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Nanoengineered Materials for Solid Oxide Cells

Edited by Katherine Develos-Bagarinao

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This book is dedicated to my teachers, advisers, colleagues, and collaborators, who have been instrumental in my pursuit of knowledge and stimulated my curiosity for the unknown; and to my family—Baggy and Aya, my sisters—Karen and Karla, and my parents—Jun and Genny, who had passionately taught me the value of perseverance and education.

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Preface

Solid oxide cells (SOCs) are one of the key technologies receiving global scientific and technological interest due to their enormous potential to alleviate the environmental problems associated with the widespread use of fossil fuels. SOCs can provide highly efficient, low-carbon power generation and constitute the core technology used to produce hydrogen, syngas, and synthetic fuels in combination with renewable electricity.

In recent years, the nanoengineering of materials used for SOCs has emerged as a versatile tool for the production of high-performance components such as electrodes, interlayers, and electrolytes with far superior properties than those of conventional materials. Over the years, several methods have been explored to tune various material structures at the nanoscale via 1D, 2D, and 3D nanostructures fabricated using advanced thin-film technology and other related nanoprocessing techniques. These developments are further complemented by significant advancements in nanocharacterization tools that can be used to elucidate the complex mechanisms governing the behavior of nanostructured materials. This strategic approach has enabled the discovery of novel structures and provided an understanding of fundamental mechanisms at the nanoscale, which are crucial in the development of next-generation devices. The use of thin-film technology and related nanotechnology techniques in the materials development of energy conversion devices such as SOCs has significantly proliferated over the last decade, but until now, no book published on this topic has consolidated the advances achieved to date into one volume. While there is a consensus among research communities that the nanoengineering of materials could enable far superior properties than those of conventional materials, there is also a general lack of awareness regarding current research activities that specifically address the issues of integrating such nanomaterials into practical devices. This book aims to bridge this gap and contribute to a better understanding of the breakthroughs achieved in this area.

With this goal in mind, I have invited active researchers and experts in the field of SOC materials development to contribute chapters covering specific topics related to the development and application of nanomaterials. Ten chapters have been selected for this volume; each chapter provides a comprehensive survey of the state-of-the-art experimental approaches and offers perspectives on the current progress achieved as well as future directions in the area. This volume covers the following topics in great detail: an overview of the various approaches used to fabricate nanostructured air electrodes and their implementation in full cells (chapter 1); the influence of surface chemistry and microstructure on the stability and performance of air electrodes (chapter 2); multilayering strategies and characterization tools used to tune the heterointerfaces of air electrodes (chapter 3); interface engineering to improve the activity and stability of SOC air and fuel electrodes (chapter 4); recent progress on atomic layer deposition, which is used to modify various cell components (chapter 5); the development of novel electrode materials and nano-oxide composite electrolytes which are different from conventional materials (chapter 6); a redox exsolution

approach for tailoring nanostructured fuel electrodes (chapter 7); an infiltration technique for engineering nanostructured fuel electrodes (chapter 8); microstructural modifications of the electrolyte/electrode interfaces via numerical and experimental approaches (chapter 9); and last but not least, an overview of synchrotron x-ray radiation techniques as advanced characterization tools for probing nanoscale structures (chapter 10).

I hope that this book will be of great interest to groups working on the development of next-generation energy conversion devices, especially those working on the materials development of solid oxide cells but also those developing oxygen separation membranes and memristive devices. Furthermore, I hope that it will be a useful reference not only for academics and researchers actively working in the field, but also for people in the industry who are currently developing systems and devices for commercial applications.

On a final note, I would like to acknowledge the valuable support and hard work of all the contributors to this volume, without which this project would have been impossible. My sincere thanks go to the Institute of Physics Publishing (specifically Caroline Mitchell and Robert Trevelyan) for providing this wonderful opportunity to work on this project.

Katherine Develos-Bagarinao Tsukuba, Japan October 2022

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I would like to thank my colleagues at the National Institute of Advanced Industrial Science and Technology (AIST) for initiating me in this exciting field and providing the opportunity for me to explore new ideas and approaches. I am also grateful to Professor Harumi Yokokawa (The University of Tokyo) for our insightful discussions and encouraging me to pursue this book project. Lastly, I would like to acknowledge the enthusiastic collaboration of all contributors, without whom this book would not have been possible.

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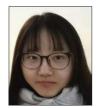
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Miao Yu is a PhD student at the Department of Energy Conversion and Storage, Technical University of Denmark, under the supervision of Professor Ming Chen. She holds an MSc in Energy Conversion and Storage from the Technical University of Denmark and a BSc in Building Environment and Energy Application Engineering from Chang'an University, Xi'an, China. Her PhD project focuses on improving the performance and durability of SOCs and interconnects at intermediate temperatures.

