Ceria-based Nanostructured Materials for Low-Temperature Solid Oxide Fuel Cells

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Ph.D. Thesis
Stockholm 2012

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Akademisk avhandling som med tillstånd av Kungliga Tekniska Högskolan framlägges till offentlig granskning för avläggande av teknologie doktorsexamen i materialkemi måndag den 11 juni 2012 klockan 10:00 i Sal C2, KTH-Electrum, Isafjordsgatan 26, Kista, Stockholm.
Abstract

As one of the most efficient and environmentally benign energy conversion devices, solid oxide fuel cells (SOFC) have attracted much attention in recent years. Conventional SOFC with yttria-stabilized zirconia as electrolyte require high operation temperature (800-1000 °C), which causes significant problems like material degradation, as well as other technological complications and economic barrier for wider applications. Therefore, there is a broad interest in reducing the operation temperature of SOFCs. One of the most promising ways to develop low-temperature SOFCs (LTSOFC) is to explore effective materials for each component with improved properties. So in this thesis, we are aiming to design and fabricate ceria-based nanocomposite materials for electrolyte and electrodes of LTSOFC by a novel nanocomposite approach and to understand the morphology/structure–property relationship.

In the first part of the thesis, novel core-shell doped ceria/Na2CO3 nanocomposite was fabricated and investigated as electrolytes materials in LTSOFC. Two types of doped ceria were selected as the main phase for nanocomposite: samarium doped ceria (SDC) and calcium doped ceria (CDC). The core-shell SDC/Na2CO3 nanocomposite particles are smaller than 100 nm with amorphous Na2CO3 shell of 4–6 nm in thickness. The ionic conductivity of nanocomposite electrolytes were investigated by electrochemical impedance spectroscopy and four-probe d.c. method, which demonstrated much enhanced ionic conductivities compared to the single phase oxides. The thermal stability of such nanocomposite has also been investigated using XRD, BET, SEM and TGA techniques after annealing samples at various temperatures. Such nanocomposite was applied in LTSOFC demonstrating an excellent power density of 0.8 Wcm⁻² at 550 °C. The high performance together with notable thermal stability proves the doped ceria/Na2CO3 nanocomposite an excellent candidate as electrolyte material for LTSOFC.

In the second part of the thesis, a novel template- and surfactant-free chemical synthetic route has been successfully developed for the controlled synthesis of hierarchically structured CeO2 with nanowires and mesoporous microspheres morphologies. The new synthetic route was designed by utilizing the chelate formation between cerium ion and various carboxylates forms of citric acid. Then, hierarchically structured cerium oxide with morphologies of nanowires and mesoporous microspheres were obtained by thermal decomposition of the two kinds of precursors. Moreover, by doping with desired elements, SDC nanowires and SDC-CuO mesoporous microspheres were prepared and used for electrolyte and anode materials, respectively, based on their unique properties due to their morphologies. When SDC nanowires/Na2CO3 composite were applied as electrolyte for single SOFC, it exhibited maximum power density of 0.52 Wcm⁻² at 600 °C, which is much higher than the state-of-the-art SOFCs using doped ceria as electrolyte. Besides, the mesoporous CuO-SDC composite anode was synthesized by microwave-assisted method, and showed good phase homogeneity of both SDC and CuO. When it was used for fuel cells, the cell had better performance than conventional CuO-SDC anode prepared by solid state method.

This thesis provides a new methodology for materials development/design for the entire SOFC community. It is notable that our work has attracted considerable attention after publication of several attached papers. The results in this thesis may benefit the development of LTSOFC and expand the related research to a new horizon.
List of Papers

This thesis is based on following publications:

1) Ying Ma, Xiaodi Wang, Shanghua Li, Muhammet S. Toprak, Bin Zhu, Mamoun Muhammed. "Samarium-doped ceria nanowires: novel synthesis and application in low-temperature solid oxide fuel cells" 

2) Ying Ma, Xiaodi Wang, Rizwan Raza, Mamoun Muhammed, Bin Zhu. "Thermal stability study of SDC/Na₂CO₃ nanocomposite electrolyte for low temperature SOFCs" 


4) Ying Ma, Xiaodi Wang, Muhammet S. Toprak, Mamoun Muhammed. "A surfactant and template-free route for controlled synthesis of hierarchically structured cerium oxides with tunable morphologies and their application for water treatment" 
   In manuscript

5) Ying Ma, Xiaodi Wang, Rizwan Raza, Bin Zhu, Mamoun Muhammed. "Microwave synthesis of mesoporous CuO-Ce₀.₈Sm₀.₂O₂₋δ composite anode for low-temperature SOFCs" 
   In manuscript

6) Xiaodi Wang, Ying Ma, Rizwan Raza, Mamoun Muhammed, Bin Zhu. "Novel core-shell SDC/amorphous Na₂CO₃ nanocomposite electrolyte for low-temperature SOFCs" 

Other work not included:

1) Xiaodi Wang, Ying Ma, Shanghua Li, Bin Zhu, Mamoun Muhammed. "SDC/ Na₂CO₃ nanocomposite: New freeze drying based synthesis and application as electrolyte in low-temperature solid oxide fuel cells" 
CERIA-BASED NANOSTRUCTURED MATERIALS FOR LTSOFCs

2) Xiaodi Wang, Ying Ma, Bin Zhu. "State of the art ceria-carbonate composites (3C) electrolyte for advanced low temperature ceramic fuel cells (LTCFCs)"

3) Xiaodi Wang, Ying Ma, Shanghua Li, Abdel-Hady Kashyout, Bin Zhu, Mamoun Muhammed. "Ceria-based nanocomposite with simultaneous proton and oxygen ion conductivity for low-temperature solid oxide fuel cells"
   J. Power Sources. 2011. 196(5). 2754-2758

