LANTHANUM STRONTIUM VANADATE IN
SOLID OXIDE FUEL CELLS

GE XIAOMING

School of Mechanical and Aerospace Engineering
Nanyang Technological University
2012
LANTHANUM STRONTIUM VANADATE IN
SOLID OXIDE FUEL CELLS

GE XIAOMING

School of Mechanical & Aerospace Engineering

A thesis submitted to the Nanyang Technological University in fulfilment
of the requirements for the Degree of Doctor of Philosophy

2011
ACKNOWLEDGEMENTS

Here I would like to express my most sincere appreciation and gratitude to my supervisor, Professor Chan Siew Hwa, for his considerate guidance and encouragement all throughout this PhD project. I have learnt so much for his expertise in the fields of solid oxide fuel cells and mathematical modelling. More than a supervisor, it is his personality, lifestyle, and working philosophy that inspire me all through this four-year odyssey.

I thank Dr. Liu Qinglin for his initial effort on launching this PhD project. I also thank Mr. Chen Xinbing, Mr. Alireza Babaei, and Dr. Zhang Lan for miscellaneous discussions. Mr. Zhao Cunlu is acknowledged for introducing me the computational tool, Wolfram Mathematica® 7. Ms. Fang Yanan (School of MSE) is acknowledged for her kindly help in X-ray powder diffraction characterization. My warmest acknowledgement goes to Dr. Fu Changjing for insightful discussions over versatile project topics. My thanks also extend to all technicians in Fuel Cell Laboratory (ERI@N), Materials Laboratory A, and Computer Aided Engineering Laboratory for technical guidance and assistance.
ABSTRACT

Solid oxide fuel cells (SOFCs) are high temperature energy conversion devices with the advantages of fuel flexibility and high efficiency. Limitations of SOFC cermet anodes have been stimulating oxide anodes. Lanthanum strontium vanadate, $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ (LSV, $0 \leq x \leq 1$), have been synthesized and examined as potential SOFC anode materials. LSV appear to be chemically compatible with yttria-stabilized zirconia (YSZ) at least up to 1300°C. Electrode performance is evaluated by impedance spectroscopy and dc polarization between 800 to 1000°C. Good electrode performance is achieved with LSV($x = 0.2, 0.3, 0.4, 0.5$)–YSZ composite anodes, in both pure H$_2$ and 3% H$_2$O humidified CH$_4$. For half-cells with $\text{La}_{0.6}\text{Sr}_{0.4}\text{VO}_3$–YSZ anode, polarization resistance is 0.85 Ω cm$^2$ and 1.38 Ω cm$^2$ at 900°C in pure H$_2$ and wet CH$_4$, respectively. When drawing a current of 0.2 A/cm$^2$ at 900°C, the overpotential is 0.13 V in pure H$_2$, and slightly higher in wet CH$_4$, 0.20 V. Further optimization of electrode microstructures is needed to maximize the performance of LSV for potential SOFC application.

LSV synthesized by soft chemistry methods show higher catalytic activity than those via solid state reactions. To elucidate the interfacial reaction behaviours, impedance responses of LSV8020 (50 wt. %)–YSZ anodes are recorded and interpreted in H$_2$–H$_2$O–He atmosphere. The typical impedance pattern corresponds to three types of physical phenomena, viz. reaction impedance, gas concentration impedance, and inductive loops that only emerge at highly biased conditions. The gas concentration impedance is significantly inhibited in wet atmosphere. A detrimental water effect is observed for up to 15 vol. % H$_2$O.

The double layer structure of solid oxide fuel cell anode/electrolyte interfaces is simulated by Markov Chain Monte Carlo methods. A case study is carried out on lanthanum strontium vanadate (LSV)/yttria-stabilized zirconia (YSZ). The density of oxygen vacancies directly adjacent to the LSV/YSZ interface is one order of magnitude higher than the bulk value of YSZ. The spatial variation of oxygen vacancies in the double layer region exhibits exponential decay behaviour. The double layer undergoes pronounced relaxations when the interfaces are under anodic biases in the range from 0
to 150 mV. The results indicate that 70–80% of the oxygen vacancies are immobilized in the Helmholtz–Perrin layer. The rationale has wide applications on elucidating anodic reaction mechanisms and potential distributions across anode/electrolyte interfaces.

The double layer of electrode/electrolyte interfaces plays a fundamental role in determining the performance of solid state electrochemical cells. The double layer capacitance is one of the most-studied descriptors of the double layer. This project examines a case study on LSV/YSZ interfaces that are exposed in solid oxide fuel cell anode environment. The apparent double layer capacitance is obtained from impedance spectroscopy. The intrinsic double layer capacitance is evaluated based on Stern’s method in conjunction with the Volta potential analysis across LSV/YSZ interfaces. Both the apparent and the intrinsic double layer capacitances exhibit right-skewed volcano patterns, when the interfaces are subjected to anodic biases from 0 to 150 mV. The apparent double layer capacitance is about one order of magnitude larger than the intrinsic double layer capacitance. This discrepancy roots in the inconsistent surface areas that are involved. This capacitance analysis would provide a more realistic estimate of the TPBs of on-running solid-state electrochemical devices.

Electrochemical reactions in solid oxide fuel cells take place around three-phase boundaries (TPBs). The electrochemically active zones (EAZs) are generated in three-dimensions around the TPBs of on-running SOFCs. This project investigates the behaviours of TPBs and EAZs via a case study on LSV–YSZ composite anode. A percolating binary particle aggregate, based on geometric random loose packing model and traditional sintering theory, is constructed to represent the LSV–YSZ anode. The TPB lengths of LSV–YSZ anodes are evaluated from the coordination numbers and sintering necks among particles in the particle aggregate. Empirical interrelations among TPBs, EAZs, active electrode thickness, in-depth penetration of electrocatalysts of polarized LSV–YSZ anode are established.

The feasibility of LSV-based SOFCs fed with practical feedstocks, e.g. syngas, town gas, coal gas, and biogas, has been proven in this project. The exchange current densities of LSV anodes in various atmospheres are in the range from 0.05 to 0.2 A/cm². The typical overpotential is about 60 mV in H₂ and at 900 ºC. LSV anodes are not coked by
deposited carbon when exposed to carbon-forming gases. More interestingly, LSV undergoes continuous activation, rather than poisoning, when exposed to gases containing 50 ppm H$_2$S. The beneficial H$_2$S effect is due to the nanostructured sulphur compounds that are in situ generated by interactions between LSV and H$_2$S. LSV-based SOFCs have demonstrated with negligible performance degradation in carbon-forming and H$_2$S-containing gases for more than 500 hours.
LIST OF PUBLICATIONS

Journal Articles


Conference Proceedings

Table of Contents

ACKNOWLEDGEMENTS ........................................................................................................ I

ABSTRACT ............................................................................................................................ II

LIST OF PUBLICATIONS ...................................................................................................... V

LIST OF TABLES .................................................................................................................. XI

LIST OF FIGURES ................................................................................................................ XII

List of Symbols .................................................................................................................... XIX

Chapter 1. Introduction ......................................................................................................... 1

1.1 Introduction of Fuel Cells ............................................................................................... 1

1.2 Fuel challenges ............................................................................................................... 2

   1.2.1 Hydrogen .................................................................................................................. 2

   1.2.2 Reforming gas .......................................................................................................... 5

1.3 Project goals .................................................................................................................. 7

1.4 Objectives of research project ....................................................................................... 8

1.5 Scope of research project ............................................................................................... 8

1.6 Thesis layout .................................................................................................................. 9

Chapter 2. Literature review ................................................................................................. 10

2.1 SOFC fundamentals ...................................................................................................... 10

2.2 Nickel cermets .............................................................................................................. 12

2.3 Copper cermets ............................................................................................................. 15

2.4 Oxides ........................................................................................................................... 18

   2.4.1 Fluorite .................................................................................................................... 19

   2.4.2 Rutile ....................................................................................................................... 21

   2.4.3 Tungsten bronze .................................................................................................... 21

   2.4.4 Pyrochlore ............................................................................................................. 22
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4.5</td>
<td>Perovskite</td>
<td>23</td>
</tr>
<tr>
<td>2.4.6</td>
<td>Double perovskite</td>
<td>28</td>
</tr>
<tr>
<td>Chapter 3</td>
<td>Synthesis, characterization, and performance of lanthanum strontium vanadate via solid state reactions</td>
<td>34</td>
</tr>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>34</td>
</tr>
<tr>
<td>3.2</td>
<td>Powder synthesis</td>
<td>35</td>
</tr>
<tr>
<td>3.3</td>
<td>Structural and thermal gravimetric characterization</td>
<td>36</td>
</tr>
<tr>
<td>3.4</td>
<td>Half-cell performance of LSV anodes</td>
<td>43</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Experimental procedures</td>
<td>43</td>
</tr>
<tr>
<td>3.4.2</td>
<td>LSV–YSZ anodes fed with pure H₂</td>
<td>45</td>
</tr>
<tr>
<td>3.4.3</td>
<td>LSV–YSZ anodes fed with wet CH₄</td>
<td>52</td>
</tr>
<tr>
<td>3.5</td>
<td>YSZ-supported single cells with LSV anodes</td>
<td>57</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Fabrication of YSZ-supported single cells</td>
<td>57</td>
</tr>
<tr>
<td>3.5.2</td>
<td>Microstructure</td>
<td>59</td>
</tr>
<tr>
<td>3.5.3</td>
<td>Single cell performance in H₂ and wet CH₄</td>
<td>59</td>
</tr>
<tr>
<td>3.6</td>
<td>Summary</td>
<td>63</td>
</tr>
<tr>
<td>Chapter 4</td>
<td>Impedance responses and the double layer structure of LSV anodes via citric route</td>
<td>65</td>
</tr>
<tr>
<td>4.1</td>
<td>Impedance identification of LSV anode in H₂–H₂O–He atmosphere</td>
<td>65</td>
</tr>
<tr>
<td>4.1.1</td>
<td>Powder synthesis, half-cell preparation, and impedance spectroscopy</td>
<td>65</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Impedance spectra, equivalent circuit, and double layer capacitance</td>
<td>66</td>
</tr>
<tr>
<td>4.1.3</td>
<td>Impedance behaviour under H₂–H₂O–He ternary atmosphere</td>
<td>73</td>
</tr>
<tr>
<td>4.1.4</td>
<td>Brief summary</td>
<td>77</td>
</tr>
<tr>
<td>4.2</td>
<td>Double layer structure in solid oxide fuel cell anode/electrolyte interfaces: a Monte Carlo study</td>
<td>78</td>
</tr>
</tbody>
</table>
4.3 Double layer capacitance of anode/solid-electrolyte interfaces ......................... 85
  4.3.1 Apparent double layer capacitance .......................................................... 88
  4.3.2 Analytical description of the Gouy–Chapman layer .................................. 92
  4.3.3 Interfacial variation of the Volta potential ................................................ 94
  4.3.4 Intrinsic double layer capacitance .......................................................... 98
  4.3.5 Double layer capacitance: apparent versus intrinsic ............................... 101
  4.3.6 Brief summary ...................................................................................... 104

4.4 Three phase boundaries and electrochemically active zones in solid oxide fuel cell
  anode/electrolyte interfaces ............................................................................ 104
  4.4.1 Materials and characterization .............................................................. 106
  4.4.2 Virtual packing .................................................................................... 107
  4.4.3 Virtual sintering .................................................................................. 114
  4.4.4 Three phase boundaries and electrochemically active zones .............. 117
  4.4.5 Brief summary .................................................................................... 122

4.5 Summary .................................................................................................... 122

Chapter 5. Sulphur tolerant and carbon resistant solid oxide fuel cells with LSV anodes
  ....................................................................................................................... 124
  5.1 Importance and current status of sulphur-tolerant and carbon-resistant SOFC anodes
  ....................................................................................................................... 124
  5.2 Experimental ............................................................................................ 125
  5.3 Structure and microstructure ....................................................................... 128
  5.4 Impedance spectroscopy and polarization of LSV anodes in clean fuels ....... 130
  5.5 LSV anodes exposed to simulated practical fuels: syngas, biogas, and coal gas 133
  5.6 Summary ................................................................................................ 143

Chapter 6. Conclusions and recommendations .................................................. 144
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Conclusions</td>
<td>144</td>
</tr>
<tr>
<td>6.2 Major achievements</td>
<td>147</td>
</tr>
<tr>
<td>6.3 Recommendations</td>
<td>147</td>
</tr>
<tr>
<td>Appendix A: Gouy–Chapman capacitance of the LSV–YSZ interfaces</td>
<td>149</td>
</tr>
<tr>
<td>REFERENCE</td>
<td>154</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 1-1 Targeted cost of hydrogen production .......................................................... 4

Table 2-1 Single cell SOFC with Ni-cermet anodes fed with hydrocarbon fuels .............. 14

Table 2-2 Single cell SOFCs with Cu-cermet anodes fed with hydrocarbon fuels .......... 17

Table 2-3 Conductivity and electrochemical properties of selected conducting oxides as SOFC anodes (Table modified from Ref. (Jiang and Chan, 2004)) ......................... 30

Table 3-1 Fitted unit cell parameters of LSV .................................................................. 40

Table 3-2 TGA data listing of LSV$_{Re}$ oxidation. $\delta$ is the oxygen non-stoichiometry parameter in the La$_{1-x}$Sr$_x$VO$_{3-\delta}$. .................................................................................. 42

Table 3-3 Data listing of single cell with configuration of LSV6040–YSZ/YSZ/(LSM–YSZ/LSM) ................................................................................................................................. 61

Table 3-4 Comparison of cell performance of SOFC using vanadate oxides. ............... 63

Table 4-1 Listing of parameters pertinent to the double layer of LSV/YSZ interfaces in LSV–YSZ(H$_2$)/YSZ/Pt(air) half cells at 950 °C. ................................................................. 100

Table 4-2 Listing of characteristic parameters of the LSV–YSZ composite anode. .......... 108

Table 4-3 Coordination numbers in the simulated LSV–YSZ packing bed ................. 112

Table 4-4 Listing of parameters of LSV for the sintering model. ...................... 116

Table 5-1 Composition and tendency of carbon formation of gases addressed in Chapter 5. The operating temperature is 900°C. The carbon formation is predicted by assuming the thermodynamic equilibrium of the gas species. .................................................. 131

Table 5-2 Exchange current density of LSV anodes exposed to various atmospheres as addressed in Chapter 5.5. ........................................................................................................ 140
LIST OF FIGURES

Figure 2-1 Flow chart of hydrocarbon utilization in SOFC (methane as example) .................. 11

Figure 3-1 XRD patterns of (a) LaVO_4 (LV_{ox}) and (b) Sr_2V_3O_7 (SV_{ox}) fitted in Jade® 5 ....... 38

Figure 3-2 XRD patterns of (a) LSV_{ox}, (b) LSV_{Re}, and (c) mixture of LSV7030_{ox} and YSZ fired at 1300°C for 3 h, with a 50:50 weight ratio................................................................. 39

Figure 3-3 XRD patterns of reduced strontium vanadate (SV_{Re}). ...................................... 40

Figure 3-4 TGA curves for the oxidation of reduced La_{1-x}Sr_xVO_3-δ (LSV_{Re}) with x= 0, 0.05, 0.2, 0.5. Note that the final products after TGA measurement were assumed to pyrovanadate, i.e., vanadium in V^{5+}................................................................. 42

Figure 3-5 Schematic illustration of the half-cell configuration. Note that the scale of all components is only guide for the eyes................................................................. 45

Figure 3-6 Impedance curves of the LSV6040 (40 wt.%)-YSZ, LSV6040 (50 wt.%)-YSZ, LSV6040 (60 wt.%)-YSZ, LSV6040 (70 wt.%)-YSZ composite anodes in pure H_2 at 1000°C. Note that LSV6040 (70 wt.%)-YSZ anode layer peels off from YSZ electrolyte, leading to unreasonably large impedance................................................................. 47

Figure 3-7 Impedance curves of LSV6040 (50 wt.%)-YSZ (50 wt.%) composite anodes sintered at 1100°C, 1150°C, 1180°C, and 1200°C. All the EIS were collected at 1000°C in pure H_2................................................................. 48

Figure 3-8 (a) OCV impedance responses in pure H_2 for LSV6040_{Re}-YSZ (50:50 wt.%) composite anode. (b) Arrhenius plot for LSV_{Re} (x = 0.2, 0.3, 0.4, 0.5)-YSZ composite anodes. Inset of (b) shows the corresponding fitted E_a estimated from 800-1000°C. .... 49

Figure 3-9 SEM images of LSV6040-YSZ composite anode (a) as-fired in air at 1180°C for 2 h; (b) in situ reduced of (a) in pure H_2 at 900°C for 2 h. Inset of (b) shows the cross-section profile of LSV6040_{Re}-YSZ with YSZ electrolyte................................................................................. 50
Figure 3-10 Anodic overpotential dependencies for LSV$_{Re}$ ($x = 0.2, 0.3, 0.4, 0.5$)-YSZ (50:50 wt. %) on (a) current density at temperature of 950°C, and (b) temperature at current density of 0.2 A/cm$^2$ in pure H$_2$. Note that LSV5050$_{Re}$-YSZ cannot reach 0.2 A/cm$^2$ at 800 °C under the potential bias of 0.8 V (maximum bias applied in this study). ............50

Figure 3-11 Impedance curves of LSV6040–YSZ (50:50 wt%) with Au and Pt as current collectors.................................................................................................................................52

Figure 3-12 Impedance curves of LSV6040 (50 wt.%)-YSZ anode in pure CH$_4$ at (a) 1000°C, (b) 950°C, and (c) 900°C..........................................................................................................................................................54

Figure 3-13 (a) OCV curves (b) impedance spectra (c) anodic overpotential of LSV6040$_{Re}$-YSZ (50:50 wt. %) in wet methane. .................................................................56

Figure 3-14 OCV impedance responses of LSV6040 (50 wt.%)-YSZ anode at 900°C in pure H$_2$ and wet CH$_4$. Legend description: “Initial pure hydrogen”, OCV impedance in H$_2$ (just before gas shifting to wet CH$_4$); “wet methane”, OCV impedance in wet methane; “final pure hydrogen”, impedance in pure H$_2$..........................................................................................56

Figure 3-15 SEM images of a dismantled single cell after running in pure H$_2$ and wet CH$_4$: (a) holistic view of the single cell; (b) EDX Linescan crossing YSZ (electrolyte) and LSV-YSZ (anode) interface, and for the lines: Zr $L_{\alpha 1}$ (turquoise); V $K_{\alpha 1}$ (bright green); La $L_{\alpha 1}$ (purple); O $K_{\alpha 1}$ (red); (c) YSZ and LSV-YSZ interface; (d) YSZ and LSM-YSZ (cathode) interface; and (d) LSM-YSZ and LSM (current collector at cathode side) interface. .........................58

Figure 3-16 Impedance curves of a cell with configuration LSV6040–YSZ /YSZ/(LSM–YSZ/LSM) when exposed to pure H$_2$.................................................................58

Figure 3-17 Cell voltage (open symbols) and powder density (closed symbols) with relation to current density for a cell with configuration LSV6040-YSZ /YSZ/(LSM-YSZ/LSM-C). The fuel was pure H$_2$ and its flow rate is 50 sccm..............................................................60

Figure 3-18 Impedance curves of a cell with configuration LSV6040–YSZ /YSZ/(LSM–YSZ/LSM) when exposed to wet CH$_4$ (CH$_4$ with 3% H$_2$O)...............................61
Figure 3-19  Cell voltage (open symbols) and powder density (closed symbols) with relation to current density for a cell with configuration LSV6040–YSZ/YSZ/(LSM–YSZ/LSM). The fuel was wet CH₄ (CH₄ with 3% H₂O) and its flow rate is 50 sccm.

Figure 4-1 XRD patterns of La₀.₈Sr₀.₂VO₃ as prepared from solid state reactions and citric route, as demonstrated in Jade® 5.

Figure 4-2 Impedance responses of LSV–YSZ anode in (a) pure H₂ under different flow rate and (b) H₂-He binary gases, both under OCV conditions, and (c) pure H₂ under different dc bias. The equivalent circuit is shown in (d). The fuel flow rate was 100 sccm. The testing temperature was 950°C.

Figure 4-3 Nominal double layer capacitance of LSV–YSZ anode obtained from EIS (a, b) and transients (c), as a function of n value in CPE of R₁/CPE₁ (a) and under small anodic dc biases (b, c). The H₂ flow rate was 100 sccm. The testing temperature was 950°C.

Figure 4-4 Current transient of LSV–YSZ anode subjected to a 200 mV potential step. The H₂ flow rate was 100 sccm. The testing temperature was 950°C.

Figure 4-5 Equivalent circuit values of LSV–YSZ anode exposed to H₂-He binary atmosphere:
(a) R₁ and nominal C₀ in (R₁CPE₁), and (b) Wₓ-R and Wₓ-T in Wₓ, with Wₓ-P fixed at 0.36. Note that in (a), only three in the five parameters in the (R₁CPE₁) subset are independent (see Eq.1).

Figure 4-6 Impedance responses of LSV–YSZ anode in H₂–H₂O atmosphere.

Figure 4-7  (a) Impedance responses of “Arc 1”, (b) estimated resistance values, and (c) relaxation frequencies of LSV-YSZ anode in H₂–H₂O–He atmosphere.

Figure 4-8  Oxygen vacancy distribution diagram in the YSZ that is adjacent to the LSV/YSZ interface, under OCV condition. The inset shows the corresponding relative oxygen vacancy density profile.

Figure 4-9 (a) Three-dimensional visualization and (b) density plot of oxygen vacancies in the...
YSZ side of LSV/YSZ interfaces under OCV condition...........................................82

Figure 4-10 Relative oxygen vacancy density profiles in the YSZ side of polarized LSV/YSZ interfaces under anodic biases from 0 to 150 mV. The profiles are shifted vertically merely for illustration purpose. .................................................................83

Figure 4-11 (a) Relative oxygen vacancy densities of the first seven charged sheets and (b) the Volta potential portion of the H–P layer in the YSZ side of polarized LSV/YSZ interfaces...........................................................................................................84

Figure 4-12 Nyquist plots of typical impedance responses of polarized LSV/YSZ interfaces. Ten impedance spectra are recorded at each potential bias. The inset shows the equivalent circuit used throughout this study.................................................................89

Figure 4-13 Equivalent circuit fitting results of (a) polarization resistance ($R_1$), (b) the CPE parameter ($Q_{CPE1}$), and (c) apparent double layer capacitance ($C_{app\,dl}$) of the $R_1$/CPE$_1$ subset. Sample A (filled square, solid line) of the four samples (A to D) corresponds to the one in Figure 1. Each error bar is generated from 10 consecutive impedance spectra. .........91

Figure 4-14 Schematic illustrations of the double layer developed across the LSV/YSZ interface: (a) microscopic structure; (b) the Volta potential distribution.........................93

Figure 4-15 (a) Gouy–Chapman capacitance versus the Volta potential of the Gouy–Chapman layer. The inset shows the magnified figure near the zero potential, where the singularity occurs according to Eq. 4-14. .................................................................94

Figure 4-16 Schematic representations of the energy-level diagrams in LSV–YSZ(H$_2$)|YSZ|Pt(air) half cells under: (a) open circuit voltage, and (b) anodically polarized conditions. The right inset in (a) shows the correlations among $\phi$, $\Psi$, $\chi$, $\mu$, $\tilde{\mu}$, $E_F$, and $\Phi$. Note that all the interfacial variations are exaggerated merely for illustration purpose. ........................................................................................................96

Figure 4-17 Spatial variations of the Volta potential across the polarized LSV/YSZ interfaces. Junctions between the Helmholtz–Perrin layer and the Gouy–Chapman layer are labelled
by embedded symbols. The inset shows a holistic view of such curves from the interface to the bulk YSZ.................................................................96

Figure 4-18 Contour plots of intrinsic double layer capacitance comprising the Helmholtz–Perrin capacitance and the Gouy–Chapman capacitance. Along the direction of the arrow, the embedded points consecutively represent the intrinsic double layer capacitance of the LSV/YSZ interfaces under anodic biases of 0, 20, 50, 70, 100, 120, and 150 mV, as shown in Table 1. The dashed line is merely a trend line.........................99

Figure 4-19 (a) Particle size distribution and (b) cumulative probability of LSV particles..108

Figure 4-20 (a) Particle size distribution and (b) cumulative probability of YSZ particles..109

Figure 4-21 SEM image of the cross-section profile of a LSV–YSZ composite anode sintered onto YSZ electrolyte.................................................................109

Figure 4-22 SEM surface morphology image of an as-reduced LSV–YSZ composite anode. The sporadic black regions represent voids while the others symbolize particle aggregates. The two-dimensional packing density of this anode is 0.78 cm²/cm³. The corresponding three-dimensional packing density, obtained from the image analyses by implementing home-build Mathematica® 7 codes, is 0.52 cm³/cm³.........................................................110

Figure 4-23 Contour plots of $N_{LSV,YSZ}^b$ as functions of $f_{LSV}^a$ and $r_p$. The light gray zone and the pastel violet zone are the non-percolation regions of LSV and YSZ, respectively. The rainbow zone is the percolating region of both LSV and YSZ. The embedded purple dot represents the simulated LSV–YSZ composite anode under investigation..................113

Figure 4-24 Sintering curves of the LSV–YSZ packing bed at 1200 ºC, controlled either by surface diffusion (green) or lattice diffusion (red) of LSV from surface sources. The inset illustrates the neck formation during the initial sintering stage. $x$ and $a$ are the radiuses of the sintering neck and the LSV particle, respectively.................................116

Figure 4-25 Schematic illustration of the microstructure and sintering necks of LSV–YSZ
composite anodes. In the figure, $x$, $w$, and $l_{0.01}$ are the radius of the sintering necks, the in-depth TPB penetration of electrocatalysts, and the active electrode thickness, respectively.

Figure 4-26 Contour plots of $A_{EAZ}$ of LSV–YSZ composite anodes as functions of $w_0$ and $l_{0.01}$. The $A_{EAZ}$ values of sample A are 3.34 (red, dashed), 3.73 (green, solid), 3.65 (blue, dashed), 3.22 (black, dotted), 3.07 (purple, solid), 2.82 (magenta, dot-dashed), and 3.31 cm$^2$ (brown, solid), under anodic biases of 0, 20, 50, 70, 100, 120, and 150 mV, respectively.

Figure 5-1 Schematic diagram of the flow channel, test rig, and half cell configuration.

Figure 5-2 X-ray diffraction pattern of La$_{0.6}$Sr$_{0.4}$VO$_x$ (LSV) that is reduced in pure H$_2$ at 900ºC for 5 hours.

Figure 5-3 Effect of composition of LSV–YSZ anodes on high-frequency resistance ($R_{h-f}$), low frequency resistance ($R_{l-f}$), and the polarization resistance ($R_p = R_{h-f} - R_{l-f}$).

Figure 5-4 Cross-section profile of the fractured LSV–YSZ electrode.

Figure 5-5 Impedance spectra of the LSV electrode as mentioned in Fig. 4a: (a) the freshly prepared electrode in pure H$_2$ and (b) the electrode after 70-hour fuel cell polarization and in the 70H$_2$–30CO–50ppm H$_2$S atmosphere.

Figure 5-6 IR-compensated polarization curve of LSV anode in pure H$_2$ and H$_2$–9H$_2$O at 900 ºC. The inset table shows the corresponding exchange current densities.

Figure 5-7 Long-term chronopotentiometry of the LSV anodes exposed to pure H$_2$ and 91H$_2$–9H$_2$O under anodic current density of 0.2 A/cm$^2$.

Figure 5-8 Long-term chronopotentiometry of the LSV electrodes under 0.2 A/cm$^2$ (fuel cell mode), with response to the gas shift from pure H$_2$ to H$_2$–50 ppm H$_2$S.

Figure 5-9 Typical low-magnification SEM images of LSV electrodes: (a) freshly reduced (a), operated in fuel cell mode and in H$_2$–50 ppm H$_2$S for 127 hours (b), and operated under alternating fuel cell and electrolyser modes and various H$_2$S-tainted and carbon-forming...
feedstocks according to Fig. 4 (c). ................................................................. 135

Figure 5-10 Long-term chronopotentiometry of the LSV electrodes exposed to H₂S-tainted feedstocks. The whole figure is divided into (a) to (d) merely for the clear illustration purpose. ................................................................. 136

Figure 5-11 Impedance spectra of the LSV electrode as mentioned in Fig. 5-9a: (a) the freshly prepared electrode in pure H₂ and (b) the electrode after 70-hour fuel cell polarization and in the 70H₂–30CO–50ppm H₂S atmosphere......................................................... 137

Figure 5-12 Impedance spectra of the LSV electrode exposed to H₂–50ppm H₂S, as mentioned in Fig. 5-9b. ...................................................................................................................... 137

Figure 5-13 Impedance spectra of the LSV electrode exposed to 60H₂–20CO₂–20CH₄–50 ppm H₂S as mentioned in Fig. 5-9c: (a) before electrolysis and (b) after the 30-hour electrolysis. ...................................................................................................................... 138

Figure 5-14 The selected area (left) and the corresponding EDX spectrum (right) of the LSV electrode after the fuel cell operation in H₂–50 ppm H₂S for 127 hours. No sulphur is found within the detection limit of EDX................................................................. 139

Figure 5-15 The selected area (left) and the corresponding EDX spectrum (right) of the LSV electrode, under alternating fuel cell and electrolyser modes and various H₂S-tainted and carbon-forming feedstock atmospheres for 498 hours, as illustrated in Fig. 5-9. Significant amount of carbon is observed. No sulphur is detected within the detection limit of EDX ...................................................................................................................... 140

Figure 5-16 Field-emission SEM images of LSV electrode surfaces: (a) freshly reduced, (b) after the fuel cell testing in H₂–50 ppm H₂S for 120 hours (Fig. 5-7), and (c) after the long term testing as given in Fig. 5-9. ...................................................................................................................... 142

Figure 5-17 High magnification surface morphology images of LSV surfaces, after the 510-h operation according to Fig. 5-9. For the deposited particles, the mean size is 5.5 nm and the standard deviation is 0.9 nm. ...................................................................................................................... 142
List of Symbols

### SUBSCRIPTS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Usual Units</th>
<th>Section Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>activation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dl</td>
<td>double layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>eff</td>
<td>effective</td>
<td></td>
<td></td>
</tr>
<tr>
<td>el</td>
<td>electronic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>Gouy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>geo</td>
<td>geometric</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>Helmholtz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i</td>
<td>ionic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>latt</td>
<td>lattice</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>melting; monosized</td>
<td></td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>maximum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ox</td>
<td>oxidized</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>polarization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re</td>
<td>reduced</td>
<td></td>
<td></td>
</tr>
<tr>
<td>surf</td>
<td>surface</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2D</td>
<td>2 dimensional</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3D</td>
<td>3 dimensional</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### SUPERSCRIPTS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Usual Units</th>
<th>Section Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>app</td>
<td>apparent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>area</td>
<td>cm²</td>
<td>4.3.5</td>
</tr>
<tr>
<td>int</td>
<td>intrinsic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>number</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>surface</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>volumetric</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### ROMAN SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Usual Units</th>
<th>Section Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>area</td>
<td>cm²</td>
<td>4.3.5</td>
</tr>
<tr>
<td>a</td>
<td>particle radius</td>
<td>μm</td>
<td>4.4.3</td>
</tr>
<tr>
<td>C</td>
<td>capacitance</td>
<td>μF/cm²</td>
<td>4.1.2</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient; dimension</td>
<td>mol/cm²; nm</td>
<td>4.1.3; 4.4.2</td>
</tr>
<tr>
<td>d</td>
<td>thickness of the double layer;</td>
<td>Nm; μm</td>
<td>4.1.2; 4.4.2</td>
</tr>
<tr>
<td>e</td>
<td>charge</td>
<td>C</td>
<td>4.3</td>
</tr>
<tr>
<td>E</td>
<td>energy;</td>
<td>eV;</td>
<td>3.3.2;</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
<td>Section</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------</td>
<td>----------------</td>
<td>---------</td>
</tr>
<tr>
<td>$f$</td>
<td>frequency;</td>
<td>$/s$;</td>
<td>3.3.2;</td>
</tr>
<tr>
<td></td>
<td>acceptance probability</td>
<td>none</td>
<td>4.2</td>
</tr>
<tr>
<td>$H$</td>
<td>Enthalpy;</td>
<td>$kJ/mol$;</td>
<td>1.2.2;</td>
</tr>
<tr>
<td></td>
<td>Hamiltonian</td>
<td>$eV$</td>
<td>4.2</td>
</tr>
<tr>
<td>$h$</td>
<td>anode layer thickness</td>
<td>$\mu m$</td>
<td>4.4.2</td>
</tr>
<tr>
<td>$i$</td>
<td>current density</td>
<td>$A/cm^2$</td>
<td>5.4</td>
</tr>
<tr>
<td>$K$</td>
<td>normalized curvature difference</td>
<td>none</td>
<td>4.4.3</td>
</tr>
<tr>
<td>$k$</td>
<td>area normalizing factor;</td>
<td>none</td>
<td>4.3.5;</td>
</tr>
<tr>
<td></td>
<td>packing density coefficient</td>
<td>none</td>
<td>4.4.2</td>
</tr>
<tr>
<td>$L$</td>
<td>thickness of the Nernst diffusion layer; grid size</td>
<td>$nm$;</td>
<td>4.1.3;</td>
</tr>
<tr>
<td>$l$</td>
<td>distance</td>
<td>$\mu m$</td>
<td>4.4.4</td>
</tr>
<tr>
<td>$N$</td>
<td>number of oxygen vacancies;</td>
<td>none</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>coordination number</td>
<td>none</td>
<td>4.4.2</td>
</tr>
<tr>
<td>$n$</td>
<td>exponential factor of constant phase element; oxygen</td>
<td>none</td>
<td>4.1.2;</td>
</tr>
<tr>
<td></td>
<td>vacancy density</td>
<td>$/cm^3$</td>
<td>4.3</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
<td>bar;</td>
<td>2.4.3;</td>
</tr>
<tr>
<td></td>
<td>transition probability</td>
<td>none</td>
<td>4.2</td>
</tr>
<tr>
<td>$q$</td>
<td>realization probability</td>
<td>none</td>
<td>4.2</td>
</tr>
<tr>
<td>$P$</td>
<td>power density</td>
<td>$W/cm^2$</td>
<td>2.2</td>
</tr>
<tr>
<td>$Q$</td>
<td>activation energy of sintering</td>
<td>$eV$</td>
<td>4.4.3</td>
</tr>
<tr>
<td>$q$</td>
<td>charge</td>
<td>$C$</td>
<td>4.2</td>
</tr>
<tr>
<td>$r$</td>
<td>ionic radius;</td>
<td>$nm$;</td>
<td>4.3.2;</td>
</tr>
<tr>
<td></td>
<td>relative particle size</td>
<td>none</td>
<td>4.4.2</td>
</tr>
<tr>
<td>$R$</td>
<td>resistance</td>
<td>$\Omega$</td>
<td>2.4.3</td>
</tr>
<tr>
<td>$s$</td>
<td>perimeter of sintering neck</td>
<td>$\mu m$</td>
<td>4.4.4</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>$^\circ C$</td>
<td>2.3</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>$s$</td>
<td>4.4.3</td>
</tr>
<tr>
<td>$w$</td>
<td>in-depth penetration of electrocatalyst</td>
<td>$nm$</td>
<td>4.4.4</td>
</tr>
<tr>
<td>$x$</td>
<td>radius of sintering neck</td>
<td>$\mu m$</td>
<td>4.4.3</td>
</tr>
<tr>
<td>$z$</td>
<td>normalized distance;</td>
<td>$nm/nm$</td>
<td>4.2</td>
</tr>
</tbody>
</table>
complex impedance $\Omega \text{ cm}^2$ 4.3

### GREEK SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Usual Units</th>
<th>Section Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>geometric factor</td>
<td>none</td>
<td>4.4.2</td>
</tr>
<tr>
<td>$\delta$</td>
<td>oxygen non-stoichiometry; surface thickness</td>
<td>$\mu$m</td>
<td>4.4.3</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>void fraction</td>
<td>none</td>
<td>4.4.2</td>
</tr>
<tr>
<td>$\eta$</td>
<td>packing density; overpotential</td>
<td>mV</td>
<td>5.4</td>
</tr>
<tr>
<td>$\theta$</td>
<td>surface coverage; constant phase angle of CPE</td>
<td>$\text{cm}^2$/cm$^2$; $^\circ$</td>
<td>4.2; 4.3</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>proportionality factor; electrode degradation rate</td>
<td>none; none</td>
<td>4.4.4; 5.4</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>line charge density</td>
<td>C/cm</td>
<td>4.2</td>
</tr>
<tr>
<td>$\mu$</td>
<td>chemical potential; shear modulus</td>
<td>eV; Pa</td>
<td>4.3; 4.4.3</td>
</tr>
<tr>
<td>$\rho$</td>
<td>charge density; materials density; radius of curvature; density of TPB</td>
<td>$\text{C/cm}^3$; $\text{g/cm}^3$; $\mu$m; $\mu$m/$\mu$m$^3$</td>
<td>4.2; 4.4.2; 4.4.3; 4.4.4</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>conductivity</td>
<td>S/cm</td>
<td>3.2</td>
</tr>
<tr>
<td>$\tau$</td>
<td>time constant</td>
<td>S</td>
<td>4.1.2</td>
</tr>
<tr>
<td>$\chi$</td>
<td>outer potential</td>
<td>V</td>
<td>4.3</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>Volta potential</td>
<td>V</td>
<td>4.2</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>atomic volume</td>
<td>nm$^3$</td>
<td>4.4.3</td>
</tr>
<tr>
<td>$\omega$</td>
<td>angular frequency</td>
<td>/s</td>
<td>4.1.2</td>
</tr>
</tbody>
</table>

### ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Meaning</th>
<th>Section References</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>alkaline fuel cell</td>
<td>1.1</td>
</tr>
<tr>
<td>APU</td>
<td>auxiliary power unit</td>
<td>1.1</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>APXPS</td>
<td>ambient pressure XPS</td>
<td>4.3.5</td>
</tr>
<tr>
<td>ATR</td>
<td>autothermal reforming</td>
<td>1.2.2</td>
</tr>
<tr>
<td>CNLS</td>
<td>complex nonlinear least squares</td>
<td>4.3</td>
</tr>
<tr>
<td>CPE</td>
<td>constant phase element</td>
<td>4.1.2</td>
</tr>
<tr>
<td>EAZ</td>
<td>electrochemical active zone</td>
<td>4.4</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray spectroscopy</td>
<td>3.4.2</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
<td>4.1.2</td>
</tr>
<tr>
<td>G–C</td>
<td>Gouy–Chapman</td>
<td>4.2</td>
</tr>
<tr>
<td>GFW</td>
<td>generalized Warburg impedance</td>
<td>4.1.3</td>
</tr>
<tr>
<td>GIR</td>
<td>gradual internal reforming</td>
<td>1.2</td>
</tr>
<tr>
<td>H–P</td>
<td>Helmholtz–Perrin</td>
<td>4.2</td>
</tr>
<tr>
<td>HT–</td>
<td>high temperature</td>
<td>1.1</td>
</tr>
<tr>
<td>IT–</td>
<td>intermediate temperature</td>
<td>1.1</td>
</tr>
<tr>
<td>LEV</td>
<td>Levenburg–Marquardt</td>
<td>5.5</td>
</tr>
<tr>
<td>LSV</td>
<td>lanthanum strontium vanadate</td>
<td>1.3</td>
</tr>
<tr>
<td>LSM</td>
<td>lanthanum strontium manganite</td>
<td>3.4.1</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo</td>
<td>4.2</td>
</tr>
<tr>
<td>MCMC</td>
<td>Markov Chain Monte Carlo</td>
<td>4.2</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
<td>5.2</td>
</tr>
<tr>
<td>MIEC</td>
<td>mixed ionic and electronic conductor</td>
<td>2.4</td>
</tr>
<tr>
<td>NDL</td>
<td>Nernst diffusion layer</td>
<td>4.1.2</td>
</tr>
<tr>
<td>OCV</td>
<td>open circuit voltage</td>
<td>2.1</td>
</tr>
<tr>
<td>oHp</td>
<td>outer Helmholtz plane</td>
<td>4.1.2</td>
</tr>
<tr>
<td>SMR</td>
<td>steam methane reforming</td>
<td>1.2.1</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
<td>3.3.2</td>
</tr>
<tr>
<td>SOC</td>
<td>solid oxide cell</td>
<td>5.5</td>
</tr>
<tr>
<td>SOFC</td>
<td>solid oxide fuel cell</td>
<td>1.1</td>
</tr>
<tr>
<td>TEC</td>
<td>thermal expansion coefficient</td>
<td>2.4.2</td>
</tr>
<tr>
<td>TPB</td>
<td>three phase boundary</td>
<td>4.1.2</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
<td>2.3</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
<td>3.2</td>
</tr>
<tr>
<td>YSZ</td>
<td>yttria-stabilised zirconia</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Chapter 1. Introduction

1.1 Introduction of Fuel Cells

Introducing the fuel cell concept over 160 years ago, Sir William Grove would have been proud of the booming fuel cell research and development all over the world. With technical breakthroughs since the last four decades, fuel cells have been demonstrating their down-to-earth applications by the reduced cost, improved performance, and increased reliability. They are also gaining commercial momentum because of human being’s continuous pursuit for sustainable energy and low-carbon economy. Fuel cells own environmental advantages against conventional power generation devices (e.g. gas turbines, internal combusive engines) with the merits of high energy utilization efficiency and reduced pollutant emissions.

Fuel cells are electrochemical energy conversion devices that directly convert chemical energy of a fuel into electrical energy. Based on the electrolyte used, fuel cells can be classified into: (i) polymer electrolyte membrane fuel cell (PEMFC), (ii) alkaline fuel cell (AFC), (iii) phosphoric acid fuel cell (PAFC), (iv) molten carbonate fuel cell (MCFC), and (v) solid oxide fuel cell (SOFC). A single SOFC consists of two porous electrodes that are separated by a dense yet oxygen ion conducting electrolyte. On the cathode (air electrode) side, oxygen is reduced to oxygen ions which are then pumped through the electrolyte. On the anode (fuel electrode) side, fuels are oxidized by the pumped oxygen ions to liberate the electrons. The Gibbs free energy difference between the two electrodes forces the electrons to flow through the external electrical circuit.

SOFC is not a heat engine and its efficiency is not limited by Carnot principle. It can achieve high efficiencies of 40-60 % (Onda et al., 2003). Over the past decades, R&D activities have focused on cheap materials and low-cost processing methods (Menzler et al., 2003; Gaudon et al., 2004; Neagu et al., 2006; Rossignol et al., 2011). Many of them were aimed to lower the operating temperature by using highly conductive oxygen ion conductors (Boulc’h and Djurado, 2002). Advanced SOFC fabrication techniques make cells with small resistance, enabling SOFCs to operate at temperatures down to
500°C (Nesaraj, 2010). The ideal SOFC operating temperature is still controversial. While intermediate temperature SOFC (IT-SOFC, 600°C < T < 800°C) can reduce the cost, high temperature SOFC (HT-SOFC, 800°C < T < 1000°C) is more efficient. Furthermore, high quality waste heat can be recuperated from HT-SOFC for heating the inlet fuels. HT-SOFC can be coupled to traditional gas turbines to make the energy efficiency even higher. SOFC is closed related to other technologies, such as ceramic ion-conducting membranes, oxygen generator, and ceramic electrochemical reactors. Such a synergy reduces investment risk and encourages entrepreneurial efforts on developing SOFC devices for stationary and distributed power generation, vehicle motive power, and auxiliary power units (APUs).

1.2 Fuel challenges

International Energy Agency (IEA) projected a series of scenarios of energy consumption and structure from now to 2030 if current legislations and policies remain unchanged. It sees global primary energy demand, e.g. on fossil fuel, nuclear fuel, solar energy, and biomass, rising by 1.5%/year on average between 2007 and 2030. World energy demand is projected to grow at an annual rate of 2.5% to 2030, in equivalent to 4,800 GW powder-generation capacity by 2030 (International Energy Agency, 2009). On the other hand, the society pays great concerns on environment issues such as global CO₂ emission and climate change. Note that how the Nobel Peace Prize for 2007 went to the Intergovernmental Panel on Climate Change (IPCC) and the former US Vice President Albert Gore. SOFC seems to be one of the solutions on tackling with these energy and environmental issues. Current status and challenges of two most common SOFC fuels, i.e. hydrogen and reforming gas, are introduced herein.

1.2.1 Hydrogen

Hydrogen is believed to be an important end-use energy carrier, in the fields of transportation, power generation, and portable power systems. Molecular hydrogen is a clean burning fuel. It is the most effective and environment-favourable feedstock to fuel cells. Hydrogen has been extensively used in industry (e.g. chemicals synthesis, refinery, electronics, and metal processing) but not as a fuel. In recent years, world-wide hydrogen demand rockets to meet rigorous government policies and regulations. Among announced projects over the world, the USA is the most ambitious
one in transiting “hydrocarbon economy” to green “hydrogen economy”. In 2001, its National Hydrogen Vision Meeting sketched a blueprint for the public confidence in hydrogen as an energy carrier. It launched a 4-year Hydrogen Fuel Initiative with budget of $1.2 billion since 2004, to develop the technology needed for commercially viable hydrogen-powered fuel cells.

