those materials that are not adequate in practical electrolyte use in terms of cost, mechanical strength and thermal expansion.

6.1 Manifest of 2PB contribution in the ionic conductive oxide anode

For cathode materials, the activation of oxygen usually can be readily measured by electrical conductivity relaxation (ECR) method. Surface exchange (k) and bulk chemical diffusion (D) coefficients are obtained by fitting the relaxation curves with governing equation. Such effective method, however, cannot be used for anode oxide like doped YCrO_3 here, because their stoichiometry will not change until a very low P_{O_2} is reached, (which is exactly one of the prerequisites with respect to the chemical stability of anode). For Cr-based materials, P_{O_2} of $10^{-18} \sim 10^{-16}$ is needed to have tangible stoichiometry change so as to conduct ECR measurement, $\text{H}_2/\text{H}_2\text{O}$ mixture at 1/500 at 700°C are needed to meet such low P_{O_2} . In the presence of H_2 , the exchange process is not so much an oxygen evolution process as a deviation from H_2/O_2 reaction equilibrium since H adsorption will take place at the surface. In addition, only a small variation of P_{O_2} (increments in 1/20~1/10 of the original P_{O_2}) can be applied in the ECR methodology so that k can be taken as a constant to simplify the governing equation. With a small P_{O_2} change, the electrical variation of those doped YCrO_3 is too small to be accurately recorded with the presence of the system noise. Therefore, ECR is not applicable here. When it comes to determine the reaction kinetics, EIS in fact shows similar functionality as ECR except that the performance is evaluated in a form of resistance, not directly expressed in forms of k and D . To handle the complexity in using EIS to clarify the oxygen activation of those doped YCrO_3 , we have to digress in the middle for a moment from H_2 oxidation to oxygen reduction on those samples so that at last a full picture of how those oxide works can be conceived. To provide more supporting evidence, samples with SSZ electrolyte were also measured to do comparison. Since the 3PB reaction take place in the vicinity of electrode/electrolyte interface, the nature of electrolyte will directly affect its kinetics. In contrast, 2PB reaction which is supported by the

MIEC electrode itself and can expand to far from the interface, is much less influenced by the electrolyte. Based on such observation, the emerged contribution from 2PB will be distinguished through using different electrolytes.

Doped $\text{YCrO}_3/\text{SSZ}/\text{doped YCrO}_3$ symmetrical cells are made using YCCC and YCCN as anode. To differ them from YSZ-based sample, hereafter, they are denoted as YCCC-SSZ, YCCN-SSZ, in comparison to YCCC-YSZ, YCCN-YSZ. Those samples were prepared with the same procedure as described in Chapter 4 except for the thickness for SSZ is set to 2~2.5 mm due to its weaker mechanical strength. The compatibility was checked first by XRD. As shown in Fig. 6.1, good chemical compatibility is confirmed between those anode compounds and SSZ electrolyte in both fabrication and testing conditions.

Fig. 6.1 XRD patterns for compatibility between YSZ and chromites in the electrode preparation condition and electrochemical testing condition.

Fig. 6.2 Microstructure of YCCC/SSZ (a), YCCN/SSZ (b) electrodes.

Fig. 6.2 displays the microstructure of the cross-section of YCCC/SSZ, YCCN/SSZ. Good adhesion and suitable porosity are verified from those pictures.

YCCN and YCCC with YSZ and SSZ were characterized in reducing and oxidizing atmospheres. The results are shown as below first, followed by the detailed analysis with respect to the lattice oxygen activation and electrolyte effect.

Fig. 6.3 P_{H_2} -dependent polarization resistances of YCCC (a) and YCCN (b) in 750°C on SSZ.

Fig. 6.3 shows the P_{H_2} dependency of both anodes. Similar to the results from YSZ electrolyte, those spectra feature a two-arc profile also, indicating two rate-determining processes in the electrode reaction. They were fitted with the EC as shown in Fig. 5.12, and the resulting resistance and capacitance are summarized in Table 6.1. According to the derived reaction orders for different elementary steps in Chapter 5, the HF and LF process is assigned to the charge transfer and surface process respectively.

Table 6.1 Fitting results for YCCC and YCCN anodes on SSZ tested in wet H_2 at 850°C, and the corresponding E_a and reaction order (n).

	In wet H_2 at 850 °C	R (Ωcm^2)	C (F/cm^2)	f_o (Hz)	E_a (eV)	n
HF arc	YCCC-SSZ	0.22	1.1×10^{-4}	2300	1.1	0.16~0.30
	YCCN-SSZ	0.96	8.3×10^{-5}	1900	1.6	0.10~0.28
LF arc	YCCC-SSZ	0.27	1.6×10^{-2}	70	0.6	0.46~0.60
	YCCN-SSZ	0.66	2.3×10^{-3}	100	0.9	0.51~0.70

Fig. 6.4 displays the dependency of overall R_p on P_{H_2} . The reaction order for YCCC-SSZ increases with decreasing P_{H_2} . Such tendency can be explained considering under lower P_{H_2} the contribution of the surface process start to weigh more than the charge transfer step since the former is explicitly affected by the concentration of H_2 in the atmosphere showing higher reaction order than the latter as derived in Table 5.3. For YCCN-SSZ, it almost keeps constant instead. Such result is actually in good agreement with the previous observation that H coverage on YCCN anode is larger than YCCC. With higher surface coverage due to the activity of Ni element, lowering P_{H_2} in the atmosphere will not apparently affect the concentration of H on the YCCN surface, therefore is not able to affect the subsequent steps significantly.

Fig. 6.4 P_{H_2} dependency of overall R_p for YCCC-SSZ (a) and YCCN-SSZ (b) from 650-850°C.

Fig. 6.5 Electrode polarization resistances of YCCC and YCCN on SSZ and YSZ.

Fig. 6.5 displays the polarization resistances for YCCC and YCCN. Using SSZ electrolyte yielded smaller R_p than YSZ. Compared to YCCC anode, it is found way more improvement is achieved with YCCN. As stated before, due to 3PB reaction takes place in the vicinity of electrolyte/anode interface, it naturally depends on the properties of both anode and electrolyte. Changing electrolyte will affect the kinetics of 3PB reaction more than 2PB. In this regard the electrode reaction pathway can be suggested majorly as 3PB for YCCN, and 2PB&3PB for YCCC. This point will be discussed with more details and supporting evidence after compared with results from the measurement conducted in oxidizing atmosphere.

Fig. 6.6 Polarization resistances of YCCC and YCCN electrodes tested under OCV condition in air at 850 °C

Fig. 6.7 Arrhenius plots for polarization resistances of four kinds of electrodes under various P_{O_2} values

Fig. 6.8 P_{O_2} dependence of the overall polarization resistances for four different electrodes measured in oxidizing atmospheres.

Table 6.2 Summary of R , C and f_0 for these four electrodes tested in air at 850°C, as well as E_a in the temperature range of 650~850°C.

In air at 850 °C		R (Ωcm^2)	C (F/cm 2)	f_0 (Hz)	E_a (eV)
YCCC-YSZ	Single arc	1.2	1.1×10^{-3}	112	2.0
YCCC-SSZ	Single arc	1.0	1.4×10^{-3}	50	2.0
YCCN-YSZ	Single arc	36.7	1.5×10^{-4}	30	2.0
YCCN-SSZ	HF arc	12.6	3.8×10^{-4}	32	2.1
	LF arc	8.7	1.2×10^{-3}	5	1.7