4) Xiaodi Wang, Ying Ma, Abhilash Sugunan, Jian Qin, Muhammet Toprak, Bin Zhu, Mamoun Muhammed. "Synthesis of uniform quasi-octahedral CeO2 mesocrystals via a surfactant-free route"

5) Bin Zhu, Ying Ma, Xiaodi Wang, Rizwan Raza, Haiying Qin, Liangdong Fan. "A fuel cell with a single component functioning simultaneously as the electrodes and electrolyte"

6) Rizwan Raza, Ying Ma, Xiaodi Wang, Xiangrong Liu, Bin Zhu. "Study on nanocomposites based on carbonate@ceria"

7) Rizwan Raza, Xiaodi Wang, Ying Ma, Bin Zhu. "Study on calcium and samarium co-doped ceria based nanocomposite electrolytes"
   J. Power Sources. 2010. 195(19). 6491-6495

8) Rizwan Raza, Xiaodi Wang, Ying Ma, Xiangrong Liu, Bin Zhu. "Improved ceria-carbonate composite electrolytes"
   Int. J. Hydrogen Energ. 2010. 35(7). 2684-2688

9) Rizwan Raza, Xiaodi Wang, Ying Ma, Bin Zhu. "A nanostructure anode (Cu0.2Zn0.8) for low-temperature solid oxide fuel cell at 400-600 °C"
   J. Power Sources. 2010. 195(24). 8067-8070

10) Rizwan Raza, Xiaodi Wang, Ying Ma, Yi Zhong Huang, Bin Zhu. "Enhancement of Conductivity in Ceria-Carbonate Nanocomposites for LTSOFCs"
    J. Nanopart Res. 2009. 6. 197-203

11) Rizwan Raza, Qinghua Liu, Jawad Nisar, Xiaodi Wang, Ying Ma, Bin Zhu. "ZnO/NiO nanocomposite electrodes for low-temperature solid oxide fuel cells."

12) Rizwan Raza, Ghazanfar Abbas, Xiaodi Wang, Ying Ma, Bin Zhu. "Electrochemical study of the composite electrolyte based on samaria-doped ceria and containing yttria as a second phase"
    Solid State Ionics. 2011. 188(1). 58-63

13) Liangdong Fan, Bin Zhu, Mingming Chen, Chengyang Wang, Rizwan Raza, Haiying
Qin, Xuetao Wang, Xiaodi Wang, Ying Ma. "High performance transition metal oxide composite cathode for low temperature solid oxide fuel cells"


**Conference presentations**

1) Ying Ma, Xiaodi Wang, Bin Zhu, Mamoun Muhammed. "A Novel Chemical Route to Synthesize CeO$_2$ nanowires" (Oral) 9th International Conference on Nanostructured Materials, June 2-6, **2008**, Rio de Janeiro/ Brazil

2) Ying Ma, Xiaodi Wang, Bin Zhu, Mamoun Muhammed. "A Novel Chemical Synthesis of SDC Nanowires - Low Temperature SOFC Electrolyte" (Oral) HyForum 2008 - International Hydrogen Forum, August 3 - 6, **2008**, Changsha/ China

3) Ying Ma, Xiaodi Wang, Shanghua Li, Bin Zhu, Mamoun Muhammed. "Novel Nanocomposite Strategy for Developing Electrolyte of Low-temperature SOFCs" (Poster) The X International Conference on Nanostructured Materials (NANO 2010), September 13-17, **2010**, Rome/ Italy

4) Xiaodi Wang, Ying Ma, Abhilash Sugunan, Jian Qin, Muhammet Toprak, Bin Zhu, Mamoun Muhammed. "Synthesis of uniform quasi-octahedral CeO$_2$ mesocrystals via a surfactant-free route." (Poster) The X International Conference on Nanostructured Materials (NANO 2010), September 13-17, **2010**, Rome/ Italy


6) Xiaodi Wang, Ying Ma, Abdel-Hady Kashyout, Bin Zhu, Mamoun Muhammed. "A Novel Fabrication of Nanochannels Metal Membrane" (Oral) 9th International Conference on Nanostructured Materials, June 2-6, **2008**, Rio de Janeiro/ Brazil

7) Rizwan Raza, Ying Ma, Xiaodi Wang, Bin Zhu "Study on Nanocomposites based on Carbonate @ Ceria" (Oral) 3rd International Conference on Surfaces, Coating and Nanostructured Materials (NanoSMat 2008), October 21-24, **2008**, Barcelona/ Spain

Contributions of the author

**Paper 1.** Planning and performing all synthetic work, parts of characterization work, evaluation of the results and writing main parts of the manuscript.

**Paper 2.** Planning and performing all synthetic work, parts of characterization work, evaluation of the results and writing main parts of the manuscript.

**Paper 3.** Developing the idea, performing parts of synthetic work and characterization work, evaluation of the results and writing main parts of the manuscript.

**Paper 4.** Planning and performing all synthetic work, parts of characterization work, evaluation of the results and writing main parts of the manuscript.

**Paper 5.** Planning and performing all synthetic work, parts of characterization work, evaluation of the results and writing main parts of the manuscript.