The future of hydrogen economy can be exciting, but it is yet to come. Some of the major barriers are cost, technological uncertainty, and infrastructure set-up. Hydrogen is just an energy carrier that must be produced by consuming energy. World-wide hydrogen production has relied on fossil fuels since 1988: 48% from natural gas, 30% from refinery/chemical off-gases, 18% from coal, and the rest from electrolysis (Armor, 1999). Hitherto, 95% of hydrogen in the USA is produced via steam methane reforming (SMR). Green technologies such as photo-electrolysis have long been considered as ultimate solutions. Nevertheless, they would be commercially available only in late 2000s or into the 22nd century (Armor, 1999). The future of hydrogen production cost is still unclear, even for mature technologies such as SMR. It is believed that the cost of hydrogen production must be reduced by a factor of 3 to 10 to make it economically competitive. As shown in Table 1-1, the cost-reduction timelines in the roadmap have always been postponed. In addition, the numbers in Table 1-1 do not include the cost of CO2 sequestration. The most updated roadmap was given in Figure 6.1 of Ref. (US Department of Energy, 2009). CO2 sequestration is not yet a proven technology, though demonstration projects for CO2 storage are on the way. In conclusion, the “green” hydrogen fuel is hitherto not so green as claimed.

Besides the hydrogen production cost, the infrastructure cost is also of great uncertainty. The infrastructure includes gas pipelines, power plants, and electricity transmission and distribution facilities. While some existing infrastructure (e.g. natural gas pipelines and distribution stations) might be utilized, specific upgrades are compulsory particularly in sectors of hydrogen storage and distribution. The technologies that are needed to convert the natural gas infrastructure for hydrogen are available now, but they are not yet cost-effective. The capital investment that was involved in order to maintain and improve the hydrogen infrastructure was estimated to be several hundred billion dollars for the USA (US Department of Energy, 2002). The cost of worldwide pipeline-based distribution systems are in the range of $0.1 to $1.0 trillion with the
assumption of large-scale and centralized hydrogen production. It would cost as high as $20 trillion till 2030 (International Energy Agency, 2007). Private capital investment is essential to build up the hydrogen infrastructure. However, the private involvement may not be forthcoming in the absence of sustained public policy supports (e.g. stringent national or international regulations on CO₂ emission) and technological advances (e.g., significant breakthroughs in hydrogen production, storage, and utilization technologies).

### Table 1-1  Targeted cost of hydrogen production

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Goal</td>
<td>Goal</td>
</tr>
<tr>
<td></td>
<td>Target Year</td>
<td>Target Year</td>
</tr>
<tr>
<td>Natural gas and fossil fuels reforming</td>
<td>$1.50 / Kg (delivered, without CO₂ sequestration)</td>
<td>$2.50 / gge (delivered) 2010</td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td>$2.00 / gge (delivered) 2015</td>
</tr>
<tr>
<td>Biomass gasification</td>
<td>$1.50 / Kg (at plant gate)</td>
<td>$3.80 / gge (delivered) 2012</td>
</tr>
<tr>
<td></td>
<td>2015</td>
<td>$3.00 / gge (delivered) 2017</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>$2.00-2.50 / Kg (at plant gate)</td>
<td>$3.70 / gge (delivered) from distributed electrolysis 2012</td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td>$3.00 / gge (at plant gate) from distributed electrolysis 2017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3.10 / gge at plant gate ($4.80 / gge delivered) from central wind electrolysis 2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;$2.00 / gge at plant gate (&lt;$3.00 / gge delivered) from central wind electrolysis 2017</td>
</tr>
<tr>
<td>Photo-electrochemical Water Splitting</td>
<td>$5.00 / Kg (at plant gate)</td>
<td>$3.00 / gge at plant gate ($4.00 / gge delivered) 2017</td>
</tr>
<tr>
<td></td>
<td>2015</td>
<td></td>
</tr>
<tr>
<td>Nuclear heat</td>
<td>Demonstration of technical Capability at competitive price</td>
<td>Commercia-scale, economically feasible production 2017</td>
</tr>
</tbody>
</table>

* A kg of hydrogen contains approximately the same amount of energy as one gallon of gasoline, or one gallon of gasoline equivalent (gge).

Ultrahigh-purity hydrogen is necessary for PEMFC, which has been developed for transportation and portable applications. Unlike PEMFC which is highly sensitive to CO poisoning, SOFC readily utilizes CO as fuel. SOFC provides a shortcut to use reforming gas instead of hydrogen, thus providing high efficiency in energy conversion. Hydrogen production via hydrocarbon reforming will be introduced in Chapter 1.2.2. Advantages and disadvantages for SOFC coupling with reforming process are subsequently discussed.
1.2.2 Reforming gas

Reforming gas, or syngas, is a gas mixture that contains varying amount of CO and H\textsubscript{2}. Typical production methods include steam reforming of hydrocarbons, coal gasification, biomass cleaning and reforming, etc. In this section only the steam reforming, which is the dominant process in industry, is discussed.

Fuel processing is the process that converts commercially available hydrocarbon fuels to fuel gas reformates (EG&G Services, 2004). It includes fuel cleaning, fuel conversion, reformate gas separation, and fuel purification. The system complexity depends on the targeted fuel cell type and the properties of raw feedstocks and deliverables. For example, in order to avoid CO poisoning ultrafine purification of reforming gases is compulsory for PEMFC. The reforming process can be classified into external reforming and internal reforming, based on whether the fuel processing is incorporated within the SOFC devices.

A typical external reforming system consists of a series of gas purification and catalytic chemical reactors, followed by impurity clean-up systems. The primary fuel reforming may be accomplished with or without a catalyst via one of three major types: (i) steam reforming; (ii) partial oxidation reforming; (iii) autothermal reforming (ATR). As mentioned in Chapter 1.2.1, natural gas is the main feedstock of hydrocarbon reforming via SMR. On an industrial scale, SMR is the cheapest and most effective method for hydrogen production. SMR is a complex process which at least includes:

\[
\begin{align*}
\text{CH}_4 + \text{steam} & \rightarrow \text{CO} + 3\text{H}_2 \quad \text{(Equation 1-1)} \\
\text{CO} + \text{steam} & \rightarrow \text{CO}_2 + \text{H}_2 \quad \text{(Equation 1-2)} \\
\text{CO}_2 + \text{H}_2 & \rightarrow \text{CO} + \text{H}_2\text{O} \quad \text{(Equation 1-3)} \\
2\text{CO} & \rightarrow \text{C} + \text{CO}_2 \quad \text{(Equation 1-4)} \\
\text{CH}_4 & \rightarrow \text{C} + 2\text{H}_2 \quad \text{(Equation 1-5)}
\end{align*}
\]

Reaction 1-1 is highly endothermic (\(\Delta H = +206.1\) kJ/mol) so that the operating...
temperature of SMR is often higher than 800°C. According to Reactions 1-1 and 1-2, excess steam is added into the reactor in order to maximize the hydrogen yield and avoid carbon deposition. However, too much steam inevitably leads to low system efficiency. These disadvantages are overweighted by its higher H₂ yield than other reforming methods, such as partial oxidation and ATR. One of the main challenges of SMR is to balance the heat input through the reformer tubes with the reaction heat. The catalysts are in a packed bed, with a series of tubes surrounded by combusting gas that supply heat to the endothermic reactions. Alternatively, reforming catalysts are applied onto the walls of heat exchanger together with a combustion catalyst on the other side to provide the heat. This arrangement requires much more active catalysts than conventional Ni-based materials. Ni-based catalysts are low-cost but are prone to carbon deposition (Reactions 1-4 and 1-5). Carbon deposition not only leads to carbon loss of the fuels, but more importantly also cokes the catalysts. Increasing steam, hydrogen, and CO₂ concentrations alleviates carbon deposition but reduces system efficiency. Furthermore, the system demands upstream sulphur removal processes. Finding cost-effective and high performance catalysts with carbon resistance and sulphur tolerance continues to be a challenge.

One of the distinguished advantages of SOFC is the possibility of utilizing practical hydrocarbon fuels, by virtue of internal reforming of hydrocarbon fuels within its anode chamber. Converting the hydrocarbon fuels directly in the anode chamber simplifies the whole system and offers cost advantages. Under practical conditions, nearly half of the heat produced by the exothermic oxidation reactions could be absorbed by the reforming processes. It lowers the cell cooling requirement and consequently reduces the required amount of air passing to the cathode side. It increases the system efficiency by eliminating the energy penalty associated with transferring the heat for the heat supply in an external reformer. The cooling effect could be harmful if the induced thermal stress leads to mechanical failure of cell components. Alternatively, gradual internal reforming (GIR) mitigates this deleterious effect by applying a slab of dry reforming agent above the anode (Klein et al., 2008a).

Carbon deposition and impurity poisoning (mostly H₂S) remain to be the critical issues for SOFC with Ni-cermet internal reforming catalysts and anodes. Conventional steam
reforming requires large quantities of steam (mostly CH$_4$:CO$_2$ < 1:3) are added to the hydrocarbon fuels in order to avoid carbon deposition. Much higher CH$_4$: CO$_2$ ratios are tolerable in the circumstance of GIR (Georges et al., 2006). Additionally, the output fuel gas from reforming process should be carefully cleaned to remove H$_2$S down to several parts per million (ppm) levels. These are undesirable because of the fuel dilution and the added processing cost. Another problem of the internal reforming is the steep temperature gradient along the fuel channels. At the inlet of a cell where the fuel concentration is high, the fuel reforming process dominates so that the inlet region is cooled significantly below the feed temperature. Meanwhile, the temperature increases when the fuel flows downstream to where the exothermic fuel oxidation dominates. Localized heating and cooling lead to significant thermal stress and, potentially, to system failure.

1.3 Project goals

SOFC technology is on the verge of commercialization now. Both research institutions and commercial organizations are launching SOFC projects for down-to-earth applications in niche markets, such as stationary power generations and auxiliary power units (APUs). Hitherto, the major hurdles for SOFC commercialization are the cost and reliability. One of the approaches on cost reduction is to feed SOFC with practical fuels, rather than using the expensive hydrogen that are actually produced from hydrocarbons. Another approach is to improve the impurity (mostly sulphur) tolerance of electrocatalysts. Advanced anode materials that are capable of hydrocarbon utilization and of high sulphur tolerance would be of great interests to SOFC community.

A technological challenge of feeding SOFC with practical hydrocarbon fuels is that conventional anodes, such as Ni–YSZ cermets, are prone to carbon deposition and sulphur poisoning. Several approaches are proposed to solve or mitigate these problems: (i) optimizing operating conditions such as temperature and voltage, (ii) tailoring the state-of-the-art Ni–cermet anodes by doping and alloying, and (iii) seeking alternative anode materials. The third approach is adopted in this project as the first two approaches both lead to system inefficiency and complexity.
This project, therefore, aims to explore a new type of anode materials that are suitable for SOFC fed on practical fuels. A class of perovskite oxides, lanthanum strontium vanadate (LSV), exhibits great potential for this kind of application. It not only suppresses carbon deposition but also withstands sulphur-containing hydrocarbon fuels such as natural gas, coal gas, and biogas. Material synthesis and preliminary electrode performance evaluation represent the Phase 1 of this project. In Phase 2, fundamental works on the reaction mechanism, interfacial structures, and electrode microstructure are investigated thoroughly. Finally in Phase 3, the optimized electrode is subjected to half cell testing and fed by various practical fuels.

1.4 Objectives of research project

- To prove the concept by feeding SOFC with practical fuels
- To synthesis, characterize, and optimize vanadate anode materials
- To establish chemical, electrochemical, and microstructural relationships
- To investigate the interfacial and fuel oxidation mechanisms

1.5 Scope of research project

The scope of the research project is outlined as below:

a. To explore new anode materials in the vanadate category for SOFC fed with practical fuels, in particular
   - Choosing the right materials
   - Powder synthesis
   - Materials characterization of the as-synthesized powders
   - Electrode engineering (e.g. power property, baking history, composition, sintering temperature, microstructure etc.)
   - Thermal, redox, and long-term operating stability

b. To establish the interrelationships between chemical, interfacial, electrochemical, and microstructural properties anode/electrode interfaces, in particular
   - Impedance spectroscopy analysis under various atmosphere
   - Monte Carlo simulation of the anode/electrolyte double layer structure
• Modified Poisson–Boltzmann theory on establishing the potential-dependent Gouy–Chapman capacitance
• The Volta potential analysis in obtaining the double layer capacitance
• Interrelationship between three phase boundaries and electrochemically active zone
c. To fabricate the half cell SOFCs with vanadate anodes
  • Running on practical fuels, e.g. simulated natural gas, syngas, biogas, and coal gas
  • Fuel impurity
  • Carbon deposition
  • Performance degradation analysis

1.6 Thesis layout

Chapter 2 reviews various anodes targeting to hydrocarbon utilizations, viz. Ni-cermet, Cu-cermet, and various oxides (zirconia-based and ceria-based fluorite, tungsten bronze, rutile, pyrochlore, chromite perovskite, titanate perovskite, double perovskite).

Chapter 3 describes the initial exploration and evaluation of lanthanum strontium vanadate (LSV) as potential SOFC anodes, including powder synthesis, materials structure and thermo-stability, half cell and single cell electrode performance.

Chapter 4 represents a comprehensive study on elucidating the interfacial structure of LSV/YSZ interfaces by impedance spectroscopy, Monte Carlo simulation, modified Poisson–Boltzmann theoretical analysis, and analytical modelling on anode microstructure, three phase boundaries, and electrochemically active zones.

Chapter 5 demonstrates the feasibility of LSV anodes for SOFCs fed with practical fuels. LSV anodes exhibit salient catalytic activity in various simulated practical fuels, e.g. syngas, coal gas, biogas, and town gas.

Chapter 6 provides conclusions, main achievements, and recommendations.
Chapter 2. Literature review

Technical challenges of hydrogen and reforming gases had been introduced in Chapter 1. Fundamental principles of SOFC operation will be introduced in Chapter 2.1. The recent research progress on hydrocarbon utilization in SOFCs is then reviewed. For SOFC operating on hydrocarbon fuels, the most critical issue is to develop anodes that do not catalyze carbon formation and have comparable performance with state-of-the-art Ni-cermet anodes.

2.1 SOFC fundamentals

The definition of “direct hydrocarbon utilization” or “direct utilization” has not been clear. The controversy pervades in literature over precisely what should be called as direct oxidation, direct conversion, or direct utilization of hydrocarbons in SOFCs. Mogensen and Kammer defined it as “conversion in the SOFC without pre-mixing the fuel gas with steam or CO₂, and without processing the fuel before it enters the cell stack.” (Mogensen and Kammer, 2003). It means that direct utilization is the direct electrochemical oxidation with the open-circuit voltage (OCV) of the fuel cell equal to the Nernst potential. So to speak, any processes that involve hydrocarbon cracking and electrochemical oxidation of the cracking products are beyond the category of “direct oxidation”. This appears to be quite a stringent definition and might not be of practical merits. Alternatively, McIntosh and Gorte envisaged that direct utilization should encompass the conventional use of hydrocarbon fuel with small amount of steam (e.g. 3% H₂O) being co-fed with hydrocarbons, regardless of the exact reaction pathways (McIntosh and Gorte, 2004). McIntosh and Gorte’s loose definition is adopted all through this study but merely for pragmatic reasons.

Oxygen molecules are reduced to oxygen ions at the cathode. Driven by the electrochemical potential difference between anode and cathode, oxygen ions are pumped through electrolyte. They finally reach the anode and are consumed in terms of electrochemical fuel oxidation,

\[ C_nH_{2n+2} + (3n + 1)O^{2-} \rightarrow nCO_2 + (n + 1)H_2O + (6n + 2)e^- \] (Equation 2-1)
Taking CH₄ as an example, Reaction (2-1), i.e., step ③ shown in Fig. 2-1, is unlikely to occur in one step. Thermal cracking of CH₄ is inevitable in typical SOFC operating temperatures. Some of the resulted compounds can be oxidized electrochemically. The cracking products include carbon, hydrogen, and some chain/cyclised hydrocarbons. The cracking process might proceed as: (i) oxidation of cracked carbon and hydrogen (Step 1 and Step 4 in Fig. 2-1) or (ii) oxidation of intermediate from free radical reactions (Step 5 and Step 7 in Fig. 2-1). Some of the reactions are proposed as below (Mogensen and Kammer, 2003):

\[
\text{CH}_4 \rightarrow C + H_2 \quad \text{(Equation 2-2)}
\]
\[
C + O^{2-} \rightarrow CO, CO_2 \quad \text{(Equation 2-3)}
\]
\[
H_2 + O^{2-} \rightarrow H_2O \quad \text{(Equation 2-4)}
\]
\[
\text{CH}_4 + O^{2-} \rightarrow \text{CH}_3\text{OH} + 2e^- \quad \text{(Equation 2-5)}
\]
\[
\text{CH}_3\text{OH} + 2O^{2-} \rightarrow \text{HCOOH} + H_2O + 4e^- \quad \text{(Equation 2-6)}
\]
\[
\text{HCOOH} + O^{2-} \rightarrow \text{CO}_2 + H_2O + 2e^- \quad \text{(Equation 2-7)}
\]

![Flow chart of hydrocarbon utilization in SOFC (methane as example)](image_url)

Figure 1-1 Flow chart of hydrocarbon utilization in SOFC (methane as example)
The exact reaction could be a combination of all the reactions mentioned above. Additionally, fuel reactions are related and influenced by other physical and chemical phenomena within the anode chamber, such as gas diffusion, gas conversion, mass transportation, and surface adsorption/desorption. In Chapter 2, literature review focuses on those cermet and conductive oxide anodes attempting for hydrocarbon utilization. Ni-cermets are introduced in Chapter 2.2. Efforts are then paid to Cu-cermets in Chapter 2.3. Conductive oxide anode materials, mainly perovskite and briefly fluorite, rutile, pyrochlore, and tungsten bronze, are finally reviewed in Chapter 2.4. Merits and drawbacks of these materials for hydrocarbon fuel utilization are analysed and commented from case to case.

### 2.2 Nickel cermet

Large amounts of steam with steam/carbon (S/C) ratio larger than 2 are routinely added into hydrocarbons that are used as fuels for SOFCs with Ni-cermet anodes. In contrast, Murray et al. demonstrated that Ni-cermet could be utilized for direct hydrocarbon SOFCs with no or little co-fed H₂O (Murray et al., 1999). Cells with Ni–YSZ anode could yield $R_p$ around 1 Ω cm² in 3% H₂O–CH₄ fuel with stable operation up to 100 h at 600°C. A temperature window between 550°C to 650°C, in which carbon is not stable, was pinpointed. The thermal cracking of methane to carbon and hydrogen was inhibited below 650°C. On the other hand, the disproportionation of CO to carbon and CO₂ was shifted to CO above 550°C. Another benefit might came from the yttria doped ceria (YDC) interlayer that were sandwiched between the 8 µm-thick YSZ electrolyte and the electrodes, noting that YDC is known to have good dry reforming ability and resistance to carbon formation. The OCV of these cells was significantly lower than the potential predicted from thermodynamics, e.g. 1.2–1.4 V in typical SOFC operating temperatures. It indicated that the dominating reactions were the oxidation of cracked compounds, either carbon and hydrogen, or light hydrocarbons from free radical reactions. That approach had fostered three well-known strategies on utilizing Ni-cermets for direct hydrocarbon utilization. The first strategy, Strategy a, is to carefully control the operating temperature and the anodic environment. The second strategy, Strategy b, is to mix or dope carbon-resistance species into Ni-cermet. The third strategy, Strategy c, is to add a buffer layer or dry reforming layer above the anode layer.
Table 2-1 Single cell SOFC with Ni-cermet anodes fed with hydrocarbon fuels

<table>
<thead>
<tr>
<th>Anode</th>
<th>Electrolyte</th>
<th>Cathode</th>
<th>Strategies for hydrocarbon utilization</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure methane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni–YSZ</td>
<td>YSZ</td>
<td>LSCF–GDC</td>
<td>*</td>
<td>(Lin et al., 2005)</td>
</tr>
<tr>
<td>Ni–GDC–Ru</td>
<td>20 µm GDC</td>
<td>SSC</td>
<td>b</td>
<td>(Hibino et al., 2002)</td>
</tr>
<tr>
<td>(1-10 wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni–YSZ (support)</td>
<td>Tubular</td>
<td>LSCF–SDC</td>
<td>c</td>
<td>(Li et al., 2007a)</td>
</tr>
<tr>
<td></td>
<td>~20 µm YSZ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDC</td>
<td>LSGM (0.5 mm)</td>
<td>LSCo</td>
<td>b</td>
<td>(Nabae et al., 2006)</td>
</tr>
<tr>
<td>Ni–SDC</td>
<td>ScSZ (2.5 mm)</td>
<td>Pt</td>
<td>c</td>
<td>(Asamoto et al., 2009)</td>
</tr>
<tr>
<td>Ni–SDC</td>
<td>SDC</td>
<td>SSC–SDC</td>
<td>b</td>
<td>(Zhu et al., 2006)</td>
</tr>
<tr>
<td>Ni–YSZ</td>
<td>YSZ (10 µm)</td>
<td>LSM–YSZ</td>
<td>c</td>
<td>(Zhan et al., 2006)</td>
</tr>
<tr>
<td>Impregnated Ni in LSC–YSZ</td>
<td>LSGM (0.5 mm)</td>
<td>LSC</td>
<td>b</td>
<td>(Nabae and Yamanaka, 2009)</td>
</tr>
<tr>
<td>Ni–YSZ–10% starch</td>
<td>YSZ</td>
<td>LSCF–GDC</td>
<td>c</td>
<td>(Lin et al., 2006)</td>
</tr>
<tr>
<td>Ni–YSZ</td>
<td>YSZ</td>
<td>LSM</td>
<td>c</td>
<td>(Klein et al., 2008b)</td>
</tr>
<tr>
<td>Wet methane (3% H₂O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni–ScSZ</td>
<td>ScSZ</td>
<td>LSM</td>
<td>a</td>
<td>(Sumi et al., 2004)</td>
</tr>
<tr>
<td>Pd/Ni/ceria impregnated YSZ</td>
<td>YSZ</td>
<td>Pt or LSM</td>
<td>b</td>
<td>(Qiao et al., 2009)</td>
</tr>
<tr>
<td>Ni–YSZ</td>
<td>YSZ (8 µm)</td>
<td>LSM</td>
<td>c</td>
<td>(Murray et al., 1999)</td>
</tr>
<tr>
<td>Sn-doped Ni–YSZ</td>
<td>YSZ (20–30 µm)</td>
<td>LSM</td>
<td>a</td>
<td>(Kan and Lee, 2010)</td>
</tr>
<tr>
<td>Ni–ScSZ</td>
<td>ScSZ</td>
<td>PCM</td>
<td>b</td>
<td>(Huang et al., 2006a)</td>
</tr>
<tr>
<td>Ni–YSZ and Ni–ScSZ</td>
<td>YSZ and ScSZ</td>
<td>LSM</td>
<td>a</td>
<td>(Sumi et al., 2010)</td>
</tr>
<tr>
<td>Wet natural gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni–YSZ</td>
<td>YSZ (10 µm)</td>
<td>LSM–YSZ</td>
<td>a</td>
<td>(Jiang and Virkar, 2003)</td>
</tr>
<tr>
<td>Butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni–LSCM–GDC</td>
<td>GDC (0.4–0.6 mm)</td>
<td>LSCF–SDC</td>
<td>b</td>
<td>(Liu et al., 2002)</td>
</tr>
<tr>
<td>Isooctane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni–YSZ</td>
<td>YSZ</td>
<td>LSCF–GDC</td>
<td>c</td>
<td>(Zhan and Barnett, 2005a, Zhan and Barnett, 2005b)</td>
</tr>
<tr>
<td>Ni–YSZ</td>
<td>YSZ (10 µm)</td>
<td>LSM–YSZ</td>
<td>a</td>
<td>(Murray et al., 2006)</td>
</tr>
</tbody>
</table>

a: operating under current loading; b: mixing or coating with carbon-resistant species; c: adding buffer layer above the anode layer.

Various hydrocarbon fuels, such as methane, natural gas, butane, and isooctane, had been used as fuels fed to SOFCs with Ni-cermet anodes. Alcohols, which carry sufficient oxygen to avoid carbon deposition, can also be utilized as fuels. Some examples are shown in Table 2-1. Thin-electrolyte cells in this category can achieve high maximum power density ($P_{\text{max}}$). $P_{\text{max}}$ as high as 2 W/cm² at 800°C had been
reported to SOFCs fed with wet methane (Sumi et al., 2004). Stable operation longer than 1000 h was achieved at 600°C with $P_{\text{max}}$ at 0.58 W/cm$^2$ for large cells (Nabae et al., 2006). Table 2-1 also shows the three strategies to mitigate the coking problem of the state-of-the-art Ni-cermet anodes for hydrocarbon fuels. It is interesting to note that ceria was always used in all the three strategies. Ceria-based oxygen ion conductors are effective in carbon removal and hydrocarbon reforming, because of their higher catalytic activity than YSZ (Trofarelli, 1996). For Strategy $a$, the two parameters under manipulation are the operating temperature and the current (or voltage). The operating temperature is usually within the range from 550 to 850°C. Otherwise, catastrophic carbon deposition on Ni reaction sites occurs and/or CO disproportionation takes place. Long-term exposure under the OCV condition, where carbon deposition is deemed to be most severe, should be avoided for Ni-cermets fed with hydrocarbon fuels. Carbon deposition could also be somewhat suppressed under current loading, as oxygen ions pumped from the cathode side might remove carbonaceous compounds if deposited. The addition of noble metals was the common practice of Strategy $b$. It utilized the excellent catalytic activity of noble metals for hydrocarbon reforming (Saeki et al., 1994; Babaei et al., 2009; Babaei and Jiang, 2010). Pd and Ru are most commonly used in SOFCs because of relatively low cost than other noble metals. For Strategy $c$, a catalyst layer (or disc) is applied above the anode layer for the purpose of dry reforming of hydrocarbon fuels. Typical catalyst discs are composed of two Ru-ceria layers on both sides of porous support (Zhan and Barnett, 2005a), or Ir-ceria pressed onto Ni–YSZ anodes (Klein et al., 2008b). Carbon deposition is thus avoided because it is hydrogen-rich gases instead of hydrocarbon fuels that reach onto the anode surface.

Though SOFC with Ni–cermet anodes has been successfully run on hydrocarbon fuels in laboratory-scale, the extension to industry-scale application is still uncertain. Carbon deposition on Ni-cermet anodes is irreversible so that any unforeseeable accident will result in catastrophic cell failure. In addition, three phase boundaries (TPBs) usually extend not more than 10 µm from the electrolyte interface to composite anode. Strategies employing high $O^{2-}$ flux through the electrolyte for carbon removal cease to function for the regions outside TPBs. This implies that Strategy $a$ cannot benefit the non-reactive areas of the Ni–cermet anodes. The protection of the anode strictly relies on the steam and CO$_2$ reforming. While it may be possible to maintain
reasonable conversions and high steam concentrations over small-scale, it becomes rather challenging for anode-supported large cells.

### 2.3 Copper cermets

The effectiveness of carbon suppression in Ni-cermet anodes, as introduced in Chapter 2.2, is still on doubt. For cermet anodes, an alternative way to avoiding carbon deposition is to replace Ni with metals that are poor catalysts for carbon formation. The metal is supposed to be stable at high operating temperatures and oxygen partial pressures (pO$_2$) of the anode atmosphere. Metals that would be oxidized by steam and metals with low melting temperatures are, therefore, excluded. Precious metals are beyond the consideration because of their high cost. As a compromise of the above two criteria Cu seems to be a good choice. Cu does not catalyze carbon formation and is stable at typical SOFC pO$_2$ range. One of the disadvantages of Cu ($T_m = 1083^\circ$C) is its low melting temperature as compared with Ni ($T_m = 1453^\circ$C). This implies that Cu may be of poor thermal stability during the SOFC operation. Another issue comes from the anode fabrication procedures. As the melting temperatures of CuO ($T_m = 1201^\circ$C) and Cu$_2$O ($T_m = 1235^\circ$C) are much lower than NiO ($T_m = 1984^\circ$C), conventional firing processes are not applicable to Cu–cermet. Furthermore, it is necessary to incorporate separated oxidation catalysts in order to achieve satisfactory electrode performance, because Cu is a very poor fuel oxidation catalyst.

Since 2000, Gorte et al. at University of Pennsylvania had pioneered Cu-based cermets for direct hydrocarbon utilization (Park et al., 2000). They developed a method for high temperature sintering of electrolyte and low temperature sintering of electrode (Park et al., 2001). The fabrication method they used is called “dual tape-casting”. In the tape casting, electrolyte powders (mostly YSZ) are mixed with various organic additives that work as binder, plasticizer, surfactants, etc. The slurry is casted into tapes over the carrier and is then slowly dried. A second layer with pore formers (e.g. graphite, PMMA, starch) is spread onto the first layer. Afterwards, the organic species and pore formers were then burnt out, leaving porous YSZ layer as electrode skeleton and dense YSZ layer as electrolyte. Cu and ceria are impregnated into the porous YSZ layer from relevant metal nitrate solutions. It is fired at right temperatures for decomposition and electrode sintering. Cell performance of Cu–YSZ anodes was poor
Table 2-2 Single cell SOFCs with Cu–cermet anodes fed with hydrocarbon fuels.

<table>
<thead>
<tr>
<th>Cell configuration</th>
<th>Fuel</th>
<th>$P_{\text{max}}$ (W/cm$^2$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu-based anodes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu–ceria–YSZ/YSZ(60 µm)/LSM–YSZ</td>
<td>C$<em>4$H$</em>{10}$</td>
<td>0.13</td>
<td>(McIntosh et al., 2002)</td>
</tr>
<tr>
<td></td>
<td>C$_3$H$_8$ (diluted by N$_2$)</td>
<td>0.1</td>
<td>(Kim et al., 2001)</td>
</tr>
<tr>
<td></td>
<td>Vegetable oil</td>
<td>0.06</td>
<td>(Zhou et al., 2007)</td>
</tr>
<tr>
<td></td>
<td>C$<em>4$H$</em>{10}$ (preoxidized in O$_2$)</td>
<td>0.12</td>
<td>(Costa-Nunes et al., 2003)</td>
</tr>
<tr>
<td>Cu–ceria–YSZ/Ni–ScSZ/ScSZ/PCM</td>
<td>C$_2$H$_5$OH</td>
<td>0.41$^b$</td>
<td>(Ye et al., 2009)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.31$^c$</td>
<td></td>
</tr>
<tr>
<td>Cu–ceria–LSGM/LSGM(440 µm)/LSCF–LSGM</td>
<td>H$_2$</td>
<td>0.22</td>
<td>(An et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>C$<em>4$H$</em>{10}$</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Cu–YSZ-ceria/YSZ/LSM–YSZ</td>
<td>C$_3$H$_8$</td>
<td>0.05</td>
<td>(Zhan and Lee, 2010)</td>
</tr>
<tr>
<td>Cu–ceria–LDC/LSGM/SCF</td>
<td>CH$_4$</td>
<td>0.1$^b$</td>
<td>(Bi and Zhu, 2009)</td>
</tr>
<tr>
<td>Cu–ceria–SDC/SDC (340 µm)/LSCF–SDC</td>
<td>C$<em>4$H$</em>{10}$</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Cu–ceria–LSGM/LSGM (440µm)/LSCF–LSGM</td>
<td></td>
<td>0.08</td>
<td>(Lu et al., 2004)</td>
</tr>
<tr>
<td>Cu–ceria–ScSZ/ScSZ(60 µm)/LSCF–ScSZ</td>
<td>C$<em>4$H$</em>{10}$</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td><strong>Cu-based anodes decorated with precious metals</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu–Pd–ceria–YSZ/YSZ(100 µm)/LSM–YSZ</td>
<td>CH$_4$</td>
<td>0.28</td>
<td>(McIntosh et al., 2003)</td>
</tr>
<tr>
<td></td>
<td>C$<em>4$H$</em>{10}$</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Cu–Co(Ru)–Zr$<em>{0.35}$Ce$</em>{0.65}$O$_{2-δ}$/YSZ (50 µm)/LSM</td>
<td>C$_2$H$_5$OH</td>
<td>0.45$^b$</td>
<td>(Cimenti and Hill, 2010)</td>
</tr>
<tr>
<td><strong>Alloyed Cu-based anodes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu–Ni–ceria–YSZ/YSZ(60 µm)/LSM–YSZ</td>
<td>CH$_4$</td>
<td>0.3$^b$</td>
<td>(Kim et al., 2002)</td>
</tr>
<tr>
<td></td>
<td>C$<em>4$H$</em>{10}$</td>
<td>0.12</td>
<td>(Lee et al., 2004)</td>
</tr>
<tr>
<td>Cu–Co–ceria–YSZ/YSZ(50 µm)/LSM–YSZ</td>
<td>CH$_4$</td>
<td>0.25$^b$</td>
<td>(Lee et al., 2005)</td>
</tr>
<tr>
<td></td>
<td>C$<em>4$H$</em>{10}$</td>
<td>0.14</td>
<td>(Lee et al., 2004)</td>
</tr>
<tr>
<td>Cu–Co–ceria/YSZ/LSM</td>
<td>CH$_4$(80%–H$_2$)</td>
<td>0.09$^c$</td>
<td>(Fuerte et al., 2011)</td>
</tr>
</tbody>
</table>

$^a$: Testing temperature is 700 ºC without explicit specifications; $^b$: 800 ºC; $^c$: 750 ºC.
even when Cu was alloyed with Ni (Kim et al., 2002). Ceria, an oxide with fast oxygen exchange kinetics, was incorporated as the fuel oxidation catalyst. Cu-ceria-YSZ anodes had been proven to be well competent for hydrocarbon utilizations (Table 2-2). Anyway, SOFCs with ceria as electrocatalyst alone is not so satisfactory. That is the reason why small amount of precious metals, e.g. Pd, were always incorporated.

Cu–cermet anodes are usually operated at intermediate temperatures. High temperatures above 800 °C are strongly prohibited with regard to the low melting temperature of Cu. After initial reduction at 700°C the Cu within the porous YSZ layer forms a electronically percolating network. After annealing at 900°C for 5 h, unfortunately, it had been sintered into unconnected particles. The Cu sintering rendered significant increase of the ohmic resistance during fuel cell operations (Gross et al., 2007b). A common practice to solve this problem is to incorporate more refractory metals into Cu cermets. As shown in Table 2-2, bimetallic electrodes such as Cu–Ni, Cu–Cr, and Cu–Co had been evaluated in terms of their effectiveness on the improvement of thermal stability. Ni was reported to loss catalytic activity after alloying with Cu. Cu–Ni cermet anodes containing more than 20 % Ni was prone to carbon deposition. The carbon cannot be removed during the loading conditions and inevitably led to cell failure (Lee et al., 2004). Cu and Cr (T\text{m} = 1907 °C) is immiscible and Cr is not expected to catalyze carbon formation. As chromium oxide was unable to be reduced in anodic environment, Cu–Cr based cermets were prepared via Cr electrodeposition onto the anode. Cu–Cr cermet anodes were tested in 80% H\textsubscript{2}–20% H\textsubscript{2}O to evaluate the redox stability in anodic environment. It was found that the Cr in Cu–Cr cermets was completely oxidized after 20-hour exposure and at 900°C (Gross et al., 2007b).

Cu–Co bimetallic anodes seem to have better performance than that of Cu–Ni and Cu–Cr. Co (T\text{m} = 1907 °C) remains reduced under similar conditions as that of Ni. Unlike Ni, Co has limited solubility with Cu at SOFC operating temperatures. Free-energy calculations indicated that Cu was segregated on to the surface of Co (Kim et al., 2000). Cu–Co cermet anodes can be prepared by co-impregnation or electrodeposition. X-ray photoelectron spectroscopy (XPS) results showed that Cu is
segregated onto the surface to form a Cu over-layer after the annealing at 600°C (Lee et al., 2005). Carbon deposition is thus suppressed because the inert Cu is segregated onto the surface. Thermal stability was also improved as a result of Co incorporation. Bimetallic anode containing 5 % electrodeposited Co and 13 % Cu did not lose its conductivity after annealing at 900°C for 50 h in wet H₂. Co-cermet anodes formed large amounts of carbon when exposed to dry methane at 800°C for 3 h, the Co-plated Cu electrode showed no observable carbon formation under the same conditions (Gross et al., 2007a).

2.4 Oxides

The limitations of cermet anodes have led to the development of oxide anode materials. Oxide anode materials are desirable to be mixed ionic and electronic conductors (MIECs), which both have high electronic conductivity and ionic conductivity. The electrochemical oxidation is then not confined to TPBs but extends to the whole oxide anode surfaces. To be a practical oxide anode material involves many more considerations besides the catalytic activity. Steele et al. proposed several empirical criteria of oxide anodes for complete methane oxidation (Steele et al., 1990). These criteria included:

1) Good electronic conductivity (preferably > 100 S/cm) at anode operating potentials (-0.7 to -0.9V). Probably n-type behaviour preferable.

2) Predominant anion lattice disorder to enhance oxygen diffusion coefficients.

3) High values for oxygen surface exchange kinetics.

4) Fabrication of porous adherent films with minimal processing problems.

5) Compatibility with solid electrolyte.

Until now there is few oxides meet all the above criteria. Ni-, Co- and Fe- based oxides are seldom used as SOFC anodes, as they easily precipitate from the corresponding oxides in reducing conditions. Typical redox couples in SOFC anode materials are Cr⁴⁺/Cr³⁺, Ti⁵⁺/Ti⁴⁺, Mn⁴⁺/Mn³⁺, Ce⁴⁺/Ce³⁺, Mo⁵⁺/Mo⁴⁺, V⁴⁺/V³⁺, Nb⁴⁺/Nb³⁺, etc. The n-type conducting oxides are favourable because the conductivity increases when the pO₂ decreases. Based on the material structure, the explored oxide anodes can be briefly classified in fluorite, rutile, tungsten bronze, pyrochlore, perovskite, and double perovskite (Table 2-3). Oxide materials, with the highlights on perovskite and double perovskite, are
reviewed in this chapter.

2.4.1 Fluorite

2.4.1.1 Zirconia-based

Coordination numbers of cation and anion in fluorite structure are 8 and 4, respectively. Low valence cations (3+ or 2+ cations) are doped into the fluorite lattice to create oxygen vacancies. At elevated temperatures the oxygen vacancies thus created may become mobile and produce ionic conductivity. Further introduction of multivalent elements could lead to mixed electronic and ionic conductor (MIEC) behaviours. Take ceria and zirconia as a comparison. Ce$^{4+}$ could be partially reduced to Ce$^{3+}$, thus doped or undoped ceria becomes MIEC at low pO$_2$. While the electronic conduction can be induced into ceria, it is difficult to reduce Zr$^{4+}$ to Zr$^{3+}$ even at low pO$_2$. The electronic conduction of zirconia has to be introduced by dopants. For this purpose many types of transition metal oxides, such as TiO$_2$, MnO$_x$, Tb$_4$O$_7$, Nb$_2$O$_5$ and WO$_3$, can be doped into zirconia (Huang and Weppner, 1996). The electronic conductivity of these materials under reducing atmosphere is, however, not high enough for SOFC anode applications.

The first row transition elements exhibit the solubility in zirconia varying from case to case, among which Ti and Nb show highest solubility. Ti, the reduction of which leads to n-type electronic conduction, has high solubility in YSZ. At 1500°C, up to 18 at% Ti$^{4+}$ can be dissolved into cubic fluorite ZrO$_2$–(7–10 at%)Y$_2$O$_3$ structure. A large region of TiO$_2$–Y$_2$O$_3$–ZrO$_2$ system had high vacancy concentrations up to 16%, e.g., Zr$_{0.21}$Y$_{0.62}$Ti$_{0.17}$O$_{1.69}$ (Feighery et al., 1999). Electronic conduction of Ti-doped zirconia was attributed to a Ti$^{4+}$/Ti$^{3+}$ small polaron hopping mechanism (Swider and Worrell, 1996). Modest electrode performance had been observed for Ti-doped zirconia anodes (Mantzouris et al., 2007). The soluble limit of Nb into zirconia was as high as 25%. The ionic conductivity of Nb-doped zirconia was rather negligible—10$^{-3}$ to 10$^{-5}$ S/cm at typical SOFC temperatures. The electronic conductivity was low because Nb was difficult to be reduced (Fagg et al., 2003a). In$_2$O$_3$ and ZrO$_2$ may form a complete solid solution at high temperatures. The ionic conductivity of 25 at% In doped ZrO$_2$ was not low ($\sim$10$^{-1}$ S/cm at 1000°C), but the material was unstable at low pO$_2$ and at high temperatures (Sasaki et al., 1994). The solubility of Fe$_2$O$_3$ in ZrO$_2$ was
about 4 at% at high temperatures (Matsui and Takigawa, 1990). 20 mol% Fe₂O₃ could be dissolved into zirconia, but zirconia with such high Fe₂O₃ content was not stable after fired at 800°C (Cao et al., 2000). The solubility of MnO in ZrO₂ was around 12 at% at high temperature, though high value up to 30 mol% had been reported (Kim and Choi, 2000). The solubility of NiO in YSZ was only about 2 at% at 1600°C (Park and Choi, 1999).

To summarize, Mn, Fe, and Ni are unsuitable dopants of zirconia. Small solubility of Fe and Ni in zirconia makes them difficult to form an effective percolation path for electron transfer. Mn-doped YSZ is likely to be a mixed p-type conductor with dominant ionic conduction at low pO₂, usually observed in various Mn-containing materials. Ti-doped ZrO₂ is more favourable, but the Ti-content is still not high enough to generate an effective percolation network for electron transfer. Nb and In also have large solubility in ZrO₂, but the solid solutions suffer structural change in typical SOFC anodic environment. Due to the high level of doping, these zirconia-based oxides exhibit fairly low ionic conductivity (<0.01S/cm). Despite of the incorporation of high-level reducible ions into ZrO₂, the electronic conductivity of doped zirconia is still quite low (<0.1 S/cm). Selected conductivity values of doped zirconia are given in Table 2-3 for reference.

2.4.1.2 Ceria-based

Ceria-based cermets, such as Cu-ceria-YSZ as introduced in Chapter 2.3, are good SOFC anodes for direct hydrocarbon utilization. In contrast, what introduced in Chapter 2.4.1.2 are pure ceria-based oxides as SOFC anodes. Doped or undoped ceria themselves could be SOFC anodes if considerable electronic conduction can be introduced into the fluorite lattice. The Ce ion of ceria is reduced from Ce⁴⁺ to Ce³⁺ in SOFC anode environments, thus resulting in the electronic conduction. Alternatively, the cation doping can also create electronic conduction in ceria. The conductivity of some doped ceria are shown in Table 2-3. High conductivity of gadolinia- and samaria-doped ceria is attributed to the good match of the ionic radii between the dopant ions and Ce ions. La-doped ceria had been synthesised via co-precipitation method, where La³⁺ were thought to be distributed randomly (Suda et al., 2006). Although the conductivity of Tb-doped ceria is lower than those with other dopants, there might be
advantageous effects of the Tb$^{4+}$/Tb$^{3+}$ redox couple in real anodic conditions (Martinez-Arias et al., 2005). The conductivity of doped ceria is relatively low but surprisingly doped ceria anodes always show modest performance even without the electronic conductor within the anode. Gadolinia doped ceria has shown good catalytic activity for the oxidation of methane with little or no carbon deposition. Modest performance was achieved for Ce$_{0.6}$Gd$_{0.4}$O$_{2-δ}$ exposed to H$_2$ instead of CH$_4$ (Marina and Mogensen, 1999; Marina et al., 1999). Anyway ceria-based cermet anodes are preferable over single phase ceria anodes, as long as the electrode conductivity is concerned.

2.4.2 Rutile

Rutile (TiO$_2$) has a tetragonal structure with a distorted hexagonal close packed anion arraying with the octahedral vacancy sites occupied by cations. Edge-sharing octahedra in rutile can facilitate electron transfer and results in high electronic conductivity (Table 2-3). Oxygen vacancies might also be introduced into the rutile lattice. However, the mobility of oxygen vacancies in rutile, if existed, is relatively low as comparing to many other oxides. The reason is that the oxygen ion octahedra have to be rotated if the oxygen vacancies are to jump from one octahedron to the next. The rotation of edge-sharing octahedra in rutile is much harder than that of corner-sharing octahedra in perovskite. This might be the reason why TiO$_2$ is a poor ionic conductor. NbO$_2$, the reduced form of Nb$_2$O$_5$, was completely miscible with TiO$_2$ from 900 to 1300°C. The conductivity of TiO$_2$–Nb$_2$O$_5$ solid solution reached $\sim$10$^2$ S/cm at 1000°C, but surprisingly its reaction kinetics was very poor both in H$_2$ and CH$_4$ (Table 2-3). The thermal expansion coefficient (TEC) of reduced TiO$_2$–NbO$_2$ was 2.3 ×10$^{-6}$/K – a quarter of that of YSZ (Tao and Irvine, 2004b). The incorporation of Cr$_2$O$_3$ into TiO$_2$–NbO$_2$ renders it redox stable but compromises the conductivity (Lashtabeg et al., 2009). These drawbacks somewhat inhibit rutile-based oxides as suitable candidates for SOFC anodes.

