Combined Cr and S Poisoning in Solid Oxide Fuel Cell Cathodes

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Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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Abstract

Solid oxide fuel cell is regarded as an electrochemical energy conversion device that can be operated at 600-1000 °C and has significant advantages over the low temperature counterparts such as fuel flexibility, non-precious metal catalysts and high efficiency. However, the durability and degradation of SOFC cathodes is one of the most critical areas for the commercial viability of the SOFC technologies. Until now, tremendous works have been done to understand the degradation mechanisms of deposition and poisoning of chromium and boron on cathodes. Sulfur, most likely from the air stream, can also accumulate at the cathode side of SOFC stacks, contaminating and degrading the cell performance. The overall objective of this PhD project is to investigate and understand the chromium and particularly sulfur deposition and poisoning mechanism of selected SOFC cathode materials under a wide range of SOFC operation conditions.

The effect of the temperature on the surface segregation and Cr$_2$O$_3$, SO$_2$, Cr$_2$O$_3$+SO$_2$ deposition on La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) cathodes is investigated in detail using confocal laser Raman spectroscopy, electrical conductivity relaxation (ECR) and X-ray photoelectron spectroscopy (XPS) method. It was found that segregation of SrO phase on the LSCF surface decreases with the decreasing of temperature. Cr deposition takes place on the LSCF surface after the heat-treatment in the presence of Cr$_2$O$_3$ at temperature range of 700 to 900 °C for 48 h, forming SrCrO$_4$ phase. As the temperature decreases, less SrCrO$_4$ phase is detected. However, Sulfur (SO$_2$) reacts with LSCF, primarily forming SrSO$_4$ at high temperatures (i.e., ≥ 700 °C) and SrS at low temperatures (i.e. <700 °C). SO$_2$ deposition shows a distinct volcano-type dependency
on the heat-treatment temperature and is most pronounced at temperatures around 700 °C, indicating that the reaction rate between the segregated SrO and SO₂ is highest at ~700 °C. Moreover, in the presence of Cr₂O₃ and SO₂ deposition and reaction products depend on the temperature: SrCrO₄ only forms on LSCF samples at 900 °C and 800 °C, while formation of SrSO₄ phase occurs at all temperatures studied. The results indicate that sulfur shows a higher activity with LSCF, as compared to gaseous Cr species. ECR results show that Cr₂O₃, SO₂, Cr₂O₃+SO₂ poisoning deteriorate significantly the surface exchange and diffusion processes for the O₂ reduction reaction on LSCF electrodes.

The mechanism of sulfur deposition and poisoning on the electrochemical activity of porous La₀.₈Sr₀.₂MnO₃ (LSM) and LSCF cathode for the O₂ reduction reaction is systematically investigated. Sulfur poisoning of the electrochemical activity of LSM electrodes is characterized by two-stage degradation processes: initial rapid degradation by the adsorption of SO₂ on the active sites on the surface of LSM electrodes, inhibiting the dissociation adsorption and diffusion processes of oxygen, followed by the irreversible and gradual degradation due to the deposition and formation of SrSO₄ on the LSM electrode surface and at the interface regions of LSM/YSZ (yttria-stabilized zirconia). However, sulfur poisoning of the electrochemical activity of LSCF electrodes is mainly caused by inhibiting the electrode surface process, followed by the irreversible and gradual degradation due to the deposition and formation of SrSO₄ and CoFe₂O₄. The amount of sulfur deposited becomes less at 800 °C than at 700 °C and 600 °C, which indicate that sulfur poisoning effect depends strongly on the temperature. The high SO₂ concentration in air accelerates the sulfur deposition and poisoning of both LSM and LSCF electrodes. The degradation due to the adsorption of SO₂ is reversible but the effect of sulfur deposition and
poisoning on the electrochemical activity of LSM cathodes cannot be reversed due to the depletion of Sr cation at the A-site of LSM as the result of the formation of SrSO$_4$. Similar sulfur deposition and poisoning on the electrochemical activity of LSCF cathodes is also proposed.

The electrochemical performance of BaCeO$_3$-LSCF cathodes was investigated in order to study the sulfur tolerance behavior. BaCeO$_3$-LSCF electrodes exhibit reduced electrode polarization resistance and better stable performance operating in the presence of accelerated SO$_2$ at 700 °C. Impregnated BaCeO$_3$ nanoparticles could react with sulfur dioxide to form BaSO$_4$ instead of SrSO$_4$ to reduce the direct contact of segregated SrO species in LSCF with SO$_2$. The BaCeO$_3$–LSCF cathodes show the promising potential as a good sulfur-tolerant oxygen electrode for SOFC.
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List of Publications

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6. **Cheng Cheng Wang**, Kongfa Chen, and San Ping Jiang, “Sulfur deposition and poisoning of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ cathode of solid oxide fuel cells”, Journal of Electrochemical Society, 161, F1133 - F1139 (2014).


8. Shikui Yao, **Cheng Cheng Wang**, Meng Li, Yi Cheng, Xing Wei, San Ping Jiang, “Practical and highly stable Ni-Fe@Co/Ti nanoporous electrodes by reactive deposition for efficient oxygen evolution reaction of water electrolysis”, International Journal of Hydrogen Energy, submitted.
Table of Contents

Acknowledgements ........................................................................................................ v
List of Publications ........................................................................................................ vi
Table of Contents ......................................................................................................... vii
List of Figures ................................................................................................................. x
List of Tables ................................................................................................................ xvi
List of Abbreviations ................................................................................................... xvii

Chapter 1: Introduction ................................................................................................. 1
  1.1 Background ....................................................................................................... 1
  1.2 Objectives and outline of the thesis ................................................................. 2

Chapter 2: Literature review ......................................................................................... 6
  2.1 Solid Oxide Fuel Cells (SOFCs) ........................................................................... 6
  2.2 SOFC performance ............................................................................................ 7
    2.2.1 Equilibrium Voltage ......................................................................................... 7
    2.2.2 Polarization Loss .............................................................................................. 8
  2.3 Traditional SOFC Cathode materials .................................................................. 9
  2.4 Deposition and poisoning of SOFC cathodes by contaminants ...................... 10
    2.4.1 Chromium Poisoning ....................................................................................... 10
    2.4.2 Sulfur Poisoning ............................................................................................. 15
    2.4.3 Other impurity poisoning ............................................................................... 19
    2.4.4 Cathode structural instability ......................................................................... 22
  2.5 Remarks and perspectives .............................................................................. 24

Chapter 3: Experimental .............................................................................................. 26
  3.1 Materials and electrode sample preparation ................................................. 26
  3.2 Chemical reactivity .......................................................................................... 27
  3.3 ECR tests .......................................................................................................... 27
  3.4 Characterization .............................................................................................. 28

Chapter 4: Impact of temperature on Cr deposition and poisoning for LSCF cathode 31
  4.1 Introduction .................................................................................................... 31
  4.2 Experimental ................................................................................................... 33
    4.2.1 LSCF bar sample preparation ......................................................................... 33
    4.2.2 ECR tests ....................................................................................................... 33
    4.2.3 Characterizations .......................................................................................... 34
  4.3 Results and Discussions .................................................................................. 35
    4.3.1 Effect of temperature on the phase of LSCF .................................................. 35
    4.3.2 Effect of temperature on the microstructure of LSCF .................................. 36
    4.3.3 Effect of temperature on the oxygen surface coefficient ............................ 40
  4.4 Conclusions ..................................................................................................... 42

Chapter 5: Impact of temperature on sulfur deposition and poisoning for LSCF
8. 2 Experimental ................................................................................................ 108
8.2.1 Half-cell preparation ....................................................................................... 108
8.2.2 Half-cell tests .................................................................................................. 109
8.2.3 Half-cell characterizations .............................................................................. 109
8. 3 Results and discussions ................................................................................ 110
8.3.1 Electrochemical performance of LSCF electrodes in the absence of SO₂ .......... 110
8.3.2 Electrochemical performance of LSCF electrodes in the presence of SO₂ ........... 111
8.3.3 Reversibility of sulfur poisoning effect of LSCF electrodes ......................... 119
8.3.4 Microstructure change of LSCF electrodes ...................................................... 120
8.3.5 XPS and XRD analysis ................................................................................... 123
8.3.6 Sulfur distribution by FIB-SEM and TOF-SIMS ................................................. 126
8.3.7 Mechanism and kinetics of sulfur deposition and poisoning on LSCF electrodes 128
8. 4 Conclusions .................................................................................................. 132

Chapter 9: Anti-sulfur poisoning of BaCeO₃-impregnated LSCF cathodes .......... 134
9.1 Introduction .................................................................................................. 134
9.2 Experimental ................................................................................................. 135
9.2.1 Half-cell preparation ....................................................................................... 135
9.2.2 Half-cell tests .................................................................................................. 136
9.2.3 Half-cell characterizations .............................................................................. 136
9.3 Results and discussions ................................................................................ 137
9.3.1 Electrochemical performance of LSCF electrodes in the absence of SO₂ ........... 137
9.3.2 Electrochemical performance of LSCF electrodes in the presence of SO₂ ........... 140
9.3.3 Microstructure change of LSCF electrodes ...................................................... 141
9.3.4 XRD analysis ................................................................................................... 142
9.3.5 Discussions .................................................................................................... 143
9. 4 Conclusions .................................................................................................. 144

Chapter 10: Conclusions and Recommendations ................................................. 146
10.1 Conclusions ..................................................................................................... 146
10.2 Recommendations ........................................................................................... 149
References: ............................................................................................................. 151
List of Figures

Fig.2.1 Schematic of the working principle of SOFCs[1]............................................................ 7
Fig.2.2 Typical current density and voltage characteristic of SOFC[2] ................................................. 8
Fig.2.3 Typical cell configuration and arrangement of investigating chromium deposition and poisoning of SOFC cathodes [4]. ..................................................................................... 11
Fig.2.4 SIMS depth profiles at LSM/GDC, LSF/GDC interface region. (a) Depth profiles of several secondary-ion signals as a function of sputtering time and (b) depth profiles of Cr concentration as a function of depth for different p(H2O)[6]. ....................................... 13
Fig.2.6 Time dependence of the rate of decrease in current under potentiostatic condition (-0.2 V vs. RE(air)). Operating temperatures are 800 °C, 700 °C and 650 °C [3]...................... 17
Fig.2.7 Dark-field scanning-TEM (DF-STEM) imaging of a near-electrolyte cathode region. EDS mapping indicates S to be incorporated into the Sr-chromate grain, confirmed by quantification results of the EDS spectrum as well as by the indexation of the diffraction [9]................................................................. 18
Fig.2.8 (Left) Bright filed image of the degraded LSCF surface (cross section view); a sample region with a relatively homogeneous Si layer thickness of approximately 20 nm; (right) Si map recorded by EFTEM[8]. ............................................................................ 21
Fig.2.9 SEM micrographs of LSCF of (a) before heat treatment and after heat treatment at (b) 600 °C, (c) 700 °C, (d) 800 °C, and (e) 900 °C for 50 h[5]. ...................................................... 23
Fig.2.10 Differentiated Auger electron spectra of the (a) LaMLL, (b)SrLMM, (c) CoLMM, (d) FeLMM, and (e) OKLL before (blue solid line) and after (red dotted line) heat treatment at 800 °C for 50 h[5]. ....................................................................................................... 23
Fig.2.11 AFM images of the LSCF+YSZ cathode s: (a) As-prepared, (b) tested for 120 h at 750 °C[7]................................................................................................................................. 24
Fig.3.1 Schematic diagram of LSCF bar samples for the ECR test in the presence of Cr2O3 and 20 ppm SO2...................................................................................................................... 27
Fig.4.1 XRD diffraction patterns of as-prepared LSCF and LSCF bar samples after heat-treatment in the presence of Cr2O3 at different temperatures for 48 h. a) fresh, b) 700°C, c) 800°C and d) 900°C. .......................................................................................... 35
Fig.4.2 XRD diffraction patterns of SrO-Cr2O3 oxide couple after heat-treatment at a) 700 °C, b) 800 °C and c) 900 °C in air for 2 h. ............................................................................................................. 36
Fig.4.3 SEM micrographs of LSCF surface after heat-treatment for 48 h in the absence (a, b, c) and presence (d, e, f) of Cr2O3 at different temperatures. (a,d) 900 °C, (b,e) 800 °C and (c,f) 700 °C. The as-prepared LSCF is shown in (g). ......................................................................................... 38
Fig.4.4 (a) Optical microscope images of as-prepared LSCF surface and (b) corresponding Raman spectra from the selected area on LSCF surface. ................................................................. 38
Fig.4.5 Optical microscope image of LSCF surface (left), Raman mapping at wavelength of 863 cm⁻¹ (middle), corresponding to SrCrO4 phase collected from the same area of optical microscope image and Raman spectra from selected particles on the LSCF surface(right). LSCF bar samples were heat-treated at (a,b,c) 900 °C, (d,e,f) 800 °C and
Fig. 4.6 Electrical conductivity relaxation profiles as a function of heat-treatment time on LSCF in the (a, b, c) absence and (d, e, f) presence of Cr$_2$O$_3$ at (a, d) 900 °C, (b, e) 800 °C and (c, f) 700 °C.

Fig. 5.1 XRD diffraction patterns of freshly-prepared LSCF and LSCF bar samples after heat-treatment for 48 h at different temperatures for 48 h. a) as-prepared, b) 900 °C, c) 800 °C, d) 700 °C, e) 600 °C, f) 500 °C, and g) 400 °C.

Fig. 5.2 SEM micrographs of LSCF surface after heat-treatment for 48 h (A) in the absence of 20 ppm SO$_2$ and (B) in the presence of SO$_2$ at (a,b) 900 °C, (c,d) 800 °C, (e,f) 700 °C, (g,h) 600 °C, (i,j) 500 °C and (k,l) 400 °C.

Fig. 5.3 Representative SEM micrographs of LSCF bar samples after heat-treatment in the presence of 20 ppm SO$_2$ at 700 °C for 48 h taken in different areas. EDX of deposited particles is shown in (d).

Fig. 5.4 (Left) Optical microscope images of LSCF surface after heat treatment in the presence of 20 ppm SO$_2$, (middle) Raman mapping at wavelength of 1000 cm$^{-1}$ corresponding to SrSO$_4$ and (right) Raman spectra from selected areas of LSCF surface. The heat treatment temperature of the LSCF bar samples was (A) 900 °C and (B) 800 °C.

Fig. 5.5 Optical microscope images of LSCF surface after heat treatment at 600 °C, 500 °C and 400 °C in the presence of 20 ppm SO$_2$ (a) Raman spectra from selected areas of the LSCF surface.

Fig. 5.6 XRD patterns of (a) La$_2$O$_3$, (b) SrO, (c) Co$_3$O$_4$ and (d) Fe$_2$O$_3$ after heat-treatment at different temperatures in the presence of 20 ppm SO$_2$ for 2 h. The numbers in the figure indicate the temperature: 4-400 °C, 5-500 °C, 6-600 °C, 7-700 °C, 8-800 °C and 9-900 °C.

Fig. 5.7 Electrical conductivity relaxation profiles of LSCF bar samples as a function of exposure time in the (a,b,c) absence and (d,e,f) presence of 20 ppm SO$_2$ at (a,d) 900 °C, (b,e) 800 °C and (c,f) 700 °C.

Fig. 5.8 Plots of occupied areas of segregated particles in the absence of SO$_2$ and sulfur-containing particles in the presence of 20 ppm SO$_2$, formed on the surface of LSCF bar samples as a function of the heat-treatment temperatures.

Fig. 6.1 XRD diffraction patterns of as-prepared LSCF and LSCF bar samples after heat-treatment in the presence of Cr$_2$O$_3$ and 20 ppm SO$_2$ at different temperatures for 48 h. a) as-prepared, b) 600 °C, c) 700 °C, d) 800 °C, e) 900 °C.

Fig. 6.2 SEM micrographs of LSCF surface after heat-treatment for 48 h in the presence of Cr$_2$O$_3$ (left), 20 ppm SO$_2$ (middle) and Cr$_2$O$_3$ and 20 ppm SO$_2$ (right) at (a,b,c) 900 °C, (d,e,f) 800 °C, (g,h,i) 700 °C, and (j,k) 600 °C. The scale bar applies to the micrographs of the same column.

Fig. 6.3 (a, b) Optical microscope images of LSCF surface after heat treatment in the presence of combined Cr$_2$O$_3$ and 20 ppm SO$_2$; (c, d) Raman mapping at wavelength of 863 cm$^{-1}$ corresponding to SrCrO$_4$; (e, f) 1000 cm$^{-1}$ corresponding to SrSO$_4$. Selected Raman
spectra is given in (g) from corresponding areas at (a, c, e) 900 °C...............................

Fig.6.4 Optical microscope images of LSCF surface after heat treatment at 700 °C (a), 600 °C
(c) in the presence of combined Cr₂O₃ and 20ppm SO₂, (b) Raman mapping at
wavelength of 1000 cm⁻¹ corresponding to SrSO₄ and (d) Raman spectra from LSCF
surface(700 °C) . Scale bar applies to all graphs. ............................................................

Fig.6.5 (a) XPS survey scan and selected high resolution XPS of (b) Sr 3d, (c) S 2p, (d) O 1s, (e)
Cr 2p and (f) La 3d of LSCF bar samples after heat treatment at different temperatures
and in the presence of Cr+S contaminants for 48 h.......................................................76

Fig.6.6 Comparison of electrical conductivity relaxation profiles of LSCF bar samples as a
function of exposure time (a) in the absence of Cr+S and in the presence of (b) Cr₂O₃, (c)
20 ppm SO₂ and (d) Cr+S at 900 °C........................................................................77

Fig.7.1 Initial polarization and impedance curves for the O₂ reduction reaction on LSM
cathodes under cathodic current passage at 200 mA cm⁻² in air at (a,b) 700 °C and (c,d)
800 °C. The electrochemical impedance curves were adjusted to the zero position.
Numbers in the figure are frequencies in Hz. .................................................................72

Fig.7.2 Initial polarization and impedance responses of O₂ reduction reaction on LSM
cathodes under cathodic current passage at 200 mA cm⁻² in the presence of 1 ppm SO₂
in air at (a,b) 700°C and (c,d) 800°C. Numbers in the figure are frequencies in Hz. ......84

Fig.7.3 Polarization and impedance curves for the O₂ reduction reaction on LSM cathodes
under cathodic current passage at 200 mA cm⁻² in the presence of 1 ppm SO₂ in air for
20 h at (a,b) 700 °C and (c,d) 800 °C. Numbers in the figure are frequencies in Hz. ......86

Fig.7.4 Polarization and impedance curves for the O₂ reduction reaction on LSM cathodes
under cathodic current passage at 200 mA cm⁻² in the presence of 10 ppm SO₂ in air at
(a,b) 700 °C and (c,d) 800 °C for 20 h. Numbers in the figure are frequencies in Hz. ......87

Fig.7.5 Comparison of Ecathode for the O₂ reduction reaction on LSM electrodes in pure air
(0 ppm SO₂), 1 ppm SO₂ and 10 ppm SO₂-containing air under cathodic current passage
of 200 mA cm⁻², measured at time intervals of 5 min and 4 h at 700 °C and 800 °C. ...89

Fig.7.6 Polarization potential curves for the O₂ reduction reaction on LSM cathodes under a
cathodic current passage at 200 mA cm⁻² in the presence of 1 ppm SO₂ in air for 20 h
and in pure air for another 15 h at (a) 700 °C and (b) 800 °C, (c) in pure air at 800 °C...91

Fig.7.7 SEM micrographs and EDS profiles of surface of (a,b) as-prepared LSM and LSM
cathodes after cathodic current passage at 200 mA cm⁻² in the presence of (c,d) 1 ppm
SO₂ and (e,f) 10 ppm SO₂ at 700 °C and 800 °C for 20 h.Typical EDS pattern taken from
the areas marked by circles is shown in (g). Bar=500 nm. .............................................93

Fig.7.8 SEM micrographs and EDS profiles of surface of YSZ electrolyte for an LSM oxygen
electrode under a cathodic current passage at 200 mA cm⁻² in the presence of (a,b) 1
ppm SO₂ and (c,d) 10 ppm SO₂ at 700 °C and 800 °C for 20 h. Typical EDS pattern taken
from the areas marked by rectangular is shown in (e) and circles is shown in (f). The
LSM electrode coatings were removed by adhesive tape. Bar=200 nm. .........................94

Fig.7.9 SEM micrographs of LSM inner surface after a cathodic current passage at 200 mA
cm⁻² in the presence of (a,b) 1 ppm SO₂ and (c,d) 10 ppm SO₂ at 700 °C and 800 °C for
20 h. Typical EDS taken from the areas marked by circles is shown in (e). Typical EDS
Fig. 7. 10SEM micrographs and EDS profiles of cross section of fresh LSM cathodes (a) and
LSM cathodes under cathodic current passage at 200 mA cm\(^{-2}\) in the presence of 1 ppm
SO\(_2\) (c,d) and 10 ppm SO\(_2\) (e,f) at 700 \(^{\circ}\)C and 800 \(^{\circ}\)C for 20 h. (b) The selected whole
image of LSM cathodes under cathodic current passage at 200 mA cm\(^{-2}\) in the presence
of 1 ppm SO\(_2\) at 700 \(^{\circ}\)C. (g) and (h) is the line scan for 700 \(^{\circ}\)C and 800 \(^{\circ}\)C.

Fig. 7. 11High resolution XPS spectra of (a) Sr3d, (b) S2p, (c) La3d and (d) Mn2p of surface of
as-prepared LSM and LSM electrode after a cathodic current passage at 200 mA cm\(^{-2}\) in
the presence of 1 ppm and 10 ppm SO\(_2\) for 20 h at 700 \(^{\circ}\)C and 800 \(^{\circ}\)C. (I) as-prepared
LSM, (II) 1 ppm SO\(_2\) at 800 \(^{\circ}\)C, (III) 1 ppm SO\(_2\) at 700 \(^{\circ}\)C, (IV) 10 ppm SO\(_2\) at 800 \(^{\circ}\)C and (V)
10 ppm SO\(_2\) at 700 \(^{\circ}\)C.

Fig. 7. 12 (a) SEM and (b) nano-SIMS image of sulfur distribution within a LSM cathode after
a cathodic current passage at 200 mA cm\(^{-2}\) in the presence of 1 ppm SO\(_2\) at 800 \(^{\circ}\)C.
Bright particles in (b) correspond to sulfur deposits.

Fig. 7. 13 Scheme of sulfur deposition and poisoning on the O\(_2\) reduction reaction on the LSM
oxygen electrodes under the SOFC operation condition at (a) 700 \(^{\circ}\)C and (b) 800 \(^{\circ}\)C.

Fig. 8. 1 Initial Polarization curves and impedance curves for the O\(_2\) reduction reaction on
porous LSCF cathodes in the absence of 1 ppm SO\(_2\) under cathodic current passage at
200 mA cm\(^{-2}\) for 1 h and (a, b) 600 \(^{\circ}\)C, (c, d) 700 \(^{\circ}\)C, (e, f) 800 \(^{\circ}\)C. The electrochemical
impedance curves were adjusted to the zero position for the purpose of comparison.
Numbers in the figure are frequencies in Hz.

Fig. 8. 2 Initial Polarization curves and impedance curves for the O\(_2\) reduction reaction on
porous LSCF cathodes in the presence of 1 ppm SO\(_2\) under cathodic current passage at
200 mA cm\(^{-2}\) for 1 h and (a, b) 600 \(^{\circ}\)C, (c, d) 700 \(^{\circ}\)C, (e, f) 800 \(^{\circ}\)C. The electrochemical
impedance curves were adjusted to the zero position for the purpose of comparison.
Numbers in the figure are frequencies in Hz.

Fig. 8. 3 Polarization curves and impedance curves for the O\(_2\) reduction reaction on porous
LSCF cathodes in the presence of 1 ppm SO\(_2\) under cathodic current passage at 200 mA
\cm\(^{-2}\) for 20 h at (a, b) 600 \(^{\circ}\)C, (c, d) 700 \(^{\circ}\)C, (e, f) 800 \(^{\circ}\)C. The electrochemical impedance
curves were adjusted to the zero position for the purpose of comparison. Numbers in the
figure are frequencies in Hz.

Fig. 8. 4 Polarization curves and impedance curves for the O\(_2\) reduction reaction on porous
LSCF cathodes in the presence of 10 ppm SO\(_2\) under cathodic current passage at 200 mA
\cm\(^{-2}\) for 20 h at (a, b) 600 \(^{\circ}\)C, (c, d) 700 \(^{\circ}\)C and (e, f) 800 \(^{\circ}\)C. The electrochemical
impedance curves were adjusted to the zero position for the purpose of comparison.
Numbers in the figure are frequencies in Hz.

Fig. 8. 5 Comparison of \(\Delta E\) cathode for the O\(_2\) reduction reaction on LSCF electrodes in 1 ppm
SO\(_2\) and 10 ppm SO\(_2\)-containing air under cathodic current passage of 200 mA cm\(^{-2}\),
measured at time intervals of 5 min and 20 h at 600 \(^{\circ}\)C, 700 \(^{\circ}\)C and 800 \(^{\circ}\)C.

Fig. 8. 6 Impedance curves for the O\(_2\) reduction reaction on LSCF cathodes under open circuit
condition in the presence of 1 ppm SO\(_2\) for 20 h at 700 \(^{\circ}\)C. The electrochemical
impedance curves were adjusted to the zero position for the purpose of comparison.
Fig. 8.7. The change of Ecathodic with time for O2 reduction reaction on LSCF cathodes under cathodic current passage at 200 mA cm² in the presence of 1 ppm SO₂ for 20 h and in pure air for 20 h at 600 °C (a), 700 °C (b) and 800 °C (c). .................................................. 119

Fig. 8.8 SEM micrographs of surface and cross section of LSCF cathodes under cathodic current passage at 200 mA cm² in the presence of 1 ppm SO₂, 10 ppm SO₂ and (i-l) as-prepared LSCF electrode at 600, 700 and 800 °C. Typical EDS pattern taken from the areas marked by circles is shown in (g). ........................................................................ 122

Fig. 8.9 SEM micrographs and EDS profiles of surface of GDC electrolyte for an LSCF oxygen electrode under cathodic current passage at 200 mA cm² in the presence of (a,b,c) 1 ppm SO₂ and (d,e,f) 10 ppm SO₂ at 600, 700 °C and 800 °C for 20 h. Typical EDS pattern taken from the areas marked by circles is shown in (g). The LSCF electrode coatings were removed by adhesive tape. .................................................................................. 123

Fig. 8.10 SEM micrographs of surface and cross section of LSCF cathodes under open circuit condition in the presence of 1 ppm SO₂ for 20 h at 700 °C (a, b). Typical EDS pattern taken from the areas marked by circles is shown in (c). ............................................... 124

Fig. 8.11 XRD patterns of LSCF electrodes under cathodic current passage at 200 mA cm² in the presence of 1 ppm SO₂ and 10 ppm SO₂ for 20 h at 700 °C and 800 °C. .................. 125

Fig. 8.12 The selected survey scan of LSCF under open circuit condition in the presence of 1 ppm SO₂ at 700 °C (a); The selected high resolution XPS of the Sr 3d (b), S 2p (c).....125

Fig. 8.13 Typical FIB-SEM elemental distributions mapping of cross section of LSCF cathodes under cathodic current passage at 200 mA cm² in the presence of 1 ppm SO₂ for 20 h at 700 °C and 800 °C. EDXs of Co and Sr element chosen with different color arrows. ....................................................................................................................................... 127

Fig. 8.14 Typical TOF-SIMS ion image of La, Sr, Co, Fe and S of LSCF cathodes under cathodic current passage at 200 mA cm² in the presence of 1 ppm SO₂ at 600 °C (A), 700 °C (B) and 800 °C (C). A SEM image of a LSCF/GDC cell is added for clarity on the left of each image. The brighter colors correspond to higher intensity. ................................. 128

Fig. 8.15 Scheme of mechanism of sulfur deposition and poisoning on the O₂ reduction reaction on LSCF oxygen electrodes under the SOFC operation condition at 600 °C and 700 °C (SO₂ adsorption on LSCF electrodes) and 800 °C (SO₂ desorption on LSCF electrodes). ................................................................. 132

Fig. 9.1 Impedance curves for the O₂ reduction reaction on LSCF (a) and BaCeO₃-LSCF (b) cathodes from 800 °C to 600 °C under the open circuit in air. The corresponding activation energies are shown in (c,d). Numbers in figures are frequencies in Hz............... 138

Fig. 9.2. Polarization and impedance curves under cathodic current passage at 200 mA cm² at 700 °C for 40 h for LSCF (a,b) and BaCeO₃-LSCF (c,d) in the absence of 1 ppm SO₂. Numbers in the figure are frequencies in Hz.............................. 139

Fig. 9.3 Polarization and impedance curves under cathodic current passage at 200 mA cm² at 700 °C for 40 h for LSCF (a,b) and BaCeO₃-LSCF (c,d) in the presence of 1 ppm SO₂. Numbers in the figure are frequencies in Hz.............................. 140

Fig. 9.4 SEM micrographs of surface and cross section of LSCF and BaCeO₃-LSCF cathodes
under cathodic current passage at 200 mA cm\(^{-2}\) in the absence (a, b, c) and presence (d, e, f) of 1 ppm SO\(_2\) at 700 °C for 40 h. (g) as-prepared LSCF electrode. The insets are the corresponding EDS spectra. ..............................................................142

Fig.9.5 XRD patterns of LSCF (b), BaCeO\(_3\)-LSCF electrodes under cathodic current passage at 200 mA cm\(^{-2}\) at 700 °C for 40 h in the absence (a) and presence (c) of 1 ppm SO\(_2\)......143
**List of Tables**

Table 4- 1. The kchem obtained by the experimental fitting at different temperatures as a function of exposure time............................................................................................................41

Table 5- 1. Reaction products of SrO heat-treated at different temperatures in the presence of 20 ppm SO₂ for 2 h.........................................................................................................................54

Table 6- 1. Phase formation and analysis by XRD, XPS and Raman spectroscopy..................74
List of Abbreviations

SOFC-Solid Oxide Fuel Cell

ORR-Oxygen Reduction Reaction

LSM-La$_{0.8}$Sr$_{0.2}$MnO$_3$

LSCF- La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$

ECR-Electrical Conductivity Relaxation

SEM-Scanning Electron Microscopy

EDS-Energy Dispersive Spectroscopy

XRD- X-ray Diffraction

XPS-X-ray Photoelectron Spectroscopy

CRS-Confocal Raman Spectroscopy

FIB/SEM-Focused Ion Beam Scanning Electron Microscopy

$\eta$-Overpotential

$E_{\text{Cathode}}$- Cathodic potential

EIS-Electrochemical impedance spectroscopy
Chapter 1: Introduction

1.1 Background

Energy crisis is becoming a globe issue around the world. Therefore, it is urgent to find sustainable energy for the sake of solving this problem. It is widely known that fuel cells can convert energy from fuels to electricity by electrochemical reaction. The electrical efficiency of fuel cell can be 60% and even exceed 70% in combined heat and power applications (CHP). Among different types of fuel cells, solid oxide fuel cells are a solid state device that can be operated at intermediate temperature of 600-800 °C and is much more fuel flexible than low temperature fuel cells and can be applied into many areas including large and small stationary power generation, and also small portable chargers. SOFCs have significant advantages over the combustion-based electricity generation with high efficiency and much low greenhouse gas emission.

However, the durability and degradation of SOFC cathodes is one of the most essential research areas that has to be paid attention to. Chromium poisoning of cathodes had been extensively investigated due to its one of major concerns for practical SOFC. Apart from a large number of studies on Cr poisoning of cathodes, studies on durability of SOFC stacks under real operation environment indicated that sulfur, most likely from the air stream can accumulate at the cathode side, contaminate and degrade the cell performance [10, 11]. However, there are relatively few studies on the sulfur deposition and poisoning process on SOFC cathodes and the mechanism of sulfur deposition and poisoning on the oxygen reduction reaction under SOFC operation.
conditions is far from clear.

Thus, the objective of the project is to investigate the effect of sulfur poisoning on SOFC cathodes such as LSM and LSCF and based on the reaction mechanism, new sulfur-tolerant cathode materials are developed.

1.2 Objectives and outline of the thesis

The main objective of the PhD project is to fundamentally understand the sulfur as well as chromium poisoning on SOFC cathodes and developing sulfur-tolerant cathode materials. Specifically, the objectives are listed as follows:

1. Investigating and understanding the deposition and poisoning of chromium on LSCF cathodes under open circuit conditions.