**Paper 6.** Participate in developing the idea, performing parts of the experiments, writing parts of the manuscript.
## Abbreviations and symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>Alkaline fuel cell</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller method for measuring surface area</td>
</tr>
<tr>
<td>CDC</td>
<td>Calcium doped ceria</td>
</tr>
<tr>
<td>CeCit</td>
<td>Cerium citrate</td>
</tr>
<tr>
<td>Celta</td>
<td>Cerium itaconate</td>
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<tr>
<td>DCO</td>
<td>Doped cerium oxide</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>EDX</td>
<td>Energy-dispersive X-rays analysis</td>
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<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
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<td>FE-SEM</td>
<td>Field-emission scanning electron microscope</td>
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<tr>
<td>GDC</td>
<td>Gadolinium doped ceria</td>
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<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
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<td>HTSOFC</td>
<td>High-temperature solid oxide fuel cell</td>
</tr>
<tr>
<td>ITSOFC</td>
<td>Intermediate-temperature solid oxide fuel cell</td>
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<tr>
<td>LSGM</td>
<td>La$<em>{0.8}$Sr$</em>{0.2}$Ga$<em>{0.8}$Mg$</em>{0.2}$O$_{2.85}$</td>
</tr>
<tr>
<td>LSM</td>
<td>La$<em>{1-x}$Sr$</em>{x}$MnO$_3$</td>
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<tr>
<td>LTSOFC</td>
<td>Low-temperature solid oxide fuel cell</td>
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<td>MCFC</td>
<td>Molten carbonate fuel cell</td>
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<td>MST</td>
<td>Materials science tetrahedron</td>
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<tr>
<td>PAFC</td>
<td>Phosphoric acid Fuel Cell</td>
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<td>PEMFC</td>
<td>Proton exchange membrane fuel cell</td>
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<tr>
<td>$P_{max}$</td>
<td>Maximum power density</td>
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<td>SAED</td>
<td>Selective area electron diffraction</td>
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<td>SDC</td>
<td>Samarium doped ceria</td>
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<td>SOFC</td>
<td>Solid oxide fuel cell</td>
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<tr>
<td>SSZ</td>
<td>Scandia-stabilized zirconia</td>
</tr>
<tr>
<td>TEC</td>
<td>Thermal expansion coefficient</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TPB</td>
<td>Triple phase boundary</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>YDC</td>
<td>Yttrium doped ceria</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttria-stabilized zirconia</td>
</tr>
</tbody>
</table>
# Table of contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td></td>
<td>I</td>
</tr>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Nanoscience and nanotechnology</td>
<td>1</td>
</tr>
<tr>
<td>1.1.1</td>
<td>Nanoscience tetrahedron</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>Fuel cell</td>
<td>3</td>
</tr>
<tr>
<td>1.3</td>
<td>Solid oxide fuel cell</td>
<td>5</td>
</tr>
<tr>
<td>1.3.1</td>
<td>Introduction of SOFC</td>
<td>5</td>
</tr>
<tr>
<td>1.3.2</td>
<td>Materials for SOFC components</td>
<td>6</td>
</tr>
<tr>
<td>1.3.3</td>
<td>Current challenges of SOFC</td>
<td>8</td>
</tr>
<tr>
<td>1.4</td>
<td>Development of low-temperature SOFC</td>
<td>9</td>
</tr>
<tr>
<td>1.4.1</td>
<td>Nanotechnology approach</td>
<td>10</td>
</tr>
<tr>
<td>1.4.2</td>
<td>Composite approach</td>
<td>10</td>
</tr>
<tr>
<td>1.5</td>
<td>Motivation and objectives</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>EXPERIMENTAL</td>
<td>15</td>
</tr>
<tr>
<td>2.1</td>
<td>Core-shell doped ceria/Na$_2$CO$_3$ nanocomposite</td>
<td>15</td>
</tr>
<tr>
<td>2.2</td>
<td>Control synthesis of hierarchically structured cerium oxides</td>
<td>15</td>
</tr>
<tr>
<td>2.3</td>
<td>SDC nanowires based nanocomposite</td>
<td>16</td>
</tr>
<tr>
<td>2.4</td>
<td>Mesoporous CuO-Ce$<em>{0.5}$Sm$</em>{0.2}$O$_{2.5}$ composite anode</td>
<td>16</td>
</tr>
<tr>
<td>2.5</td>
<td>Characterization</td>
<td>16</td>
</tr>
<tr>
<td>2.6</td>
<td>Single cell fabrication and electrochemical measurement</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>RESULTS AND DISCUSSION</td>
<td>21</td>
</tr>
<tr>
<td>3.1</td>
<td>Core-shell doped ceria/Na$_2$CO$_3$ nanocomposite electrolyte</td>
<td>21</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Core-shell SDC/Na$_2$CO$_3$ nanocomposite (Paper VI)</td>
<td>21</td>
</tr>
<tr>
<td>3.1.2</td>
<td>CDC/Na$_2$CO$_3$ nanocomposite (Paper III)</td>
<td>22</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Thermal stability study (Paper II)</td>
<td>24</td>
</tr>
<tr>
<td>3.2</td>
<td>Shape-tunable synthesis of ceria and their application in LTSoFC</td>
<td>25</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Controlled synthesis of hierarchically structured ceria (Paper IV)</td>
<td>25</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>3.2.2 SDC nanowires based nanocomposite electrolyte (Paper I)</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>3.2.3 Mesoporous CuO-Ce_{0.8}Sm_{0.2}O_{2-δ} composite anode (Paper V)</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>CONCLUSIONS</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>FUTURE WORK</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>REFERENCES</td>
<td>37</td>
<td></td>
</tr>
</tbody>
</table>
1 Introduction

World energy demand has been increasing continually and is projected for a strong growth by 50 percent from 2005 to 2030. As major challenges for global economy and climate change, energy supply security, high oil prices and growing greenhouse gases emission are the most critical issues today in the world. In order to solve these problems, some clean sources of energy, such as hydrogen, which don't produce pollutants or greenhouse gases need to be developed. As an energy converter of hydrogen, fuel cells harness the chemical energy of hydrogen to generate electricity, which are considered as more efficient, quiet, and pollution-free power sources in comparison with other systems.