Fig. 6.6 shows the polarization resistance of those electrodes measured in air. Fig. 6.7 and 6.8 display the corresponding E_a and P_{O_2} -dependency of the overall R_p . Table 6.2 summarizes the fitting results of measurement conducted in oxidizing atmospheres with different P_{O_2} . For measurement in oxidizing atmospheres, the excellent catalytic activity of Co is well-known and it is very common to obtain decent oxygen reduction reaction (ORR) performance from Co based perovskite materials. Similarly, the Ni-based ABO_3 and K_2NiF_4 structure materials such as $LaNiO_{3-\delta}$ and $La_2NiO_{4+\delta}$ have been reported to be electro-catalytically active even if the stability is an issue.[125-127] As a result, it is not surprising to achieve performance enhancement on $YCrO_3$ after Co and Ni doping. From cathode study a number of different reaction models have been developed in literature and may lead to different reaction orders in specific scenarios. However, in general, the processes dependent on P_{O_2} less than 1/4 are most likely attributed to the charge transfer process and those displaying more than 1/2 dependency are often attributed to processes involving diatomic oxygen species.[128-130] Judging from the reaction order for both YCCC-YSZ and -SSZ cathodes in Fig. 6.8a and b, the main process associated with the single arc is therefore attributed to the oxygen dissociative adsorption or surface diffusion of atomic oxygen, but not a charge transfer process since the capacitance of the single arc for each YCCC electrode in the order of mF is generally larger than those associated with charge transfer process, typically $10^{-3} \sim 10^{-1}$ mF. In addition, in the spectra of an $YCr_{0.8}Co_{0.2}O_3$ -YSZ electrode (not shown here) made in the same routine as in this work, three suppressed arcs were observed when tested in the same conditions and the one with the lowest characteristic frequency (60 Hz) possessed very similar capacitance (1.3 mF/cm^2) and E_a (1.8~2.0 eV) as the YCCC electrodes in this work, which cannot be the charge transfer process obviously. The dissociative adsorption of oxygen on $YCrO_3$ can be enhanced after Co doping as $LaCoO_3$ exhibits much better oxygen dissociative

adsorption activity than LaCrO_3 . [117, 131-132] But in most cases the corresponding adsorption E_a for either LaCrO_3 or LaCoO_3 is less than what we obtained here. A similar E_a of 2.3 eV has been obtained for doped LaCoO_3 cathode, [133-134] but was attributed to the charge transfer process in that specific case due to the $1/4 P_{\text{O}_2}$ dependency. On the other hand, given the enhanced adsorption ability of doped YCrO_3 , the diffusion process could possibly arise as a limiting factor because even though Co doping can be expected to increase the diffusion kinetics as well, the 20% Co doping level is not enough to overcome the penetrating threshold. The performance of $(\text{LaSr})\text{CrO}_3$ has been reported to be controlled by the surface diffusion process, it however showed a much smaller E_a of $\sim 1.3\text{eV}$. [133] A similar situation can be found in LSM. An arc with E_a of 1.5~2.0 eV is often observed in medium or low frequency EIS for LSM. The medium frequency arc with E_a of 2.0 eV in Kim 's work [135] was related to the surface diffusion of O^- .

Based on the n values in Fig. 6.8 c and d as well as the fact that two suppressed arcs are present in the spectra of YCCN cathodes, we assign the same surface process in YCCC along with another atomic oxygen process to these spectra of YCCN. Considering the poor surface adsorption/diffusion ability of Cr and the low level of Ni doping, the limitation of such surface processes on YCCN should not be less severe than YCCC. As the overall reaction order is smaller than other atomic processes (for O^- diffusion, $n=3/8$), such an atomic process in YCCN is possibly related to the charge transfer process ($n=0$ or $1/8$). Another interesting phenomenon for the YCCN is that the E_a in Fig. 6.7c and d increase with temperature, which is also visible for YCCC electrodes at lower P_{O_2} . It cannot be explained by the change in ratio of two limiting processes with different E_a , because the overall E_a will predictably approach the smaller one as

temperature increases. A possible cause could be the enlarged active sites resulting from the formation of oxygen vacancy at lower P_{O_2} . Low P_{O_2} at high temperature facilitates the formation of oxygen vacancy in yttrium chromites,[136] leading to the increase in surface/bulk oxygen defect, which may in turn broaden the active zone due to enhanced mass transportation. The corresponding E_a then not only includes the reaction activation energy but also is influenced by the formation energy of oxygen vacancy.

The chemical capacity featured at low frequency has been observed in a number of electrode studies. Such capacitance is attributed either to the surface adsorption of reactive species or the dissolution of O_2 into metal electrode bulk (Ag or even Pt) or the change of stoichiometry of the oxide electrodes when they experience the change of overpotential during EIS testing.[137-139] For a typical (LaSr)CoO₃ cathode, such capacitance ranges from 10~500 mF which are too big to be associated to any other process without involvement of the electrode bulk, and it also increases with the thickness of electrode until 10~50 μm . Alder et al.[140] have addressed this issue in detail and formulated a relationship between the chemical capacitance and the oxygen non-stoichiometry δ . It was also used by Kawada to directly determine the oxygen vacancy concentration in the Sr doped LaCoO₃ material.[137] As the chemical capacity corresponds to the ease of stoichiometry change and oxygen vacancy concentration, it was used by Adler as an indicator suggesting the involvement of electrode bulk in the electrode reaction.[140] Based on these observations, the small capacitance of YCCC and YCCN cathodes as shown in Table 6.2 suggests that the activation of lattice oxygen under oxidizing atmosphere is difficult for those compounds and the involvement of electrode bulk must be limited due to

lack of ionic conductivity, and therefore 3PB is the primary active zone when without lattice oxygen vacancy.

One may question, since 3PB is the essential active zone for both YCCC and YCCN in cathode conditions, why the charge transfer process that is a rate-limiting process in YCCN electrodes just disappears in the YCCC electrodes. Van et al.[108, 141] systematically investigated LSM/YSZ electrode to visualize 3PB area. Two possible 3PB areas, (1) extension from electrode/electrolyte boundary to the electrolyte bare surface, (2) extension into the electrode/electrolyte interface, were proposed. The weight of each depends mainly on the ionic conductivity of electrode. In this sense, owing to the different nature between YCCC/YSZ and YCCN/YSZ interfaces and/or the difference between YCCC and YCCN surface nature, the charge transfer kinetics could vary from one to another. Such supposition is actually supported by the results obtained in the reducing atmosphere, showing different charge transfer E_a for YCCC and YCCN.

When it comes back to anode condition, the activity of O in YCCC and YCCN lattice will manifest itself in the performance of those anodes. The reducibility introduced by Co doping activates lattice O in YCCC to react with H adsorbed on the surface. This is more significant to the performance when part of the YCCC bulk is activated as described above and the O^{2-} can be transported through YCCC bulk to 2PB. The activity of O will directly affect the charge transfer step carried out on electrodes. Ni doping is expected to work in a similar manner, but with a lower doping level, higher charge transfer E_a was obtained. As clearly shown in Table 6.1 and 6.2, the capacitances of LF arcs for YCCC are much greater under reducing than oxidizing

atmospheres, which clearly indicates the involvement of YCCC bulk as an active site for the H_2 oxidation reactions. Since the hypostoichiometry of oxygen for $\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_{3-\delta}$ under P_{O_2} of 10^{-18} at 1000 °C is 0.06,[68] for $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$ at $10^{-4} P_{\text{O}_2}$ and 800°C 0.12,[142] it is reasonable to expect more vacancy after B site Co doping then the resultant enhancement in ionic conductivity of YCCC in the reducing atmosphere compared to oxidizing one. Indeed, the reactants now are different in reducing atmosphere after switching from oxidizing conditions. Species like OH^- , H and H_2O will be newly present. But the capacitance from surface adsorption of neither OH^- nor H is sufficient to solely account for the big capacitances for the LF arc listed in Table 6.1.[111] Furthermore, neither YCCC nor YCCN are believed to possess proton conductivity. As a result, the chemical capacitance mainly originates from the incorporation/exsolution of oxygen from the electrode bulk, thus indicating apparent 2PB contribution in YCCC. Unlike the YCCC electrodes, the capacitance of YCCN electrodes did not change much in the reducing atmospheres (note: we used one arc to represent YCCN-YSZ electrode in air in Table 6.2, which is actually two arcs in series. If fitted into two arcs, the capacitance for the LF arc would display a similar value to that of YCCN-SSZ electrode). That implies the ionic conductivity of YCCN in reducing condition is still very limited. Despite the fact that the reducibility of Ni-based perovskite is very good, the enhancement of ionic conductivity and stoichiometric flexibility are limited by the low doping level in YCCN. The active zone for H_2 oxidation reaction in this case is essentially the 3PB area.