2. Investigating and understanding the mechanism and kinetics of sulfur poisoning on the electrocatalytic activity of LSCF and LSM cathodes for the oxygen reduction reaction.

3. Investigating and understanding fundamentally the effect of combined chromium and sulfur poisoning on LSCF cathodes.

4. Developing sulfur-tolerant poisoning cathodes materials by using impregnation technique.

Based on the objectives as shown above, the thesis is consisting of 10 chapters. Here is the brief outline of the chapters.

Chapter 2: Literature review

In this chapter, the durability and degradation of SOFC cathodes as reported in the literature were reviewed and discussed. This includes the effect of chromium poisoning on SOFC cathodes in various test conditions like the temperature, air atmosphere, polarization and chromium
concentration; sulfur deposition and poisoning on SOFC cathodes, and deposition and poisoning of boron, moisture and other minor elements on SOFC cathodes.

Chapter 3: Experimental

In this chapter, the experimental procedure of studying the effect of chromium poisoning, sulfur poisoning of SOFC cathodes were described in details.

Chapter 4: Impact of temperature on Cr deposition and poisoning for LSCF cathode (This chapter is published in Electrochemica Acta)

In this chapter, the effect of Cr deposition on the microstructure and electrochemical activity of LSCF cathodes for the oxygen reduction reaction at different temperatures is studied using electrical conductivity relaxation. The present study demonstrates that the temperature has a significant effect on the Sr segregation, Cr deposition and formation of SrCrO₄ phase on the LSCF surface. Surface exchange coefficients of LSCF after being exposed to Cr₂O₃ are significantly lower than that in the absence of Cr₂O₃.

Chapter 5: Impact of temperature on sulfur deposition and poisoning for LSCF cathode (This chapter is published in Journal of the Electrochemical Society)

In this chapter, the deposition and poisoning of sulfur on the microstructure and surface diffusion properties of LSCF cathode materials is investigated in the temperature range of 900 – 400 °C on dense bar samples in air using confocal Raman spectroscopy, scanning electron microscopy as well as ECR methods. The results indicate the deposition of sulfur species on the LSCF surface and formation of SrSO₄ depends strongly on the temperature. Sulfur deposition and poisoning becomes most pronounced at temperatures around 700 °C.

Chapter 6: Impact of temperature on Cr/ S Co-deposition and poisoning for LSCF cathode
In real SOFC stack operation conditions, both chromium and sulfur sources exist. In this chapter, the presence of both Cr and S contaminants on the microstructure and surface diffusion properties of LSCF cathode materials is also investigated from 900 to 600 °C on LSCF dense bar samples in air. The results indicate that sulfur deposition and poisoning effect is more dominant as compared to the chromium particularly at low temperatures (700 °C) under the conditions of this study.

**Chapter 7: Mechanism and kinetics of SO₂ poisoning on the electrochemical activity of LSM cathodes.**

The focus is on the mechanism and kinetics of the sulfur poisoning and deposition on the LSM cathodes at different temperatures and SO₂ content. The results show that the presence of SO₂ in air poisons the electrochemical activity of LSM electrodes by inhibiting the oxygen dissociation and diffusion process on the surface of LSM and by the formation of strontium sulfate in the LSM bulk and at the LSM/YSZ interface region. The deposition processes of sulfur species is most likely controlled by the nucleation reaction between the SrO and the gaseous sulfur species, forming SrSO₄.

**Chapter 8: Mechanism and kinetics of SO₂ poisoning on the electrochemical activity of LSCF cathodes**

In this chapter, the mechanism and kinetics of sulfur poisoning and deposition on the LSCF cathodes are also investigated at different temperatures and SO₂ content using electrochemical analysis, FIB-SEM and TOF-SIMS. The results show that the presence of SO₂ in air poisons the electrochemical activity of LSCF electrodes by inhibiting the electrode bulk process and by the
formation of SrSO₄ as well as CoFe₂O₄. The deposition processes of sulfur species is most likely controlled by the nucleation reaction between the segregated SrO and the gaseous sulfur species.

Chapter 9: Sulfur-tolerant BaCeO₃-impregnated LSCF cathodes

For the first time, infiltration of proton conductors like barium cerate (BaCeO₃) into LSCF electrodes is investigated as sulfur-tolerant cathodes. The results indicate that BaCeO₃ impregnation can inhibit sulfur poisoning by forming barium sulfate compound on the electrode surface at 700 °C, enhancing the sulfur-tolerance of LSCF electrodes.

Chapter 10: Conclusions and Recommendations

The achievements of this project are summarized and the suggestions for future studies are listed in this chapter.

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Chapter 2: Literature review

2.1 Solid Oxide Fuel Cells (SOFCs)

Recent years, a lot of attention has been paid on sustainable energy for the sake of solving the energy crisis issue around the globe. It is widely known that fuel cells can convert energy from fuels to electricity by electrochemical reaction [12-14]. The energy converting process is not limited by Carnot efficiency, which is different from normal combustion engines. The electrical efficiency of fuel cell can be 60% and even exceed 70% in combined heat and power applications (CHP) [15, 16]. NASA space programs used the first commercial fuel cells to generate power for spacecraft.

Fuel cells can be classified into many types such as alkaline fuel cells (AFCs), molten carbonate fuel cells (MCFCs), proton exchange membrane fuel cells (PEMFCs) and solid oxide fuel cells [12]. SOFC is a solid device that can be operated at intermediate temperature of 600-800 °C [16-20]. Fig.2-1 shows the diagram of the basic working principle of SOFC. It is usually consisted of three parts including cathode, anode and electrolyte. Electrolyte is an ionic conductor that can separate air from fuel gases and prevent the combustion between gases [21]. The porous cathode is the electrode where oxygen reduction reaction (ORR) can occur to reduce, the oxygen molecules oxygen ions (O²⁻) [22]. O²⁻ ions are transferred by electrolyte to the porous anode [23] where they combine with fuels like H₂ to form water. Both cathode and anode must be porous for the sake of increasing reaction areas and promoting mass transport of reactants. In the case, H₂ as
fuel chemical reactions can be written as below:

Cathode \( \frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}[2-1] \)

Anode \( H_2 + O^{2-} \rightarrow H_2O + 2e^-[2-2] \)

If the fuel is CH₄, the reaction is \( CH_4 + 6O^{2-} \rightarrow CO_2 + 2H_2O + 12e^- \) [2-3]

Whole reaction: \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \) [2-4]

Or \( CH_4 + 3O_2 \rightarrow CO_2 + 2H_2O \) [2-5]

Fig.2.1 Schematic of the working principle of SOFCs [1].

2.2 SOFC performance

2.2.1 Equilibrium Voltage

Open circuit voltage (OCV) means the potential difference of the cell when no external electrical current flows. OCV of SOFC is closely related with O₂ partial pressure for anode and cathode, so it can also be calculated using the Nernst equation. Take the hydrogen fuel cell for example; the theoretical OCV is 1.103 V at 800 °C [24].

\[
OCV = \frac{RT}{4F} \ln \left( \frac{P_{O_2,\text{anode}}}{P_{O_2,\text{cathode}}} \right) \quad [2-6].
\]
2.2.2 Polarization Loss

In reality, the cell voltage will decrease starting from OCV when the current density increases. It is mainly attributed to the various polarization losses. Normally, there are at least four major polarization losses including the loss of activation polarization, the loss of ohmic resistance, the loss of concentration polarization and other losses due to the electronic conductivity of electrolytes or sealing leakage. Fig.2 lists the typical current density and voltage characteristic of SOFC.

Firstly, activation polarization loss is related to the limit of electrode reaction kinetics because of the activation energy barrier (Ea). Especially, the main factors are the kinetic losses of the adsorption/dissociation as well as charge transfer for active species in the triple phase boundary (TPB). The famous Butler-Volmer equation (Eq2-7) clearly defines the relation between current density (j) and activation overpotential (η). In the equation, α means transfer coefficient, of which value depending on the symmetry of the activation barrier. Exchange current density (j_0) is related to the reactant as well as activation barriers. Improvement of the exchange current density can be achieved by using appropriate catalysts and increasing reactant concentrations.

\[
    j = j_0 \left( \frac{\alpha n F n_{act}}{RT} - e^{-\frac{(1-\alpha) n F n_{act}}{RT}} \right)
\]

[2-7]

Fig.2.2 Typical current density and voltage characteristic of SOFC[2].
Secondly, loss of ohmic polarization is due to the resistance of electrolyte as well as electrode materials, and the contact resistance. Thus, electrodes need to be good electronic conductors and to reduce the ohmic resistance of electrolyte, thin electrolyte layer can be applied or high oxygen ionic conductor materials like doped CeO$_2$ and doped Bi$_2$O$_3$ are used [25], which has already been demonstrated for the application of high performance SOFC in the intermediate temperature range.

Thirdly, concentration polarization loss is mainly due to the mass transfer process that is caused by the gas diffusion in the porous electrodes at high current densities. The concentration near the electrode/electrolyte interface would be depleted because of the electrochemical reaction of oxygen reduction at the cathode or fuel oxidation at the anode. Concentration overpotential generates from reduced concentration of reactants and shows rapid increase with the current density.

2.3 Traditional SOFC Cathode materials

There are some requirements for a SOFC cathode, which should include the good ORR activity, high temperature stability, compatible thermal expansion coefficient (TEC) that can match well with other components, required porosity, low cost and so on [26]. Understanding ORR is also essential in developing cathode materials. Normally, there are several elementary steps for ORR including gas phase diffusion, adsorption of oxygen molecules, dissociation into oxygen atoms, charge transfer and incorporation of oxygen ions. Among all the cathode materials, LSM is one of the most common cathodes for SOFCs because it has a high electrical conductivity.
at higher temperature and its thermal expansion coefficient with electrolyte material YSZ. LSCF has also been extensively investigated because of its much higher ionic and electronic conductivity [27-30], compatible TEC with electrolyte material GDC.

2.4 Deposition and poisoning of SOFC cathodes by contaminants

2.4.1 Chromium Poisoning

In the past 15 years, chromium poisoning of cathodes had been extensively investigated due to its importance in the development of durable SOFC stack technologies. It is widely known that metallic materials based alloys are often regarded as the primary candidates of the interconnect materials for intermediate temperature SOFC because of some obvious benefits like economic, easy processing, high electrical and thermal conductivities [31]. However, these alloys are generally composed of Cr or Cr based alloys such as Ni-Fe-Cr based heat resistant alloys and chromia-forming ferric stainless steels. When operating at high temperatures, volatile Cr species will be produced in the oxidizing atmosphere [31]. Volatile Cr species can also originate from the balance of plant (BoP) system. Without protective coatings, volatile Cr species could lead to rapid performance degradation for SOFC cathodes of oxygen reduction reaction.

Since 2000, many researchers have done a lot of work on investigating the fundamental mechanism for chromium poisoning of SOFC cathodes. S. P. S. Badwal [32] pointed out that the chromium poisoning mechanism is driven by electrochemical deposition of Cr species between the cathode and electrolyte/electrode interface area in competition with oxygen reduction reaction [33]. However, Jiang investigated the Cr deposition mechanism on cathodes using typical setup below (Fig.2-3) and showed that chromium deposition is correlated to chemical dissociation
reaction instead of electrochemical reduction of high valence Cr species in competition with the oxygen reduction reaction. And the deposition of Cr₂O₃ and (Cr,Mn)₃O₄-type spinel phases is due to manganese ions segregated when being polarized or operating at higher temperature [4].

Jiang did a comprehensive study on Cr deposition at air electrodes like LSM, LSCF and Pt air electrodes of SOFC at 900 °C [34] and pointed that for LSM electrodes, Cr deposition preferentially occurred on YSZ and formed the deposited ring, however, Cr deposited on the surface of LSCF to form SrCrO₄. But for Pt electrodes, no detected Cr deposition can be found in the places mentioned above. All the results clearly indicate that chromium deposition is not an electrochemical reduction and it is a chemical reaction in nature.

In our group (S. P. Jiang), Cr deposition and poisoning was also investigated on new cathode materials like Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃ (BSCF) [35]. The results indicate that the BSCF cathodes are stable in the absence of metallic interconnects, however, degrade quickly in the presence of Fe-Cr alloy interconnect, due to the Cr deposition at surface of BSCF forming barium chromate, strontium chromate or other compounds after 20 h polarization at 900 and 800 °C. In addition, the Sr amount of BSCF plays an important role in Cr deposition [36]. Cr poisoning on cathode materials under different operating conditions such as air atmosphere, temperature, cathodic
current density, and Cr concentration and so on was also investigated. For instance, Xinbing Chen [37] investigated Cr poisoning on a LSM cathode in pure and moisturized air at 900 °C and reported that oxyhydroxide Cr species formed accelerated degradation of LSM cathode in moisturized air. It is also widely known that operating temperature is playing a vital role on Cr deposition. Jiang et al. [34] investigated Cr deposition on cathodes from 700 °C to 900 °C and found that Cr deposition decreased with the decrease of the temperature. However, Krumpelt [38] reported the Cr deposition on LSM cathodes and found Cr deposited at the LSM and YSZ interface is much more severe at 700 °C than that at 800 °C. Bo Wei [39] also did detailed study of chromium deposition on LSCF electrode under OCV condition from 900 °C to 700 °C and clearly identified that the formation of SrCrO4 phase at 900 °C for 20 h under OCV by Confocal Raman spectroscopy technique, in addition, the magnitude of Cr deposition decreased with the decrease in temperature. All these results were in accordance with the mechanism was proposed by Jiang [34].

Moreover, traditional composite cathodes were also studied in details. For instance, J.J.Bentzen [40] investigated Cr poisoning of LSM/YSZ and LSCF/GDC composite cathodes by using Cr2O3 pellet source in pure air and moisturized air at 750 °C and 850 °C with 0.2 and 0.4 A cm−2 for over 300-3000 h. They found that cathode degradation for both composite cathodes was related to water partial pressure and the current density, which can indicate that the more humid air, the higher current density, the much higher degradation. Nevertheless, the effect of temperature seemed to depend on the humidity. Horita investigated Cr poisoning at LSM and (La,Sr)FeO3 (LSF) cathodes using secondary-ion mass spectrometry (SIMS) for the first time (Fig.2.4) and they concluded that cathodic polarization currents decreased with time mainly due to the deposition of Cr at the active sites of cathodes. Also, they content that the difference in the
polarization resistance was related to the difference in Cr degradation mechanism between these cathode materials. For LSM electrode, Cr poisoning normally accumulated in the triple phase boundary area, while in LSF, it happened in the chemical and electrochemical reaction area.

![SIMS depth profiles at LSM/GDC, LSF/GDC interface region](image)

**Fig.2.** 4 SIMS depth profiles at LSM/GDC, LSF/GDC interface region. (a) Depth profiles of several secondary-ion signals as a function of sputtering time and (b) depth profiles of Cr concentration as a function of depth for different p(H2O)[6].

The effect of Cr poisoning on LaNi0.6Fe0.4O3 (LNF) cathodes under current load were also studied by M.K.Stodolny [41, 42]. Similar to BSCF, LNF cathode was stable in Cr-free atmosphere; however, LNF cathode performance decreased because of Cr species by extrinsic degradation. It is also worth mentioning that Eunjoo Park [43] did a comparison work on the chromium poisoning on different kinds of cathode materials like LSM, and BSCF. They found that Cr mainly deposit near the cathode/electrolyte interface for LSM, while Cr deposition occurred primarily on the surface of BSCF due to increased activity of BSCF with Cr vapor. Moreover, as for the relationship between chromium poisoning and electrode/electrolyte materials, some companies like Tokyo gas [44] did some work on understanding the relationship between the resistance against Cr poisoning and compositions for electrode as well as electrolyte, and found
that the resistance was dependent on the composition of the electrolyte and the electrode
degradation was mainly caused by the precipitation of Cr$_2$O$_3$ at the interface.

The effect of cathodic polarization on chromium poisoning of cathode performance has been
studied. Eunjoo Park et al studied the influence of cathode polarization on chromium poisoning of
LSM, LSCF and LNF [45] by SEM-WDX (Wavelength Dispersive X-ray spectroscopy), and the
results showed that chromium deposition was affected by cathodic polarization. However, it also
indicated that there was no obvious difference among three electrodes regarding the effect of
polarization on chromium deposition under large cathodic polarization condition. E.Yu.Konysheva
[46] studied that effect of current density on poisoning rate of cathodes by chromium and found
that at 800 °C, the highest degradation rate occurred under open circuit conditions due to the direct
formation of SrCrO$_4$ layer on LSCF surface compared with results for adding cathodic current,
however, after applying cathodic current at 0.2 A/cm$^2$, the overall amount of chromium was twice
as large as under OCV condition. He also compared the amount of chromium in LSCF and LSM
cathode under the same situation and concluded that the amount was larger in LSCF than LSM
electrodes. Due to the higher oxygen ionic conductivity of LSCF electrodes, the degradation rate
of LSCF was lower than LSM electrodes in the presence of chromium. M.Kornely [47] also
investigated the degradation of SOFC cathode (LSM) by Cr poisoning under open circuit
conditions at 800 °C by electrochemical impedance spectroscopy technique and he found that there
was an obvious increase of cathodic polarization resistance after switching on Cr source, so it
clearly identified that chromium poisoning of LSM cathode can occur under OCV. To verify the
existence of Cr on the triple phase boundary area [TPB], Horita [48] used secondary ion mass
spectrometry (SIMS) technique analyzed Cr distribution in LSM; they found that the degradation
of LSM was due to the Cr deposited on the triple phase boundary area (TPB). In addition, they also observed that the increase of Cr concentration on the surface areas. S.C. Paulson [49] also did study on the chromium distribution at a porous LSM cathode and found that deposited Cr containing compounds were distributed in both triple-phase boundary (TPB) interface region and the edge of LSM film on the YSZ surface.

2.4.2 Sulfur Poisoning

Recently, people found that sulfur, most likely from the air stream can accumulate at the cathode side, contaminate and degrade the cell performance [10, 11]. Sulfur in the air stream can affect significantly the performance and durability of SOFCs [50-53]. One possible source of sulfur contamination is the sulfur from a trace amount of SOx in air, which could be accumulated by reacting with cathode in the vicinity of the air entrance of the cells.

On the other hand, people also found that sulfur is one of the major contaminants in the anode aide of SOFCs. For example, one of the major challenges for the direct use of hydrocarbon fuels in SOFCs is the poisoning of Ni-based anodes by sulfur existed as impurities in readily available hydrocarbon fuels [54, 55]. The presence of H2S degrades the performance of the Ni-based anodes such as Ni/Y2O3-ZrO2 (Ni/YSZ) and Ni/Gd2O3-CeO2 (Ni/GDC) cermet anodes [56-58]. The mechanism and kinetics of the deposition and poisoning of sulfur on the anodes of SOFCs has been studied [59], however, much less attention has been paid on the mechanism of sulfur deposition and poisoning on the cathode materials.

Xiong et al. studied the polarization behavior of (La0.85Sr0.15)0.95MnO3 (LSM) and Sm0.5Sr0.5CoO3 (SSC) cathodes after the heat-treatment of the electrodes to 100 ppm SO2 at 800
C and found that the performance of SSC declined rapidly while LSM was more stable in SO2-contained air [52]. The significant difference in the polarization performance of SSC and LSM in SO2-contained air for the O2 reduction reaction has been explained by the difference in the activity of SrO in the LSM and SSC perovskites. K.Yamaji [60] investigated the effect of SO2 concentration on degradation of SSC cathodes (100 ppm, 1 ppm and 5 ppb) at 800 °C and it clearly showed that the degradation of the cell accelerated due to the increase content of SO2, SrSO4 was also formed on the surface of SSC cathode. A.J.Schuler [61] did some studies on investigating sulfur as pollutant species on LSM/YSZ cathodes with LSC as current collection layer and they found that there was a preferential reaction between sulfur with LSC compared with LSM. These results can be explained by the higher thermodynamic activity of SrO in LSC rather than LSM and the difference is 4 orders of magnitude between La0.6Co0.2O3 and La0.6Mn0.2O3. Sasaki Kazunari [62] investigated the chemical durability of SOFC and an accelerated SO2 (20 ppm) test was done to clarify the sulfur poisoning on degradation of LSM cathode materials. It clearly showed that SrSO4 was formed in the LSM by FESEM-EDX analysis and can indicate the reaction between Sr and SO2 at 800 °C.

Liu et al. [50] showed that the performance of cells with La0.6Sr0.4Co0.2Fe0.8O3-δ (LSCF) electrode becomes unstable in the presence of 1 ppm SO2 and drops significantly when the SO2 concentration increased to 20 ppm. The performance degradation is most likely due the poisoning of SO2 and the formation of SrSO4. Ishihara et al. [63] reported that the degradation of LSCF is accelerated at low partial pressure of O2 in the presence of sulfur and the degradation is considered to be caused by the Sr segregation and the subsequent formation of SrSO4. On the other hand, Wang et al. [64] studied the polarization performance behavior of LSCF in the presence of 0.1
ppm SO₂ and two-stages of performance degradation were found. A degradation mechanism based on the occupation of SO₂ in the oxide ion vacancies and subsequent formation of SO₃²⁻ and SrSO₄ was proposed for the irreversible poisoning effect of SO₂. Xie [63] also showed that Sr segregation and the subsequent formation of SrSO₄ is the main cause of the performance degradation of LSCF cathodes at low partial pressure of O₂ in the presence of sulfur at 973 K.

There are some studies on investigating factors like temperature affecting the sulfur poisoning on cathode materials. For instance, Kishimoto [3] reported that SO₂-induced degradation of LSCF is affected by SO₂ concentration and the operating temperature, and performance degradation is characterized by a rapid degradation at an early stage, followed by a relatively slow degradation stage. The degradation rates for the slow degradation step were nearly the same although the operating temperature was different (as shown in Fig.2.6). Mori [65] also found that the sulfur deposition in LSCF depends on temperature and current density and degradation rate of the cell voltage at 800 °C is lower than that operated at 700 °C. They also observed that sulfur is deposited over the entire LSCF cathode at 800 °C, while at 700 °C sulfur is mainly concentrated in the areas close to the GDC barrier layer and this was considered to be related to the concentrated electrochemical reactions area near the GDC barrier layer.

Fig.2.5 Time dependence of the rate of decrease in current under potentiostatic condition (-0.2 V vs. RE(air)). Operating temperatures are 800 °C, 700 °C and 650 °C [3].
F.Wang [66] studied the effect of water vapor on sulfur distribution within LSCF cathode and the results showed that degradation speed was accelerated around 10 times in the presence of 1 ppm SO$_2$ with water vapor at 800 °C for 100 h. It is also worth mentioning that combined CrO$_3$ and SO$_2$ effect on the degradation mechanism of SOFC cathodes was studied by T.Horita [66]. It clearly shows that the cathode degradation performance was mainly due to the formation of SrCrO$_4$ and SrSO$_4$ on the surface of LSCF as well as electrochemical active sites. In addition, J.Andreas Schuler [9] also studied combined Cr and S poisoning in LSM cathodes and Sr(Cr, S)O$_4$ compounds were detected by SEM/TEM techniques (Fig.2-7), which could result in the decrease of active sites in LSM and lead to the performance degradation.

Edith Bucher [67] used an in-situ dc conductivity relaxation measurement technique to investigate the sulfur poisoning on cathode materials La$_{0.6}$Sr$_{0.4}$CoO$_3$ at 700 °C. After performing for 1000 h in an O$_2$-Ar atmosphere with and without 50 ppm SO$_2$, the chemical oxygen exchange coefficient $K_{chem}$ decreased by a factor of 10 and SrSO$_4$ was also clearly identified by x-ray photoelectron spectroscopy (XPS). SEM with EDX and TEM also detected the La$_2$O$_2$SO$_4$ within the first 500 nm of the surface and Co-rich phase. The same experiment was also applied to investigate the atmosphere with either a few ppb or 2 ppm SO$_2$ under the same situation [68]. It
shows that SrSO₄ were observed at the surface as well as thick nanocrystal-line layer. And this region was assumed to consist of the phases SrSO₄, La₂O₂SO₄, and Co₃O₄, which could exhibit low electronic conductivity as well as low surface oxygen exchange activity. Although there are many works of sulfur contamination on SOFC cathode, these works are rather scattered, there is no fundamental study on chemical reactivity between SO₂ and cathode materials, and there is a lack of systematic work on the operating temperature, SO₂ concentration on the initial electrochemical performance of cathode materials. However, these works are essential to understand sulfur contamination on cathode which is worthy of dedicated investigation.

2.4.3 Other impurity poisoning

It is widely known that glass ceramics are suitable seals for SOFCs because of their tailorable structure as well as properties [69-72]. However, the disadvantages for the glass ceramics are their volatility and reaction with other cell components like interconnect and electrode materials at the operating temperature. Batfalsky et al. studied chemical reactions among glass sealant and Fe-Cr alloy that leads to the severe corrosion of the alloy, and then finally leads to the short circuit of the cell [72]. In addition, for the glass components, boron oxide (B₂O₃) is one of the suitable raw materials due to its controlling viscosity and suitable softening temperature [73]. Nevertheless, the high volatility of boron species such as BO₂ and B₃H₆O₆ under the dry and wet conditions could probably poison the electrodes [74]. Kongfa Chen [75] did study on the effect of boron on microstructure, composition, electro catalytic activity of traditional electrodes. SIMS technique was used to detect the boron deposition in the LSM and LSCF bar samples. It was found that there were significant microstructure and composition changes after boron deposition. SrB₂O₄ can be
detected for two samples on the outmost surface, while LaBO3 was also formed in the LSM bar samples. All these results clearly identify that volatile boron species lead to the microstructure change of cathode materials like LSM and LSCF. Regarding to the effect of boron on the electrocatalytic activity of LSM and LSCF electrode, Kongfa Chen [75] found that the significant degradation of LSM electrode occurred due to the chemical incompatibility between boron and LSM, also the reaction happened on the surface of LSM electrodes. While for LSCF electrode, the electrode polarization resistance increased significantly after being treated in the presence of glass, and it is also mainly due to the chemical incompatibility as well as formation of LaBO3 and Fe2O3.

There are studies on the water on the electrochemical performance and durability for cathodes [76-78]. It has been found that higher humidity at the cathode side can result in the significant voltage drop at 0.2 A/cm² and some La2O3 nano particles were detected on LSM electrodes at the same time. Shen F. et al. [79] studied the moisture on degradation for LSM and combined moisture degree; interconnect interface and the cathode together to investigate the degradation of LSM and LSCF electrode by deconvoluting the electrochemical impedance spectroscopy (EIS). They found that the ohmic resistance and polarization resistance of LSM electrode was largely influenced by the moisture compared with LSCF electrode. In addition, more chromium could diffuse from interconnect to cathode for both cathodes in the moisture atmosphere. Eric D.Wachsman [80] studied the effect of H2O and CO2 on the cathode degradation mechanism by establishing the cathode composition/structures and operating condition. A focused ion beam (FIB)/SEM technique was used to quantify the change of microstructure before and after poisoning. They found that competitive adsorption/desorption process among CO2, H2O and O2, and finally they mentioned that rationally design stable low polarization cathodes will be studied.
in the future.

Some minor elements such as Ca, Al and Si could affect the performance of SOFC. Junya Oishi [81] et al. studied these additionally added minor elements on the properties of LSCF cathode. Conductivity relaxation measurements were adopted to measure both $D_{\text{chem}}$ and $K_{\text{chem}}$ of LSCF electrodes and their results clearly showed that Al and Si could decrease $D_{\text{chem}}$ and $K_{\text{chem}}$, but Ca as well as Ba don’t influence $D_{\text{chem}}$ and $K_{\text{chem}}$ too much that is probably due to the formation of oxygen vacancy on LSCF after additions of Ca and Ba detected by XPS. Silica (Si) poisoning on the LSCF cathode was studied using TEM by Edith Bucher [8] and the results showed that Si contamination can occur in around 20 nm thick at the surface of LSCF electrode (as shown in Fig.2-8).

![Fig.2. 7 (Left) Bright filed image of the degraded LSCF surface (cross section view); a sample region with a relatively homogeneous Si layer thickness of approximately 20 nm; (right) Si map recorded by EFTEM [8].](image)

$\text{Al}_2\text{O}_3$ additions in YSZ electrolyte were also studied to understand the degradation of interface of LSM-YSZ. Ruth Knibbe [82] found that cubic $(\text{Mn,Al})_3\text{O}_4$ phase formed at the interface and caused the delamination between the cathode and electrolyte. Moreover, Eui-Hyun Kim [83] used atomic layer deposition to investigate $\text{Al}_2\text{O}_3$ on the degradation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSC) cathode and found that the deposited $\text{Al}_2\text{O}_3$ into the porous electrode could block the triple phase boundary in LSCF and caused the disruption at the interface between the charge collector
and cathode.

**2.4.4 Cathode structural instability**

S.P. Simner [84] studied the stability for anode supported YSZ electrolyte SOFC using LSCF cathodes operating at 750 °C and 0.7 V for 500 h. It shows that there were no discernible microstructural changes by SEM; however, XPS results clearly showed that significant Sr enrichment can be observed on the interface between cathode and electrolyte, and then finally leading to the substantial increase of ohmic and nonohmic resistances. In addition, Dongjo Oh [5] did study on understanding the mechanism of LSCF cathode degradation by observing the behavior on the surface of dense sintered LSCF sample from 600 to 900 °C. SEM results showed that there were some micron sized particles formed on the grain surface (Fig.2-9). Moreover, Auger electron spectroscopy (as shown in Fig.2.10) and TEM clearly identified the formation of Sr-O based precipitate and it increased with the increase of temperature as well as oxygen partial pressure. They proposed the two-step mechanism of Sr-O formation that can be included the formation of oxygen vacancies as well as the enriched Sr phase formation. Consequently, it can lead to the obvious degradation of LSCF cathodes.
Some researchers also studied the deteriorated behavior at interface of LSCF with rare doped ceria electrolytes (RDC, M₀.₂Ce₀.₈O₁.₉, M=Gd, La). For instance, it is known that RDC was used as the interlayer between LSCF and YSZ in order to prevent the La₂Zr₂O₇ formation. Natsuko Sakai [85] studied the effect of RDC on the long term reliability of SOFC performance and a secondary phase was also formed at the interface due to the reaction of rare earth element with the transition metals in cathodes. In addition, transition metals (Co, Fe) as well as Sr can also diffuse from LSCF to ceria electrolytes. This entire phenomenon can strongly affect the stability of

Fig.2.8 SEM micrographs of LSCF of (a) before heat treatment and after heat treatment at (b) 600 °C, (c) 700 °C, (d) 800 °C, and (e) 900 °C for 50 h[5].

Fig.2.9 Differentiated Auger electron spectra of the (a) LaMLL, (b)SrLMM, (c) CoLMM, (d) FeLMM, and (e) OkLL before (blue solid line) and after (red dotted line) heat treatment at 800 °C for 50 h[5].

Some researchers also studied the deteriorated behavior at interface of LSCF with rare doped ceria electrolytes (RDC, M₀.₂Ce₀.₈O₁.₉, M=Gd, La). For instance, it is known that RDC was used as the interlayer between LSCF and YSZ in order to prevent the La₂Zr₂O₇ formation. Natsuko Sakai [85] studied the effect of RDC on the long term reliability of SOFC performance and a secondary phase was also formed at the interface due to the reaction of rare earth element with the transition metals in cathodes. In addition, transition metals (Co, Fe) as well as Sr can also diffuse from LSCF to ceria electrolytes. This entire phenomenon can strongly affect the stability of
impurity phase, diffusion in ceria and the degradation of LSCF cathodes as well. Recent years, Yihui Liu [7] investigated the degradation for impregnated LSCF-YSZ for SOFC operating at 750 °C up to 120 h and found that the cathode polarization resistance increased after long time test. In addition, the microstructural of LSCF particles changed from well-connected shape to dispersive and flattened shape that leaded to the degradation of cathodes. AFM technique was used to demonstrate the microstructure change of impregnated LSCF-YSZ cathodes (Fig.2-11). It shows that the surface diffusion of atoms in the LSCF cathode happened after high temperature heat treatment to reduce the overall energy of LSCF. Yihui Liu [86] also did extensive study on understanding the degradation mechanism of LSCF as LSCF impregnated GDC cathodes at 750 °C for 120 h. there was obvious grain growth of LSCF and GDC-LSCF cathodes; SrCoOₓ particles can be detected on LSCF surface under polarization that could contribute to the deterioration of LSCF cathodes.