Xiangling Yue



Xiangling Yue is a Rutherford Fellow at the School of Chemistry, University of St Andrews. She was awarded a master's degree in chemical engineering by the Dalian Institute of Chemical Physics, Chinese Academy of Sciences in 2009 and in 2014, she obtained a PhD in Chemistry at the University of St Andrews. Her PhD thesis focused on development of alternative materials for high-temperature electrolysis. After her PhD, she continued to work with professor John Irvine as a postdoctoral researcher for a few years before being

awarded the EPSRC UKRI Innovation Fellowship to start her independent research in 2018. She has developed expertise in SOC manufacture, ceramic processing, electrochemical characterisations, and the microstructural engineering of the solid-state materials used in fuel cells and electrolysers for low-carbon energy storage and conversion, in particular for applications involving CO₂ utilisation. She is also working on biomass combustion and understanding the biomass ash deposition process in order to alleviate ash accumulation in biomass boilers and plants, which is a project undertaken in close collaboration with industry.

Mengzhen Zhou



Mengzhen Zhou is currently pursuing her PhD degree at the School of Environment and Energy at the South China University of Technology. Her research focuses on the cathodes of solid oxide fuel/electrolysis cells.

Glossary

 p_{O_2} Oxygen partial pressure

V_O Oxygen vacancies
3D Three-dimensional
ALD Atomic layer deposition

A-PBC A-site deficient PrBa_{0.94}Co₂O_{5+δ}

APHAXPES Ambient-pressure hard x-ray photoelectron spectroscopy

APT Atom probe tomography
APUs Auxiliary power units

AP-XPS Ambient-pressure x-ray photoelectron spectroscopy

ASR Area-specific resistance (Ω cm²)

 $\begin{array}{cc} BCO & BaCoO_{3-x} \\ BL & Barrier \ Layer \end{array}$

 $\begin{array}{ll} BMCNO & PrBaMn_{1.7}Co_{0.1}Ni_{0.2}O_{5+\delta} \\ BSCF & Ba_{1-x}Sr_xCo_{1-\nu}Fe_{\nu}O_{3-\delta} \end{array}$

BSCFZY $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.2}Zr_{0.1}Y_{0.1}O_{3-\delta}$

 $BSFM \qquad \qquad Ba_{0.3}Sr_{0.7}Fe_{0.9}Mn_{0.1}O_{3-\delta}$

CB Conduction band

CHP Combined heat and power
COBRA Coherent Bragg rod analysis
CR Crystal reconstruction

CTECoefficient of thermal expansionCVDChemical vapor deposition c_{ν} Oxygen vacancy concentration

D Oxygen diffusivity

D* Oxygen self-diffusion coefficient (cm² s⁻¹)
DCMS Direct current magnetron sputtering

DFT Density functional theory
DOS Electron density of states
DPB Double phase boundary
DRM Dry reforming of methane
DRT Distribution of relaxation times D_{ν} Oxygen vacancy diffusivity

EELS Electron energy loss spectroscopy
EIS Electrochemical impedance spectroscopy

 E_k Apparent activation energy \hat{k} ESM Electrochemical strain microscopy $E_{\mathrm{Sr,vac}}$ Vacancy formation energy of Sr

EXAFS Extended x-ray absorption fine structure

FE Fuel electrodes

FEM Finite element method

FIB-SEM Focused ion beam-scanning electron microscopy

FSM $SrFe_{0.75}Mo0.25O_{3-\delta}$

FT-IR Fourier transform infrared spectroscopy

GDC Gadolinia-doped ceria (alternatively, CGO), $Gd_xCe_{1-x}O_{2-\delta}$

GLAD Glancing angle deposition GSTF Gradient structured thin films

HAADF STEM High-angle annular dark field scanning transmission electron microscopy

HOR Hydrogen oxidation reaction HRXRD High-resolution x-ray diffraction

IE Isotope exchange

IE-APT Isotope exchange atomic probe tomography

IEDP Isotope exchange depth profiling

IT-SOC Intermediate temperature solid oxide cell

IV-IP Current/voltage-current/power

k* Oxygen surface exchange coefficient (cm s⁻¹)

 k_{chem} Chemical oxygen surface exchange coefficient (cm s⁻¹)

KFM Kelvin force microscopy

 $k^{\rm q}$ Electrical oxygen surface exchange coefficient (cm s⁻¹)