Recalling the judgment of 2PB or 3PB-dominant based on the improvement from changing electrolyte, it is found that the analysis from chemical capacitance (associated to the readiness of stoichiometry change) finally converges with it in terms of the 2PB/3PB reaction pathways on those two different candidates: only the one with 3PB dominant feature can be

apparently changed in R_p by using different electrolyte, e.g. YCCN; if the reaction pathway is mixed 2PB/3PB, less apparent effect is observed, like YCCC.

Nevertheless, the LF part which is associated to the surface process is improved as well by changing the electrolyte, which seems not quite possible since electrolyte is not likely involved in adsorption/diffusion process directly. In this regard, the next section is focused to explain such phenomenon.

6.2 Extended surface adsorption area due to active electrolyte

The improvement of electrode performance testing with YSZ and SSZ as shown in Table 6.1 on the LF resistances is to be derived to associate with the enlargement of the surface active areas on the electrode in following.

It was reported by Watanabe et al.[143] that in the Sm doped CeO_2 anode not only the ohmic loss but also the polarization resistances were reduced by using an electrolyte with higher ionic conductivity. The influence of the electrolyte was also observed on the cathode part.[144-145] Uchida et al.[146] obtained the highest performance for a Pt cathode by using the electrolyte with the best ionic conductivity. While the DC polarization measurement used in the above studies effectively displayed the enhancement of polarization, it cannot decisively distinguish which part of the polarization resistance has been changed. A possible explanation for this improvement proposed by Watanabe was that the electrode kinetics could be limited by the rate of O^{2-} supply to the anode via the electrolyte. Such an explanation unless implies that the resistance of O^{2-} transfer between electrode/electrolyte interface belongs to the polarization

resistance, otherwise it is merely talking out ohmic resistance and therefore not really relevant to the finding. With the EIS technique, more features of such an effect can be revealed. Kungas et al.[147] studied the effect of electrolyte in a composite cathode. The impedance varied not only in the magnitude but also in the profile when coupling the cathode with different electrolytes. Liu [148] observed in the investigation of the importance of 3PB in LSCF cathode that both HF and LF arcs in the spectra changed a lot in size and shape upon changing electrolytes. However, neither of the works has stated explicitly how the properties of the electrolytes will affect the polarization resistance. The ohmic resistance will of course be reduced due to high conductivity. The charge transfer (Eq. 6.1 or 6.2) and ionic transfer (Eq. 6.3) processes since related to electrolyte will also be affected by the nature of electrolyte because it is one of the sources for reactant components.

But can the electrolyte impact any processes which we suppose here are not directly related to the electrolyte, such as surface adsorption or diffusion on electrode itself?

Fig. 6.9 Schematic diagram of reactions for LSCF electrode.

Since really good MIEC anode is rarely reported, let us look at the case of ORR on a mixing conductive cathode---a dense LSCF electrode supported by YSZ or SSZ electrolyte. The results derived from cathode is applicable to anode because the principle behind is the same. As shown in Fig. 6.9, the exchange current density j_i for interface ion transfer reaction will be enhanced by using an electrolyte with higher ionic conductivity, or more relevantly, has a readier availability of $V_{\text{O electrolyte}}^{\bullet\bullet}$. The $V_{\text{O LSCF}}^{\bullet\bullet}$ will keep the same in equilibrium condition because the oxygen vacancy in LSCF depends only on the ambient atmosphere. Significant amounts of oxygen vacancies may only be obtained under a very large overpotential. Consequently, the oxygen exchange reaction on the dense LSCF surface (that is, 2PB area) won't be directly influenced by the kinetics at the interface since it is only determined by ambient atmosphere and the activity of $V_{\text{O LSCF}}^{\bullet\bullet}$. Such reasoning can be verified by the similar case in Baumann's study of LSCF surface kinetics.[92] After inserting a thin GDC layer in between YSZ and a dense LSCF electrode, the medium frequency arc corresponding to an interface ion transfer resistance

disappeared, but the LF arc corresponding to oxygen exchange on LSCF surface remained virtually unchanged.

For a charge transfer reaction occurring at 3PB, the exchange current density j_{ct}^0 will certainly increase when using a higher ion conducting electrolyte just as stated before. Let's now imagine a reaction chain to clarify the effect of such an enhancement in charge transfer on other surface processes not directly related to the electrolyte. Supposing charge transfer is one of the rate-limiting steps of the LSCF/YSZ cathode, the net current can be expressed as:

$$j_{ct} = j_{ct}^0 \left\{ \frac{c_o}{c_o^0} \exp(-\alpha f) - \exp[(1-\alpha) f] \right\} \quad (6.4)$$

Under a given applied cathodic overpotential η_1 (in the linear polarization zone), the net current is j_1 and the corresponding O^- concentration outside of the electrolyte is c_1 . Then, keep everything else the same, but suddenly change the electrolyte from YSZ to SSZ. With the same O^- concentration and then the same overpotential η_1 , the charge transfer reaction on LSCF/SSZ electrode now must proceed faster (j_{ct}^0 in Eq. 6.4 for SSZ is larger than that for YSZ under the same initial concentration of O^-). The net current increases to j_2 and the steady state is lost. The O^- concentration starts to reduce accompanied by reducing current. But the O^- gradient keeps increasing, extending the surface diffusion area in order to collect more O^- to balance the change. Meanwhile, the declining current reduces the consumption of O^- , and the enlarged active surface area provides more O^- . A new steady state will be established in the midpoint soon, with O^- concentration outside electrolyte of c_2 ($c_2 < c_1$) and net current of j_2' ($j_2 > j_2' > j_1$). The polarization

resistance $\eta/(j_2')^2$ is finally reduced and the active zone for surface diffusion and adsorption enlarged by changing YSZ to SSZ. From this point of view, the nature of the electrolyte will

affect not only the reactions involving the electrolyte but also those related to it indirectly. Such change works out in a chain, just as the variation of P_{O_2} changes each step in the ORR process. Obviously, such reasoning is not only valid in cathode but also applicable to the oxidation reaction at the anode simply by rearranging Eq. 6.4. What may need to be stressed here is that, when mentioning ionic conductivity of the electrolyte, we are not dealing with the ohmic resistance change of electrolyte at all, but just using it as the indicator of the availability of O source in the electrolyte, which is intrinsically associated to the apparent conductivity.

Fig. 6.10 Improvement of electrode performance for YCCC and YCCZ upon change YSZ to SSZ electrolyte

Fig. 6.10 shows the comparison of performance for YCCC and YCCN as either anode or cathode on YSZ vs. on SSZ electrolyte. In anode part, besides the HF charge transfer process, the LF process ascribed to the diffusion process was also improved by using SSZ electrolyte on both materials as predicted above. Much more significant enhancement was achieved on the YCCN anode. It is because the active zone for YCCN is limited to 3PB, but in YCCC anode it extends

to a small portion of electrode bulk. Changing have a less significant effect on the processes that take place at the 2PB area as stated before. In the cathode part, even though improvement still can be observed, it is less substantial, especially for the YCCC cathode. The RDS for YCCC was ascribed to either surface dissociative adsorption or the diffusion process, but not the charge transfer step. Therefore, the first ring in the chain is missing, thus less improvement can be anticipated.

6.3 Demonstration of practical application for active electrolyte

The above illustrated electrolyte effect opens a wide door for the application of novel electrolyte materials (in a form of coupling with other refractory electrolyte into bilayer or sandwich structure) that otherwise cannot be used by themselves alone due to instability in either oxidizing or reducing atmospheres, mechanical fragility, high cost or etc. For example, stabilized bismuth electrolyte showing excellent ionic activity cannot be exposed to the anode compartment directly since its instability below $10^{-13} P_{O_2}$. [149] However, if coupled with other electrolyte to protect it from anode atmosphere, bismuth can be a superior electrolyte decoration layer to promote the polarization resistance drastically. In a wider perspective, even those materials which are not technically electrolyte due to their tangible electronic conductivity can be used as electrolyte decoration based on this idea as long as they show sufficient ionic activity for the purpose of electrode performance enhancement.