![Fig.2. 10 AFM images of the LSCF+YSZ cathodes: (a) As-prepared, (b) tested for 120 h at 750 °C [7].](image)

2.5 Remarks and perspectives

Solid oxide fuel cells (SOFCs) operating at 600-800 °C is much more fuel flexible and can be applied into many areas that has been investigated for decades. The most essential challenges for the application for SOFC are the durability. In the past few years, there are many studies on
understanding the degradation mechanism of SOFC cathode side and trying to solve the deterioration issue. The effect of different contaminations on the degradation of SOFC cathodes was reviewed. Among all the contaminants, Cr from the metallic interconnects materials leading to the poisoning of SOFC cathodes is most widely known and extensively studied. The mechanism of Cr deposition and poisoning on traditional LSM, LSCF cathodes were proposed and researchers have clearly identified Cr poisoning is a chemical reaction. The effect of temperature, oxygen partial pressure and current density on Cr poisoning of SOFC cathodes were also investigated and reviewed.

Some recent studies on durability of SOFC stacks under real operation environment have indicated that sulfur, most likely from the air stream can accumulate at the cathode side, contaminate and degrade the cell performance. Researchers did study on understanding the sulfur poisoning mechanism of SOFC cathode by investigating the current density, the sulfur content and operating temperature on the degradation performance. Although there are many works of sulfur contamination on SOFC cathode, these works are rather scattered, there is no fundamental study on chemical reactivity between SO₂ and cathode materials, and there is a lack of systematic work on the operating temperature, SO₂ concentration on the initial electrochemical performance of cathode materials. However, these works are essential to understand sulfur contamination on cathode which is worthy of dedicated investigation. Hence, understanding the sulfur deposition and poisoning mechanism of traditional LSM and LSCF cathode materials will be quite meaningful for the real application of SOFC.
Chapter 3: Experimental

3.1 Materials and electrode sample preparation

LSCF powders (Fuel Cell Materials) were pressed into a rectangular bar at 300 MPa, and then fired at 1350 °C for 5 h in air to form dense LSCF bar samples with the dimension of 25 mm × 6.6 mm × 0.62 mm. LSCF bar sample and Cr$_2$O$_3$ powder alumina boat were placed side by side in a close-end quartz tube in a furnace and there was no direct contact between the LSCF bar samples and Cr$_2$O$_3$ powder. Bar samples were treated at different temperatures from 900 °C to 700 °C in the presence and absence of Cr$_2$O$_3$ for the sake of investigating the surface segregation as well as chromium deposition on LSCF. For investigating sulfur poisoning effect on LSCF bar sample, the samples were placed side by side in a close-end quartz tube in a furnace. The sulfur deposition and poisoning experiments were carried out on dense LSCF bar samples by heat-treatment at temperatures from 900 to 400 °C in the presence and absence of 20 ppm SO$_2$ (20 ppm SO$_2$ in dry air). In the case of investigating Cr and S poisoning effect on LSCF bar sample, the samples were heat treated at temperatures from 900 °C to 600 °C in the presence and absence of Cr$_2$O$_3$ and 20 ppm SO$_2$ (SO$_2$ in N$_2$, BOC Ltd.).

Y$_2$O$_3$-ZrO$_2$ (YSZ) electrolyte pellets were prepared from 8 mol% Y$_2$O$_3$-doped ZrO$_2$ powder (Tosoh, Japan) by die pressing and sintered at 1450 °C for 5 h. The YSZ electrolyte was 0.5–0.9 mm thick and 20 mm in diameter. La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM, Fuel Cell Materials, USA) cathode ink was painted on the center of YSZ pellet and fired at 1100 °C for 2 h. The electrode area was 0.5 cm$^2$ and the electrode thickness was 20 µm.

Gd$_{0.1}$Ce$_{0.9}$O$_{1.95}$ (GDC) electrolyte pellets were prepared from Fuel Cell Materials, USA by die
pressing and sintered at 1450 °C for 5 h. The pellets were 0.5–0.9 mm in thickness and 19–20 mm in diameter. LSCF (Fuel Cell Materials, USA) cathode was applied onto the GDC pellets by slurry coating and sintered at 1050 °C for 2 h. The thickness of the LSCF electrodes was 20–30 µm and the geometric area was 0.5 cm².

3.2 Chemical reactivity

In order to understand the chemical reaction between Cr poisoning and LSCF cathode materials, it is more meaningful to use Cr₂O₃ and SrO raw powders to study the thermodynamic reaction rate. The chemical reactivity between Cr₂O₃ and SrO was studied by calcination of Cr₂O₃-SrO (mixed 50/50 in weight ratio) oxide couple at 700, 800 and 900 °C for 2h. For the same reason, the chemical reactivity between La₂O₃, SrO, Co₃O₄ and Fe₂O₃ oxides and sulfur was also investigated by calcination of the oxide powders at different temperatures (from 400 to 900 °C) in the presence of 20 ppm SO₂ for 2 h. More details will be introduced next.

3.3 ECR tests

The effect of contaminants on the electrochemical activity of LSCF cathodes can be conveniently assessed by the surface exchange and oxygen bulk diffusion properties. The electrical conductivity relaxation (ECR) is an effective technique to measure the bulk diffusion coefficient (D_chem) and chemical oxygen exchange coefficient (k_chem) of LSCF cathode because of the high sensitivity of electrical conductivity to changes in oxygen partial pressure and relatively simple experimental setup. The conductivity of LSCF bar samples was measured by a four-probe method using a system consisting of a Digital Multimeter (Keithley 2001) equipped with a
computer and a program written using the LBVIEW 8.5 software. Silver wires were used as the lead wires, which were attached to the Ag electrode using silver paste. The measurements were carried out at the temperatures of 700, 800 and 900 °C in the presence and absence of gaseous Cr species or in the presence of 20 ppm SO₂ with oxygen partial pressure changes from 0.05 bar to 0.21 bar in a quartz tube. For electrical conductivity relaxation measurement, LSCF bar samples were completely equilibrated at the atmosphere of P₀₂ = 0.02 bar and then the oxygen partial pressure was abruptly changed to 0.21 bar while recording the electrical conductivity of the LSCF bar samples with time until a new equilibrium was reached. The total gas flow rate was maintained at 100 ml min⁻¹ to ensure that the P₀₂ of the gas achieved equilibrium in no more than 20 s. The change in conductivity with time is plotted as \( \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} \), where \( \sigma(0) \), \( \sigma(t) \) and \( \sigma(\infty) \) denote the initial, time dependent and final conductivities, respectively. The electrical conductivity data of the bar samples were recorded as a function of time and the experimental data was fitted to the theoretical equations to calculate the oxygen surface exchange coefficients.

### 3.4 Characterization

A Pt counter electrode (Pt ink, Gwent Group of Companies, United Kingdom) was coated on the opposite surface of the electrolyte and fired at 800 °C. A Pt reference electrode was attached on the edge of the electrolyte. Pt mesh was placed on the surface of LSM or LSCF cathodes as the current collector. The cell was symmetrically placed between double alumina tubes. A glass seal was used for the cathode side for avoiding leakage of SO₂-air mixture gas. For LSM electrodes, the operation temperature for the cell tests was 700 °C and 800 °C, respectively. In the case of LSCF electrodes, the operation temperature for the cell tests was 600 °C, 700 °C and 800 °C,
respectively. During the cell tests, dry SO₂-containing air with SO₂ concentration of 1 and 10 ppm was supplied to the cathode.

Electrochemical performance and impedance responses were measured at 800 and 700 °C on a three-electrode cell, using a Gamry Reference 3000 Potentiostat. Impedance curves were recorded under open circuit with frequency range from 0.1 Hz to 100 kHz and the signal amplitude of 10 mV. The electrode was stabilized in air for 1 h before the electrochemical measurement. Electrode polarization resistance (Rₑ) was obtained by the differences between the high and low frequency intercepts, and electrode ohmic resistance (Rₒ) was obtained from the high frequency intercept. The cathodic polarization potential (Eₑₐ₉ₜ₉oₜ) was measured between LSM cathode and Pt reference electrode. Thus, the overpotential, η of the reaction on a LSM cathode can be obtained from the cathodic polarization current, j:

\[ E_{\text{Cathode}} = jR_\Omega + \eta \]  \hspace{1cm} (1)

The phase composition of LSCF bar samples was examined by XRD (D8 Advance, Bruker, Germany) and confocal laser Raman spectroscopy (WITec GmbH, Ulm Germany). Raman measurements were performed with a frequency-doubled NdYAG laser with an excitation wavelength of 532 nm and the 100x objective of the confocal microscope (Zeiss EC "Epiplan-Neofluar"; WD=0.31 mm). The system captures full Raman spectra at each pixel of an imaging area with an integration time of 50 ms. The spectra were corrected using a built-in background subtraction function of the system; images were re-calculated with the software’s analysis function.

Scanning electron microscopy and energy dispersive spectrometer using a Zesis EVO with 15 keV was used to observe the microstructure of the bar samples treated at different temperatures in
the presence and absence of Cr sources. The phases of the mixed oxide powders were checked by XRD.

The electrodes before and after the electrochemical tests were examined by scanning electron microscopy (SEM, NEON 40EsB) and energy dispersive X-ray analysis (EDX, INCA, Oxford, England). Epoxy resin was infiltrated under vacuum. A thin wafer sample was lifted out in a focused ion beam-SEM (FIB-SEM, FEI Quanta 200i 3D) and polished in another FIB-SEM (HI-TACHI MI4000L). Microstructure observation and elemental mapping analysis of the wafer sample were carried out using both HITACHIMI4000L and scanning electron microscopy (SEM, JEOL JEM-ARM200F, 200kV) equipped with energy dispersive X-ray spectroscopy (EDS) detectors.

XRD was used to examine the phase change of LSCF electrodes before and after the electrochemical tests. X-ray photoelectron spectroscopy (XPS) was also performed using a Kratos AXIS Ultra DLD instrument using monochromated Al Kα X-rays (energy 1486.7 eV). Pass energy of 40 eV was used for the core level spectra.

TOF-SIMS (ION-TOF GmbH, Münster, Germany) was then used to investigate the sulfur distribution in different LSCF cathodes in details. The measurement mode combined spectrum and fast imaging modes together. For the spectrum mode, analysis beam was 30 keV Bi⁺ with spot size (ca. 5 um), while for the fast imaging mode, analysis beam was 30 keV Bi⁺ with spot size (ca. 150 nm). Sputter beam was 2 keV Cs⁺ for two modes. The sulfur distribution in LSM cathode was examined by Nano SIMS (CAMECA, AMETEK, Inc., USA).
Chapter 4: Impact of temperature on Cr deposition and poisoning for LSCF cathode

(This Chapter is reproduced from paper titled “Effect of temperature on the chromium deposition and poisoning of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ cathodes of solid oxide fuel cells” published in Electrochimica Acta 139(2014)173-179).

4.1 Introduction

Lanthanum strontium cobalt ferrite, La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) is one of the most investigated and commonly used cathodes of intermediate temperature solid oxide fuel cells (IT-SOFCs) due to its high mixed electronics and ionic conductivities (MIEC) and high catalytic activity for O$_2$ reduction reaction in the temperature range 600 - 800 °C [87-90]. However, one of the main challenges for the practical application of LSCF cathodes is the durability of the electrode under SOFC operating conditions [91, 92]. It has been well known that strontium in LSCF tends to segregate to the cathode surface under the operating temperature of SOFCs and the segregation and formation of Sr-enriched layers could be a potential reason for the performance degradation of LSCF cathodes as reported in the literature [5, 91].

The durability of a SOFC cathode is also critically related to the deposition and poisoning of various contaminant species such as sulfur from the air stream [18], chromium from the chromia-forming metallic interconnect [93], silica originated from the electrode sintering process or from the raw materials [94], boron from the glass or ceramic-glass sealants [75]. Among various contaminants, chromium deposition and poisoning is probably the most investigated [95]. We studied in detail the mechanism of the deposition and poisoning of chromium species at the
cathodes of SOFCs including (La,Sr)MnO$_3$ (LSM) [93, 96], LSCF [97], (Ba,Sr)(Co,Fe)O$_3$ (BSCF) [98]. For the O$_2$ reduction reaction on LSCF electrodes, the deposition of Cr species preferentially takes place on the surface of LSCF electrode, forming SrCrO$_4$ and Cr$_2$O$_3$ phase. The preferential deposition of Cr species on the surface of the LSCF electrode is most likely due to the interaction between the segregated SrO and gaseous Cr species [97, 99].

In addition to the significant detrimental effect of water or humidity on the Cr deposition, the operating temperature is expected to have a significant effect on the kinetics of the chromium deposition as the partial pressure of gaseous chromium species as well as the Sr segregation is dependent of the temperature. Krumpelt et al. [38] studied the Cr deposition on LSM cathodes and showed that Cr deposited at the LSM/YSZ region is higher at 700 °C than that at 800 °C under the same polarization current for 500 h. On the other hand, we studied the Cr deposition at 200 mA cm$^{-2}$ for 20 h at 700-900 °C and SEM examination qualitatively shows that the amount of Cr at the interface decreases with the temperature. However, there appears no report on the effect of temperature on the Cr deposition on the LSCF cathodes. It is important to clarify the Cr deposition and poisoning processes on the O$_2$ reduction reaction on LSCF cathodes as a function of temperature under SOFC operating conditions.

The effect of contaminants on the electrochemical activity of LSCF cathodes can be conveniently assessed by the surface exchange and oxygen bulk diffusion properties. The electrical conductivity relaxation (ECR) is an effective technique to measure the bulk diffusion coefficient ($D_{chem}$) and chemical surface exchange coefficient ($k_{chem}$) of LSCF cathode because of the high sensitivity of electrical conductivity to changes in oxygen partial pressure and relatively simple experimental setup [100, 101]. However, ECR method is sensitive to the surface
microstructure and properties (such as grain size, density, etc.). For example, Cox-Galhotra et al.[102] reported that the $k_{\text{chem}}$ of LSCF with grain size of 1-3 µm is $2.0 \times 10^{-3}$ cm s$^{-1}$ at 800 °C. Hong et al. [103] showed that $k_{\text{chem}}$ of LSCF samples with grain size of 5-30 µm is $2.5 \times 10^{-5}$ cm s$^{-1}$ at 800 °C. Nevertheless, under identical experimental conditions, ECR is a good technique to assess the effect of contaminant or impurities on the surface properties of LSCF[104]. In this study, the effect of Cr deposition on the microstructure and electrochemical activity of LSCF cathodes for the O₂ reduction reaction at different temperatures is studied using ECR and confocal laser Raman spectroscopy.

4.2 Experimental

4.2.1 LSCF bar sample preparation

LSCF powders (Fuel Cell Materials) were pressed into a rectangular bar at 300 MPa, and then fired at 1350 °C for 5 h in air to form dense LSCF bar samples with the dimension of 25 mm × 6.6 mm × 0.62 mm. LSCF bar sample and Cr₂O₃ powder alumina boat were placed side by side in a close-end quartz tube in a furnace and there was no direct contact between the LSCF bar samples and Cr₂O₃ powder. Bar samples were treated at different temperatures from 900 °C to 700 °C in the presence and absence of Cr₂O₃ for the sake of investigating the surface segregation as well as chromium deposition on LSCF.

4.2.2 ECR tests

The conductivity of LSCF bar samples was measured by a four-probe method using a system consisting of a Digital Multimeter (Keithley 2001) equipped with a computer and a program
written using the LABVIEW 8.5 software. Silver wires were used as the lead wires, which were attached to the Ag electrode using silver paste. The measurements were carried out at the temperatures of 700, 800 and 900 °C in the presence and absence of gaseous Cr species with oxygen partial pressure changes from 0.05 bar to 0.21 bar in a quartz tube. The electrical conductivity data of the bar samples were recorded as a function of time and the experimental data was fitted to the theoretical equations [105] to calculate the oxygen surface exchange coefficients.

4.2.3 Characterizations

The phase composition of LSCF bar samples was examined by XRD (D8 Advance, Bruker, Germany) and confocal laser Raman spectroscopy (WITec GmbH, Ulm Germany). Raman measurements were performed with a frequency-doubled NdYAG laser with an excitation wavelength of 532 nm and the 100x objective of the confocal microscope (Zeiss EC "Epiplan-Neofluar"; WD=0.31 mm). The system captures full Raman spectra at each pixel of an imaging area with an integration time of 50 ms. The spectra were corrected using a built-in background subtraction function of the system; images were re-calculated with the software’s analysis function.

Scanning electron microscopy and energy dispersive spectrometer using a Zesis EVO with 15 keV was used to observe the microstructure of the bar samples treated at different temperatures in the presence and absence of Cr sources. The reactivity between Cr₂O₃ and SrO was studied by calcination of Cr₂O₃-SrO (mixed 50/50 in weight ratio) oxide couple at 700, 800 and 900 °C for 2h and the phased of the mixed oxide powders were also checked by XRD.
4.3 Results and Discussions

4.3.1 Effect of temperature on the phase of LSCF

Fig.4.1 XRD diffraction patterns of as-prepared LSCF and LSCF bar samples after heat-treatment in the presence of Cr$_2$O$_3$ at different temperatures for 48 h. a) fresh, b) 700˚C, c) 800˚C and d) 900˚C.

Fig.4.1 shows the XRD patterns of as-prepared LSCF as well as LSCF bar samples after heat-treatment in the presence of Cr$_2$O$_3$ at different temperatures for 48 h. The as-prepared LSCF shows XRD patterns typically associated with rhombohedral perovskite structure. After heat treatment at 700 and 800 ˚C in the presence of Cr$_2$O$_3$, there is no change in the XRD patterns, suggesting that the main phase is still the perovskite structure. However, for the LSCF bar sample treated at 900 ˚C in the presence of Cr$_2$O$_3$, small peak at 29˚ is clearly visible, which can be identified as the formation of SrCrO$_4$ [106]. This indicates the reaction between the gaseous Cr species and LSCF bar samples, resulting in the formation of second phase, SrCrO$_4$.

The reactivity between SrO and Cr$_2$O$_3$ was studied by heat treatment of the oxide couples at 700, 800, and 900 ˚C, for 2 h and results are shown in Fig.4.2. In the case of SrO/Cr$_2$O$_3$ oxide couple, XRD peaks belonging to the SrCrO$_4$ phase were observed after the heat-treatment at 700-900 ˚C. The XRD results indicate that SrO is very active with Cr$_2$O$_3$, forming SrCrO$_4$ phase in
the temperature range studied.

![XRD diffraction patterns of SrO-Cr2O3 oxide couple after heat-treatment](image)

Fig. 4.2 XRD diffraction patterns of SrO-Cr2O3 oxide couple after heat-treatment at a) 700 °C, b) 800 °C and c) 900 °C in air for 2 h.

4.3.2 Effect of temperature on the microstructure of LSCF

Fig.4.3 shows the SEM micrographs of the surface of the LSCF samples after the heat treatment in the absence and presence of Cr2O3 in air at 900, 800 and 700 °C for 48 h. The surface of the as-prepared LSCF sample is relatively dense and smooth and the grain size is in the range of 2-5 µm (Fig.4.3g). The large grain size of the LSCF is most likely due to the high sintering temperature (1350 °C for 5 h). There are some clear and visible changes in the surface morphology of LSCF bar samples after heat treatment in the absence of Cr2O3 atmosphere, indicated by the formation of isolated small particles on the LSCF surface (Fig.4. 3a-c). More specifically, for the LSCF samples treated at 900 °C for 48 h, particles as large as 2 µm were formed (Fig.4.3a) and the formation of such large particles is most likely due to the segregated strontium and/or cobalt species [99]. As the temperature decreases, the size of the segregated particles decreases significantly (0.1-0.3 µm, Fig.4.3b and c), indicating that the surface segregation decreases significantly with the temperature. These results are in accordance with the reported strontium
segregates and surface morphological behavior of LSCF samples after heat-treatment from 600 °C to 900 °C [62].

After the heat-treatment in the presence of Cr₂O₃ in air for 48 h, there is a significant increase in both the size and number of segregated particles on the LSCF surface (Fig.4.3d-f). In the case of LSCF samples treated at 900 °C in the presence of Cr₂O₃, the size of deposited particles is as large as 3 µm (Fig.4.3d). There is also significant increase in the surface roughness. This indicates that gaseous Cr species from Cr₂O₃ is detrimental to the microstructure and morphology of LSCF. Nevertheless, the size and number of these segregated particles becomes smaller with the decrease of temperature (Fig.4.3e and f), similar to that observed in the absence of Cr₂O₃. This indicates that the deposition of Cr species on the segregated particles is related to the temperature. As the temperature decreases, the partial pressure of gaseous chromium species decreases significantly [33, 106]. As shown in Fig.4.3a-c, the surface segregation of Sr and/or Co also decreases significantly with the decrease of temperature. The reduction in operation temperature can significantly slow the deposition process of chromium species on LSCF cathodes.

The formation of segregated particles on the surface of LSCF bar samples was further investigated using confocal Raman spectroscopy. For the as-prepared LSCF samples, the surface is dense, clean and Raman spectrum of the LSCF surface is featureless (see Fig.4.4) as the near-cubic perovskite phase of LSCF has little Raman activity.

Fig.4.5a-c is the optical microscopy images and Raman spectra of the LSCF surface after heat treatment at 900 °C in the presence of Cr₂O₃ for 48 h. The formation of segregated particles can be clearly observed (circled particles, Fig.4.5a). The bright yellow colored areas in the Raman mapping with wavelength of 863 cm⁻¹ (Fig.4.5b) are due to the formation of SrCrO₄ [107]. This is
Fig. 4.3 SEM micrographs of LSCF surface after heat-treatment for 48 h in the absence (a, b, c) and presence (d, e, f) of Cr₂O₃ at different temperatures. (a,d) 900 °C, (b,e) 800 °C and (c,f) 700 °C. The as-prepared LSCF is shown in (g).

Fig. 4.4 (a) Optical microscope images of as-prepared LSCF surface and (b) corresponding Raman spectra from the selected area on LSCF surface.

also supported by the detection of characteristic Raman peaks with wavelength of 863 and 892
cm$^{-1}$ on the LSCF bar samples (Fig.4.5c). Zhang et al.[108] used confocal Raman spectroscopy to study the strontium chromate pigment in coatings and observed two Raman bands for SrCrO$_4$ at 863 and 892 cm$^{-1}$. Based on Raman mapping (Fig.4.5b), majority of the particles formed on the surface of LSCF bar samples belong to the SrCrO$_4$ oxides.

Fig.4.5 Optical microscope image of LSCF surface (left), Raman mapping at wavelength of 863 cm$^{-1}$ (middle), corresponding to SrCrO$_4$ phase collected from the same area of optical microscope image and Raman spectra from selected particles on the LSCF surface(right). LSCF bar samples were heat-treated at (a,b,c) 900 °C, (d,e,f) 800 °C and (g,h,i) 700 °C in the presence of Cr$_2$O$_3$ for 48 h.

As the temperature decreases to 800 and 700 °C, the formation of SrCrO$_4$ occurs along the grain boundaries and the density or the number of bright yellow colored areas (i.e., SrCrO$_4$ phase) in general decrease (Fig.4.5d,e and Fig.4.5g,h). Although SrCrO$_4$ phase was not detected at 800
and 700 °C by XRD (Fig.4.1), the formation of the SrCrO₄ particles is identified by the Raman spectroscopy at these temperatures. The characteristic Raman band with wavelength of 863 cm⁻¹ is clearly visible with reduced intensity for the Raman band at 892 cm⁻¹ on the LSCF bar samples heat-treated at 800 and 700 °C (Fig.4.5f and i). The observation of Raman characteristic peak due to the formation of the SrCrO₄ particles on the LSCF surface is consistent with the reports of the observation of SrCrO₄ on the surface of LSCF electrode [97, 109]. The observation of SrCrO₄ also suggests that the Cr deposition on LSCF preferentially takes place on segregated SrO in the temperature range of the present study. The detection of SrCrO₄ phase by the Raman spectroscopy and not by XRD at temperatures of 800 and 700 °C indicates the high sensitivity of Raman spectroscopy techniques in the study of Cr deposition on LSCF electrode system, particularly in the cases where the quantities of the secondary phase are very small.

4.3.3 Effect of temperature on the oxygen exchange coefficient

Fig.4.6 is the electrical conductivity relaxation profiles of LSCF samples measured at different temperatures as a function of exposure time in the absence and presence of Cr₂O₃. Oxygen partial pressure changes from 0.05 bar to 0.21 bar. Variation of oxygen partial pressure in the ambient atmosphere leads to a change in the oxygen vacancy as well as the charge carrier concentration of the MIEC material, and this can be reflected as a relaxation of the apparent macroscopic electrical conductivity [102, 104, 110]. The initial relaxation time of LSCF bar samples measured at 900, 800 and 700 °C in the absence of Cr₂O₃ was 400, 1000, and 2000 s, respectively (Fig.4.6a-c). The change in the relaxation time is relatively small for the LSCF bar samples in the absence of Cr₂O₃. In the case of the electrical conductivity relaxation profiles of
LSCF samples measured in the presence of Cr$_2$O$_3$, the relaxation time increases significantly with the increase in the exposure time for LSCF samples (Fig.4.6d-f). For example, the relaxation time increased from 700 to 2500 s after being exposed to Cr$_2$O$_3$ for 48h at 900 °C (Fig.4.6d), and it increased from 1700 s to over 25,000 s after the heat-treatment at 700 °C for 48 h (Fig.4.6f). The significant increase in the relaxation time implies the reduction in the oxygen reduction kinetic after the exposure to chromium source evidently due to the chromium deposition and poisoning.

These results are consistent with the SEM results.

Table 4-1. The Oxygen exchange coefficient ($k_{chem}$) obtained by the experimental fitting at different temperatures as a function of exposure time.

<table>
<thead>
<tr>
<th>Time</th>
<th>$a_k_{chem}/ \times 10^{-3}$ cm.s$^{-1}$</th>
<th>$b_k_{chem}/ \times 10^{-3}$ cm.s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature</td>
<td>Temperature</td>
</tr>
<tr>
<td>900 °C</td>
<td>800 °C</td>
<td>700 °C</td>
</tr>
<tr>
<td>0 h</td>
<td>6.0</td>
<td>0.50</td>
</tr>
<tr>
<td>12 h</td>
<td>5.0</td>
<td>0.40</td>
</tr>
<tr>
<td>24 h</td>
<td>4.0</td>
<td>0.30</td>
</tr>
<tr>
<td>48 h</td>
<td>3.0</td>
<td>0.20</td>
</tr>
</tbody>
</table>

$^a$ in the absence of Cr$_2$O$_3$;
$^b$ in the presence of Cr$_2$O$_3$.

The $k_{chem}$ values obtained by the experimental fitting at different temperatures as a function of exposure time are given in Table 4-1. The initial $k_{chem}$ of as-prepared LSCF is $6 \times 10^{-3}$, $5 \times 10^{-4}$ and $2 \times 10^{-4}$ cm.s$^{-1}$ at 900, 800 and 700 °C, respectively, and decreases slightly with the heat-treatment time in the absence of Cr$_2$O$_3$. The small decrease in $k_{chem}$ may be due to the surface segregation and formation of isolated particles on the LSCF surface as shown by SEM analysis. On the other hand, the decrease of $k_{chem}$ from $6 \times 10^{-3}$ cm.s$^{-1}$ measured at 900 °C to $2 \times 10^{-4}$ cm.s$^{-1}$ measured at 700 °C indicates that the kinetics of the surface diffusion of oxygen species becomes much slower as the temperature decreases. Very different from that in the absence of Cr$_2$O$_3$, $k_{chem}$ decreased rather quickly after the heat-treatment in the presence of Cr$_2$O$_3$. The $k_{chem}$ value is $1.5 \times 10^{-4}$, $1 \times 10^{-4}$.
and $4 \times 10^{-5}$ cm s$^{-1}$ at 900, 800 and 700 $^\circ$C in the presence of gaseous Cr species for 48 h, respectively. The relative decrease in $k_{chem}$ (i.e. the ratio of reduction in $k_{chem}$ to initial $k_{chem}$ value) is in the range of 70-75% in the temperature range studied. The significant reduction in $k_{chem}$ is clearly related to the deposition and formation of SrCrO$_4$ on the surface of LSCF.

![Graphs showing electrical conductivity relaxation profiles](image)

Fig.4.6 Electrical conductivity relaxation profiles as a function of heat-treatment time on LSCF in the (a, b, c) absence and (d, e, f) presence of Cr$_2$O$_3$ at (a, d) 900 $^\circ$C, (b, e) 800 $^\circ$C and (c, f) 700 $^\circ$C.

4.4 Conclusions

LSCF bar samples were used to investigate the effect of temperature on the surface segregation and deposition and poisoning of Cr. The SEM and Confocal laser Raman spectroscopy shows that there is clear change in the microstructure and the formation of SrCrO$_4$
particles on the surface of LSCF was clearly identified after the samples were exposed to Cr$_2$O$_3$-containing atmosphere at different temperatures for 48 h. The present study demonstrates that the temperature has a significant effect on the Sr segregation, Cr deposition and formation of SrCrO$_4$ phase on the LSCF surface. Decrease in the operating temperature significantly reduced the segregated SrO and partial pressure of gaseous Cr species, leading to the significant reduction in Cr deposition. There is close correlation between the strontium segregation and chromium deposition on the LSCF surface as a function of temperature. Oxygen exchange coefficients of LSCF after being exposed to Cr$_2$O$_3$ are also significantly lower than that in the absence of Cr$_2$O$_3$ as a result of the Cr deposition and formation of SrCrO$_4$.

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5.1 Introduction

Sulfur is one of the major contaminants in SOFCs. For example, one of the major challenges for the direct use of hydrocarbon fuels in SOFCs is the poisoning of Ni-based anodes by sulfur existed as impurities in readily available hydrocarbon fuels [54, 55]. The presence of H$_2$S degrades the performance of the Ni-based anodes such as Ni/Y$_2$O$_3$-ZrO$_2$ (Ni/YSZ) and Ni/Gd$_2$O$_3$-CeO$_2$ (Ni/GDC) cermet anodes [56-58]. Sulfur in the air stream can also affect significantly the performance and durability of SOFCs [51, 52, 59]. One possible source of sulfur contamination is the sulfur from a trace amount of SO$_x$ in air, which could be accumulated by reacting with cathode in the vicinity of the air entrance of the cells. In contrast with the extensive studies on the mechanism and kinetics of the deposition and poisoning of sulfur on the anodes of SOFCs [59], much less attention has been paid on the sulfur deposition and poisoning on the cathode materials. Understanding the SO$_2$ poisoning mechanism is critical to develop contaminant-tolerant and durable cathodes for SOFCs.

Xiong et al. studied the polarization behavior of (La$_{0.85}$Sr$_{0.15}$)$_{0.95}$MnO$_3$ (LSM) and Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ (SSC) cathodes after the heat-treatment of the electrodes to 100 ppm SO$_2$ at 800 °C and found that the performance of SSC declined rapidly while LSM was more stable in
SO$_2$-contained air [52]. The significant difference in the polarization performance of SSC and LSM in SO$_2$-contained air for the O$_2$ reduction reaction has been explained by the difference in the activity of SrO in the LSM and SSC perovskites. Liu et al. [50] showed that the performance of cells with La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF) electrode becomes unstable in the presence of 1 ppm SO$_2$ and drops significantly when the SO$_2$ concentration increased to 20 ppm. The performance degradation is most likely due the poisoning of SO$_2$ and the formation of SrSO$_4$. Sitte et al. measured the surface exchange kinetics of a dense La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ sample at 700°C and observed the decreases in the surface exchange coefficient, $k_{chem}$ with the presence of a small amount of sulfur (ppb) [67]. Ishihara et al. [63] reported that the degradation of LSCF is accelerated at low partial pressure of O$_2$ in the presence of sulfur and the degradation is considered to be caused by the Sr segregation and the subsequent formation of SrSO$_4$. On the other hand, Wang et al. [64] studied the polarization performance behavior of LSCF in the presence of 0.1 ppm SO$_2$ and two-stages of performance degradation were found. A degradation mechanism based on the occupation of SO$_2$ in the oxide ion vacancies and subsequent formation of SO$_3^{2-}$ and SrSO$_4$ was proposed for the irreversible poisoning effect of SO$_2$. However, there appears no consensus on the mechanism and kinetics of the deposition and poisoning of sulfur on SOFC cathodes such as LSCF.