 $\begin{array}{lll} L2NO4 & La_2NiO_{4\pm\delta} \\ LAO & LaAlO_3 \\ LC95 & La_{0.95}CoO_{3-\delta} \end{array}$

LCCFC Lithium compounds ceramic fuel cell

 $\begin{array}{lll} LCeNT & La_{0.8}Ce_{0.1}Ni_{0.4}Ti_{0.6}O_3 \\ LCNT & La_{0.43}Ca_{0.37}Ni_{0.06}Ti_{0.94}O_{3-\gamma} \end{array}$

LCO LiCoO₂

LCTCF $La_{0.43}Ca_{0.37}Ti_{0.8}Co_{0.1}Fe_{0.1}O_{3-\delta}$

LEIS Low energy ion scattering spectroscopy

LMO LiMnO₂

 $\begin{array}{ccc} LNF & LaNi_{0.6}Fe_{0.4}O_{3-\delta} \\ LNO & La_2NiO_{4+\delta} \end{array}$

LNZ Lithium nickel zinc oxide

LPNO $La_{2-x}Pr_xNiO_{4+\delta}$ LSC $La_{1-x}Sr_xCoO_3$ LSC₁₁₃ $La_{1-x}Sr_xCoO_3$ LaSrCoO_{4 $-\delta$} LSC_{214} $La_{2-x}Sr_xCoO_4$ LSC₂₁₄ LSC64, LSC₁₁₃ $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ LSC82 **LSCF** $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ **LSCM** $(La_{0.75}Sr_{0.25})Cr_{0.5}Mn_{0.5}O_3$ **LSCNi** $(La_{0.7}Sr_{0.3})(Cr_{0.85}Ni_{0.15})O_{3-x}$ LSCNi-Fe $(La_{0.7}Sr_{0.3})(Cr_{0.85}Ni_{0.15-x}Fe_x)O_{3-\delta}$

LSCoT $La_{0.3}Sr_{0.7}Co_{0.07}Ti_{0.93}O_{3-\delta}$

LSCr $La_{1-x}Sr_xCrO_3$

 $\begin{array}{lll} LSCrFeCo & La_{0.3}Sr_{0.7}Cr_{0.3}Fe_{0.6}Co_{0.1}O_{3-\delta} \\ LSCrT & (La_{0.75}Sr_{0.25})Cr_{0.5}Ti_{0.5}O_3 \\ LSCuT & La_{0.43}Sr_{0.37}Cu_{0.12}Ti_{0.88}O_{3-\delta} \end{array}$

 $\begin{array}{lll} LSF & La_{1-x}Sr_xFeO_3 \\ LSF_{113} & La_{0.8}Sr_{0.2}FeO_{3-\delta} \\ LSF_{214} & (La,Sr)_2FeO_{4-\delta} \end{array}$

LSFCNb $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.15}Nb_{0.05}O_{3-\delta}$

LSFN $La_{0.6}Sr_{0.4}Fe_{0.8}Ni_{0.2}O_{3-\delta}$

LSM $La_{1-x}Sr_xMnO_3$

LSMF $La_{1,2}Sr_{0.8}Mn_{0.4}Fe_{0.6}O_{4-\delta}$

LSNT $La_{0.4}Sr_{0.4}Ni_{0.06}Ti_{0.94}O_{3-\delta}, La_{0.52}Sr_{0.28}Ni_{0.06}Ti_{0.94}O_3$

LST $La_{0.4}Sr_{0.4}TiO_{3-\delta}$

LSTN $La_{0.4}Sr_{0.4}Ti_{0.94}Ni_{0.06}O_{3-\delta}$

MDC $Mo_{0.1}Ce_{0.9}O_{2+\delta}$

MIEC Mixed ionic electronic conductor
MLLS Multiple linear least squares
MPD Maximum power density

NAP-XPS Near-ambient-pressure x-ray photoelectron spectroscopy

NBMO $NdBaMn_2O_{5+\delta}$

NCAL $Ni_{0.8}Co_{0.15}Al_{0.05}LiO_{2-\delta}$

NEXAFS Near-edge x-ray absorption fine structure

Ni/GDC Nickel/gadolinia-doped ceria Ni/SDC Nickel/samaria-doped ceria Ni/YSZ Nickel/yttria-stabilized zirconia

 $\begin{array}{lll} NLM & La_{0.9}Mn_{0.8}Ni_{0.2}O_{3} \\ NPs & Nanoparticles \\ NSC_{113} & Nd_{0.5}Sr_{0.5}CoO_{3-\delta} \\ NSC_{214} & Nd_{0.8}Sr_{1.2}CoO_{4\pm\delta} \end{array}$