2.4.3 Tungsten bronze

Oxides with the general formula A$_2$BM$_5$O$_{15}$ (with M= Nb, Ta, Mo, W; A and B= Ba, Na, etc.) show the tungsten bronze structure. It can be obtained from the perovskite by rotating some of the MO$_6$ octahedra. In so doing 40% of the large cation sites (A2 sites)
are increased in size from tetra-capped square prisms to penta-capped pentagonal prisms, 20% remains essentially unchanged (A1 site), and the remaining 40% of the sites are decreased in size (C site). The formula may be written as $A_{0.6}BO_3$ when the small size A-sites are left empty (Tao and Irvine, 2004b). The distortion of the octahedra means that some B-O bonds is extended and some are short than the average. The connection of the short B-O bond may supply a percolation path for charge transfer, possibly leading to high electronic conductivity.

The conductivity of tungsten bronze in reducing environment is about four orders higher than that in air. Among the various $(Ba, Sr, Ca, La)_{0.6}M_xNb_{1-x}O_3$ ($M = Ni, Mg, Mn, Fe, Cr, In, Sn)$ tungsten bronzes, $Sr_{0.2}Ba_{0.4}Ti_{0.2}Nb_{0.8}O_3$ exhibits the highest conductivity (10 S/cm at $pO_2 = 10^{-20}$ bar and at 930°C), as shown in Table 2-3. In contrast, the conductivity in air is only around $10^{-3}$ S/cm at 930°C, as oxygen vacancies are generated only under reducing conditions. The conductivity increases with decreasing $pO_2$ and reaches 1–10 S/cm at $pO_2 < 10^{-17}$ bar. The electrochemical performance of tungsten bronze anodes is poor. Polarization resistance ($R_p$) of $(Sr_{1-x}Ba_x)_{0.6}Ti_{0.2}Nb_{0.8}O_3-\delta$ is around 28 Ω cm$^2$ at 930 °C (Kaiser et al., 2000). The introduction of Mn into the tungsten bronze structure is supposed to reduce $R_p$. Even though, the corresponding reaction kinetics is still inferior to fluorite oxides, such as doped zirconia and doped ceria. In addition, the TEC of these compounds (e.g., $6.7\times10^{-6}$ K$^{-1}$ for $Sr_{0.2}Ba_{0.4}Ti_{0.2}Nb_{0.8}O_{3-\delta}$) are significantly lower than that of zirconia (Kaiser et al., 2000). The TEC mismatch of these tungsten bronze oxides with YSZ poses sheer problems.

**2.4.4 Pyrochlore**

Pyrochlore-type oxides, $A_2B_2O_7$, can be derived from fluorite by removing 1/8 of the oxygen ions, ordering the two cations, and ordering the oxygen vacancies. $A_2B_2O_7$ pyrochlore structure is formed of the cation radius of the two cations falls into a specific range. Readers who are interested in structural studies on pyrochlore are recommended to study Wuensch’s exhaustive review on $A_2B_2O_7$ (A= Y, Gd, Sc, Yb, Ca, etc.; B= Sn, Ti, Zr, etc.) structures (Wuensch et al., 2000). Substituting B sites with larger B’ ions progressively drive the pyrochlore structure to complete disorder, producing oxygen ion conductivity greater than $10^{-2}$ S/cm at 1000°C. The pyrochlore, $Gd_2Ti_2O_7$ (GT), were considered as potential SOFC anodes. Both the magnitude and the type of conduction
(ionic and/or electronic) was found to be influenced by dopant size, site location (A or B cation sublattice) and net dopant density (Kramer et al., 1994). Ca doping into the A site was found to increase the ionic conductivity up to two orders of magnitude. In contrast, other alkaline earth dopants (Sr and Mg) induced a drop in ionic and an enhancement in electronic conductivity due to the large dopant-host size mismatch.

High ionic conductivity and mixed ionic and electronic conductivity pyrochlore had been reported, such as (Gd$_{0.98}$Ca$_{0.02}$)$_2$Ti$_2$O$_7$. It could be a potential parent phase. $R_p$ as low as 0.2 $\Omega$ cm$^2$ at 950 $^\circ$C had been reported for pyrochlore anodes exposed to H$_2$S-containing hydrogen atmosphere (Zha et al., 2005a). Table 2-3 lists doped pyrochlore for potential SOFC anode applications, among which Mo doped titanate pyrochlore was especially promising. The Gd$_2$Ti$_2$O$_7$–Gd$_2$Mo$_2$O$_7$ solid solution, with the advantage of stabilizing Gd$_2$Mo$_2$O$_7$ at high pO$_2$, is the popular parent pyrochlore structure. These solid solutions do exhibit high electrical conductivity, but they are stable only within a certain pO$_2$ range. The pO$_2$ boundary largely depends on the temperature. The Gd$_2$(Ti$_{1-x}$Mo$_x$)$_2$O$_7$ solid solution phase is, therefore, not a redox stable material at high temperatures. A chemical compatibility study between Gd$_2$(Ti$_{1-x}$Mo$_x$)$_2$O$_7$ and YSZ indicated no significant reactions in the reducing environment at 1000°C (Porat et al., 1997c; Porat et al., 1997b). So far, the studied pyrochlore phases are either redox unstable or poorly conducting. It needs more efforts to find an ideal redox stable mixed conductor in the pyrochlore category.

2.4.5 Perovskite

Perovskite is the name of the mineral CaTiO$_3$. Its structure consists of corner-shared TiO$_6$ octahedra with the large Ca$^{2+}$ situating at corners of the unit cell. More generally, ABO$_3$ compounds having structure based on this architecture are also called perovskite. The powerful perovskite structure can adapt considerable lattice mismatch between the (A–X) and (B–X) bond lengths, even in the cases that more than one A-site cation and/or M-site cation species are present. In addition, the large tolerance of atomic vacancies and the formation of intergrowth structures extend this family even further. Some perovskites can accommodate a large content of oxygen vacancies, thus making them as potential oxygen ion conductors. Perovskite always allows first-row transition metal ions to be introduced into the B-site lattices and rare-earth and lanthanoid ions into
A-site lattices. First-row transition metal ions usually exhibit multi-valence under different fuel atmospheres. This might represent the origin of high electronic conductivity if the electrons are well delocalized. Good ionic and mixed conductivity has been found in several perovskite oxides. A systematic review of the transport phenomena in perovskites had been given (Goodenough, 2004).

Perovskite covers the whole spectrum of SOFC components—electrolyte, anode, cathode, and interconnector. Single cells entirely based on perovskites had been demonstrated (Tao et al., 2005). Sr- and Mg-doped LaGaO$_3$ (LSGM) exhibit high oxygen ionic conductivity and are used as electrolyte materials (Haavik et al., 2004), though their mechanical strength and chemical stability is inferior to YSZ. Manganite, ferrite, and cobaltite perovskites have modest ionic but high electronic conductivity. They have been proven to be good SOFC cathode materials. Sr-doped LaMnO$_3$ and Sr-doped LaCo(Fe)O$_3$ are used as cathodes for HT-SOFC and IT-SOFC, respectively (Berenov et al., 2010; Laguna-Bercero et al., 2010). Doped lanthanum chromites, like Sr-doped LaCrO$_3$, are extensively used as interconnect materials. In contrast, not so many perovskites are competent for SOFC anode application, as far as the chemical stability in reducing environment and electrical conductivity are concerned. In Chapter 2.4.5.1 and 2.4.5.2, chromite and titanate single perovskites used as SOFC anodes are reviewed, respectively. Further discussions also cover double perovskites and Ruddlesden–Popper series that belong to an extended definition of perovskite.

2.4.5.1 Chromite
Lanthanum-chromite (LC)-based materials have been used as SOFC interconnect materials, where Sr and Ca are the typical dopants. The electrical conductivity of Sr-doped LaCO$_3$ (LSC) was around 20 S/cm in air but was decreased when exposed to reducing environments (Simner et al., 2000). A good TEC match between the LSC with YSZ is achieved by tailoring the Sr content of LSC. The sinterability of LSC to electrolyte (e.g., YSZ) is very poor so that it is essentially inert to fuel oxidation. Little or no reforming activity or direct oxidation of CH$_4$ had been observed on lanthanum chromites (Metcalfe and Baker, 1996). Anyway, this group of materials can be used as the parent material for SOFC anode application, as long as the excellent chemical stability of LSC is retained.
Chapter 2. Literature review

$R_p$ of bare Ca-doped LaCO$_3$ (LCC) was around 86 Ω cm$^2$ at 850°C in H$_2$. $R_p$ is reduced to 21 Ω cm$^2$ with 10% Mg doping in M-site, i.e. replacing Cr. $R_p$ can be further reduced to 5 Ω cm$^2$ in H$_2$ via 3% V doped into M site, but it was as high as 30 Ω cm$^2$ in CH$_4$ (Primdahl et al., 2001). Multivalent first row transition metals, such as Fe, Mn, Co, Ni, Ti, form redox couples that facilitate electron transfer when doped into LSC. Slight doping of Ru into LSC had also been attempted (Combemale et al., 2009). Promising results were reported for Fe, Ni and Co doped LSC. However, all of them cannot withstand the SOFC anodic environment for long time, either second phases form or metal precipitates from the perovskite structure. Ti and Mn are believed to be the more effective dopants than Fe, Co, and Ni in low pO$_2$ conditions.

The conductivity of Ti-doped LSC (LSCT) was around $10^{-4}$–$10^{-2}$ S/cm, much lower than 0.1 S/cm that was required for the SOFC electrode application (Steele et al., 1990). $R_p$ of LSCT, with Ti content in LSCT in the range from 20% to 50%, was higher than 40 Ω cm$^2$ in H$_2$ at 857°C (Pudmich et al., 2000). Mn is supposed to be another promising dopant, as LaMnO$_3$-based oxides are good cathode materials for HT-SOFCs. The Mn$^{3+}$/Mn$^{4+}$ redox couple seems to have good electrochemical reaction kinetics. However, 20% Mn doping in LSC did not show significant improvement of electrode performance. $R_p$ of La$_{0.8}$Sr$_{0.2}$Cr$_{0.8}$Mn$_{0.2}$O$_3$ was still as high as 50–70 Ω cm$^2$ in H$_2$ at 850°C (Vernoux et al., 2001). Surprisingly, good electrochemical performance was achieved by increasing the Mn doping to 50% in LSC, i.e., La$_{0.8}$Sr$_{0.2}$Cr$_{0.5}$Mn$_{0.5}$O$_3$ (LSCM). LSCM exhibited comparable electrochemical performance to Ni–YSZ cermets. It was stable both in fuel and air conditions and showed stable electrode performance in methane. The electrode polarization resistance approached 0.8 Ω cm$^2$ at 900°C in wet CH$_4$ (Tao and Irvine, 2003). Isotopic exchange experiments indicated that the oxygen tracer diffusion coefficient ($D^*$) of LSCM under oxidising and reducing conditions at 1000 ºC were $4\times 10^{-10}$ cm$^2$/s and $3\times 10^{-8}$ cm$^2$/s, respectively. Under the same conditions the surface exchange coefficient ($k^*$) were $5\times 10^{-8}$ cm/s and $4\times 10^{-8}$ cm/s, respectively (Raj et al., 2006). The electrode performance of LSCM can be further improved via electrode engineering of composite electrodes and the impregnation methods (Jiang et al., 2006a; Jiang et al., 2006b; Lu and Zhu, 2007). One of the
drawbacks of LSCM is its low electronic conductivity. The total conductivity of LSCM in air is less than 30 S/cm and not higher than 1 S/cm in the reducing environment (Jiang et al., 2008). It implies that the current collection comes to be an issue for fuel cells with LSCM anode.

2.4.5.2 Titanate

Titanates that are stable in reducing conditions are another group of potential SOFC anode materials. The most popular parent structure is strontium titanate (SrTiO$_3$). It is n-type conductor when donor-doped (e.g. La$^{3+}$, Y$^{3+}$) and/or exposed to reducing atmospheres. La$^{3+}$ is an appropriate donor dopant because of similar ionic radii with Sr$^{2+}$. The initial electrical conductivity of La$_x$Sr$_{1-x}$TiO$_3$ (LST) strongly depends on the pO$_2$ during the sample sintering. The samples sintered in air exhibited an electrical conductivity on the order of magnitude of 10$^1$ S/cm. In contrast, LST that was sintered in hydrogen at 1650°C showed conductivity in the order of magnitude of 10$^2$ S/cm under typical SOFC operating temperatures (Marina et al., 2002). LST could be used as the anode support due to the high electronic conductivity (Pillai et al., 2008; Ma et al., 2010). The conductivity of LST increases together with increasing La concentration but levels off at the La content around 0.4. Depending on the percentage of La dopant the conductivity of LST can reach ~10$^2$ S/cm. At low pO$_2$ the electronic conduction is reinforced when Ti$^{4+}$ is reduced to Ti$^{3+}$. Meanwhile, oxygen vacancies are generated because of the electroneutrality. This is the reason why the conductivity LST in reducing conditions is much higher than that in air. LST has been doped with transition metals (Ni, Co, Cu, Cr and Fe) and Ce, among which Ce seems to be the most effective one (Cumming et al., 2011). LST is also compatible to YSZ even when subjected to oxidation/reduction cycling.

LST can also form complex perovskite phases if with oxygen excess. La$_2$Sr$_4$Ti$_6$O$_{19-\delta}$ and its derivatives, which has a unit cell consisting of six ordered perovskite primate cells and with about 1/19 oxygen excess, had been regarded as potential anode for SOFC fed with hydrocarbons. Their conductivities strongly depend on the oxygen stoichiometry. They exhibit n-type conduction behaviour when more Ti$^{3+}$ is generated. While the conductivity was negligible in air, it could be increased to ~10$^2$ S/cm in 5% H$_2$/Ar atmosphere at 900°C. An anodic $R_p$ of 8.93 $\Omega$ cm$^2$ and $P_{max}$ of 0.02 W cm$^2$ were
achieved in wet CH\textsubscript{4} when using pure La\textsubscript{2}Sr\textsubscript{4}Ti\textsubscript{6}O\textsubscript{19.5} as anode (Canales-Vazquez \textit{et al.}, 2003). La\textsubscript{4}Sr\textsubscript{n-4}Ti\textsubscript{n}O\textsubscript{3n+2} \((n > 7)\) are layered phases and have oxygen planes in the form of crystallographic shears joining octahedron blocks. These planes became more sporadic with increasing \(n\) (i.e., decrease of oxygen content) until they were no longer in crystallographic features. It finally resulted in local oxygen-rich defects randomly distributed within a perovskite framework when \(n > 11\). Optimized titanates with disordered oxygen defects were proven to be excellent SOFC anode materials. For SOFCs using the engineered La\textsubscript{4}Sr\textsubscript{8}Ti\textsubscript{11}Mn\textsubscript{0.5}Ga\textsubscript{0.5}O\textsubscript{37.5}, the \(n = 12\) member in the La\textsubscript{4}Sr\textsubscript{n-4}Ti\textsubscript{n}O\textsubscript{3n+2} series, as anode, high OCV and very low \(R_p\) both in H\textsubscript{2} and CH\textsubscript{4} were reported (Ruiz-Morales \textit{et al.}, 2007).

The electrode performance was greatly improved by replacing 1/12 Ti by Mn in La\textsubscript{4}Sr\textsubscript{n-4}Ti\textsubscript{n}O\textsubscript{3n+2} series \((n = 12)\). For SOFCs with La\textsubscript{4}Sr\textsubscript{8}Ti\textsubscript{11}Mn\textsubscript{0.5}Ga\textsubscript{0.5}O\textsubscript{37.5} composite anode, \(R_p\) was as low as 0.7 \(\Omega\) cm\textsuperscript{2} in wet CH\textsubscript{4} and at 950°C. The overpotential was lower than 0.1 V at a drawn current density of 0.6 A/cm\textsuperscript{2} (Ovalle \textit{et al.}, 2006). Comparable cell performance was achieved with a large replacement of Ti with Mn, such as La\textsubscript{0.4}Sr\textsubscript{0.6}Ti\textsubscript{0.4}Mn\textsubscript{0.6}O\textsubscript{3-δ} (Fu \textit{et al.}, 2006). \(R_p\) around 0.57 \(\Omega\) cm\textsuperscript{2} at 900°C in CH\textsubscript{4} was achieved by sophisticated doping with Sc or Ga into Ti site (Table 2-3). However, the chemical expansion of these materials is irreversible during the redox cycling, though the expansion itself is not high. This property would restrict their applications in electrolyte-supported and/or small-sized SOFCs, such as the integrated planar-type SOFC.

An unusual increase of electrical conductivity was observed in Y-doped SrTiO\textsubscript{3}. The electrical conductivity of Sr\textsubscript{1-1.5x}Y\textsubscript{x}TiO\textsubscript{3-δ} increased with increasing yttrium level and reached a maximum value of 64 S/cm with \(x = 0.08\) at 800°C (Hui and Petric, 2002a). Its conductivity was influenced by both the oxygen partial pressure of the reducing atmosphere and the saturation level of the dopant. It also underwent a transition from p-type to n-type conduction under decreased pO\textsubscript{2}. The conductivity was increased from 64 S/cm for the charge-neutral Sr\textsubscript{0.88}Y\textsubscript{0.08}TiO\textsubscript{3-δ} composition to a maximum of 82 S/cm for Sr\textsubscript{0.86}Y\textsubscript{0.08}TiO\textsubscript{3-δ} at 800°C. However, cell performance with optimized Y-doped SrTiO\textsubscript{3} anodes was still not higher than 0.05 W/cm\textsuperscript{2} in wet H\textsubscript{2} (Hui and Petric,
2.4.6 Double perovskite

Double perovskites contain different B-site cations that are ordered. The degree of cation order strongly influences the oxygen self-diffusion in double perovskites such as GdBaCo$_2$O$_{5+δ}$ (Parfitt et al., 2011). Early results indicated that SrCu$_{0.4}$Nb$_{0.6}$O$_{2.9}$ was not stable in H$_2$ as metallic Cu precipitated from the double perovskite structure (Tao and Irvine, 2002b). Sr$_2$Mn$_{0.8}$Nb$_{1.2}$O$_{6-δ}$ had a total conductivity of 0.36 S/cm and exhibited p-type behaviour in low pO$_2$ (Tao and Irvine, 2002a). Replacing Mn and Nb with Mg and Mo, Sr$_2$Mg$_{1-x}$Mo$_x$O$_{6-δ}$ (SMMO) seemed to be a good material for hydrocarbon utilization with modest sulphur tolerance. The conductivity of SMMO reached 10 S/cm at 800°C in H$_2$ and CH$_4$, and the system gave satisfactory anode performance in H$_2$ and CH$_4$ as well as moderate sulphur tolerance (Huang et al., 2006b). With 300 mm-thick LSGM as electrolyte and SrCo$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ as cathode, $P_{\text{max}}$ of single cells could reach 0.84 W/cm$^2$ and 0.45W/cm$^2$ at 800°C and 700°C in H$_2$, respectively. $P_{\text{max}}$ was around 0.44 W/cm$^2$ and 0.34 W/cm$^2$ in dry and wet CH$_4$ at 800°C. The sulphur tolerance of SMMO enabled the use of natural gas as fuel. Single SOFCs with SMMO anodes showed negligible performance degradation up to 50 power cycles (Huang et al., 2006c). La-substituted SMMO, i.e. Sr$_{2-x}$La$_x$MgMoO$_{6-δ}$ (0.6≤x≤0.8), showed better performance than SMMO. Differential scanning calorimetry (DSC) results showed that SMMO underwent phase transition at 275 ºC in air. The phase transition, however, did not occur if SMMO was exposed to wet H$_2$ (Marrero-Lopez et al., 2009). One of the issues of Mo-containing oxides is that Mo might easily diffuse to other cell components (Marrero-López et al., 2007). Therefore, the long-term stability of SOFCs using Mo-containing anodes is of concern. In addition, SMMO reacts with the three major SOFC electrolyte materials, i.e. YSZ, GDC, and La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-δ}$ above 1000 ºC, among which the reaction with YSZ is most severe (Marrero-Lopez et al., 2010).

Various doping approaches of SMMO had been reported in literature, e.g. Co (Zhang et al., 2011), Fe (Xiao et al., 2010; Liu et al., 2010b), and Ni (Huang et al., 2009) replacing Mg and Mo, La (Ji et al., 2007) and Ca and Ba (Zhang et al., 2010b)
replacing Sr. The electronic conductivity seem to be improved by replacing Mg with Fe in the double perovskite structure. The conductivity of Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_{6-\delta}$ (SFM) reached 300–600 S/cm in air and hydrogen. Surprisingly, however, that both positive (Liu et al., 2010b) and negative temperature (Xiao et al., 2010) effects had been observed in Fe-doped SMMO. Generally speaking, the conductivity of SMMO and its derivatives are in the range of several to hundreds of S/cm for various doped SMMO (Table 2-3). Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_{6-\delta}$ (Liu et al., 2010b) showed $P_{\text{max}}$ around 0.1 W/cm$^2$ at 850 °C in wet CH$_4$. In comparison, much higher $P_{\text{max}}$ had been reported to be 0.55, 0.57, and 0.23, for Sr$_{1.2}$La$_{0.8}$MgMoO$_{6-\delta}$ (Ji et al., 2007), Sr$_2$CoMoO$_{6-\delta}$, Sr$_2$NiMoO$_{6-\delta}$ at 800 °C and in wet CH$_4$, respectively. More conductivity and electrode performance results are shown in Table 2-3.

Table 2-3  Conductivity and electrochemical properties of selected conducting oxides as SOFC anodes (Table modified from Ref. (Jiang and Chan, 2004))

<table>
<thead>
<tr>
<th>Composition</th>
<th>Electrical conductivity (S/cm)</th>
<th>Polarization resistance ($\Omega$ cm$^2$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature/reduced $^a$</td>
<td>Temperature/Oxidized $^b$</td>
<td>Temperature/hydrogen $^c$</td>
</tr>
<tr>
<td><strong>Fluorite-zirconia based</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y$<em>{0.20}$Ti$</em>{0.18}$Zr$<em>{0.62}$O$</em>{1.90}$</td>
<td>-</td>
<td>-</td>
<td>16.8 (932)</td>
</tr>
<tr>
<td>Y$<em>{0.16}$Zr$</em>{0.75}$Ti$<em>{0.13}$O$</em>{2-x}$</td>
<td>-</td>
<td>-</td>
<td>0.303 (900)</td>
</tr>
<tr>
<td>Y$<em>{0.11}$Zr$</em>{0.75}$Ti$<em>{0.13}$O$</em>{2-x}$</td>
<td>-</td>
<td>-</td>
<td>0.462 (900)</td>
</tr>
<tr>
<td>Y$<em>{0.22}$Zr$</em>{0.71}$Ti$<em>{0.07}$O$</em>{2-x}$</td>
<td>-</td>
<td>-</td>
<td>0.715 (900)</td>
</tr>
<tr>
<td>Y$<em>{0.24}$Zr$</em>{0.65}$Ti$<em>{0.35}$O$</em>{2-x}$</td>
<td>-</td>
<td>-</td>
<td>0.159 (900)</td>
</tr>
<tr>
<td>Y$<em>{0.087}$Zr$</em>{0.813}$Ti$<em>{0.13}$O$</em>{2-x}$</td>
<td>-</td>
<td>-</td>
<td>0.246 (900)</td>
</tr>
<tr>
<td>Y$<em>{0.165}$Zr$</em>{0.66}$Ti$<em>{0.17}$O$</em>{2-x}$</td>
<td>-</td>
<td>-</td>
<td>0.134 (900)</td>
</tr>
<tr>
<td>Y$<em>{0.165}$Zr$</em>{0.806}$Ti$<em>{0.094}$O$</em>{2-x}$</td>
<td>-</td>
<td>-</td>
<td>0.070 (900)</td>
</tr>
<tr>
<td>Ti$<em>{1/4}$Zr$</em>{0.786}$O$_{1.89}$</td>
<td>-</td>
<td>-</td>
<td>0.002–0.005 (900)</td>
</tr>
<tr>
<td><strong>Fluorite-ceria based</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.6}$Gd$</em>{0.4}$O$_2$</td>
<td>0.7 (800)</td>
<td>$10^{12}$–$10^{13}$ (800)</td>
<td>-</td>
</tr>
<tr>
<td>Ce$<em>{0.5}$Gd$</em>{0.4}$O$_2$</td>
<td>0.6 (800)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ce$<em>{0.5}$Gd$</em>{0.5}$O$_{2-\delta}$</td>
<td>0.16 (800)</td>
<td>8.6×10$^{-2}$ (800)</td>
<td>-</td>
</tr>
<tr>
<td>Ce$<em>{0.5}$Gd$</em>{0.4}$O$_{1.8}$</td>
<td>-</td>
<td>-</td>
<td>0.39 (1000)</td>
</tr>
<tr>
<td>Ce$<em>{0.5}$Gd$</em>{0.5}$O$_{1.9}$</td>
<td>~$10^{10}$ (800)</td>
<td>~$10^{13}$ (800)</td>
<td>-</td>
</tr>
<tr>
<td>Ce$<em>{0.5}$Sm$</em>{0.5}$O$_{1.9}$</td>
<td>~$10^{17}$ (800)</td>
<td>~$10^{13}$ (800)</td>
<td>-</td>
</tr>
<tr>
<td>Ce$_2$O$_2$</td>
<td>-</td>
<td>1.31×10$^{-6}$ (500)</td>
<td>-</td>
</tr>
</tbody>
</table>
### Tungsten bronze

| Composition | $\text{Ce}_0.95\text{La}_{0.05}\text{O}_{1.975}$ | $\text{Rutile}$ | $\text{Ba}$ | $\text{Ba}$ | $\text{Ba}$ | $\text{Ba}$ | $\text{Gd}$ | $\text{Gd}$ | $\text{Gd}$ | $\text{Sr}$ | $\text{Sr}$ | $\text{Sr}$ | $\text{Sr}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}$ | $\text{Ti}
### (ii) Titanate

| Formula | Pr$_{2}$Ce$_{0.2}$Zr$_{1.8}$O$_{7.6}$ | Pr$_{2}$Zr$_{0.7}$O$_{7.5}$ | Single perovskite
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01 (1000)</td>
<td>3×10$^{-3}$ (1000)</td>
<td>(Holtappels et al., 2000)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>2×10$^{-4}$ (1000)</th>
<th>6×10$^{-3}$ (1000)</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Holtappels et al., 2000)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### (i) Chromite

<table>
<thead>
<tr>
<th>Formula</th>
<th>86 (850)</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{2}$Ca$</em>{0.3}$CrO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>1.15 (850)</th>
<th>1.79 (850)</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.75}$Sr$</em>{0.25}$CrO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>0.256 (850)</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.75}$Sr$</em>{0.25}$Cr$<em>{0.2}$O$</em>{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>1.3 (900)</th>
<th>38 (900)</th>
<th>0.26 (900)</th>
<th>0.85 (900)</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$Cr$<em>{0.8}$V$</em>{0.03}$O$_{3}$</td>
<td>-</td>
<td>-</td>
<td>0.18 (900)</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>1.4(800)</th>
<th>2.3 (800)</th>
<th>-</th>
<th>-</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.75}$Sr$</em>{0.25}$Cr$<em>{0.3}$Mn$</em>{0.5}$O$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>2.5 (800)$^d$</th>
<th>11 (800)</th>
<th>-</th>
<th>-</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.75}$Sr$</em>{0.25}$Cr$<em>{0.3}$Mn$</em>{0.5}$O$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>0.22 (800)</th>
<th>28.8 (800)</th>
<th>-</th>
<th>-</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.75}$Sr$</em>{0.25}$Cr$<em>{0.3}$Mn$</em>{0.5}$O$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### (ii) Titanate

<table>
<thead>
<tr>
<th>Formula</th>
<th>3 (1000)</th>
<th>1 (1000)</th>
<th>-</th>
<th>-</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$TiO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>1.79 (850)</th>
<th>28 (850)</th>
<th>1.79 (850)</th>
<th>-</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$TiO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>0.004 (1000)</th>
<th>-</th>
<th>-</th>
<th>510 (800)</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.1}$Sr$</em>{0.9}$TiO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>200 (1000)</th>
<th>0.03 (1000)</th>
<th>-</th>
<th>-</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$TiO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>4 (1000)</th>
<th>1.3 (1000)</th>
<th>-</th>
<th>-</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$TiO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>200 (1000)</th>
<th>0.01 (1000)</th>
<th>-</th>
<th>-</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$TiO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>16 (1000)</th>
<th>0.004 (1000)</th>
<th>-</th>
<th>-</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$TiO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>360 (1000)</th>
<th>0.03 (1000)</th>
<th>-</th>
<th>-</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$TiO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>$3.02^{+2}$ (900)</th>
<th>$10^{+3.76}$ (900)</th>
<th>-</th>
<th>-</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$TiO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>350 (800)</th>
<th>-</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTi$<em>{0.97}$Nb$</em>{0.03}$O$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>700 (800)</th>
<th>-</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTi$<em>{0.94}$Nb$</em>{0.06}$O$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>9–28 (800)</th>
<th>-</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTi$<em>{0.9}$Nb$</em>{0.1}$O$_{3}$ (0.01 &lt;x&lt;0.08)</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>7–64 (800)</th>
<th>-</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$<em>{0.88}$Y$</em>{0.07}$TiO$_{3}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 2. Literature review

<table>
<thead>
<tr>
<th>Formula</th>
<th>ΔE (eV)</th>
<th>ΔK (eV)</th>
<th>ΔG (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr&lt;sub&gt;0.85&lt;/sub&gt;Y&lt;sub&gt;0.15&lt;/sub&gt;Ti&lt;sub&gt;0.95&lt;/sub&gt;Ca&lt;sub&gt;0.05&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>37 (800)</td>
<td>-</td>
<td>-</td>
<td>Hui and Petric, 2001</td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.85&lt;/sub&gt;Y&lt;sub&gt;0.15&lt;/sub&gt;Ti&lt;sub&gt;0.95&lt;/sub&gt;Co&lt;sub&gt;0.05&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>45 (800)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.85&lt;/sub&gt;Y&lt;sub&gt;0.15&lt;/sub&gt;Ti&lt;sub&gt;0.95&lt;/sub&gt;Zr&lt;sub&gt;0.05&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>13 (800)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.85&lt;/sub&gt;Y&lt;sub&gt;0.15&lt;/sub&gt;Ti&lt;sub&gt;0.95&lt;/sub&gt;Mg&lt;sub&gt;0.05&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>6 (800)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.88&lt;/sub&gt;Y&lt;sub&gt;0.08&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>64 (800)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SrT&lt;sub&gt;i0.99&lt;/sub&gt;Nb&lt;sub&gt;0.01&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>~10&lt;sup&gt;14&lt;/sup&gt; (800)</td>
<td>~10&lt;sup&gt;12&lt;/sup&gt; (800)</td>
<td>-</td>
<td>Horikiri et al., 2008</td>
</tr>
<tr>
<td>SrT&lt;sub&gt;i0.99&lt;/sub&gt;Nb&lt;sub&gt;0.01&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>~10&lt;sup&gt;15&lt;/sup&gt; (800)</td>
<td>~10&lt;sup&gt;13&lt;/sup&gt; (800)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SrT&lt;sub&gt;i0.99&lt;/sub&gt;Nb&lt;sub&gt;0.01&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10–11</td>
<td>(600-900)</td>
<td>-</td>
<td>(Gross et al., 2009)</td>
</tr>
<tr>
<td>SrT&lt;sub&gt;i0.99&lt;/sub&gt;Nb&lt;sub&gt;0.01&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>6–10</td>
<td>(600-900)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SrT&lt;sub&gt;i0.99&lt;/sub&gt;Nb&lt;sub&gt;0.01&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>70–90</td>
<td>(600-900)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.88&lt;/sub&gt;Y&lt;sub&gt;0.08&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>~10&lt;sup&gt;17&lt;/sup&gt; (800)</td>
<td>~0.1 (800)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.85&lt;/sub&gt;Y&lt;sub&gt;0.10&lt;/sub&gt;Ti&lt;sub&gt;0.99&lt;/sub&gt;Co&lt;sub&gt;0.01&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>45 (800)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>La&lt;sub&gt;0.4&lt;/sub&gt;Sr&lt;sub&gt;0.6&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1</td>
<td>2×10&lt;sup&gt;-3&lt;/sup&gt; (800)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>La&lt;sub&gt;0.4&lt;/sub&gt;Sr&lt;sub&gt;0.6&lt;/sub&gt;Ti&lt;sub&gt;0.3&lt;/sub&gt;Mn&lt;sub&gt;0.2&lt;/sub&gt;O&lt;sub&gt;1.4&lt;/sub&gt;</td>
<td>0.1 (800)</td>
<td>2×10&lt;sup&gt;-2&lt;/sup&gt; (800)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>La&lt;sub&gt;0.4&lt;/sub&gt;Sr&lt;sub&gt;0.6&lt;/sub&gt;Ti&lt;sub&gt;0.6&lt;/sub&gt;Mn&lt;sub&gt;0.4&lt;/sub&gt;O&lt;sub&gt;1.8&lt;/sub&gt;</td>
<td>0.1 (800)</td>
<td>2 (800)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>La&lt;sub&gt;0.4&lt;/sub&gt;Sr&lt;sub&gt;0.6&lt;/sub&gt;Ti&lt;sub&gt;0.4&lt;/sub&gt;Mn&lt;sub&gt;0.6&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2 (800)</td>
<td>20 (800)</td>
<td>0.35 (855)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.8 (855)&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>La&lt;sub&gt;0.4&lt;/sub&gt;Sr&lt;sub&gt;0.6&lt;/sub&gt;Ti&lt;sub&gt;0.4&lt;/sub&gt;Fe&lt;sub&gt;0.3&lt;/sub&gt;O&lt;sub&gt;1.3&lt;/sub&gt;</td>
<td>10&lt;sup&gt;12.4&lt;/sup&gt;–10&lt;sup&gt;13.8&lt;/sup&gt; (800)</td>
<td>10&lt;sup&gt;0.1&lt;/sup&gt;–1 (800)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.88&lt;/sub&gt;Y&lt;sub&gt;0.02&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
<td>10 (900)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.9&lt;/sub&gt;Y&lt;sub&gt;0.08&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
<td>65 (900)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.9&lt;/sub&gt;Y&lt;sub&gt;0.09&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
<td>70 (900)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.88&lt;/sub&gt;Y&lt;sub&gt;0.12&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
<td>50 (900)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.88&lt;/sub&gt;Y&lt;sub&gt;0.08&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>2.9 (800)&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.9&lt;/sub&gt;Ti&lt;sub&gt;0.12&lt;/sub&gt;Nb&lt;sub&gt;0.08&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>350 (800)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.84&lt;/sub&gt;Y&lt;sub&gt;0.04&lt;/sub&gt;Ti&lt;sub&gt;0.86&lt;/sub&gt;Nb&lt;sub&gt;0.12&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>250 (800)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sr&lt;sub&gt;0.88&lt;/sub&gt;Y&lt;sub&gt;0.08&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>100 (800)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>La&lt;sub&gt;2&lt;/sub&gt;Sr&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;19.8&lt;/sub&gt;</td>
<td>30 (900)</td>
<td>8.5×10&lt;sup&gt;-4&lt;/sup&gt; (900)</td>
<td>2.97 (900)</td>
<td>8.93 (900)</td>
</tr>
<tr>
<td>La&lt;sub&gt;4&lt;/sub&gt;Sr&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;12&lt;/sub&gt;MnO&lt;sub&gt;38.6&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>0.3 (950)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.7 (950)&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>La&lt;sub&gt;2&lt;/sub&gt;Sr&lt;sub&gt;3&lt;/sub&gt;Ti&lt;sub&gt;11&lt;/sub&gt;Mn&lt;sub&gt;0.5&lt;/sub&gt;Ga&lt;sub&gt;0.5&lt;/sub&gt;O&lt;sub&gt;16.8&lt;/sub&gt;</td>
<td>0.5 (900)</td>
<td>10&lt;sup&gt;-3&lt;/sup&gt; (900)</td>
<td>0.2 (900)</td>
<td>0.57 (900)</td>
</tr>
<tr>
<td>La&lt;sub&gt;2&lt;/sub&gt;Sr&lt;sub&gt;3&lt;/sub&gt;Ti&lt;sub&gt;5&lt;/sub&gt;Sc&lt;sub&gt;0.1&lt;/sub&gt;O&lt;sub&gt;19.2&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>0.5 (900)</td>
<td>1.2 (900)</td>
</tr>
</tbody>
</table>

### Double perovskite

<table>
<thead>
<tr>
<th>Formula</th>
<th>ΔE (eV)</th>
<th>ΔK (eV)</th>
<th>ΔG (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr&lt;sub&gt;2&lt;/sub&gt;MnO&lt;sub&gt;3&lt;/sub&gt;Nb&lt;sub&gt;1.2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
<td>8×10&lt;sup&gt;-3&lt;/sup&gt; (900)</td>
<td>0.36 (900)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SrMnO&lt;sub&gt;3&lt;/sub&gt;Nb&lt;sub&gt;0.5&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.1×10&lt;sup&gt;-2&lt;/sup&gt; (900)</td>
<td>1.23 (900)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sr&lt;sub&gt;2&lt;/sub&gt;Mg&lt;sub&gt;1.3&lt;/sub&gt;MnO&lt;sub&gt;6&lt;/sub&gt;</td>
<td>4.8 (800)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sr&lt;sub&gt;2&lt;/sub&gt;MgMoO&lt;sub&gt;6&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>0.41 (900)</td>
<td>-</td>
</tr>
<tr>
<td>Sr&lt;sub&gt;2&lt;/sub&gt;MgMoO&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.19 (800)</td>
<td>7.7×10&lt;sup&gt;-4&lt;/sup&gt; (800)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

---

Chapter 2. Literature review

Marrero and Petric, 2007

---

<table>
<thead>
<tr>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fu et al., 2006</td>
</tr>
<tr>
<td>Li et al., 2007b</td>
</tr>
<tr>
<td>(Fagg et al., 2003b)</td>
</tr>
<tr>
<td>(Kurokawa et al., 2007a)</td>
</tr>
<tr>
<td>(Kolodiazhnyi and Petric, 2005)</td>
</tr>
<tr>
<td>(Ovalle et al., 2006)</td>
</tr>
<tr>
<td>(Ruiz-Morales et al., 2007)</td>
</tr>
<tr>
<td>(Canales-Vazquez et al., 2003)</td>
</tr>
<tr>
<td>(Canales-Vazquez et al., 2005)</td>
</tr>
<tr>
<td>Material</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>Sr₂CoMoO₆₋₄δ</td>
</tr>
<tr>
<td>Sr₂Feₓ/₃Mo₂/₃O₆₋₄δ</td>
</tr>
<tr>
<td>Ca₂FeMoO₆₋₄δ</td>
</tr>
<tr>
<td>Sr₂FeMoO₆₋₄δ</td>
</tr>
<tr>
<td>Ba₂FeMoO₆₋₄δ</td>
</tr>
<tr>
<td>Sr₂NiMoO₆₋₄δ</td>
</tr>
<tr>
<td>Sr₂CoMoO₆₋₄δ</td>
</tr>
</tbody>
</table>

- **a.** Testing in reducing atmosphere (e.g. forming gas)
- **b.** Testing in oxidizing atmosphere (e.g. air)
- **c.** Hydrogen and methane correspond to wet hydrogen and wet methane that are humidified at room temperatures.
- **d.** Temperatures in parentheses are of Celsius degree (°C).
- **e.** Sample sintered or annealing in hydrogen.
- **f.** 10 vol.% H₂–H₂S fuels.
- **g.** Composite electrode used.
Chapter 3. Synthesis, characterization, and performance of lanthanum strontium vanadate via solid state reactions

3.1 Introduction

Historically, lanthanum strontium vanadate La$_{1-x}$Sr$_x$VO$_3$ (LSV, $0 \leq x \leq 1$) are of interests because of their metal-insulator transition (Sayer et al., 1975) and hence, plausible candidates of high-$T_c$ superconductors (Mahajan et al., 1992). Electrical conductivity of LSV ($0 \leq x \leq 0.4$) changes from semiconducting to metallic behaviour with strontium content around 0.2. LSV ($x \geq 0.2$) reach $10^2$-$10^3$ S/cm of electronic conductivity in a typical SOFC operating at temperatures between 500 and 1000°C (Sayer et al., 1975; Webb and Sayer, 1976). For the two ends of LSV (i.e. LaVO$_3$ and SrVO$_3$), orthorhombic LaVO$_3$ is a Mott insulator, while cubic SrVO$_3$ is an oxide conductor with metallic behaviour (Inaba et al., 1995).

Both high electrical conductivity and catalytic activity on fuel oxidation are prerequisites for potential SOFC anodes. It was found that vanadium-based oxides had already been widely used in the catalytic industry. Supported vanadia had been investigated extensively because of its technological importance in industrial heterogeneous catalytic processes, such as oxidative dehydrogenation of hydrocarbons like propane (Daniell et al., 2002), toluene (Bulushev et al., 2000) and butadiene (Bond et al., 1979) and selective catalytic reduction of nitrogen oxides (Georgiadou et al., 1998). Complex pyrovanadate, such as La–Mn–V–O (Varma et al., 2001) and La–Fe–V–O (Varma et al., 2003), had been proven to be good catalysts for CO oxidation at temperatures above 200°C. SrVO$_3$ had also been attempted as an oxidation catalyst for methanol and benzene, but without success (De and Balasubramanian, 1983). The binary perovskite containing V$^{3+}$ and V$^{4+}$, exhibiting good catalytic performance on selective oxidation of alcohols has also been reported (Trikalitis and Pomonis, 1995).
Despite the unique properties of vanadate, it has not been widely used in SOFCs. Small proportion of strontium pyrovanadate, Sr$_3$(VO$_4$)$_2$, is routinely added into strontium-doped lanthanum chromite to produce high density interconnect materials (Simner et al., 2000). It is only in recent years that vanadate is being explored to be an anode material for SOFC. It was reported that “Strontium doped LaVO$_3$ is stable under SOFC fuel outlet conditions..., however… is unlikely to be useful as anode materials” (Hui and Petric, 2001). However, studies showed that LSV was active in electrochemical H$_2$S oxidation (Aguilar et al., 2004b; Aguilar et al., 2004a; Cheng et al., 2005; Cheng et al., 2006). SOFC with La$_{0.7}$Sr$_{0.3}$VO$_3$ anode is among the best of all reported results, with excellent sulphur tolerance up to percentage level (Aguilar et al., 2004b). Nevertheless, it seems that La$_{0.7}$Sr$_{0.3}$VO$_3$ (LSV7030) has low catalytic activity for H$_2$ and CH$_4$ oxidation. The polarization resistance at 1000°C is about 5 Ω cm$^2$ for such cells running on H$_2$ (Aguilar et al., 2004a). Maximum power density can reach 150 mW/cm$^2$ for the cell with LSV7030/YSZ (250 µm)/La$_{0.85}$Sr$_{0.15}$MnO$_3$ configuration fed with pure H$_2$ at 900°C. Recently, LaCrO$_3$–VO$_x$–YSZ anode containing 40 wt.% reduced vanadium oxide (VO$_x$) was tested using tainted syngas derived from coal gasification, but no results on pure fuel gases were reported (Xu et al., 2007). While vanadate has been proven to be excellent in sulphur tolerance, low catalytic activity to fuel oxidation undermines its candidature of SOFC anode.

### 3.2 Powder synthesis

A literature survey shows that there are four methods employed for synthesizing LSV$_{Re}$, i.e., (i) reduction from LSV$_{Ox}$ (Trikalitis and Pomonis, 1995; Khan et al., 2004); (ii) arc melting of reduced raw materials (Sayer et al., 1975; Bordet et al., 1993); (iii) annealing of LSV$_{Ox}$ in vacuum (Mahajan et al., 1992; Shinike et al., 1976; Hur et al., 1994); and (iv) directly sintering in reducing environment (Inaba et al., 1995; Nakamura et al., 1979). Early researchers synthesized dense polycrystalline LSV$_{Re}$ because of their interests in the electrical and magnetic properties. The corresponding operating temperature was extremely high, i.e., 1400–1800°C. Such a high temperature process not only led to equipment complexity, but also reduced the catalytic activity because of increased crystal size and decreased surface area of materials. A modified method (i) was used in the present study. This method had been reported in early works on selective isopropanol oxidation (Trikalitis et al., 1998).
A series of LSV (0 ≤ x ≤ 1) powders were synthesized by solid state reactions in air followed by reduction in the forming gas. The raw materials for oxidized LSV (LSV\textsubscript{Ox}) synthesis were lanthanum (III) oxide, strontium (II) carbonate, and vanadium (V) oxide. La\textsubscript{2}O\textsubscript{3} (Advanced Materials, 99.995%) was calcined at 1000°C for 4 h to remove the moisture and carbonaceous compounds. The decomposition of SrCO\textsubscript{3} (Advanced Materials, 99.5+%) was carried out at 1000°C for 6 h. V\textsubscript{2}O\textsubscript{5} (Sigma-Aldrich, 99.6+%) was firstly ball milled for 10 min and then dried at 300°C for 2 h. Stoichiometric amounts of La\textsubscript{2}O\textsubscript{3}, decomposed SrCO\textsubscript{3}, and V\textsubscript{2}O\textsubscript{5} were put into a rolling jar. Roll milling was carried out in isopropanol with YSZ media up to 24 h. The slurry was dried at 80°C in air. The dried powders were compacted into pellets with diameter of 24 mm. They were calcined at 600°C for 48 h to minimize vanadium loss. They were finally fired at 800°C for 24 h to form the right phases. Yellowish powders (LSV\textsubscript{Ox}) were obtained after crushing and milling the sintered pellets in an agate mortar. The reduction experiment of LSV\textsubscript{Ox} was carried out in a tube furnace. To yield reduced LSV (LSV\textsubscript{Re}), LSV\textsubscript{Ox} were compacted into pellets and reduced in forming gas (5% H\textsubscript{2}/Ar) at 1000°C for 24 to 48 h with intermediate grinding. The pellets were crushed into powders after reduction. There are two reasons why forming gas rather than pure H\textsubscript{2} was used in this project. The first reason is the stringent safety regulation in Singapore. The second reason is to ensure the stability of the material in reducing atmosphere. p\textsubscript{O2} is not always low at SOFC anode chamber, especially under high current loading operation conditions where a lot of steam is generated. If LSV\textsubscript{Ox} cannot be reduced in forming gas, it will definitely fail under practical SOFC operating conditions. La-rich LSV\textsubscript{Re} are black and Sr-rich LSV\textsubscript{Re} are black with bluish tint.