In this study, the deposition and poisoning of sulfur on the microstructure and surface diffusion properties of LSCF cathode materials is investigated in the temperature range of 900 – 400 °C on dense bar samples in air using confocal Raman spectroscopy, scanning electron microscopy as well as electrical conductivity relaxation (ECR) methods. Use of dense bar samples would facilitate the observations of microstructure changes and surface property characterizations.
The results indicate the deposition of sulfur species on the LSCF surface and formation of SrSO₄ depends strongly on the temperature. Sulfur deposition and poisoning becomes most pronounced at temperatures around 700 °C.

5.2 Experimental

5.2.1 LSCF bar sample preparation

The procedure of preparing LSCF sintered bar samples was the same as the experimental procedure in Chapter 4. While LSCF bar sample were placed side by side in a close-end quartz tube in a furnace. The sulfur deposition and poisoning experiments were carried out on dense LSCF bar samples by heat-treatment at temperatures from 900 to 400 °C in the presence and absence of 20 ppm SO₂ (20 ppm SO₂ in dry air).

5.2.2 Chemical reactivity

The chemical reactivity between La₂O₃, SrO, Co₃O₄ and Fe₂O₃ oxides and sulfur was investigated by calcination of the oxide powders at different temperatures in the presence of 20 ppm SO₂ for 2 h.

5.2.3 ECR tests

The procedure of testing the electrical conductivity relaxation curves of LSCF bar samples in the presence of 20 ppm SO₂ from 900 to 700 °C was the same as the experiment procedure in Chapter 3. However, the samples that were heat treated at temperatures from 600 to 400 °C in the presence of 20 ppm SO₂ were not evaluated by ECR due to the very low conductivity value of the
LSCF samples at these low temperatures.

5.2.4 Characterizations

XRD (D8 Advance, Bruker, Germany) and confocal laser Raman spectroscopy (WITec GmbH, Ulm Germany) techniques were also used to examine the phase formation and composition of oxides and LSCF bar samples. The morphology and microstructure of the bar samples after the heat-treatment at different temperatures in the presence and absence of 20 ppm SO2 were studied by scanning electron microscopy (SEM) and energy dispersive spectroscopy using a Zesis EVO with 20 keV.

5.3 Results

5.3.1 Effect of temperature on the phase of LSCF

Fig.5.1 is the XRD patterns of LSCF bar samples after heat-treatment in the presence of 20 ppm SO2 at different temperatures for 48 h. The as-prepared LSCF shows typical XRD patterns associated with rhombohedral perovskite structure. After heat treatment at 800 and 900 °C in the presence of 20 ppm SO2, XRD patterns of LSCF remained the same, suggesting that the main phase is the perovskite structure. However, prominent XRD peaks associated with the formation of SrSO4 phase [112] were observed for the LSCF bar sample treated at 700 °C in the presence of 20 ppm SO2 (curve d, Fig.5.1). This indicates the reaction between the SO2 and LSCF bar samples, forming SrSO4 phase. As the heat-treatment temperatures decreased to 600 °C-400 °C, a distinct peak at 29.5° was detected, which is associated with the formation of SrS phase [113]. The XRD results indicate that the formation of the SrSO4 is most favorable at a temperature of ~700 °C,
while the formation of SrS occurs at temperatures below 700 °C.

![XRD diffraction patterns](image)

**Fig.5.1** XRD diffraction patterns of freshly-prepared LSCF and LSCF bar samples after heat-treatment in the presence of 20 ppm SO₂ at different temperatures for 48 h. a) as-prepared, b) 900 °C, c) 800 °C, d) 700 °C, e) 600 °C, f) 500 °C, and g) 400 °C.

### 5.3.2 Effect of temperature on the microstructure of LSCF

Fig.5.2 is the SEM micrographs of the surface of the LSCF bar samples after heat treatment in the absence and presence of 20 ppm SO₂ in air at different temperatures for 48 h. As shown previously, the surface of as-prepared LSCF sample is characterized by the dense LSCF grains with smooth surface and the grain size is in the range of 2-5 µm [104]. After heat treatment in the absence of SO₂, there is a clear formation of isolated small particles on the LSCF surface (Fig.5.2A). For LSCF samples treated at 900 °C for 48 h, particles as large as 2 µm are formed (Fig.5.2a) and the formation of such particles is most likely due to the segregated cobalt and in particular strontium species [114]. With the decrease in the temperature, the size and number of the segregated particles are reduced significantly. In the case of the LSCF bar sample heat-treated at 400 °C for 48 h, the surface is very clean (Fig.5.2k), similar to that of as-prepared LSCF sample.
These results are in accordance with the surface morphological behavior of LSCF samples after heat-treatment from 600 °C to 900 °C as reported by Oh et al. [5] and Bucher et al [92]. The significant reduction in the segregated particles indicates that the strontium and/or cobalt segregation on the LSCF electrode is kinetically controlled by the temperature.

Very different from that in the absence of SO₂, the size and number of particles formed on the LSCF surface varied significantly with the temperature (Fig.5.2B). For the LSCF sample heat-treated at 900 °C in the presence of SO₂ for 48 h, there is a formation of large number of small (~80 nm) and large (~700 nm) particles and the formation of the particles appears to be random on both the grain boundaries and the surface of LSCF grains (Fig.5b). Significant deposition and formation of large and small particles were also observed for the LSCF bar sample heat-treated at 800 °C (Fig.5.2d). However, the most remarkable formation of particles was observed for the LSCF after heat-treatment in the presence of SO₂ at 700 °C (Fig.5.2f). The surface of LSCF sample is almost completely covered by the particles formed on the surface of LSCF grains. The particles formed on the LSCF surface were most likely strontium sulfate, SrSO₄, indicated by the prominent phase formation of SrSO₄ as detected by XRD (Fig.5.1). When the temperature decreased to 600 °C, the numbers of the particles formed on the LSCF surface decreased substantially with few isolated large particles (400 nm) and numerous fine particles (35 nm) (Fig.5.2h). As the temperature is reduced to 400 °C, the surface of LSCF bar sample is very clean (Fig.5.2l), similar to that in the absence of SO₂ (Fig.5.2k). This indicates the significantly reduced activity between the SO₂ and LSCF at temperatures below 700 °C.

Fig5.3 is the enlarged micrographs of the deposited particles formed at 700 °C, taking on different LSCF bar samples. The deposited particles are characterized by smooth surface without
clear crystalline facets (Fig. 5.3b and c). The size of these particles is in the range of 0.5 to 5 µm, much larger than the particles formed at 800 and 900 °C. EDX analysis indicates that the particles

(A) In the absence of SO$_2$  
(B) In the presence of SO$_2$
Fig. 5.2 SEM micrographs of LSCF surface after heat-treatment for 48 h (A) in the absence of 20 ppm SO₂ and (B) in the presence of SO₂ at (a,b) 900 °C, (c,d) 800 °C, (e,f) 700 °C, (g,h) 600 °C, (i,j) 500 °C and (k,l) 400 °C.

Fig. 5.3 Representative SEM micrographs of LSCF bar samples after heat-treatment in the presence of 20 ppm SO₂ at 700 °C for 48 h taken in different areas. EDX of deposited particles is shown in (d).

are enrichment of the Sr and S (Fig. 5.3d) with atomic ratio of 1:1, consistent with the SrSO₄ phase as identified by XRD.

The phase of the deposited particles on the surface of LSCF bar samples was further investigated using confocal Raman spectroscopy. Fig. 5.4 is the optical microscopy images and Raman spectra of the LSCF surface after heat treatment at 900 and 800 °C in the presence of 20 ppm SO₂ for 48 h. The formation of irregular particles can be clearly observed. SrSO₄ has a
characteristic Raman adsorption peak at 450, 600 and 1000 cm\(^{-1}\), consistent with that reported in [112]. The bright yellow-colored areas in the Raman mapping with wavelength of 1000 cm\(^{-1}\) are due to the formation of SrSO\(_4\) [115]. For the reaction at 900 °C, there were formations of large number of small particles along the grain boundaries and based on Raman mapping (Fig.5.4A), majority of the particles in the optical microscopy images belonged to the SrSO\(_4\) oxides. As the temperature decreased to 800 °C, formation of SrSO\(_4\) was also clearly identified (Fig.5.4B), similar to that observed for the LSCF bar samples at 900 °C. The Raman mapping results evidently show the formation of SrSO\(_4\) on the LSCF surface after the heat-treatment in the presence of 20 ppm SO\(_2\) at 800 and 900 °C. The detection of SrSO\(_4\) phase by the Raman spectroscopy and not by XRD also indicates the high sensitivity of Raman spectroscopy techniques in the study of sulfur poisoning on LSCF electrode system, particularly in the cases where the quantities of the secondary phase are very small.

Fig.5.4 (Left) Optical microscope images of LSCF surface after heat treatment in the presence of 20ppm SO\(_2\), (middle) Raman mapping at wavelength of 1000 cm\(^{-1}\) corresponding to SrSO\(_4\) and (right) Raman spectra from selected areas of LSCF surface. The heat treatment temperature of the LSCF bar samples was (A) 900 °C and (B) 800 °C.

As the temperature decreased to the range of 600-400 °C, number of particles observed on the
surface of the bar samples decreased significantly (Fig. 5.5). The Raman spectra taken on the surface of LSCF samples after heat-treatment at 600, 500 and 400 °C in the presence of 20 ppm SO₂ were similar and no characteristic peaks at 450, 600 and 1000 cm⁻¹ for SrSO₄ were observed (Fig. 5.5d). No other Raman peak was observed most likely due to the little Raman activity of near-cubic perovskite phase of LSCF and the face-centered cubic structure of SrS [113]. Both Raman and XRD results indicate that reactivity between the LSCF and SO₂ at temperatures below 700 °C to form SrSO₄ would be very low or negligible. Nevertheless, the detection of SrS by XRD (see Fig. 5.1) clearly indicates that SrS has been formed at temperatures below 700 °C.

Fig. 5.5 Optical microscope images of LSCF surface after heat treatment at 600 °C, 500 °C and 400 °C in the presence of 20 ppm SO₂ (a) Raman spectra from selected areas of the LSCF surface.

The clear observation of SrSO₄ and SrS sulfur-containing compounds by XRD, SEM and Raman studies suggest that the sulfur deposition on LSCF depends strongly on the temperature and the reaction with SO₂ is most pronounced at temperatures around 700 °C.
5.3.3 Activity of constituent oxides of LSCF with SO₂

The reactivity between the constituent oxides of LSCF and SO₂ was studied by heat-treatment of La₂O₃, SrO, Co₃O₄ and Fe₂O₃ oxide powders at 900, 800, 700, 600, 500 and 400 °C for 2 h in the presence of 20 ppm SO₂ and the XRD patterns of oxides after the treatment are

![XRD patterns of (a) La₂O₃, (b) SrO, (c) Co₃O₄ and (d) Fe₂O₃ after heat-treatment at different temperatures in the presence of 20 ppm SO₂ for 2 h. The numbers in the figure indicate the temperature: 4-400 °C, 5-500 °C, 6-600 °C, 7-700 °C, 8-800 °C and 9-900 °C.](image)

Table 5-1. Reaction products of SrO heat-treated at different temperatures in the presence of 20 ppm SO₂ for 2 h.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>SrSO₄</th>
<th>SrCO₃</th>
<th>Sr(OH)₂</th>
<th>SrSO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>√</td>
<td>√</td>
<td>√</td>
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<tr>
<td>700</td>
<td>√</td>
<td></td>
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<td></td>
</tr>
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<td>600</td>
<td>√</td>
<td>√</td>
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<td>√</td>
</tr>
<tr>
<td>500</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
shown in Fig. 5.6. In the case of SrO, the major phase was SrCO$_3$ and Sr(OH)$_2$ formed in the temperature range studied, probably due to the facile reaction of SrO with CO$_2$ and H$_2$O in the air. However, distinctive SrSO$_4$ peaks were detected between 900 to 700 °C and SrSO$_3$ peaks between 600 to 400 °C. The phases formed for the SrO-SO$_2$ oxide couples are summarized in Table 5-1. According to the literature, La$_2$O$_3$ is reactive with SO$_2$ to form La$_2$(SO$_4$)$_3$ in the temperatures lower than 237 °C [116], while Fe$_2$O$_3$ can react with SO$_2$ in the temperature range of 100 to 750 °C but Fe$_2$(SO$_4$)$_3$ could decompose above 600 °C [117]. Zhao et al. [118] showed that Co$_3$O$_4$ reacted with SO$_2$ at 300 °C. However, under the conditions of this study, no additional peaks or new phases were observed for the reaction between La$_2$O$_3$, Co$_3$O$_4$ and Fe$_2$O$_3$ oxides and SO$_2$ (Fig. 5.6b-d). The results indicate that SrO is most reactive with SO$_2$, while the activity of La$_2$O$_3$, Co$_3$O$_4$ and Fe$_2$O$_3$ oxides with SO$_2$ is very low.

### 5.3.4 Effect of temperature on the oxygen exchange coefficient

Fig. 5.7 is the electrical conductivity relaxation profiles of LSCF samples measured at 900, 800 and 700 °C as a function of exposure time in the absence and presence of 20 ppm SO$_2$. Oxygen partial pressure changes from 0.05 bar to 0.21 bar. In the absence of SO$_2$, the initial relaxation time is around 400 s, 1000 s, 2000 s, respectively (Fig. 5.7a-c). The initial oxygen exchange coefficients, $k_{chem}$ of as-prepared LSCF measured in the absence of SO$_2$ is $6 \times 10^{-3}$, $5 \times 10^{-4}$ and $2 \times 10^{-4}$ cm s$^{-1}$ at 900, 800 and 700 °C, respectively, and decreased slightly with the heat-treatment time in the absence of SO$_2$. The small decrease in $k_{chem}$ might be due to the surface segregation of isolated particles on the LSCF surface as shown by SEM analysis (Fig. 5.2A). However, the relaxation time increases with the exposure time for LSCF samples in the presence
of SO₂. For example, the relaxation time increased from 1500 s to 3500 s after exposed to SO₂ from 3 h to 48 h at 900 °C (Fig.5.7d), while the relaxation time increased from 10000 s to 20000 s after exposed to SO₂ from 3 h to 48 h at 800 °C. Similar trend was also observed for the samples heat-treated at 700 °C, the relaxation time increased from 8000 s to 18000 s (Fig.5.7f).

In the presence of 20 ppm SO₂, $k_{chem}$ decreased rather quickly. After the exposure to the sulfur for 48 h, the $k_{chem}$ of LSCF at 900 °C, 800 °C and 700 °C is $9 \times 10^{-5}$, $8 \times 10^{-6}$ and $2 \times 10^{-6}$ cm s⁻¹, respectively, two orders of magnitude lower than that of the freshly-prepared LSCF. The significant reduction in $k_{chem}$ is clearly related to the sulfur poisoning and formation of SrSO₄ on the surface of LSCF cathode materials. As compared to the chromium and boron poisoning, sulfur poisoning is also very significant on the surface exchange properties of the LSCF cathodes. For example, at 800 °C, $k_{chem}$ of LSCF after the heat-treatment in the presence of 20 ppm SO₂ for 48 h is $8 \times 10^{-6}$ cm s⁻¹, significantly lower than $1.0 \times 10^{-6}$ cm s⁻¹ and $6 \times 10^{-5}$ cm s⁻¹ measured after the heat-treatment in the presence of Cr₂O₃ and borosilicate glass for 48 h [104].
Fig. 5.7 Electrical conductivity relaxation profiles of LSCF bar samples as a function of exposure time in the (a,b,c) absence and (d,e,f) presence of 20 ppm SO₂ at (a,d) 900 °C, (b,e) 800 °C, and (c,f) 700 °C.

5.4 Discussions

The most significant finding of the study is the unusual dependence of the sulfur deposition or reaction with LSCF bar samples on temperature. As shown in Fig. 5.2A, the Sr segregation of the LSCF decreased with the decrease of temperature, consistent with that reported in the literature [5, 92]. Very different from the significant reduction in the surface segregated Sr particles, the sulfur deposition occurred most significantly at temperatures around 700 °C (Fig. 5.2f). The apparent inconsistent relationship between the Sr segregation and sulfur deposition, i.e., the amount of sulfur-containing compounds/particles formed on the LSCF surface can be semi-quantitatively evaluated, as shown in Fig. 5.8. In the figure, the degree or magnitude of the Sr surface segregation and sulfur deposition was estimated by measuring the occupied areas of the segregated particles and areas of sulfur-containing compounds/particles formed on the surface of LSCF bar samples. The occupied areas of particles on the surface were obtained by counting the individual particles per unit area based on the SEM images (similar to that shown in Fig. 5.2). The areas of the segregated Sr/Co particles on the LSCF surface decreased with the temperature, as expected, however, the areas of sulfur-containing particles shows a reversed V-shape dependence on the
temperature. The areas of the sulfur-containing particles increase with temperature from 900 to 700 °C and then decrease very quickly when the temperature decreases from 600 to 400 °C.

In the study of the chromium deposition on LSCF cathode, it is well known that the deposition of Cr species occurs preferentially on the surface of the LSCF cathode and at the LSCF cathode and metallic interconnect interface rather than at the cathode/electrolyte interface, forming primarily SrCrO$_4$ [34, 97, 109, 119, 120]. The interaction between the SrO and gaseous Cr species would lead to the formation of Sr-Cr-O nuclei on the surface of LSCF and subsequent crystallization and grain growth of SrCrO$_4$ and/or Cr$_2$O$_3$ solid phases [97, 121]. The nucleation theory based on the segregated species is also consistent with the observation that the Cr deposition on LSCF decreases significantly with the temperature, as shown recently. The predominant formation of SrSO$_4$ at high temperatures of 900-700 °C and SrS at low temperatures of 600-400 °C indicates that the segregated Sr also plays an important role in the sulfur deposition and poisoning, similar to that observed in the chromium deposition in the LSCF cathodes [97]. When the temperature is reduced below 700 °C, the surface segregation of Sr species is significantly decreased. XRD data shows the existence of SrS instead of SrSO$_4$ on the LSCF bar.

![Fig.5.8 Plots of occupied areas of segregated particles in the absence of SO$_2$ and sulfur-containing particles in the presence of 20 ppm SO$_2$, formed on the surface of LSCF bar samples as a function of the heat-treatment temperatures.](image)
samples after the heat-treatment at 600 to 400 °C in the presence of 20 ppm SO₂ and the intensity of the SrS phase increases with the decrease of the treatment temperature (Fig. 5.1). The complete disappearance of SrS peaks for the LSCF bar samples heat-treated at temperatures ≥ 700 °C indicates that SrSO₄ is more stable than SrS particularly at high temperatures. Madarasz et al. studied the oxidation behavior of SrS in air and oxidation of SrS starts slowly at 700 °C, forming SrSO₄ [122].

In the present study, the sulfur deposition was carried out on LSCF dense bar sample under no polarization. Therefore, the degradation model based on the occupation of SO₂ in the oxide ion vacancies and subsequent formation of SO₃²⁻ and SrSO₄ for the sulfur deposition and poisoning [59, 64] would not be applicable in this case. However, the reversed V-shape dependence of the sulfur deposition as a function of temperature (Fig. 5.8) implies that kinetically the nucleation and grain growth for the formation of SrSO₄ phase is a complicated function of temperature, and the rate of nucleation and grain growth for the formation of SrSO₄ and SrS phases is the highest at 700 °C. In a recent study of the effect of SO₂ on the oxygen permeation properties of LSCF hollow fiber membranes, Gao et al. also reported that the sulfur content of the LSCF membrane surface layer after exposed to SO₂ decreased with increase in temperature from 800 °C to 1000 °C [123]. The decrease in sulfur content indicates the reduced sulfur-containing particles (i.e., SrSO₄) with the increase of temperature, consistent with the reduced SrSO₄ when the temperature increased from 700 °C to 900 °C in this study. Based on the classical nucleation theory, the nucleation and crystal growth is a competition between the effective diffusion coefficient and energy barrier for the formation and growth of nuclei [124]. For example, in the study of crystal nucleation and growth of NaF in photo-thermo-refractive glass, Dyamant et al. [125] observed the parabolic
relationship between the nucleation rates of NaF and temperature with the maximum rate at ~485 °C. The SrSO₄ phase exhibits an excellent stability from room temperature to 1400 °C with a structural transformation at 1158.3 °C [126]. Thus, once SrSO₄ is formed, the growth of the formed SrSO₄ phase would be determined by reaction between SrO and SO₂. One hypothesis is that the reaction between the SO₂ and segregated SrO could strongly depend on the temperature with the highest activity at temperatures of 700 °C. This appears to be indicated that at high temperatures of 800 and 900 °C the dominant phase formed between SrO and SO₂ is SrCO₃ and Sr(OH)₂ rather than SrSO₄ and SrSO₃ (see Fig. 5.6).

The standard Gibbs free energy, ΔG of possible sulfur compounds of the reaction between LSCF and SO₂ such as SrSO₄, CoSO₄ and Fe₂(SO₄)₃ can be calculated based on the thermodynamic database [127]. For example, at 700 °C, the ΔG of SrSO₄, CoSO₄ and Fe₂(SO₄)₃ is -561.74, -171.88 and -57.77 kJ mol⁻¹, respectively. Despite the negative ΔG values, no CoSO₄ and Fe₂(SO₄)₃ phases were observed by the XRD as well as Raman spectroscopy analysis of the LSCF bar samples after the heat-treatment in the presence of 20 ppm SO₂ under the conditions of the present study. This indicates that kinetically, the reactivity of cobalt and iron oxides with SO₂ is very low. The low activity of cobalt and iron oxides with sulfur is also confirmed by oxide couple study (see Fig.4-6) and the reported observation of SrSO₄ and CoFe₂O₄ and not CoSO₄ and Fe₂(SO₄)₃ phase for the sulfur poisoned LSCF cathodes [59, 64].

5.5 Conclusions

Sulfur deposition and poisoning mechanism were investigated on dense LSCF bar samples after exposed to 20 ppm SO₂ in the temperature range of 900 to 400 °C, using XRD, SEM,
confocal Raman and ECR techniques. SO₂ reacts with LSCF, forming SrSO₄ phase at temperatures \( \geq 700 \, ^oC \) and SrS at temperature below 700 °C. The surface segregation of Sr and/or Co species on the LSCF bar samples decreases significantly with the temperature, however, the sulfur deposition as measured by the formation of sulfur-containing particles on the LSCF surface shows a reversed V-shaped dependence on the temperature. Sulfur reaction and deposition to form sulfate, SrSO₄ is most pronounced at 700 °C. ECR results indicate that the surface exchange coefficient of LSCF after exposed to 20 ppm SO₂ at 700-900 °C for 48 h is 9×10⁻⁵ cm s⁻¹, 8×10⁻⁶ cm s⁻¹ and 2×10⁻⁶ cm s⁻¹, which is much lower than 2.8×10⁻⁴ cm s⁻¹, 5×10⁻⁴ cm s⁻¹ and 6×10⁻⁴ cm s⁻¹ of the sample tested in the absence of SO₂. Temperature is the one of the major contributing factors that controls the mechanism of sulfur poisoning for LSCF cathode on SOFC in terms of reaction efficient and the surface exchange and diffusion processes for O₂ reduction reaction at typical temperature range.

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Chapter 6: Impact of temperature on Cr/ S Co-deposition and poisoning for LSCF cathode

(This Chapter is reproduced from paper titled “Co-Deposition and Poisoning of Chromium and Sulfur Contaminants on La₉₀ₓSrₓCo₀₂Fe₀₇ₓO₃₋ₓ Cathodes of Solid Oxide Fuel Cells” published in Journal of the Electrochemical Society, 162 (6) F507-F512 (2015)).

6.1 Introduction

The durability of a solid oxide fuel cell (SOFC) is critically related to the degradation behavior of its cathodes such as La₀.₈Sr₀.₂MnO₃ (LSM) and La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋ₓ (LSCF) in the presence of impurity species such as chromium from the chromia-forming interconnect, silica, boron and volatile alkaline elements from the glass seals sealant and sulfur from air [17-20, 121, 128, 129]. Among them, gaseous chromium species vaporized from the chromium oxide scale of chromia-forming metallic interconnect are probably the most investigated contaminants affecting the performance of SOFCs’ cathodes. The mechanism and process of the deposition and poisoning of chromium species at the cathodes of SOFCs have been extensively investigated, including LSM [6, 96], LSCF [120] and Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋ₓ (BSCF) [98]. In the case of LSCF electrodes, deposition of Cr species preferentially take place on the surface of the LSCF electrode, resulted from the interaction between the segregated SrO and gaseous Cr species [97, 114]. Both the humidity in the air stream and operation temperature have a significant effect on the Cr deposition[130]. Cr deposition decreases significantly with the decrease of temperature, most likely due to the reduced Sr segregation as well as the decrease of the partial pressure of gaseous Cr species at reduced temperatures [131].
The sulfur in the form of SO₂ or H₂S in the air stream is another important contaminant affecting the performance stability of SOFC cathodes. Wang et al. [64] studied the polarization performance behavior of LSCF in the presence of 0.1 ppm SO₂ and observed two-stages of performance degradation. A degradation mechanism based on the occupation of SO₂ in the oxide ion vacancies and subsequent formation of SO₃²⁻ and SrSO₄ was proposed for the irreversible poisoning effect of SO₂. Liu et al. [50] showed that the performance of cells with La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃-δ (LSCF) electrode becomes unstable in the presence of 1 ppm SO₂ and drops significantly when the SO₂ concentration increased to 20 ppm. The performance degradation is most likely due to the poisoning of SO₂ and the formation of SrSO₄. We studied recently the sulfur deposition and poisoning mechanism of LSCF electrodes and found that sulfur (i.e., SO₂) reacts with LSCF, primarily forming SrSO₄ phase at high temperatures (i.e., ≥ 700 °C) and SrS at low temperatures (i.e. <700 °C) [131]. Sulfur deposition shows a reversed V-shape dependence on the heat-treatment temperature and is most pronounced at temperatures around 700 °C, indicating that sulfur deposition and poisoning on LSCF are closely related to the operating temperature of fuel cells.

In SOFC stack operation conditions, both chromium and sulfur source exists. Horita et al [18] studied the effect of impurities on the performance stability of the flatten tubular SOFC stack and found that the concentrations of contaminants like Cr, Si and S increase with the operation time. This indicates the presence of deposition and poisoning of multiple impurities on the cell performance. Schuler et al [4] studied the air side contaminants under SOFC stack configuration. Post-analyses of the cells showed that performance degradation is mainly due to cathode contaminants originated from the upstream of the cell. Further studies [9] on the Ni-YSZ
anode-supported thin YSZ electrolyte cell with the LSM/YSZ composite cathodes indicate the formation of Sr(Cr,S)O₄ in the LSM/YSZ composite cathode layer after tested for 1900 h at 800 °C, indicating the presence of Cr and S contaminants. Malzbende et al. [132] reported a post-test analysis of an SOFC stack with anode supported cells with Ni/YSZ anode, YSZ electrolyte, and a LSM cathode operated under steady-state conditions for 19,000 h, and found that the ultimate failure of the stack is the result of a weakening and fracture of the YSZ electrolyte along grain boundaries due to the local Mn enrichment. However, there appear no reports on the deposition and poisoning of LSCF cathodes in the presence of both Cr and S contaminants.

In this study, the presence of both Cr and S contaminants on the microstructure and surface diffusion properties of LSCF cathode materials is investigated from 900 to 600 °C on LSCF dense bar samples in air. The results indicate that sulfur deposition and poisoning effect is more dominant as compared to the chromium particularly at low temperatures, ie. ≤ 700 °C under the conditions of this study. Electrical conductivity relaxation (ECR) results also indicate that Cr and S poisoning strongly deteriorate the surface exchange and diffusion processes for the O₂ reduction reaction on LSCF electrodes.

6.2 Experimental

6.2.1 LSCF bar sample preparation

The procedure of preparing LSCF sintered bar samples was the same as the experimental procedure in Chapter 3. The LSCF bar samples were heat treated at temperatures from 900 °C to 600 °C in the presence and absence of Cr₂O₃ and 20 ppm SO₂ (SO₂ in N₂, BOC Ltd.). Cr₂O₃ was used as the source of gaseous Cr species and flow rate of SO₂ was 20 sccm.
6.2.2 ECR tests

The procedure of testing the electrical conductivity relaxation curves of LSCF bar samples in the presence of 20 ppm SO₂ was the same as the experiment procedure in Chapter 3. For comparison, the measurements were carried out at a selected temperature of 900 °C with oxygen partial pressure changing from 0.05 bar to 0.21 bar in the presence of Cr and S, respectively, and in the presence of both Cr and S (or Cr+S).

6.2.3 Characterizations

XRD (D8 Advance, Bruker, Germany) and Confocal laser Raman spectroscopy (WITec GmbH, Ulm Germany) techniques were used to examine the phase composition of LSCF bar samples. The morphology and microstructure of the bar samples after the heat-treatment at different temperatures in the presence of Cr and S species were studied by scanning electron microscopy (SEM) and energy dispersive spectroscopy using a Zesis EVO with 20 keV.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS Ultra DLD instrument using monochromated Al Kα X-rays (energy 1486.7 eV). A pass energy of 40 eV was used for the core level spectra. The binding energy (BE) scale was calibrated with respect to the adventitious carbon component of the C 1s peak fixed at 284.8 eV. Background subtraction and peak fitting were done performed with Casa XPS.

6.3 Results and discussions

6.3.1 Effect of temperature on the phase of LSCF

Fig.6.1 shows the XRD pattern of as-prepared LSCF as well as LSCF bar samples after
heat-treatment in the presence of Cr$_2$O$_3$ and 20 ppm SO$_2$ (or Cr+S) at different temperatures for 48 h. The as-prepared LSCF shows typically XRD patterns associated with rhombohedral perovskite structure (curve a, Fig. 6.1). Diffraction peak at 29° was observed for LSCF samples heat treated at 900 °C and 800 °C and can be identified as the formation of SrCrO$_4$ phase [106], while for the sample heat treated at 700 °C and 600 °C, peak at 27° associated with the formation of SrSO$_4$ [112] was detected. The formation of SrSO$_4$ phase is also observed on LSCF samples after the heat-treatment in the presence of SO$_2$ when the temperature is equal to and lower than 700°C [131].

![Fig. 6.1 XRD diffraction patterns of as-prepared LSCF and LSCF bar samples after heat-treatment in the presence of Cr$_2$O$_3$ and 20 ppm SO$_2$ at different temperatures for 48 h. a) as-prepared, b) 600 °C, c) 700 °C, d) 800 °C, e) 900 °C.](image)

6.3.2 Effect of temperature on the microstructure of LSCF

Fig. 6.2 is the SEM micrographs of the LSCF surfaces after the heat treatment in the presence of Cr$_2$O$_3$ and 20 ppm SO$_2$ in air at different temperatures for 48 h. For the purpose of comparison, the SEM micrographs of LSCF surface after the heat treatment in the presence of Cr$_2$O$_3$ or 20 ppm SO$_2$ in air at different temperatures [131] were also shown in the figure. There are significant
increases in both the size and number of deposits on the LSCF surface. In the case of LSCF samples treated at 900 °C in the presence of Cr₂O₃ only, the size of deposited particles is as large as 2 µm (Fig.6-2a), indicating the significant reaction of the gaseous Cr species from Cr₂O₃ with LSCF. For the LSCF sample heat-treated at 900 °C in the presence of SO₂ for 48 h, there is a formation of large number of small (~80 nm) and large (~700 nm) particles and the formation of the particles appears to be random on both the grain boundaries and the surface of LSCF grains (Fig.6-2b). However, for the samples heat-treated at 900 °C in the presence of Cr and S for 48 h, a large number of deposited particles in the size ~1.0 µm was observed. Compared with the one in the presence of Cr or S (Fig.6-2a and 2b), significantly more deposited particles were formed on the surface, which indicates the additive deposition effect of Cr and S contaminants in the presence of both Cr and S species.