Nanotechnology, a broad and interdisciplinary field involving solid state physics and chemistry, solid state ionics, materials engineering, medical science, biotechnology, etc., is considered to be one of the most important future technologies. Nanotechnology makes it possible to design and create new materials with unprecedentedly novel or improved properties by manipulating matter at the nanometer scale, which in turn will profoundly impact our economy, our environment, and our society. Nanostructured materials have a significant fraction of grain boundaries and a large surface-to-volume ratio, which exhibit unique properties arising from their size or shape in nanoscale region, e.g. “quantum size effect”, where the electronic properties of solids are altered due to confinement of charge carriers.

The enhancement of ionic conductivity in the nanostructured solid conductors, known as “nanoionics”, recently become one of the hottest fields, since they can be used in advanced energy conversion and storage devices, such as solid oxide fuel cell (SOFC). In this thesis, ceria-based nanomaterials with different morphologies are studied and applied as different components for low-temperature SOFC. This thesis is a continuation and an extended version of a previously published thesis titled “ceria-based nanocomposite electrolyte for low-temperature solid oxide fuel cells” (ISBN 978-91-7415-497-9), submitted towards partial fulfillment of the requirements for Technical Licentiate degree in Materials Chemistry at Royal Institute of Technology (KTH) in 2009.

1.1 Nanoscience and nanotechnology

Nanoscience and nanotechnology primarily deal with the synthesis, characterization, exploration, and exploitation of nanostructured materials. These materials are characterized
by at least one dimension in the nanometer (1 nm = 10^{-9} m) range. Individual nanostructures include nanocrystals, nanowires, quantum dots, clusters, and nanotubes, while collections of nanostructures involve arrays, assemblies, and superlattices of the individual nanostructures.\textsuperscript{13,14} Nanoparticles possess large surface areas and essentially no inner mass, that is, their surface-to-mass ratio is extremely high. Therefore, the physical and chemical properties of nanomaterials can differ significantly from those of the bulk materials of the same composition. The uniqueness of the structural characteristics, energetics, dynamics and chemistry of nanostructures is the foundation of nanoscience. Nanoscale materials and devices can be fabricated using either “bottom-up” or “top-down” fabrication approaches. In bottom-up methods, nanomaterials or structures are fabricated from buildup of atoms or molecules in a controlled manner that is regulated by thermodynamic means such as self-assembly.\textsuperscript{15,16} While top-down fabrication technologies include photolithography, dip-pen lithography, nanomolding and nanofluidics, etc.\textsuperscript{17,18}

Size effects are an essential aspect of nanomaterials.\textsuperscript{19,20} Size effects are of two types: one is concerned with specific size effects (e.g., magic numbers of atoms in metal clusters, quantum mechanical effects at small sizes) and the other with size-scaling applicable to relatively larger nanostructures.\textsuperscript{5} One example is the “quantum size effect” where the electronic properties of solids are altered with great reductions in particle size due to the confinement of the movement of electrons.\textsuperscript{21,22} Shapes of nanoparticles also play a role in determining properties,\textsuperscript{23} such as reactivity and electronic spectra. For example, the position of the plasmon band of metal nanorods is sensitive to the aspect ratio.\textsuperscript{24,25}

Nanotechnology has an extremely broad range of potential applications from nanoscale electronics and optics, to nanobiological systems and nanomedicine, to new materials, and therefore it requires formation of and contribution from multidisciplinary teams of chemists, materials scientists, physicists, engineers, molecular biologists, pharmacologists and others to work together on (i) synthesis and processing of nanomaterials and nanostructures, (ii) understanding the physical properties related to the nanometer scale, (iii) design and fabrication of nano-devices or devices with nanomaterials as building blocks, and (iv) design and construction of novel tools for characterization of nanostructures and nanomaterials.\textsuperscript{26}

1.1.1 Nanoscience tetrahedron

The term materials science tetrahedron (MST) was first conceived to guide research and development in the field of materials science and engineering.\textsuperscript{27} MST describes the interplay of the four elements, structure, properties, process, and performance. The four elements are closely connected to each other and form a fundamental basis for understanding and engineering new materials to meet needs. The performance of a new material is what is desired and also the reason for developing new materials. Performance
is determined by properties of the material that are in turn determined by its structure. In fact, the understanding the structure–property relationship is at the heart of materials science and engineering. Once the relationship is clear, material properties can be modified by changing structure of the matter through engineering approaches, that is, processing, and thereby delivering the desired performance.28 The MST is very useful in solving many problems in materials science research.

An analogous tetrahedron (Fig. 1-1) can be used to describe the four elements in nanoscience and nanotechnology field as well: structure (morphology), properties, synthesis and application (performance). In fact, in the past couple of decades, this tetrahedron has been widely used in nanotechnology field, although not explicitly or completely. Synthesis and processing of nanomaterials with different sizes and morphologies are the essential aspect of nanotechnology, which are the main activities in this field now, as reported by several review papers.29,30 Studies on new physical properties and applications of nanomaterials and nanostructures are possible only when nanostructured materials are made available with desired size, morphology, crystal and microstructure and chemical composition. Once we understand how the structure of nanomaterials affects the properties and performance, we can further modify the desired performance by synthesis and processing. The four elements constitute a complete nanotechnology development loop. In this process, advanced characterization tools play vital role in connecting the four elements, e.g. it helps to understand the structure–property relationship, which is critical for any successful application of nanomaterials.