Even for the SSZ used in this study, due to the fragility, it is usually not adequate to be made into thin electrolyte pellet in the electrolyte-supported fuel cell. A YSZ/SSZ/YSZ sandwich structure has been adopted by some co-workers to gain both high ionic conductivity

from SSZ and mechanical strength from YSZ. However, after the finding in this above section, the advantage from SSZ is far more than its higher ionic conductivity but majorly the so-called ionic activity. Thus, it is wiser to design a SSZ/YSZ/SSZ sandwich to utilize good support from YSZ and at the same time outstanding polarization resistance from electrode/SSZ interface. According to the explanation on the presented finding, what alters the R_p is only related to the interface composition of electrode/electrolyte. No necessarily a bulk SSZ pellet, a very thin layer of SSZ deposited on thicker YSZ should also be able to realize the same effect. In the following such concept is demonstrate on the SSZ/YSZ/SSZ sandwich structure using YCCN anode. The sandwich structure is produced by a spray-modified pressing method.

SSZ 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 30 mL ethanol), then ball-milled for 24 h to produce suspension which was air-brushed onto both sides of YSZ electrolyte to fabricate thin layer SSZ. In brief, YSZ in ~2 g were dry pressed under 50 MPa in a 31 mm die. The suspension was evenly sprayed to YSZ surface, followed by an intermediate pressing of 200 MPa. The sample was taken out and inserted back to the die carefully with the uncoated surface facing outside this time. The spray process was repeated, followed by a final pressing at 300 MPa. The thickness of SSZ layers can be controlled by the volume of suspension served to the gun and was set to ~50 μm for all samples. SSZ/YSZ/SSZ sandwich were sintered to 1400°C 4h for densification.

Fig. 6.11 Comparison between R_p for YCCN-SSZ (a), YCCN-SSZ/YSZ/SSZ (b) and YCCN-YSZ symmetrical cells (c) measured in wet H_2 at different temperatures.

Fig. 6.11 shows R_p for YCCN on pure SSZ, SSZ/YSZ/SSZ sandwich and pure YSZ measured at wet H_2 . The resistance obtained from SSZ/YSZ/SSZ sandwich in Fig. 6.11 b is very close to that obtained from pure SSZ electrolyte. In contrast, pure YSZ electrolyte yielded much

larger R_p , ~4 times bigger than the other two. Those results clearly demonstrate that the electrolyte effect is really associated with the electrode/electrolyte interface composition. Thus, thin layer decoration of active electrolyte is indeed able to promote the electrode performance as well as bulk of pure electrolyte of the same kind, which can conserve the use of expensive electrolyte material, and also make fragile electrolytes like erbium doped bismuth adequate in real application.

6.4 Summary

In this chapter, by extending the electrode response from P_{H_2} in Chapter 5 to P_{O_2} when measuring in O_2 -containing gases and using SSZ to replace YSZ electrolyte, the activation of lattice oxygen, the contribution from 2PB and 3PB and the beneficial effect of electrolyte in R_p for those oxide anodes were investigated. Judged by the chemical capacitance along with the improvement from changing electrolyte, YCCC was confirmed to be both 2BP and 3PB active, and YCCN 3PB dominant. The activation of 2PB depended on the ionic conductivity and then the nonstoichiometry of oxide under reducing atmospheres. A big capacitance for YCCC was observed and associated to the variation of lattice oxygen under EIS measurement, confirming the activity of bulk transport. The overall performance was less affected by the nature of electrolyte when both 3PB and 2PB pathways were effectively working, but on the 3PB dominant YCCN, reaction kinetics was largely influenced by the electrolyte. What's more, for YCCN, not only the charge transfer step, but also the surface process anode was promoted. Such effect of electrolyte on surface process was explained by a chain-transmit mechanism. Basically, by enlarging the exchange current of charge transfer reaction at the electrolyte/anode interface, bigger gradient in the adsorbed species was resulted, which in turn broadened the adsorption area

then diffusion and adsorption rates. The significance of this phenomenon in practical application was demonstrated on the SSZ/YSZ/SSZ sandwich electrolyte which showed almost the same R_p as from pure SSZ electrolyte. Such results could be able to rewrite the concept of electrolyte design and open a wide door for the utilization of novel electrolyte materials that otherwise cannot be used by themselves alone due to instability in either oxidizing or reducing atmospheres, mechanical fragility, high cost or etc.

ACTIVATION/DEACTIVATION AND STABILITY OF THE BULK PATHWAY UNDER OVERPOTENTIAL

The reaction kinetics of H_2 oxidation is investigated on equilibrium in those chapters above. While the basic principles governing the reaction rates can be extrapolated into non-equilibrium condition with steady net current after taking into account the effect of overpotential in the form of Butler-Volmer (B-V) equation at the activation polarization region, the change of physical properties locally in the materials bulk is not covered either in the equilibrium state treatment or B-V equation application. It is well-known that overpotential is capable of changing the surface adsorption composition of electrodes, which has been documented by Fleig et al. into dedicated models to illustrate the surface overpotential. On the other hand, the other side of the coin, e.g. the bulk properties of oxide anode, has not been address under the influence of potential before to the best of our knowledge. Under service condition usually ~ 0.3 V overpotential, significant electronic current is transformed into ionic current through the electrodes. For those oxide anodes, as proven in chapter 6, it occur through both traditional 3PB area and also newly emerged 2PB area. In the 2PB area, a big portion of the overpotential will be consumed by the bulk transport, which can possibly alter the local chemical composition of the electrode materials and electrical boundary conditions. The consequence of such alternation would be able to cast a great impact on both performance and stability of the electrode. In this regard, the present chapter is dedicated to the influence of overpotential on the bulk pathway,

which will be discussed and compared to the Nernst equation that is generally applied to treat any oxide electrodes under equilibrium. The relevant potentials controlling electrode processes include electrostatic potential, electrochemical potential of electron and ion. The distributions of those potentials and resultant influence on electrode processes are treated with drift diffusion equations. It is found that the electrode bulk is not locally electroneutral and the resultant electrostatic gradient can be established in the region near electrolyte due to the uneven distributions of ions and electrons. Therefore, besides the concentration gradient, electrical field force produced by the electrostatic potential is also the driving forces in the ion diffusion and introduces new concepts in handling chemical and electrical contributions in the overall electrochemical response of electrode system.

7.1 Oxygen transport at oxide anode bulk: 1-dimensional model

Considering oxygen reduction reaction as an example, the electrode process under steady state on MIEC is schematically sketched in Fig. 7.1a. The oxygen ions are transported through the MIEC bulk and react with H_2 on the surface. A column drawn arbitrarily at the left shows the transition from electronic current to ionic current through H_2 oxidation on the inner surface within the active length. Such electron-ion current transition starts from the upper boundary of the active length, finishes outside electrolyte with electronic current finally blocked. The active length estimated from chemical capacitance for cathode material (not available now for oxide anodes) by Adler et al. can be as big as 7~15 μm depending mainly on D/k and microstructure. The transport path in MIEC near electrolyte actually can be illustrated as in Fig. 7.1b. Though 3PB reaction in lots of cases is important to the overall electrode kinetics as well, it is ignored here in order to focus our topic to 2PB exclusively. Oxygen ions are transported inside the MIEC

from the MIEC/electrolyte interface to MIEC inner surface, as indicated by the red lines. According to the current density inside different portion of MIEC, the electrochemical equipotential lines (ELs) for oxygen is drawn qualitatively also. For segment between any two ELs, the transport behavior inside it can be simplified into a 1-dimensional case as shown in Fig. 7.1c, which renders simpler mathematical treatment without loss the important physical essence. The driving force of such transport has in lots of cases been ascribed to the oxygen vacancy gradient alone, and the influence or even the existence of electrical field was neglected, most probably because it seems impossible to build electrical field inside the bulk of a conductive material. The existence of electrical field in MIEC bulk and the distributions of defects and potentials herein will be analytically derived first; then independently solved from the governing equations also based on the 1-dimensinoal model.

Fig. 7.1 Schematic diagram for MIEC anode operation (a), the ionic flowing and equipotential lines at MIEC anode near the interface area (b), and the 1-D model derived based on it (c).