In the case of the presence of Cr contaminant, the size and number of the deposits decrease significantly with the decrease of temperature (Fig.6-2d, g), indicating that the deposition of Cr species on the LSCF depends strongly on the temperature, as shown early [131]. The significant decrease in the Cr deposition on LSCF electrodes is mainly due to the fact that as the temperature decreases from 900 °C to 700 °C, both the partial pressure of gaseous chromium species and surface segregation of Sr decrease significantly, thus significantly slowing the deposition process of chromium species. Significant deposition and formation of large and small particles were also observed for the LSCF bar sample heat-treated at 800 °C in the presence of SO₂ (Fig.6-2e). Very different from that observed for the Cr deposition, the most remarkable formation of deposited particles occurs on the LSCF electrodes after heat-treatment in the presence of SO₂ at 700 °C (Fig.6-2h). The surface of LSCF sample is almost completely covered by the deposits formed on
the surface of LSCF grains and the particles formed are strontium sulfate, SrSO₄, as shown previously. As the temperature reduced to 600 °C, the sulfur deposition is substantially reduced with isolated deposits on the LSCF electrode surface (Fig. 6-2j).

![Figure 6.2 SEM micrographs of LSCF surface after heat-treatment for 48 h in the presence of Cr₂O₃ (left), 20 ppm SO₂ (middle) and Cr₂O₃ and 20 ppm SO₂ (right) at (a,b,c) 900 °C, (d,e,f) 800 °C, (g,h,i) 700 °C, and (j,k) 600 °C. The scale bar applies to the micrographs of the same column.](image)

The deposition behavior in the presence of both Cr and S (Cr+S) contaminants is very different from that observed in the presence of individual Cr or S. In the temperature range studied,
the deposit formation on the surface of LSCF electrodes appears to be most significant at 900 and 700 °C (Fig.6-2c and i). The significant deposit formation for the reaction at 900 °C is most likely dominated by the Cr deposition and this is supported by the prominent phase formation of SrCrO₄ (see Fig.6-1). The substantial deposit formation also occurs on the LSCF electrodes in the presence of Cr+S contaminants for the reaction at 700 °C (Fig.6-2i). The phase of the deposited particles is dominated by strontium sulfate, SrSO₄, rather than SrCrO₄ as detected by XRD (Fig.6-1). It is in accordance with the severe sulfur poisoning effect on LSCF as a function of temperature (700 °C). Nevertheless, the size of the deposits formed on the surface of the LSCF electrode is in the range of 1~3.5 µm, very different from that formed in the presence of S after the heat-treatment at the same temperatures (Fig.6-2h). This may indicates the complex effect of the co-presence of Cr and S contaminants on the deposition and grain growth of the SrSO₄ dominated deposit phase. When the temperature decreased to 600 °C, the numbers of the particles formed on the LSCF surface decreased substantially with numerous fine particles (35 nm) (Fig.6-2k). This indicates the significantly reduced activity between LSCF and Cr+S at temperatures below 700 °C.

6.3.3 The phase deposits

The formation of deposited particles on the surface of LSCF bar samples was further investigated using confocal Raman spectroscopy. Figure 6-3 is the optical microscopy images and Raman spectra of the LSCF surface after heat treatment at 900 °C and 800 °C in the presence of Cr and S contaminants for 48 h. As shown in Figure 6-3g, the Raman spectra of the deposits on the LSCF surface with a wavelength of 865 cm⁻¹ and 1000 cm⁻¹ correspond to the phases of SrCrO₄
and SrSO₄ [133]. From the Raman mapping image in Figure 6-3c-f, it can be easily seen that isolated and large SrCrO₄ particles were formed on the LSCF surface at 900 °C, while as the SrCrO₄ particles formed at 800 °C were much smaller most likely due to the reduced partial pressure of gaseous Cr species. The reduction in operation temperature can significantly slow the deposition process of chromium species on LSCF cathodes. The detection of SrSO₄ phase by the Raman spectroscopy and not by XRD also indicates the high sensitivity of Raman spectroscopy techniques for the study of sulfur deposition. However, when the temperature decreased to 700 °C, the Raman spectroscopy only detects the presence of SrSO₄ and no Raman shift signal associated with SrCrO₄ is observed (Fig.6-4d), consistent with the XRD result. Raman image mapping with wavelength of 1000 cm⁻¹ shows the dominant formation of SrSO₄ phase (Fig.6-4b). The results indicate that sulfur poisoning is dominant at lower temperatures (i.e., 700 °C) with the formation of the SrSO₄ as the reaction products.

The composition and phase of the deposits on the LSCF surface was further investigated by XPS. Figure 6-5a shows the selected survey scan of the deposits on the LSCF surface at 800 °C, indicating the presence of Sr, Cr, S, La and O elements. The deconvolution of Sr 3d₅/₂₋₃/₂ in LSCF generally shows that the Sr 3d peaks are mainly consisted of two distinctive peaks of 3d₅/₂ at lower binding energy (BE) ranges and 3d₃/₂ at relatively higher BE ranges [134] (see Fig.6-5b). For the LSCF samples heat-treated at 900 °C, deconvolution analysis was carried out and the results of the deconvoluted Sr 3d spectra were comprised of 4 peaks at 134.0 eV, 135.8 eV, 131.7 eV and 134.5 eV at, respectively. Based on the XPS data that the BE of Sr in SrO is 132.8 eV [135] and 133.8 eV in SrCO₃ [136], the main peaks in LSCF measured at about 134.0 eV and 135.8 eV are originated from Sr 3d₅/₂ and Sr 3d₃/₂, which corresponds to the SrSO₄ phase [137]; while the BE at
about 131.7 eV (Sr 3d\textsubscript{5/2}) and 134.5 eV (Sr 3d\textsubscript{3/2}) is correlated to the formation of the perovskite phase showing a charge state of Sr\textsuperscript{2+} [138]. At 800 °C, the Sr 3d spectra was comprised of 4 peaks at 134.1 eV (Sr 3d\textsubscript{5/2}), 135.8 eV(Sr 3d\textsubscript{3/2}), 131.2 eV(Sr 3d\textsubscript{5/2}) and 132.9 eV(Sr 3d\textsubscript{3/2}). At 700 °C, the Sr 3d spectra is dominated by peaks at 134.3 eV (Sr 3d\textsubscript{5/2}) and 136.1 eV (Sr 3d\textsubscript{3/2}), and the peak intensity at 131.3 eV(Sr 3d\textsubscript{5/2}) and 133.0 eV(Sr 3d\textsubscript{3/2}) is relatively weak. At 600 °C, the Sr 3d spectra is mainly comprised of 2 peaks at 134.2 eV(Sr 3d\textsubscript{5/2}) and 135.9 eV(Sr 3d\textsubscript{3/2}).

![Graph showing Raman shift vs. intensity at different temperatures](image)

- **900 °C**
- **800 °C**
Fig. 6.3 (a, b) Optical microscope images of LSCF surface after heat treatment in the presence of combined $\text{Cr}_2\text{O}_3$ and 20ppm $\text{SO}_2$; (c, d) Raman mapping at wavelength of 863 cm$^{-1}$ corresponding to $\text{SrCrO}_4$; (e, f) 1000 cm$^{-1}$ corresponding to $\text{SrSO}_4$. Selected Raman spectra is given in (g) from corresponding areas at (a, c, e) 900 °C.

Fig. 6.5c shows the S 2p spectra of LSCF bar samples after heat treatment in the presence of Cr and S at different temperatures. Normally, for each type of sulfur species, there is a doublet consisting of S 2p$_{3/2}$ and S 2p$_{1/2}$ (spin-orbit coupling) with the intensity ratio of 2:1 [139]. Deconvolution analysis was carried out and the BE of the deconvoluted S 2p$_{3/2}$ spectra was 168.5 eV, 168.6 eV, 169.2 eV and 168.7 eV at 900 °C, 800 °C, 700 °C and 600 °C, respectively, which is in accordance with the XPS results of $\text{SrSO}_4$ [137] and the BE of the S 2p$_{3/2}$ is 169.0 eV for sulfate. Due to the detection of the main peaks of Sr and S spectra associated with $\text{SrSO}_4$, it can be concluded that $\text{SrSO}_4$ has been formed on the surface of LSCF at the temperature range in this study. This is in excellent agreement with the Raman spectroscopy results.

Fig. 6.5d shows the deconvoluted O 1s spectra of LSCF bar samples. The oxygen species of oxide materials can be mainly classified with the binding energy difference. The O 1s peak, typical of perovskite materials, consists of three components at about 529, 531 and 532 eV which are usually attributed to lattice, surface, and adsorbed oxygen, respectively [140]. For the samples that were heat treated at 900 °C and 800 °C, the BE of the deconvoluted O 1s spectra is 529.5-529.6 eV (low BE) associated with the oxygen in the lattice; 531.7-531.8 eV (intermediate BE) associated with surface oxygen 533.2-533.1 eV; (high BE) with adsorbed oxygen, respectively. The high BE is due to the oxygen-containing species which occurs relatively near the surface containing species and/or surface OH group caused by hydroxyl environment [141-146]. For the sample that were heat-treated at 700°C, the BE of the deconvoluted O 1s spectra is 532.5 eV, which could be correlated to the adsorbed oxygen species or carbonate. At low temperature of
600 °C, the BE of the deconvoluted O1s (531.7 eV, 533.1 eV) would correspond to the chemisorbed oxygen in the form of $O^{2-}$ and the oxygen-containing species.

Fig.6.5e shows in the case of Cr 2p spectra at different temperatures. No obvious Cr 2p spectra was detected at 600 °C and 700 °C, which means that the deposition and formation of Cr species at temperatures equal to or below 700 °C is not favorable. Cr 2p spectra were observed for the LSCF samples heat-treated at 900 and 800 °C. After deconvolution, the BE of the Cr 2p$_{1/2}$ is 585.6 eV and 585.7 eV at 900 °C and 800 °C, respectively, while the BE of the Cr 2p$_{3/2}$ is 575.9 eV and 576.3 eV at 900 °C and 800 °C, respectively. This is consistent with the BE of 586.2-586.9 eV for Cr 2p$_{1/2}$ and 576.4-577.0 eV for Cr 2p$_{3/2}$ in Cr$^{3+}$ compounds[147]. However, it is difficult to identify BE of 588.1-589.1 eV for Cr 2p$_{1/2}$ peak and 578.3-579.8 eV for Cr 2p$_{3/2}$ peak associated with Cr$^{6+}$ compounds. The XPS analysis data confirm the presence of Cr$^{3+}$, but not Cr$^{6+}$ on the LSCF surface at 900 and 800 °C. XPS technique provides both elemental and, to a certain extent, chemical information in the top 3-30 atomic layers (10-100Å) of the samples. The dominant spectra associated with Cr$^{3+}$ may indicate that surface of the Cr deposit particles is covered by Cr$_2$O$_3$ while the core is the SrCrO$_4$ as detected by XRD.

Fig.6.5f shows the La 3d spectra of LSCF bar samples. The La 3d$_{5/2}$ peak was observed at 833.0 eV for the sample heat-treated at 900 °C (similar to the as-prepared sample of 833.8 eV [148]) and it is shifted to 834.1 eV, 836.3 eV and 835.4 eV from 800 °C to 600 °C. The binding energy of the La 3d$_{5/2}$ peaks agrees with values reported by Wu et al[149] for La$_{0.5}$Sr$_{0.5}$MnO$_3$ pellets with a main line at 834.1 eV. The exposure at lower temperatures, especially 700 °C, resulted a shift to even a higher BE (836.3 eV). The spectrum of La 3d$_{5/2}$ for the sample is in a good agreement with that for La$_2$(SO$_4$)$_3$[148] whereas the diffraction lines associated with
La$_2$O$_2$(SO$_4$) was observed for 100 ppm SO$_2$ by Wang.

Table 6-1 summarizes the phases formed on the surface of LSCF dense bar samples after heat-treatment in the presence of Cr+S at different temperatures, based on XRD, Raman and XPS analysis. The results indicate that in the presence of Cr and 20 ppm SO$_2$, the deposition and reaction products between LSCF and contaminants are dependent on the temperature: SrCrO$_4$ only forms at high temperature of 900 and 800 °C, while SrSO$_4$ forms at the temperature ranges studied.

Table 6-1. Phase formation and analysis by XRD, XPS and Raman spectroscopy.

<table>
<thead>
<tr>
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<th>900 °C</th>
<th>800 °C</th>
<th>700 °C</th>
<th>600 °C</th>
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<td>SrCrO$_4$</td>
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<td>SrSO$_4$</td>
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<td><strong>Raman</strong></td>
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<tr>
<td>La$_2$(SO$_4$)$_3$</td>
<td>nd</td>
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*nd-not detected.*
Fig. 6.4 Optical microscope images of LSCF surface after heat treatment at 700 °C (a), 600 °C (c) in the presence of combined Cr₂O₃ and 20ppm SO₂, (b) Raman mapping at wavelength of 1000 cm⁻¹ corresponding to SrSO₄ and (d) Raman spectra from LSCF surface (700 °C). Scale bar applies to all graphs.
Fig. 6.5 (a) XPS survey scan and selected high resolution XPS of (b) Sr 3d, (c) S 2p, (d) O 1s, (e) Cr 2p and (f) La 3d of LSCF bar samples after heat treatment at different temperatures and in the presence of Cr+S contaminants for 48 h.

6.3.4 Oxygen surface coefficient

Fig. 6.6 is the electrical conductivity relaxation profiles of LSCF samples measured at 900 °C as a function of exposure time in the absence and presence of Cr, S and Cr+S. In the absence of contaminants, the initial relaxation time is around 400 s. The initial oxygen exchange coefficients, $k_{chem}$ of as-prepared LSCF measured is $6\times10^{-3}$ cm s$^{-1}$ at 900 °C, respectively, and decreased slightly with the heat-treatment time. In the case of the ECR relaxation profiles of LSCF samples measured in the presence of contaminants, the relaxation time increased from 700 s to 2500 s after being exposed to Cr$_2$O$_3$ for 48 h at 900 °C, while in the presence of 20 ppm SO$_2$, the relaxation time increased from 1500 s to 3500 s. However, the relaxation time increased from 1500 to 4500 s after being exposed to both Cr+S. The $k_{chem}$ value is $1.5\times10^{-4}$ cm s$^{-1}$, $9\times10^{-5}$ cm s$^{-1}$, $5\times10^{-5}$ cm s$^{-1}$ at 900 °C in the presence of Cr, S and Cr+S after exposed for 48 h, respectively. The results also show that the $k_{chem}$ of LSCF after being exposed to the combined Cr+S at 900 °C is two orders of magnitude lower than that of the freshly-prepared LSCF ($6\times10^{-3}$ cm s$^{-1}$). The deposition and
formation of SrCrO$_4$ and SrSO$_4$ on the surface of LSCF cathode materials can greatly attribute to the significant reduction in $k_{chem}$ for the O$_2$ reduction on LSCF electrodes, indicating that the co-presence of chromium and sulfur contaminants is significant detrimental to the electrocatalytic activity of LSCF cathodes of SOFCs.

![Graphs showing electrical conductivity relaxation profiles](image)

**Fig.6.6** Comparison of electrical conductivity relaxation profiles of LSCF bar samples as a function of exposure time (a) in the absence of Cr+S and in the presence of (b) Cr$_2$O$_3$, (c) 20 ppm SO$_2$ and (d) Cr+S at 900 °C.

### 6.4 Conclusions

The deposition and poisoning of the co-presence of chromium and sulfur contaminants were investigated on LSCF bar samples at temperature range of 900-600 °C. SEM microstructure analysis indicates that the interaction between LSCF and chromium and sulfur contaminant species depends strongly on the temperature and deposit formation on the surface of LSCF surface is most pronounced at temperature of 700 °C. XRD, Raman and XPS analysis demonstrated that in
the presence of Cr and 20 ppm SO₂, the deposition and reaction products between LSCF and Cr+S contaminants are dependent on the temperature: SrCrO₄ only forms at high temperature of 900 and 800 °C, while formation of SrSO₄ phase occurs at the temperature ranges tested in the present study. The $k_{\text{chem}}$ value is $1.5 \times 10^{-4}$ cm s⁻¹, $9 \times 10^{-5}$ cm s⁻¹, $5 \times 10^{-5}$ cm s⁻¹ at 900 °C in the presence of gaseous Cr, S and Cr+S, respectively. The results indicate that the co-presence of chromium and sulfur contaminants can cause the significant deposition and formation of SrCrO₄ and/or SrSO₄, which are detrimental to the oxygen exchange and surface diffusion process on the LSCF electrode materials.

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Chapter 7: Mechanism and kinetics of SO$_2$ poisoning on the electrochemical activity of LSM cathodes.

7.1 Introduction

Solid oxide fuel cells (SOFCs) operating at intermediate temperature of 600-800 °C offer an attractive option that is much more fuel flexible than low temperature fuel cells and is suitable for a wide range of applications [17-20]. One of the main challenges for the practical application of SOFC is the durability of the system under long-term operation conditions [150, 151]. In addition to the microstructural stability, one main factor affecting the durability of SOFC is the deposition and poisoning of impurities such as chromium species from the Fe-Cr alloy metallic interconnect boron from borosilicate glass sealants and sulfur from the air stream on the performance and activity of the cathodes. It is well known that volatile chromium species can deposit on the electrode surface and/or at the electrode/electrolyte interface, significantly poisoning and degrading the electrochemical activity of SOFC cathodes such as La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ (LSCF), Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (BSCF) and La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) [121]. One of the important issues of borosilicate glass-based sealants is the high volatility of boron species in the glass under SOFC operating conditions [73], which shows significant deposition and poisoning effect on the electrochemical activity of SOFC cathodes [62, 94, 129, 152-154]. Recent studies on the durability of SOFC stacks under real operation environment have indicated that sulfur in the air stream can accumulate at the cathode side, contaminate and degrade the cell performance [50-52, 59].

Sulfur deposition and poisoning behaviors have been investigated on different cathode
materials including LSCF and LSM [50-52, 59, 63, 64]. Recently, Kishimoto et al. [65] reported that SO2-induced degradation of LSCF is affected by SO2 concentration and the operating temperature, and performance degradation is characterized by an initial rapid degradation, followed by a relatively slow degradation stage. Mori et al. also found that the sulfur deposition in LSCF depends on the operating temperature and current density and the degradation rate of the cell voltage at 800 °C is lower than that operated at 700 °C [65]. They observed that sulfur is deposited over the entire LSCF cathode at 800 °C, while at 700 °C sulfur is mainly concentrated in the areas close to the Gd-doped ceria (GDC) barrier layer, which was considered to be related to the concentrated electrochemical reactions area near the GDC barrier layer. Wang et al [64]. showed that (La0.85Sr0.15)0.95MnO3 cathode is more stable than Sm0.5Sr0.5CoO3 (SSC) cathode in SO2-containing air. The high performance degradation rate of SSC electrode was explained by the high activity of SrO in SSC as compared to that in LSM [155]. Xie et al. [63] showed that Sr segregation and the subsequent formation of SrSO4 is the main cause of the performance degradation of LSCF cathodes at low partial pressure of O2 in the presence of sulfur. Liu et al. [50] reported that the performance of cells with LSCF/GDC composite cathodes becomes unstable in the presence of 1 ppm SO2 in air and drops significantly when the SO2 concentration increased to 20 ppm. We also studied the sulfur deposition and poisoning on dense LSCF bar samples and found that sulfur poisoning effect depends strongly on the operating temperature and concentration of SO2, and the SO2 deposition is most pronounced at 700 °C [131]. However, there appears no detailed study on the mechanism and kinetics of O2 reduction reaction on LSM cathode, despite the fact that LSM is regarded as one of the most commonly used and important cathodes of SOFC [156].
In this study, the focus will be on the mechanism and kinetics of the sulfur poisoning and deposition on the LSM cathodes at different temperatures and SO₂ content. The results show that the presence of SO₂ in air poisons the electrochemical activity of LSM electrodes by inhibiting the oxygen dissociation and diffusion process on the surface of LSM and by the formation of strontium sulfate on the LSM electrode surface and at the LSM/YSZ interface region. The deposition processes of sulfur species are most likely controlled by the nucleation reaction between the SO₂ and segregated SrO, forming SrSO₄.

7.2 Experimental

7.2.1 Half-cell preparation

Y₂O₃-ZrO₂ (YSZ) electrolyte pellets were prepared from 8 mol% Y₂O₃-doped ZrO₂ powder (Tosoh, Japan) by die pressing and sintered at 1450 °C for 5 h. The YSZ electrolyte was 0.5–0.9 mm thick and 20 mm in diameter. La₀.₈Sr₀.₂MnO₃ (LSM, Fuel Cell Materials, USA) cathode ink was painted on the center of YSZ pellet and fired at 1100 °C for 2 h. The electrode area was 0.5 cm² and the electrode thickness was 20 µm. Pt counter electrode (Pt ink, Gwent Group of Companies, United Kingdom) was painted on the opposite side of the electrolyte and fired at 800 °C. A Pt reference electrode was attached on the edge of the electrolyte. Pt mesh was placed on the surface of LSM cathodes as the current collector.

7.2.2 Half-cell tests

The cell was symmetrically placed between two alumina tubes with a glass seal on the cathode side in order to avoid leakage of SO₂-air mixture gas. During the cell tests, dry
SO₂-containing air with SO₂ concentration of 1 and 10 ppm was supplied to the cathode. The air flow rate was 100 mL min⁻¹.

Electrochemical performance and impedance responses were measured at 800 and 700 °C on a three-electrode cell, using a Gamry Reference 3000 Potentiostat. Impedance curves were recorded under open circuit with frequency range from 0.1 Hz to 100 kHz and the signal amplitude of 10 mV. The electrode was stabilized in air for 1 h before the electrochemical measurement. Electrode polarization resistance (Rₑ) was obtained by the differences between the high and low frequency intercepts, and electrode ohmic resistance (Rₒ) was obtained from the high frequency intercept. The cathodic polarization potential (Eₐ) was measured between LSM cathode and Pt reference electrode. Thus, the overpotential, η of the reaction on a LSM cathode can be obtained from the cathodic polarization current, j:

\[ E_{\text{Cathode}} = jR_{\Omega} + \eta \]  

7.2.3 Half-cell characterizations

LSM electrodes before and after the electrochemical tests were examined by scanning electron microscopy (SEM, NEON 40EsB) and energy dispersive X-ray analysis (EDX, INCA, Oxford, England). X-ray photoelectron spectroscopy (XPS) was also performed using a Kratos AXIS Ultra DLD instrument using monochromated Al Kα X-rays (energy 1486.7 eV). Pass energy of 40 eV was used for the core level spectra. The sulfur distribution in LSM cathode was examined by Nano SIMS (CAMECA, AMETEK, Inc, USA).
7.3 Results and discussions

7.3.1 *Electrochemical performance of LSM electrodes in the absence of SO₂*

Fig. 7.1 shows the initial polarization and impedance responses of a LSM electrode as a function of time under cathodic current passage at 200 mA cm⁻² at 700 and 800 °C in air. Under a cathodic current of 200 mA cm⁻², $E_{\text{Cathode}}$ decreases with the current passage for the O₂ reduction reaction. For example, at 700 °C, the initial $E_{\text{Cathode}}$ was 1053 mV and decreased rather rapidly to ≈930 mV after polarization for ≈10 min (Region I), followed by a slow decrease with further current passage (Region II) (Fig. 7-1a). The change in $E_{\text{Cathode}}$ in Region I was negative, $\Delta E = 930-1053 = -123$ mV. After current passage for about 60 min, $E_{\text{Cathode}}$ became more or less stable and reaches ≈800 mV after cathodic current passage for 120 min. The significant reduction in the polarization potential is also supported by the corresponding impedance behavior (Fig. 7-1b). At 700 °C, the impedance response for the O₂ reduction reaction is characterized by a large and depressed arc. The initial $R_E$ was 12 Ω cm² and decreased significantly with the application of cathodic current passage. After polarization at 200 mA cm⁻² for 5 min, $R_E$ was reduced to 5.2 Ω cm² and reached 3.2 Ω cm² after being polarized for 60 min. On the other hand, $R_\Omega$ was 3.5 Ω cm² and more or less stable during the polarization period. Thus, the reduction in the $E_{\text{Cathode}}$ is mainly due to the decrease in $\eta$. Similar reduction in the cathodic polarization potential and electrode polarization resistance was also observed for the reaction on LSM cathodes at 800 °C (Fig. 6-1c and d). The significant reduction in $E_{\text{Cathode}}$ or negative $\Delta E$ values and $R_E$ with the application of a cathodic polarization current passage is due to the well-known activation effect of cathodic
polarization on the enhancement of the electrochemical activity of LSM electrodes [157-162].

7.3.2 Electrochemical performance of LSM electrodes in the presence of 1 ppm SO₂

Fig. 7.2 shows the initial polarization and impedance responses for the O₂ reduction reaction on a LSM cathode under cathodic current passage at 200 mA cm⁻² in the presence of 1 ppm SO₂ in air at 700 °C and 800 °C. The E_Cathode changes significantly with the cathodic current passage.

However, at 700 °C, very different from that observed in the absence of SO₂, E_Cathode increased very rapidly with the cathodic current passage initially (i.e., Region I) and reached a plateau after polarization for ~3 min where the increase in E_Cathode is much slower (i.e., Region II) (Fig.7-2a).
For example, after the cathodic current passage for 5 min, $E_{\text{Cathode}}$ increased rapidly from an initial value of 1100 mV to 1280 mV within 2 min of applying the cathodic current passage. The change in $E_{\text{Cathode}}$ in Region I is positive, $\Delta E = 1280 - 1100 = 180$ mV. After interruption of the current and switching on the current again, $E_{\text{Cathode}}$ started at 1080 mV, almost the same as the initial $E_{\text{Cathode}}$ value. Such change of $E_{\text{Cathode}}$ with the cathodic current passage is more or less reproducible. The remarkable difference in the change and magnitude of $E_{\text{Cathode}}$ with the cathodic current passage for the $O_2$ reduction reaction in the absence and presence of 1 ppm $SO_2$ in air is a clear indication of the poisoning effect of $SO_2$ on the electrochemical activity of the LSM electrodes for the $O_2$ reduction reaction. Such distinct two-stage degradation behavior for the reaction on the LSM electrodes in $SO_2$-containing air is very similar to that reported for the $O_2$ reduction reaction on LSM electrodes in the presence of Fe-Cr metallic interconnect [121, 163-165]. The initial rapid increase in $E_{\text{Cathode}}$ in Region I for the reaction in the presence of $SO_2$ indicates that $SO_2$ poisons the $O_2$ reduction reaction by inhibiting the dissociation and diffusion of oxygen on the LSM electrode surface, similar to the inhibiting and poisoning effect of the gaseous Cr species [4, 121, 163-165]. On the other hand, the electrochemical impedance responses of LSM cathodes in the presence of 1 ppm $SO_2$ in air behave differently to the polarization potential. $R_E$ decreased with the cathodic current passage. For example, initial $R_E$ was $12 \ \Omega \ \text{cm}^2$ and decreased to $7 \ \Omega \ \text{cm}^2$ after current passage from 5 min. The decrease in $R_E$ measured at open circuit conditions is similar to the impedance behavior of LSM electrode in the presence of Fe-Cr metallic connect under a cathodic current density of 200 mA cm$^{-2}$ at 900 °C[163]. Nevertheless, the reduction in the $R_E$ values is relatively moderate as compared to that in the absence of $SO_2$ (Fig.7-1).
Fig. 7.2 Initial polarization and impedance responses of O₂ reduction reaction on LSM cathodes under cathodic current passage at 200 mA cm⁻² in the presence of 1 ppm SO₂ in air at (a,b) 700°C and (c,d) 800°C. Numbers in the figure are frequencies in Hz.
Fig. 7.3 Polarization and impedance curves for the $O_2$ reduction reaction on LSM cathodes under cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm SO$_2$ in air for 20 h at (a,b) 700 °C and (c,d) 800 °C. Numbers in the figure are frequencies in Hz.

When the test temperature increased to 800 °C, the change in $E_{\text{Cathode}}$ with the cathodic current passage is much smaller. For example, after the cathodic current passage for 60 min, $E_{\text{Cathode}}$ increased from 628 mV to 656 mV within 2 min of applying the cathodic current passage, $\Delta E = 28$ mV, which is much smaller than 255 mV measured at 700 °C under identical conditions. This indicates that the inhibiting effect of SO$_2$ on the oxygen dissociation and diffusion process is smaller at 800 °C, as compared for the reaction at 700 °C. Initial $R_E$ was 5.7 $\Omega$ cm$^2$ and decreased rapidly to 1.5 $\Omega$ cm$^2$ after polarization for 5 min. Then $R_E$ increased with the current passage, reaching 3.2 $\Omega$ cm$^2$ after current passage for 60 min (Fig. 7-2d).

Fig. 7.3 shows the polarization and impedance curves under a cathodic current of 200 mA cm$^{-2}$ at 700 and 800 °C in the presence of 1 ppm SO$_2$ in air for a longer period of 20 h. The characteristic of $E_{\text{Cathode}}$ with current passage for the reaction at 700 °C can also be divided into two distinct regions (Regions I and II). The change in $E_{\text{Cathode}}$ is generally reproducible but becomes less stable after polarization for 12 h (Fig. 7.3a). $R_E$ increased with the polarization time, reaching 7.2 $\Omega$ cm$^2$ after polarized in the presence of 1 ppm SO$_2$ in air for 20 h (Fig. 7.3b). For the reaction at 800 °C, the two-stage degradation polarization phenomena can also be clearly identified, though the magnitude of the $E_{\text{Cathode}}$ change is significantly smaller as compared to that at 700 °C. For example, after polarization for 4 h, $\Delta E$ in Region I is 100 mV, much smaller than 400 mV observed for the reaction on the LSM at 700 °C measured under similar conditions. Similar to that observed for the reaction at 700 °C, $R_E$ also increases with the cathodic polarization time in the presence of 1 ppm SO$_2$ in air (Fig. 7.3d).
Fig. 7.4 Polarization and impedance curves for the O₂ reduction reaction on LSM cathodes under cathodic current passage at 200 mA cm⁻² in the presence of 10 ppm SO₂ in air at (a,b) 700 °C and (c,d) 800 °C for 20 h. Numbers in the figure are frequencies in Hz.

Fig. 7.4 shows polarization and impedance curves for the O₂ reduction reaction on a LSM cathode under cathodic current passage at 200 mA cm⁻² in the presence of 10 ppm SO₂ in air at 700 °C and 800 °C. Similar to the reaction in the presence of 1 ppm SO₂, the polarization potential for the reaction on LSM electrode is also characterized by two-stage degradation behavior. For example, for the reaction at 700 °C after polarization for 4 h, the initial Ecathode of the LSM electrode was 1053 mV and increased to 1653 mV within 2 min (Region I), ΔE = 600 mV (Fig. 7-4a). This is larger than the ΔE value of 400 mV measured under identical condition in the presence of 1 ppm SO₂ in air at 700 °C. For the reaction at 800 °C, the ΔE was typically in the range of 200 mV (Fig. 7-4b), which is also higher than ΔE value of 100 mV measured for the
reaction in the presence of 1 ppm SO$_2$ in air. Increase in the SO$_2$ concentration also led to the increase in both $R_E$ and $R_\Omega$. For example, at 700 °C, $R_E$ increased significantly to 13 $\Omega$ cm$^2$ after being polarized for 20 h. In addition, $R_\Omega$ also increased from $\sim$3 $\Omega$ cm$^2$ to $\sim$3.6 $\Omega$ cm$^2$ at the end of the test. The significant increase of both electrode polarization and ohmic resistances indicates the serious sulfur deposition and poisoning effect under the high content of SO$_2$ in air. This result is in general in accordance with that reported by Wang et al[59], who found that the resistances increased rapidly at higher SO$_2$ concentration at 800 °C.

![Fig. 7.5 Comparison of Ecathode for the O$_2$ reduction reaction on LSM electrodes in pure air (0 ppm SO$_2$), 1 ppm SO$_2$ and 10 ppm SO$_2$-containing air under cathodic current passage of 200 mA cm$^{-2}$, measured at time intervals of 5 min and 4 h at 700 °C and 800 °C.](image)

Fig. 7.5 compares $\Delta E$ measured in Region I in air and in 1 and 10 ppm SO$_2$-containing air under current passage at 200 mA cm$^{-2}$ at 700 °C and 800 °C, measured at different time intervals. The $\Delta E$ behaves very differently for the O$_2$ reduction reaction in pure air and in SO$_2$-containing air. In pure air, $\Delta E$ is negative, -70 mV and -53 mV for the reaction at 700 and 800 °C, due to the activation effect of cathodic polarization on the electrochemical activity of LSM electrodes. However, for the reaction in the SO$_2$-containing air, $\Delta E$ is positive, a clear indication of SO$_2$ poisoning effect. However, the magnitude of $\Delta E$ for the O$_2$ reduction reaction in SO$_2$-containing air at 700 °C is significantly higher than that at 800 °C. The significantly higher $\Delta E$ value for the
O₂ reduction reaction at 700 °C indicates the more severe poisoning effect of SO₂ on the electrocatalytic activity of LSM electrodes as compared to that at a higher temperature of 800°C. This is in a good agreement with the observed most pronounced sulfur deposition on the dense LSCF bar samples at 700 °C[131].