3.3 Structural and thermal gravimetric characterization

LSV powders were pressed onto a specially designed XRD sample holder for XRD characterization. Phase screening of LSV was carried out with X-ray diffraction (XRD, Philips PW1830). Another diffractometer, Shimadzu 6000 with Cu K\textsubscript{α} radiation, was used for phase identification. The step size was 0.02° with a scan rate of 0.5°/min. Profile refinement was carried out with the commercial Jade 5 software. To check the thermal stability of LSV, LSV\textsubscript{ox}–YSZ mixture was calcined at 1300°C for 3 h for XRD characterization.
Light yellow LaVO$_4$ is monoclinic (Monazite type), and yellowish Sr$_2$V$_2$O$_7$ is triclinic (Figure 3-1 and Table3-1). Figure 3-2a shows the XRD patterns of as-synthesized LSV$_{Ox}$. Single phase can be obtained at the two ends of LSV$_{Ox}$. LV$_{Ox}$ and SV$_{Ox}$ are hard to dissolve in each other due to their distinct crystalline structures. Not surprisingly, any attempt to achieve a single phase LSV$_{Ox} (0 < x < 1)$ will fail. As shown in Fig. 3-2a, trace of LaVO$_4$ is visible even in LSV0595$_{Ox}$. In present study LSV$_{Ox} (0 < x < 1)$ are treated as a mixture of LaVO$_4$ and Sr$_2$V$_2$O$_7$. In Fig. 3-2b, single phase can be readily synthesized for slightly Sr-doped LV$_{Re}$. LSV$_{Re} (0 \leq x \leq 0.1)$ are refined as orthorhombic, with increasing cell volume when more Sr$^{2+}$ (1.44 Å) replace La$^{3+}$ (1.36 Å) (Shannon, 1976). LSV5050$_{Re}$ profile could be fitted to cubic $(La_{0.50}Sr_{0.50})VO_{2.95}$ (PDF#33-1343). With caution, it can be orthorhombic because the differences in lattice parameters are very close to each other, as in the case of LaVO$_3$. LaVO$_3$ was once believed to be cubic, but Bordet et al. noticed the distorted VO$_6$ octahedral network and thus classified it as orthorhombic GdFeO$_3$ type (Bordet et al., 1993). As shown in Fig. 3-2b, the peak width at half height of LSV5050$_{Re}$ is quite large. Such a peak broadening can be ascribed to lattice disorder or fine grain size down to nano-scale. It seems impossible that powders prepared from solid state reaction are nano-sized. Thus the peak broadening is empirically ascribed to random occupation of strontium and lanthanum in the perovskite A-site lattice. Unlike LSV$_{Re} (x= 0, 0.05, 0.1)$ and LSV5050$_{Re}$, LSV$_{Re} (x= 0.2, 0.3, 0.4)$ are binary phase structure between LaVO$_3$ and $(La_{0.50}Sr_{0.50})VO_{2.95}$.

For the Sr-rich LSV$_{Re}$, it is futile to eliminate the impurities from LSV$_{Re} (0.8 \leq x \leq 1)$ even with repeated grinding and firing. Impurities are identified as Sr$_3$(VO$_4$)$_2$-, Sr$_6$V$_6$O$_{19}$-, or Sr(V$_6$O$_{11}$)-like phases. Figure 3-3 shows a typical XRD pattern of SV$_{Re}$, the toughest composition within the LSV category. Even after a 1000°C reduction for 2 days with intermediate grinding, Sr$_3$(VO$_4$)$_2$ is still the dominant phase while almost no SrVO$_3$ diffraction peaks were detected. It is not easy to identify the other peaks in the Fig. 3-4, noting that there are at least 29 La–Sr–V oxides in the standard powder diffraction (PDF) files. The valence of vanadium is 5+ in Sr$_3$(VO$_4$)$_2$, which implies that it may be impossible to obtain vanadate with V$^{3+}$/V$^{4+}$ for the conditions used here. In contrast to SrVO$_3$, LaVO$_3$ is much easier to be prepared. This is possibly because the V$^{4+}$ state is less stable than the V$^{3+}$ state. Nakamura et al. prepared LaVO$_3$ by reducing V$_2$O$_5$ and La$_2$O$_3$ at 1200°C for 12 h in a CO$_2$/H$_2$ gas (PO$_2$ = 10$^{-10}$ bar)
(Nakamura et al., 1979). It is believed that LaVO₃ can also form in the present experimental conditions, i.e., 1000°C for 24 h in 5% H₂/Ar, noting that P O₂ is around 10⁻²¹ bar for 5% H₂/Ar at 900°C (Tao and Irvine, 2004a).

Figure 3-1  XRD patterns of (a) LaVO₄ (LV₉₀₃) and (b) Sr₂V₂O₇ (SV₉₀₃) fitted in Jade® 5.
Figure 3-2  XRD patterns of (a) LSV\textsubscript{Ox}, (b) LSV\textsubscript{Re}, and (c) mixture of LSV7030\textsubscript{Ox} and YSZ fired at 1300°C for 3 h, with a 50:50 weight ratio.
Table 3-1  Fitted unit cell parameters of LSV

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice setting</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>LV$_{Ox}$</td>
<td>Monoclinic</td>
<td>$a = 7.019(4)$ Å, $b = 7.260(3)$ Å, $c = 6.714(3)$ Å, $\beta = 104.878(1)$ °, $V = 330.62$ Å$^3$, $Z = 4$</td>
</tr>
<tr>
<td>SV$_{Ox}$</td>
<td>Triclinic</td>
<td>$a = 7.087(5)$ Å, $b = 12.964(1)$ Å, $c = 7.044(4)$ Å, $\alpha = 93.806(1)$ °, $\beta = 90.925(3)$ °, $\gamma = 99.384(1)$ °, $V = 636.84$ Å$^3$, $Z = 4$</td>
</tr>
<tr>
<td>LV$_{Re}$</td>
<td>Orthorhombic</td>
<td>$a = 5.513(2)$ Å, $b = 7.883(1)$ Å, $c = 5.537(1)$ Å, $V = 239.14$ Å$^3$, $Z = 4$</td>
</tr>
<tr>
<td>LSV9505$_{Re}$</td>
<td>Orthorhombic</td>
<td>$a = 5.545(3)$ Å, $b = 7.834(1)$ Å, $c = 5.521(1)$ Å, $V = 239.82$ Å$^3$, $Z = 4$</td>
</tr>
<tr>
<td>LSV9010$_{Re}$</td>
<td>Orthorhombic</td>
<td>$a = 5.545(5)$ Å, $b = 7.835(2)$ Å, $c = 5.528(9)$ Å, $V = 240.16$ Å$^3$, $Z = 4$</td>
</tr>
<tr>
<td>LSV5050$_{Re}$</td>
<td>Cubic</td>
<td>$a = 3.869(1)$ Å, $V = 57.93$ Å$^3$, $Z = 1$</td>
</tr>
</tbody>
</table>

![Figure 3-3](image-url)  
Reduction of SV$_{Ox}$ to SV$_{Re}$:  
1000°, 1 day in 5%H$_2$/Ar  
1000°, 1 day in 5%H$_2$/Ar  

Note that the powders are sintered two days with intermediate grinding (1 day+ 1 day route).
SrVO₃ can be reduced from Sr₂V₂O₇ at 1250°C in 7% H₂–Ar. At 800°C, it is stable only when PO₂ < 10⁻¹⁰ bar (Hui and Petric, 2001). With arbitrary single phase of Sr-rich LSV_{Re} is thought to be impossible at present conditions, i.e., 1000°C in 5% H₂/Ar. This is different from the reported results that single phase can be obtained for the whole range of LSV (0 ≤ x ≤ 1) via 1500°C vacuum annealing and arc-melting (Mahajan et al., 1992). It seems that the pyrovanadate impurities are not detrimental to the catalytic activities of LSV_{Re}. Trikalitis et al. obtained LSV_{Re} as a mixture of LaVO₃, SrVO₃ and Sr₃V₂O₈, which were quite active for isopropanol selective oxidation (Trikalitis et al., 1998). As our objective is to select some materials for catalytic fuel oxidation in SOFC, any pursuits on single phase materials and detailed investigation on phase structure are beyond the scope of the present study.

To study the chemical compatibility of LSV with YSZ, LSV was mixed with YSZ powder in 50:50 wt% and fired at 1300°C for 3 h in air. One of the XRD patterns of LSV-YSZ after calcination is shown in Fig. 3-2c. No Bragg peaks were observed other than the expected peaks arising from LSV_{Ox} and YSZ. This indicates that no significant reactions had occurred between the two materials, at least within XRD detection limitations.

The oxidation behaviour of LSV_{Re} was investigated by thermal gravimetric analysis (TGA) via TGA 2950 (TA Instruments). 15 mg of LSV_{Re} was put into the Pt pan. N₂ was purged into the thermobalance chamber with a flow rate of 80 sccm. The TGA system was heated up from room temperature to 1000°C in air at a scan rate of 5 °C/min. Figure 3-4 shows the oxidation behaviour of LSV_{Re} in air. It can be seen in Fig. 3-4 that the onset temperature (T_{onset}) of oxidation strongly depends on the composition. T_{onset} of slightly Sr-doped LSV is around 340–360°C, and it is around 486°C for the oxidation of LSV_{50}Re. As shown in the Fig. 3-4, only a single step is observed in all the TGA curves. It is assumed that the vanadate (III) is completely oxidized to vanadate (V). The oxidation seems to complete at 600°C. After that no noticeable weight change is observed. The weight gain between 300 to 600°C is attributed to the vanadate oxidation. The oxygen non-stoichiometry parameter δ is calculated as:

\[
\text{LaVO}_{3-\delta} + \frac{1+\delta}{2}\text{O}_2 \rightarrow \text{LaVO}_4
\]  
(Equation 3-1)
Chapter 3. Synthesis, characterization, and Performance of LSV via solid state reactions

\[
\text{La}_{0.93}\text{Sr}_{0.03}\text{VO}_{3-\delta} + \frac{0.975+\delta}{2}\text{O}_2 \rightarrow \text{La}_{0.93}\text{Sr}_{0.03}\text{VO}_{3.975}
\]  (Equation 3-2)

\[
\text{La}_{0.8}\text{Sr}_{0.2}\text{VO}_{3-\delta} + \frac{0.9+\delta}{2}\text{O}_2 \rightarrow \text{La}_{0.8}\text{Sr}_{0.2}\text{VO}_{3.9}
\]  (Equation 3-3)

\[
\text{La}_{0.5}\text{Sr}_{0.5}\text{VO}_{3-\delta} + \frac{0.75+\delta}{2}\text{O}_2 \rightarrow \text{La}_{0.5}\text{Sr}_{0.5}\text{VO}_{3.75}
\]  (Equation 3-4)

---

Figure 3-4 TGA curves for the oxidation of reduced \( \text{La}_{1-x}\text{Sr}_x\text{VO}_{3-\delta} \) (LSV\(_\text{Re}\)) with \( x = 0, 0.05, 0.2, 0.5 \). Note that the final products after TGA measurement were assumed to pyrovanadate, i.e., vanadium in \( \text{V}^{5+} \).

Table 3-2 TGA data listing of LSV\(_\text{Re}\) oxidation. \( \delta \) is the oxygen non-stoichiometry parameter in the \( \text{La}_{1-x}\text{Sr}_x\text{VO}_{3-\delta} \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_{\text{onset}} ) (°C)</th>
<th>( T_{\text{offset}} ) (°C)</th>
<th>Weight increase (wt. %)</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSV(_\text{Re})</td>
<td>364</td>
<td>494</td>
<td>6.127</td>
<td>-0.084</td>
</tr>
<tr>
<td>LSV9505(_\text{Re})</td>
<td>342</td>
<td>439</td>
<td>6.184</td>
<td>-0.062</td>
</tr>
<tr>
<td>LSV8020(_\text{Re})</td>
<td>348</td>
<td>513</td>
<td>6.202</td>
<td>-0.017</td>
</tr>
<tr>
<td>LSV5050(_\text{Re})</td>
<td>486</td>
<td>547</td>
<td>5.658</td>
<td>( 4.06 \times 10^{-4} )</td>
</tr>
</tbody>
</table>
The δ values of LSV_{Re} are given in Table 3-2. The obtained δ values scatter from -0.084 to 4.06 × 10^{-4}. The large discrepancy of δ might be due to the system error of the low-accuracy TGA instrument. Whether LSV_{Re} is of oxygen-deficient or oxygen-excess is, therefore essentially unknown. Literature results showed that LSV was predominantly of oxygen-deficient. Hur et al. obtained LaVO_{2.92} (δ = 0.08) via 1600°C vacuum annealing of raw mixed V_{2}O_{3} and La_{2}O_{3} powders (Hur et al., 1994). Mahajan et al. showed that δ of LV_{Re}, LSV8020_{Re}, and LSV5050_{Re} were 0.02, 0.01, and -0.05, respectively (Mahajan et al., 1992).

With caution, it can be inferred that the oxygen nonstoichiometry of LSV is non-negligible. The ionic conductivity (σ_{i}) of LSV_{Re}, though not measured in this study, might not be low. While little ionic conductivity data had been reported in literature, the electronic conductivity (σ_{el}) of LSV_{Re} was reported to be high. In a typical SOFC temperature range, LSV_{Re} (0 ≤ x ≤ 0.2) shows the semiconductor behaviour with conductivity around 0.1-1 S/cm. For the case of LSV_{Re} (0.2 ≤ x ≤ 0.4), σ_{el} is in the order of 10^{2}-10^{4} S/cm (Webb and Sayer, 1976). The increased conductivity results from the introduction of V^{4+} together with the Sr^{2+} in LSV_{Re}. The electronic transfer of V^{3+/4+} redox couple should contribute to the high conductivity of LSV_{Re}(0.2 ≤ x).

### 3.4 Half-cell performance of LSV anodes

#### 3.4.1 Experimental procedures

Electrode performance of LSV anodes was evaluated by electrochemical impedance spectroscopy (EIS) and dc polarization. A schematic illustration of the three-electrode configuration is shown in Fig. 3-5. This kind of configuration had been proven in minimizing the artefacts arisen from the electrode misalignment. It had been used in our group for many years. The YSZ electrolyte in this configuration was 18 mm in diameter and 1 mm in thickness. LSV_{Ox} and YSZ were mixed in a 50:50 weight ratio, and the LSV_{Ox}–YSZ paste was screen printed onto YSZ electrolyte. It was fired at 1180°C for 2h to form an anode layer with thickness of 30 µm. A “just cover” Pt current collection layer was brush-painted onto the LSV–YSZ anode. As Pt is susceptible to be catalytically active, gold paste (Fuel Cell Materials, USA) was also used as current collector. Pt was used as the counter and reference electrodes (CE and
RE, respectively) on the opposite side of YSZ, where the gap between CE and RE is at least 4 mm. The active area of the working surface was 0.46 cm². The cell was sealed onto an alumina tube using a ceramic sealant (Ceramabond 552, Aremco). It was cured at 90°C and 200°C for 2 h each. A gas-tight pre-test was carried out by passing N₂ with very slow flow rate. During the electrochemical testing, the anode side was fed with either pure H₂ or wet CH₄. The fuel flow rate was 50 sccm. The opposite side, i.e. the side with CE and RE, was exposed to ambient air. LSV anode was in situ reduced for 2 h at 900°C. Electrochemical testing was carried out between 800 to 1000°C, with a heating and cooling rate of 2°C/min.

EIS was carried out using a Solartron 1255B frequency response analyzer coupled to a 1287 electrochemical interface. The impedance spectra were recorded at open-circuit voltage (OCV) with 10 mV ac amplitude over the frequency range 10⁵-10⁻² Hz. Ohmic resistance of the electrochemical cell, \( R_Ω \), was estimated from the high frequency (high-\( f \)) intercept on the impedance curves. Electrode polarization resistance, \( R_p \), was extracted from the difference between its low-\( f \) and high-\( f \) intercepts. Potential dynamic polarization was carried out by sweeping from OCV to 0.8 V anodic biases at a scan rate of 1 mV/s. Microstructure of the anodes was inspected by scanning electron microscopy (SEM, JEOL JSM-6340F). The impedance data and potentiodynamic polarization data were analyzed by commercial Zview and Corrview software, respectively.
Figure 3-5 Schematic illustration of the half-cell configuration. Note that the scale of all components is only a guide for the eyes.

3.4.2 LSV–YSZ anodes fed with pure H₂

Steele proposed several criteria decades ago for oxide anodes attempting to complete methane oxidation (Steele et al., 1990). The first given rule was “Good electronic conductivity (preferably > 10² S/cm) at anode operating potentials (-0.7 to -0.9 V). Probably n-type behaviour preferable.” LSVₐ is metallic (Webb and Sayer, 1976) and slightly n-type (Hui and Petric, 2001). At a typical temperature range of SOFC (600 to 1000°C), the dc conductivity of LSV₈₀₂₀ₐ was 10¹.⁹ - 10².² S/cm while around 10¹.⁵ S/cm for LSV₉₀₁₀ₐ (Webb and Sayer, 1976). LSVₐ (x < 0.2) were ruled out as far as electronic conductivity was concerned. Recalling the discussion in Section 3.3, Sr-rich LSVₐ were also unfavourable due to its chemical instability in oxidizing environment. For these reasons, only LSVₐ (0.2 ≤ x ≤ 0.5) were chosen for electrochemical testing. LSV is good electronic conductor but its ionic conductivity is assumed to be negligible. The three phase boundaries (TPBs) are thus confined to LSV–YSZ interface if pure LSV anode is used. TPB is the place where the electronic component, ionic component, and fuel meet and electrochemical reactions take place. Initial efforts on fabricating pure LSV anodes had failed because they delaminated from YSZ electrolyte during in situ reduction. The reason is that LSV undergoes considerable lattice shrinkage during reduction, when orthorhombic LaVO₄ and triclinic Sr₂V₂O₇ release lattice oxygen to
Experimental results showed that the use of composite anodes of LSV and YSZ alleviated the delamination problem. The YSZ component in LSV–YSZ composite anodes provided a rigid skeleton to withhold the LSV component. In addition, the TEC mismatch between LSV and YSZ was minimized. Furthermore, the TPB was extended from 2D interface to 3D reaction zones once LSV–YSZ composite anodes were employed. The detailed investigation on three phase boundaries (TPBs), both experimental and theoretical, will be discussed in Chapter 4.

Electrode engineering is a complex that at least includes particle size, particle size ratio, firing history, electrode composition, conductivity, porosity, thickness, and fuel compositions. In this chapter, the effects of electrode composition and firing history on the electrochemical performance of LSV–YSZ composite electrodes are investigated. Modelling works pertaining to electrode optimization was again given in Chapter 4. Unreasonably large $R_p$ and $R_\Omega$ were observed in LSV$^1$ (70 wt. %)–YSZ and LSV(80 wt. %)–YSZ. $R_p$ of LSV–YSZ anodes with LSV contents at 40 wt.%, 50 wt.%, and 60 wt.% are 1.2, 0.38, 0.35 $\Omega$ cm$^2$, respectively (Fig. 3-6). The delamination problem of LSV (60 wt.%)–YSZ is occasionally observed. It appears that LSV (50 wt.%)–YSZ is the best composition. Figure 3-7 shows the impedance responses of LSV6040 (50 wt. %)–YSZ anodes sintered at different temperatures. The ohmic resistance, $R_\Omega$, varied significantly with the anode sintering temperatures. $R_\Omega$ is the lumped resistance at least consisting of electrolyte ohmic resistance, electrode ohmic resistance, and various contact resistances. Based on the conductivity of YSZ from literature (Ciacchi et al., 1994), the ohmic resistance of 1 mm thick YSZ should be around 0.54 $\Omega$ cm$^2$. For LSV6040–YSZ anode sintered at 1100°C, $R_\Omega$ was more than 2 $\Omega$ cm$^2$ at 1000°C (Fig. 3-7). A sintering temperature of 1100°C was thus too low. Increasing the sintering temperature to 1150°C readily reduced $R_\Omega$ to 1.4 $\Omega$ cm$^2$. $R_\Omega$ is further decreased to 0.5 $\Omega$ cm$^2$ in the sintering temperature range of 1180 to 1200°C (Fig. 3-7).

---

1 LSV in LSV-YSZ are not marked explicitly as LSV$_{\text{ox}}$ or LSV$_{\text{re}}$. Note that LSV is LSV$_{\text{ox}}$ during electrode preparation and it is LSV$_{\text{re}}$ during electrochemical testing after in situ reduction.
Figure 3-6  Impedance curves of the LSV6040 (40 wt.%)–YSZ, LSV6040 (50 wt.%)–YSZ, LSV6040 (60 wt.%)–YSZ, LSV6040 (70 wt.%)–YSZ composite anodes in pure H₂ at 1000°C. Note that LSV6040 (70 wt.%)–YSZ anode layer peels off from YSZ electrolyte, leading to unreasonably large impedance.

Figure 3-8a shows the impedance spectra of a typical LSV-YSZ anode (LSV6040Re–YSZ) in pure H₂ and under the OCV condition. The corresponding $R_p$ is in the range from 1.31 to 0.34 Ω cm² between 800 to 1000°C. As reported by Tao and Irvine, LSCM anode showed a $R_p$ of 0.47 Ω cm² in wet H₂ (3% H₂O-H₂) at 925°C (Tao and Irvine, 2004a). Our early works also demonstrated that $R_p$ of LSCM-YSZ (50:50 wt.%) composite anode reached 2.4 Ω cm² at 800°C in wet H₂ (Jiang et al., 2006a). Doped tertiary titanates were also reported as potential anode materials. At the operating temperature of 900°C in wet H₂, $R_p$ reached 0.3 Ω cm² for LaSrTiMnOₓ (Ovalle et al., 2006; Fu et al., 2006), while 0.5 Ω cm² for La₂Sr₄Ti₆₋ₓScₓO₁₉₋ₚ (Canales-Vazquez et al., 2005). LSV–YSZ was thus considered as comparable to these more well-established oxide anode materials. Low-$f$ arcs at a characteristic frequency of 0.1 Hz were shown in Fig. 3-8a. These arcs were tentatively ascribed to gas conversion impedance. The low-$f$ arcs at 1 Hz were reported to the gas conversion impedance between H₂ and H₂O, in the case of hydrogen oxidation in cermet anodes fed with H₂/H₂O mixture (Brown et al., 2000). Due to the imperfect ceramic sealant, gas conversion also exists in present material system, though pure H₂ instead of wet H₂ was used. Based upon the measured OCV and employing Nernst equation, it was estimated that H₂O can reach as high as 7 % in the vicinity of anode. The assumption of gas conversion is supported by the observed low-$f$ arcs up to 1000°C, as gas conversion was usually more significant at high temperature due to the more water produced. This is
because the ceramic sealants become more and more leaking at elevated temperatures. Intermediate-\(f\) arcs peaked around 20–100 Hz were clearly visible at 800°C and 850°C, while they fade away at temperatures higher than 900°C. Impedance arcs peaked around 10–100 Hz were classified as the diffusion over a stagnant gas layer, in the case of \(\text{H}_2\) oxidation in Ni-based cermet anodes (Primdahl and Mogensen, 1999). The intermediate-\(f\) arcs here observed are tentatively regarded to thermal-activated gas diffusion induced impedance. Unobvious high-\(f\) arcs that peaked around several kHz were consistently observed in the spectra. Its real axis part was smaller than the gas conversion arc (low-\(f\) arc) and diffusion arc (intermediate-\(f\) arc).

As shown in Fig. 3-9a, as-fired LSV anode is fine and uniform with particle size in the range of 0.5-2 µm but the porosity is low. The porosity has been increased by in situ reduction from \(\text{LSV}_{\text{ox}}\) to \(\text{LSV}_{\text{Re}}\). Good adhesion and thermal compatibility between the \(\text{LSV}_{\text{Re}}\) and YSZ electrolyte is shown in the inset of Fig. 3-9b, in consistent with the low contact resistance shown in Fig. 3-8a. It seemed difficult to sinter a well-contact \(\text{LSV}_{\text{Re}}\text{-YSZ}\) interface at 1000°C (Aguilar et al., 2004b, Aguilar et al., 2004a), as the melting point of \(\text{LSV}_{\text{Re}}\) is as high as 2050°C (Sayer et al., 1975). In contrast, the melting point of \(\text{LSV}_{\text{ox}}\) components, such as \(\text{Sr}_2\text{V}_2\text{O}_7\), is not higher than 1200 °C, thus enabling good sinterbility in the samples investigated in this study. Taken in account the ionic conductivity of YSZ (Ciacchi et al., 1994), \(R_\Omega\) shown in Fig. 3-8a is reasonable.
for half-cells with 1 mm thick YSZ electrolyte. The ohmic resistance of electrode and the contact resistance between the electrode and the electrolyte contribute 0.1 Ω cm² to the total ohmic resistance at 900°C, but this value become negligible at 1000°C. The low contact resistance is the reason for small high-f arcs obtained in this study (Fig. 3a).

Figure 3-8 (a) OCV impedance responses in pure H₂ for LSV6040$_{Re}$–YSZ (50:50 wt. %) composite anode. (b) Arrhenius plot for LSV$_{Re}$ ($x = 0.2, 0.3, 0.4, 0.5$)–YSZ composite anodes. Inset of (b) shows the corresponding fitted $E_a$ estimated from 800–1000°C.
Chapter 3. Synthesis, characterization, and Performance of LSV via solid state reactions

Figure 3-9  SEM images of LSV6040-YSZ composite anode (a) as-fired in air at 1180°C for 2 h; (b) in situ reduced of (a) in pure H₂ at 900°C for 2 h. Inset of (b) shows the cross-section profile of LSV6040-Re-YSZ with YSZ electrolyte.

![SEM images of LSV6040-YSZ composite anode](image)

Figure 3-10 Anodic overpotential dependencies for LSV₉ₓ₋₅₀ (x = 0.2, 0.3, 0.4 0.5)-YSZ (50:50 wt. %) on (a) current density at temperature of 950°C, and (b) temperature at current density of 0.2 A/cm² in pure H₂. Note that LSV5050₉ₓ₋₅₀-YSZ cannot reach 0.2 A/cm² at 800 °C under the potential bias of 0.8 V (maximum bias applied in this study).
As shown in Figs. 3-8 and 3-10, LSV_{Re}(x = 0.2, 0.3, 0.5)–YSZ (50:50 wt.%) are of inferior but comparable performance as compared to that of x = 0.4. $R_p$ of LSV_{Re}(x = 0.5)–YSZ, the weakest in this category, decreases from 1.92 $\Omega$ cm$^2$ at 800°C to 0.92 $\Omega$ cm$^2$ at 1000°C. $R_p$ of the four examined anodes are fitted to the Arrhenius equation. The apparent activation energies ($E_a$) range from 0.42 to 0.71 eV (inset of Fig. 3-10b). A wide spread values of $E_a$ had been reported in the literature for the state-of-the-art Ni-based anodes. Anodes with fine structure such as Ni film and fine cermet, usually have low $E_a$, e.g. 0.49 eV (Nakagawa et al., 1995) and 0.5 eV (Brown et al., 2000). Large $E_a$ was reported in coarse cermet (1.2 eV) and Ni felt electrodes (1.2-1.6 eV) (Brown et al., 2000). In literature, usually only thermal-dependent impedance arcs were used to abstract $E_a$. In contrast, in this study $E_a$ is estimated from the total polarization resistance. Preliminary analysis shows coarse powders and hence coarse microstructure (coarsening YSZ powder at 1200°C for 1 hour) has higher $E_a$. For example, $E_a$ of LSV_{Re}(x = 0.4)–YSZ (coarsened) with 50:50 weight ratio is 0.85 eV, which is higher than the fine microstructure of $E_a = 0.71$ eV (inset of Fig. 3-10b). Though there might be other factors contributing to the activation energy, it is believed that a fine microstructure of LSV–YSZ contributes to low $E_a$.

Figure 3-10a shows the polarization behavior of LSV_{Re} (x = 0.2, 0.3, 0.4, 0.5)–YSZ (50:50 wt. %) in pure H$_2$ at 950°C. The anodic overpotential of LSV_{Re}(x = 0.4)–YSZ, the best of the four materials, is 0.2 V for a current density of 0.64 A/cm$^2$. For all the four materials, the overpotential is not higher than 0.15 V at a current density of 0.2 A/cm$^2$ at 950°C (Fig. 3-10b). When drawing a current density of 0.2 A/cm$^2$, the overpotential of LSCM-YSZ (50:50 wt. %) was reported to 0.38 V (Jiang et al., 2006a) and 0.18 V (Ye et al., 2008). The polarization performance of LSV is considered to be better than that of LSCM at 950 °C.

Before moving to discussions on wet CH$_4$, it is necessary to diagnose the catalytic effort of Pt. It is surmised that Pt is catalytically active while Au is not. Figure 3-11 shows the impedance spectra of half cells with Pt and Au current collectors (cc). It is surprisingly to note that the whole impedance ($R_G+R_p$) are almost the same. This result
indicates that the catalytic effect of Pt is negligible for LSV–YSZ anodes. A fatal disadvantage of Au cc is the high $R_\Omega$, which is 0.62 Ω cm$^2$ and 0.09 Ω cm$^2$ larger than Pt cc (Fig. 3-11). Actually the Au paste peels off from the electrode very easily during sample preparation (Bek, 2009). Hereafter in this study Pt instead of Au is used as current collector.

3.4.3 LSV–YSZ anodes fed with wet CH$_4$

One of the advantages of SOFC is its capability of utilizing hydrocarbon as fuel, in contrast to PEMFC where only extremely pure H$_2$ can be used. The dominant paraffin in fossil fuel is the natural gas. Natural gas consists of methane together with small amount of ethane, propane, butane, and pentane, as well as traces of carbon dioxide, nitrogen, helium and hydrogen sulphide. From the thermodynamic point of view, methane is more reluctant to be reduced than other alkenes. It is also least prone to carbon deposition because of the stable structure and high hydrogen-to-carbon ratio. According to BP’s annual report on world energy, the reserves-to-production (R/P) ratio is 62.8 (British Petroleum, 2010). Natural gas is extensively used in Singapore for power generation and residential utilization.

![Figure 3-11](image-url)  
**Figure 3-11**  
Impedance responses of La$_{0.6}$Sr$_{0.4}$VO$_3$–YSZ (50:50 wt. %) with Au and Pt as current collectors.
Figure 3-12 shows the impedance responses of LSV6040 (50 wt.%)–YSZ anodes fed with pure CH₄. $R_p$ at 900°C, 950°C, and 1000°C are found to be 13.5 Ω cm², 11.5 Ω cm², and 4.8 Ω cm², respectively, at OCV conditions. The $R_p$ in pure CH₄ is about 14 times larger than that in pure H₂, indicating the large energy barrier of CH₄ oxidation. Nevertheless, the $R_p$ plunges under polarized conditions and shows significant dependency on temperature. At the operating temperature of 900°C, a 52 % drop of $R_p$ is observed under only 100 mV bias. The drop reaches 74 % as the temperature is increased to 1000°C. The activation under potential biases indicates that LSV is a potential candidate for CH₄ oxidation, though the reaction resistance is rather large.

Weakly humidified CH₄ instead of pure CH₄ is routinely used in SOFCs. The incorporation of steam helps in reforming CH₄ into CO and H₂ rich gases. The reforming effect is, nevertheless, less pronounced when CH₄ is only weakly humidified and the fuel flow rate is high. Steam incorporation may play both physical and chemical roles. From the physical aspect, steam improves the adsorption of CH₄ onto the TPB—usually the rate-limiting step in the whole fuel oxidation pathways. From the chemical aspect, absorbed steam on TPBs facilitates fuel dissociation and various spillover reactions. It may also accelerate surface diffusion of the intermediates. All these proposed mechanisms are similar to the case in humidified H₂ fuel. With the absence of direct and in-situ investigation tools, the exact reaction pathways of steam-aided reaction mechanisms are still uncertain. Open circuit voltage (OCV) is the electromotive force, which indicates to what extent energy can be drawn from electrochemical systems. Practical cell potential at open circuit conditions, i.e OCV, is always much lower than the Nernst potential. For example, the Nernst potential of wet CH₄ oxidation in typical SOFC temperatures was in the range from 1.2 to 1.4 V (Jiang et al., 2006b). In contrast, OCV was just about 0.8 to 1.1 V using LSCM–YSZ composite anodes (Jiang et al., 2006b). It is possibly due to incomplete CH₄ oxidation to CO/CO₂ and H₂/H₂O. Experiments showed that it took nearly 30 minutes for the system to become stable when the fuel is shifted from H₂ and CH₄, vice versa.
Figure 3-12  Impedance curves of LSV6040 (50 wt. %)-YSZ anode in pure CH$_4$ at (a) 1000°C, (b) 950°C, and (c) 900°C.

Figure 3-13 shows the OCV of LSV6040$_{Re}$–YSZ (50:50 wt. %) anode fed with wet CH$_4$ at temperatures between 800 to 1000°C. The OCV is dependent on the operating temperature. It increases from -0.91 V at 800°C to -1.09 V at 1000°C. Some glitches consistently appear in the OCVs between 800°C to 850°C, and occasionally at temperatures higher than 850°C. These glitches are likely related to reversible surface oxidation/reduction of LSV species during methane conversion, either internal reforming or direct oxidation. Significant potential oscillation under dc bias was observed in Ni–YSZ fed with CO/CO$_2$ fuel (Holtappels et al., 1999). It was ascribed to periodic carbon deposition and removal on Ni surface. Naked-eye observations on the
tested LSV–YSZ anodes did not find any trace of carbon deposition, thus a surface reconstruction model based on carbon deposition is unlikely relevant to present study. Early works demonstrated that LSCM (Jiang et al., 2006b; Wang et al., 2008) and LSCM–YSZ (Wang et al., 2008) also showed OCV oscillation when fed with wet CH₄. It was phenomenally ascribed to CH₄-H₂O interaction and creation/annihilation of surface oxygen vacancy (Wang et al., 2008). It was plausible since most conducting oxide, like LSCM and LSV₆₆₇₅, are thought to be poor ionic conductors.

As shown in Fig. 3-13b, $R_p$ of LSV₆₆₇₅–YSZ (50:50 wt. %) anodes are 3.53, 1.91, 1.44, 1.17, 1.07 $\Omega$ cm² from 800°C to 1000°C with a temperature increment of 50°C. Figure 3-13c shows the corresponding polarization curves. While the limiting current was observed for the case of 800°C and 850°C, the potential-current curve at 1000°C indicated signs of activation at large polarized conditions. As practical fuel cells are operated under polarized rather than OCV conditions, such kind of kinetic activation of LSV₆₆₇₅–YSZ (50:50 wt. %) anodes is promising. For half-cells tested in wet CH₄ at 900°C, $R_p$ of engineered LSCM–YSZ were around 0.85 $\Omega$ cm² (Tao and Irvine, 2004a) and 2.6 $\Omega$ cm² (Jiang et al., 2006b). LSV₆₆₇₅–YSZ is thus thought to be comparable to LSCM-related materials.

It is believed that the impedance curves in H₂, before switched to and after switched back from wet CH₄, should be the same if LSV–YSZ anode is not coked by deposited carbon. Otherwise, the deposited carbon from CH₄ pyrolysis carbon will block the reaction sites thus rendering larger $R_p$. Figure 3-14 shows the three impedance curves in initial H₂, wet CH₄, and again H₂ after switching back from the exposure in wet CH₄ after sufficient time. It was fairly normal for the larger $R_p$ in wet CH₄ than that in H₂. What of interest is that the $R_p$ of the two impedance curves in H₂, before and after CH₄ exposure, are almost the same, albeit slightly different at high frequency regions. It is evident that the LSV anodes are carbon-resistant. While the low-frequency impedance arc is almost unchanged, the high-frequency arc distinctly different. This change of high-frequency impedance, which is most probably related to interfacial charge transfer, indicates subtle alternation of the anode/electrolyte interfaces.
Chapter 3. Synthesis, characterization, and Performance of LSV via solid state reactions

Figure 3-13  (a) OCV curves (b) impedance spectra (c) anodic overpotential of LSV6040$_{Re}$-YSZ (50:50 wt. %) in wet methane.

Figure 3-14  OCV impedance responses of LSV6040 (50 wt. %)-YSZ anode at 900°C in pure H$_2$ and wet CH$_4$. Legend description: “Initial pure hydrogen”, OCV impedance in H$_2$ (just before gas shifting to wet CH$_4$); “wet methane”, OCV impedance in wet methane; “final pure hydrogen”, impedance in pure H$_2$. 

56
3.5 YSZ-supported single cells with LSV anodes

In this section electrolyte-supported single cells were fabricated and tested. Modest single cell performance had been demonstrated. These preliminary but promising results pave the way for practical SOFCs with LSV-based anodes. The cathode material is chosen from well-established materials. In this study it is LSM. LSM is routinely used for high temperature SOFC with the operating temperature higher than 800°C. To reduce the ohmic losses, the most effective way is to use thin film electrolyte instead of thick electrolyte support, as long as the contact of the SOFC components is already good enough. In this preliminary stage, thin YSZ-supported single cells with LSV anodes were constructed and evaluated.

3.5.1 Fabrication of YSZ-supported single cells

The electrolyte was prepared from YSZ (Tosoh, Japan) by a ceramic route as given in Section 3.4. The thickness of as-sintered YSZ disc is around 500 µm. It was mechanically polished down to 300 µm. The LSV–YSZ composite powders were prepared identical to that described in Section 3.4. The cathode powders, La$_{0.85}$Sr$_{0.15}$MnO$_3$, are commercially available from Nextech (the USA). Our early work showed that A-site deficient LSM had much better catalytic activity than stoichiometry LSM (Leng et al., 2004; Leng et al., 2006). To produce 10% A-site deficiency, say (La$_{0.85}$Sr$_{0.15}$)$_{0.9}$MnO$_3$, La$_{0.85}$Sr$_{0.15}$MnO$_3$ was mixed with the appropriate amount of MnCO$_3$ and calcined at 900°C for 1 hour. (La$_{0.85}$Sr$_{0.15}$)$_{0.9}$MnO$_3$ (LSM)–YSZ composite cathode with 50 wt.% LSM was used as the cathode. LSM added with 10 wt.% graphite powders were applied used as current collection. All the powders are mixed with ink vehicle (Fuel Cell Materials, the USA) to form the corresponding electrode inks.

The two-electrode configuration was used in single cell performance evaluation. It was modified from the three-electrode configuration mentioned in Section 3.4 by shorting the RE and CE. LSV6040–YSZ ink was screen-printed onto the YSZ disc and sintered at 1180°C for 2 hours. The cathode, LSM–YSZ, was subsequently screen-printed to the opposite side of YSZ disc and baked at 600°C for 1 h. A LSM current collection layer with 10 wt.% graphite was applied onto the cathode side. The LSM–YSZ and
LSM were co-sintered at 1150°C for 2 h. Pt meshes were used on both sides for current collection. Pt paste was applied onto anode surface to form a “just cover” fine layer, to ensure good current collection between the anode and Pt mesh. The experimental setup was similar to that mentioned in Section 3.4. They are omitted herein for the sake of simplicity.

Figure 3-15 SEM images of a dismantled single cell after running in pure H₂ and wet CH₄: (a) holistic view of the single cell; (b) EDX Line scan crossing YSZ (electrolyte) and LSV-YSZ (anode) interface, and for the lines: Zr Lα₁ (turquoise); V Kα₁ (bright green); La Lα₁ (purple); O Kα₁ (red); (c) YSZ and LSV-YSZ interface; (d) YSZ and LSM-YSZ (cathode) interface; and (d) LSM-YSZ and LSM (current collector at cathode side) interface.

Figure 3-16 Impedance curves of a cell with configuration LSV6040–YSZ/YSZ/(LSM–YSZ/LSM) when exposed to pure H₂.
3.5.2 Microstructure

The single cell with configuration of LSV–YSZ/YSZ (300 µm)/ LSM–YSZ/LSM was run on pure H₂ and wet methane for more than two days. To visualize how a single cell was constructed, SEM observation was taken after the single cell was disassembled. A holistic view of the single cell is shown in Fig. 3-15a, where the four component layers are clearly visible. The thickness of LSV–YSZ, LSM–YSZ, and LSM layers were 30 µm, 30 µm, and 40 µm, respectively. Good adherence between the neighbouring layers was confirmed by the enlarged SEM images, as shown in Figs. 3-15c, 3-15d, and 3-15e. The pores in the LSV–YSZ anode are homogeneously distributed. Within the detection limit, the energy dispersive X-ray spectroscopy (EDX) analysis is not able to discriminate the ionic (YSZ) and electronic parts (LSV or LSM) of the electrodes. For the LSV–YSZ anode, EDX mapping analysis shows that vanadium is uniformly distributed on the whole surface. The porosity of LSM current collector was higher than LSM–YSZ, because 10 wt. % carbon was added into LSM for mitigating mass transportation problems. The anodic current collector was platinum. Compositional analysis was used to check whether Pt had penetrated into TPB regions. As already discussed in Section 3.4, the thickness of TPB was normally less than 10 µm even for good MIECs. Thus the region that stretched from 10 µm to 20 µm away from the anode-electrolyte interface was probed (Fig. 5-1b). The line-scan and mapping analysis did not detect any Pt in regions adjacent to the YSZ electrolyte. Exhaustive EDX point analysis on more than 10 points in the Pt detection region also did not reveal any Pt. It is concluded that Pt does not penetrate to the Pt detection region, not to mention the TPB regions.

3.5.3 Single cell performance in H₂ and wet CH₄

High OCV values in the range of -1.14 V to -1.17 V are observed for the single cell fed with H₂. This indicates that the sealing condition of the test rig is satisfactory. The temperature dependency of the impedance curves are shown in Fig. 3-16. It gives an activation energy of 0.67 eV, which is comparable to $E_a=0.62$ eV of LSV6040–YSZ anode measured from a three-electrode configuration (Section 3.4.2). It should be emphasized that the impedance curves were collected in a two-electrode configuration. Thus, so-obtained $R_\Omega$ and $R_p$ were a combination of the impedance from all cell components: YSZ electrolyte support, LSV–YSZ anode, LSM–YSZ cathode, current...
collectors, etc. In the present study, the fuel utilization is still below 9% even at the maximum current density of 1.2 A/cm² (See Chapter 9 of Ref. (EG&G Services, 2004) for related tutorials of these calculations). Figure 3-17 shows the current-voltage (I-V) responses for a 300-µm thick YSZ-supported SOFC consisting of LSV6040–YSZ composite anode and LSM–YSZ/LSM bi-layer cathode. The fuel used is pure H₂ and its flow rate is 50 sccm. No signs of activation polarization at low I and mass-transport limited polarization at high I are observed in Fig. 3-17. The OCV, $R_\Omega$, $R_p$, and $P_{\text{max}}$ at various temperatures are listed in Table 3-3. $P_{\text{max}}$ are 0.12, 0.19, 0.28, 0.39, 0.52 W/cm² for temperatures at 800°C, 850°C, 900°C, 950°C, and 1000°C, respectively. To the best of the author’s knowledge, such kind of performance is among the best of single cells employing vanadate anodes with 300-µm YSZ electrolyte support.

![Figure 3-17](image)

**Figure 3-17**  Cell voltage (open symbols) and powder density (closed symbols) with relation to current density for a cell with configuration LSV6040-YSZ/YSZ/(LSM-YSZ/LSM-C). The fuel was pure H₂ and its flow rate is 50 sccm.