1.2 Fuel cell

Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy.31-34 The basic physical structure of a fuel cell consists of an
INTRODUCTION

electrolyte layer in contact with a porous anode and cathode on each side. A fuel cell has
electrochemistry mechanisms similar to a battery; however, it uses externally supplied
fuels, while a battery consumes internal fuels to generate electricity. A fuel cell can
produce electricity continuously as long as the fuel is supplied; by contrast a battery needs
to be recharged. The conversion efficiency of fuel cells is much higher than current
thermo-mechanical methods. In addition, fuel cells are environmental friendly, with much
lower CO₂, sulfur and nitrogen oxides emissions. Therefore, fuel cells are considered as
one of the most promising power generation devices.35

There are a variety of fuel cells in different stages of development. The major
successful types of fuel cells are proton exchange membrane fuel cell (PEMFC), alkaline
fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and
solid oxide fuel cell (SOFC), classified by type of electrolyte materials they use. Fig. 1-2
illustrates the basic principle of the above five kinds of fuel cells.36

The applications for fuel cells are mainly on mobile or stationary applications.32,34 The
mobile applications primarily include transportation systems and portable electronic
equipment, while stationary applications primarily include combined heat and power
systems for both residential and commercial needs. On transportation application, all the
world leading car manufacturers have designed at least one prototype vehicle using fuel
cells. In addition, miniature fuel cells could replace batteries for electronic products such
as cellular telephones, portable computers, and video cameras. The primary stationary
application of fuel cell technology is for the combined generation of electricity and heat,
for buildings, industrial facilities or stand-by generators.35
1.3 Solid oxide fuel cell

1.3.1 Introduction of SOFC

Solid oxide fuel cell (SOFC) is characterized by having a solid ceramic electrolyte (hence the alternative name, ceramic fuel cell), which is usually a metal oxide. The basic components of SOFC are a cathode, an anode and an electrolyte. At the cathode, where oxidant, normally oxygen in the air is supplied, oxygen is reduced to oxygen ions. Then the oxygen ions are transported through the electrolyte under electrical load, to the anode and react with the hydrogen to form water. Thus the final products of SOFC are electricity, heat and water. The process is shown schematically in Fig. 1-3. The half-cell reactions at the cathode and anode can be expressed by Kröger-Vink Notation as follows, where \( V_{O}^{\circ} \) is the oxygen ion vacancy and \( O_{O}^{\circ} \) is the oxygen ion in the electrolyte:

**Cathode Reaction:**

\[
\frac{1}{2}O_{2}(g) + 2e^{\circ} + V_{O}^{\circ} \rightarrow O_{O}^{\circ}
\]  \hspace{1cm} (1-1)

**Anode Reaction:**

\[
H_{2}(g) + O_{O}^{\circ} \rightarrow H_{2}O(g) + V_{O}^{\circ} + 2e^{\circ}
\]  \hspace{1cm} (1-2)

So the overall reaction can be expressed as:

\[
H_{2}(g) + \frac{1}{2}O_{2}(g) \rightarrow H_{2}O(g)
\]  \hspace{1cm} (1-3)

The relatively high operating temperature of SOFC allows for highly efficient conversion to power, internal reforming, and high quality by-product heat for cogeneration. The most important feature of SOFC is fuel flexibility, i.e. in principle it can utilize a variety of fuels, such as hydrocarbon fuels, bio-ethanol, bio-gas, etc., without the need for external reforming. Unlike low temperature fuel cells like PEMFC, SOFC does not rely on noble metal catalyst, so that CO can be used as a fuel rather than a poison. These capabilities have made SOFC an attractive emerging technology for stationary power.

![Fig. 1-3 Scheme of the operating principle of a solid oxide fuel cell.](image-url)
1.3.2 Materials for SOFC components

1.3.2.1 Electrolyte

The electrolyte is the principal component of importance for SOFC. An ideal SOFC electrolyte should have the following characteristics: high ionic conductivity; low electronic conductivity; good thermal and chemical stability in relation to the reactant environment and the contacting electrode materials; closely matched thermal expansion coefficient (TEC) between the electrodes and contacting components; fully dense structure to maximize conductivity and minimize reactant cross-over; be low cost and environmentally benign. Currently fluorite structure materials, such as zirconia-based and ceria-based oxide, and perovskite LaGaO$_3$ based materials are widely used as electrolytes for SOFC. Fig. 1-4 shows how the specific ionic conductivity of different solid oxide electrolytes varies with temperature.

Vacancies randomly distributed throughout the oxide sublattice are an essential element required for oxygen-ion conduction in SOFC electrolyte materials. The fluorite oxides are the classical oxygen ion conductors, with the general formula of AO$_2$, where A is a tetravalent cation. This structure is a face-centered cubic arrangement of cations with oxygen ions occupying all the tetrahedral sites, leading to a large number of octahedral interstitial voids. Thus this structure is a rather open one and rapid ion diffusion can be expected. The addition of lower valence cations produces oxygen vacancies, resulting in improved oxygen ion conductivity. Zirconia (ZrO$_2$) has the fluorite structure and has been studied extensively for SOFCs electrolytes. Yttria stabilised zirconia (YSZ) is the most...
widely used electrolyte for SOFCs and possesses good chemical and physical stability as well as negligible electronic conductivity. Addition of 8 mol% of yttria i.e. \((\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}\) (8YSZ) has the highest oxide ion conductivity.

Doped cerium oxide (DCO), also with the fluorite structure, is considered to be a promising electrolyte for low temperature SOFC.\(^{49,50}\) Samarium doped ceria (SDC) and gadolinium doped ceria (GDC) are the most extensively studied ceria based electrolytes, with the maximum ionic conductivity occurring at 10–20 mol% dopants. Compared to YSZ, DCO has a high conductivity and lower activation energy below 800 °C. However, DCO suffers from the partial reduction of Ce\(^{4+}\) to Ce\(^{3+}\) in reducing atmosphere and at high temperature (>600 °C), which leads to undesirable structural change, as well as electronic conductivity which reduces performance due to electronic leakage currents between the anode and cathode. Therefore, the operation of SOFCs with a DCO electrolyte is considered most effective in the 500–600 °C temperature range.