7.3.3 Stability of LSM electrodes in SO₂-containing air

Fig.7.6 shows the polarization performance of a LSM electrode under a cathodic current passage at 200 mA cm⁻² in 1 ppm SO₂-containing air for 20 h, followed by the polarization in the pure air for 20 h at 700 °C and 800 °C. The electrode was stabilized in air before the introduction of SO₂. LSM electrodes are very stable in air as shown in Fig.7-6c for a typical example of the polarization performance at 200 mA cm⁻² at 800 °C for 40 h. The presence of SO₂ has a significant effect on the performance stability of LSM electrodes. At 700 °C, after introducing 1 ppm SO₂-containing air, E_Cathode increases continuously from 898 mV to 1840 mV after polarization for 25 h. After change to clean air, E_Cathode does not change but the increase in E_Cathode becomes very slower, reaching 1888 mV after polarization in clean air for 20 h.

The polarization behavior of the LSM electrodes at 800 °C is different to that polarized at 700 °C. With the introduction of 1 ppm SO₂ in air, E_Cathode increased from 419 mV to 838 mV after polarization for 15 h. After switching off SO₂ and changing to clean air, E_Cathode decreased to 566 mV initially and started increasing slowly to 644 mV after polarization for 20 h, which is still significantly higher than 419 mV before the introduction of SO₂. The results clearly indicate that the deteriorated electrochemical activity of LSM electrodes due to the SO₂ poisoning cannot be recovered by polarization in clean air.
7.3.4 Microstructure of LSM electrodes

Fig.7.6 shows the SEM micrographs of the surface of as-prepared LSM electrodes and LSM cathodes after cathodic current passage at 200 mA cm$^{-2}$ at 700 °C and 800 °C in the presence of 1 ppm and 10 ppm SO$_2$ in air for 20 h. In the case of as-prepared LSM electrodes, the LSM particle size is in the range of 0.3-1 µm and the surfaces of LSM particles is generally clean and smooth.
However, there is clear microstructural change after the exposure to the 1 ppm and 10 ppm SO2-containing air at both temperatures. Irregularly shaped small particles were formed on the surface and grain boundaries of the LSM electrodes (indicated by the circles in the figure). The size of the small particles formed is in range of 20-100 nm. The morphology change of the LSM electrodes indicates the sulfur deposition and reaction on the LSM electrode surface. However, EDS didn’t detect the presence of sulfur species probably due to the low limit of the technique (Fig.7-7g). Similar microstructure change also occurred in the bulk of the LSM electrodes after a cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm SO$_2$ and 10 ppm SO$_2$ for 20 h at 700 °C and 800 °C.

Fig.7.8 shows the SEM micrographs of YSZ electrolyte surface after a cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm and 10 ppm SO$_2$ in air for 20 h at 700 and 800 °C for 20 h. The LSM electrodes were removed by adhesive tape. The contact rings on the YSZ electrolyte surface (indicated by arrow, Fig.7-8a) are the contact areas between LSM particles and YSZ electrolyte, formed during the high temperature sintering of the LSM electrodes[166]. In the case of the LSM electrode after polarization in the presence of 1 ppm SO$_2$ in air, the YSZ electrolyte surface is generally clean with formation of few nanoparticles on the surface and grain boundary areas (indicated by a circle, Fig.7.8a and b). With the increase of the concentration of SO$_2$ to 10 ppm, there is a significant increase of the formation of nanoparticles on the electrolyte surface particularly for the reaction at 700 °C. Nanoparticles are in the range of 20-100 nm in diameter and cover the entire YSZ electrolyte surface including the areas within the contact rings (Fig.7.8c). The deposition of nanoparticles also occurs on the YSZ electrolyte surface for the reaction at 800 °C (Fig.7.8d). EDS could not detect the presence of sulfur on the deposited
nanoparticles (Fig.7.8f) and only in the case of particles within the contact ring areas (marked by a rectangular, Fig.7.8b), EDS detected the presence of trace amount of sulfur (Fig.6-8e), indicating the deposition of sulfur species on the YSZ electrolyte surface.

Fig.7. 7 SEM micrographs and EDS profiles of surface of (a,b) as-prepared LSM and LSM cathodes after cathodic current passage at 200 mA cm$^{-2}$ in the presence of (c,d ) 1 ppm SO$_2$ and (e,f ) 10 ppm SO$_2$ at 700 °C and 800 °C for 20 h.Typical EDS pattern taken from the areas marked by circles is shown in (g). Bar=500 nm.
Fig. 7.8 SEM micrographs and EDS profiles of surface of YSZ electrolyte for an LSM oxygen electrode under cathodic current passage at 200 mA cm$^{-2}$ in the presence of (a,b) 1 ppm SO$_2$ and (c,d) 10 ppm SO$_2$ at 700 ºC and 800 ºC for 20 h. Typical EDS pattern taken from the areas marked by rectangular is shown in (e) and circles is shown in (f). The LSM electrode coatings were removed by adhesive tape. Bar=200 nm.

Fig. 7.9 shows the SEM micrographs of LSM electrode surface in contact with YSZ electrolyte (i.e. the inner surface). The LSM electrodes were polarized at 200 mA cm$^{-2}$ in the presence of 1 ppm and 10 ppm SO$_2$ for 20 h at 700 and 800 ºC for 20 h and removed by adhesive tape method. The inner surface in direct contact with the YSZ electrolyte surface is characterized by the formation of nano-sized particles. The size of the nanoparticles is in the range of 20 nm (see the inset). There is also formation of particles with very different crystal facets and
morphology to the LSM particles (indicated by arrow, Fig. 7-9c). However, EDS analysis couldn’t
detect the deposition of sulfur species on the inner surface of LSM particles (Fig. 7-9e).
Nevertheless, the significant change of the morphology of the inner surface of the LSM particles
in direct contact with the YSZ electrolyte surface clearly indicate the sulfur deposition and/or
reaction at the interface regions between LSM particles and YSZ electrolyte, especially at lower
temperature of 700 °C and higher concentration of SO₂ of 10 ppm.

Fig. 7.9 SEM micrographs of LSM inner surface after a cathodic current passage at 200 mA cm⁻² in the
presence of (a,b) 1 ppm SO₂ and (c,d) 10 ppm SO₂ at 700 °C and 800 °C for 20 h. Typical EDS taken
from the areas marked by circles is shown in (e). Typical EDS taken from the areas marked by circles is
shown in (e). Bar=200 nm.

Fig. 7.10 shows SEM micrographs of cross section of as-prepared LSM cathodes and LSM
cathodes under cathodic current passage at 200 mA cm⁻² in the presence of 1 ppm SO₂ and 10 ppm
SO₂ for 20 h at 700 °C and 800 °C for 20 h. For as-prepared LSM cathodes, there is good contact
between the LSM particles and YSZ electrolyte, which is due to the high sintering temperature. Under cathodic current passage at 200 mA cm\(^{-2}\) in the presence of 1 ppm SO\(_2\) for 20 h at 700 \(^\circ\)C and 800 \(^\circ\)C (Fig. 10 c, d), there were less pores inside the LSM electrode bulk and the surface of LSM particles were not as smooth as the fresh samples. When the concentration of SO\(_2\) increased to 10 ppm (as shown in Fig. 7.10 e, f), especially at 700 \(^\circ\)C, the LSM bulk became more dense than other samples. However, EDS didn’t detect the sulfur species in the bulk of LSM electrode, which might be due to the quite low concentration of sulfur in the bulk of LSM electrodes.
Fig. 7.10 SEM micrographs and EDS profiles of cross section of fresh LSM cathodes (a) and LSM cathodes under cathodic current passage at 200 mA cm\(^{-2}\) in the presence of 1 ppm SO\(_2\) (c,d) and 10 ppm SO\(_2\) (e,f) at 700 °C and 800 °C for 20 h. (b) The selected whole image of LSM cathodes under cathodic current passage at 200 mA cm\(^{-2}\) in the presence of 1 ppm SO\(_2\) at 700 °C. (g) and (h) is the line scan for 700 °C and 800 °C.

7.3.5 XPS and Nano-SIMS results of LSM

Fig. 7.11 shows the XPS spectra of Sr3d, S2p, La3d and Mn2p for the as-prepared LSM and
LSM electrodes after a cathodic current passage at 200 mA cm\(^{-2}\) in the presence of 1 ppm and 10 ppm SO\(_2\) at 700 and 800°C for 20 h. The deconvolution analysis shows that the Sr3d spectrum is comprised of four peaks. The main Sr3d\(_{5/2}\) peak in as-prepared LSM samples at 132.4 eV can be attributed to the Sr\(^{2+}\) ions in LSM lattice\[167\], while the Sr3d\(_{5/2}\) peak appeared at 133.2 eV can be ascribed to SrO on LSM surface\[137\]. For the LSM samples after cathodic current passage at 200 mA cm\(^{-2}\) in the presence of 1 ppm SO\(_2\), two Sr3d\(_{5/2}\) peaks were observed at 132.5 eV and 133.5 eV at 700°C, and 132.5 eV and 133.1 eV at 800°C, respectively. The one at 132.5 eV can also be ascribed to the Sr\(^{2+}\) ions in LSM lattice and the one at 133.5/133.1 eV can be ascribed to the SrCO\(_3\)/SrO on LSM surface. However, in the case of high content of 10 ppm SO\(_2\) at 700 °C, a Sr3d\(_{5/2}\) peak was obtained at 134.3eV and can be attributed to the Sr species in SrSO\(_4\), indicating the formation of strontium sulfate on the electrode surface. The ratio of SrSO\(_4\) in Sr3d peaks accounted for 40.94% and can illustrate the severe sulfur poisoning of LSM electrode. However, when the temperature increased to 800 °C, two Sr3d\(_{5/2}\) peaks were measured at 132.6 eV and 133.6 eV, which can be ascribed to Sr\(^{2+}\) ions in LSM lattice and SrO on LSM surface. Table 6-1 listed the XPS result of Sr3d peak after deconvolution analysis.

Sulfur was detected on the surface of LSM electrodes after a cathodic current passage at 200 mA cm\(^{-2}\) in the presence of 1 ppm and 10 ppm SO\(_2\) at both 700 and 800 °C for 20 h. The results show that the binding energy of deconvoluted S2p\(_{3/2}\) peak is 169.0 eV, which is in accordance with the XPS results of SrSO\(_4\) and the binding energy of the S2p\(_{3/2}\) is 169.0 eV for sulfate. It has been reported that strontium sulphate is formed after the exposure of La\(_{0.6}\)Sr\(_{0.4}\)CoO\(_{3-\delta}\) to >1ppm SO\(_2\) for 24 h at 700 °C [67]. The binding energies and the multiple splitting of La3d agree well with reported values for La\(_{0.8}\)Sr\(_{0.2}\)BO\(_3\) (B=Cr, Mn, Fe, Co or Y) compounds [168, 169]. The shape
and position of La3d peaks are almost the same with as-prepared LSM and LSM after the polarization in SO2-containing air at both temperatures, indicating no reaction between sulfur and lanthanum under the conditions of this study. As Mn2p spectra are difficult to be analyzed by a simple deconvolution analysis concerning the contribution of Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ compounds[169], the exact oxidation state of Mn ions is not calculated from Mn2p spectra in this case.

![Graphs showing XPS spectra](image)

**Fig.7.11** High resolution XPS spectra of (a) Sr3d, (b) S2p, (c) La3d and (d) Mn2p of surface of as-prepared LSM and LSM electrode after a cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm and 10 ppm SO$_2$ for 20 h at 700 °C and 800 °C. (I) as-prepared LSM, (II) 1ppm SO$_2$ at 800 °C, (III) 1 ppm SO$_2$ at 700 °C, (IV) 10 ppm SO$_2$ at 800 °C and (V) 10 ppm SO$_2$ at 700 °C.
Fig. 7. 12 (a) SEM and (b) nano-SIMS image of sulfur distribution within a LSM cathode after a cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm SO$_2$ at 800 °C. Bright particles in (b) correspond to sulfur deposits.

Fig.7-12 shows the Nano-SIMS imaging of the sulfur distribution on a LSM cathode after a cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm SO$_2$ in air at 800 °C for 20 h. The bright particles show the deposition of sulfur in the electrode bulk and at the interface of LSM/YSZ. The sulfur deposition at the LSM/YSZ interface is consistent with the observation of significant nanoparticle formation on the YSZ electrolyte surface and on the inner surface of LSM in direct contact with the YSZ electrolyte, as shown in Fig.7-8 and 9.

7.3.6 Mechanism and kinetics of sulfur poisoning and deposition on LSM electrodes

As shown in this study, the results for SO$_2$ deposition and poisoning on the electrochemical performance and microstructure of LSM electrodes can be summarized below.

1. For the O$_2$ reduction of LSM electrodes in the absence of SO$_2$, $E_{\text{Cathode}}$ and $R_{\text{e}}$ decreases with the cathodic current passage, showing typically the activation effect of cathodic current on the electrochemical activity of LSM electrodes at both 700°C and 800°C.

2. In the presence of SO$_2$ in air, the LSM electrode behaves very differently to that in the
clean air for the O₂ reduction reaction. E\textsubscript{Cathode} increases with the cathodic current passage and is characterized by a distinctive two-stage degradation behavior, a rapid initial increase in Region I, followed by a much slow increase in Region II. The ΔE value in Region I is much smaller for the O₂ reduction reaction at 800 °C, as compared to that at 700 °C.

3. The stability results of LSM electrodes in SO₂-containing air and in pure air indicate that the deteriorated electrochemical activity of LSM electrodes due to the SO₂ poisoning cannot be recovered by polarization in the pure or clean air.

4. Both SEM and XPS results indicate the sulfur deposition and formation of SrSO₄ on the surface and interface region between LSM particles and YSZ electrolyte after polarization at 200 mAcm\(^{-2}\) in the SO₂-containing air at 700 and 800 °C. This is further demonstrated by a preliminary Nano-SIMS result, showing the sulfur deposition in the bulk of LSM electrode as well as the LSM/YSZ interface region.

The very different behavior of the polarization potential for the O₂ reduction reaction on the LSM electrodes in the absence and presence of SO₂ in air at both 700 and 800 °C demonstrates the significant poisoning effect of sulfur on the electrochemical activity of LSM for the O₂ reduction reaction. The SO₂ deposition and poisoning on the electrochemical activity of LSM electrodes is characterized by a distinct two-stage degradation behavior (Fig.7-2), similar to that reported for the O₂ reduction reaction on LSM electrodes in the presence of Fe-Cr metallic interconnect [121, 163-165]. Detailed study of O₂ reduction on porous LSM electrode in the presence of Fe-Cr metallic interconnect indicated that the rapid increase of the E\textsubscript{Cathode} is due to the poisoning effect of gaseous Cr species on the dissociative adsorption and diffusion of oxygen on the surface of
LSM electrodes[4]. The similarity of the polarization behavior of LSM electrodes in the presence of SO$_2$ in this study and in the presence of Cr species [4, 121, 163-165] implies that SO$_2$ would first adsorb on the active sites of LSM surface:

$$SO_2 + S_{LSM} \rightleftharpoons SO_2 - S_{LSM}$$  \hspace{1cm} (2)

where $S_{LSM}$ is an active site on the electrode surface. The O$_2$ reduction reaction on LSM electrodes is primarily controlled by the oxygen dissociative adsorption and diffusion on the LSM surface [170-172]. Thus, the adsorbed SO$_2$ on the active sites of LSM electrode, $SO_2$-$S_{LSM}$ would be most effective to inhibit the dissociation and diffusion of oxygen and this is indicated by the rapid increase of $E_{\text{Cathode}}$ in Region I, i.e., $\Delta E$. The much slower increase in $E_{\text{Cathode}}$ in Region II is most likely due to the saturation of adsorbed SO$_2$ on the electrode surface. However, the adsorbed SO$_2$, $SO_2$-$S_{LSM}$ can also be desorbed and this is indicated by the almost reproducible initial polarization behavior of $E_{\text{Cathode}}$ as a function of cathodic current passage. Thus, the overall process of the adsorption and desorption of SO$_2$ on the active sites on the LSM electrode surface can be written as:

$$SO_2 + S_{LSM} \rightleftharpoons SO_2 - S_{LSM}$$  \hspace{1cm} (3)

Both the adsorption and desorption rates of SO$_2$ would depend on the temperature. Overbury et al.[173] studied the temperature effect on the interaction of SO$_2$ with ceria films and found that the principle interaction is chemisorption of SO$_2$ at oxygen anions, which reversibly desorbs as SO$_2$ over a broad temperature range from 200 to 600 K. Annealing of ceria in SO$_2$ can lead to the formation of S$_2$ which desorb from the surface at temperatures above 850 K[173]. Sun et al.[174] also found that SO$_2$ adsorbs on Pt(111) through S and O atom, but upon heating to 300 K, SO$_2$ molecules underwent desorption and dissociation. Thus high temperature would favor the
desorption process of SO\textsubscript{2} due to the increased thermal energy of the sulfur species. The shift of reaction (3) to the left at a higher temperature of 800 °C would release the active sites, $S_{\text{LSM}}$ on the LSM electrode surface for the reaction and reduce the inhibiting effect of SO\textsubscript{2}. This explains the much smaller $\Delta E$ for the reaction at 800 °C as compared to that at 700 °C (Fig.7-5).

SEM results indicate the significant sulfur deposition and reaction on the surface of LSM electrodes and at the LSM/YSZ interface regions (Fig. 7-7-9). Though EDS could not detect the deposition of sulfur, XPS results identify the formation of SrSO\textsubscript{4} phase on the LSM electrode surface after polarization in the SO\textsubscript{2}-contained air. The deposition of sulfur in the electrode bulk and at the interfaces is also confirmed by the preliminary Nano-SIMS (Fig.7-11). The formation of SrSO\textsubscript{4} phase has been reported on LSCF electrodes after exposed to SO\textsubscript{2}-containing air[175]. The formation of SrSO\textsubscript{4} is most likely related to the interaction between SO\textsubscript{2} and segregated SrO on the LSM electrode surface:

$$\text{SO}_2 + \text{SrO} + \frac{1}{2}\text{O}_2 \rightarrow \text{SrSO}_4$$

Madarasz et al studied the oxidation of SrS powders and found that SrS completely oxidizes to SrSO\textsubscript{4} up to 1300 °C [122]. This indicates that SrSO\textsubscript{4} phase formed is stable under the conditions of the study. The stability of the SrSO\textsubscript{4} phase formed on the electrode surface and at the LSM/YSZ interface explains the irreversibility of the sulfur deposition and poisoning on the electrochemical activity of LSM electrodes, as shown in Fig.6-6.

Based on the discussion above, the mechanism and kinetics of SO\textsubscript{2} deposition and poisoning on the O\textsubscript{2} reduction reaction on LSM electrodes can be schematically illustrated in Fig.7-12. More favorable desorption of $SO_2-S_{\text{LSM}}$ at 800 °C would leave more active sites for the dissociative adsorption and diffusion of oxygen species for the O\textsubscript{2} reduction reaction with reduced SO\textsubscript{2}.
poisoning effect, as compared to the reaction at 700 °C. However, at the same time, the adsorbed SO₂ will react with segregated SrO, forming SrSO₄ on the LSM electrode surface and at the three phase boundary areas. The deposition of SrSO₄ will significantly lead to the acceleration of Sr segregation and consequently the Sr deficient at the A-site of the LSM. The A-site deficiency in Sr will in turn reduce the electronic conductivity and deteriorate the electrocatalytic activity of LSM electrodes for the O₂ reduction reaction[156]. The deposition of SrSO₄ phase at the three phase boundary area would drive the reaction to the interface between LSM particle and YSZ electrolyte as LSM is essentially electronic conductor with negligible oxygen ionic conductivity[176]. This will further accelerate the Sr segregation at the LSM/YSZ interface, resulting in the interaction between SO₂ and SrO and the deposition of sulfur species. This appears to be supported by the nanoparticles formation on the inner surface of LSM and within the contact ring areas on the YSZ electrolyte surface (Fig.7-8 and 9). The observation of nanoparticle formation indicates that the deposition of sulfur on the LSM electrode surface and at the electrode/electrolyte interface is most likely initiated by the nucleation reaction between the SrO nuclei and gaseous SO₂ in air.

Fig.7. 13 Scheme of sulfur deposition and poisoning on the O₂ reduction reaction on the LSM oxygen electrodes under the SOFC operation condition at (a) 700 °C and (b) 800 °C.
7.4 Conclusions

The mechanism and kinetics of sulfur deposition and poisoning on LSM electrodes was investigated at 700 and 800 °C. Sulfur species that initially played a dominant role in inhibiting the dissociation adsorption and diffusion processes of oxygen on the LSM surface, especially at 700 °C. Sulfur poisoning effect of LSM electrodes increased with higher concentration of SO₂. SEM/EDX combined XPS results show that the formation of small rough particles on the surface of LSM electrodes is SrSO₄ and the amount of SrSO₄ formation was the highest at higher concentration of SO₂ (10 ppm) at 700 °C, which can finally lead to the performance degradation. Nano-SIMS result indicates that sulfur is distributed in the whole LSM electrode and more obvious on the interface of LSM/YSZ at 800 °C. The O₂ reduction reaction kinetics of LSM electrodes is affected by the sulfur inhibiting species on the surface process and also the temperature due to the adsorption/desorption rate, and then the kinetics of the deposition processes of sulfur species is controlled by the nucleation reaction between the SrO and the gaseous sulfur species, forming SrSO₄. Finally, sulfur species not only has significant inhibiting effect on the kinetics for the O₂ reduction reactions at the LSM electrodes but also has a significant effect on the reaction mechanism.

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Chapter 8: Mechanism and kinetics of SO$_2$ poisoning on the 
electrochemical activity of LSCF cathodes

8.1 Introduction

Solid oxide fuel cells (SOFCs) operating at intermediate temperature of 600-800 °C are 
promising electrochemical devices due to the high energy conversion efficiency and fuel flexibility. They are suitable for a wide range of areas like transportation as well as stationary and mobile application [17-20]. However, for the sake of commercialization of SOFC, one of the most important technical issues is to solve the gradual degradation and deactivation of the cathodes by contaminants such as moisture, sulfur, chromium and boron which can be either in the moisture containing air stream or from the volatile species of cell components, such as metallic interconnect, sealant and manifold [79, 121, 129, 154]. For instance, recently, C.Pellegrinelli [177] studied the degradation mechanism of (La$_{0.4}$Sr$_{0.2}$)$_{1.92}$MnO$_3$-(Y$_2$O$_3$)$_{0.8}$(ZrO$_2$)$_{0.92}$ (LSM-YSZ) cathode in H$_2$O environments by testing the symmetrical cell with in-situ electrochemical impedance spectrometry (EIS) and focused ion beam-scanning electron microscopy (FIB-SEM) 3D reconstructions technique and categorized three impedance arcs corresponding to various cathode mechanism, and they also analyzed the relationship between polarization resistance and temperature under various PO$_2$ conditions to distinguish different electrode degradation contributions. Moreover, some studies on durability of SOFC stacks under practical operation situation have indicated that sulfur, most likely from the air can accumulate at the cathode side, contaminate and degrade the cell performance [50-52, 59, 65].

La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$(LSCF) perovskite material has been extensively studied and regarded
as one of the most promising cathode candidates for intermediate-temperature SOFCs due to its high mixed electronic and ionic conductivities and high catalytic activity for the O₂ reduction reaction[87, 178, 179]. However, despite the promising potential of the LSCF material as the IT-SOFC cathode, few studies are reported on the interaction between the LSCF electrode and sulfur dioxide. The mechanism of the sulfur deposition at the LSCF cathode is not clear. Murata Manufacturing Co., Ltd. has been developing single step co-fired planar type solid oxide fuel cells (SOFCs) and they reported [65] that sulfur distribution in LSCF depended on the air stream, operating temperature and current density. The degradation of the cell voltage operating at 800 °C was lower than that operating at 700 °C. They also found that sulfur was homogeneously detected whole in the LSCF cathode at 800 °C, however, sulfur was detected in the LSCF near the GDC barrier layer at 700 °C due to electrochemical reactions area near the GDC barrier, which could result in greater degradation of the cathode in operation at 700 °C. Xie et al. [63] reported that Sr segregation and the subsequent formation of SrSO₄ is the main reason of the performance degradation of LSCF cathodes at low partial pressure of O₂ in the presence of sulfur. Wang et al. [64] studied the polarization performance behavior of LSCF in the presence of 0.1 ppm SO₂ and two-stages of performance degradation are found. A degradation mechanism based on the occupation of SO₂ in the oxide ion vacancies and subsequent formation of SO₃²⁻ and SrSO₄ was proposed for the irreversible poisoning effect of SO₂.

In this paper, the mechanism and kinetics of sulfur poisoning and deposition on the LSCF cathodes are discussed at different temperatures and SO₂ content using electrochemical analysis, FIB-SEM and time-of-flight secondary ion mass spectrometry (TOF-SIMS) [175, 176, 180-186]. The results show that the presence of SO₂ in air mainly poisons the electrochemical activity of
LSCF electrodes by inhibiting the electrode bulk process and to a less extent by the electrode surface process and then by the formation of SrSO₄ as well as CoFe₂O₄ on the surface and the bulk of LSCF electrode. The deposition processes of sulfur species at LSCF electrodes is essentially a chemical reaction and is kinetically controlled by the nucleation reaction between the gaseous sulfur species and the segregated SrO on the LSCF electrode surface.

8.2 Experimental

8.2.1 Half-cell preparation

Electrolyte pellets were prepared by die pressing Gd₀.₁Ce₀.₉O₁.₉₅ (GDC, Fuel Cell Materials, USA) powder, followed by sintering at 1450 °C for 5 h. The pellets were 0.5–0.9 mm in thickness and 19–20 mm in diameter. LSCF (Fuel Cell Materials, USA) cathode was applied onto the GDC pellets by slurry coating and sintered at 1050 °C for 2 h. The thickness of the LSCF electrodes was 20–30 µm and the geometric area was 0.5 cm². A Pt counter electrode (Pt ink, Gwent Group of Companies, United Kingdom) was coated on the opposite surface of the electrolyte and fired at 800 °C. A Pt reference electrode was attached on the edge of the electrolyte. Pt mesh was placed on the surface of LSCF cathodes as the current collector. The cell was symmetrically placed between double alumina tubes. A glass seal was used for the cathode side for avoiding leakage of SO₂-air mixture gas. The operation temperature for the cell tests was 600 °C, 700 °C and 800 °C, respectively. During the cell tests, dry SO₂-containing air with SO₂ concentration of 1 and 10 ppm was supplied to the cathode.
8.2.2 Half-cell tests

Electrochemical performance and impedance responses were measured on a three-electrode cell using Gamry Reference 3000 Potentiostat. Impedance curves were recorded under open circuit with frequency range from 0.1 Hz to 100 kHz and the signal amplitude of 10 mV. Electrode polarization resistance ($R_E$) was then measured by the differences between the high and low frequency intercepts, and ohmic resistance ($R_Ω$) was obtained from the high frequency intercept. The electrode was stabilized in air for 1 h before introducing SO$_2$. SO$_2$ gas was switched to clean air after exposure in SO$_2$-containing air in order to study the recovery effect of LSCF electrodes.

8.2.3 Half-cell characterizations

The surface microstructure of LSCF cathodes before and after the electrochemical tests were examined by scanning electron microscopy (SEM, NEON 40EsB) and energy dispersive X-ray analysis (EDX, INCA, Oxford, England). Moreover, the cross section of LSCF cathodes after polarization at 200 mA.cm$^{-2}$ for 20 h in the presence of 1 ppm SO$_2$ at 600 °C, 700 °C and 800 °C were investigated in details. Epoxy resin was infiltrated under vacuum. A thin wafer sample was lifted out in a focused ion beam-SEM (FIB-SEM, FEI Quanta 200i 3D) and polished in another FIB-SEM (HI-TACHI MI4000L). Microstructure observation and elemental mapping analysis of the wafer sample were carried out using both HITACHI MI4000L and scanning electron microscopy (SEM, JEOL JEM-ARM200F, 200kV) equipped with energy dispersive X-ray spectroscopy (EDS) detectors.

XRD (D8 Advance, Bruker, Germany) was used to examine the phase change of LSCF electrodes before and after the electrochemical tests. X-ray photoelectron spectroscopy (XPS) was
further performed using a Kratos AXIS Ultra DLD instrument using monochromated Al Kα X-rays (energy 1486.7 eV). Pass energy of 40 eV was used for the core level spectra. TOF-SIMS (ION-TOF GmbH, Münster, Germany) was then used to investigate the sulfur distribution in different LSCF cathodes in details. The measurement mode combined spectrum and fast imaging modes together. For the spectrum mode, analysis beam was 30 keV Bi+ with spot size (ca. 5 um), while for the fast imaging mode, analysis beam was 30 keV Bi+ with spot size (ca. 150 nm). Sputter beam was 2 keV Cs+ for two modes.

8.3 Results and discussions

8.3.1 Electrochemical performance of LSCF electrodes in the absence of SO2

Fig.8.1 shows the initial polarization and impedance curves for the O2 reduction reaction on LSCF electrodes as a function of cathodic current passage at 200 mA cm\(^{-2}\) at 600, 700 and 800 °C in the absence of 1 ppm SO2. Under a cathodic current of 200 mA cm\(^{-2}\), the cathodic polarization potential, \(E_{\text{cathode}}\), was more or less stable with the current passage for the O2 reduction reaction. For instance, at 600 °C, after polarization for 1h, initial \(E_{\text{cathode}}\) was \(\sim 600\) mV (Fig.8.1a). The relatively stable polarization potential is also supported by the corresponding impedance behavior (Fig.8.1b). At 600 °C, electrode polarization resistance (\(R_E\)) of LSCF electrode and ohmic resistance (\(R_\Omega\)) were 3.3 Ω cm\(^2\) and 5.2 Ω cm\(^2\), respectively. They were almost stable during the polarization period. Similar phenomenon in the cathodic polarization potential and polarization resistance was also observed for the reaction on LSCF cathodes at 700 and 800 °C (Fig.8.1c-f). At 700 °C, \(E_{\text{cathode}}\) was \(\sim 430\) mV, \(R_E\) and \(R_\Omega\) were \(\sim 0.6\) Ω cm\(^2\) and 1.7 Ω cm\(^2\). While at 800 °C, the
$E_{\text{cathode}}$ was $\sim$220 mV, $R_\Omega$ and $R_{\text{cathode}}$ were $\sim$0.15 $\Omega$ cm$^2$ and 0.8 $\Omega$ cm$^2$, respectively. All these results can indicate that the cathodic polarization has little activation effect on the electro catalytic activity of the LSCF electrode, which is different from the enhancement of cathodic polarization on LSM electrodes [157]. The initial impedance and polarization behavior of LSCF electrode for the $O_2$ reduction reaction under a cathodic current of 200 mA cm$^{-2}$ at 900 °C in the absence of Fe-Cr alloy interconnect was also investigated and the results showed that the cathodic polarization potential changed very little with the cathodic current passage [97].