7.2 Qualitative analysis on c_e , c_v and ϕ in bulk pathway

The motion of chemical species in MIEC electrode is governed by the Nernst-Planck equation. For one-dimension case, the mass flux of species i under steady state takes the form as:

$$j_i^{\text{mass}}(x) = -D_i \frac{dc_i(x)}{dx} - \frac{f_i(x)}{z_i e} \frac{d\phi(x)}{dx} \quad (7.1)$$

where x is the position, D_i the chemical diffusion coefficient, c_i the concentration, σ_i the conductivity, ϕ the galvanic potential, z_i the valence, e the electron charge. The first term in RHS represents the diffusion, and second term migration.

According to the Nernst-Einstein relationship, the equation above can be rearranged as:

$$j_i^{\text{mass}}(x) = \frac{\int_i \tilde{\mu}_i}{(z_i e)^2 \frac{dx}{x}} \quad (7.2)$$

where

$$\tilde{\mu}_i(x) = \mu_i(x) + z_i e \phi(x) \quad (7.3)$$

$$\mu_i(x) = \mu_i^0(x) + k_B T \ln c_i(x) \quad (7.4)$$

is the electrochemical and chemical potentials, respectively. k_B and T remain the usual physical meanings.

The current density, $I_i = z_i e j_i^{\text{mass}}$, is then

$$I_i(x) = \frac{\int_i \tilde{\mu}_i(x)}{z_i e \frac{dx}{x}} \quad (7.5)$$

The current of charged species in the solid bulk is determined by its electrochemical potential gradient.

For clarity, the electronic species is henceforth indicated by the subscript “e”, and the ionic one by “v” in view of oxygen vacancy being the most common ionic defect in MIEC electrode materials. Assuming the electrolyte is purely ionic conductive at this moment, when a certain current, I_0 , is flowing through the electrolyte, the ionic and electronic currents in the MIEC film will be I_0 and 0, respectively, given that there is no sink or source for either electrons or ions in MIEC under steady state. According to Eq. 7.5, the electrochemical potential of electrons, $\tilde{\mu}_e(x)$, is constant along the thickness of electrode.

Partial differentiation of Eq. 7.3 with respect to x for electron is

$$\frac{\tilde{\mu}_e(x)}{x} = -\frac{\mu_e(x)}{x} \quad e \frac{\psi(x)}{x} = 0 \quad (7.6)$$

In order to investigate the galvanic potential term above, let us make an assumption on the electron chemical potential as $\frac{\mu_e(x)}{x} = 0$, that is, the electrons are evenly distributed in the anode bulk. Such assumption yields $\frac{\psi(x)}{x} = 0$ accordingly, meaning no electrical field inside the bulk.

With this result, for the ionic current on the other hand, the ionic concentration gradient in anode bulk serves as the only driving force for ionic flux as in Eq. 7.7:

$$\frac{\tilde{\mu}_v(x)}{x} = -\frac{\mu_v(x)}{x} + 2e \frac{\psi(x)}{x} = -\frac{\mu_v(x)}{x} = \frac{2e}{\int_v} i_0 \quad (7.7)$$

Inserting Eq. 4 for ion into Eq. 7.7, one obtains

$$\frac{k_B T}{c_v(x)} \frac{c_v(x)}{x} = \frac{2e}{\int_v} i_0 \quad (7.8)$$

As a result, the oxygen ion defects are not uniformly distributed in the anode bulk. Given the even cation charge background and the assumed uniform distribution of electrons, the local charge density at position x in the bulk, $\rho(x)$, is

$$\psi(x) = \odot z_{\text{cations}} e c_{\text{cations}} - c_e - 2eA_0 + 2ec_v(x) = 2ec_v(x) + \text{const} \neq 0 \quad (7.9)$$

where A_0 is the theoretical volume density of oxygen lattice sites.

Poisson's equation for one-dimension case writes

$$\frac{\partial^2 \phi(x)}{\partial x^2} = \frac{\rho(x)}{\epsilon_0 \epsilon} \quad (7.10)$$

Inserting Eq. 7.9 into Poisson's equation, it ends up with $\frac{\rho(x)}{x} = 0$, which is contradictory to the deviation before under the assumption of $c_e(x)=\text{constant}$. Such contradiction clearly demonstrates this assumption is not self-consistent, therefore cannot be true. There exist local net charges and electrical field inside the MIEC anode bulk. Such logical reasoning is illustrated in Fig. 7.2

Fig. 7.2 logical flow chart for the possible distribution of electronic defects and the existence of galvanic potential in MIEC bulk.

With regard to the theoretical analysis above, a couple of points in the reasoning process need to be remarked. The first is the purely ionic conductivity for electrolyte. In reality, no matter how small it is, the electronic conductivity in electrolyte material will not be 0 strictly. The significance of the electronic conductivity in electrolyte has been addressed by Virkar.[150] It was shown that such conductivity is one of the most important parameters for one to determine

the profile of $\tilde{\mu}_e(x)$ and the equivalent oxygen partial pressure inside electrolyte. However, assuming an ideal ion-conductive electrolyte will not affect the validity of the analysis above, because, in principle, the ion transport from electrolyte to anode and the building-up of voltage difference between cathode and anode in Fig. 7.1c, or in other words, the applicability of Nernst equation, do not exclude the existence of electronic conductivity in the electrolyte. Secondly, we leave out the charges located at boundaries but only focus on the local charges in bulk. The abrupt change in electrical properties at the boundary of two phases leads to the relocation of charges, which breaks the local neutrality as a result. From the viewpoint of traditional electrode investigation, where the charge neutrality is always assumed in the bulk, one would believe that those boundary charges may strongly affect the specific value of electrical field inside the anode. However, in the present case, studied is the very relationship between charges and electrical field. The local neutrality assumption is not adopted here, since it is actually one of the subjects to be addressed as will be shown later. Poisson's equation is the governing law, theoretically formulizing the relationship between charges and the change of electrical field. Therefore, making use of this equation will neither omit nor double-count the influence from any relevant charges. In this regard, boundary charges need not to be considered additionally. At last, the conductivities have been implicitly taken as constant and independent to the concentration of charge carriers. Such practice is adopted to keep equations tidy and will not affect the nature of this problem qualitatively. With those issues clarified, it is clear to us now that the analysis above is physically rigorous and the electrical field is built inside the anode bulk regardless of the high electrical conductivity the anode materials may possess.

To determine the correct electron distribution profile and other related properties in MIEC bulk, three simplified scenarios are tried. The first scenario is drawn as Fig. 7.3a. For uneven distribution, the population of electrons is assumed to decrease from anode surface (S) to anode/electrolyte interface (I), which leads to a tendency of electron flux from S to I due to the concentration gradient. Cancelling out such tendency to reach a zero net electron current requests the electrical field to be established as illustrated in Fig. 7.3a. The corresponding local positive and negative charges inside the bulk come from the relocation of electronic and ionic defects.

Then, the population of ionic defects, V° , must increase from I to S in order to yield the electrical field as such. The ionic current corresponding to the influence from vacancy gradient and electrical field is denoted as I_{grad} and I_{fld} respectively. One can easily find both I_{grad} and I_{fld} flow from S to I in this circumstance, and the overall ionic current as a sum of I_{grad} and I_{fld} will be from S to I also, which is in consistence with the real situation at marked by the arrow above. The second scenario is drawn as Fig. 7.3b. The population of electrons is assumed to increase from S to I this time. With the same routine, it ends up with two ionic current flowing from I to S, making the overall current opposite with the real one in direction, therefore is impossible. Monotonic change of electron population from one side to the other has been used in those two cases. In the last case, a nonmonotonic change will be tried. As displayed in Fig. 7.3c, the electron population from S to I first increases to the peak then starts to decrease. Likewise, it can be readily determined that the overall current will flow from the middle of the MIEC to the sides, which is nonsense. Of course, the electron population can decreases first, and then rises back from S to I, which just changes the detail and will not bring anything new. In fact, there are countless different examples for the nonmonotonic case, but the particular example used here along with those two monotonic ones can represent all scenarios. Among them, only the case

shown in Fig. 7.3a coincides with the real situation. The finding that electrons cannot be uniformly distributed in the anode bulk and an electrical field must exist is obtained without any boundary condition restriction, which simply means that the MIEC segment subject to study can be the whole anode bulk, or any pieces of volume inside the bulk. Therefore, whatever the specific nonmonotonic distribution looks like, it will end up with contradictory result.