 $\begin{array}{ll} NSC_{214/113} & Nd_{0.8}Sr_{1.2}CoO_{4\pm\delta}/Nd_{0.5}Sr_{0.5}CoO_{3-\delta} \\ ECR & Electrochemical conductivity relaxation \end{array}$

OCV Open circuit voltage OE Oxygen electrodes

OER Oxygen evolution reactions ORR Oxygen reduction reactions

O-SOCs Oxygen ion-conducting solid oxide cells

OTR Optical transmission relaxation

 $\begin{array}{lll} PBCC & PrBa_{0.8}Ca_{0.2}Co_2O_{5+\delta} \\ PBCFN & PrBaCo_{1.6}Fe_{0.2}Nb_{0.2}O_{5+\delta} \\ PBCM & Pb_{0.5}Ba_{0.5}Co_{0.1}Mn_{0.9}O_x \\ PBMCo & PrBaMn_{1.7}Co_{0.3}O_{5+\delta} \\ PBMF & PrBaMn_{1.7}Fe_{0.3}O_{5+\delta} \\ PBMO & PrBaMn_2O_{5+\delta} \end{array}$

PEMS Plasma-enhanced magnetron sputtering

pFIB Plasma focused ion beam PLD Pulsed laser deposition

PNM $PrNi_{0.5}Mn_{0.5}O_3$

 $\begin{array}{lll} PSCFN & Pr_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta} \\ PSFM & (Pr_{0.4}Sr_{0.6})_3(Fe_{0.85}Mo_{0.15})_2O_7 \\ P-SOCs & Proton-conducting solid oxide cells \\ \end{array}$

PVD Physical vapor deposition QCM Quartz crystal microbalance

RFMS Radio frequency magnetron sputtering

 R_p Polarization resistance (Ω cm²)

RP Ruddlesden-Popper

R-PCECs Reversible protonic ceramic electrochemical cells

 R_s Surface polarization resistance (Ω cm²)

RVE representative volume element R_{Ω} Ohmic resistance (Ω cm²) SAED Selected area electron diffraction

SCF $Sr_{0.8}Ce_{0.2}FeO_3$

SCN10 $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$

ScSZ Scandia-stabilized zirconia

SDC Samaria-doped ceria, $Sm_xCe_{1-x}O_{3-\delta}$

SEM Scanning electron microscopy

SEM-WDS Scanning electron microscopy-wavelength dispersive x-ray spectroscopy

SERS Surface enhanced Raman spectroscopy
SIMS Secondary ion mass spectrometry
SMT Semiconductor-to-metal transition

SOCs Solid oxide cells

SOECs Solid oxide electrolysis cells

SOFCs Solid oxide fuel cells

SPM Scanning probe microscopy

SSC $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$

SSOFC Symmetrical solid oxide fuel cell
SSPM Scanning surface potential microscopy
STEM Scanning transmission electron microscopy

STEM-EDS or Scanning transmission electron microscopy-energy dispersive x-ray

EDX spectroscopy STF $SrTi_{1-x}Fe_xO_3$

STFN $Sr_{0.95}(Ti_{0.3}Fe_{0.7-x}Ni_x)O_{3-\delta}$

STM/STS Scanning tunneling microscopy and spectroscopy

STO SrTiO₃

SYTN $Sr_{0.92}Y_{0.08}Ti_{1-x}Ni_xO_{3-\delta}$

SZ SrZrO₃

SZY Yttrium-doped SrZrO₃
t Tolerance factor

TEM Transmission electron microscopy

TGA-DSC Thermogravimetric analyzer-differential scanning calorimetry

ToF-SIMS Time-of-flight secondary ion mass spectrometry

TPB Triple-phase boundary

TPD Temperature programmed oxidation TPR Temperature programmed reduction

TRF-XAS Total-reflection fluorescence x-ray absorption spectroscopy

TXM Transmission x-ray microscopy
UV-Vis Ultraviolet–Visible absorption spectra
VAN Vertically aligned nanocomposite

VB Valence band

XANES X-ray absorption near-edge structure
XAS X-ray absorption spectroscopy
XCT X-ray computed tomography
XPS X-ray photoelectron spectroscopy

XRD X-ray diffraction XRF X-ray fluorescence XRR X-ray reflectivity

YSZ Yttria-stabilized zirconia, (YO_{1.5})_{0.16}(ZrO₂)_{0.84}

ZDC $Zr_{0.35}Ce_{0.65}O_{2-\delta}$