The impedance spectra of the single cell exposed to wet CH₄ are shown in Fig. 3-18. $R_p$ is much higher in wet CH₄ than that in H₂, though $R_\Omega$ is similar in both fuels. At 900°C, $R_p$ from wet CH₄ is 1.22 Ω cm², in comparison to 0.84 Ω cm² in H₂. It indicates that LSV, like most anode materials, has much higher electrochemical activity in H₂ than in
The exact oxidation mechanisms of CH₄ oxidation are still unclear because of the complex reaction pathways. In literature two reaction pathways for CH₄ oxidation in SOFCs had been proposed: (i) indirect oxidation, i.e. cracking of the methane on the anode followed by the electro-oxidation of the cracked species (Mogensen and Kammer, 2003); (ii) direct oxidation, i.e. directly electro-oxidizing the methane to CO, CO₂ and H₂O (Steele et al., 1988; Steele et al., 1990). The OCV at 850°C, 900°C, and 950°C are found to be -0.919 V, -0.951 V, and -0.989 V, respectively. Thermodynamic equilibrium analysis indicates that OCV should be in the range from -1.2 V to -1.4 V at temperatures from 850°C to 950°C. Direct oxidation mechanism seems implausible in the case of LSV anodes, as reflected from the low OCVs observed here.

Table 3-3  Data listing of single cell with configuration of LSV6040–YSZ /YSZ/(LSM–YSZ/LSM) /YSZ/(LSM–YSZ/LSM)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>R₀ (Ω cm²)</th>
<th>Rₚ (Ω cm²)</th>
<th>OCV (V)</th>
<th>Pₚₘₓ (W/cm²)</th>
<th>R₀ (Ω cm²)</th>
<th>Rₚ (Ω cm²)</th>
<th>OCV (V)</th>
<th>Pₚₘₓ (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td>0.85</td>
<td>1.99</td>
<td>-1.173</td>
<td>0.12</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>850°C</td>
<td>0.63</td>
<td>1.24</td>
<td>-1.165</td>
<td>0.19</td>
<td>0.64</td>
<td>3.19</td>
<td>-0.919</td>
<td>0.05</td>
</tr>
<tr>
<td>900°C</td>
<td>0.54</td>
<td>0.84</td>
<td>-1.153</td>
<td>0.28</td>
<td>0.53</td>
<td>1.22</td>
<td>-0.951</td>
<td>0.13</td>
</tr>
<tr>
<td>950°C</td>
<td>0.42</td>
<td>0.70</td>
<td>-1.147</td>
<td>0.39</td>
<td>0.41</td>
<td>0.90</td>
<td>-0.989</td>
<td>0.18</td>
</tr>
<tr>
<td>1000°C</td>
<td>0.32</td>
<td>0.65</td>
<td>-1.143</td>
<td>0.52</td>
<td>0.34</td>
<td>---*</td>
<td>-1.005</td>
<td>0.25</td>
</tr>
</tbody>
</table>

* Rₚ at 1000°C in wet CH₄ was not shown because of severe distortion in the low-f impedance arc.
Chapter 3. Synthesis, characterization, and Performance of LSV via solid state reactions

Figure 3-19 shows the DC polarization curves of the single cell in wet CH₄. \( P_{\text{max}} \) at 850°C, 900°C, and 950°C are 0.05, 0.13, and 0.18 W/cm², respectively. Relatively low cell performance of LSV anodes in wet CH₄ calls for further anode engineering. Though still inferior to Ni-cermet based SOFCs, the single cell performance achieved in this study has been quite encouraging. Table 3-4 lists a brief literature survey of single cell performance using vanadate anodes. It can be seen that vanadate anodes are active in electrochemical H₂S oxidation (Aguilar et al., 2004a; Aguilar et al., 2004b; Cheng et al., 2005; Cheng et al., 2006). SOFC with La₀.₇Sr₀.₃VO₃ anode was of excellent sulphur tolerance up to percentage level (Aguilar et al., 2004b). Nevertheless, it seems that La₀.₇Sr₀.₃VO₃ (LSV7030) has low catalytic activity towards H₂ and CH₄ oxidation. Polarization resistance at 1000°C was as large as 5 \( \Omega \) cm² for such cells running on H₂ (Aguilar et al., 2004a). \( P_{\text{max}} \) reaches 150 mW/cm² for the cell with LSV7030/YSZ (250 \( \mu \)m)/La₀.₈₅Sr₀.₁₅MnO₃ configuration fed with pure H₂ at 900°C. Recently, LaCrO₃-Vo₃-YSZ anode containing 40 wt.% reduced vanadium oxide (Voₓ) was tested using tainted syngas derived from coal gasification (Xu et al., 2007). All of these works did not report the performance results on clean CH₄ fuel oxidation. Vanadate had been reported to be excellent in sulphur tolerance. In this chapter, LSV is also proved to have promising performance both in pure H₂ and wet CH₄.

![Cell voltage (open symbols) and power density (closed symbols) with relation to current density for a cell with configuration LSV6040–YSZ/YSZ/(LSM–YSZ/LSM). The fuel was wet CH₄ (CH₄ with 3% H₂O) and its flow rate is 50 sccm.](image-url)
Table 3-4 Comparison of cell performance of SOFC using vanadate oxides.

<table>
<thead>
<tr>
<th>Half cell anode performance $(R_p$ from EIS)</th>
<th>Single cell Performance</th>
<th>Maximum power density (W/cm$^2$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70 (H$_2$, 950°C); 0.90 (wet CH$_4$, 950°C)</td>
<td>LSV6040-YSZ/YSZ (300 µm)/(LSM-YSZ/LSZ-M-C)</td>
<td>0.52(H$_2$, 1000°C); 0.25 (wet CH$_4$, 1000°C)</td>
<td>This work</td>
</tr>
<tr>
<td>~ 9 (H$_2$, 950°C)</td>
<td>~2 (10 % H$_2$S-H$_2$, 950°C)</td>
<td>LSV7030-YSZ/YSZ (250 µm)/SSC-GDC</td>
<td>0.14 (5% H$_2$S-CH$_4$, 950°C)</td>
</tr>
<tr>
<td>2.3 (wet H$_2$, 1000°C)</td>
<td>1.0 (wet 10% H$_2$S-H$_2$, 950°C)</td>
<td>LSV7030/YSZ (250 µm)/LSM-YSZ</td>
<td>0.11 (5% H$_2$S-H$_2$, 950°C)</td>
</tr>
<tr>
<td>~12 (0.5 % H$_2$S-H$_2$, 900°C)</td>
<td>LaCrO$_3$-VO$_x$-YSZ (300µm)/ Pt</td>
<td>LSV7030/YSZ (120 µm)/LSM-YSZ</td>
<td>0.17 (0.5 % H$_2$S-H$_2$, 900°C)</td>
</tr>
<tr>
<td>~ 5.5 (H$_2$, 800°C)</td>
<td>~8.3 (syngas, 800°C)</td>
<td>LSV7030/YSZ (120 µm)/LSM-YSZ</td>
<td>~1 (H$_2$, 800°C)</td>
</tr>
</tbody>
</table>

3.6 Summary

Research works on crystalline structure, electrical conductivity and magnetic behaviour of LSV can be dated back to a half century ago. Extension of LSV into catalytic application was, however, little reported. In this chapter, La$_{1-x}$Sr$_x$VO$_3$ (LSV) with $x = 0.0$, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, 0.9, 0.95, 1.0 were synthesized by solid state reactions, either in oxidized or reduced form. LSV$_{Ox}$ was regarded as a mixture of LaVO$_4$ and Sr$_2$V$_2$O$_7$. Single phase can be obtained only for LSV$_{Re}$ ($x = 0, 0.05, 0.1$) and LSV5050$_{Re}$, and LSV$_{Re}$ ($x = 0.2, 0.3, 0.4$) was a binary phase structure between LaVO$_3$ and (La$_{0.50}$Sr$_{0.50}$)VO$_{2.95}$. Chemical compatibility with YSZ had been confirmed at least up to 1300°C. The TGA analysis showed that the oxygen vacancy in LSV$_{Re}$ is non-negligible.

Composite anodes of LSV$_{Re}$ ($x=0.2$, 0.3, 0.4, 0.5) with YSZ showed comparable electrode performance with more well-studied oxide anodes such as LSCM. Electrode engineering was carried out by means of sintering temperature and electrode
composition. LSV anodes were not able to be sintered satisfactorily below 1150°C. Composite anodes with LSV more than 70 wt.% peeled off from YSZ electrolyte when exposed to pure H₂. Composite anodes with LSV less than 40 wt.% failed to form a percolation network for electron transfer. In this study LSV6040 (50 wt. %)–YSZ was used for electrode performance evaluation. LSV–YSZ anodes achieved $R_p$ of 0.7–1.1 $\Omega$ cm$^2$ in pure H$_2$ at 900°C for 2h. The anodic overpotential was lower than 0.2 V when drawing a current density of 0.2 A/cm$^2$. Apparent activation energies were in the range from 0.42 to 0.71 eV for the four LSV$_{Re}$ ($x= 0.2, 0.3, 0.4, 0.5$)–YSZ anodes. Preliminary study indicated that LSV–YSZ anodes, at least LSV6040$_{Re}$–YSZ, were active for CH$_4$ oxidation. For half cells fed with 3% H$_2$O–CH$_4$ at 900°C, polarization resistance of LSV6040$_{Re}$–YSZ anode reached 1.4 $\Omega$ cm$^2$ at open circuit conditions. Polarization curves showed that the current density can reach 0.2 A/cm$^2$ with the anodic overpotential less than 0.2 V.

Electrolyte-supported single cells with configuration of LSV6040–YSZ/YSZ (300 $\mu$m)/LSM–YSZ/(LSM) were constructed. Satisfactory single cell performance had been demonstrated. When fed with pure H$_2$ and operated at 900°C, $R_p$ of the single cell was 0.84 $\Omega$ cm$^2$ and $P_{max}$ was 0.28 W/cm$^2$. When the fuel gas was switched to 3% H$_2$O humidified CH$_4$, polarization resistance was 1.22 $\Omega$ cm$^2$ and the $P_{max}$ was 0.13 W/cm$^2$. Single cell performance achieved in this study was among the best results of SOFCs employing vanadate anodes. The single cell exhibited great temperature dependency in H$_2$ and wet CH$_4$. Further electrode engineering is desirable in order to achieve high performance. These preliminary but promising results paved the way for further exploration on high performance SOFCs with LSV-based anodes.
Chapter 4. Impedance responses and the double layer structure of LSV anodes via citric route

4.1 Impedance identification of LSV anode in $\text{H}_2$–$\text{H}_2\text{O}$–$\text{He}$ atmosphere

Lanthanum strontium vanadate (LSV) had been attempted to be a plausible SOFC anode material since 2001 (Hui and Petric, 2001). LSV suffers phase transformation between cubic and low symmetric forms under redox cycling. The steep lattice change thus incurred might render LSV an unsuitable candidate. Later, LSV anodes were found with excellent sulphur tolerance but rather modest catalytic activity in clean fuels (Aguilar et al., 2004a, Aguilar et al., 2004b, Cheng et al., 2005, Cheng et al., 2006). In Chapter 3, the lattice mismatch problem was alleviated by in situ reduction of LSV–YSZ composite— the same strategy applied to the state-of-the-art Ni cermet anodes (Ge and Chan, 2009b). With that recipe we demonstrated salient electrode performance of LSV–YSZ composite anodes in pure $\text{H}_2$ and wet methane. To understand this kind of anodes further, fundamental works regarding to fuel oxidation mechanism had been carried out. In this study, the impedance behaviour was investigated via electrochemical impedance spectroscopy (EIS). A series of impedance spectra were collected in deliberately designed $\text{H}_2$–$\text{He}$–$\text{H}_2\text{O}$ ternary atmosphere. The impedance arcs were identified as reaction impedance at high frequencies, concentration impedance at medium-to-low frequencies, and occasionally inductive loops at extremely low frequencies.

4.1.1 Powder synthesis, half-cell preparation, and impedance spectroscopy

LSV powders were synthesized successfully from three soft chemistry methods, i.e. glycine nitrate combustion and two citric routes. All LSV powders mentioned in this chapter are 20 at% strontium doped lanthanum vanadate ($\text{La}_{0.8}\text{Sr}_{0.2}\text{VO}_3$, or simply LSV). $\text{La}_{0.8}\text{Sr}_{0.2}\text{VO}_3$ is preferred based on a trade-off of catalytic activity and redox stability. They were prepared via a citric route with lanthanum nitrate, strontium nitrate, ammonium metavanadate, and citric acid as starting materials. The
as-prepared LSV powders were annealed stepwise to 600°C for 12 hours. They were then mixed thoroughly with YSZ (Tosoh, Japan) in a 50:50 weight ratio. The anodic ink composed of LSV–YSZ and commercial ink vehicle (Fuel Cell Materials, USA). It was screen-printed onto YSZ electrolyte disc (1 mm thick). It was fired for 2 hours at 1210°C to form an anode layer. Its geometric area was 0.46 cm² and its thickness was 30 µm. Pt paste was brush-painted to the opposite side and sintered at 900°C for 30 minutes as counter and reference electrodes.

The electrochemical testing was carried out in the same test rig as given in Chapter 3. A small amount of Pt paste was applied to improve the “point” current collection on the anode side. Both the counter and reference electrode were exposed to air. The fuel gas, consisting of H₂ and He, was modulated from the corresponding pure gases via a Brooks® multi-channel mass flow controller. To yield the H₂–He–H₂O tertiary gas, H₂–He was channelled through a humidifier with temperature control of ± 0.1°C. The half-cell was heated to 950°C at 3°C/min and hold for 4 hours before electrochemical testing. EIS was carried out using a Solartron 1255B frequency response analyzer coupled to a Solartron 1287 electrochemical interface. The impedance spectra were recorded with 10 mV ac amplitude over the frequency range of 10⁻⁵ – 10⁻² Hz, under 0–500 mV anodic dc bias. Before the collection of impedance spectra, the half-cell was subjected to potentiostatic polarization at the desired dc bias for 20 minutes. The potential transients were obtained by chronoamperometry undergoing potential step from open circuit voltage (OCV) to 500 mV anodic bias, with a sampling rate of 30 points/sec.

4.1.2 Impedance spectra, equivalent circuit, and double layer capacitance

Figure 4-1 shows the XRD patterns of La₀.₈Sr₀.₂VO₃ (LSV in short hereafter in this chapter) prepared from solid state reactions and citric route. As mentioned in Chapter 3, LSV prepared from solid state reactions contains ineradicable impurities. In contrast, XRD analysis shows that (Shimadzu 6000, Cu Kα radiation) the LSV prepared from citric route is of single phase after reduction in H₂ at 900°C for 12 hours. This indicates that citric route yields more homogenous and catalytically active LSV particles.
The OCV impedance spectra recorded in pure H\(_2\) generally contain two depressed and poorly separated arcs, besides the parasitic inductance caused by the lead wires at extremely high frequencies (Fig. 4-2a). The high frequency arc, Arc 1, peaks around 500 to 2000 Hz (i.e., relaxation frequency at 500–5000 Hz). Such kind of impedance arcs usually correspond to reaction steps with fast kinetics, such as double layer charging, spillover reaction, charge transfer, and surface adsorption/desorption. Relaxation frequency of the middle-to-low frequency arc, Arc 2, scatters around 0.5 to 2 Hz. With regard to SOFC anodes, middle and low frequency arcs are usually ascribed to gas diffusion in the porous electrode and gas channels, gas conversion, and OCV modulation due to the change of gas compositions. It can be called as concentration impedance. For impedance spectra collected under biases larger than 250 mV, small inductive loops, Arc 3, begin to emerge at extremely low frequencies below 0.1 Hz. This sluggish phenomenon can be either a potential-driven or an activation process from adsorbate intermediates, especially water that is generated in considerable quantity under large dc biased conditions.
Figure 4-2 Impedance responses of LSV–YSZ anode in (a) pure H\textsubscript{2} under different flow rate and (b) H\textsubscript{2}-He binary gases, both under OCV conditions, and (c) pure H\textsubscript{2} under different dc bias. The equivalent circuit is shown in (d). The fuel flow rate was 100 sccm. The testing temperature was 950°C.
While too early to draw a conclusion on the physical causes of Arc 3, it is not trivial to do an analogy with other energy conversion systems also with low frequency inductive loops. Such phenomenon had been observed in “all solid” secondary battery (Kahil et al., 1986) and polymer fuel cells (Roy et al., 2007; Schneider et al., 2008). Arc 3 is also fairly common in SOFC cathodes. While it might be due to enhanced electronic conductivity of electrolyte surface (Schouler and Kleitz, 1987), theoretic investigations on oxygen reduction on Au/YSZ interface indicated that Arc 3 may be aroused from stepwise multi-electron transfer with adsorbed intermediates (Vanhassel et al., 1991). Besides the mechanism mentioned above, for LSM-YSZ cathode it may also due to the improved interface structure after current passage. In terms of more relevant Ni anodes, Arc 3 was seldom found in Ni pattern anodes but not uncommon in Ni paste and Ni cermet anodes. Controversy still exists: Bieberle claimed no inductive loops (Bieberle and Gauckler, 2001; Bieberle, 2000) while Boer observed Arc 3 in Ni pattern anodes (Boer, 2000). Generally, Arc 3 only exists in porous anodes with low electrode impedance.

After this rather qualitative discussion on the shapes and possible contributions, impedance spectra are fitted to certain equivalent circuits. A subset of inductance and negative resistance in parallel, $L_i/R_i$, describes the parasitic inductance aroused from Pt lead wires at extremely high frequencies. Arc 1 is simulated routinely by a $R/CPE$ subset. The high frequency part of Arc 2 is generally of linear relationship. In contrast, the low frequency part is somewhat a depressed arc—typical appearance of O element, which is also named as finite length Warburg or porous bounded Warburg element (Consultrsr.com, 2011). O element is used extensively to depict the impedance of rotating disk electrode (RDE), where the reactants simply diffuse through the Nernst Diffusion Layer (NDL). In our gas channel design the inlet gases are supplied perpendicular to the anode surface, which produces similar fluid flow field to RDE. Fig. 4-2a shows the impedance responses of the LSV–YSZ anode with different H$_2$ flow rate. With the decreasing flow rate, it is worth noting how Arc 2 changes from finite length Warburg to some symptoms of infinite Warburg while Arc 1 almost remains unchanged. Arc 2 is also reduced significantly with increasing dc biases (Fig. 4-2c), which may be due to the compacted NDL or buffering effect of the generated water. The change of fuel flow rate only alters the hydrodynamic force, i.e., the NDL thickness. In contrast, fuel dilution not only changes NDL thickness
but also the H2 partial pressure on the NDL surface. Both Arc 1 and Arc 2 are increased due to fuel dilution (Fig. 4-2b), implying that H2 concentration in NDL affects the fuel oxidation reactions. Arc 3 is not included in the equivalent circuit because its physical nature is still undetermined. Impedance curves are deconvoluted through a $R_s(W_s)$ equivalent circuit, where $R_s$ is the series resistance and $W_s$ is an O element.

All electrochemical reactions must take place at the electrified interface, the double layer. The nature of double layer at LSV–YSZ interface and the magnitude of its capacitance are the keystones to understand the anode behaviour towards H2 oxidation. In this section the double layer capacitance ($C_{dl}$) is obtained from two methods: one is EIS method and the other is transient method. In the EIS method, each impedance curve is fitted to an equivalent circuit and the $C_{dl}$ is assigned to be the capacitance ($C$) calculated from $(R_1/CPE_1)$. The relationship between $C$, impedance $Z$, and angular relaxation frequency $\omega_{\text{max}}$ of $(R_1/CPE_1)$ can be described by

$$C = \frac{\sqrt[4]{R_T T_1}}{R_1} = T_i R_{\text{max}}^{n-1} \quad \text{(Equation 4-1)}$$

$$Z = \frac{1}{T_i (i\omega)^n} \quad \text{(Equation 4-2)}$$

where $R_1$ is the resistance, $T_1$ (CPE1-T) and $n$ (n equivalent to CPE1-P) are parameters of constant phase element #1 in ZView©, $\omega$ is the angular frequency, and $i$ is the imaginary unit. The circuit used in transient method, $R_u$ ($C_{dl}/R_p$), includes uncompensated resistance ($R_u$), double layer capacitance ($C_{dl}$), and the polarization resistance ($R_p$). Though sometimes the values of parameters obtained from the two methods are quite similar (e.g., $R_u$ to $R_s$ and $R_p$ to $R_1$), it is worth to highlight that their physical meanings are always different. For current transients responding to a potential step, $C_{dl}$ can be obtained from integration, i.e.

$$C_{dl} = \frac{\Delta Q}{\Delta U} = \int_{t=0}^{t=t_s} \frac{[i(t) - i_s]}{\Delta U} dt \quad \text{(Equation 4-3)}$$
where \( \Delta U \) is the difference between the OCV and applied potential step, \( t_s \) is the time interval, and \( i_s \) is the current density where the current decay saturates. \( C_{dl} \) can also be estimated from non-linear fitting. If a potential step \( U \) is applied to the system at \( t = 0 \), the current transient fulfills

\[
C_{dl} R_u \frac{di(t)}{dt} + \left(1 + \frac{R_u}{R_p}\right)i_t(0) = \frac{U}{R_p} 

\]

(Equation 4-4)

Solve Eq. 4-4 to yield its analytical solution,

\[
i_t(t) = \frac{t(R_p + R_u)}{C_{dl} R_p R_u} \left( U + e^{\frac{t(R_p + R_u)}{C_{dl} R_p R_u}} \right) \]

(Equation 4-5)

With certain initial conditions on the \( R_u \) and \( R_p \), \( C_{dl} \) is easily available from commercial tools like Wolfram Mathematica©. The nominal \( C_{dl} \) obtained from EIS method ranges from 0.3 to 0.7 mF/cm\(^2\) (Fig. 4-3a). The large fitting error of \( C_{dl} \) calculated from Arc 1 is resulted from the overlapped impedance arcs, noting that the magnitude of Arc 1 is 2 to 4 times smaller than that of Arc 2. A pattern of \( n - C_{dl} \) dependency appears to exist but is still within the fitting error. In the transient method, this problem is even more severe because of the nature of current transients. The current signals oscillate all through the experiment (Fig. 4-4). It is surprising that \( C_{dl} \) varies almost 2 orders of magnitude from different methods—0.5±0.2, 4.3±0.3, and 18.3±1.6 mF/cm\(^2\) for EIS method (Fig. 4-3a), non-linear fitting (Fig. 4-3c), and integration (Fig. 4-3c), respectively. Typical \( C_{dl} \) for solid state electrodes, especially Ni cermet SOFC anodes, are in the order of \( 10^{-1} \) mF/cm\(^2\) (Gewies et al., 2007; Robertson and Michaels, 1991; Primdahl and Mogensen, 1997). \( C_{dl} \) from the EIS method may be envisaged to be “correct” double layer capacitance, which will be discussed in Sections 4.2 to 4.4 in detail. It is, however, necessary to explain why so large discrepancy is observed in the three methods. One explanation is that \( C_{dl} \) obtained from the transients is tainted by pseudo-capacitance that is resulted from bulk phenomena. For gas diffusion within the porous electrode,
it could contribute to a capacitance in the order of $10^1 \text{ mF/cm}^2$ (Primdahl and Mogensen, 1999). Its relaxation frequency is generally around several Hz, equivalent to a time constant in the order of $10^{-1} \text{ s}$ ($\tau = 1/(2\pi f)$). Other bulk phenomena, such as gas conversion, give even larger values ca $10^3 \text{ mF/cm}^2$ (Primdahl and Mogensen, 1998). As shown in Fig. 4-4, the time constants of transient experiments are around 1–2 seconds, a value large enough to trigger phenomena other than double layer charging, such as gas diffusion and gas conversion.

![Figure 4-3](image)

Figure 4-3 Nominal double layer capacitance of LSV–YSZ anode obtained from EIS (a, b) and transients (c), as a function of $n$ value in CPE of $R_1$/CPE (a) and under small anodic dc biases (b, c). The H$_2$ flow rate was 100 sccm. The testing temperature was 950°C.
With some confidence on the $C_{\text{dl}}$ values around 0.3 to 0.7 mF/cm$^2$, here the double layer structure is briefly discussed. Most researchers adopt the Helmholtz-Perrin theory to explain double layer capacitance in SOFC anodes. This theory treats the double layer to a parallel-plate capacitor. Area-specific $C_{\text{dl}}$ is thus represented as

$$C = \frac{\Delta Q}{\Delta U} = \frac{\varepsilon \varepsilon_0}{d},$$

(Equation 4-6)

where $d$ is the distance between the oHp and YSZ surface, $\varepsilon$ is the relative permittivity of the material in-between, and $\varepsilon_0$ is the permittivity of free space. Eq. 4-6 implies constant $C_{\text{dl}}$ with no dependency on voltage. However, $C_{\text{dl}}$ of LSV–YSZ anode does change with different dc biases (Fig. 4-3b). Reliable and ubiquitous $C_{\text{dl}}$–$U$ relationship is yet to be identified. In literature, positive $C_{\text{dl}}$–$U$ dependency had been reported (Bieberle et al., 2001). Helmholtz-Perrin theory also predicts unrealistic small double layer distance. Some modification must be applied to the theory. At least, the diffusive nature of the electrified layer, exact charged species, and extension of three phase boundary (TPB) should be taken into account. More works should be addressed on these problems.

### 4.1.3 Impedance behaviour under H$_2$–H$_2$O–He ternary atmosphere

Fig. 4-5 shows the fitted results of elements in ($L_i/R_i$) $R_s$ ($R_1$/CPE$_1$) $W_s$ equivalent circuit. For Arc 1 simulated by ($R_1$/CPE$_1$), both $R_1$ and $C_{\text{dl}}$ increase with increasing H$_2$ content in H$_2$–He atmosphere. Strong dependency of $R_1$ to H$_2$ content implies that surface adsorption or dissociation of H$_2$ onto LSV surface could be the rate determining step in H$_2$ oxidation. The nominal $C_{\text{dl}}$ rises slightly with increasing H$_2$ content, indicating an extension of the reaction sites or accumulation of charged species on LSV side of TPB. It is not clear whether the fuel dilution effect is of chemical or physical nature, bearing in mind how it can alter LSV surface structure and gas diffusivity. Arc 2 is described by an O element, Generalized Finite Warburg element (GFW, $W_s$), whose impedance is

$$Z = R \frac{\tanh(ioT)^p}{(ioT)^p},$$

(Equation 4-7)
where \( R (W_s R) \), \( T (W_s T) \) and \( P (W_s P) \) are the parameters of GFW in ZView\textsuperscript{©}. The Warburg resistance \( R \) increases significantly from 0.8 Ω cm\(^2\) to 1.8 Ω cm\(^2\) but \( T \) decreases consistently for almost 25%, when the fuel composition changes from 10 vol. % He to 90 vol. % He. While the increase of \( R \) is straightforward to understand, it is confusing for the decreasing \( T \). In the diffusion interpretation, \( T \) stands for

\[
T = \frac{L^2}{D_{\text{eff}}} = \frac{\tau L^2}{D_{\text{AB}} \phi},
\]

(Equation 4-8)

where \( L \) is the NDL thickness, \( \tau \) is the tortuosity, \( \phi \) is the porosity, and \( D_{\text{AB}} \) is the binary diffusion coefficient. \( T \) should increase according to fuel dilution, with the assumption of constant effective diffusion coefficient (\( D_{\text{eff}} \)). Anyway, an order-of-magnitude evaluation of the \( L \) value should still be meaningful. In present experiments \( L \) is estimated to be around 5–10 mm, with the assumption of \( 0.25 < \tau < 0.35 \) (Williford et al., 2003), \( 0.3 < \phi < 0.5 \) (this study), and \( 11 \times 10^{-4} < D_{\text{H}_2, \text{He}} < 13 \times 10^{-4} \) m\(^2\)/s (McCourt et al., 2005).

**Figure 4-4** Current transient of LSV–YSZ anode subjected to a 200 mV potential step. The \( \text{H}_2 \) flow rate is 100 sccm. The testing temperature is 950°C.
Impedance spectra of LSV–YSZ anodes recorded in wet atmosphere (H₂-H₂O gases) are distinct to their counterparts in dry atmosphere. The impedance points collapse below 1 Hz. Arc 1 dominates and Arc 2 appears to die out. The grouped polarization resistance, $R_p$, is comparable to that in dry H₂. The whole spectra cannot be fitted to relevant equivalent circuit given in Figure 4-2d. The $\omega_{\text{max}}$ of Arc 1, 200–600 Hz, is one order lower and the corresponding reaction resistance, $R_1$, is however larger than that in pure H₂. H₂ oxidation is somewhat retarded but the gas diffusion problem is alleviated significantly. This detrimental steam effect on Arc 1 emerges even with a small addition of water. It continues at least up to 15 vol. % H₂O, as shown in Fig. 4-6. To incorporate small amount of steam into fuels has been a common practice for SOFCs with Ni-cermet anodes. A beneficial water effect is
with little controversy for most SOFC anodes. It is rather impressive for the detrimental water effect as observed in LSV–YSZ anodes. It seems little to do with the change of electrode conductivity, as far as the negligible variation of $R_s$ is concerned (Fig. 4-6). As steam facilitates the surface conduction of YSZ (Sakai et al., 2003), the water effect of LSV–YSZ anodes must come from the subtle alternation of LSV surface structure but not that of YSZ. Much works on the interfacial structure of LSV have to be carried out.

![Impedance responses of LSV–YSZ anode in H$_2$–H$_2$O atmosphere.](image)

Fig. 4-7 exhibits how the LSV–YSZ anode responses under both water and fuel dilution effects. For impedance spectra recorded at wet atmosphere (here “wet” means H$_2$ humidified at room temperature, i.e. 3 vol. % H$_2$O–H$_2$), all the spectra are not able to be fitted to equivalent circuit given in Figure 4-2d. Any discussions relying on equivalent circuit, like capacitance, are thus not meaningful. When the fuel is shifted to wet atmosphere, with caution it is assumed that Arc 1 remains and Arc 2 converges at low frequencies. With this assumption the resistance values are roughly estimated from the corresponding impedance spectra. Comparing the spectrum obtained from wet H$_2$ to that from the dry H$_2$, $R_s$ is identical (0.67 Ω cm$^2$) and $R_1$ slightly increases from $0.13 \pm 0.02$ to $0.15 \pm 0.03$ Ω cm$^2$ (Fig. 4-7a and 4-7b). The $R_2$ slumps from 0.73 to 0.09 Ω cm$^2$, an impressive result exhibiting on how only 3 % H$_2$O almost eliminates the dominant diffusion impedance in dry atmosphere. In the case of fuel dilution of wet H$_2$, the relaxation frequency shows a decreasing trend and is one order lower than that in dry atmosphere, indicating more sluggish reaction
kinetics at low hydrogen partial pressure atmosphere (Fig. 4-7c). Furthermore, \( R_1 \) increases nearly three times when wet \( H_2 \) relinquishes gradually to \((10H_2-90He)-3 \% H_2O\) (Fig. 4-7b), comparing to only one time increase of dry \( H_2-He \) atmosphere in that case (Fig. 4-5). High electrode degradation rate in wet fuels may be due to its oxidizing atmosphere. Note that the oxygen partial pressure jumps 2–3 three orders to \( 10^{-15} - 10^{-18} \) bar with the introduction of only 3 \% \( H_2O \).

![Figure 4-7](image)

(a) Impedance responses of “Arc 1”, (b) estimated resistance values, and (c) relaxation frequencies of LSV-YSZ anode in \( H_2-H_2O-He \) atmosphere.

### 4.1.4 Brief summary

The impedance behaviour of composite anodes of 20 at \% strontium doped lanthanum vanadate (LSV) and yttoria-stabilized zirconia (YSZ) was investigated in \( H_2-H_2O-He \) atmosphere. Impedance spectra in \( H_2-He \) binary atmosphere mostly contain two depressed and poorly separated arcs, and occasionally inductive loops at extremely low frequencies under biased conditions. The high frequency arc, Arc 1, was ascribed to reaction resistance. The middle-to-low frequency arc, Arc 2, was identified to concentration impedance in the porous electrode or gas channels. Small inductive loops, Arc 3, begin to emerge for dc biases larger than 250 mV. Significant efforts were contributed to obtain the double layer capacitance. The EIS method might have given “correct” capacitance in the order of \( 10^{-1} \) mF/cm\(^2\). The capacitance
obtained from the transient method is contaminated and its value is 1–2 orders higher than normal double layer capacitances. In wet atmosphere, the impedance spectra still include Arc 1 but Arc 2 collapses together at low frequencies. A detrimental water effect that seldom observed in most SOFC anodes was identified up to 15 vol. % H₂O.

4.2 Double layer structure in solid oxide fuel cell anode/electrolyte interfaces: a Monte Carlo study

Solid oxide fuel cells (SOFCs) are high temperature energy conversion devices owning the advantages of high efficiency and fuel flexibility (McIntosh and Gorte, 2004; Goodenough and Huang, 2007). The electrochemical fuel oxidation is believed to occur around three phase boundaries (TPBs), influenced at least by materials properties, fuel composition, operating conditions, impurities (Hansen et al., 2004), and water (Sakai et al., 2003). The reaction mechanisms can thus be fairly complicated. Some reaction paths have been proposed but the underlying mechanisms are hitherto still unclear (Raz et al., 2001; Mogensen et al., 2007). Surprisingly, little attention has been paid to the double layer of anode/electrolyte interfaces. The double layer plays a fundamental role in determining the electrode kinetics and has attracted broad interests in various electrochemical systems (Pajkossy and Kolb, 2007; Rufford et al., 2009). A clear understanding on the double layer structure should be helpful in elucidating the interfacial structures and reaction processes in SOFCs. This work was dedicated to provide a quantitative picture of the double layer in SOFC anode/electrolyte interfaces. A case study was carried on lanthanum strontium vanadate (La₀.₈Sr₀.₂VO₃, LSV)/8 mol % yttria-stabilized zirconia (YSZ) interfaces. LSV is a highly conducting oxide and has great potential to be SOFC anode fed with tainted fuels (Ge and Chan, 2009b).

The solid electrolyte interface usually has a more compact double layer than the liquid electrolyte interface. Furthermore, charged particles in solid crystalline electrolytes are mobile only in certain directions. The primitive model method initially proposed by Torrie and Valleau (Torrie and Valleau, 1979), which successfully describes the Gouy–Chapman (G–C) layer in liquid electrolytes (Wang and Ma, 2010a; Fedorov et al., 2010), therefore seems insufficient to depict the whole double layer in solid electrolyte
interfaces. Generally speaking, solid electrolyte interfaces are conceptually simpler than their liquid counterparts due to confined lattice ions and diminished ion-dipole interactions. These kinds of simplifications enabled us to simulate the oxygen vacancy distribution in YSZ as the stochastic evolution of randomized charged particles on well-defined lattices.

This work simulated 2-dimensional double layer structure of LSV/YSZ interfaces in LSV–YSZ(H$_2$)|YSZ|Pt(air) half cells at 950 °C, with an open circuit voltage (OCV) of -1.18 V. The electrons on the LSV side were aligned compactly along the LSV/YSZ interface. The oxygen vacancy distributions on the YSZ side of the interface were simulated by the Markov chain Monte Carlo (MCMC) technique. The square grid ($L\times L$) was subsumed to (400) planes of YSZ. The grid size $L$ was assigned as 40, as a trade-off of computing time and adequate description of the double layer. The normalized distance ($z$) away from the LSV/YSZ interface was in unit of the nearest neighbouring distance among oxygen vacancies (0.257 nm, PDF #30–1468). Impenetrable walls at $z = 0$ and $z = L$ represented the LSV/YSZ interface and the bulk YSZ, respectively. The $L\times L$ grid was translated with periodic boundary conditions in the direction perpendicular to the LSV/YSZ interface. The Hamiltonian of canonical ensemble comprises (i) the attraction between the reference particle and the charged line ($H_{p-l}$) and (ii) the repulsion due to neighbouring particles ($H_{p-p}$). $H_{p-l}$ is due to the long-range Coulombic attractions between the electron reservoirs at the LSV side and the reference oxygen vacancy in the YSZ side of the LSV/YSZ interfaces,

$$H_{p-l} = \sum_{k}^{N} \left[ \frac{q\lambda}{2\pi\varepsilon_0\varepsilon_r} \ln \frac{L + \sqrt{L^2 + 4z_k^2}}{z_k} \right],$$

(Equation 4-9)

where $N$ is the total numbers of oxygen vacancies, $\lambda$ the line charge density, $q$ the charge of oxygen vacancy ($q=2e$), $\varepsilon_0$ the vacuum permittivity, and $\varepsilon_r$ the relative static permittivity. $H_{p-p}$ is simply due to the Coulombic repulsions among oxygen vacancies,

$$H_{p-p} = \sum_{k}^{N} \sum_{l}^{N} \frac{q^2}{4\pi\varepsilon_0\varepsilon_r r_{kl}},$$

(Equation 4-10)

where $r_{kl}$ is the distance between a $k$ and a $l$ oxygen vacancies. Let the probability of a transition from state $i$ to $j$ is $p_{ij}$ ($i \neq j$), of a trial realizing this transition is $q_{ij}$, and of an
acceptance of this trial is $f_{i,j}$. It is then found that

$$p_{i,j} = q_{i,j} f_{i,j}.$$  \hspace{1cm} \text{(Equation 4-11)}

The $q_{i,j}$ fulfils the uniform distribution. In this study, the $f_{i,j}$ is according to the Metropolis algorithm,

$$f_{i,j} = \min \left\{ 1, \alpha \exp \left[ -\frac{(1 - \beta \theta^2) \Delta H_{p^{i,j}} + \Delta H_{p^{p,j}}}{kT} \right] \right\},$$  \hspace{1cm} \text{(Equation 4-12)}

where $\theta$ is the coverage rate of the outer Helmholtz plane (oHp), $\alpha$ a factor related to the effective double layer thickness, $\beta$ ($0 < \beta < 1$) a degenerated factor accounting for the driving force decay, $k$ the Boltzmann constant, $T$ the absolute temperature. The rapid prototyping was implemented on Mathematica® 7. All MCMC simulations were run at $1 \times 10^6$ iterations, which had been proved to be sufficient to reach the invariant distribution. It took nearly 40 hours to run the code on a Hewlett–Packard® Z400 workstation.

Figure 4-8 shows a typical oxygen vacancy diagram in the YSZ side of LSV/YSZ interfaces under OCV condition. Oxygen vacancies in the first several charged sheets seem to be strongly attracted by the interface. The oxygen vacancy distribution gradually becomes stochastic along the direction towards the bulk YSZ. Figure 4-9 shows the three-dimensional visualization and the density plot constructed by superimposing 16 such diagrams that are generated from the same code. As shown in Fig. 4-9, the oxygen vacancies exhibit no catastrophic agglomerations and are uniformly distributed at places far away from the interface ($z > 10$). It is worth to highlight that the oxygen vacancy concentrations adjacent to the interface is one order of magnitude larger than that in the bulk YSZ, mostly probably due to the double layer charging effect. This interfacial accumulation of oxygen vacancies should be incorporated into any analyses on electrode kinetics and reaction mechanisms around TPBs (e.g. adsorption, spillover, and desorption). The double layer region extends about 6 to 8 sheets (i.e. 1.5 to 2.1 nm), beyond which the background concentration is reached. The border between the double layer and the bulk YSZ is nevertheless very obscure.

The inset of Fig. 4-10 gives the one-dimensional relative oxygen vacancy density ($\rho / \rho_0$)
profile of the corresponding diagram. \( \rho/\rho_0 \) is defined as the ratio of summed oxygen vacancy densities of each sheet (\( \rho \)) over the background density (\( \rho_0 \)). \( \rho/\rho_0 \) of the first five sheets, as shown in Fig. 4-8, are 12.32, 6.02, 4.17, 2.32, and 1.58. Comparing to the cases of liquid electrolyte interfaces (Fawcett, 2009) (Torrie and Valleau, 1980), these \( \rho/\rho_0 \) values are comparable but the \( \rho/\rho_0 \) profile decays much faster. Figure 4-10 shows the \( \rho/\rho_0 \) profiles of polarized LSV/YSZ interfaces under anodic biases (\( E_{bias} \)) from 0 to 150 mV. Each profile is averaged from 7 independent MCMC runs. The \( \rho/\rho_0 \) profiles of heavily biased interfaces are “steeper” than those of lightly biased interfaces. The inset of Fig. 4-10 shows listed fitting results of the \( \rho/\rho_0 \) profiles according to an exponential decay, \( \rho/\rho_0 = 1 + a \times \exp(-k \times z) \). \( a \) and \( k \) are in the ranges from 22.9–23.1 and 0.71–0.73, respectively. Both of them exhibit descendent behaviours towards the increase of \( E_{bias} \), implying the gradual relaxations of the double layer. This phenomenon roots in the dwindling Volta potential difference of LSV/YSZ interfaces, \( \Psi_{LSV}^{YSZ} \), when the interfaces are subjected to changing \( E_{bias} \). The effect of \( E_{bias} \) on \( \Psi_{LSV}^{YSZ} \) is nontrivial and deserves the electrochemical potential analysis on half cells.

![Figure 4-8](image-url) Oxygen vacancy distribution diagram in the YSZ that is adjacent to the LSV/YSZ interface, under OCV condition. The inset shows the corresponding relative oxygen vacancy density profile.
Figure 4-9 (a) Three-dimensional visualization and (b) density plot of oxygen vacancies in the YSZ side of LSV/YSZ interfaces under OCV condition.
Figure 4-10 Relative oxygen vacancy density profiles in the YSZ side of polarized LSV/YSZ interfaces under anodic biases from 0 to 150 mV. The profiles are shifted vertically merely for illustration purpose.
The separation of the Helmholtz–Perrin (H–P) layer and the G–C layer has an important application on calculating the Volta potential distributions across polarized interfaces. It is however difficult to pinpoint the “boundary” between the two layers. It might only be conceptually separable because the charge distribution is continuous even around the boundary. To present the double layer clearly, Fig. 4-11a shows the $\rho/\rho_0$ values of the charged sheets that are supposed within the double layer region. In this study, the first two charged sheets are tentatively regarded to compose the H–P layer. The Volta potential portion of the H–P layer over the whole double layer ($\Psi_H/\Psi^{LSV}$) are thus found to be $0.80\pm0.01$, $0.77\pm0.01$, $0.77\pm0.02$, $0.77\pm0.01$, $0.76\pm0.02$, $0.74\pm0.01$, and $0.74\pm0.01$, under $E_{bias}$ of 0, 20, 50, 70, 100, 120, and 150 mV, respectively (Fig. 4-11b). A typical double layer structure therefore looks like: 70–80% of oxygen vacancies are immobilized in the outer Helmholtz plane, with a distance of 0.5–0.8 nm away from the LSV/YSZ interface; 20–30% of oxygen vacancies decay stochastically into thermal
disarray, with an effective region that extends about 2 nm into the bulk YSZ. Further work on the effects of dielectric mismatch (Jho et al., 2008; Wang and Ma, 2010b), temperature, and fuel atmosphere will be considered in future to establish a complete understanding of SOFC anode/electrolyte interfaces.

4.3 Double layer capacitance of anode/solid-electrolyte interfaces

Solid electrolytes have been widely used in solid state energy conversion systems like batteries and fuel cells. Among various energy conversion systems, solid oxide fuel cells (SOFCs) own the advantages of high efficiency and fuel flexibility. The interfacial reaction mechanisms across the electrolyte and the electrode in SOFCs, however, are still in controversy (Mogensen et al., 2007; Bessler et al., 2010). One of the reasons may be the insufficient understanding on the double layer under SOFC operating conditions.

The double layer consists of an electron layer on the electrode and an oxygen vacancy layer on the electrolyte. One of the most-studied descriptors of the double layer is the double layer capacitance ($C_{dl}$). The electrocapillary technique represents the most classic method of measuring $C_{dl}$ in mercury/solution interfaces (Grahame, 1947). Direct-current measurements of $C_{dl}$ in solid electrode/liquid electrolyte interfaces became feasible after the invention of potentiostat (Hickling, 1942). These dc voltammetry methods are, however, limited to low sensitivity and poor resolution. For example, our previous work demonstrated that they failed to resolve $C_{dl}$ from various pseudo-capacitances (Ge and Chan, 2009a). In situ characterization techniques, including infrared spectroscopy (Ashley et al., 1991), Raman spectroscopy (Macomber et al., 1982), atomic force microscopy (Wang and Bard, 2001), neutron diffraction (Williams et al., 1998), and various synchrotron radiation methods (Tikhonov, 2006; Luo et al., 2006), had been used to investigate the double layer in recent years. Recently, encouraging works on in situ Raman and infrared spectroscopy had been carried out in SOFCs (Pomfret et al., 2008; Lu et al., 2002).