Perovskite is another type of oxygen ion conductor, which has ABO\(_3\) stoichiometry. Typically, the A-site cation is large, such as a rare earth, and will be 12-coordinated by anions in the lattice. The B-site cation is typically smaller and six-coordinate, forming BO\(_6\) octahedra. There are two cation sites in the perovskite oxides upon which to substitute lower valence cations, leading to a much wider range of possible oxygen ion conducting materials. Until now lanthanum gallate is the most widely studied perovskite conductor that is stable in air and hydrogen.\(^{51-53}\) Lanthanum gallate with strontium doping on the A-site of the perovskite and magnesium on the B-site could be used at temperatures as low as 600 °C.\(^{54}\) A favored composition in terms of ionic conductivity is \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}\) (LSGM). However, LSGM is substantially more expensive than ceria based electrolytes, and it has also proved difficult to prepare pure single phase electrolytes of LSGM. Besides, challenges of matching the thermal expansion coefficients, mechanical strength, and chemical compatibilities need further development.

1.3.2.2 Anode

The role of an anode in SOFC is electro-oxidation of fuel by catalyzing the reaction, and facilitating fuel access and product removal. Therefore, the anode materials should meet several requirements\(^{55-58}\): stability in reducing environment; sufficient electronic and ionic conductivity; porous structure; thermal expansion coefficient (TEC) matching with electrolyte materials and high catalytic activity.

These requirements together with elevated operating temperature limit the choice of the anode materials to nickel and the noble metals. The vast majority of SOFCs have a nickel anode because of its low cost. The most commonly used anode materials are cermet composed of nickel and solid electrolyte, such as Ni-YSZ, Ni-SDC, aiming at maintaining porosity of anode by preventing sintering of the Ni particles and giving the anode a TEC
INTRODUCTION

comparable to that of the solid electrolyte. However, direct exposure of hydrocarbon fuels to the conventional nickel based anodes has been problematic due to their high catalysis for hydrocarbon cracking reactions at the operating temperatures, leading to carbon accumulation in the anode and thus eventually degrading the cell performance.\textsuperscript{59,60} Alternative anode materials, i.e. replacing nickel by copper in the cermet anode, were thus developed,\textsuperscript{61} since copper does not catalyze the cracking process.

1.3.2.3 Cathode

Cathode in SOFC carry out several roles: reduction of molecular oxygen, transport of charged species to the electrolyte and distribution of the electrical current associated with the oxygen reduction reaction.\textsuperscript{55,62-64} Therefore, the cathode materials should meet the following requirement:

1) Stability in oxidizing environment;
2) Sufficient electronic and ionic conductivity;
3) Porous structure and stable at high temperature;
4) Comparable TEC to that of electrolyte materials;

Numerous oxides have been studied as cathode materials for SOFC. Strontium-doped lanthanum manganite (LSM), La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3}, with intrinsic p-type conductivity, is the most commonly used cathode material for YSZ based SOFC.\textsuperscript{65,66} The conductivity of LSM varies with strontium content, with an apparent optimum strontium level. Another perovskite material that has been extensively studied is doped lanthanum cobaltite, LaCoO\textsubscript{3}.\textsuperscript{67} The conductivity can be increased by substituting cations on the lanthanum and cobalt site. For example, La\textsubscript{1-x}Sr\textsubscript{x}Co\textsubscript{1-y}Fe\textsubscript{y}O\textsubscript{3-δ}, has been identified as promising materials in terms of both ionic and electronic conductivity.\textsuperscript{68} Furthermore, there are a number of new materials that have been proposed as cathode materials for SOFC operating at lower temperature. These include perovskite-type materials [(Sm, Sr)CoO\textsubscript{3}, (Ba, Sr)(Co, Fe)O\textsubscript{3-δ}], layered perovskite-related structures (La\textsubscript{n+1}Ni\textsubscript{3}O\textsubscript{3n+1}) and double perovskites (GdBaCoO\textsubscript{5+δ}), all of which have shown encouraging performance at lower temperatures.\textsuperscript{69}

1.3.3 Current challenges of SOFC

High temperature SOFC (HTSOFC), which operates in the temperature region of 850–1000 °C, has been successfully demonstrated by developers such as Siemens Westinghouse and Rolls-Royce.\textsuperscript{37} However, this high temperature presents not only material degradation problems, but also technological complications and economic obstacles.\textsuperscript{70,71} From standpoint of costs, expensive high temperature alloys are used to house the cell, and expensive ceramics are used for the interconnections, thus increasing the cost of the SOFC substantially.\textsuperscript{70} Besides, material degradation is another critical issue prohibitive for broad commercialization. For example, the high operating temperature
leads to sintering of the nickel particles, which deteriorates the anode porosity and catalytic activity. Therefore, reducing the operation temperature of SOFC to the so-called intermediate temperature (IT) range of 600–800 °C, or even low temperature range of below 600 °C, is a grand challenge in SOFC field.

1.4 Development of low-temperature SOFC

The development of intermediate-temperature SOFC (ITSOFC) or low-temperature SOFC (LTSOFC) is now a global tendency for SOFC commercialization. However, with decreased operating temperature, the internal resistance of SOFC increases tremendously, which results in decrease of the cell performance. Therefore, to decrease the internal resistance of SOFC is the key point for LTSOFC. There are several factors leading to SOFC internal resistance: first and foremost is the resistance of electrolyte, due to low oxygen ion conductivity of electrolyte materials. Second, polarization resistances of electrodes, especially cathode, are magnified with the decrease of temperature.

There are two main approaches by which SOFCs can be operated at lower temperatures, while still attaining comparable performance to the higher temperature technology. The dimensional thickness of the electrolyte can be reduced, so reducing the area specific resistance of the fuel cell, and/or materials development can bring about the same result by improving the ionic conductivity of the electrolyte at lower temperatures and bring about improvements in the performance of electrodes.