8.3.2 Electrochemical performance of LSCF electrodes in the presence of $SO_2$

Fig.8.2 is the initial polarization and impedance curves for the $O_2$ reduction reaction on LSCF electrodes as a function of cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm $SO_2$ in air at 600, 700 and 800 °C. The time behavior of the cathodic potential, $E_{\text{cathode}}$, behaves different from that in the absence of $SO_2$. For example, at 600 °C, after polarization for 5 min, initial $E_{\text{cathode}}$ increased from 610 to 614 mV within 2 min of applying the cathodic current passage (Fig.8.2a) and then $E_{\text{cathode}}$ kept increasing to 767 mV within 1 hour of polarization. While at 700 °C, after polarization for 5 min, initial $E_{\text{cathode}}$ increased from 414 to 445 mV within 2 min of applying the cathodic current passage (Fig.8.2c), however, $E_{\text{cathode}}$ kept nearly stable within 1 hour of polarization. The difference in the change of $E_{\text{cathode}}$ with the cathodic current passage for the $O_2$ reduction reaction in the absence and presence of 1 ppm $SO_2$ in air is a clear indication of the poisoning effect of sulfur species on the reaction at the LSCF electrodes, especially at lower temperature (600 °C). The similarity of the initial polarization behavior of LSCF electrodes in the
presence of SO₂ in this study and in the presence of Cr species as shown early [34], an indication of inhibiting effect of sulfur species on the surface process such as the dissociative adsorption and diffusion reaction on the electrode surface for the O₂ reduction at early stages of the Fig. 8.1 Initial Polarization curves and impedance curves for the O₂ reduction reaction on porous LSCF cathodes in the absence of 1 ppm SO₂ under cathodic current passage at 200 mA cm⁻² for 1 h and (a, b) 600 °C, (c, d) 700 °C, (e, f) 800 °C. The electrochemical impedance curves were adjusted to the zero position for the purpose of comparison. Numbers in the figure are frequencies in Hz.

diffusion reaction on the electrode surface for the O₂ reduction at early stages of the
polarization. On the other hand, the electrochemical impedance responses of LSCF cathodes in the presence of 1ppm SO₂ behave similarly to the polarization potential. At 600 °C, initial $R_E$ increased from $\sim3.5 \, \Omega \, \text{cm}^2$ to 4.8 $\Omega \, \text{cm}^2$. Moreover, at 700 °C, initial $R_E$ increased from $\sim0.4 \, \Omega \, \text{cm}^2$ to 0.5 $\Omega \, \text{cm}^2$.

When the temperature increased to 800 °C, the cathodic polarization potential behaved differently to the one observed at 600 and 700 °C. For example, after polarization for 5 min, initial $E_{\text{cathode}}$ decreased from 250 mV to 215 mV within 2 min of applying cathodic polarization. And $E_{\text{cathode}}$ kept the similar decreasing trend within 1 hour polarization. It might illustrate that at a higher temperature of 800 °C, SO₂ can go into the desorption process due to the increased thermal energy of the sulfur species and desorb from the active sites of LSCF electrode surface, thus reducing the inhibiting effect of SO₂ and causing the decrease in $E_{\text{cathode}}$. The electrode polarization resistance increased with the cathodic current passage. After current passage for 1 h, $R_E$ increased gradually from 0.12 $\Omega \, \text{cm}^2$ to 0.18 $\Omega \, \text{cm}^2$.

Fig.8.3 shows the polarization and impedance curves under a cathodic current of 200 mA cm⁻² at 600, 700 and 800 °C in the presence of 1 ppm SO₂ in air for a longer period of 20 h. The characteristics of $E_{\text{cathode}}$ with current passage for the reaction at 600 °C is similar from the initial $E_{\text{cathode}}$ behavior and $E_{\text{cathode}}$ kept increasing from 626 to 811 mV with cathodic current passage for 20 h and $\Delta E_{\text{cathode}}$ was 202 mV, which can indicate that the significant sulfur poisoning effect on LSCF electrodes with the increased polarization time. $R_E$ increased from 3.5 $\Omega \, \text{cm}^2$ to 7.3 $\Omega \, \text{cm}^2$ after polarized for 20 h (Fig.8.3b). At 700 °C, the characteristic of $E_{\text{cathode}}$ with current passage for the reaction is slightly different from the initial $E_{\text{cathode}}$ behavior. For instance, with cathodic current passage for 4 h, initial $E_{\text{cathode}}$ increased from 452 mV to 462 mV within 1 min and became
more or less stable with further current passage. Moreover, \( E_{\text{cathode}} \) obviously increased to 581 mV and \( \Delta E_{\text{cathode}} \) was 129 mV after cathodic current passage for 20 h. Compared with the value of \( \Delta E_{\text{cathode}} \) (202 mV) observed at 600 °C, it can indicate that the sulfur poisoning effect was more

Fig8.2 Initial Polarization curves and impedance curves for the \( \text{O}_2 \) reduction reaction on porous LSCF cathodes in the presence of 1 ppm SO\(_2\) under cathodic current passage at 200 mA cm\(^{-2}\) for 1 h and (a,
b) 600 °C, (c, d) 700 °C, (e,f) 800 °C. The electrochemical impedance curves were adjusted to the zero position for the purpose of comparison. Numbers in the figure are frequencies in Hz.

severe at lower temperature. $R_E$ also increased with the polarization time and changed from 0.4 $\Omega$ cm$^2$ to 1.3 $\Omega$ cm$^2$ after polarized for 20 h (Fig.8.3d). While for the reaction at 800 °C after polarization for 20 h, the characteristics of $E_{\text{cathode}}$ with current passage is similar to the initial polarization behavior observed in Fig. 7-2e. For instance, with cathodic current passage for 4 h, initial $E_{\text{cathode}}$ decreased from 291 mV to 281 mV within 1 min and reached 308 mV with polarization for 20 h. The increase of $\Delta E_{\text{cathode}}$ was 17 mV, much smaller than the value observed (129 mV) at 700 °C. In terms of impedance behavior, $R_E$ increased from 0.12 $\Omega$ cm$^2$ to 0.25 $\Omega$ cm$^2$ after being polarized from 4 h to 20 h in the presence of 1 ppm SO$_2$ (Fig.8.3f)[187].
Fig. 8.3 Polarization curves and impedance curves for the O\textsubscript{2} reduction reaction on porous LSCF cathodes in the presence of 1 ppm SO\textsubscript{2} under cathodic current passage at 200 mA cm\textsuperscript{-2} for 20 h at (a, b) 600 °C, (c, d) 700 °C, (e, f) 800 °C. The electrochemical impedance curves were adjusted to the zero position for the purpose of comparison. Numbers in the figure are frequencies in Hz.

Fig. 8.4 shows polarization and impedance curves for the O\textsubscript{2} reduction reaction on LSCF cathodes under cathodic current passage at 200 mA cm\textsuperscript{-2} in the presence of 10 ppm SO\textsubscript{2} in air at 600, 700 °C and 800 °C. The polarization potential behaves similar to the reaction in the presence of 1 ppm SO\textsubscript{2}. For example, for the reaction at 600 °C, initial $E_{\text{cathode}}$ increased from 750 mV to 1023 mV and then $E_{\text{cathode}}$ increased to $\sim$2500 mV with polarization for 20 h and $\Delta E_{\text{cathode}}$ was 1600 mV. While at 700 °C, initial $E_{\text{cathode}}$ increased from 565 mV to 600 mV within 1 min and then $E_{\text{cathode}}$ increased to 700 mV with polarization for 20 h and $\Delta E_{\text{cathode}}$ was 135 mV. For the reaction at 800 °C, initial $E_{\text{cathode}}$ decreased from 453 mV to 445 mV within 1 min and then $E_{\text{cathode}}$ increased to 501 mV with polarization for 20 h and $\Delta E_{\text{cathode}}$ was $\sim$48 mV, which was much smaller than the value observed at 600 and 700 °C. Increase in the SO\textsubscript{2} also led to the increase in $R_E$. $R_E$ increased from 3.5 $\Omega$ cm\textsuperscript{2} to 10 $\Omega$ cm\textsuperscript{2} at 600 °C after polarization for 20 h. At 700 °C, $R_E$ increased from 0.4 $\Omega$ cm\textsuperscript{2} to 1.6 $\Omega$ cm\textsuperscript{2} after polarization for 20 h. $R_\Omega$ also increased gradually from 2.5 $\Omega$ cm\textsuperscript{2} to 3 $\Omega$ cm\textsuperscript{2}. While at 800 °C, $R_E$ increased from 0.12 $\Omega$ cm\textsuperscript{2} to 0.45 $\Omega$ cm\textsuperscript{2} after polarization for 20 h, and $R_\Omega$ also increased gradually from 1.46 $\Omega$ cm\textsuperscript{2} to 1.52 $\Omega$ cm\textsuperscript{2}. This result is in accordance with Wang FF’s[59] result, who found that the resistances increased rapidly at the
beginning and followed by a gradual increase with time due to the increase of SO₂ concentration.

Fig. 8.5 compares $\Delta E_{\text{cathode}}$ in air and in 1 and 10 ppm SO₂-containing air under current passage at 200 mA cm⁻² at 600, 700 °C and 800 °C, measured at different time intervals. The $\Delta E_{\text{cathode}}$ behavior is very different for the O₂ reduction reaction in SO₂-containing air at two temperatures. At 600 °C, in the case of 1 ppm SO₂ in air, $\Delta E_{\text{cathode}}$ is 10 mV and 200 mV measured at time intervals of 5 min and 20 h, respectively. At 700 °C, $\Delta E_{\text{cathode}}$ is 31 mV and 129 mV measured at time intervals of 5 min and 20 h, respectively, while for the reaction at 800 °C, $\Delta E_{\text{cathode}}$ is -35 mV and 17 mV, respectively, significantly smaller than that measured at a lower temperature of 600 and 700 °C. Similar $\Delta E_{\text{cathode}}$ behavior was also observed for the reaction in 10 ppm SO₂-containing air. The significantly higher value of $\Delta E_{\text{cathode}}$ for the O₂ reduction reaction on the LSCF electrodes at 600 °C indicates the more serious poisoning effect of SO₂ on the electrocatalytic activity of LSCF electrodes.
Fig. 8.4 Polarization curves and impedance curves for the O₂ reduction reaction on porous LSCF cathodes in the presence of 10 ppm SO₂ under cathodic current passage at 200 mA cm⁻² for 20 h at (a, b) 600 °C, (c, d) 700 °C and (e, f) 800 °C. The electrochemical impedance curves were adjusted to the zero position for the purpose of comparison. Numbers in the figure are frequencies in Hz.

Fig. 8.6 is the impedance responses of the O₂ reduction reaction on LSCF electrodes and under open circuit condition for 20 h in the presence of 1 ppm SO₂ at 700 °C. The initial Rₑ was ~0.35 Ω cm² and gradually increased to 0.8 Ω cm² after test under OCV for 20 h. The increase of polarization resistance shows the degradation of electrochemical activity of LSCF electrode, due to the poisoning effect of sulfur species that deposited in the LSCF electrode, which is similar to the recent result of Cr poisoning of LSCF electrodes under open circuit condition [39], and their results clearly demonstrated that the mechanism of Cr deposition in the LSCF electrodes is controlled most likely by the nucleation reaction instead of electrochemical process.

Fig. 8.5 Comparison of ΔEcathode for the O₂ reduction reaction on LSCF electrodes in 1 ppm SO₂ and 10 ppm SO₂-containing air under cathodic current passage of 200 mA cm⁻², measured at time intervals 600°C, 700°C, and 800°C.
of 5 min and 20 h at 600 °C, 700 °C and 800 °C.

Fig. 8.6 Impedance curves for the O₂ reduction reaction on LSCF cathodes under open circuit condition in the presence of 1 ppm SO₂ for 20 h at 700 °C. The electrochemical impedance curves were adjusted to the zero position for the purpose of comparison. Numbers in the figure are frequencies in Hz.

8.3.3 Reversibility of sulfur poisoning effect of LSCF electrodes

Fig. 8.7 The change of Ecathodic with time for O₂ reduction reaction on LSCF cathodes under cathodic current passage at 200 mA cm⁻² in the presence of 1 ppm SO₂ for 20 h and in pure air for 20 h at 600 °C.
Fig. 8.7 shows the polarization performance of a LSCF electrode under a cathodic current passage at 200 mA cm$^{-2}$ in 1 ppm SO$_2$-containing air for 20 h, followed by the polarization in the pure air for 20 h, measured at 600, 700 °C and 800 °C. At 600 °C, with polarization for 1 h, $E_{\text{cathode}}$ was $\sim$640 mV and kept stable. In the presence of 1 ppm SO$_2$, $E_{\text{cathode}}$ increased from $\sim$645 mV to $\sim$790 mV with polarization for 20 h and then $E_{\text{cathode}}$ finally reached to $\sim$800 mV after switching off SO$_2$ under the same condition. At 700 °C, with polarization for 1 h, $E_{\text{cathode}}$ was $\sim$440 mV and $E_{\text{cathode}}$ increased to $\sim$524 mV with polarization for 20 h and then $E_{\text{cathode}}$ was $\sim$559 mV after switching off SO$_2$. At 800 °C, $E_{\text{cathode}}$ was $\sim$261 mV within 1 h of applying cathodic current. $E_{\text{cathode}}$ increased from $\sim$259 mV to $\sim$279 mV with polarization for 20 h, and then $E_{\text{cathode}}$ finally increased to $\sim$290 mV after switching off SO$_2$. All these results indicate the electrochemical performance of LSCF electrodes is significantly deteriorated by sulfur dioxide due to the formation of SrSO$_4$ and CoFe$_2$O$_4$ and can’t be recovered by introducing clean air. However, in Wang FF’s result [64], they reported that The SO$_2$ was removed from the air after 2 h, which caused about 1.5% degradation recovery for LSCF electrode at the early stage (<10 h) due to the SO$_2$ adsorption initially took place. In our case, SO$_2$ was removed after being polarized for 20 h and the results showed that sulfur poisoning on the LSCF electrodes is not a reversible process.

### 8.3.4 Microstructure change of LSCF electrodes

Fig. 8.8 shows the SEM micrographs of the surface and cross-section of the LSCF electrodes after cathodic current passage at 200 mA cm$^{-2}$ at 600 °C, 700 °C and 800 °C in the presence of 1 ppm SO$_2$ and 10 ppm SO$_2$ in air for 20 h. For as-prepared LSCF electrodes (Fig. 8-8j), the particles are uniformly shaped and distributed with grain size of $\sim$0.2-1 µm and the surfaces of
LSCF particles are quite smooth, and there is also a good distribution of large and small pores. However, there is significant microstructural change after the exposure to the presence of 1 ppm SO$_2$ and 10 ppm SO$_2$ at 600 and 700 °C. At 600 °C, the surfaces of LSCF particles were not as smooth as the as-prepared LSCF particles and there were some particles deposited on the surface (as shown in Fig.8-8a). At 700 °C, the surface of LSCF particles appears to be quite rough and was covered by some small particles in the range of ~20 nm (indicated by the arrow in Fig.8-8d). When the concentration of SO$_2$ increased to 10 ppm in air, the morphology of LSCF particles obviously changed (indicated by the circle in Fig.8-8e) and the surface seemed to be covered by some thin deposited films. EDX results show that the existence of sulfur (Fig.8-8l), indicating sulfur deposition on the surface of LSCF electrodes. While at 800 °C, the microstructure change of surface of LSCF electrodes was not as obvious as at 700 °C that can indicate that sulfur poisoning effect on LSCF electrodes is less severe, which is consistent with the observation on dense LSCF bar samples [188]. There is less microstructural change in the bulk of LSCF electrodes after a cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm SO$_2$ at three temperatures for 20 h (Fig.8-8c and f). Wang et al also reported [64] that there was no obvious microstructure change within the whole cathode layer at 800 °C.

Fig.8.9 shows SEM micrographs of GDC electrolyte surface after a cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm and 10 ppm SO$_2$ for 20 h at 600, 700 and 800 °C for 20 h. With the increase of the concentration of SO$_2$ to 10 ppm, the electrolyte surface seemed to become rougher. However, EDS didn’t detect the sulfur species on the surface of GDC electrolyte and this indicates that isolated small particles were the LSCF left on the GDC electrolyte surface. This also shows that sulfur does not preferentially deposit on the GDC electrolyte surface, which is
consistent with the SEM results of GDC electrolyte under chromium deposition and poisoning on LSCF electrode [97].

Fig. 8.10 shows the SEM micrographs of the surface and cross section of LSCF electrodes in the presence of 1 ppm SO$_2$ under open circuit voltage (OCV) at 700 °C for 20 h. There are also some small particles in the range of ~10 nm deposited on the surface of LSCF electrodes (as indicated by the arrows in Fig. 8-10a). However, EDS didn’t detect the presence of sulfur species. There is also less microstructural change in the bulk of LSCF electrodes under OCV condition at 700 °C for 20 h.

![Figure 8.8 SEM micrographs of surface and cross section of LSCF cathodes under cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm SO$_2$, 10 ppm SO$_2$ and (j-l) as-prepared LSCF electrode at 600, 700 and 800 °C. Typical EDS pattern taken from the areas marked by circles is shown in (g).](image-url)

Fig. 8.8 SEM micrographs of surface and cross section of LSCF cathodes under cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm SO$_2$, 10 ppm SO$_2$ and (j-l) as-prepared LSCF electrode at 600, 700 and 800 °C. Typical EDS pattern taken from the areas marked by circles is shown in (g).
8.3.5 XPS and XRD analysis

Fig. 8.11 shows the XRD result of porous LSCF electrodes under cathodic current passage at 200 mA cm\(^{-2}\) in the presence of 1 ppm SO\(_2\) and 10 ppm SO\(_2\) for 20 h at 600, 700 °C and 800 °C. The main peaks were LSCF and GDC. However, prominent XRD peaks associated with the formation of SrSO\(_4\) phase were observed for all samples and the intensity of SrSO\(_4\) also became stronger with the increase of SO\(_2\) content as well as the decrease of temperature. For instance, at 600 °C, the intensity of SrSO\(_4\) was the highest one among other temperatures. In addition, CoFe\(_2\)O\(_4\) phase was also observed, which is in agreement with other researchers [59], who reported that for the cell exposed to SO\(_2\) with high concentration (>1 ppm), the diffraction lines associated with SrSO\(_4\) and CoFe\(_2\)O\(_4\) appeared. Bucher et al also confirmed the CoFe\(_2\)O\(_4\) formation when LSCF reacted with SO\(_2\) [67].
circles is shown in (g). The LSCF electrode coatings were removed by adhesive tape.

Fig. 8.12 shows the selected survey scan of the LSCF electrode surface under open circuit condition in the presence of 1 ppm SO$_2$ for 20 h at 700 °C. All related elements like La, Sr, Co, Fe, O, S were observed on the surface of LSCF electrodes. After deconvolution analysis, the results of the deconvoluted Sr 3d spectra were comprised of four peaks (Fig. 8.12 b). The main peaks in LSCF electrode measured at about 131.9 eV and 133.60 eV were originated from Sr 3d$_{5/2}$ and 3d$_{3/2}$, which corresponded to the perovskite structure [138]. Other two peaks in LSCF measured at about 133.1 eV, 134.8 eV that may be ascribed to SrO on LSCF surface [189]. And the binding energy of the deconvoluted S 2p$_{3/2}$ spectra was $\sim$169.4 eV, which is in accordance with the XPS results of SrSO$_4$ [137]. So it can be concluded that SrSO$_4$ was formed on the surface of LSCF electrode even under OCV condition. This can indicate the deposition of sulfur species on the LSCF electrode has no direct relationship with cathodic polarization.

Fig. 8.10 SEM micrographs of surface and cross section of LSCF cathodes under open circuit condition in the presence of 1 ppm SO$_2$ for 20 h at 700 °C (a, b). Typical EDS pattern taken from the areas...
marked by circles is shown in (c).

Fig. 8.11 XRD patterns of LSCF electrodes under cathodic current passage at 200 mA cm\(^{-2}\) in the presence of 1 ppm SO\(_2\) and 10 ppm SO\(_2\) for 20 h at 700 °C and 800 °C.

In other words, the deposition of sulfur species on the LSCF electrode is not limited by the electrochemical reaction, which is also consistent with Bo Wei’s result\([39]\) that points out the mechanism of Cr deposition on LSCF electrodes under open circuit condition is a chemical process in nature that is initiated most likely by the nucleation reaction between surface segregated SrO\(_x\) and gaseous Cr species.

Fig. 8.12 The selected survey scan of LSCF under open circuit condition in the presence of 1 ppm SO\(_2\) at 700 °C (a); The selected high resolution XPS of the Sr 3d (b), S 2p (c).
8.3.6 Sulfur distribution by FIB-SEM and TOF-SIMS

Fig. 8.13 shows FIB-SEM mapping of cross section of LSCF electrodes after being poisoned by 1 ppm SO$_2$ under cathodic current passage at 200 mA cm$^{-2}$ at 700 °C and 800 °C for 20 h. At 700 °C, it clearly shows that sulfur existed heterogeneously in the LSCF layer, especially ~15 μm from the surface and formation of SrSO$_4$ (as indicated by EDXS result in Fig. 8-13C). However, Sr and S elements seemed not appearing in the same position in the bulk. Also, there are also some Co enriched particles (as indicated by the arrows in Fig. 8-13 A), which is in accordance with Ling’s result about Co segregation from chromium poisoning of LSCF bar samples at 800 °C. EDXS clearly shows that cobalt aggregations occurred and CoFe$_2$O$_4$ was detected (Fig. 8-13D). While at 800 °C, cobalt aggregations and formation of SrSO$_4$ can also be observed.

Sulfur distribution as a function of depth from cathode surface was further obtained using TOF-SIMS to qualitatively analyze the sulfur distribution from cathode surface layer to the interface. Fig. 8.14 shows the TOF-SIMS image of the La, Sr, Co, Fe and S signals recorded of the electrode under cathodic current passage at 200 mA cm$^{-2}$ in the presence of 1 ppm SO$_2$ for 20 h at 600, 700 °C and 800 °C. At 600 °C, sulfur is not only deposited on the surface of LSCF electrode but also found in the bulk of LSCF cathode. Similar phenomenon can also be observed at 700 °C. Compared with intensity of sulfur signal, it can be seen that sulfur is more likely to deposit on the surface of LSCF electrodes. While at 800 °C, the intensity of S signal is lower than the one at 600 and 700 °C, which means that the severe sulfur poisoning effect occurs at lower temperature.
Fig. 8.13 Typical FIB-SEM elemental distributions mapping of cross section of LSCF cathodes under cathodic current passage at 200 mA cm^{-2} in the presence of 1 ppm SO\textsubscript{2} for 20 h at 700 °C and 800 °C. EDXs of Co and Sr element chosen with different color arrows.
Fig. 8.14 Typical TOF-SIMS ion image of La, Sr, Co, Fe and S of LSCF cathodes under cathodic current passage at 200 mA cm\(^{-2}\) in the presence of 1 ppm SO\(_2\) at 600 °C (A), 700 °C (B) and 800 °C (C). A SEM image of a LSCF/GDC cell is added for clarity on the left of each image. The brighter colors correspond to higher intensity.

### 8.3.7 Mechanism and kinetics of sulfur deposition and poisoning on LSCF electrodes

As shown in the study, the results for sulfur deposition and poisoning on the electrochemical performance and microstructure of LSCF electrodes are summarized below.

1. For the O\(_2\) reduction of LSCF electrodes in the absence of SO\(_2\), \(E_{\text{cathode}}\) and \(R_e\) kept nearly stable with cathodic current passage, showing that cathodic polarization has
little activation effect on the electrocatalytic activity of the LSCF electrode.

2. In the presence of SO2 in air, the LSCF electrodes behaved differently from that in clean air for the O2 reduction reaction. ECathode increased with cathodic current passage and the ΔE value is much smaller for the O2 reduction reaction at 800 °C as compared to that at 600 and 700 °C. This also indicates the pronounced poisoning effect of SO2 on the electrochemical activity of LSCF electrodes at 600 °C.

3. Deposition of sulfur species occurred on the LSCF electrode surface with and without cathodic current passage at 700 °C. This clearly indicates that the deposition of sulfur species at the LSCF electrode has no intrinsic relationship with the electrochemical polarization.

4. The stability results of LSCF electrodes in SO2 indicate the deteriorated electrochemical activity of LSCF electrodes (ECathode) due to the SO2 poisoning cannot be recovered by polarization in the pure air or clean air.

5. Both EDXS and XRD results indicate the sulfur deposition and formation of SrSO4 as well as CoFe2O4 on the surface after polarization at 200 mAcm⁻² in the SO2-containing air at 600, 700 and 800 °C. Under the present testing condition, sulfur species preferentially deposited on the surface and bulk of LSCF electrode rather than at the LSCF electrode/GDC electrolyte interface, which is due to that there is no formation of deposit bands or rings on the GDC electrolyte surface as well as TOF-SIMS result.

The very different behavior of the polarization potential for the O2 reduction reaction on the LSCF electrodes in the absence and presence of SO2 in air at 600, 700 and 800 °C demonstrates
the significant poisoning effect of sulfur on the electrochemical activity of LSCF for the O₂ reduction reaction. Such degradation behavior for the reaction on the LSCF electrodes in SO₂-containing air at 600 and 700 °C is similar to that reported for the O₂ reduction reaction on LSCF electrodes in the presence of Fe-Cr metallic interconnect [34, 97, 190]. Detailed study of O₂ reduction on porous LSCF electrode in the presence of Fe-Cr metallic interconnect indicated that the rapid increase of the final E_{Cathode} is due to the poisoning effect of gaseous Cr species on the oxygen reduction reaction on LSCF electrodes. The similarity of the polarization behavior of LSCF electrodes in the presence of SO₂ in this study and in the presence of Cr species can imply that SO₂ would first adsorb on the active sites of LSCF surface at 600 and 700 °C. However, the much smaller initial E_{Cathode} compared to the gaseous Cr species on LSM electrode under the same situation [190] at 700 °C might indicate that the kinetics of O₂ reduction reaction on LSCF electrodes is mostly dominated by the electrode bulk process and to a less extent by the electrode surface. The adsorbed SO₂ on the active sites of LSCF can also be desorbed and this is indicated by the almost reproducible initial polarization behavior of E_{Cathode} as a function of cathodic current passage. Both the adsorption and desorption rates of SO₂ would depend on the temperature. At a higher temperature of 800 °C, the active sites would be released on the LSM electrode surface for the reaction and reduce the inhibiting effect of SO₂. This explains the much smaller ∆E for the reaction at 800 °C as compared to that at 600 and 700 °C.

The deposition of sulfur species on the LSCF electrode surface under open circuit also indicates that sulfur deposition in the LSCF/GDC system is not controlled by the electrochemical process. Consequently, the deposition of sulfur species at the LSCF electrode is in nature a chemical process. This conclusion is consistent with the proposed mechanism of the Cr deposition
process at the LSCF electrode [97]. SEM results indicate the significant sulfur deposition and reaction on the surface and bulk of LSCF electrodes (Fig.8-13). The deposition of sulfur in the electrode bulk is also confirmed by the TOF-SIMS (Fig.8-14). XRD and XPS results identify the formation of SrSO$_4$ phase and CoFe$_2$O$_4$ on the LSCF electrode surface after polarization in the SO$_2$-contained air. The formation of SrSO$_4$ phase has already been reported on LSCF electrodes after exposed to SO$_2$-containing air [59]. So the driving force behind the nucleation theory is the surface segregation and migration of cationic species on the surface of perovskite oxide cathodes. The decomposition of LSCF would also lead to the formation of (La,Sr)$_2$(Co,Fe)O$_4$ and CoO, as shown by Hashimoto et al. [188]. The accelerated migration and segregation of SrO from the bulk to the surface and subsequent reaction between SrO and SO$_2$ species can be written as follows:

\[
(\text{La, Sr})(\text{Co, Fe})\text{O}_3 + \text{SO}_2 \rightarrow \text{SrSO}_4 + (\text{La, Sr})_1-x(\text{Co, Fe})\text{O}_3 \quad [1]
\]

\[
(\text{La, Sr})_1-x(\text{Co, Fe})\text{O}_3 \rightarrow (\text{La, Sr})_2(\text{Co, Fe})\text{O}_4 + \text{CoO} \quad [2]
\]

\[
(\text{La, Sr})_2(\text{Co, Fe})\text{O}_4 + \text{SO}_2 + \text{CoO} \rightarrow \text{SrSO}_4 + \text{CoFe}_2\text{O}_4 + \text{other amorphous phase} \quad [3]
\]

In terms of differences in the manner of the sulfur deposition process between LSCF/GDC and LSM/YSZ system, for LSCF electrodes, sulfur species poisons the O$_2$ reduction reaction on LSCF electrodes mainly by inhibiting the electrode bulk process and to a less extent by the surface process. For LSM electrode, at 700 °C, sulfur poisons the electrochemical activity of LSM electrode by SO$_2$ adsorption at the active sites on the surface of LSM grains, which in turn inhibits the oxygen dissociation and diffusion processes, while at 800 °C, SO$_2$ desorption process could take place, releasing the occupied active site, then the reaction between SO$_2$ and SrO segregated on the LSM surface occurs, resulting in the formation of SrSO$_4$. Similar to the effect of the sulfur deposition on the O$_2$ reduction reaction in the LSM/YSZ system, the formation of SrSO$_4$ and
CoFe$_2$O$_4$ species on the surface of LSCF would unavoidably result in the degradation of LSCF electrode performance.

Based on the discussion above, the mechanism and kinetics of SO$_2$ deposition and poisoning on the O$_2$ reduction reaction on LSCF electrodes can be illustrated in Fig.8-15. As compared to the reaction at 600 and 700 °C, more favorable desorption of SO$_2$ on the LSCF active sites at 800 °C would occur and reduced SO$_2$ poisoning effect could be observed by the smaller increase of $E_{\text{cathode}}$. However, at the same time, the adsorbed SO$_2$ will react with segregated SrO, forming SrSO$_4$ on the surface and bulk of LSCF electrode. In addition, CoFe$_2$O$_4$ will also be formed. Then it will in turn reduce the electronic conductivity and deteriorate the electrocatalytic activity of LSCF electrodes for the O$_2$ reduction reaction. So the observation of nanoparticle formation indicates that the deposition of sulfur on the LSCF electrode surface and bulk is most likely initiated by the nucleation reaction between the SrO nuclei and gaseous SO$_2$ in air.

![Fig.8.15 Scheme of mechanism of sulfur deposition and poisoning on the O2 reduction reaction on LSCF oxygen electrodes under the SOFC operation condition at 600 °C and 700 °C (SO2 adsorption on LSCF electrodes) and 800 °C (SO2 desorption on LSCF electrodes).]

### 8.4 Conclusions

The mechanism and kinetics sulfur deposition and poisoning on LSCF electrodes was
investigated at 600, 700 and 800 °C. Sulfur species poisons the O₂ reduction reaction on LSCF electrodes by inhibiting the electrode bulk process, especially at 600 °C. Sulfur poisoning effect of LSCF electrodes increased with higher concentration of SO₂. FIB-SEM as well as EDX results show that sulfur exists heterogeneously in the LSCF layer, especially ~15 μm from the surface and the amount of sulfur becomes less at 800 °C, which indicate that sulfur poisoning effect is most pronounced at lower temperature. The deposition of sulfur on the LSCF electrode and under open circuit condition at 700 °C indicates that sulfur poisoning in the LSCF/GDC system is essentially a chemical reaction. The O₂ reduction reaction kinetics of LSCF electrodes is affected by the sulfur inhibiting species on the electrode bulk process and also the temperature, and then the kinetics of the deposition processes of sulfur species is controlled by the nucleation reaction between the SrO and the gaseous sulfur species, forming SrSO₄ and CoFe₂O₄ was also formed due to the decomposition of LSCF perovskite oxides. The effect of sulfur deposition and poisoning on the electrochemical activity of LSCF cathodes is not reversible after changing to SO₂-free air.

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Chapter 9: Anti-sulfur poisoning of BaCeO$_3$-impregnated LSCF cathodes

9.1 Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFCs) operating at 600-800 °C are quite promising due to the fuel flexibility than low temperature fuel cells and is also appropriate for wide applications [17-20]. However, one of the most essential challenges promoting the commercialization of SOFC is to develop cathode materials with high electrochemical activity for O$_2$ reduction reaction, high stability as well as optimum tolerance to impurities like chromium, sulfur, moisture under the real operation condition [34, 52, 177]. Nowadays, there are extensive studies on sulfur deposition and poisoning on different cathode materials like LSCF, La$_{0.6}$Sr$_{0.4}$CoO$_{3-δ}$ (LSC) and LSM [50, 59, 65, 67, 187]. Their results show that a ppm level of sulfur dioxide in the air can deposit and poison the cathodes, forming SrSO$_4$ and then finally leading to the electrochemical performance degradation.

Solution impregnation technique is one of the most useful ways to obtain SOFC cathodes with better electrochemical performance [191-197]. It is also widely used in enhancing the performance of cathodes towards chromium poisoning. For instance, infiltration of oxygen ionic conductors like gadolinium-doped ceria (GDC) nanoparticles or alkaline oxide like BaO can significantly enhance the LSCF electrode performance and reduce Cr deposition and poisoning of LSCF by lowering the contact opportunity between LSCF and gaseous Cr species or preferentially forming BaCrO$_4$ instead of SrCrO$_4$ that was caused by the reaction of nucleation agent Sr with gaseous Cr species [104, 198]. Hence, it is also urgent to try alternative ways to minimize the sulfur deposition and poisoning of cathodes by reducing the direct contact between LSCF and sulfur.
dioxide as well as eliminating nucleation agents such as Sr in the LSCF cathode materials to avoid the formation of SrSO₄, thus significantly reducing the sulfur deposition and interaction with the cathode.