Impedance spectroscopy has hitherto been very popular on measuring $C_{dl}$ in various interfaces. Impedance responses of SOFC electrode/electrolyte interfaces are always
severely depressed due to the frequency dispersion of electrochemical reactions. The frequency dispersion rarely occurs in homogeneous and clean interfaces, e.g. adsorbate-free mercury (Grahame, 1947) and single crystal surfaces (Eberhardt et al., 1996). It is largely ascribed to inhomogeneity: (i) fractal disorder (Pajkossy, 2005), including surface roughness (Jarzabek and Borkowska, 1997), electrode porosity (Hitz and Lasia, 2001), and atomic scale irregularity (Kerner and Pajkossy, 1998); (ii) non-uniform potential and current distribution (Jorcin et al., 2006); and (iii) anion adsorption (Pajkossy and Kolb, 2007). The frequency dispersion has been fairly common in SOFCs because of their porous electrodes and corrugated electrode/electrolyte interfaces. The constant phase element (CPE) is a non-intuitive circuit element that can be used to describe depressed impedance spectra. The frequency dispersion makes the CPE exponent \( n \) difficult to be obtained from impedance spectra, because the constant phase angle of CPE \( \theta \) becomes ambiguous due to the overlapping of impedance arcs. This might be one of the reasons why diverse \( C_{dl} \) values have always been reported. Take the Ni–yttria-stabilized zirconia cermet, a typical high temperature SOFC anode, as an example. Primdahl and Mogensen reported that \( C_{dl} \) of Ni–8-mol% yttria-stabilized zirconia (YSZ\(^{\ddagger} \)) anodes was in the range from 200 to 700 \( \mu F/cm^2 \) in 3% \( H_2O-H_2 \) and at 1000 °C (Primdahl and Mogensen, 1997). Jiang and Badwal noted that \( C_{dl} \) of Ni–3-mol% yttria-stabilized zirconia anodes at 1000 °C was ca 100 \( \mu F/cm^2 \), slightly increasing with the increase of \( H_2 \) concentration in 2% \( H_2O-H_2-N_2 \) atmosphere (Jiang and Badwal, 1999). Holtappels et al. showed that \( C_{dl} \) of Ni–YSZ anodes was of several tens of \( \mu F/cm^2 \) from 725 to 890 °C but could jump to several hundred \( \mu F/cm^2 \) at 950 °C, exhibiting complex dependencies on temperature and fuel composition (\( H_2 \) balanced with \( H_2O \) and \( Ar \)) (Holtappels et al., 1999). The extrapolated \( C_{dl} \) at 1000 °C appears to be in the capacitance range given in Ref. (Primdahl and Mogensen, 1997). Besides the frequency dispersion, it is worth noting that the differences in SOFC architectures could also be responsible for the reported discrepancies. As shown in Ref. (Jiang and Badwal, 1999), \( C_{dl} \) of 80% Ni–zirconia anodes could be 30% and 150% larger than the anodes containing 70% of Ni and pure Ni, respectively. These results imply that the double layer of SOFC anode/electrolyte interfaces is fairly complicated. The underlying mechanism is still unclear and relevant capacitance models are yet to be developed.

\( C_{dl} \) can also be evaluated theoretically according to Stern’s method (Stern, 1924),
consisting of the Helmholtz model (Helmholtz, 1853) and Gouy–Chapman model (Gouy, 1910; Chapman, 1913). In this work, the experimentally measured and theoretically obtained \( C_{dl} \) are hereafter denoted as \( C_{app}^{dl} \) and \( C_{int}^{dl} \), respectively. The derivation of the Gouy–Chapman capacitance \( (C_G) \) is the most critical task in calculating \( C_{int}^{dl} \). Firstly, it involves an investigation on the potential distributions across electrode/electrolyte interfaces. Then, the Helmholtz–Perrin layer (the H–P layer) and the Gouy–Chapman layer (the G–C layer) must be separated.

It is worth noting that \( C_{dl}^{app} \) of SOFC electrode/electrolyte interfaces are always much larger than those involving liquid electrolytes (Brett and Brett, 1994; Kisza, 2006). In addition, conventional capacitance models, e.g. the parallel-plate condenser model, predicate unrealistically small thicknesses of the double layer. Furthermore, they fail to account the changing capacitance behaviour of polarized SOFC interfaces. To address these problems, a case study was carried out on lanthanum strontium vanadate (LSV)/YSZ interfaces exposed in SOFC anodic environment. LSV is a conducting oxide and has great potential to be robust SOFC anodes (Ge and Chan, 2009b). In this study, \( C_{dl}^{app} \) was obtained from impedance spectroscopy and \( C_{dl}^{int} \) was evaluated via Stern’s method. The numeric inconsistency between \( C_{dl}^{app} \) and \( C_{dl}^{int} \) was discussed.

La\(_{0.8}\)Sr\(_{0.2}\)VO\(_x\) (LSV) powders were synthesized via a citric route with \( \text{La(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \) (Fluka, 99.0%), \( \text{Sr(NO}_3\text{)}_2 \) (Fluka, 99.0%), \( \text{NH}_4\text{VO}_3 \) (Sigma-Aldrich, 99.5%), and \( \text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O} \) (Fluka, 99.5%) as starting materials. Mixed raw materials were dissolved in deionised water. The solution was then heated at 70 °C and under magnetic stirring. A dark blue gel was obtained after dissipating excess water. It was dehydrated overnight at 100 °C and carefully ground in an agate mortar. The precursor was baked stepwise to 800 °C for 12 hours in order to match the particle size of YSZ (Tosoh). Anodic inks were formed by mixing LSV–YSZ powders (50:50 by weight) together with the ink vehicle (Fuel Cell Materials). Green anodes were fabricated by screen-printing the ink onto a 1-mm-thick YSZ disc. LSV–YSZ composite anodes were sintered at 1200 °C for 2 hours. LSV is of single phase after reduction in H\(_2\) at 900 °C for 12 hours, as checked by X-ray powder diffraction (Shimadzu 6000, Cu K\(_\alpha\) radiation). The geometric area of anodes was 0.46 cm\(^2\). Pt paste was brush-painted on
the other side of YSZ and sintered at 900 °C for 30 minutes. The test rig configuration had been given in Ref. (Ge and Chan, 2009b). The operating temperature was 950 °C. The H₂ flow rate was 100 sccm. The open circuit voltage of half cells was -1.18 V.

Half cells were polarized potentiostatically at desired anodic biases until the system became stable. The anodic biases selected in this study were 0, 20, 50, 70, 100, 120, and 150 mV. Impedance responses were recorded via a Solartron 1255B frequency response analyzer coupled to a 1470E electrochemical interface. The frequency range was 100,000–0.05 Hz. The sampling rate was 10 points/decade of frequency. For a given equivalent circuit, the complex nonlinear least squares (CNLS) fitting algorithm was used to fit in the complex impedance plane (Macdonald et al., 1982). Impedance spectra were fitted via Zview® 3.2c. Under each given anodic bias, impedance spectra were collected in batches with a batch size of 10. The whole batch was discarded and re-recorded unless the Chi-squared (χ²) of every fitting result is lower than 3×10⁻⁴. In this study, impedance spectra of four samples prepared from the same batch, Samples A to D, were recorded.

Electrons in the LSV side of LSV/YSZ interfaces were assumed to be uniformly distributed and compactly aligned. Oxygen vacancies in the YSZ side followed Stern’s picture: the H–P layer locating on the outer Helmholtz plane (oHp) and the G–C layer decaying continuously along the direction towards the bulk YSZ. The Volta potential difference across the LSV/YSZ interface was evaluated from its relationship with the electrochemical potential and the work function. The H–P layer was described by a parallel–plate condenser model. The G–C layer was depicted by a modified Poisson–Boltzmann theory (Appendix A).

4.3.1 Apparent double layer capacitance

Figure 4-12 shows typical impedance spectra of polarized LSV/YSZ interfaces at 950 °C and under H₂ atmosphere, comprising an inductive impedance arc at high frequencies and two severely depressed and overlapped capacitive impedance arcs at intermediate and low frequencies. The high-frequency impedance arc (high-f arc) is triggered by Pt lead wires. The intermediate-f arc, of great interest in this study, results from two concurrent phenomena: the double layer charging and the faradaic reaction.
The low-\(f\) arc is attributed to gas diffusion and conversion processes. (Primdahl and Mogensen, 1998) (Primdahl and Mogensen, 1999) All impedance spectra were fitted to a Voigt-type equivalent circuit \((R_i/L_i)R_s(R_1/CPE_1)(R_2/CPE_2)\) (MacDonald, 1987). In the equivalent circuit, \((R_i/L_i)\), \(R_s\), \((R_1/CPE_1)\), and \((R_2/CPE_2)\) represent the high-\(f\) arc, the lumped ohmic resistance, the intermediate-\(f\) arc, and the low-\(f\) arc, respectively. Impedance spectra collected under small applied anodic biases (\(E_{bias} < 150\) mV) are highly reproducible (Fig. 4-12). Once the \(E_{bias}\) is larger than 150 mV, however, the low-\(f\) arcs become so unstable that they cannot be fitted satisfactorily. As indicated in Fig. 4-12, polarization resistance of the intermediate-\(f\) arc \((R_1)\) ranges from 0.15 to 0.20 \(\Omega\) cm\(^2\) and is somewhat independent on \(E_{bias}\). It implies that the interfacial reaction mechanism remains unchanged under these \(E_{bias}\). In contrast, polarization resistance of the low-\(f\) arc \((R_2)\) ranges from 0.4 to 0.9 \(\Omega\) cm\(^2\) and has a negative dependency on \(E_{bias}\). Such behaviours are mostly due to the water effect in gas transport phenomena (Primdahl and Mogensen, 1998). Detailed discussions on the water effect of LSV–YSZ anodes have given in Section 3.1 and are beyond the scope of the present section (Ge and Chan, 2009a).

Figure 4-12 Nyquist plots of typical impedance responses of polarized LSV/YSZ interfaces. Ten impedance spectra are recorded at each potential bias. The inset shows the equivalent circuit used throughout this study.
The CNLS fitting results with unrestricted parameters indicate that $n_1$ of CPE$_1$ are approximately 0.60. For the sake of mechanistic consistency, all CNLS fitting procedures were therefore carried out with fixed $n_1$ of 0.60. $C_{\text{dl}}^{\text{app}}$ can be expressed as

$$C_{\text{dl}}^{\text{app}} = \frac{nRQ}{R_1}$$

by using Eq. 3 in Ref. (Hsu and Mansfeld, 2001), where $Q$ is the CPE parameter together with $n$ that define CPE ($Z_{\text{CPE}}=Q^{-1}(j\omega)^{-n}$). Figure 4-13 shows the fitting results of four samples produced from the same batch, among which sample A corresponds to the one shown in Fig. 4-12.

Figures 4-13a and 4-13b show $R_1$ and $Q_{\text{CPE1}}$ as a function of $E_{\text{bias}}$, respectively. Figure 4-13c shows the corresponding $C_{\text{dl}}^{\text{app}}$ that are converted according to Eq. 4-13. $C_{\text{dl}}^{\text{app}}$ of LSV/YSZ interfaces, taking sample A as an example, are $171\pm 13$, $240\pm 10$, $218\pm 11$, $178\pm 6$, $172\pm 8$, $165\pm 10$, and $165\pm 20$ μF/cm$^2$ under $E_{\text{bias}}$ of 0, 20, 50, 70, 100, 120, and 150 mV, respectively. These $C_{\text{dl}}^{\text{app}}$ values of LSV/YSZ interfaces are in the same order of magnitude as those of metal(air)/YSZ interfaces (Hendriks et al., 2002a; Robertson and Michaels, 1991), an order of magnitude higher than those of interfaces with aqueous (Brett and Brett, 1994) or supercritical organic electrolytes (Abbott and Harper, 1999), and two orders of magnitude higher than those of metal/non-aqueous electrolyte interfaces e.g. molten salts (Kisza, 2006), ionic liquids (Lockett et al., 2010; Costa et al., 2010), and organic electrolytes (Feng et al., 2010). The occurrence of such large $C_{\text{dl}}^{\text{app}}$ values is not thought to be experimental artefacts mainly from two reasons. Firstly, consistent results had been observed for all the four samples investigated in this study (samples A to D, Fig. 4-13). Secondly, such occurrence is not uncommon: many high temperature SOFC anodes also had been reported to exhibit large $C_{\text{dl}}^{\text{app}}$ values (Holtappels et al., 1999; Primdahl and Mogensen, 1997; Jiang and Badwal, 1999).

The pronounced feature of all $C_{\text{dl}}^{\text{app}} - E_{\text{bias}}$ curves is their right-skewed volcano (or called “capacitance surge”) patterns. These bump-shaped patterns peak around $E_{\text{bias}}=20$ mV and gradually restore after $E_{\text{bias}}=100$ mV. Samples A to D exhibit similar
trends, albeit with different $C_{dl}^{app}$ values (Fig. 4-13c). The poor reproducibility of $C_{dl}^{app}$ is well-known for electrochemical systems involving solid electrolytes, e.g. silver halides (Armstrong and Mason, 1973) and YSZ (Hendriks et al., 2002b). As the curves in Fig. 4-3c are somewhat reproducible, these patterns are thought to own some intrinsic merits rather than merely experimental errors. $C_{dl}^{app}$ had been reported to be positively dependent on $E_{bias}$ in lithographically patterned (Bieberle et al., 2001) and point-contact (Kek et al., 2001) Ni/YSZ interface. The exact mechanism of the “capacitance surge” phenomenon is still under investigation. The possibilities of charging microstructure and electrode failure are excluded since the impedance spectra are reversible and reproducible. The results, nevertheless, imply that double-plate condenser models, predicting constant capacitance regardless of applied biases, are insufficient.

Figure 4-13  Equivalent circuit fitting results of (a) polarization resistance ($R_1$), (b) the CPE parameter ($Q_{CPE1}$), and (c) apparent double layer capacitance ($C_{dl}^{app}$) of the $R_1$/CPE$_1$ subset. Sample A (filled square, solid line) of the four samples (A to D) corresponds to the one in Figure 1. Each error bar is generated from 10 consecutive impedance spectra.
4.3.2 Analytical description of the Gouy–Chapman layer

The double layer of LSV/YSZ interfaces is formed by closely packed electrons on the LSV side and oxygen vacancies on the YSZ side. The oxygen vacancies can be further divided into two sub-layers: the compact H–P layer and the diffusive G–C layer (Fig. 4-14a). The Volta potential of LSV/YSZ interfaces ($\Psi_{LSV}^{YSZ}$) is the Volta potential difference between LSV and YSZ,

$$\Psi_{LSV}^{YSZ} = \Psi_{LSV} - \Psi_{YSZ},$$  \hspace{1cm} (Equation 4-14)

where $\Psi_{LSV}$ and $\Psi_{YSZ}$ are the Volta potential in the LSV side and the YSZ side, respectively. All the terms in Eq. 4-15 are negative as the interface is exposed in anodic environment. Away from the interface, $\Psi_{YSZ}$ increases linearly within the oHp and asymptotically approach zero from the oHp to the bulk YSZ (Fig. 4-14b). The portion of $\Psi_{YSZ}$ in the G–C layer is denoted as $\Psi_{G}$. The spatial variation of $\Psi_{G}$ fulfils a modified Poisson–Boltzmann equation,

$$\frac{d^2 \Psi}{dz^2} = -\frac{4e_0 n_{0}^{G}}{\varepsilon_{r,G} \varepsilon_0} \sinh \left( \frac{e_0 \Psi}{kT} \right) \exp \left( -\frac{e_0 \Psi}{kT} \right),$$  \hspace{1cm} (Equation 4-15)

where $z$ is the distance away from the LSV/YSZ interfaces, $e_0$ the elementary charge, $\varepsilon_0$ the vacuum permittivity, $\varepsilon_{r,G}$ the relative static permittivity of YSZ in the G–C layer, $n_{0}^{G}$ the free oxygen vacancy concentration of YSZ, $k$ the Boltzmann’s constant, and $T$ the absolute temperature. Reduce Eq. 4-15 to first-order,

$$\left( \frac{d\Psi}{dz} \right) = \sqrt{\frac{2n_{0}^{G}}{\varepsilon_{r,G} \varepsilon_0}} \sqrt{kT \left[ \exp \left( -\frac{2e_0 \Psi_{G}}{kT} \right) - 1 \right] + 2e_0 \Psi_{G}}.$$

According to the Gauss’s law of electrostatics the surface charge density in the G–C layer ($\sigma_G$) is given by

$$\sigma_{G} = \sqrt{\frac{2e_0 \varepsilon_{r,G} n_{0}^{G}}{\varepsilon_0}} \sqrt{kT \left[ \exp \left( -\frac{2e_0 \Psi_{G}}{kT} \right) - 1 \right] + 2e_0 \Psi_{G}}.$$  \hspace{1cm} (Equation 4-17)

Differentiating $\sigma_G$ against $\Psi$ gives the Gouy–Chapman capacitance ($C_G$),
Mathematical derivations that lead to Eqs. 4-15 to 4-18 are given in Appendix A.

Figure 4-15 shows the relationship between $C_G$ and $\Psi_G$ with Eq. 4-18 solved numerically, by substituting reasonable values of $\varepsilon_{r,G}$ and $n^0_{\varepsilon G}$. $C_G$ increases with the increasing absolute value of $\Psi_G$. In reality, the singularity shown in the inset of Fig. 4-15 never occurs because the Volta potential develops in any electrode/electrolyte interfaces. As a rough evaluation, $C_G$ ranges from 300 to 700 $\mu$F/cm$^2$ in a typical $\Psi_G$ range of most SOFC materials (e.g. 100 to 200 mV). Note that $C_G$ is distinct to $C_{app}$, though their numerical values seem similar. The occurrence of large values of $C_G$ might be attributed to the solid structure of YSZ, which results in a more compact G–C layer than that in aqueous electrolytes.

\[
C_G = e_0 \left[ \exp \left( -\frac{2e_0 \Psi_G}{kT} \right) -1 \right] \sqrt{\frac{2\varepsilon_{r,G}e_0 n^0_{\varepsilon G}}{kT \left[ \exp \left( -\frac{2e_0 \Psi_G}{kT} \right) -1 \right] + 2e_0 \Psi_G}}.
\]

(Equation 4-18)

Figure 4-14 Schematic illustrations of the double layer developed across the LSV/YSZ interface: (a) microscopic structure; (b) the Volta potential distribution.
4.3.3 Interfacial variation of the Volta potential

Deterministic $C_G$ values, however, are still unavailable from Eq. 4-18 unless $\Psi_{LSV}^{YSZ}$ is known and $\Psi_G$ is separated from the Volta potential in the H–P layer ($\Psi_H$). As shown in Fig. 4-14b, $\Psi_{LSV}^{YSZ}$ comprises $\Psi_G$ and $\Psi_H$.

$$\Psi_{LSV}^{YSZ} = \Psi_G + \Psi_H.$$  \hspace{1cm} (Equation 4-19)

The problem of determining $\Psi_G$ therefore consists of two sub-problems: (i) how to obtain $\Psi_{LSV}^{YSZ}$ under given polarized conditions and (ii) how to split $\Psi_{LSV}^{YSZ}$ into $\Psi_G$ and $\Psi_H$.

To obtain $\Psi_{LSV}^{YSZ}$ under given polarized conditions (the problem i), first consider the LSV/YSZ interface under the OCV condition. As shown in the inset of Fig. 4-16a, $\Psi_{LSV}^{YSZ}$ is related to the Galvani potential $\phi$, the outer potential $\chi$, the chemical potential $\mu$, the electrochemical potential $\tilde{\mu}$ (i.e. the Fermi level $E_F$), and the work function $\Phi$. 

Figure 4-15  (a) Gouy–Chapman capacitance versus the Volta potential of the Gouy–Chapman layer. The inset shows the magnified figure near the zero potential, where the singularity occurs according to Eq. 4-16.
Detailed explanations are omitted here for simplicity. Interested readers are recommended with thorough works on metal/aqueous (Trasatti, 1974; Trasatti, 1982; Trasatti, 1990), semiconductors (Reiss, 1985; Reiss, 1988), metal/solid electrolyte (Riess, 1997; Riess and Vayenas, 2003), and ionic solid interfaces (Nowotny, 1997).

In this work $\Psi$ is expressed by $\tilde{\mu}$ and $\Phi$, both of which are experimentally measurable (Schindler et al., 1989; Tsiplakides et al., 2007; Tsiplakides and Vayenas, 2001; Tsiplakides and Vayenas, 2002; Frantzis et al., 2000; Nowotny et al., 1989; Nowotny and Sloma, 1991). $\Psi_{YSZ}^{LSV}$ is thus given by

$$\Psi_{YSZ}^{LSV} = -\frac{\tilde{\mu}_{c,YSZ}^{LSV} + \Phi_{YSZ}^{LSV}}{e_0},$$  \hspace{1cm} \text{(Equation 4-20)}

where $\tilde{\mu}_{c,YSZ}^{LSV}$ and $\Phi_{YSZ}^{LSV}$ are the electrochemical potential difference and work function difference between LSV and YSZ across the LSV/YSZ interface, respectively. As the electrochemical state of the bulk YSZ is set as the reference state, Eq. 4-20 is simplified to

$$\Psi_{LSV} = -\frac{\tilde{\mu}_{c,YSZ}^{LSV} + \Phi_{YSZ}^{LSV}}{e_0},$$  \hspace{1cm} \text{(Equation 4-21)}

For LSV–YSZ($H_2$)|YSZ|Pt(air) half cells investigated in this study, $\tilde{\mu}_{c}^{LSV}$ is experimentally given by

$$e_0E_{emf} = -\left(\tilde{\mu}_{c}^{LSV} - \tilde{\mu}_{c}^{Pt}\right),$$  \hspace{1cm} \text{(Equation 4-22)}

where $E_{emf}$ is the electromotive force (Fig. 4-16a).

A brief literature survey was conducted on the electrochemical potential and the work function of YSZ, Pt, and LSV. The absolute potential of standard YSZ oxygen electrode was $5.07 \pm 0.05$ V at $400 \, ^\circ C$ and under oxygen partial pressure ($p_{O_2}$) of $1.2 \times 10^{-2}$ bar (Riess and Vayenas, 2003; Tsiplakides and Vayenas, 2001; Tsiplakides and Vayenas, 2002; Vayenas, 2000; Vayenas et al., 2001). A rudimentary evaluation considering atmospheric effect from the Nernst equation and temperature effect from Ref. (Riess and Vayenas, 2003) suggests $\tilde{\mu}_{c}^{YSZ} = -5.23$ eV at $950 \, ^\circ C$ and in air. $\tilde{\mu}_{c}^{Pt}$ is
Chapter 4. Impedance responses and the double layer structure of LSV anodes via citric route

Figure 4-16  Schematic representations of the energy-level diagrams in LSV–YSZ(H₂)|YSZ|Pt(air) half cells under: (a) open circuit voltage, and (b) anodically polarized conditions. The right inset in (a) shows the correlations among \( \phi \), \( \Psi \), \( \chi \), \( \mu \), \( \bar{\mu} \), \( E_F \), and \( \Phi \). Note that all the interfacial variations are exaggerated merely for illustration purpose.

Figure 4-17  Spatial variations of the Volta potential across the polarized LSV/YSZ interfaces. Junctions between the Helmholtz–Perrin layer and the Gouy–Chapman layer are labelled by embedded symbols. The inset shows a holistic view of such curves from the interface to the bulk YSZ.
estimated to be -5.72 eV at 950 °C and in air, based on work function data of Pt \( p_{O_2} = 1.2 \times 10^{-2} \) bar|YSZ|Ag\( p_{O_2} = 1.2 \times 10^{-2} \) bar) electrochemical cells (Tsiplakides and Vayenas, 2002; Tsiplakides and Vayenas, 2001), and temperature coefficients given in Ref. (Seely, 1941). \( \Phi^{LSV} \) is evaluated to be 3.79 eV at 950 °C and in reducing environment, with temperature and atmospheric coefficients bought from Refs. (Kurtz and Henrich, 1983; Smith and Henrich, 1990; Egdell et al., 1984). According to Eqs. 4-21 and 4-22, \( \Psi^{LSV}_{YSZ} \) under the OCV condition is thus found to be -0.75 V.

When half cells are polarized and subjected to non-negligible faradaic currents, every throughout the bulk YSZ becomes no longer uniform (Fig. 4-16b). The measured potential difference \( (E_m) \) is given by

\[
E_m = E_{emf} + E_{bias} = -\frac{\mu^{LSV}_{e} - \mu^{Pt}_{e}}{e_0}.
\]

(Equation 4-23)

Note that in Eq. 4-23 \( E_m \) and \( E_{emf} \) are negative but \( E_{bias} \) is positive. \( \Psi^{LSV}_{YSZ} \) with non-negligible faradaic currents is thus given by

\[
\Psi^{LSV}_{YSZ} = -\frac{\mu^{LSV}_{e,YSZ} + \Phi^{LSV}_{YSZ}}{e_0} + R_\Omega i_{ion},
\]

(Equation 4-24)

where \( R_\Omega \) is the ohmic resistance and \( i_{ion} \) is the ionic current across the bulk YSZ \( (i_{ion} \geq 0) \). \( R_\Omega \) and \( i_{ion} \) were obtained from impedance spectroscopy and potentiostatic polarization, respectively. Typical \( \Psi^{LSV}_{YSZ} \) values, taking sample A as an instance, are -0.750, -0.739, -0.723, -0.714, -0.699, -0.690, and -0.678 V, under \( E_{bias} \) of 0, 20, 50, 70, 100, 120, and 150 mV, respectively. It is worth to highlight that the exertion of \( E_{bias} \) on LSV/YSZ interfaces leads to reduced \( \Psi^{LSV}_{YSZ} \), and consequently, the loosened double layer.

To split \( \Psi^{LSV}_{YSZ} \) into \( \Psi_G \) and \( \Psi_H \) (the problem ii), the microscopic structure of the H–P layer and the G–C layer must be analysed. In a simplified Monte Carlo simulation, the oxygen vacancies on the YSZ side of the LSV/YSZ interfaces is described as the evolving charged particles on \( a priori \) defined lattices. The Hamiltonian of canonical
ensemble comprises (i) the attraction between oxygen vacancies in YSZ and the electrons in LSV (ii) the repulsion among nearest neighbouring oxygen vacancies in YSZ. The jump frequencies and acceptance rules are based on the Metropolis algorithm (Shonkwiler and Mendivil, 2009). The Monte Carlo simulation results indicated that the Volta potential portion of the H–P layer over the whole double layer ($\Psi_H / \Psi_{LSV}^{YSZ}$) were $0.80\pm0.01$, $0.77\pm0.01$, $0.77\pm0.02$, $0.77\pm0.01$, $0.76\pm0.02$, $0.74\pm0.01$, and $0.74\pm0.01$, under $E_{bias}$ of 0, 20, 50, 70, 100, 120, and 150 mV, respectively. Note that the Volta potential portion of the G–C layer over the whole double layer ($\Psi_G / \Psi_{LSV}^{YSZ}$) is complementary to $\Psi_H / \Psi_{LSV}^{YSZ}$.

Finally, the spatial variation of $\Psi_G$ can be obtained by solving Eq. 4 numerically, after both the two problems i and ii answered. On the other hand, the spatial variation of $\Psi_H$ is linear because the H–P layer has been modelled as a double-plate capacitor. Figure 4-17 shows the spatial variations of $\Psi_{LSV}^{YSZ}$ of polarized LSV/YSZ interfaces by utilizing the continuous and derivable boundary conditions near $\Psi_{oHp}$ (Appendix A, Eqs. A10–1 and A10–2). The $\Psi_{LSV}^{YSZ} – z$ curves of various polarized LSV/YSZ interfaces exhibit similar patterns: a linear increase that accounts for about 70–80% of $\Psi_{LSV}^{YSZ}$ and an asymptotical increase to zero potential. A structural relaxation of the double layer is evident when the LSV/YSZ interfaces are subjected to increasing $E_{bias}$ (Fig. 4-17).

4.3.4 Intrinsic double layer capacitance

Every $\Psi_{LSV}^{YSZ} – z$ curve in Fig. 4-17 incorporates a separator between the H–P layer and the G–C layer. The separators are obtained after solving Eq. 4-16 with initial and boundary conditions from Eq. A10. Thicknesses of the H–P layer ($d_H$) of polarized LSV/YSZ interfaces are thus known as $0.355\pm0.003$, $0.280\pm0.003$, $0.302\pm0.006$, $0.325\pm0.003$, $0.320\pm0.008$, $0.306\pm0.005$, $0.358\pm0.003$ nm, under $E_{bias}$ of 0, 20, 50, 70, 100, 120, and 150 mV, respectively. These $d_H$ values are equivalent to 2.0–2.6 times of the ionic radius of oxygen ions in YSZ ($r_{2O^{2-}}$) (Shannon, 1976). If the cut-off where the double layer ceases is 100 μV, thicknesses of the G–C layer ($d_G$) are 1.10, 1.23, 1.26, 1.32, 1.48, 1.64, and 1.88 nm, respectively (Table 4-1). In other words, typical values of $d_H$ and $d_G$ are equivalent to 1.1–1.4 and 5.7–8.7 times of the lattice spacing of (400) planes of YSZ (PDF #30–1468), respectively. The double layer thickness, i.e. $d_H + d_G$,
Chapter 4. Impedance responses and the double layer structure of LSV anodes via citric route

increases monotonically with $E_{\text{bias}}$. Under an $E_{\text{bias}}$ of 150 mV, $d_{\text{H}}+d_{\text{G}}$ is almost 50% larger than that under the OCV condition. It is surprising to note that the double layer has such a compact structure and it is significantly sensitive to external stimuli.

![Figure 4-18 Contour plots of intrinsic double layer capacitance comprising the Helmholtz–Perrin capacitance and the Gouy–Chapman capacitance. Along the direction of the arrow, the embedded points consecutively represent the intrinsic double layer capacitance of the LSV/YSZ interfaces under anodic biases of 0, 20, 50, 70, 100, 120, and 150 mV, as shown in Table 1. The dashed line is merely a trend line.]

The intrinsic double layer capacitance ($C_{\text{dl}}^{\text{int}}$) consists of $C_{\text{H}}$ and $C_{\text{G}}$ connected in series (Stern, 1924),

$$\frac{1}{C_{\text{dl}}^{\text{int}}} = \frac{1}{C_{\text{H}}} + \frac{1}{C_{\text{G}}} \quad . \quad \text{(Equation 4-25)}$$

$C_{\text{G}}$ is potential dependent and has been given in Eq. 4-18. In contrast, $C_{\text{H}}$ is potential independent and is routinely expressed as (Helmholtz, 1853)

$$C_{\text{H}} = \frac{\varepsilon_{\text{rH}}\varepsilon_0}{d_{\text{H}}} \quad , \quad \text{(Equation 4-26)}$$
where $\varepsilon_{r,H}$ is the relative static permittivity of YSZ in the H–P layer. For LSV/YSZ interfaces subjected to 0, 20, 50, 70, 100, 120, and 150 mV, $C_H$ are 24.9, 31.6, 29.3, 27.2, 27.6, 28.9, and 24.7 $\mu$F/cm$^2$, respectively (Eq. 4-16); $C_G$ are 417.8, 477.8, 433.9, 401.7, 384.3, 384.4, and 321.6 $\mu$F/cm$^2$, respectively (Eq. 4-18); and finally $C_{dl}^{int}$ are 23.5, 29.6, 27.4, 25.5, 25.7, 26.9, and 22.9 $\mu$F/cm$^2$, respectively (Eq. 4-25, inset of Fig. 4-18). Figure 4-18 shows contour plots of $C_{dl}^{int}$ as functions of $C_H$ and $C_G$, indicating the dominant role of $C_H$ on $C_{dl}^{int}$. The relative difference between $C_H$ and $C_{dl}^{int}$, defined as $(C_H - C_{dl}^{int})/C_{dl}^{int}$, is less than 8%. The whole rationale should still be adopted whenever $C_H$ is used as the estimator of $C_{dl}^{int}$. The reason is that $d_H$ heavily depends on the Volta potential difference and the thickness of the double layer. Table 4-1 summarizes the parameters, i.e. the Volta potential, thickness, and capacitance, which describe the H–P layer, the G–C layer, and the double layer of polarized LSV/YSZ interfaces.

<table>
<thead>
<tr>
<th>Applied anodic biases (mV)</th>
<th>The compact layer</th>
<th>The diffusive layer</th>
<th>The double layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Psi_{H}^{LSV}$</td>
<td>$\Psi_{YSZ}$</td>
<td>$\Psi_{LSV}$</td>
</tr>
<tr>
<td>Volta potential portion</td>
<td>$\Psi_{an}$</td>
<td>$\Psi_{LSV}$</td>
<td>$\Psi_{YSZ}$</td>
</tr>
<tr>
<td>Thickness $d$ (nm)</td>
<td>$d_{H}$</td>
<td>$d_{G}$</td>
<td>$d_{H}$</td>
</tr>
<tr>
<td>Helmholtz–Pe rrin capacitance $C_H$ ($\mu$F/cm$^2$)</td>
<td>24.9</td>
<td>1.10</td>
<td>417.8</td>
</tr>
<tr>
<td>Gouy–Chap man capacitance $C_G$ ($\mu$F/cm$^2$)</td>
<td>31.6</td>
<td>1.23</td>
<td>477.8</td>
</tr>
<tr>
<td>Intrinsic double layer capacitance $C_{dl}^{int}$ ($\mu$F/cm$^2$)</td>
<td>29.3</td>
<td>1.26</td>
<td>433.9</td>
</tr>
<tr>
<td>Apparent double layer capacitance $C_{dl}^{app}$ ($\mu$F/cm$^2$)</td>
<td>27.2</td>
<td>1.32</td>
<td>401.7</td>
</tr>
<tr>
<td>Table 4-1 Listing of parameters pertinent to the double layer of LSV/YSZ interfaces in LSV–YSZ(H$_2$)</td>
<td>YSZ</td>
<td>Pt(air) half cells at 950 °C.</td>
<td></td>
</tr>
</tbody>
</table>
4.3.5 Double layer capacitance: apparent versus intrinsic

The $C_{\text{dl}}^{\text{app}} - E_{\text{bias}}$ curves show a right-skewed volcano pattern that peaks around 20–50 mV (Fig. 4-13c). Surprisingly, the $C_{\text{dl}}^{\text{int}} - E_{\text{bias}}$ curves also exhibit a “capacitance surge” at small $E_{\text{bias}}$ (Fig. 4-18). It is of great interest to note that the theoretical approaches have satisfactorily depicted the changing double layer capacitance behaviours of polarized LSV/YSZ interfaces. Generally speaking, the “capacitance surge” phenomenon results from the Volta potential variations and the changing double layer structure. When half cells are subjected to a small $E_{\text{bias}}$, oxygen vacancies once trapped at oHp become relaxed and permeate towards the bulk YSZ. The LSV/YSZ interfaces therefore undergo a minute decrease of $\Psi_{\text{LSV}}^{\text{YSZ}}$ and accordingly a slight relaxation of the double layer. These effects lead to an expansion of the G–C layer and an increase of $\Psi_{G} / \Psi_{\text{LSV}}^{\text{YSZ}}$. Note that the increase of $\Psi_{G} / \Psi_{\text{LSV}}^{\text{YSZ}}$ counteracts the decrease of $\Psi_{\text{LSV}}^{\text{YSZ}}$ that leads to it. In other words, it competes with the loosened H–P layer that is resulted from the dwindling coulombic attractions. These two counterbalancing effects results in a local maximum in $C_{\text{dl}} - E_{\text{bias}}$ curves. The exact position of the local maximum, however, is currently unknown due to insufficient data explored in this study. To locate the local maximum, sophisticated materials characterization techniques that measure the surface states (and therefore, the Volta potentials) of on-running SOFCs must be involved. It is of great interest to note that in situ ambient-pressure X-ray photoelectron spectroscopy (APXPS) has been adopted recently, which successfully measures the surface states in ceria/YSZ/Pt single chamber cells under H$_2$–H$_2$O atmosphere and at 750 °C (DeCaluwe et al., 2010; Zhang et al., 2010a). The rationale of the Volta potential analysis could be tested and verified, if APXPS is employed to obtain the electrochemical states of electrode/solid-electrolyte interfaces.

Notwithstanding similar $E_{\text{bias}}$ effects on $C_{\text{dl}}^{\text{app}}$ and $C_{\text{dl}}^{\text{int}}$, $C_{\text{dl}}^{\text{app}}$ are basically one order of magnitude larger than $C_{\text{dl}}^{\text{int}}$ (Table 4-1). This discrepancy roots in the inconsistent surface areas that are used in the two approaches: $C_{\text{dl}}^{\text{app}}$ adopts the geometric area ($A_{\text{geo}}$) but $C_{\text{dl}}^{\text{int}}$ embraces the real area ($A_{\text{real}}$). The relationship between $C_{\text{dl}}^{\text{app}}$ and $C_{\text{dl}}^{\text{int}}$ can be simply connected by
impedance responses and the double layer structure of LSV anodes via citric route

\[ C_{\text{app}}^{\text{dl}} = k \; C_{\text{int}}^{\text{dl}} = \frac{A_{\text{real}}}{A_{\text{geo}}} \; C_{\text{int}}^{\text{dl}}, \]  

(Equation 4-27)

where \( k \) is the area normalizing factor. Typical \( k \) values, take sample A as an example, are 7.3±0.5, 8.1±0.4, 7.9±0.4, 7.0±0.2, 6.7±0.3, 6.1±0.4, 7.2±0.9, under \( E_{\text{bias}} \) of 0, 20, 50, 70, 100, 120, and 150 mV, respectively. It is surprisingly to find that \( A_{\text{real}} \) is about 6–8 times of \( A_{\text{geo}} \), at least for the case of LSV–YSZ composite anode exposed in \( \text{H}_2 \) at 950 º C. Historically, models pertinent to \( A_{\text{real}} \) rely on assumptions about charge transfer and electrode microstructure, involving parameters that are notoriously difficult to determine and verify. \( A_{\text{real}} \) represents the area where electrochemical fuel cell reactions take place. These reactions occur only at three phase boundaries (TPBs) where gas (fuel or oxygen), electrode (anode or cathode), and electrolyte meet. If a composite electrode is used, as the case of LSV–YSZ anode, only the TPBs that are not far away from the anode–electrolyte interface contribute to the reactions. An active layer therefore exists and the remainder of the composite electrode merely functions as current collector and gas diffusion layer. Apparently, \( A_{\text{real}} \) is composed of the TPBs within the active layer. In other words, \textit{in situ} detection and monitoring of \( A_{\text{real}} \) become feasible by merely recording the impedance responses of on-running SOFCs and utilizing the apparent and intrinsic double layer capacitance analysis, even without \textit{a priori} knowledge on the electrode microstructure and the conductivity of electrode and electrolyte materials.

This work describes a combined experimental and modelling study of the electrochemical characteristics associated with the double layer in high temperature SOFCs via a case study on LSV/YSZ interfaces. Impedance responses of electrode/solid-electrolyte interfaces are recorded. \( C_{\text{app}}^{\text{dl}} \) is obtained by appropriate fitting processes to the impedance spectra. To fully understand the capacitive behaviour of the interfaces, modelling works decouple contributions from the two different regions of the double layer—the tightly bound H–P layer and the more diffuse G–C layer. As a result of the modelling efforts, \( C_{\text{app}}^{\text{dl}} \) is found to be around 1 order of magnitude higher than \( C_{\text{int}}^{\text{dl}} \) that the models predict. This difference is ascribed to differences between the anode’s electrochemically active area and the anode’s two-dimensional geometric footprint. To fully generalize this rationale, the double
layer of SOFCs operated under various fuel atmospheres and lower operating temperatures needs to be addressed. The fuel atmosphere exerts pronounced influences on the impedance responses and the \( C_{\text{app}} \) consequently obtained from impedance spectra. The fuel composition effect had been widely observed in, e.g. Ni cermet anodes with \( \text{H}_2-\text{H}_2\text{O} \) atmosphere (Jiang and Badwal, 1999; Matsui et al., 2007; Kim et al., 2009) and LSV–YSZ anodes with \( \text{H}_2-\text{H}_2\text{O}-\text{He} \) atmosphere (Ge and Chan, 2009a).

Fundamentally, the change of fuel atmosphere alters \( \chi, \Phi, \) and \( \bar{\mu} \) of the electrocatalysts. The variation of \( \bar{\mu} \) can be easily measured for SOFCs in half cell configurations, provided that the electrochemical states of the reference electrode are readily known. In contrast, detecting the variations of \( \chi \) and \( \Phi \) of SOFC components is challenging because of the high operating temperatures, fuel atmospheres, and the difficulty of attaching probes across each component. \( \chi \) and \( \Phi \) could possibly be measured by in situ APXPS (Zhang et al., 2010a; DeCaluwe et al., 2010). As the alternation of surface states due to the change of fuel atmosphere varies from case to case, no general rules about the fuel composition effect on \( C_{\text{int}} \) can be drawn.

The decrease of operating temperature would result in sluggish electrochemical fuel cell reactions. As reflected in impedance spectra, the impedance arc pertinent to electrochemical reactions is enlarged and the time constant of the arc increases. The \( C_{\text{app}} \) of anode/electrolyte interfaces at low temperatures should thus be smaller than those at high temperatures. This trend has been observed in Ni–YSZ cermet anodes (Holtappels et al., 1999), and had also been reported in point-contact metal (Ni, Pt, Au)/9 mol% yttria-doped zirconia single crystal interfaces (Bieberle et al., 2001). This effect, however, might not be obvious for electrodes with low thermal activation energy and complex electrode architecture. To determine \( C_G \) and \( C_H \) at low temperatures, the temperature effects of \( \varepsilon_{r,G}, \varepsilon_{\text{cH}}, n_{\text{p}G}^{0}, \Psi, \Psi/G/\Psi, \Phi, \) and \( \bar{\mu} \) must be known, as indicated in Eqs. 4-18 to 4-26. Take the LSV/YSZ interfaces under the OCV condition as an example. The change of \( \Phi_{\text{LSV}}^{\text{YSZ}} \) might be insignificant for operating temperatures down to 800ºC, mainly because of the small temperature dependency of \( \Phi \) (Langmuir, 1936; Potter, 1940; Smith, 1949). \( \hat{\mu}_{\text{LSV}} \) is experimentally measurable according to Eq.10, where \( E_{\text{emf}} \) fulfils the Nernst equation. The Nernst equation predicts increased OCVs at
lower temperatures. To summarize and according to Eqs. 4-20 to 4-22, $\Psi_{LSV}^{YSZ}$ is somewhat increased if SOFC operating temperatures are decreased. The G–C layer has also been enlarged because of less oxygen vacancies in YSZ are freely mobile at lower temperatures, resulting in the increase of $\Psi_{G}/\Psi$ (in other words, the decrease of $\Psi_{H}/\Psi$). Therefore, $\Psi_{G}$ definitely becomes larger due to the increases of $\Psi_{LSV}^{YSZ}$ and $\Psi_{G}/\Psi$. In contrast to $\Psi_{G}$, the changing behaviour of $\Psi_{H}$ is unable to be predicated unambiguously, noting that $\Psi_{LSV}^{YSZ}$ has been increased but $\Psi_{H}/\Psi$ has been decreased. It should bear in mind that $C_{dl}^{int}$, as indicated in Table 4-1 and Fig. 4-18, is controlled by the property of the H–P layer. Therefore, the behaviour of $C_{dl}^{int}$ at low temperatures is difficult to predict due to the uncertainty of $\Psi_{H}$. The complete capacitance and Volta potential analyses, as proposed in Section 3.2 to 3.5, should be adopted to resolve this ambiguity.

### 4.3.6 Brief summary

The double layer capacitance of solid electrode/solid-electrolyte interfaces was investigated via a case study on LSV/YSZ interfaces in SOFC anodic environment. The magnitude of apparent double layer capacitance was of several hundreds of $\mu$F/cm$^2$. Under anodic polarized conditions, it exhibited a right-skewed volcano pattern that peaks around 20 to 50 mV. The intrinsic double layer capacitance exhibited similar “capacitance surge” behaviour. The phenomenon was ascribed to mutual competitions between the loosened H–P layer and the increase of Volta potential in the G–C layer. The numeric values of intrinsic double layer capacitance were, however, almost one order of magnitude lower than the apparent. Such kind of discrepancy was ascribed to the inconsistent areas that were used in the two cases. The capacitance analysis enables in situ detection of active areas and TPBs of composite electrode–electrolyte interfaces in various solid state electrochemical systems.

### 4.4 Three phase boundaries and electrochemically active zones in solid oxide fuel cell anode/electrolyte interfaces

Solid oxide fuel cells (SOFCs) are highly efficient energy conversion devices with advantages of fuel flexibility and long-term stability. Electrochemical fuel cell reactions in SOFC electrodes take place around three phase boundaries (TPBs), where
gas, electrode, and electrolyte meet. Numerous analytical (Costamagna et al., 1998; Chan and Xia, 2001), numerical (Abbaspour et al., 2010; Martinez and Brouwer, 2008), and experimental (Wilson et al., 2006; Shearing et al., 2010) works on TPBs had been reported. Avoiding the structural complexity of porous and composite electrodes, some characteristics of TPBs have been obtained from unitary, dense, and two-dimensionally patterned electrodes (Bieberle and Gauckler, 2000; Mizusaki et al., 1994). The microstructure and TPBs of composite electrodes had been reported to be quantified by stereological measurements (Zhao et al., 2001). In the case of composite electrodes, only those TPBs adjacent to the electrode/electrolyte interface contribute to electrochemical reactions. An active electrode layer therefore exists (Fukunaga et al., 2007; Sakamoto et al., 1996; Abudula et al., 1996; Nakamura et al., 2008; Menzler and Haanappel, 2010). The remainder above the active electrode layer merely functions as current collectors and gas diffusion layers. When SOFCs are subjected to external loads (i.e. in polarized conditions), this scenario becomes more complicated because the active TPBs fluctuate in accordance with the applied stimulus. Meanwhile, studying solid electrode/solid electrolyte interfaces by in situ techniques is difficult because of these systems’ opaque and sealed geometries. Several in situ techniques on SOFCs have been developed recently (Pomfret et al., 2010; DeCaluwe et al., 2010). These in situ techniques are, however, constrained to the characterization on materials’ surface states. Any fuel cell reaction paths beneath the sintered electrode/electrolyte interfaces are still difficult to be detected.