In recent years, there has been an enormous increase in the developing of thin film technologies for SOFC to reduce its internal resistance in order to decrease the operation temperature. There are several advantages on synthesizing SOFC electrolyte components by thin film processes, e.g. ohmic losses can be reduced, sintering temperature can be decreased and interfaces can be easily controlled. By using a thin electrolyte layer, the electrolyte can no longer mechanically support the cell. Instead an anode/substrate is usually used for supporting the cell. So far many studies have been done to deposit an yttria stabilized zirconia (YSZ) electrolyte film using various physical or chemical thin film technologies, such as electrophoretic deposition, spin coating method, radio-frequency sputtering, atomic layer deposition, pulsed laser deposition, etc. However, there are still some drawbacks on these methods, such as long production period, very high cost, difficulty on scaling up, as well as difficulties on control of film growth, which make it difficult to realize the commercialization of LTSOFC.

Another practical way to exploit LTSOFC is exploring new electrolyte materials with enhanced ionic conductivity by nanotechnology approach or composite approach, as well as developing compatible electrode materials, which is the main topic of the thesis.
1.4.1 Nanotechnology approach

The conductivity of micro-sized polycrystalline electrolyte is contributed to both grain-interior and grain-boundary. The specific grain-boundary resistivity is known to be two to three orders of magnitude higher than the grain-interior resistivity. This blocking effect comes from the oxygen vacancy depletion near the grain-boundary.\(^{82}\) Therefore, many efforts have been taken on the engineering of grain-boundary to lower its resistance, and improve the performance of polycrystalline electrolytes. However, ion transport across or along grain boundaries in solids with nanometer-sized grains may differ distinctly from that in conventional polycrystalline solids.\(^{82,83}\) In recent years, the enhancement of ionic conductivity in the nanostructured solid electrolytes, known as “nanoionics”,\(^6,7\) has been rapidly recognized as an emerging new scientific area and widely applied on rechargeable lithium-ion batteries, gas sensors and solid oxide fuel cells.\(^8\) The enhancement of ionic conductivity in nanoionics is explained by predominance of grain-boundary conductivity, because of faster diffusion than bulk and larger volume fraction of grain boundary in nanostructured electrolytes.\(^{83}\)

Some works have been done to study the enhanced oxide ion conductivity of nanostructured electrolyte for SOFCs. For example, Bellino et.al\(^ {10,11}\) observed the total ionic conductivity of nanostructured, heavily doped ceria solid electrolyte increases about one order of magnitude compared to microcrystalline materials. Conductivity enhancement has also been found in nanostructured YSZ materials; e.g. Tuller et.al prepared YSZ thin films with nanometric sized grains and enhanced oxygen ion conductivities were observed when compared to bulk YSZ.\(^ {84}\) In addition, oxygen diffusivity in the grain boundaries of YSZ was found to be about 3 orders of magnitude higher than in single crystals.\(^ {12}\) Nanoionics, as a combination of nanotechnology and ionics, have pioneered a new direction in the solid state ionic research field.

Furthermore, regarding the morphology effect of nanomaterials, the grain boundary of nanostructured ionic conductors can be tuned by manipulating their nano-architecture. For example, as one of the attractive nanomaterials with unique chemical and physical properties, 1D nanowires may achieve higher ionic conductivity compared to their nanoparticles analogues, due to their longer continuous grain-boundary from high aspect ratio. Therefore, the study on performance of nanostructured electrolyte with respect to the shape or size effect are of great significance and opens a new area in R&D leading to new electrolyte materials for LTSOFC.

1.4.2 Composite approach

Composite electrolytes are basically physical mixtures consisting of two or more solid phases that possess different ionic conductivity properties.\(^ {85}\) This kind of composite materials usually show enhanced conductivity, but the effects are not simply additive;
rather they are synergistic that the overall conductivity is significantly higher than in both of the constituent phases. The conductivity enhancement effects of composite electrolyte were first reported on LiI:Al₂O₃ composite in 1973 by Liang,⁸⁶ that the incorporation of Al₂O₃ substantially increased almost 50 times of the Li⁺ ion conductivity for LiI. Since then, enormous work has been done to study the enhancement effects of diverse composite system, such as insulator-conductor systems (dispersing an oxide like Al₂O₃, SiO₂ in a moderate ion conductor),⁸⁷⁹₂ or conductor-conductor system (Ag⁺ conductivity enhancement in AgBr-Agl; nano-sized ionic CaF₂/BaF₂ heterostructures).⁹³⁹₆ This conductivity enhancement, the so-called composite effect, is suggested to be due to high ionic conductivity in the interface region between components.⁸³⁹⁷

In recent years, composite effect has also been utilized on developing new electrolytes materials for LT-SOFC. In 2000, Zhu et al. reported for the first time the ceria-based composite electrolyte for SOFC, since then plenty of work has been done to develop functional electrolytes for low-temperature SOFC by composite approach.⁹₈-¹₀² These composite materials commonly consist of two phases; host phase (ceria-based oxide) and second phase (various salt, proton conductor, etc.). Many efforts have been made on various ceria-based composite ceramics, such as SDC (samarium doped ceria), GDC (gadolinium doped ceria) and YDC (yttrium doped ceria) etc. incorporated with different salts and hydrates, such as chlorides, fluorites, carbonates, sulphates and sodium or potassium hydrates (as shown in Table 1-1).¹⁰³-¹¹₀ Ceria-based composite electrolyte materials have displayed high ionic conductivity at 400–600 ºC, where the conductivity has been increased about one to two magnitudes compared to conventional single-phase electrolyte, like YSZ, GDC, etc. Development on ceria-based composite electrolyte has