Fig. 7.3 Three scenarios for the defects distribution in MIEC anode under steady state with current I_0 .

By making use of Eq. 7.4 and 7.5, the scenario in Fig. 7.3a can be interpreted into Fig. 7.4b with specific parameters including c_v , c_e , ϕ and etc. The situation under OCV is also described in Fig. 7.4a for comparison. As the ion transport behavior in MIEC cathode is not different from anode here in terms of the governing equations, those properties are extended into the cathode for the sake of completeness. The transition of those parameters from anode to cathode through electrolyte is arbitrarily illustrated. And the complexity concerning the interface properties, though very important, is left out here in order to focus on the MIEC bulk. For more informative study regarding the interface and electrolyte, one is recommended to refer to Virkar's work.[150-151] Under OCV, all parameters display a uniform profile through out the MIEC film in both cathode and anode sides. The Nernst potential E_N represented as

$$E_N = \frac{RT}{4F} \ln \frac{P_{O_2}^I}{P_{O_2}^{II}} \quad (7.11)$$

is equal to V_{ocv} under the assumption of zero electronic conductivity in electrolyte.

$$E_N = V_{ocv} = \frac{\tilde{\mu}_e - \tilde{\mu}_e}{F} \quad (7.12)$$

As can be seen in Fig. 7.4a, both E_N and the galvanic potential are built up inside the electrolyte. Under steady state with a certain current flowing, the transport of ion is positively driving by both electrical field and c_v gradient. The contribution from each of them trade off with one another to yield a certain difference in $\tilde{\mu}_v$ from surface to interface that can be determined from impedance measurement. Decreasing in c_v from surface to interface may limit the MIEC performance by a resultant reduced ionic conductivity in the most active area, but on other hand also be able to stabilize the material near interface if c_v is small enough. Therefore, c_v is of particular interest with respect to the performance reduction/enhancement upon polarization and electrode reliability under large load. As $c_v(x)$ is tied to $\phi(x)$, it cannot be simply determined from the material stoichiometry data at the calculated P_{O_2} through Eq. 7.11, since the contribution from ϕ will decrease the change in c_v . Quantification of c_v and ϕ requires to solve those equations analytically or numerically.

Fig. 7.4 Distributions of concentrations and potentials under OCV (a) and steady state (b).

7.3 Quantitative solutions for c_e , c_v and ϕ

In the 1-dimensional MIEC cathode model, if assuming electron and oxygen vacancy as charge carrier, the governing equation set under steady state can be rearranged as:

$$-\frac{c_v(x)}{x} + \frac{2F}{RT} c_v \frac{\psi(x)}{x} = \frac{j_v^{\text{mass}}}{D_v} \quad (7.13)$$

$$-\frac{c_e(x)}{x} - \frac{F}{RT} c_e \frac{\psi(x)}{x} = 0 \quad (7.14)$$

$$\frac{\psi^2(x)}{x^2} = \frac{\psi(x)}{\sum_0} \quad (7.10)$$

The difficulty in solving such so-called Nernst-Planck-Poisson system lies in the non-linearity. To obtain analytical solutions, assumptions need to be made to replace Poisson's equation. Two assumptions have been used widely in the pertaining studies, namely electroneutrality and constant field assumption. As one can readily find that electroneutrality leads to constant field and vice versa when inserting it back to Poisson's equation, it may be confusing to understand the difference between those two assumptions. In this regard, the related background will be briefly reviewed here. Electroneutrality was adopted by Planck himself in 1890 to develop solution for the steady state Nernst-Planck equation. Such assumption seems largely reasonable in view of basic physical conceptions on conductive materials. And justification for it is usually realized by the fact that if under appropriate use, inserting back the obtained galvanic potential into Poisson's equation yields small, though not constantly zero, charge density. On the other hand, Goldman in 1943 introduced the constant field assumption to solve the transport properties in a conductive membrane under steady state.[152] Such assumption reduces the 2-order differential Poisson's equation into 1-order, and allows one to integrate the Nernst-Planck equations (7.13) and (7.14) directly. Despite the simplicity brought by these two assumptions, the fundamental concerns associated with the validity of them can be summarized as: (1) why in the first place they can be consistent with Poisson's equation; (2) and

if they are, do they cover all the circumstances where Eq.7.10 is applicable. Later on, MacGillivray et al. clarified above concerns,[153] and demonstrated with the perturbation theory that the electroneutrality and constant field assumptions are nothing else but two extreme cases of Poisson's equation. The applicability of each hypothesis can be evaluated based on a dimensionless factor,

$$\alpha^2 = \left(\frac{\sum \sum_0 k_B T}{\lambda_D^2 e^2 c} / l^2 \right) \text{ or } \alpha = \frac{\sum \sum_0 k_B T}{\lambda_D^2 e^2 c l^2} \quad (7.15)$$

where λ_D is the Debye length and l sample thickness.

When

$\alpha \ll 1$, local electroneutrality applicable;

$\alpha \gg 1$, constant field applicable;

$\alpha \cong 1$, neither assumption is correct.

As can be seen now, electroneutrality and constant field hypotheses are used under totally opposite circumstances.

In the present case, for most MIEC materials in SOFC's application, assuming $T=1000\text{K}$, $c_e \cong c_v \cong 4000 \text{ mol/m}^3$ (i.e. ~ 0.5 /unit cell), λ_D can be calculated as $4 \times 10^{-8} \text{ m}$, a value far smaller than the active length of $1 \sim 10 \text{ }\mu\text{m}$ for MIEC cathode given ε in the range of $10^{12} \sim 10^{14}$.

Therefore the electroneutrality can be the appropriate approximation here. Poisson's equation is replaced by

$$2c_v - c_e - c_a = 0 \quad (7.16)$$

where c_a is positive for the acceptor dopant and negative for donor dopant.

Inserting Eq. 7.16 into 7.13 to eliminate c_v , then subtracting 0.5×Eq. 7.14, one obtains

$$\left(\frac{3}{2} \frac{c_e + c_a}{c_e} \right) \frac{F}{RT} = \frac{j_v^{\text{mass}}}{D_v} \quad (7.17)$$

Inserting Eq. 7.14 into Eq. 7.17,

$$\left(\frac{3}{2} + \frac{c_a}{c_e} \right) \frac{c_e}{x} = \frac{j_v^{\text{mass}}}{D_v} \quad (7.18)$$

Integrating Eq. 7.18 yields

$$x = \frac{D_v}{j_v^{\text{mass}}} \left(\frac{3}{2} c_e + c_a \ln c_e \right) + \text{const} \quad (7.19)$$

where *const* is a constant determined by boundary conditions.

The explicit solution of c_e towards x cannot be developed as the inverse function is not applicable. Therefore Matlab computing is introduced to display the profiles of c_e , then c_v and ϕ . In particular, the contribution comparison between electrical field and chemical gradient for ion transport can be evaluated now. According to Eq. 7.13, the ratio can be represented as

$$r = \frac{f_{\text{ele}}}{f_{\text{che}}} = \frac{\frac{2F}{RT} c_v}{c_v} = \frac{4c_v}{c_e} \quad (7.20)$$

x

—

For a clear contrast, the distribution of c_v under the assumption of no electrical field contribution is also provided based on Fick's 1st law,

$$\overline{D_v \frac{dc_v(x)}{dx}} = j_v^{\text{mass}} \quad \text{or} \quad c_v(x) = \frac{j_v^{\text{mass}}}{D_v} x + \text{const} \quad (7.21)$$

In principle, there are four combinations of electronic/ionic defects in MIEC materials (though not all can be found in or belong to the presently available anode category):

- 1) e-V, electron-vacancy, e.g. (LaSr)TiO₃ anode;
- 2) h-V, hole-vacancy, e.g. YCCC, YCCN anodes, or (LaSr)(CoFe)O_{3-δ} cathode;
- 3) e-O, electron-interstitial oxygen;
- 4) h-O, hole-interstitial oxygen, e.g. La₂NiO_{4+δ} in O-hyperstoichiometry regime;

Similar to the e-V case, the solutions for the rest combinations can be derived via the same route. To answer the question whether the results solved from equations above and that from the previous qualitatively analysis as in Fig. 7.4 is consistent with each other or not, e-V case is exhibited first.