TPBs instead of electrochemically active zones (EAZs) have long been attributed to the places where fuel cell reactions occur. This argument appears especially plausible for composite electrodes comprising purely ionic and electronic components. Generally speaking, three-dimensional EAZs are generated by the out-of-plane extensions of the corresponding one-dimensional TPB lines. The extent of such extensions depends on the materials properties of electrodes and electrolytes, gas atmosphere, operating temperature, external loads, etc. Electrochemical reactions thus take place in three-dimensional EAZs beyond one-dimensional TPBs. The cross-sections of EAZs, to some extent, represent the interfaces where the electrochemical double layer develops. Surprisingly, the correlation between TPBs and EAZs has hitherto been poorly known.

This work is dedicated to investigate the relationship between TPBs and EAZs, by
employing the electrode microstructural modelling and the apparent and intrinsic double layer capacitance analysis. The TPBs of composite anodes are obtained from the microstructure models of virtually sintered packing beds. On the other hand, the capacitance analysis provides the real reaction areas of on-running SOFCs (Ge et al., 2011), which are regarded as the cross-section areas of EAZs. To fully demonstrate the rationale, a case study was carried out on half-cells with lanthanum strontium vanadate (LSV)–yttria-stabilized zirconia (YSZ) as composite anode and YSZ as electrolyte. LSV is a conducting oxide and has great potential to be robust SOFC anodes (Ge and Chan, 2009b). The rationale is thought to be suitable for various parametric analyses on TPBs and EAZs, though only the electrical potential effect has been discussed herein.

4.4.1 Materials and characterization

$La_{0.8}Sr_{0.2}VO_x$ (LSV) powders were synthesized via a citric route as described in Section 4.3. The sample preparation and half cell testing procedures had been given in Ref. (Ge and Chan, 2009b) and are omitted for simplicity. To prepare samples for particle size measurement, firstly the powders were ultrasonically dispersed in isopropanol. The suspension was then dripped onto clean Si wafer and dried in air. Hundreds of particles were counted from scanning electron microscopy (SEM, JEOL JSM-6340F) images. The particle sizes are fitted to a normal distribution function. The mean of the normal distribution function is used as the mean particle size of the corresponding particles. A home-built Mathematica® 7 code interpreted SEM surface morphology images of sintered LSV–YSZ anodes and provided the two-dimensional porosity. A standard calibration sample with large surface area, known electrode thickness and composition, was used to convert the two-dimensional porosity into three-dimensional porosity. The anode thickness was obtained from the cross-section profiles via SEM.

The LSV–YSZ green anode was described analytically as a binary random loose particle aggregate. The packing bed was constructed geometrically based on a set of experimental inputs, consisting of particle size, particle size ratio, powder composition, and packing density. The particles were supposed to be distributed in the packing bed homogeneously and statistically. The coordination numbers of particles in the packing bed were analyzed on the basis of geometric arguments. Finally, the green packing bed was sintered according to a particle-to-plate sintering model.
4.4.2 Virtual packing

Table 4-2 lists the parameters describing the LSV–YSZ composite anode, comprising electrode thickness, electrode composition, electrode porosity, particle size, and particle density. These parameters serve as the initial inputs in establishing the packing bed. The particle size distributions of LSV and YSZ are shown in the Figs. 4-19 and 4-20, respectively. The LSV and YSZ powders have similar particle sizes and both of them exhibit the normal distribution behaviour. Note that the spread of particle sizes are not considered in this simplified packing model. Figure 4-21 shows the cross-section profile of the LSV–YSZ/YSZ interface, from which the anode layer thickness is readily known. The mass loss due to the reduction of LSV provides a precise way of determining the composition of LSV–YSZ anode. The two-dimensional packing density ($\eta_{2D}$) is calculated from surface morphology images as those shown in Fig. 4-22. $\eta_{2D}$ is converted to the three-dimensional packing density ($\eta_{3D}$) because practical SOFC anodes are three-dimensional. A linear relationship is assumed to exist between $\eta_{3D}$ and $\eta_{2D}$,

$$\eta_{3D} = k_{2D \rightarrow 3D} \eta_{2D} \quad \text{(Equation 4-28)}$$

where $k_{2D \rightarrow 3D}$ is the packing density coefficient. $k_{2D \rightarrow 3D}$ was obtained from a calibration sample with deliberated large surface area. It is worth to mention that the exact microstructure beneath the electrode surface is poorly known. $\eta_{3D}$, which is determined by simply measuring the weight and dimensions, could have slightly overestimated the open porosity of the electrodes. The $\eta_{3D}$ given in Table 4-2 was averaged from five samples produced from the same batch with the one shown in Fig. 4-22.
Table 4-2 Listing of characteristic parameters of the LSV–YSZ composite anode.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode layer thickness, $h$</td>
<td>23.0 μm</td>
</tr>
<tr>
<td>Particle size of LSV, $d_{LSV}$</td>
<td>0.23 ± 0.04 μm</td>
</tr>
<tr>
<td>Particle size of YSZ, $d_{YSZ}$</td>
<td>0.27 ± 0.05 μm</td>
</tr>
<tr>
<td>Density of reduced LSV, $\rho_{LSV}$</td>
<td>6.606 g/cm³</td>
</tr>
<tr>
<td>Density of YSZ, $\rho_{YSZ}$</td>
<td>5.942 g/cm³</td>
</tr>
<tr>
<td>Geometric surface area of LSV–YSZ composite anodes, $A_{geo}$</td>
<td>0.46 cm²</td>
</tr>
<tr>
<td>Two-dimensional packing density, $\eta_{2D}$</td>
<td>0.79 ± 0.03 cm²/cm²</td>
</tr>
<tr>
<td>Packing density coefficient, $k_{2D\rightarrow 3D}$</td>
<td>0.67</td>
</tr>
<tr>
<td>Three-dimensional packing density, $\eta_{3D}$</td>
<td>0.53 cm³/cm³</td>
</tr>
<tr>
<td>Volume fraction of LSV (void exclusive), $f_{LSV}^v$</td>
<td>0.42 cm³/cm³</td>
</tr>
<tr>
<td>Number fraction of LSV (void exclusive), $n_{LSV}^f$</td>
<td>0.54 particles/particles</td>
</tr>
<tr>
<td>Area fraction of LSV (void exclusive), $A_{LSV}^f$</td>
<td>0.46 cm²/cm²</td>
</tr>
</tbody>
</table>

Figure 4-19 (a) Particle size distribution and (b) cumulative probability of LSV particles.
Figure 4-20 (a) Particle size distribution and (b) cumulative probability of YSZ particles.

Figure 4-21 SEM image of the cross-section profile of a LSV–YSZ composite anode sintered onto YSZ electrolyte. The apparent poor adhesion may be incurred during the preparation of the fractured sample.
Figure 4-22 SEM surface morphology image of an as-reduced LSV–YSZ composite anode. The sporadic black regions represent voids while the others symbolize particle aggregates. The two-dimensional packing density of this anode is 0.78 cm$^2$/cm$^2$. The corresponding three-dimensional packing density, obtained from the image analyses by implementing home-build Mathematica® 7 codes, is 0.52 cm$^3$/cm$^3$.

Among various packing modes the random loose packing seems most relevant (Jaeger and Nagel, 1992), as the void fraction ($\varepsilon$=1-$\eta_{3D}$) of LSV–YSZ anodes is as high as 0.47 (Table 4-2). It considers how many randomized LSV and YSZ particles can be accommodated, i.e. coordination numbers, around a specific particle. The coordination numbers of a reference particle rely on the relative particle size ($r_p$) and the area fraction ($f_A$) in packing beds (Suzuki and Oshima, 1983). Without loss of generality, take LSV as the reference particle. The total coordination numbers of a LSV reference particle ($N_{LSV}^b$) is the sum of that in contact with LSV particles ($N_{LSV,LSV}^b$) and that in contact with YSZ particles ($N_{LSV,YSZ}^b$),

$$N_{LSV}^b = N_{LSV,LSV}^b + N_{LSV,YSZ}^b \quad \text{(Equation 4-29)}$$

In Eq. 4-29, $N_{LSV,LSV}^b$ is given by coordination numbers in the corresponding monosized LSV packing bed ($N_{LSV,LSV}^m$, or simply $N^m$) weighted by the area fraction of LSV ($f_{LSV}^A$),
\[ N_{LSV,LSV}^b = f_{LSV}^A N_{LS}^m . \]  \hspace{1cm} (Equation 4-30)

\( N_{LS}^m \) is 6.50 as \( \eta_{3D} \) is 0.53 in this work, as shown in Table 4-2 (Suzuki, 2007). Note that in Eq. 4-30 the particle segregation behaviours are not considered. \( f_{LSV}^A \) is related with the number fraction of LSV (\( f_{LSV}^n \)) as

\[ f_{LSV}^A = \frac{f_{LSV}^n r_p^2}{f_{LSV}^n r_p^2 (r_p^2 - 1) + 1} . \]  \hspace{1cm} (Equation 4-31)

In Eq. 4-31, \( r_p \) is the particle size ratio of LSV over YSZ,

\[ r_p = \frac{d_{LSV}}{d_{YSZ}} , \]  \hspace{1cm} (Equation 4-32)

where \( d_{LSV} \) and \( d_{YSZ} \) are particle sizes of LSV and YSZ, respectively. \( N_{LSV,YSZ}^b \) is obtained in the same manner with \( N_{LSV,LSV}^b \),

\[ N_{LSV,YSZ}^b = (1 - f_{LSV}^A) N_{LSV,YSZ}^m , \]  \hspace{1cm} (Equation 4-33)

where \( N_{LSV,YSZ}^m \) is the coordination numbers of a reference LSV particle embedded in the YSZ packing bed. \( N_{LSV,YSZ}^m \) is related with \( r_p \) and \( N_{LS}^m \) as

\[ N_{LSV,YSZ}^m = \frac{2\alpha}{1 - (r_p^2 + 2r_p)^{1/2}} , \]  \hspace{1cm} (Equation 4-34)

where \( \alpha \) is a geometric factor directly proportional to \( N_{LS}^m \),

\[ \alpha = \frac{2 - \sqrt{3}}{4} N_{LS}^m . \]  \hspace{1cm} (Equation 4-35)

The coordination numbers of YSZ can be obtained via the same arguments as that of LSV. Table 4-3 lists the coordination numbers of LSV and YSZ particles in the LSV–YSZ packing bed. It can be found in Table 4-3 that larger particles always have bigger coordination numbers, albeit with sophisticated and non-linear interdependences.
Table 4-3 Coordination numbers in the simulated LSV–YSZ packing bed.

<table>
<thead>
<tr>
<th>Coordination numbers</th>
<th>Values (contacts/particle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{LSV,YSZ}^{w}$</td>
<td>5.50</td>
</tr>
<tr>
<td>$N_{LSV,LSV}^{b}$</td>
<td>2.99</td>
</tr>
<tr>
<td>$N_{LSV,YSZ}^{b}$</td>
<td>2.97</td>
</tr>
<tr>
<td>$N_{LSV}^{b}$</td>
<td>5.96</td>
</tr>
<tr>
<td>$N_{YSZ,LSV}^{w}$</td>
<td>7.78</td>
</tr>
<tr>
<td>$N_{YSZ,YSZ}^{b}$</td>
<td>3.51</td>
</tr>
<tr>
<td>$N_{YSZ,LSV}^{b}$</td>
<td>3.58</td>
</tr>
<tr>
<td>$N_{YSZ}^{b}$</td>
<td>7.09</td>
</tr>
</tbody>
</table>

For any correctly–designed composite anodes, both the electronic and ionic components must form electrical percolating networks. For binary packing beds composed of purely electronic (e.g., LSV) and ionic (e.g., YSZ) particles, the formation of percolating networks solely depends on whether the coordination numbers of homogenous particles ($N_{ii}^{b}$) are larger than the percolation threshold ($N_{i,i}^{*}$). $N_{i,i}^{*}$ is defined as the minimum coordination numbers that render particles long-range interconnected. It was reported to be $(D^2 + D)/(2D-1)$ for the rigid particle aggregates, where $D$ is the dimension (Kuo and Gupta, 1995). Generally speaking, larger particles involve smaller number fraction ($f^n$) to render $N_{i,i}^{b} > N_{i,i}^{*}$. Figure 4-23 shows contour plots of $N_{LSV,YSZ}^{b}$ together with the percolating regions of LSV and YSZ, as functions of $f^n_{LSV}$ and $r_p$. The whole region is divided into three sub-regions by the two contours of $N_{LSV,LSV}^{b}$ and $N_{YSZ,YSZ}^{b}$, viz. the non-percolating region of LSV (light gray), the percolating region of both LSV and YSZ (rainbow), and the non-percolating region of YSZ (pastel violet). The largest percolating region obviously occurs when a monosized packing bed (i.e. $r_p = 1$) with equal amount of LSV and YSZ particles (i.e. $f^n_{LSV} = 0.5$) forms. The percolating region shrinks when particle aggregates deviate
from \( r_p = 1 \) and \( f_{LSV}^{n} = 0.5 \). Accordingly, the percolating region shown in Fig. 4-23 is merely a small portion of the whole crescent-shaped percolating region. As can be seen in Table 4-3 and Fig. 4-22, both LSV and YSZ situate within the percolating region. Fig. 4-23 also implies that \( r_p \) and \( f^n \) should not deviate strongly from 1 and 0.5, respectively. Otherwise, the risk of obtaining non-percolating composite electrodes is high because the percolating region becomes too narrow to manipulate. Contour plot diagrams like Fig. 4-23 are useful in designing and evaluating coordination numbers and percolation thresholds of binary particle aggregates.

Figure 4-23 Contour plots of \( N^b_{LSV,YSZ} \) as functions of \( f_{LSV}^{n} \) and \( r_p \). The light gray zone and the pastel violet zone are the non-percolation regions of LSV and YSZ, respectively. The rainbow zone is the percolating region of both LSV and YSZ. The embedded purple dot represents the simulated LSV–YSZ composite anode under investigation.

Packing beds constructed by coordination number theories were largely based on Bouvard and Lange’s method (Chan et al., 2004; Jeon et al., 2006; Janardhanan et al., 2008; Mori et al., 2008; Chen et al., 2011). Their packing method involves an implicit assumption that the coordination number of monosized packing beds \( (N^m) \) is exactly 6
(Bouvard and Lange, 1991). Unlike Bouvard and Lange’s method, the void fraction effect on $N^m$ has been incorporated in our packing model. As summarized by Suzuki (Suzuki, 2007), $N^m$ is in principle a monotonically decreasing function on the void fraction $\varepsilon$.

### 4.4.3 Virtual sintering

The necks among heterogeneous particles in the packing bed represent the sintering necks among electronic and ionic particles in realistic SOFC composite anodes. In contrast, the necks among homogeneous particles are of little interests as long as percolating networks have already formed. This work therefore considers the LSV–YSZ necks under the conditions of percolating LSV–LSV and YSZ–YSZ networks. The neck formation between two LSV and YSZ particles is considered from: (i) adhesion at room temperature and (ii) sintering at elevated temperatures. The adhesion of contacting LSV and YSZ particles occurs in order to minimize the surface energy. The surface energy of both particles should be quite low because of organic surface films. The lower limit of the radius of adhesion necks ($x_0$) formed by Van der Waals forces is given by

$$x_0 = \left( \frac{r_a a^3}{10\mu} \right)^{1/3}$$

(Equation 4-36)

where $\gamma_s$ is the surface energy, $a$ the particle radius, and $\mu$ the shear modulus of LSV particles (Ashby, 1974). According to Eq. 4-36, the normalized radius of adhesion necks ($x_0/a$) is 0.04.

This lightly (i.e. 4%) contacting LSV–YSZ particle aggregate is subsequently sintered in the initial sintering stage, thus preventing abnormal particle growth and maintaining considerable electrode porosity (Figs. 4-22 and 4-25). The YSZ should be inert as the electrode sintering temperature (1200 °C) is significantly lower than its melting point. Note that the constrained sintering between the YSZ substrate and the thin electrode and the free surface sintering are not considered in this study. A sphere-to-plate model that considers a LSV sphere sintered to YSZ plate should be reasonable, because the effective curvature of inert YSZ is almost zero. The normalized curvature difference ($K$) for diffusion from a surface source (e.g., surface diffusion and lattice diffusion) is
where \( \rho \) is the radius of curvature of the sintering neck and \( x \) is the radius of the sintering neck (inset of Fig. 6) (Ashby, 1974). By simple geometry,

\[
\rho = \frac{x^2}{2(a-x)}
\]

Under quasi steady state conditions, the grow rate of sintering necks controlled by lattice diffusion \( (dx_{\text{latt}}/dt) \) is

\[
\frac{dx_{\text{latt}}}{dt} = \frac{2D_v^p \gamma \Omega K^2}{kT},
\]

where \( D_v \) and \( \Omega \) are the lattice diffusion coefficient and the ionic volume of LSV, respectively (Kuczynski, 1949; Wilson and Shewmon, 1966). In contrast, the surface diffusion leads to a sintering neck grow rate \( (dx_{\text{surf}}/dt) \) given by

\[
\frac{dx_{\text{surf}}}{dt} = \frac{2D_s^p \delta_s \gamma \Omega K^3}{kT},
\]

where \( D_s \) and \( \delta_s \) are the surface diffusion coefficient and the effective surface thickness of LSV, respectively (Kuczynski, 1949; Wilson and Shewmon, 1966). The diffusion coefficients in Eqs. 4-39 and 4-40 fulfil the Arrhenius behaviour,

\[
D_i = D_0^i \exp \left( -\frac{Q_0^i}{RT} \right), \quad i = v, s
\]

where \( D_0^i \) and \( Q_0^i \) are the pre-exponential factor and the activation energy for the specific diffusion mode, respectively. Table 4-4 lists the sintering parameters of LSV. Figure 4-24 shows the normalized radius of sintering necks \( (x/a) \) in function of sintering time. The neck growth is quite fast in the first 10 minutes but relatively sluggish after 3 hours. \( x/a \) is 0.14 for a sintering time of 2 hours if the sintering is lattice diffusion controlled. In comparison, \( x/a \) is 0.54 if the sintering is surface diffusion controlled. It is thus inferred that the sintering of LSV–YSZ particle aggregate is dominated by the surface diffusion.
Figure 4-24 Numerical sintering curves of the LSV–YSZ packing bed at 1200 °C, controlled either by surface diffusion (green) or lattice diffusion (red) of LSV from surface sources. The inset illustrates the neck formation during the initial sintering stage. $x$ and $a$ are the radiuses of the sintering neck and the LSV particle, respectively.

Table 4-4 Listing of parameters of LSV for the sintering model.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic volume, $\Omega$</td>
<td>$9.24 \times 10^{-21}$ cm$^3$</td>
</tr>
<tr>
<td>Melting point, $T_m$</td>
<td>1953 K</td>
</tr>
<tr>
<td>Density, $\rho_{\text{LSV-ox}}$</td>
<td>4.89 g/cm$^3$</td>
</tr>
<tr>
<td>Surface energy, $\gamma_s$</td>
<td>700 mJ/m$^2$</td>
</tr>
<tr>
<td>Effective surface thickness, $\delta_d$</td>
<td>$7 \times 10^{-8}$ cm</td>
</tr>
<tr>
<td>Pre-exponential factor for lattice diffusion, $D_0^p$</td>
<td>$3.2 \times 10^7$ cm$^2$/s</td>
</tr>
<tr>
<td>Activation energy for lattice diffusion, $Q_0^p$</td>
<td>378 kJ/mol</td>
</tr>
<tr>
<td>Pre-exponential factor for surface diffusion, $D_0^s$</td>
<td>$2 \times 10^3$ cm$^2$/s</td>
</tr>
<tr>
<td>Activation energy for surface diffusion, $Q_0^s$</td>
<td>370 kJ/mol</td>
</tr>
<tr>
<td>Sintering temperature, $T$</td>
<td>1473 K</td>
</tr>
<tr>
<td>Sintering time, $t$</td>
<td>7200 s</td>
</tr>
</tbody>
</table>
In literature, the description on TPBs of SOFC electrodes was mostly modelled by the intersection of two overlapping heterogeneous particles (Abbaspour et al., 2010; Golbert et al., 2008; Kenney et al., 2009; Nishida and Itoh, 2011; Sanyal et al., 2010). To the best of our knowledge, Costamagna and coworkers first proposed this particle-overlapping method (Costamagna et al., 1998). The method involves a priori knowledge on the extent of particle overlapping. In addition, the role of materials properties in the neck formation has been somewhat overlooked. Numerical sintering models had also been proposed for externally compacted SOFC composite electrodes (Schneider et al., 2006). In contrast, the analytical sintering model used in this work is free of external pressure.

### 4.4.4 Three phase boundaries and electrochemically active zones

Figure 4-25 shows a schematic configuration of the half-cell consisting of YSZ electrolyte, LSV–YSZ composite anodes, and enlarged EAZs of two sintered LSV and YSZ particles. It is worth noting that EAZs are, in principle, the sum of numerous tiny and discontinuous active zones around the sintering necks. As sketched in Fig. 7, the dimensions of EAZs are defined by three length scales, viz. the length specific TPB length ($l_{TPB}$), the in-depth TPB penetration of electrocatalysts ($w$), and the distance away from the interface between the LSV–YSZ anode and the YSZ electrolyte, i.e. LSV–YSZ/YSZ interface ($l$). Without loss of generality, let LSV be the reference particle. The length specific $l_{TPB}$ is thus given by

$$l_{TPB} = sN_{LSV,YSZ}^b \rho_{LSV}^l,$$

(Equation 4-42)

where $s$ is the perimeter of sintering necks of two as-sintered LSV and YSZ particles ($s = 2\pi x$) and $\rho_{LSV}^l$ is the line density of LSV along the direction away from the LSV–YSZ/YSZ interface. Unless addressed explicitly, the TPB length used all through this study is length specific, which is the TPB length normalized to the direction away from the composite electrode-electrolyte interface. The $s$ and $\rho_{LSV}^l$ of the LSV–YSZ anodes are 0.4 μm/contact and $1.53 \times 10^{13}$ particles/cm, respectively. The corresponding $l_{TPB}$ is thus found to be $1.8 \times 10^9$ cm/cm, equivalent to a volume-specific TPB length of $3.9 \times 10^9$ cm/cm$^3$. The TPB length reported herein is one order of
magnitude larger than those experimentally determined values (Wilson et al., 2006). This discrepancy might be because LSV particles are much finer than NiO particles. Furthermore, the particle agglomeration, particle segregation, and dead-sintered interfaces have not been considered in this study.

Figure 4-25 Schematic illustration of the microstructure and sintering necks of LSV–YSZ composite anodes. In the figure, $x$, $w$, and $l_{0.01}$ are the radius of the sintering necks, the in-depth TPB penetration of electrocatalysts, and the active electrode thickness, respectively.

$w$ is assumed to decay exponentially along $l$,

$$w = w_0 \exp(-k l)$$  \hspace{1cm} (Equation 4-43)

where $w_0$ is the $w$ at the LSV–YSZ/YSZ interface and $k$ is a proportionality factor that fulfils

$$k l_{0.01} = \ln 100$$  \hspace{1cm} (Equation 4-44)

In Eq. 44, $l_{0.01}$ is defined empirically as the $l$ where $w$ decays 99%. It is worth to mention that the selection of 99% decay is arbitrary. To some extent, $l_{0.01}$ could be regarded as the active electrode thickness, beyond which fuel cell reactions become so sluggish that $w$ is negligible. In summary, the cross-section area of EAZs ($A_{EAZ}$) is given by integrating $l_{TPB}$, $w$, and $l$ from the LSV–YSZ/YSZ interface ($l = 0$) to the active electrode thickness ($l = l_{0.01}$),
\[ A_{E\text{AZ}} = \int_{0}^{l_{\text{TPB}}} f_{c} w_{0} e^{-x} \, dl \]  

(Equation 4-45)

where \( f_{c} = 1.15 \) is a correction factor that accounts for particle coarsening on the basis of cumulative distribution functions (Suzuki, 2007). The ratios of \( A_{E\text{AZ}} \) over \( A_{\text{geo}} \) of the LSV–YSZ composite anode had been known to be 7.3±0.5, 8.1±0.4, 7.9±0.4, 7.0±0.2, 6.7±0.3, 6.1±0.4, 7.2±0.9, under anodic biases (\( E_{\text{bias}} \)) of 0, 20, 50, 70, 100, 120, and 150 mV, respectively (Ge et al., 2011). The \( A_{E\text{AZ}} \) of polarized LSV–YSZ composite anodes can thus be readily known. Except \( w_{0} \) and \( l_{0.01} \), the parameters in Eqs. 15–18 have been known from the virtual packing and sintering data (Tables 4-2 and 4-3).

The magnitude of \( w_{0} \) has been rarely reported in literature. Nakagawa et al. observed no performance changes of Ni films ranging from 0.8 μm to 12.9 μm (Nakagawa et al., 1995). They thus inferred that the EAZs of Ni–YSZ cermet anodes were less than 1 μm away from the Ni–YSZ/YSZ interface. Horita et al. examined active sites of cathodically polarized La\(_{0.9}\)Sr\(_{0.1}\)MnO\(_{3}\) (LSM)/YSZ interfaces under \(^{16}\)O/\(^{18}\)O atmosphere. They concluded with caution that the length scale of the active sites for O\(_{2}\) reduction was less than 1 μm (Horita et al., 1998). While the experiments largely delimit the upper bound that is around 1 μm, the lower bound of \( w_{0} \) might have to be simulated. Adler et al. discussed the cathodic behaviours of mixed ionic and electronic conductors (MIECs) and found that the penetration depth of poor ionic conductors (e.g. LSM) was essentially less than 100 atomic unit cells (Adler et al., 1996). By analyzing electrochemical potential distributions of patterned MIEC cathodes, Fleig found that the ionic current density dropped by 80% at a distance of several nanometres away from TPBs (Fleig, 2002). Generally speaking, \( w_{0} \) of SOFC cathodes depends on the oxygen ionic conductivity and oxygen surface exchange rate. If the same argument also applies to SOFC anodes, \( w_{0} \) of LSV particles should not be larger than 16 nm (Fleig, 2002; Liu, 1998). In this work \( w_{0} \) is thus thought to be in the order of magnitude of \( 10^{0} \) nanometres.

An empirical way on estimating \( l_{0.01} \) is to examine the electrode thickness effect on fuel cell performance. Take the state-of-the-art Ni cermet anodes as an example. It is interesting to note that most experimental results advocate \( l_{0.01} \) in two categories: 100 μm (Fukunaga et al., 2007; Abudula et al., 1996) and 10μm (Sakamoto et al., 1996;
Menzler and Haanappel, 2010; Brown et al., 2000; Primdahl and Mogensen, 1999). Our previous works suggested an optimal anode thickness around 100 μm for submicron-sized particle aggregates (Chan and Xia, 2001). As it tackled with the mass transport behaviour in porous media and was irrelevant to interfacial chemistry, that “optimal” anode thickness might not be the active anode thickness. In contrast, Zhu and Kee stated charge transfer regions extending over a distance of 10–20 μm away from electrolyte surfaces (Zhu and Kee, 2008). Jiang et al. simulated equal-sized and equal-composition LSM–YSZ cathodes and reported the effective thickness of 10–20 μm (Jiang et al., 2010). In this work, $l_{0.01}$ is tentatively regarded to be in the order of magnitude of $10^1$ μm.

Figure 4-26  Contour plots of $A_{EAZ}$ of LSV–YSZ composite anodes as functions of $w_0$ and $l_{0.01}$. The $A_{EAZ}$ values of sample A are 3.34 (red, dashed), 3.73 (green, solid), 3.65 (blue, dashed), 3.22 (black, dotted), 3.07 (purple, solid), 2.82 (magenta, dot-dashed), and 3.31 cm$^2$ (brown, solid), under anodic biases of 0, 20, 50, 70, 100, 120, and 150 mV, respectively.
Figure 4-26 shows the contour plots of $A_{\text{EAZ}}$ as functions of $w_0$ and $l_{0.01}$ after solving Eq. 4-35 numerically. It should be borne in mind that in Fig. 4-26 $w_0$ and $l_{0.01}$ are treated as two independent parameters, although the exact interrelationship between $w_0$ and $l_{0.01}$ is hitherto unknown. In addition, exact values of $w_0$ and $l_{0.01}$ are unable to be obtained within the scope of the present study. Notwithstanding these limitations, it is still meaningful to discuss the behaviours of EAZs in polarized LSV–YSZ anodes. For instance, under the open circuit voltage (OCV) condition $w_0$ is 3.61 nm if $l_{0.01}$ is given as 10 μm, vice versa. If $w_0$ is assigned as 5 nm and it remains constant under polarized conditions, $l_{0.01}$ are 7.23, 8.07, 7.90, 6.96, 6.64, 6.10, and 7.16 μm, under $E_{\text{bias}}$ of 0, 20, 50, 70, 100, 120, 150 mV, respectively. On the other hand, $l_{0.01}$ would be 12.04, 13.45, 13.16, 11.61, 11.07, 10.17, 11.94 μm, respectively, if $w_0$ was 3 nm instead of 5 nm (Fig. 8). SOFCs are certainly operated under more sophisticated conditions with either independent or interrelated $w_0$ and $l_{0.01}$. Unfortunately, this kind of uncertainty has not been able to be minimized without convincing experimental evidences. This work therefore merely provides some technical guidelines on these hard-to-measure interfacial parameters (Fig. 4-26). It is worth to highlight that either the active electrode thickness or the TPB length, which has been used extensively in literature, is not sufficient in describing the reactive regions in on-running SOFCs alone.

To summarize, the rationale on establishing the relationship between TPBs and EAZs, though derived based on LSV–YSZ composite anodes in SOFCs, is suitable for various solid state electrode/electrolyte interfaces, e.g. fuel cells with solid electrolytes, solid state electrolytic cells, oxygen sensors, and batteries. Besides purely academic interests, it is thought to be useful for technical designs on electrodes and electrode/electrolyte interfacial structures. $l_{0.01}$ represents the optimized thickness of the functional layer in SOFC anodes. Note that the use of functional layers has been very popular in Ni-cermet supported SOFC stacks. In addition, $w_0$ sets the design target on the shell thickness of (inert) core-(active) shell structures. These kinds of structures have being used extensively in polymer electrolyte membrane fuel cells (PEMFCs) (Wang et al., 2010). Notwithstanding with these merits, the theory should be judged critically on some inherent assumptions and limitations. A fundamental assumption, albeit made tacitly, is that the electrocatalyst is purely electronic and the electrolyte is purely ionic. The whole theory needs further corrections in order to be suitable for MIECs. The significance of MIECs should not be overlooked, as they have...
been quite common in intermediate and low temperature SOFCs. Furthermore, the virtual packing neglects problems like particle segregation and particle size distribution. These problems become significant if $r_p$ strongly deviates from the unity. This work could be further improved by employing in situ techniques to characterize the electrode microstructure (Wilson et al., 2006; Shearing et al., 2010; Bouvard and Lange, 1991; Kanno et al., 2011). Sophisticated materials characterization techniques (e.g. in situ Raman spectroscopy (Cheng et al., 2007), in situ X-ray photoelectron spectroscopy (DeCaluwe et al., 2010; Zhang et al., 2010a), and synchrotron X-ray scattering (Nagy and You, 2009) should also be involved in order to measure $w$ and $l_{0.01}$ experimentally.

4.4.5 Brief summary

The interrelationship between TPBs and EAZs was investigated via a case study on LSV–YSZ composite anodes in SOFCs. The TPB lengths were calculated from a virtually packed and sintered particle aggregate. The packing and sintering methods were suitable for the optimization of SOFC composite electrodes. The length specific TPB length was $1.8\times10^9$ cm/cm, equivalent to a volume-specific TPB length of $3.9\times10^9$ cm/cm$^3$. The cross-section area of EAZs was basically 6 to 8 times of the geometric area. Empirical correlations among EAZs, TPBs, active electrode thickness, and in-depth penetration of electrocatalysts were established. Under the circumstance of polarized LSV–YSZ anodes, the active electrode thickness and in-depth penetration of electrocatalysts were typically in the range of 5–20 μm and 2–8 nm, respectively.

4.5 Summary

The double layer and electrochemically active zones of solid state electrode/solid-electrolyte interfaces were investigated via a case study on LSV/YSZ interfaces in solid oxide fuel cell anodic environments. A comprehensive theory had been elaborated by addressing the double layer structure, the double layer capacitance, and the electrochemically active zones. The double layer structure was described by a modified Poisson–Boltzmann theory and Monte Carlo simulations. The apparent double layer capacitance was obtained from impedance spectroscopy. Its magnitude was of several hundreds of μF/cm$^2$. The Helmholtz–Perrin capacitance was ca 22 to 30 μF/cm$^2$ while the Gouy–Chapman capacitance was ca 320 to 480 μF/cm$^2$. The intrinsic double layer capacitance was dominated by the Helmholtz–Perrin capacitance.
Thicknesses of the compact layer were around 0.28 to 0.36 nm; thicknesses of the diffusive layer were around 1.1 to 1.9 nm. Under anodic biases from 0 to 150 mV, the “capacitance surge” phenomenon was ascribed to mutual competitions between the loosened compact layer and the increase of Volta potential in the diffusive layer. Synergic capacitance analyses enabled in situ detections of electrochemically active zones. With electrode microstructures described by the sintered LSV–YSZ particle packing beds, correlations among electrochemically active zones, three phase boundaries, in-depth penetration of electrocatalysts, and effective anode thickness were established.
Chapter 5. Sulphur tolerant and carbon resistant solid oxide fuel cells with LSV anodes

5.1 Importance and current status of sulphur-tolerant and carbon-resistant SOFC anodes

The international commitment on sustainable society and low-carbon future demands green energy conversion technologies (International Energy Agency, 2010). In an idealized scenario, primary energy sources are converted to secondary energy sources, mostly in electrical energy, with high energy conversion efficiency and low carbon footprint. Such kinds of energy conversion devices are thought to be incorporated into smart grids, in order to improve the system efficiency and stability towards demand fluctuations and intermittent electrical sources. Currently available technologies, e.g. wind (Li, 2010), nuclear (Muradov and Veziroglu, 2008), solar (Pagliaro et al., 2010), metal hydrides (Aguey-Zinsou and Ares-Fernandez, 2010), and batteries (Baker, 2008) largely fail to meet at least one of the key targets including cost, reliability, flexibility, efficiency, and large scale deployment. One of the technologies that generally fulfil these requirements is SOFC. SOFC has been extensively studied since the last three decades (Minh, 1993; Jacobson, 2010). Distinctive advantages of SOFCs are the high energy conversion and storage efficiency and the fuel flexibility. SOFC electrical efficiencies ranging from 40% (simple and small systems) to 50% (hybrid systems) had been demonstrated, and the theoretical efficiency is projected up to 60% (Energy, 2004). SOFCs employing robust hydrogen electrodes can be fed with H₂, CO, syngas, gasified reformates from natural gas, coal, and heavy hydrocarbons. Direct hydrocarbon fed SOFCs had also been demonstrated (McIntosh and Gorte, 2004).

The fuel flexibility, however, has been somewhat constrained by the lack of carbon resistance and sulphur tolerance. The state-of-the-art Ni–cermet electrodes are prone to carbon filament precipitation (Toebes et al., 2002), dusting, and dry corrosion when exposed to hydrocarbon fuels. Ni–cermets are also known to be poisoned by parts per million (ppm) levels of H₂S, though they can be regenerated when exposed to low concentrations and temporarily high concentrations of H₂S (Matsuzaki and Yasuda, 2000; Zha et al., 2007). In literature, various mitigation approaches on Ni–cermet
SOFC anodes had been proposed, including the addition of water (Lakshminarayanan and Ozkan, 2011; Yang et al., 2010) or low melting point metals (Marina et al., 2011) into fuels, and decoration of NiO particles with ceria (Kurokawa et al., 2007b; Yun et al., 2010; Lohsoontorn et al., 2008) or niobia (Choi et al., 2008). Sulphide (Pujare et al., 1987; Yates and Winnick, 1999; Liu et al., 2003) and oxide (Mukundan et al., 2004; Aguilar et al., 2004a; Zha et al., 2005a; Xu et al., 2007; Lu and Zhu, 2008; Danilovic et al., 2009; Zha et al., 2005b; Cooper et al., 2010) anodes had also been explored extensively. Many practical SOFC feedstocks, e.g. natural gas, coal gas, syngas, town gas, biogas, and reformed military fuels, contain several to thousands ppm of H_2S. In this chapter, lanthanum strontium vanadate-based SOFCs are tested and they exhibit salient catalytic activity and long-term stability when exposed to various feedstocks out of the H_2–H_2O–CO–CO_2–CH_4–H_2S system.

5.2 Experimental

In this chapter La_{0.6}Sr_{0.4}VO_x (LSV) was used because of its higher catalytic activity than La_{0.8}Sr_{0.2}VO_x. LSV powders were synthesized via a citric route. The starting materials were La(NO_3)_3·6H_2O (Fluka, 99.0%), Sr(NO_3)_2 (Fluka, 99.0%), NH_4VO_3 (Sigma-Aldrich, 99.5%), and C_6H_8O_7·H_2O (Fluka, 99.5%). The molar ratio of total metal ions over citric acid was 2:3. Stoichiometric amounts of the raw materials were dissolved in deionised water. The solution was heated at 70 ºC under magnetic stirring. A dark blue gel was obtained after dissipating excess water. It was dehydrated overnight at 100 ºC and carefully ground in an agate mortar. The precursor was baked at 600 ºC for 2 hours in a pristine alumina crucible (Coorsteck, the USA). The LSV powders were re-ground in the agate mortar. The LSV powders were further baked at 600°C for 2 hours and at 800 ºC for 6 hours. The YSZ powders (Tosoh, Japan) were used as-received.

Right amounts of LSV and YSZ powders were roll-milled overnight in isopropanol with YSZ balls. Subsequently, the slurry was dried at 80 ºC in ambient air to obtain a homogeneous LSV–YSZ mixture. The powder mixture was added with ink vehicles (Fuel Cell Materials, the USA) and ground in the agate mortar to form the electrode paste. Green electrodes were prepared by screen-printing the ink onto 1-mm-thick YSZ electrolyte substrates. The geometric area of electrodes was 0.46 cm^2. The
electrochemically catalytic layer, LSV (50 wt.%)–YSZ, were sintered at 1215 °C for 2 hours. The gas diffusion layer, LSV (70 wt.%)–YSZ, was screen-printed onto the catalytic layer and sintered at 1205 °C for another 2 hours. A piece of Au gauze (Alfa Aesar, 52 mesh woven from 0.102 mm diameter wire, 99.99% metal basis) with a small amount of Pt paste in discrete dots was pressed onto the electrode to improve the contact quality. The Pt paste was also applied on the opposite side of YSZ substrate to represent the counter and the reference electrodes. All the Pt layers were sintered at 900 °C for 30 minutes.

Figure 5-1  Schematic diagram of the flow channel, test rig, and half cell configuration.
The half cell configuration is given in Fig. 5-1. The lead wires on the hydrogen electrode side are made of Au (Alfa Aesar, 0.5 mm diameter, 99.9985% metal basis). The lead wires on the oxygen electrode side are made of Pt (Alfa Aesar, 0.5 mm diameter, annealed, 99.95% metal basis). The half cell was sealed onto an alumina tube with ceramic paste (Aremco 552, the USA). The testing tube was cured at 120 ºC for 2 hours. Both the counter and reference electrodes are exposed to ambient air. After purging with N₂, the test rig was heated up in H₂ with a ramping rate of 2 ºC/min. The operating temperature was 900 ºC. At the hydrogen electrode side, the H₂S-free feedstock was modulated from the corresponding pure gases via Brooks® 4-channel mass flow controller (MFC). H₂S was introduced to the feedstock by using a certified gas blend of H₂S and H₂ (1000 ppm H₂S balanced with H₂). To obtain H₂O-containing feedstock, the gas blend was channelled through a humidifier with temperature control of ±0.1ºC. The wet gas blend was further mixed with 1000ppm H₂S–H₂ to get the desired composition. The total flow rate of feedstock was maintained at 100 sccm.

Impedance responses were recorded under given anodic biases via a Solartron 1255B frequency response analyzer coupled to a 1470E electrochemical interface. The frequency range was 100,000–0.05 Hz. The sampling rate was 10 points/decade of frequency. Impedance spectra were fitted via Zview® 3.2c according to complex nonlinear least squares (CNLS) algorithm. Quasi-steady state polarization was performed by sweeping from -0.3 V (vs OCV) to 0.6 V (vs OCV), with a ramping rate of 0.1 mV/s and a sampling rate of 1 point/mV. Long-term stability tests were performed by chronopotentiometry, i.e. monitoring the electric potentials under given current densities. The sampling rate was 0.2 points/sec.

The X-ray diffraction pattern was recorded on a Shimadzu 6000 with Cu Ka radiation. The step size was 0.02º. The scan rate was 2º/min. Low vacuum scanning electron microscopy (SEM, JEOL JSM–6360) and field-emission SEM (FESEM, JEOL 7600F) were used for low and high magnification surface morphology observations, respectively. Qualitative element detection in the electrodes was carried out via the energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments X-Max), which are coupled to the JEOL JSM–6360.
5.3 Structure and microstructure

Figure 5-2 shows the XRD pattern of LSV powders that were reduced at 900 °C in pure H₂ for 5 hours. The single phase LSV is well fitted to cubic structure, with $a = 3.8815(6)$ Å, $V = 58.48$ Å³, and space group Pm-3m. It is stated that LSV is of “pseudo” cubic perovskite structure. The reason is that it might be of orthorhombic structure but with very similar lattice parameters (Bordet et al., 1993; Ge and Chan, 2009b). As shown in Chapter 3, LSV prepared from solid state reactions contains eradicable impurities. In contrast, LSV synthesized via citric route is of single phase (Fig. 5-2). This is possibly attributed to the better reactivity of finer LSV powders.

![Figure 5-2 X-ray diffraction pattern of La₀.6Sr₀.4VO₄ (LSV) that is reduced in pure H₂ at 900°C for 5 hours.]

Figure 5-3 shows the electrode performance of LSV–YSZ anodes in the effect of LSV contents. The high-frequency resistances represent the ohmic resistances of LSV–YSZ anodes. The difference between the low-frequency resistance and the high-frequency resistance is the polarization resistance ($R_p$). As seen in Fig. 5-3, the lowest $R_p$ occurs when the LSV content is 50 wt. %. The microstructure of graded LSV anodes is shown
in Fig. 5-4. The catalytic layer and the gas diffusion layer are 30 μm and 15 μm, respectively. Good adhesion between the electrolyte substrate and the catalytic layer and between the catalytic layer and the gas diffusion layer is evident.

Figure 5-3  Effect of composition of LSV–YSZ anodes on high-frequency resistance ($R_{hf}$), low frequency resistance ($R_{lf}$), and the polarization resistance ($R_p = R_{hf} - R_{lf}$).

Figure 5-4  Cross-section profile of the fractured LSV–YSZ electrode.
5.4 Impedance spectroscopy and polarization of LSV anodes in clean fuels

Impedance spectroscopy shows good electrode performance of the LSV anodes. The polarization resistances ($R_p$) of the LSV electrode in $\text{H}_2$ are 0.54, 0.43, 0.44 $\Omega \text{ cm}^2$ under the potential biases ($E_{bias}$) of -100, 0, and 100 mV, respectively (Fig. 5-5a). The high $R_p$ under $E_{bias}$=-100 mV is due to the severe starvation of $\text{H}_2\text{O}$. With the $\text{H}_2\text{O}$ content of the feedstock increased to 9 vol. % (Table 5-1), $R_p$ are 0.11, 0.22, 0.44, 0.56 $\Omega \text{ cm}^2$ under $E_{bias}$ of -300, -100, 0, 100 mV, respectively (Fig. 5-5b). These results indicate that LSV seems to be of higher catalytic activity as electrolyser than fuel cell. Under the open circuit voltage (OCV) condition, the La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$ (LSCM) and La$_4$Sr$_8$Ti$_{11}$Mn$_{0.5}$Ga$_{0.5}$O$_{37.5}$ SOFC anode showed $R_p$ of 0.47 (Tao and Irvine, 2003) and 0.20 (Ruiz-Morales et al., 2006) $\Omega \text{ cm}^2$ in 97$\text{H}_2$–3$\text{H}_2\text{O}$ at 900º C, respectively. LSV is thought to be comparable to these more well-established SOFC oxide anode materials. In contrast, only a few half cell results were reported for oxide solid oxide electrolysis cell (SOEC) negative electrodes. Based on a rough comparison with the single cell result of LSCM (Yang and Irvine, 2008; Jin et al., 2011) and symmetric cell result of Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_6$–$\delta$ (Liu et al., 2010a), LSV could be regarded as one of the best oxides for SOEC negative electrodes. It is worth to mention that only the fuel cell operations are discussed in this chapter, as SOEC is beyond the scope of this PhD project.