It is known that doped barium cerate electrolytes show high protonic conductivity due to their low activation energy for proton conduction [199-201] and BaCeO₃-based compositions also exhibit high ionic conductivity at intermediate or lower temperatures [202], however, they can easily react with acidic gases (CO₂, SO₂) and steam [203-205]. Doped BaCeO₃ materials have been proved to be chemically unstable in acidic and amphoteric gases, including CO₂, SO₂ and H₂O, which form carbonates, sulfates and hydroxides. For instance, the decomposition of BaCeO₃ in CO₂ and H₂O to BaCO₃ and Ba(OH)₂ were proposed earlier by Gopalan and Virkar [206], and Tanner and Virkar [207] respectively. Here, for the first time, infiltration of proton conductors like barium cerate (BaCeO₃) into LSCF electrodes was investigated against sulfur deposition and poisoning on cathodes. The results indicate that BaCeO₃ impregnation can significantly enhance LSCF performance and inhibit sulfur poisoning by forming some barium sulfate compound on the electrode surface at 700 °C, so it is highly effective to enhance the sulfur-tolerance of LSCF electrodes.

9.2 Experimental

9.2.1 Half-cell preparation

Electrolyte pellets were prepared by die pressing Gd₀.₁Ce₀.₉O₁.₉₅ (GDC, Fuel Cell Materials, USA) powder, followed by sintering at 1450 °C for 5 h. The pellets were around 0.5–0.9 mm in thickness and 20 mm in diameter. LSCF (Fuel Cell Materials, USA) cathode ink was painted onto
the center of GDC pellets and sintered at 1050 °C for 2 h. The thickness of the LSCF electrodes was 20–30 µm and the geometric area was 0.5 cm². BaCeO₃ with a stoichiometric amount of Ba(NO₃)₂, Ce(NO₃)₂·6H₂O (99%, Alfa-Aesar) solution (0.2 mol L⁻¹) was infiltrated into the LSCF cathodes and heat-treated at 1050 °C for 3 h. The infiltrated BaCeO₃ loading was 1.8 mg cm⁻².

9.2.2 Half-cell tests

The electrochemical stability of LSCF and BaCeO₃-LSCF cathodes were tested using a Gamry Reference 3000 Potentiostat. Pt paste was used as the counter electrode and reference electrode. Pt mesh was placed on the surface of LSCF and BaCeO₃-LSCF cathodes as the current collector. The cell was symmetrically placed between double alumina tubes. A glass seal was used for the cathode side in order to avoid leakage of SO₂-air mixture gas. During the cell tests, dry SO₂-containing air with SO₂ concentration of 1 ppm was supplied to the cathode. The electrode was stabilized in air for 1 h before introducing SO₂. The air flow rate was 100 mL min⁻¹. IR-free overpotential as a function of cathodic current passage time at 200 mA cm⁻² was recorded at 700 °C. Impedance responses were measured with the frequency range from 0.1 Hz to 100 kHz and the signal amplitude of 10 mV. Electrode polarization resistance (Rₑ) was obtained from the differences of the low and high frequency intercepts, and electrode ohmic resistance (Rₒ) was obtained from the high frequency intercept from the impedance curves.

9.2.3 Half-cell characterizations

XRD (D8 Advance, Bruker, Germany) was used to examine the phase composition of BaCeO₃-LSCF after being poisoned by SO₂ at 700 °C. The surface and cross section of cathodes
before and after the tests were examined by scanning electron microscopy (SEM, NEON 40EsB) and an X-ray energy dispersion spectrometer (EDS).

9.3 Results and discussions

9.3.1 Electrochemical performance of LSCF electrodes in the absence of SO₂

Figure 8-1 shows the electrochemical impedance responses of LSCF and BaCeO₃ impregnated LSCF (BaCeO₃-LSCF) electrodes for oxygen reduction reaction from 800 °C to 600 °C. The high frequency (100K Hz) was corresponding to the ohmic resistance of the electrolyte and only electrode polarization resistance (R_p) was made for comparison in this study. It can be clearly seen that BaCeO₃-LSCF electrode depicted an obvious decreased of R_p at lower temperature. For instance, R_p was ∼0.88 Ω cm² at 600 °C, smaller than the value of ∼3.7 Ω cm² that was observed for pure LSCF electrodes under the same condition. Moreover, it is also similar to GDC-impregnated LSCF electrode (R_p with ∼0.52 Ω cm² at 600 °C) with those reported before. However, at higher temperature (800 °C), R_p for LSCF and BaCeO₃-LSCF was ∼0.08 Ω cm² and ∼0.07 Ω cm², respectively. It can be observed that the activation energy of R_p for pure LSCF electrode was ∼1.54 eV (Fig.9-1c), which was similar with the value of 1.2-1.6 eV reported before. The activation energy of R_p for BaCeO₃-LSCF electrode, is ∼0.96 eV (Fig.9-1c), which was smaller than pure LSCF electrode, which could indicate that a certain amount of proton conductor BaCeO₃ could lower the activation energy.
Fig. 9.1 Impedance curves for the O₂ reduction reaction on LSCF (a) and BaCeO₃-LSCF (b) cathodes from 800 °C to 600 °C under the open circuit in air. The corresponding activation energies are shown in (c,d). Numbers in figures are frequencies in Hz.

Fig. 9.2 is the polarization and impedance curves of LSCF and BaCeO₃-LSCF electrode as a function of cathodic current passage at 200 mA cm⁻² at 700 °C for 40 h in the absence of 1 ppm SO₂. For LSCF electrodes, under a cathodic current passage of 200 mA cm⁻² at 700 °C for 40 h, the initial overpotential (η) was ~40 mV and increased to ~70 mV. Rₚ increased from 0.2 Ω cm² to 0.83 Ω cm² after being polarized for 40 h (Fig. 9-2b). And ohmic resistance (Rₒ) slightly increased from 1.2 Ω cm² to 1.25 Ω cm². This can indicate that the electrocatalytic activity of LSCF electrodes for the O₂ reduction reaction degrades under cathodic polarization at 200 mA cm⁻², as indicated by the continuous increase of Rₚ, Rₒ and η, which is in consistent with Yihui Liu’s result about investigating the degradation mechanism of LSCF cathodes under a cathodic current passage of 200 mA cm⁻² at 750 °C for 120 h, which shows that the polarization losses for the O₂
reduction reaction on LSCF under a cathodic current of 200 mA cm\(^{-2}\) are mainly related to the low
frequency electrode process associated with the oxygen adsorption, dissociation and diffusion
[86]. However, BaCeO\(_3\)-LSCF electrode showed a better and stable polarization performance (\(\eta\)
slightly increased from 16 mV to 26 mV) (Fig.9-2c). The relatively stable polarization potential is
also supported by the corresponding impedance behavior. \(R_p\) slightly increased from 0.25 \(\Omega\) cm\(^2\)
to 0.4 \(\Omega\) cm\(^2\) at 700 °C. The impedance responses are characterized by an arc with a low frequency
inductance loop that this low-frequency loop is often seen for the reaction in nanostructured
electrodes, and the low-frequency loop could be due to significant dissociation and adsorption of
oxygen species on the electrode surface, enhanced by the nanostructure and the presence of
catalytic promoter [197].

Fig.9.2. Polarization and impedance curves under cathodic current passage at 200 mA cm\(^{-2}\) at 700 °C
for 40 h for LSCF (a,b) and BaCeO\(_3\)-LSCF (c,d) in the absence of 1 ppm SO\(_2\). Numbers in the figure are
frequencies in Hz.
9.3.2 Electrochemical performance of LSCF electrodes in the presence of SO\textsubscript{2}

Fig. 9.3 is the polarization and impedance curves of LSCF and BaCeO\textsubscript{3}-LSCF electrode as a function of cathodic current passage at 200 mA cm\textsuperscript{-2} at 700 °C for 40 h in the presence of 1 ppm SO\textsubscript{2}. The time behavior of overpotential behaves differently for LSCF and BaCeO\textsubscript{3}-LSCF. For the reaction on LSCF electrodes, η obviously increased from 53 mV to 180 mV with the polarization time for 40 h, an increase in overpotential by around 3 times. \( R_p \) also increased from 0.25 Ω cm\textsuperscript{2} to 1.6 Ω cm\textsuperscript{2}. However, in the presence of 1 ppm SO\textsubscript{2}, the electrochemical performance of BaCeO\textsubscript{3}-LSCF performed better and η increased from 63 mV to 80 mV after being polarized for 40 h (Fig. 9-2c). \( R_p \) also increased from 0.4 Ω cm\textsuperscript{2} to 0.7 Ω cm\textsuperscript{2}. All these electrochemical performance results can obviously indicate that BaCeO\textsubscript{3}-LSCF electrode presented a higher tolerance towards sulfur poisoning at 700 °C.
for 40 h for LSCF (a,b) and BaCeO$_3$-LSCF (c,d) in the presence of 1 ppm SO$_2$. Numbers in the figure are frequencies in Hz.

### 9.3.3 Microstructure change of LSCF electrodes

Fig. 9.4 shows the SEM micrographs of the surface and cross-section of the LSCF and BaCeO$_3$–LSCF electrodes after cathodic current passage at 200 mA cm$^{-2}$ at 700 °C in the absence and presence of 1 ppm SO$_2$ for 40 h. For as-prepared LSCF electrodes (Fig. 9-4g), the particles are uniformly shaped and the average size is 200±20 nm and the surfaces of LSCF particles are quite smooth, and also there is also a good distribution of large and small pores. Under 200 mA cm$^{-2}$ at 700 °C for 40 h in the absence of 1 ppm SO$_2$ for LSCF electrodes, the size of LSCF particles increased to 220±30 nm (Fig. 9-4a). However, there is significant microstructural change after the exposure to the presence of 1 ppm SO$_2$ at 700 °C. The surfaces of LSCF particles were not smooth and there were some nanoparticles can be deposited on the surface (as shown in Fig. 9-4d). EDX results show that the existence of sulfur (inset in Fig. 9-4d), which is most likely due to the formation of SrSO$_4$ [187] on the surface of LSCF electrode. This result is in accordance with others’ reported the sulfur poisoning on LSCF electrodes [67].

In the case of BaCeO$_3$-LSCF electrode, fine round nanoparticles (~40nm) are distributed uniformly on the LSCF surface after being polarized at 200 mA cm$^{-2}$ at 700 °C for 40 h in the absence of 1 ppm SO$_2$ (as indicated by arrow in Fig.9-4b). However, after polarized for 40 h in the presence of 1 ppm SO$_2$, those nanoparticles changed from round to needle shape and the length was around 30 nm (Fig. 9-4e). The distribution of the nanoparticles was relatively random, different from the infiltrated BaCeO$_3$ particles. Such change is most likely due to the formation of new phase. This indicates that the presence of BaCeO$_3$ nanoparticles might affect the interaction
between sulfur species and LSCF electrodes. However, EDX results didn’t obtain any detailed information about these particles due to the detection limit. There is less microstructural change in the bulk of BaCeO₃-LSCF electrodes after a cathodic current passage at 200 mA cm⁻² in the absence and presence of 1 ppm SO₂ at 700 °C for 40 h (Fig. 9-4c and f). Wang et al also reported that there was no microstructure change within the whole cathode layer for LSCF electrodes at 800 °C [59].

![Fig.9.4 SEM micrographs of surface and cross section of LSCF and BaCeO₃-LSCF cathodes under cathodic current passage at 200 mA cm⁻² in the absence (a, b, c) and presence (d, e, f) of 1 ppm SO₂ at 700 °C for 40 h. (g) as-prepared LSCF electrode. The insets are the corresponding EDS spectra.](image)

### 9.3.4 XRD analysis

Fig.9.5 shows the XRD pattern recorded on the surface of LSCF and BaCeO₃-LSCF electrodes (0.36 mg/cm²) as a function of cathodic current passage at 200 mA cm⁻² at 700 °C for 40 h in the presence of 1 ppm SO₂. For LSCF electrode (Fig.9-5b), in addition to the typical LSCF and GDC diffraction peaks, additional SrSO₄ and CoFe₂O₄ peaks were observed, which was
similar to those reported that for the cell exposed to SO$_2$ with high concentration (>1 ppm), the diffraction lines associated with SrSO$_4$ and CoFe$_2$O$_4$ appeared. Bucher et al [67] also confirmed the CoFe$_2$O$_4$ formation when LSCF reacted with SO$_2$. For BaCeO$_3$–LSCF electrodes in the absence of SO$_2$, however, pure perovskite BaCeO$_3$ phase can’t be detected by XRD that is due to the low amount of BaCeO$_3$ impregnated in LSCF cathodes (Fig. 9-5a). While for BaCeO$_3$–LSCF electrodes in the presence of SO$_2$, the formation of BaSO$_4$ peak instead of SrSO$_4$ can explain the different morphologies of the deposited particles on the electrode surface (as shown in Fig. 9-4e). In addition, there are also some small peaks that can’t be easily identified at the moment, and more analysis ought to be done in the future.

![Fig.9.5 XRD patterns of LSCF (b), BaCeO$_3$-LSCF electrodes under cathodic current passage at 200 mA cm$^{-2}$ at 700 $^\circ$C for 40 h in the absence (a) and presence (c) of 1 ppm SO$_2$.](image)

**9.3.5 Discussions**

As shown in the present study, sulfur deposition and poisoning on LSCF electrodes preferentially occurs on the surface, which is consistent with the Cr deposition and poisoning of LSCF electrodes. The sulfur poisoning mechanism is mainly related to the surface segregated species like Sr in the LSCF cathodes. Hence, the driving force behind the nucleation theory is the surface segregation and migration of cationic species on the surface of LSCF cathodes, leading to
the formation of SrSO$_4$ and CoFe$_2$O$_4$ species, which would unavoidably result in the degradation of LSCF electrode performance.

It is widely known that proton conductor BaCeO$_3$ is very active with acidic gas such as SO$_2$, and infiltration of the nanoscale BaCeO$_3$ particles could lead to the formation of BaSO$_4$ nanoparticles and thus inhibiting the formation of SrSO$_4$ (as can be seen in XRD results). It clearly shows the XRD peak shift from SrSO$_4$ to BaSO$_4$. So this can effectively prevent Sr segregation and then the excess Sr efficiency at the A-site, which is evidently supported by the negligible change in the $R_p$ for the reaction on BaCeO$_3$–LSCF that is obviously contrast to that observed on the LSCF electrodes.

The stabilization effect of Sr at the A-site of the LSCF perovskite structure by the BaCeO$_3$ infiltration is ascribed to the increase of electrode activity and durability of BaCeO$_3$–LSCF cathodes. As BaCeO$_3$ could act as a reacting barrier to sulfur species, the BaCeO$_3$ nanoparticles would finally be exhausted to the formation of BaSO$_4$ and the protecting properties to LSCF electrode could be finished. The high sulfur tolerance of the BaCeO$_3$ infiltrated LSCF for 40 h tested under the accelerated sulfur poisoning and deposition conditions shows its promising potential as a highly active and sulfur-tolerance cathode for SOFCs.

9. 4 Conclusions

In this study, the electrochemical performance and tolerance towards sulfur deposition and poisoning were investigated on pure LSCF and BaCeO$_3$–LSCF electrodes. For the oxygen reduction reaction on BaCeO$_3$–LSCF electrodes, the electrode polarization resistance and the activation energy was smaller than the pure LSCF electrodes that are mainly due to the
impregnation of BaCeO$_3$ nanoparticles. Compared with the pure LSCF electrode, BaCeO$_3$-LSCF showed a better sulfur tolerance and higher stability. The XRD results shows that impregnated BaCeO$_3$ nanoparticles could easily react with sulfur dioxide to form BaSO$_4$ instead of SrSO$_4$ for the sake of reducing the direct contact of segregated SrO species in LSCF with SO$_2$. The BaCeO$_3$-LSCF cathodes could become a promising oxygen electrode for SOFC when operating in the presence of SO$_2$.

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Chapter 10: Conclusions and Recommendations

10.1 Conclusions

This thesis includes a comprehensive study on the degradation of SOFC cathodes in terms of chromium, sulfur poisoning, and develop sulfur tolerant cathode materials by using impregnation technique. The conclusions are shown below.

1. LSCF bar samples were used to investigate the effect of temperature on the surface segregation and deposition and poisoning of Cr. The SEM and confocus laser Raman spectroscopy shows that there is clear change in the microstructure and the formation of SrCrO₄ particles on the surface of LSCF was clearly identified after the samples were exposed to Cr₂O₃-containing atmosphere at different temperatures for 48 h. The present study demonstrates that the temperature has a significant effect on the Sr segregation, Cr deposition and formation of SrCrO₄ phase on the LSCF surface. There is close correlation between the strontium segregation and chromium deposition on the LSCF surface as a function of temperature. Surface exchange coefficients of LSCF after being exposed to Cr₂O₃ are also significantly lower than that in the absence of Cr₂O₃ as a result of the Cr deposition and formation of SrCrO₄.

2. Sulfur deposition and poisoning mechanism were investigated on dense LSCF bar samples after exposed to 20 ppm SO₂ in the temperature range of 900 to 400 °C, using XRD, SEM, confocal Raman and ECR techniques. SO₂ reacts with LSCF, forming SrSO₄ phase at temperatures ≥ 700 °C and SrS at temperature below 700 °C. The surface segregation of Sr and/or Co species on the LSCF bar samples decreases significantly with the temperature,
however, the sulfur deposition as measured by the formation of sulfur-containing particles on the LSCF surface shows a reversed V-shaped dependence on the temperature. Sulfur reaction and deposition to form sulfate, SrSO$_4$ is most pronounced at 700 °C. ECR results indicate that the surface exchange coefficient of LSCF after exposed to 20 ppm SO$_2$ at 700-900 °C for 48 h is $9 \times 10^{-5}$ cm s$^{-1}$, $8 \times 10^{-6}$ cm s$^{-1}$ and $2 \times 10^{-6}$ cm s$^{-1}$, which is much lower than $2.8 \times 10^{-4}$ cm s$^{-1}$, $5 \times 10^{-4}$ cm s$^{-1}$ and $6 \times 10^{-3}$ cm s$^{-1}$ of the sample tested in the absence of SO$_2$. Temperature is the one of the major contributing factors that controls the mechanism of sulfur poisoning for LSCF cathode on SOFC in terms of reaction efficient and the surface exchange and diffusion processes for O$_2$ reduction reaction at typical temperature range.

3. The deposition and poisoning of the co-presence of chromium and sulfur contaminants were investigated on LSCF bar samples at temperature range of 900-600 °C. SEM microstructure analysis indicates that the interaction between LSCF and chromium and sulfur contaminant species depends strongly on the temperature and deposit formation on the surface of LSCF surface is most pronounced at temperature of 700 °C. XRD, Raman and XPS analysis demonstrated that in the presence of Cr and 20 ppm SO$_2$, the deposition and reaction products between LSCF and Cr+S contaminants are dependent on the temperature: SrCrO$_4$ only forms at high temperature of 900 and 800 °C, while formation of SrSO$_4$ phase occurs at the temperature ranges tested in the present study. The $k_{\text{chem}}$ value is $1.5 \times 10^{-4}$ cm s$^{-1}$, $9 \times 10^{-5}$ cm s$^{-1}$, $5 \times 10^{-5}$ cm s$^{-1}$ at 900 °C in the presence of gaseous Cr, S and Cr+S, respectively. The results indicate that the co-presence of chromium and sulfur contaminants can cause the significant deposition and formation of SrCrO$_4$ and/or SrSO$_4$, which are detrimental to the oxygen exchange and surface diffusion process on the LSCF electrode materials.
4. The mechanism and kinetics of sulfur deposition and poisoning on LSM electrodes was investigated at 700 and 800 °C. Sulfur species that initially played a dominant role in inhibiting the dissociation adsorption and diffusion processes of oxygen on the LSM surface, especially at 700 °C. Sulfur poisoning effect of LSM electrodes increased with higher concentration of SO₂. SEM/EDX combined XPS results show that the formation of small rough particles on the surface of LSM electrodes is SrSO₄ and the amount of SrSO₄ formation was the highest at higher concentration of SO₂ (10 ppm) at 700 °C, which can finally lead to the performance degradation. Nano-SIMS result indicates that sulfur is distributed in the whole LSM electrode and more obvious on the interface of LSM/YSZ at 800 °C. The O₂ reduction reaction kinetics of LSM electrodes is affected by the sulfur inhibiting species on the surface process and also the temperature due to the adsorption/desorption rate, and then the kinetics of the deposition processes of sulfur species is controlled by the nucleation reaction between the SrO and the gaseous sulfur species, forming SrSO₄. Finally, sulfur species not only has significant inhibiting effect on the kinetics for the O₂ reduction reactions at the LSM electrodes but also has a significant effect on the reaction mechanism.

5. The mechanism and kinetics sulfur deposition and poisoning on LSCF electrodes was investigated at 600, 700 and 800 °C. Sulfur species poisons the O₂ reduction reaction on LSCF electrodes by inhibiting the electrode bulk process, especially at 600 °C. Sulfur poisoning effect of LSCF electrodes increased with higher concentration of SO₂. FIB-SEM as well as EDX results show that sulfur exists heterogeneously in the LSCF layer, especially ~15 μm from the surface and the amount of sulfur becomes less at 800 °C, which indicate that sulfur poisoning effect is most pronounced at lower temperature. The deposition of sulfur on
the LSCF electrode and under open circuit condition at 700 °C indicates that sulfur poisoning in the LSCF/GDC system is essentially a chemical reaction. The O₂ reduction reaction kinetics of LSCF electrodes is affected by the sulfur inhibiting species on the electrode bulk process and also the temperature, and then the kinetics of the deposition processes of sulfur species is controlled by the nucleation reaction between the SrO and the gaseous sulfur species, forming SrSO₄ and CoFe₂O₄ was also formed due to the decomposition of LSCF perovskite oxides. The effect of sulfur deposition and poisoning on the electrochemical activity of LSCF cathodes is not reversible after changing to SO₂-free air.

10.2 Recommendations

This thesis mainly focus on investigating the mechanism of sulfur poisoning on traditional SOFC cathodes in terms of surface microstructural change, phase compositions, sulfur distribution and electrochemical performance. Future work can be done in the following area.

1. Exploring the interface between LSM and YSZ after SO₂ poisoning in details by FIB-TEM.
2. Exploring the relationship between combined Cr and S poisoning on SOFC cathode in terms of electrochemical performance analysis, and thus can provide enough evidence in real SOFC operation.
3. Developing new sulfur tolerant cathode materials with better and stable performance.
4. Developing new Cr/S tolerant cathode materials to be applied into real SOFC tests in the future.
5. Exploring the sulfur poisoning of cathode materials when SOFC operating at low
temperature.

6. Adopting impregnation technique into develop novel cathode materials in SOFC and other research areas regarding to the renewable energy.

7. It could provide deeper insights into the mechanism by using molecular simulation to study Cr and S poisoning.

8. It could be more useful to study the moisture poisoning effect on SOFC cathode.

9. It could be also meaningful to study the CO₂ effect on BaCeO₃-impregnated LSCF cathode due to the higher concentration of CO₂ than SO₂ in the air.
References:

[7] Liu Y, Chi B, Pu J, Li J. Performance degradation of impregnated La0.6Sr0.4Co0.2Fe0.8O3+Y2O3 stabilized ZrO2 composite cathodes of intermediate temperature solid oxide fuel cells. International Journal of Hydrogen Energy. 2012;37:4388-93.
[8] Bucher E, Gspan C, Hofer F, Sitte W. Post-test analysis of silicon poisoning and phase decomposition in the SOFC cathode material La0.6Sr0.4Co0.2Fe0.8O3-delta by transmission electron microscopy. Solid State Ionics. 2013;230:7-11.


[35] Kim Y-M, Chen X, Jiang SP, Bae J. Chromium Deposition and Poisoning at Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3-deltas Cathode of Solid Oxide Fuel Cells. Electrochemical and Solid State Letters. 2011;14:B41-B5.

[36] Kim Y-M, Chen X, Jiang SP, Bae J. Effect of Strontium Content on Chromium Deposition and Poisoning in Ba_{1-x Sr_x}Co_{0.8}Fe_{0.2}O_3-deltas (0.3 <= x <= 0.7) Cathodes of Solid Oxide Fuel Cells. Journal of the Electrochemical Society. 2012;159:B185-B94.

[37] Chen X, Zhen Y, Li J, Jiang SP. Chromium deposition and poisoning in dry and humidified air at (La_{0.8}SrO_{0.2})_{0.8}MnO_3-s cathodes of solid oxide fuel cells. International Journal of Hydrogen Energy. 2010;35:2477-85.

[39] Wei B, Chen K, Wang CC, Lü Z, Jiang SP. Cr deposition on porous La$_0.6$Sr$_0.4$Co$_0.2$Fe$_{0.8}$O$_3$·δ electrodes of solid oxide cells under open circuit condition. Solid State Ionics. 2015;281:29-37.


[41] Stodolny MK, Boukamp BA, Blank DHA, van Berkel FPF. Cr-poisoning of a LaNi$_{0.6}$Fe$_{0.4}$O$_3$ cathode under current load. Journal of Power Sources. 2012;209:120-9.


[53] Wang FF, Yamaji K, Cho DH, Shimonosono T, Kishimoto H, Brito ME, et al. Sulfur Poisoning on La$_0.6$Sr$_0.4$Co$_0.2$Fe$_{0.8}$O$_3$ Cathode for SOFCs. Journal of the Electrochemical Society. 2011;158:B1391-B7.


[57] Cheng Z, Zha SW, Liu ML. Influence of cell voltage and current on sulfur poisoning behavior of


[63] Xie J, Ju YW, Ishihara T. Influence of sulfur impurities on the stability of La0.6Sr0.4Co0.2Fe0.8O3 cathode for solid oxide fuel cells. Solid State Ionics. 2013;249:177-83.


[67] Bucher E, Gspan C, Hofer F, Sitte W. Sulphur poisoning of the SOFC cathode material La0.6Sr0.4CoO3.5. Solid State Ionics. 2013;238:15-23.

[68] Bucher E, Gspan C, Sitte W. Degradation and regeneration of the SOFC cathode material La0.6Sr0.4CoO3.5 in SO2-containing atmospheres. Solid State Ionics. 2015;272:112-20.


[76] Nielsen J, Mogensen M. SOFC LSM:YSZ cathode degradation induced by moisture: An impedance
[79] Shen F, Lu K. Moisture Effect on La0.8Sr0.2MnO3 and La0.6Sr0.4Co0.2Fe0.8O3 Cathode Behaviors in Solid Oxide Fuel Cells. Fuel Cells. 2015;15:105-14.
[81] Oishi J, Otomo J, Oshima Y, Koyama M. The effects of minor elements in La0.6Sr0.4Co0.2Fe0.8O3 cathodes on oxygen reduction reaction. Journal of Power Sources. 2015;277:44-51.
[86] Liu Y, Chen K, Zhao L, Chi B, Pu J, Jiang SP, et al. Performance stability and degradation mechanism of La0.6Sr0.4Co0.2Fe0.8O3 cathodes under solid oxide fuel cells operation conditions. International Journal of Hydrogen Energy. 2014;39:15868-76.
[87] Esquirol A, Brandon NP, Kilner JA, Mogensen M. Electrochemical Characterization of La0.6Sr0.4Co0.2Fe0.8O3 Cathodes for Intermediate-Temperature SOFCs. Journal of The Electrochemical Society. 2004;151:A1847-A55.
[92] Bucher E, Sitte W. Long-term stability of the oxygen exchange properties of La0.6Sr0.4Co0.2Fe0.8O3 in dry and wet atmospheres. Solid State Ionics. 2011;192:480-2.
[95] Fergus JW. Effect of cathode and electrolyte transport properties on chromium poisoning in solid


[98] Kim YM, Chen XB, Jiang SP, Bae J. Effect of Strontium Content on Chromium Deposition and Poisoning in BaₓSrₐₐCoₓFeₓO₃⁺δ (0.3 <= x <= 0.7) Cathodes of Solid Oxide Fuel Cells. Journal of the Electrochemical Society. 2012;159:B185-B94.


[114] Zhao L, Drennan J, Kong C, Amarasinghe S, Jiang SP. Insight into surface segregation and chromium deposition on La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} cathodes of solid oxide fuel cells. Journal of Materials Chemistry A. 2014;2:11114 - 23.


[123] Gao J, Li LP, Yin Z, Zhang JC, Lu SM, Tan XY. Poisoning effect of SO₂ on the oxygen permeation behavior of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} perovskite hollow fiber membranes. Journal of Membrane Science. 2014;455:341-8.


[128] Chen X, Zhang L, Liu E, Jiang SP. A fundamental study of chromium deposition and poisoning at (La_{0.5}Sr_{0.5}){Mn_{1-x}Co_{x}}O_{3-δ} (0.0 ≤ x ≤ 1.0) cathodes of solid oxide fuel cells. International Journal of Hydrogen Energy. 2011;36:805-21.


[130] Chen XB, Zhen YD, Li J, Jiang SP. Chromium deposition and poisoning in dry and humidified air at (La_{0.5}Sr_{0.5})MnO₃ cathodes of solid oxide fuel cells. International Journal of Hydrogen Energy. 2010;35:2477-85.

[131] Wang CC, Chen KF, Jiang SP. Sulfur Deposition and Poisoning of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} Cathode Materials of Solid Oxide Fuel Cells. Journal of the Electrochemical Society. 2014;161:F1133-F9.


[141] Ivanovskaya MI, Kotikov DA, Pan’Kov VV, Zyryanov VV. Structure of SrCo0.5Fe0.5O3 - δ-based composites prepared by sol-gel and mecha nochemical processes. Inorganic Materials. 2009;45:910-5.


[171] Matsuzaki Y, Yasuda I. Relationship between the steady-state polarization of the SOFC air electrode, La$_{0.6}$Sr$_{0.4}$MnO$_{3+δ}$/YSZ, and its complex impedance measured at the equilibrium potential. Solid State Ionics. 1999;126:307-13.


[187] Wang CC, Chen K, Jiang SP. Sulfur Deposition and Poisoning of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ Cathode Materials of Solid Oxide Fuel Cells. Journal of The Electrochemical Society. 2014;161:F1133-F9.

[188] Hashimoto S-i, Fukuda Y, Kuhn M, Sato K, Yashiro K, Mizusaki J. Oxygen nonstoichiometry and
thermo-chemical stability of La$_{0.6}$Sr$_{0.4}$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ ($y= 0; 0.2, 0.4, 0.6, 0.8$). Solid State Ionics. 2010;181:1713-9.


[193] Chen J, Liang F, Chi B, Pu J, Jiang SP, Jian L. Palladium and ceria infiltrated La$_{0.6}$Sr$_{0.4}$Co$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ cathodes of solid oxide fuel cells. Journal of Power Sources. 2009;194:275-80.

[194] He HQ, Zhang L, Babaei A, Wang X, Jiang SP. Co$_2$MnO$_4$ spinel-palladium co-infiltrated La$_{0.6}$Ca$_{0.4}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ cathodes for intermediate temperature solid oxide fuel cells. Journal of Alloys and Compounds. 2011;509:9708-17.


[198] Chen K, Ai N, O’Donnell KM, Jiang SP. Highly chromium contaminant tolerant BaO infiltrated La$_{0.6}$Sr$_{0.4}$Co$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ cathodes for solid oxide fuel cells. Physical Chemistry Chemical Physics. 2015;17:4870-4.


[204] Chen F, Sorensen OT, Meng G, Peng D. Chemical stability study of BaCe$_{0.8}$Nd$_{0.2}$O$_{3-\delta}$ high-temperature proton-conducting ceramic. Journal of Materials Chemistry. 1997;7:481-5.

[205] Zakowsky N, Williamson S, Irvine JTS. Elaboration of CO$_2$ tolerance limits of BaCe$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ electrolytes for fuel cells and other applications. Solid State Ionics. 2005;176:3019-26.

[206] Gopalan S, Virkar Anil V. Thermodynamic stabilities of SrCeO$_3$ and BaCeO$_3$ using a molten salt

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