Fig. 7.5 Electron (a) and vacancy (b) and galvanic potential distributions in a 1 μm $\text{La}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ anode film as the e-V type.

Using $\text{La}_{0.3}\text{Sr}_{0.6}\text{TiO}_3$ (LST) to represent the e-V type, and setting the boundary condition $c_e=0.5/\text{unit cell}$ at the anode surface, and $i=0.5 \text{ A/cm}^2$, $D_v=10^{-7} \text{ cm}^2/\text{s}$, $T=1000 \text{ K}$, the local concentration of charge carriers and galvanic potential in LST can be solved. The results are displayed in Fig. 7.5. Under steady state c_e , c_v , ϕ all increase from surface to interface, showing perfect agreement with the case in Fig. 7.4b. The galvanic potential ϕ is set as 0 at the anode/electrolyte surface since only the potential difference matters. Obviously ϕ is not even

inside the MIEC bulk, challenging the usual wisdom that no electrical field is possible inside such a conductor. It should be point out that D_v for LST is roughly set since the real number is still not available in literature. However, it is good enough to show the theoretical principle here. When increasing the current to 1 A/cm^2 , the corresponding change in those parameters can be shown in Fig. 7.6.

Fig. 7.6 Limiting current in LST and the electron (a) and vacancy (b) and galvanic potential distributions (c).

In Fig. 7.6, the current is increased from 0.5 to 1 A/cm² compared to Fig. 7.5 with other parameters remain unchanged. Those curves are found to stop at 0.2 μm instead of reaching the interface. Surface instead of interface is chosen as boundary to yield boundary conditions since during electrode operation under different conditions, surface exposed to fixed P_{O_2} or P_{H_2} is more likely to be known in term of the charge carriers densities. Therefore, such phenomenon in fact means the limiting current is arrived with those given parameters for LST, which reasonably represents the real situation that the bulk diffusion process does not literally obey ohm's law (appears in the polarization response of EIS instead of x-axis intercept), and limiting current can be reach easily with small ion diffusion coefficient.

The results for the rest three cases are displayed in Fig. 7.7-9. Cell volumes are set to 200 Å³ and $D_v=10^{-6}$ cm²/s, $T=1000$ K, $i=1$ A/cm² and thickness 10 μm. The others parameters used in calculation are listed behind.

Fig. 7.7 Profiles for c_h (a), V^0 (b), ϕ (c) and $r_{E/C}$ (d) in h-V type with acceptor doping 0.4/unit cell and 0.02/unit cell of c_h at surface.

Fig. 7.8 Profiles for c_e (a), O_i'' (b), ϕ (c) and $r_{E/C}$ (d) in e-O type with donor doping 0.3/unit cell and 0.1/unit cell of c_e at surface.

Fig. 7.9 Profiles for c_h (a), O_i (b), ϕ (c) and $r_{E/C}$ (d) in h-O type with acceptor doping 0.1/unit cell and 0.2/unit cell of c_h at surface.

From those figures, it is found that if hole as the opponent of electron is the charge carriers, e.g. in YCCC, the profile shows exactly opposite tendency of electron as shown in Fig. 7.7, the same is also valid when O_i replacing V'' as the ionic defects as shown in Fig. 7.8. That is in good consistence with the qualitative analysis where only the net charge matters regardless of

what the specific form the charge carrier takes. It is also noted that the galvanic potential built inside the bulk with given current 1 A/cm^2 is not small at all, but could account for a big portion of the total anode overpotential. The contribution from electrical field in ion transport shown by those figures is even bigger than that from chemical diffusion.

It is worth noting that in the derivation above D_v in Eq. 7.13 is taken as constant regardless of the change of c_v along MIEC film. According to the random-walk theory by Goodenough,

$$D_v = D_v^0 \exp\left(\frac{\Delta G_m}{k_B T}\right) \quad (7.22)$$

$$D_v^0 = \frac{l^2}{6} z(1 - n_v) f v_0 \quad (7.23)$$

where l is distance between two oxygen sites, z the number of near-neighbor oxygen sites surrounding one oxygen, n_v the fraction of vacancy site (proportional to c_v), f a geometrical factor depending on the jump path, v_0 the attempt frequency. As $c_v(x) \ll 3$ under the present situation for perovskite MIEC, $1 - n_v \approx 1$, thus making D_v being constant a reasonable approximation.

7.4 Experimental verification through the h-V type MIEC electrode

To verify those results experimentally, LSCF/GDC half cells were measured. Though anode bulk transport is the subject here, experiment was conducted in the cathode mode, because firstly, the principle in the above qualitative/quantitative treatment is not unique to anode but also applicable to cathode; secondly, there is a large body of data regarding MIEC cathode but

almost nothing there for anode part, from which the necessary input parameter is readily available.

An $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (~1.2 mm)/GDC(~30 μm) bilayer was fabricated through the spray-modified dry pressing method as described in experimental section. The sample was tested in the configuration shown in Fig. 7.10a. In order to avoid the electronic conductivity in GDC, testing was carried out in air instead in anode- H_2 /cathode-air. To simulate cathode mode on LSCF, positive and negative potential was applied to Pt counter electrode and LSCF, respectively. Constant currents flow through this bilayer. Fig. 7.10b shows the microstructure of the cross-section. The adhesion between GDC/LSCF is good and GDC was successfully densified to ensure no electron current or gas leaking. The goal of this experiment is to see whether a current which is too high to be realized by mere chemical diffusion in LSCF/GDC pellet can be flow through it without damaging the sample, therefore proving the extra contribution from electrical field.

Fig. 7.10 The configuration of LSCF/GDC measurement (a) and cross-sectional LSCF/GDC (d).

Fig. 7.11 EIS of LSCF/GDC bilayer in air 700°C

Fig. 7.12 DC resistance under constant current loading for LSCF/GDC bilayers (a), and the variation of applied voltage (b).

Fig. 7.11 shows the EIS of such bilayer measured in air at 700°C. The arc represents the surface reaction, i.e. $14 \Omega\text{cm}^2$, and the tail the transport resistance that cannot be known from this spectrum. Fig. 7.12a shows the DC resistance under a constant current loading, 7 mA/cm^2 , on the sample. The total resistance is $\sim 66 \Omega$ (or $46 \Omega\text{cm}^2$), which means $32 \Omega\text{cm}^2$ is for oxygen transport. Fig. 7.12b shows voltage vs. time, which clearly demonstrates the stability of this sample under this current. The potential applied to the transport process can be calculated as 226 mV. Based on this condition, the distribution of charge carriers under traditional chemical

diffusion only assumption and chemical diffusion/electrical field driving co-control assumption can be resolved.

Fig. 7.13 Calculated profiles for V'' (b) in LSCF under chemical diffusion only assumption based on the same experimental conditions.

According to literature data, the boundary condition on V^0 is set to 0.05/unit cell, D_v $2.5 \times 10^{-6} \text{ cm}^2/\text{s}$ at 700°C . Fig. 7.13 shows the profile of V_0 under the chemical diffusion only assumption with the same input conditions as in experiment. The vacancy concentration increases linearly from surface to interface. The final concentration near interface is ~ 1.2 /unit cell, which in fact is high enough to give rise to decomposition of LSCF, therefore is not consistent with experiment result. On the other hand, Fig. 7.14 shows the corresponding calculations on those charge carriers and potentials according to the analytic solutions above with the same condition. It can be found that in most of the active length ion migration driven by electrical field instead of chemical diffusion dominates the ion transport as shown in Fig. 7.14d.

Due to such contribution, the concentration gradient turns less steep accordingly and yields much smaller vacancy concentration at the interface; therefore avoid the decomposition of LSCF.