Typical polarization curve of LSV anode with IR compensation are given in Fig. 5-6. The ohmic resistance used in the IR compensation was obtained via impedance spectroscopy at OCV conditions. It can be found that the reaction kinetics is strongly affected by only incorporating 9 vol.% $\text{H}_2\text{O}$ into the feedstock. As indicated in Fig. 5-6, the polarization behaviour of LSV anodes seems asymmetric between the cathodic and the anodic side. The exchange current density ($i_0$), obtained from the low overpotential ranges near the OCV, are given in the inset of Fig. 5-6. It is surprisingly to find that $i_0$ at the anodic side ($i_{0-a}$) is always larger than that in the cathodic side ($i_{0-c}$). This is in contradiction with the impedance results shown in Fig. 5-5. One of the plausible reasons may be that the absorbed water impedes fuel cell reactions. The exact mechanism is, however, still unknown. Figure 5-7 shows the chronopotentiometry
Chapter 5. Sulphur-tolerant and carbon-resistant solid oxide fuel cells with LSV anodes

Figure 5-5 Impedance spectra of the LSV electrode as mentioned in Fig. 4a: (a) the freshly prepared electrode in pure H$_2$ and (b) the electrode after 70-hour fuel cell polarization and in the 70H$_2$–30CO–50ppm H$_2$S atmosphere.

Table 5-1 Composition and tendency of carbon formation of gases addressed in Chapter 5. The operating temperature is 900ºC. The carbon formation is predicted by assuming the thermodynamic equilibrium of the gas species.

<table>
<thead>
<tr>
<th>Feedstock (100 sccm in total)</th>
<th>Carbon formation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>H$_2$O</td>
<td>CO</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>91</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>36</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>73</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>55</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>70</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>70</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>65</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>97</td>
<td>3</td>
<td>-</td>
</tr>
</tbody>
</table>

| | | | |
| - | H$_2$-rich biogas (humidified) | H$_2$-rich biogas with low CO$_2$ concentration (humidified) | CH$_4$-rich biogas |
| No | Yes | Yes | Yes |
| Coal gas from hydrogasification | Syngas; desulphurized town gas | town gas | Coal gas |
| Mixture of H$_2$-rich biogas and CH$_4$-rich biogas | |
| | | | |
curves of the LSV electrode in pure H\(_2\) and 91H\(_2\)–9H\(_2\)O, where the half cell is polarized under anodic current density of 0.2 A/cm\(^2\). The fresh LSV electrode has the overpotential (\(\eta\)) of 89 mV in H\(_2\) and a degradation rate (\(\kappa\)) of 0.023%/hour (h). A potential drop can be seen in Fig. 5-7 when the fuel gas is shifted from H\(_2\) to 91H\(_2\)–9H\(_2\)O. This potential drop is mostly due to the reduction of OCV. Potential oscillation is observed after 2-hour exposure to 91H\(_2\)–9H\(_2\)O. This phenomenon might be due to the surface reconstruction of LSV under oxidising environment.

![Figure 5-6](image)

**Figure 5-6** IR-compensated polarization curve of LSV anode in pure H\(_2\) and H\(_2\)–9H\(_2\)O at 900 \(^\circ\)C. The inset table shows the corresponding exchange current densities.
5.5 LSV anodes exposed to simulated practical fuels: syngas, biogas, and coal gas

50 ppm H₂S was added to H₂ to test the sulphur tolerance of LSV. Figure 5-8 shows the electrode behaviour under a current density of 0.2 A/cm². η suddenly jumps from 91 mV to 102 mV when the H₂ fuel is tainted by 50 ppm H₂S. This fast electrode degradation is most probably related to the H₂S adsorption onto LSV, which consequently blocks the electrochemical reaction sites. This type of degradation lasts for 3 h and results in the η change of 1 mV, where the adsorption/desorption equilibrium of H₂S has been established. The LSV electrode undergoes a performance improvement of 0.012%/h (i.e. κ = -0.012%/h), rather than degradation, in the following 112 h. η finally reaches 97 mV after the 130h fuel cell operation, which is only 6 mV higher than that in pure H₂. The salient long-term stability is also evident in the microstructural analysis. As can be seen in Figs. 5-9a and 5-9b, little change of the microstructure has been observed for the microstructure between the freshly prepared
electrode and the electrode subjected to 130h polarization. It is of great interest to note that LSV is catalytically active in H₂–50ppm H₂S and has being continuously improved at least up to a few hundred hours.

To further demonstrate the suitability of LSV towards practical gases, it is subjected to a continuous testing on simulated town gas, biogas, and coal gas with 50 ppm H₂S (Table 5-1). The LSV electrode exhibits non-negligible performance degradation (κ = 0.090%/h) under the circumstance of fuel cell polarization in 70H₂–30CO (Fig. 5-10a), a typical composition of syngas. Interestingly, the LSV electrode enjoys performance improvement (κ = -0.003%/h) merely by adding the feedstock with 50 ppm H₂S. After the 52h fuel cell operation, R_p of this syngas is only 0.07 Ω cm² larger than that of the freshly made electrode in H₂ (Fig. 5-11). A coal gas composition is simulated by replacing 5% of H₂ with CO₂ in the previous feedstock, i.e. 65H₂–30CO–5CO₂–50 ppm H₂S. η of the electrode exposed to this coal gas is -68 mV. It decreases to -61 mV after the 10-h electrolysis (Fig. 5-10a). After 3h standby exposure to H₂–50 ppm H₂S the LSV electrode is subjected to fuel cell polarization in H₂–50 ppm H₂S and then 75H₂–25CO₂–50 ppm H₂S, a typical H₂–rich biogas with low CO₂ concentration. η and R_p in H₂–50 ppm H₂S is almost unchanged as comparing to fresh electrodes exposed to H₂ (cf. Figs. 5-10a and 5-10b for η; cf. Figs. 5-11 and 5-12 for R_p). The LSV electrode exhibits slight activation through the following 12 h, with κ of -0.087%/h in H₂–50 ppm H₂S and -0.069%/h in 75H₂–25CO₂–50 ppm H₂S (Fig. 5-10b). The results indicate that LSV SOFC anode performs satisfactorily in practical gases where carbon deposition can hardly occur, even with intermittent electrolysis processes.

Figure 5-8 Long-term chronopotentiometry of the LSV electrodes under 0.2 A/cm² (fuel cell mode), with response to the gas shift from pure H₂ to H₂–50 ppm H₂S.
Figure 5.9  Typical low-magnification SEM images of LSV electrodes: (a) freshly reduced (a), operated in fuel cell mode and in H₂–50 ppm H₂S for 127 hours (b), and operated under alternating fuel cell and electrolyser modes and various H₂S-tainted and carbon-forming feedstocks according to Fig. 4 (c).
Figure 5-10  Long-term chronopotentiometry of the LSV electrodes exposed to H₂S-tainted feedstocks. The whole figure is divided into (a) to (d) merely for the clear illustration purpose.
Figure 5-11  Impedance spectra of the LSV electrode as mentioned in Fig. 5-10a: (a) the freshly prepared electrode in pure H₂ and (b) the electrode after 70-hour fuel cell polarization and in the 70H₂–30CO–50ppm H₂S atmosphere.

Figure 5-12  Impedance spectra of the LSV electrode exposed to H₂–50ppm H₂S, as mentioned in Fig. 5-10b.
Once the feedstock is shifted to $60\text{H}_2\text{–}20\text{CO}_2\text{–}20\text{CH}_4\text{–}50\text{ppm H}_2\text{S}$, a simulated gas blend of $\text{H}_2$-rich and $\text{CH}_4$-rich biogases that is prone to carbon formation, the electrode potential is suddenly increased from -0.868 V to -0.692 V. This is mainly due to the OCV reduction after the gas shifting. Nevertheless, large $k$ of 0.377%/h has been observed during the 12h fuel cell polarization (Fig. 4-9b). Two degradation mechanisms might exist: (i) carbon coking of electrodes and (ii) surface oxidation of LSV. To eliminate the ambiguity, the LSV electrode is subsequently subjected to electrolysis for 25 h. The dry reforming of $\text{CH}_4$ by $\text{CO}_2$ is suppressed because $\text{CO}_2$ is reduced to $\text{CO}$ during the electrolysis. Therefore, $\text{CH}_4$ pyrolysis dominates and the carbon deposition is more remarkable in electrolyser than that in fuel cell. If the degradation is controlled by the carbon coking mechanism, the electrode degradation after the 25h electrolysis should be more serious than that before the electrolysis. In contrast to this prediction, the electrode potential and $R_p$ have been little changed before and after the electrolysis (-0.664 V vs -0.639 V, cf. Fig. 4-9b and Fig. 4-9c; $R_p$ in Fig. 5-13). More distinctively and interestingly, continuous electrode activation with $k = -0.05\%$/h has been observed in the 300h fuel cell operation (Fig. 4-9c). These results clearly rule out the carbon coking mechanism. The most probable mechanism is that the “oxidized” LSV surface has been reconstructed by the reducing environment that is created by electrolysis. Table 5-2 shows the exchange current densities of LSV anodes.
Chapter 5. Sulphur-tolerant and carbon-resistant solid oxide fuel cells with LSV anodes

exposed to various atmospheres. In line with the results shown in Fig. 5-6, $i_{0-a}$ is systematically larger than $i_{0-c}$ in all the fuels. It is surprising to note that the $i_0$ from the Levenburg–Marquardt (LEV) Tafel fitting method is several times larger than that from traditional Tafel fitting. The underlying reasons are unknown of this moment.

Improved microstructure could be a plausible reason for the continuous electrode activation. It is, however, difficult to explain why both electrodes are activated but their microstructures are distinct for two LSV electrodes that are addressed in Figs. 5-8 and 5-10. The “fine” microstructure of the electrode exposed to carbon-forming gases might be the artefact from deposited carbon particles (cf. Figs. 5-9b and 5-9c; cf. Figs. 5-14 and 5-15). The exact mechanism of the electrode activation is currently unknown. These promising results, nevertheless, demonstrate that LSV performs satisfactorily at least up to a few hundreds of hours even with the presence of carbon deposition.

![Figure 5-14](image)

Figure 5-14 The selected area (a) and the corresponding EDX spectrum (b) of the LSV electrode after the fuel cell operation in H$_2$–50 ppm H$_2$S for 127 hours. No sulphur is found within the detection limit of EDX.
Figure 5-15  The selected area (left) and the corresponding EDX spectrum (right) of the LSV electrode, under alternating fuel cell and electrolyser modes and various H₂S-tainted and carbon-forming feedstock atmospheres for 498 hours, as illustrated in Fig. 5-10. Significant amount of carbon is observed. No sulphur is detected within the detection limit of EDX.

Table 5-2  Exchange current density of LSV anodes exposed to various atmospheres as addressed in Chapter 5.5.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Cathodic (i_0) (i_{0,c}) (A/cm(^2))</th>
<th>Anodic (i_0) (i_{0,a}) (A/cm(^2))</th>
<th>LEV (i_0) (A/cm(^2))</th>
<th>(\chi^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>0.108</td>
<td>0.122</td>
<td>0.525</td>
<td>9.339</td>
</tr>
<tr>
<td>30CO(_2)-70H(_2)-50ppm H(_2)S</td>
<td>0.113</td>
<td>0.153</td>
<td>0.755</td>
<td>47.74</td>
</tr>
<tr>
<td>20CO(_2)-20CH(_4)-60H(_2)-50 ppm H(_2)S</td>
<td>0.069</td>
<td>0.102</td>
<td>0.257</td>
<td>0.266</td>
</tr>
<tr>
<td>20CO(_2)-20CH(_4)-60H(_2)-50 ppm H(_2)S</td>
<td>0.058</td>
<td>0.090</td>
<td>0.152</td>
<td>0.486</td>
</tr>
<tr>
<td>H(_2)-50ppm H(_2)S</td>
<td>0.091</td>
<td>0.129</td>
<td>0.572</td>
<td>46.24</td>
</tr>
<tr>
<td>97H(_2)-3H(_2)O-50ppm H(_2)S</td>
<td>0.060</td>
<td>0.132</td>
<td>0.223</td>
<td>0.343</td>
</tr>
</tbody>
</table>
While LSV is excellent in carbon resistance, it is still not clear why it is activated, instead of poisoned, by $\text{H}_2\text{S}$-containing feedstock. Scanning electron microscopy (SEM) analyses show negligible contributions of $\text{H}_2\text{S}$ on modifying electrode microstructure (Figs. 5-9a and 5-9b). This is conceivable because the $\text{H}_2\text{S}$ concentration is only 50 ppm and most sulphur-containing species, e.g. S, $\text{CS}_2$, are volatile at 900ºC. One of the possible mechanisms is the formation of metal sulphides that are catalytically active for fuel cell and electrolysis reactions. Figures 5-16a, 5-16b, and 5-16c show high-resolution surface morphology images of LSV electrodes that are freshly prepared, exposed to $\text{H}_2$–50 ppm $\text{H}_2\text{S}$ as corresponding to Fig. 5-8, and various feedstocks as corresponding to Fig. 5-9, respectively. No fine structures are observed in the freshly prepared electrode (Fig. 5-16a). Modest amount of nanoparticles are observed in the electrode with 120-h exposure to $\text{H}_2\text{S}$ (Fig. 5-16b). Large quantity of relatively uniform-sized nanoparticles, with diameter of $5.5 \pm 0.9$ nm (Fig. 5-17), exists on electrode surfaces that were exposed to $\text{H}_2\text{S}$ for 510 h (Fig. 5-16c). The nanoparticles are tentatively regarded as certain metal sulphides. The matrix of these nanoparticles should be LSV, as vanadium-based oxides have good affinity to $\text{H}_2\text{S}$ while YSZ is essentially inert towards $\text{H}_2\text{S}$. The concentration of these nanoparticles is still below the detection limit of energy-dispersive X-ray spectroscopy (EDX, Figs. 5-14 and 5-15). In literature, various vanadium-based sulphides had been reported with high electrical conductivity (Kijima et al., 1996) and catalytic activity towards $\text{H}_2\text{S}$ oxidation (Li et al., 1996). These nanoparticles may lead to enlarged reaction areas and enhanced reaction kinetics, e.g. adsorption/desorption, dissociation, and spillover of surface species.
Chapter 5. Sulphur-tolerant and carbon-resistant solid oxide fuel cells with LSV anodes

Figure 5-16 Field-emission SEM images of LSV electrode surfaces: (a) freshly reduced, (b) after the fuel cell testing in \( \text{H}_2 - 50 \text{ ppm H}_2\text{S} \) for 120 hours (Fig. 5-8), and (c) after the long term testing as given in Fig. 5-10.

Figure 5-17 High magnification surface morphology images of LSV surfaces, after the 510-h operation according to Fig. 5-10. For the deposited particles, the mean size is 5.5 nm and the standard deviation is 0.9 nm.
To some extent, the nanoparticle decoration on LSV surface is very similar to the extensively-studied impregnation method (Jiang, 2006). The ultimate goal of impregnation is to decorate the electrocatalyst surfaces with highly active nanoparticles. One of the fatal disadvantages of impregnated nanoparticles is their thermal instability. In contrast, the in situ “sulphur-decorated” nanoparticles that precipitate on LSV surfaces seem to be very stable for more than 500 hours. The nanoparticles are generated continuously by interactions between LSV and H2S during the course of high temperature SOFC operation. This is in distinct contrast to impregnated nanoparticles under elevated temperatures, which are largely eliminated due to particle sintering. This approach represents a novel route for fabricating nanostructured electrodes in high temperature energy and conversion devices.

5.6 Summary

The feasibility of SOFCs fed with practical feedstocks has been proven by utilizing LSV-based hydrogen electrodes. LSV is catalytically active in various gases, e.g. H2, syngas, biogas, town gas, and coal gas, under fuel cell and electrolyser modes. LSV electrodes are not coked by deposited carbon when exposed to carbon-forming gases. More interestingly, LSV undergoes continuous activation, rather than poisoning, when exposed to gases containing 50 ppm H2S. The beneficial H2S effect is probably due to the nanostructured sulphur compounds that are in situ generated by interactions between LSV and H2S. LSV-based reversible SOCs, operated under fuel cell and electrolyser modes, have been demonstrated with negligible performance degradation in carbon-forming and H2S-containing gases for more than 500 hours.
Chapter 6. Conclusions and recommendations

6.1 Conclusions

The objective of this project is to explore satisfactory anodes for SOFCs fed with hydrocarbon fuels and to investigate the interfacial properties of anode/electrolyte junctions in SOFCs. Based on the results and discussion of this project, the following conclusions can be drawn:

- La\textsubscript{1-x}Sr\textsubscript{x}VO\textsubscript{3} (LSV) with \(x = 0.0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, 0.9, 0.95, 1.0\) were synthesized by solid state reactions, both in oxidized and reduced form. LSV\textsubscript{ox} was regarded as a mixture of LaVO\textsubscript{4} and Sr\textsubscript{2}V\textsubscript{2}O\textsubscript{7}. Single phase can be obtained only for LSV\textsubscript{re} (\(x = 0, 0.05, 0.1\)) and LSV\textsubscript{50-50}\textsubscript{re}. LSV\textsubscript{re} (\(x = 0.2, 0.3, 0.4\)) was a binary phase structure between LaVO\textsubscript{3} and (La\textsubscript{0.50}Sr\textsubscript{0.50})VO\textsubscript{2.95}. Chemical compatibility with YSZ had been confirmed at least up to 1300°C. TGA analysis indicated non-negligible oxygen nonstoichiometry of LSV\textsubscript{re}. Impedance spectroscopy indicated the necessity of incorporating ionic components into LSV in order to extend the TPBs from the anode/electrolyte interface.

- LSV\textsubscript{re} (\(x = 0.2, 0.3, 0.4, 0.5\))–YSZ Composite anodes showed comparable electrode performance to those more well-studied conducting oxide anodes, such as LSCM. Electrode engineering was conducted by means of sintering temperature and electrode composition. LSV anodes were not able to be sintered satisfactorily below 1150°C. Once exposed to pure H\textsubscript{2}, composite anodes with more than 70 wt.% of LSV peeled off from the YSZ electrolyte substrate. Composite anodes with LSV less than 40 wt.% failed to form an electronically percolating network. LSV6040 (50 wt. %)–YSZ anodes achieved \(R_p\) of 0.7–1.1 Ω cm\textsuperscript{2} in pure H\textsubscript{2} at 900°C. The anodic overpotential was lower than 0.2 V when drawing a current density of 0.2 A/cm\textsuperscript{2}. The apparent activation energies were in the range from 0.42 to 0.71 eV for the four LSV\textsubscript{re} (\(x = 0.2, 0.3, 0.4, 0.5\))–YSZ anodes. Good thermal stability had been achieved. Preliminary studies indicated that LSV–YSZ anodes, at least LSV6040 (50 wt. %)–YSZ, were active for CH\textsubscript{4} oxidation. For half-cells fed with 3% H\textsubscript{2}O saturated CH\textsubscript{4} at 900°C, polarization resistance of LSV6040 (50
wt. %)–YSZ anode reached 1.4 Ω cm$^2$ at the open circuit condition. Polarization curves showed that the current density reached 0.2 A/cm$^2$ with the anodic overpotential less than 0.2 V.

- Modest single cell performance, with the configuration of LSV6040–YSZ/YSZ (300 µm)/LSM–YSZ/(LSM), had been demonstrated. When fed with pure H$_2$ and operated at 900°C, $R_p$ of the single cell was 0.84 ohm cm$^2$ and $P_{max}$ was 0.28 W/cm$^2$. When the fuel gas was switched to 3% H$_2$O humidified CH$_4$, $R_p$ was increased to 1.22 ohm cm$^2$ and $P_{max}$ was 0.13 W/cm$^2$. Single cell performance achieved in this study was among the best of SOFCs using vanadate anodes. Whatever the fuels were the cell performance, nevertheless, showed great temperature dependencies.

- Impedance behaviours of LSV8020(50 wt. %)–YSZ composite anodes, with LSV8020 synthesized from citric route, were investigated in H$_2$–H$_2$O–He atmosphere. Impedance spectra in H$_2$–He binary atmosphere mostly contained two depressed and poorly separated impedance arcs, and occasionally inductive loops at extremely low frequencies and under large potential biases. The high frequency arc, Arc 1, was ascribed to the reaction resistance. The middle-to-low frequency arc, Arc 2, was identified as the concentration impedance due to the porous electrodes or gas channels. Small inductive loops, Arc 3, came to emerge when dc potential biases were larger than 250 mV. Great efforts were paid to the double layer capacitance. The EIS method gave “correct” capacitance in the order of $10^{-1}$ mF/cm$^2$. In contrast, capacitance obtained from the transient methods was contaminated by the double layer charging phenomenon. For impedance spectra collected in wet fuel atmosphere, Arc 1 was still maintained but Arc 2 collapsed together at low frequencies. A detrimental water effect, which had been seldom observed in most SOFC anodes, was identified up to 15 % H$_2$O.

- Two-dimensional oxygen vacancy distributions in the YSZ side of polarized LSV/YSZ interfaces had been successfully constructed via Markov Chain Monte Carlo simulations. The oxygen vacancy concentration directly adjacent to the interface was one order of magnitude larger than that in the bulk YSZ. The spatial $\rho/\rho_0$ profile could be empirically modelled as an exponential decay. The thickness of the H–P layer was in the range of 0.5 to 0.8 nm. The double
layer region extended about 2 nm into the bulk YSZ. The oxygen vacancy diagrams and \( \rho/\rho_0 \) profiles indicated the H–P layer accommodates 70–80% of the oxygen vacancies.

- The double layer capacitance of solid electrode/solid-electrolyte interfaces was investigated via a case study on LSV/YSZ interfaces in SOFC anodic environment. The magnitude of apparent double layer capacitance was of several hundreds of \( \mu \text{F/cm}^2 \). Under anodic polarized conditions, it exhibited a right-skewed volcano pattern that peaks around 20 to 50 mV. The intrinsic double layer capacitance exhibited similar “capacitance surge” behaviour. The phenomenon was ascribed to mutual competitions between the loosened H–P layer and the increase of Volta potential in the G–C layer. The numeric values of intrinsic double layer capacitance were, however, almost one order of magnitude lower than the apparent. Such kind of discrepancy was ascribed to the inconsistent areas that were used in the two cases. The capacitance analysis enabled in situ detection of active areas and TPBs of composite electrode/electrolyte interfaces in various solid state electrochemical systems.

- The interrelationship between TPBs and EAZs was investigated via a case study on LSV–YSZ composite anodes in SOFCs. The TPB lengths were calculated from a virtually packed and sintered particle aggregate. The packing and sintering methods were suitable for the optimization of SOFC composite electrodes. The length specific TPB length of LSV–YSZ composite anodes was 1.8x10^9 cm/cm, equivalent to a volume-specific TPB length of 3.9x10^9 cm/cm^3. The cross-section area of EAZs was basically 6 to 8 times of the geometric area. Empirical correlations among EAZs, TPBs, active electrode thickness, and in-depth penetration of electrocatalysts were established. Under the circumstance of polarized LSV–YSZ anodes, the active electrode thickness and in-depth penetration of electrocatalysts were typically in the range of 5–20 \( \mu \text{m} \) and 2–8 nm, respectively.

- The feasibility of SOFCs fed with practical fuels had been proven by utilizing LSV-based anodes. LSV was catalytically active in various gases, e.g. \( \text{H}_2 \), syngas, biogas, town gas, and coal gas. The polarization resistances were typically smaller than 0.4 \( \Omega \text{ cm}^2 \) in these fuel atmospheres. LSV anodes were not coked by deposited carbon when exposed to carbon-forming gases. More interestingly, LSV undergone continuous activation, rather than poisoning, when
Chapter 6. Conclusions and recommendations

exposed to gases containing 50 ppm H$_2$S. The beneficial H$_2$S effect was probably due to the nanostructured sulphur compounds that were in situ generated by the reactions between LSV and H$_2$S. LSV-based reversible SOCs had been demonstrated with negligible performance degradation in carbon-forming and H$_2$S-containing gases for more than 500 hours.

6.2 Major achievements

- Proof-of-concept demonstration of LSV anodes, synthesized via either solid state reactions and citric route, as competitive candidates for SOFC anodes.
- Mechanistic investigation of impedance responses of LSV anodes in fuel dilution and high water content environment.
- Markov Chain Monte Carlo simulation of anode/solid electrolyte interfaces
- Modified Poisson–Boltzmann theory and the Volta potential analysis of the anode/solid electrolyte interfaces
- Established interrelationship between three phase boundary and electrochemically active zones
- Demonstration of the suitability of LSV anodes in practical hydrocarbon fuels.

6.3 Recommendations

- Integrating the double layer structure and reaction kinetics of anode/solid oxide interfaces. In this project, significant efforts had been paid to the interfacial structures, mainly the double layer structure, of anode/electrolyte interfaces via Monte Carlo simulation and analytical Poisson–Boltzmann theory. The ultimate merits of these kinds of interfacial analysis rely on the integration of them with interfacial reaction kinetics. This integration is of great importance simply by noting that practical fuel cells are operated under loading conditions. Such integration calls for the knowledge of electron transfer electrodics and relevant analysis on the gas diffusion and conversion phenomena.
- Expanding the series: doping into V-site of LSV. LSV can be further improved, in terms of structural stability, redox stability, and catalytic activity, by sophisticated and systematic tailoring. The priority goes to two of these issues: one is cell performance and the other is redox stability. To improve the cell
performance, a small amount of precious metals can be doped into V-site. Ruthenium, an economically competitive noble metal, may be able to be incorporated into V-site because of similar ionic radii with $V^{3+}/V^{4+}$. Some alternative dopants are transition metals. Fe, Co, and Ni are not in consideration because of their chemical instability in reducing atmosphere. The effects of Mn should be similar to Ru (i.e., to improve the catalytic performance), as some manganite (e.g., LSM and LSCM) are well-known to be catalytically effective. On the other hand, several titanates and chromites have been proved to be conductive and stable in SOFC anodic environments, as introduced in Chapter 2. Doping Ti and Cr into V sites could stabilize the LSV structure at oxidising environments.

- Electrode-supported SOFCs with LSV anodes. Decreasing electrolyte thickness is critical to minimize the overall cell losses. Thin electrolyte cells can be anode-supported, cathode-supported, interconnector-supported, or inert porous substrate supported. LSM-supported single cells with thin YSZ electrolyte and vanadate anodes seem most relevant. Alternatively, dual tape-casted YSZ electrolyte supported by porous YSZ substrate and impregnated electrodes can be used.

- The sulphur-tolerant mechanism. It is currently unknown whether the excellent sulphur tolerance of LSV anodes is of chemical or of electrochemical nature, though the formation of metal sulphide appears to be quite possible. Chemically speaking, metal sulphide could improve the conducting percolation networks or the adsorption/desorption behaviours of gas species. Electrochemically speaking, metal sulphide might have better charge transfer kinetics than LSV. Synergic chemical, electrochemical, and materials structure investigations should be carried out to resolve the ambiguity.
Appendix A: Gouy–Chapman capacitance of the LSV–YSZ interfaces

The Volta potential difference of the Gouy–Chapman (G–C) layer is divided into two parts: one is the linear part starting from the electrode/electrolyte interface to outer Helmholtz plane (oHp), and the other is the non-linear part decaying asymptotically into bulk electrolyte (Fig. 4-13a). While the linear part is described by the double-plate condenser model, the non-linear part calls for a Debye and Hückel’s treatment. Main assumptions in this study are: (i) charge cloud approximation. Some oxygen vacancies are immobilized on the outer Helmholtz plane (oHp). The others beyond the oHp are smeared into continuous thermal disarray, thus creating a charge cloud from oHp to the bulk YSZ; (ii) continuum. The bulk YSZ is treated as a continuous dielectric medium; (iii) one dimension. The charge distribution is uniform in directions parallel to the LSV/YSZ interface; (iv) time-invariant. All treatments are in steady state conditions. Transient states with electric-magnetic interactions are not taken into account; (v) negligible electron and hole effects. Electron and hole concentrations are in orders lower than that of oxygen vacancies. The electroneutrality is maintained by $Y_{rz}$ and $V_{0}^{-}$.

For the sake of mechanistic lucidity we start from the derivation of Poisson’s equation. Consider a Gaussian pillbox with radius $r$ and length $l$ (Fig. 3a). One of its two lateral surfaces situates in the LSV side and the other locates in the YSZ side. At a distance $x$ away from oHp we denote the volumetric net charge density as $\rho_{(z)}$ and the Volta potential difference as

$$\Delta \Psi_{(z)} = \Psi_{(z)} - \Psi_{YSZ}, \quad (A1)$$

where $\Psi_{(z)}$ and $\Psi_{YSZ}$ are the Volta potential at position $z$ and the bulk YSZ ($z \to \infty$), respectively. In this study the Volta potential of the bulk YSZ is set to zero. $\Delta \Psi_{(z)}$ is therefore reduced to $\Psi_{(z)}$. The relationship between $\rho_{(z)}$ and $\Psi_{(z)}$ is derived from the Gauss’s law of electrostatics,
\[ \sum \Phi_i = \oiint_E G \, dS = q_{\text{enclosed}} \] 

\[ \Phi_{E_0, \text{face-left}} + \Phi_{E_0, \text{face-right}} + \Phi_{\text{side}} = \frac{\rho(z) \, dV}{\varepsilon_0 \varepsilon_r} \]  

(A2)

where \( \Phi_{E_0} \) is the electric flux, \( S \) the surface area of the Gaussian pillbox, \( V \) the volume of the Gaussian pillbox, \( \varepsilon_0 \) the vacuum permittivity, \( \varepsilon_r \) the relative static permittivity of YSZ in the G–C layer, \( E \) the electric field in the G–C layer, and \( q_{\text{enclosed}} \) the electric charges enclosed by the Gaussian pillbox, \( i.e. \) the net electric charges at LSV side (with vanishingly small distance away from the LSV/YSZ interface) balanced with oxygen vacancies at oHp. Differentiating the last right hand of Eq. A2 against \( z \) leads to Poisson’s equation,

\[ \frac{d^2 \Psi}{dz^2} = -\frac{\rho(z)}{\varepsilon_r \varepsilon_0} \]  

(A3)

In Eq. A3 and also in below, the subscript \( (z) \) is omitted merely for notational simplicity (\( e.g. \) \( \Psi(z) \) as \( \Psi \)). The relationship between \( \rho \) and \( \Psi \) lies in the defect chemistry of YSZ. The charged species in YSZ are created by doping \( \text{Y}_2\text{O}_3 \) into \( \text{ZrO}_2 \) according to the overall reaction (using Kröger–Vink notations),

\[ \text{Y}_2\text{O}_3 \xrightarrow{2\text{ZrO}_2} 2\text{Y}_{\text{Zr}}' + \text{V}_{\text{O}}'' + 3\text{O}_0' \]  

(A4)

\( \text{Y}_{\text{Zr}}' \) and \( \text{V}_{\text{O}}'' \) dominants according to the Assumption \( v \). Under SOFC operating conditions \( \rho \) is then given by

\[ \rho_{(z)} = e_0 \sum n_i z_i = e_0 \left( n_{\text{Y}_{\text{Zr}}} z_{\text{Y}_{\text{Zr}}} + n_{\text{V}_{\text{O}}} z_{\text{V}_{\text{O}}} \right) = e_0 \left( -n_{\text{Y}_{\text{Zr}}} + 2n_{\text{V}_{\text{O}}} \right) \]  

(A5)

where \( n_{\text{Y}_{\text{Zr}}} \) and \( n_{\text{V}_{\text{O}}} \) are the concentration of \( \text{Y}_{\text{Zr}}' \) and \( \text{V}_{\text{O}}'' \), respectively. Eq. A4 implies \( n_{\text{Y}_{\text{Zr}}} \) and \( n_{\text{V}_{\text{O}}} \) fulfils

\[ n_{\text{Y}_{\text{Zr}}}^0 = 2n_{\text{V}_{\text{O}}}^0 \]  

(A6)
where $n_{\text{Yz}}^0$ and $n_{\text{O}}^0$ are the bulk concentration of $Y_{\text{z}}^{-}$ and $V_{\text{O}}^{\ast}$, respectively. As the mobility of $Y_{\text{z}}$ is in orders of magnitude lower than that of $V_{\text{O}}^{\ast}$ at elevated temperatures, $n_{\text{Yz}}$ is assumed to remain constant (as $n_{\text{Yz}}^0$) while $n_{\text{O}}$ is potential-dependent and follows the Boltzmann distribution law. This behaviour of charged species in YSZ is distinct to that in aqueous solutions where both cations and anions are freely mobile. Charge concentrations of YSZ are then expressed as

$$n_{\text{Yz}} = n_{\text{Yz}}^0, \quad (A7-1)$$

$$n_{\text{O}} = n_{\text{O}}^0 \exp \left( -\frac{U}{kT} \right), \quad (A7-2)$$

where $U$ is the potential energy, $k$ the Boltzmann constant, and $T$ the absolute temperature. Here $U$ is negative because $V_{\text{O}}^{\ast}$ has to be accumulated to balance the electrons in the LSV. $U$ simply becomes the coulombic potential energy of $V_{\text{O}}^{\ast}$ with the exclusion of short-range interactions (e.g. dispersion forces), $U = z_{\text{Yz}} e_0 \Psi = 2e_0 \Psi$ ($\Psi < 0$). (A8)

Incorporating Eqs. A3, A5, A6, A7, and A8 one gets

$$\frac{d^2 \Psi}{dz^2} = \frac{2e_0 n_{\text{O}}^0}{\varepsilon \varepsilon_0} \left[ 1 - \exp \left( -\frac{2e_0 \Psi}{kT} \right) \right], \quad (A9-1)$$

or in another form

$$\frac{d^2 \Psi}{dz^2} = -\frac{4e_0 n_{\text{O}}^0}{\varepsilon \varepsilon_0} \sinh \left( \frac{e_0 \Psi}{kT} \right) \exp \left( -\frac{e_0 \Psi}{kT} \right), \quad (A9-2)$$

with the initial condition

$$\Psi_{z = z_{\text{ab}}} = \Psi_{\text{olp}} - \Psi_{\text{YSZ}} = \Psi_{\text{olp}}, \quad (A10-1)$$

and the boundary conditions

$$\lim_{z \to z_{\text{ab}^{-}}} \frac{d\Psi_G}{dz} = \lim_{z \to z_{\text{ab}^{-}}} \frac{d\Psi_H}{dz} \quad (A10-2)$$

and
\[ \lim_{z \to \infty} \Psi = 0, \quad \lim_{z \to \infty} \frac{d\Psi}{dz} = 0. \quad (A10-3) \]

Eq. A9 has been the quintessential form that describes the spatial Volta potential variations of the G–C layer. It can be linearized if \( 2e_0 \Psi \) is much smaller than \( kT \) (say, ten times), which is equivalent to a \( \Psi \) value not higher than 5 mV. Here the difficulty is that \( \Psi(z) \) is hard to be determined experimentally. To a rather qualitative guesstimate, \( \Psi \) is highly implausible of only several mV, taking typical OCV values (ca 1.2 V) under H\(_2\) atmosphere into account. To conclude, Eq. A9 cannot be linearized under SOFC operating conditions. The boundary condition, Eq. A10–3, is provided only for an explanatory purpose. It is useless in solving Eq. A9, albeit useful to derive the differential capacitance (see below).

The following session is dedicated to derive the Gouy–Chapman capacitance (\( C_G \)) in function of the Volta potential. Recall the well-known relationship between \( E \) and \( \Psi \)

\[ E = -\frac{d\Psi}{dz}. \quad (A11) \]

The \( \Psi - E \) relationship is obtained by substituting Eq. A11 into Eq. A9–1,

\[ E \frac{dE}{d\Psi} = \frac{2e_0 n_0^0}{\varepsilon_i \varepsilon_0} \left[ 1 - \exp \left( -\frac{2e_0 \Psi}{kT} \right) \right]. \quad (A12) \]

One of the analytical solutions of Eq. A12 that is physically meaningful is

\[ E = -\frac{d\Psi}{dz} = -\sqrt{\frac{2kT n_0^0}{\varepsilon_i \varepsilon_0}} \exp \left( -\frac{2e_0 \Psi}{kT} \right) + \frac{4e_0 n_0^0}{\varepsilon_i \varepsilon_0} \Psi + C, \quad (A13) \]

where \( C \) is the constant to be determined. Applying Eq. A10–3 to Eq. A13 one gets

\[ C = \frac{-2kT n_0^0}{\varepsilon_i \varepsilon_0}. \quad (A14) \]

Substituting Eq. A14 back into Eq. A13 one yields
\[ \left( \frac{d\Psi}{dz} \right) = \sqrt{\frac{2n_0^0}{\varepsilon \varepsilon_0}} \sqrt{kT \left[ \exp \left( -\frac{2e_0}{kT} \Psi \right) -1 \right] + 2e_0 \Psi} \quad . \quad (A15) \]

Eq. A15 cannot be solved analytically anymore. Fortunately Eq. A15 is quite enough to obtain \( C_G \). According to the Gauss’s law of electrostatics it reads

\[ \sigma_G = \varepsilon \varepsilon_0 \left( \frac{d\Psi}{dz} \right)_{z=z_{0p}} , \quad (A16) \]

where \( \sigma_G \) is the area specific charge density on the faces of Gaussian pillbox (Fig. 3a). Substituting Eq. A15 into Eq. A16 one obtains

\[ \sigma_G = \sqrt{2\varepsilon \varepsilon_0 n_0^0 \sqrt{kT \left[ \exp \left( -\frac{2e_0}{kT} \Psi_G \right) -1 \right] + 2e_0 \Psi_G}} \quad . \quad (A17) \]

\( C_G \) is obtained by differentiating \( \sigma_G \) against \( \Psi \),

\[ C_G = \frac{d\sigma_G}{d\Psi_G} . \quad (A18) \]

Finally, one gets the relationship between \( C_G \) and \( \Psi_G \) by substituting Eq. A17 into Eq. A18, \[ C_G = e_0 \left[ \exp \left( -\frac{2e_0}{kT} \Psi_G \right) -1 \right] \sqrt{\frac{2\varepsilon \varepsilon_0 n_0^0}{kT \left[ \exp \left( -\frac{2e_0}{kT} \Psi_G \right) -1 \right] + 2e_0 \Psi_G}} \quad . \quad (A19) \]
REFERENCES


BLENNOW, P., HANSEN, K. K., WALLENBERG, L. R. & MOGENSEN, M. 2009.


the Electrochemical Society, 148, A388-A394.


CIMENTI, M. & HILL, J. M. 2010. Direct utilization of methanol and ethanol in solid oxide fuel cells using Cu-Co(Ru)/Zr0.35Ce0.65O2-delta anodes. Journal of Power Sources, 195, 3996-4001.

COMBEMALE, L., CABOCHE, G. & STUERGA, D. 2009. Flash microwave synthesis and sintering of nanosized La0.75Sr0.25Cr0.93Ru0.07o3-[delta] for fuel cell application. Journal of Solid State Chemistry, 182, 2829-2834.


COSTA, R., PEREIRA, C. M. & SILVA, F. 2010. Double layer in room temperature


DANIOVIC, N., LUO, J. L., CHUANG, K. T. & SANGER, A. R. 2009. Ce0.9Sr0.1VOx (x=3, 4) as anode materials for H2S-containing CH4 fueled solid oxide fuel cells. *Journal of Power Sources*, 192, 247-257.


FU, Q. X., TIETZ, F. & STOVER, D. 2006. La0.4Sr0.6Ti1-xMnxO3-delta perovskites as anode materials for solid oxide fuel cells. *Journal of the Electrochemical Society*, 153, D74-D83.


FUKUNAGA, H., ISHINO, M. & YAMADA, K. 2007. Effective thickness of


INTERNATIONAL ENERGY AGENCY, 2010. Energy Technology Perspectives 2010-Scenarios & Strategies to 2050.


JIANG, S. P., CHEN, X. J., CHAN, S. H. & KWOK, J. T. 2006a. GDC-impregnated, (La0.75Sr0.25)(Cr0.5Mn0.5)O-3 anodes for direct utilization of methane in solid oxide fuel cells. *Journal of the Electrochemical Society*, 153, A850-A856.

JIANG, S. P., CHEN, X. J., CHAN, S. H., KWOK, J. T. & KHOR, K. A. 2006b. (La0.75Sr0.25)(Cr0.5Mn0.5)O-3/YSZ composite anodes for methane oxidation reaction in solid oxide fuel cells. *Solid State Ionics*, 177, 149-157.


JIN, C., YANG, C. H., ZHAO, F., CUI, D. & CHEN, F. L. 2011. La0.75Sr0.25Cr0.5Mn0.5O3 as hydrogen electrode for solid oxide electrolysis cells. *International Journal of Hydrogen Energy*, 36, 3340-3346.


KAISER, A., BRADLEY, J. L., SLATER, P. R. & IRVINE, J. T. S. 2000. Tetragonal tungsten bronze type phases (Sr1-xBax)(0.6)Ti0.2Nb0.8O3-delta: Material characterisation and performance as SOFC anodes. *Solid State Ionics*, 135, 519-524.


LAGUNA-BERCERO, M.A., KILNER, J. A. & SKINNER, S. J. 2010. Performance and Characterization of (La,Sr)MnO3/YSZ and La0.6Sr0.4Co0.2Fe0.8O3 Electrodes for Solid Oxide Electrolysis Cells. *Chemistry of Materials*, 22, 1134.


LENG, Y. J., CHAN, S. H., KHOR, K. A. & JIANG, S. P. 2006. (La0.8Sr0.2)(0.9)MnO3-Gd0.2Ce0.8O1.9 composite cathodes prepared from
(Gd, Ce)(NO2)(x)-modified (La0.8Sr0.2)(0.9)MNO3 for intermediate-temperature solid oxide fuel cells. Journal of Solid State Electrochemistry, 34, 409-415.


LU, X. C. & ZHU, J. H. 2007. Cu(Pd)-impregnated La0.75Sr0.25Cr0.5Mn0.5O3-delta anodes for direct utilization of methane in SOFC. *Solid State Ionics*, 178, 1467-1475.


Structural, electronic, and magnetic properties of LaxSr1-xVO3 (0.1≤x≤1.0). *Physical Review B*, 46, 10973-10985.


RAJ, E. S., KILNER, J. A. & IRVINE, J. T. S. 2006. Oxygen diffusion and surface exchange studies on (La0.75Sr0.25)0.95Cr0.5Mn0.5O3−δ. Solid State Ionics, 177, 1747-1752.


dispersed on Sm-doped ceria for the application to internal reforming solid oxide fuel cells operated at medium-temperature. *Catalysis Letters*, 26, 149-157.


SHEARING, P. R., GELB, J., YI, J., LEE, W. K., DRAKOPOLOUS, M. & BRANDON,


SLATER, P. R. & IRVINE, J. T. S. 1999b. Synthesis and electrical characterisation of the tetragonal tungsten bronze type phases, (Ba/Sr/Ca/La)(0) 6MxNb1-xO3-delta (M = Mg, Ni, Mn, Cr, Fe, In, Sn): evaluation as potential anode materials for solid oxide fuel cells. *Solid State Ionics*, 124, 61-72.


SUDA, E., PACAUD, B. & MORI, M. 2006. Sintering characteristics, electrical


TAO, S. W. & IRVINE, J. T. S. 2002a. Study on the structural and electrical properties of the double perovskite oxide SrMn0.5Nb0.5O3-delta. *Journal of Materials Chemistry*, 12, 2356-2360.


TAO, S. W. & IRVINE, J. T. S. 2004a. Synthesis and characterization of (La0.75Sr0.25)Cr0.5Mn0.5O3-delta, a redox-stable, efficient perovskite anode for SOFCs. *Journal of the Electrochemical Society*, 151, A252-A259.


TAO, S. W. & IRVINE, J. T. S. 2004c. Catalytic properties of the perovskite oxide La0.75Sr0.25Cr0.5Fe0.5O3-delta in relation to its potential as a solid oxide fuel cell anode material. *Chemistry of Materials*, 16, 4116-4121.

TIETZ, F., RAJ, I. A. & STOVER, D. 2004. Statistical design of experiments for


WANG, W., ZHANG, L. & JIANG, S. P. 2008. Potential oscillation of methane oxidation reaction on (La0.75Sr0.25)(Cr0.5Mn0.5)O3 electrodes of solid oxide fuel cells. *Journal of Power Sources*, 178, 92-96.


WILSON, T. L. & SHEWMON, P. G. 1966. Role of the interfacial diffusion in sintering
of copper. Transactions of the Metallurgical Society of Aime, 236, 48-4&.


YANG, X. & IRVINE, J. T. S. 2008. (La0.75Sr0.25)(0.95)Mn0.5Cr0.5O3 as the cathode of solid oxide electrolysis cells for high temperature hydrogen production from steam. Journal of Materials Chemistry, 18, 2349-2354.


Pd-promoted La0.75Sr0.25Cr0.5Mn0.5O3/YSZ composite anodes for direct utilization of methane in SOFCs. *Journal of the Electrochemical Society*, 155, B811-B818.


ZHA, S. W., TSANG, P., CHENG, Z. & LIU, M. L. 2005b. Electrical properties and sulfur tolerance of La0.75Sr0.25Cr1-xMnxO3 under anodic conditions. *Journal of Solid State Chemistry*, 178, 1844-1850.