Fig. 7.14 Calculated profiles for c_h (a), V_O (b), ϕ (c) and $r_{E/C}$ (d) in LSCF based on the experimental conditions.

In the above content, the transport behavior is studied independently by analysis based on sound physical knowledge and by solving the Nernst-Planck-Poisson equations mathematically.

Two routes are confirmed to be consistent with each other without sharing common restrictive assumptions, lending credibility to those treatments. However, the role of the first route is more than being used to check the consistency. It shows the basic concept in the MIEC bulk transport that the mathematical treatment is not able to convey. Since the electroneutrality is adopted in the latter (as also in lots of similar studies), it then becomes superfluous to ask and also impossible to answer whether the MIEC bulk is really electroneutral or in fact locally charged but with electroneutrality being an appropriate approximation in some cases. Through the first route, it is clearly demonstrated that MIEC bulk under steady state is not neutral but with local charges anywhere, which could be viewed as a complement to the conventional conception on this subject that only chemical diffusion is believed to be true. The validity of analytical solutions for c_e , c_v and ϕ is further verified through experiment, given without E contribution, either the current flow of 7 mA/cm in the dense LSCF pellets measured here or the constant current load ~ 0.6 A/cm² in the practical porous LSCF cathode can be realized. It is unveiled by those results that E contribution is significant in most cases and usually greater than the chemical diffusion.

In the other hand, for local chemical composition, it has been shown by above calculations and can be briefly summarized that the real concentration of ionic defects (vacancy or interstitial oxygen) under service condition in either anode or cathode are less deviated from the as-prepared composition compared to estimated from the Nernst equation using equivalent P_{O_2} -stoichiometry data. The schematic diagram is displayed in Fig. 7.15. As a result, the stability of anode material toward the relatively high P_{O_2} in anode/electrolyte interface, or cathode towards the relatively low P_{O_2} in cathode/electrolyte interface is less severe due to the existence of electrical field in the bulk.

Fig. 7.15 schematic drawing of oxygen defect profiles in anode and cathode, vacancy in anode (a), interstitial oxygen in anode (b), vacancy in cathode (c), interstitial oxygen in cathode (d).

According to the profiles of ϕ in Fig. 7.6-9 representing all types of MIEC materials, it is clear that the electrical fields in both anode and cathode work to facilitate the transport of oxygen defects. However, as shown in Fig. 7.15, only for anode materials with O_i^a and cathode materials with V_O^c defects, the overpotential and then the electrical field will maintain higher ionic conductivities for those materials under polarization relative to equilibrium status, while for the

mode to verify the theoretical results experimentally. The results disproved the general chemical diffusion-only conception in SOFC community, and proved the newly introduced chemical diffusion&electrical field driving co-determined ion transport process. Due to the presence of electrical field, the real stoichiometry variation in ionic defects under service conditions in either anode or cathode was much smaller than estimated from the Nernst equation using equivalent P_{O_2} -stoichiometry data. The stability concern in terms of high P_{O_2} at anode/electrolyte interface and low P_{O_2} at cathode/electrolyte interface was therefore much less severe. The electrical fields in both anode and cathode worked positively to facilitate the transport of oxygen defects.

However, only for anode materials with O_i or cathode materials with V_o defects, it maintained higher ionic conductivities under polarization with the presence of electrical field compared to equilibrium status. In other words, overpotential would broaden the electrode pathway effectively for those electrodes. The electrical field also opens a new concept for the cation transport in electrode, for it not only drives the anions but inevitably also drives the cations movement in the electrode. With such framework exhibited here, the cation movement proposed in electrode performance relaxation is well-grounded.

CONCLUSIONS

The anode oxidation reaction pathway was investigated on YCrO_3 -based perovskites materials in terms of the origin of catalytic activity for oxide anode, the reactive area and rate determining steps, the effect of electrolyte on interface resistance and the evolution of bulk pathway under overpotential in practical operation conduction.

In Chapter 5, Sr, Co and Ni were doped into YCrO_3 to enable a systematic variation in terms of B site element, electrical conductivity and catalytic activity. Good performance was yielded from YCCC, $0.9 \text{ } \Omega\text{cm}^2$ at 850°C which was among the best performance presently available from oxide anodes. Charge transfer and hydrogen surface adsorption/diffusion were identified as limiting factors in those doped YCrO_3 anode. B site element worked as a decisive role in determining catalytic activity. Such activity was proven to be H-related, e.g. H surface adsorption/coverage was dependent to those B site elements. Compared to metal Ni, the oxides displayed lower H adsorption ability judged by the apparent P_{H_2} -dependent resistance. YCCN showed higher adsorption ability than YCCC even with less dopant content at B site. A model was presented to describe the elementary steps in H_2 oxidation. It was suggested that for the charge transfer step, any hypothesis models presented without taking H into account were invalid. It was also found that high electrical conductivity ($>100 \text{ S/cm}$), though usually cited as a prerequisite, was not necessary in those chromites to obtain a good electrode performance. High

performance came from combination of decent electrical conductivity (>1 S/cm) and B site active element.

In Chapter 6, by extending the electrode response from P_{H_2} in Chapter 5 to P_{O_2} measuring in O_2 -containing gases and using SSZ to replace YSZ electrolyte, the activation of lattice oxygen, the contribution from 2PB and 3PB and the beneficial effect of electrolyte in R_p for those oxide anodes was investigated. Judging from the chemical capacitance along with the improvement from changing electrolyte, YCCC was confirmed to be both 2BP and 3PB active, and YCCN 3PB dominant. The activation of 2PB depended on the ionic conductivity and then the nonstoichiometry of oxide under reducing atmospheres. A big capacitance for YCCC was observed and associated to the variation of lattice oxygen under EIS measurement, confirming the activity of bulk transport. The overall performance was less affected by the nature of electrolyte when both 3PB and 2PB pathways were effectively working, but on the 3PB dominant YCCN, reaction kinetics was largely influenced by the electrolyte. For YCCN, not only the charge transfer step, but also the surface process anode was promoted. Such effect of electrolyte on surface process was explained by a chain-transmit mechanism. Basically, by enlarging the exchange current of charge transfer reaction at the electrolyte/anode interface, bigger gradient in the adsorbed species was resulted, which in turn broadened the adsorption area then the adsorption rates. The significance of this phenomenon in practical application was demonstrated on the SSZ/YSZ/SSZ sandwich electrolyte which showed almost the same R_p as from pure SSZ electrolyte. Such results could be able to rewrite the concept of electrolyte design and open a wide door for the utilization of novel electrolyte materials that otherwise cannot be

used by themselves alone due to instability in either oxidizing or reducing atmospheres, mechanical fragility, high cost or etc.

In Chapter 7, the influence of the overpotential on the bulk reaction pathway was investigated. The bulk overpotential in MIEC anode was consumed in form of concentration gradient driven diffusion and electrical field driven migration. As only the former is appreciated by co-workers on the transport studies, the existence of electrical field and then the resultant impact on the bulk reaction pathway and durability of electrode under service were thoroughly studied here. Qualitative analysis was conducted first, followed by quantitative treatment for analytical solutions. It was proven that the electrode bulk was not electroneutral through the qualitative analysis. With electron blocked at the electrode/electrolyte interface, the appearance of electrical field was an inevitable consequence of the ion transport process. The analytic solutions were pursued independently with appropriate assumption taken. Results from both methods were compared, and show perfect consistency with one another, lending credibility to those treatment. Ion transport in LSCF/GDC as h-V type MIEC was measured under cathode mode to verify the theoretical results experimentally. The results disproved the general chemical diffusion-only conception in SOFC community, and proved the newly introduced chemical diffusion&electrical field driving co-determined ion transport process. Due to the presence of electrical field, the real stoichiometry variation in ionic defects under service conditions in either anode or cathode was much smaller than estimated from the Nernst equation using equivalent P_{O_2} -stoichiometry data. The stability concern in terms of high P_{O_2} at anode/electrolyte interface or low P_{O_2} at cathode/electrolyte interface was therefore much less severe. The electrical fields in both anode and cathode worked positively to facilitate the transport of oxygen defects. However,

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 With such framework exhibited here, the cation separation proposed in electrode performance
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