<table>
<thead>
<tr>
<th>Doped Ceria</th>
<th>Salt</th>
<th>Conductivity (S cm⁻¹)</th>
<th>Performance (W cm⁻²)</th>
<th>Temperature (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDC</td>
<td>20wt%(1LiCl: 1 SrCl₂)</td>
<td>0.015-0.21</td>
<td>0.10-0.58</td>
<td>400-660</td>
</tr>
<tr>
<td>GDC</td>
<td>15wt%NaOH</td>
<td>0.02-0.45</td>
<td>0.10-0.62</td>
<td>380-620</td>
</tr>
<tr>
<td>GDC</td>
<td>22wt%(2Li₂CO₃:1 Na₂CO₃)</td>
<td>0.01-0.80</td>
<td>0.20-0.78</td>
<td>400-660</td>
</tr>
<tr>
<td>SDC</td>
<td>20wt%(1LiCl: 1 SrCl₂)</td>
<td>0.02-0.24</td>
<td>0.10-0.60</td>
<td>400-660</td>
</tr>
<tr>
<td>SDC</td>
<td>15wt%NaOH</td>
<td>0.03-0.50</td>
<td>0.20-0.66</td>
<td>380-620</td>
</tr>
<tr>
<td>SDC</td>
<td>22wt%(2Li₂CO₃:1 Na₂CO₃)</td>
<td>0.002-0.90</td>
<td>0.20-1.00</td>
<td>400-660</td>
</tr>
<tr>
<td>YDC</td>
<td>20wt%(1LiCl: 1 SrCl₂)</td>
<td>0.01-0.18</td>
<td>0.10-0.52</td>
<td>400-660</td>
</tr>
<tr>
<td>YDC</td>
<td>15wt%NaOH</td>
<td>0.02-0.40</td>
<td>0.20-0.58</td>
<td>380-620</td>
</tr>
<tr>
<td>YDC</td>
<td>22wt%(2Li₂CO₃:1 Na₂CO₃)</td>
<td>0.01-0.78</td>
<td>0.20-0.70</td>
<td>400-660</td>
</tr>
</tbody>
</table>
opened up a new horizon in the LTSOFCs research field.\textsuperscript{35}

With enhanced ionic conductivity, ceria–based composite electrolyte materials could achieve good performance as long as electrode materials are compatible. So far, the mixture of NiO and composite electrolyte has been widely used as the anode materials; while (La,Sr)CoO\textsubscript{3}, (Sm,Sr)CoO\textsubscript{3}, or lithiated NiO are commonly used cathode materials. Table 1-1 gives the summary of the conductivity and the relevant FC performance for various ceria-based composite electrolytes.\textsuperscript{100} However, the development of more compatible anode and cathode materials with structural superiority and better properties will further improve the overall fuel cell performance.

The enhanced ionic conductivity of ceria–based composite electrolyte is preliminarily explained by interface conduction mechanism.\textsuperscript{100,101,111} Compared with single phase electrolyte (SDC, YSZ), composite electrolyte contains lots of interface regions between the two constituent phases. The interface supplies high conductivity pathway for ionic conduction, which have the capacity to increase mobile ion concentration than that of the bulk. There are highly conducting contributions in parallel due to space charge zones near phase boundaries. The defect concentrations are much higher in these zones than that in the bulk, which accounts for higher ionic diffusivity and mobility than bulk. Up to now the interfacial conduction mechanism is widely recognized in the ceria-based composites research field. However, more detailed mechanism still needs to be investigated, especially in terms of charge carriers (proton or oxygen ion).

### 1.5 Motivation and objectives

As we introduced previously, in order to develop LTSOFCs, there are two ways to implement the aim: first, to decrease the area specific resistance of cells by developing new electrolyte materials with higher ionic conductivity; second, to further improve the performance of electrodes that are compatible to the electrolyte materials. To further improve the ionic conductivity of electrolyte, there are two possible ways: nanotechnology approach and composite approach. Both of them have advantages and drawbacks: nanostructured ionic conductors possess enhanced ionic conductivity due to predominance of grain boundary, but their stability at high temperature is a serious issue; ceria-based composite materials created a big breakthrough in LTSOFCs field while the detailed conduction mechanism of composite materials is still not clear. However, when composite materials meet “nano”, there will be a synergistic effect. For nanostructured ionic conductors, grain growth can be effectively suppressed by incorporating another phase into interparticle region; while for composite materials with nanostructure, the grain boundary/interface conduction is dominant in overall transport, which will give rise to an enormous conductivity enhancement. Therefore, nanocomposite approach is a novel effective way to develop electrolyte materials for LTSOFC. Regarding to the enhancement of electrode
properties, a promising way is to further improve the materials architecture, like fabrication of mesoporous structure for electrode materials.

In this thesis, we are aiming at developing a novel nanocomposite approach to design and fabricate ceria-based composite materials for both electrolytes and anode of LTSoFC. Based on the interfacial effect, both size and morphology of the host particles will influence the volume of interface, which will further affect the ionic conductivity of the composite electrolytes. For this purpose, we studied two ceria-based nanocomposite systems with different composition and morphologies. First, SDC/Na₂CO₃ and CDC/Na₂CO₃ were fabricated and applied as electrolyte in low-temperature SOFC, and the thermal stability of the core-shell SDC/Na₂CO₃ nanocomposites was studied and its long-term durability was evaluated. Second, a novel method for controlled synthesis of hierarchically structured ceria nanowires and mesoporous microspheres were developed, and the detailed formation mechanism were investigated. Based on the uniqueness of the two morphologies, distinctive properties are expected to further enhance the performance of electrolyte and anode, respectively. Therefore, by doping with desired elements, the SDC nanowires and SDC-CuO mesoporous microspheres were prepared and applied as electrolyte and anode materials for LTSoFC. The whole work carefully investigated the synthesis–structure–property relationship, which has explicitly exemplified the use of nanoscience tetrahedron as a guideline to develop functional nanomaterials for LTSoFC applications.
2 Experimental

2.1 Core-shell doped ceria/Na$_2$CO$_3$ nanocomposite

2.1.1 Fabrication of doped ceria/Na$_2$CO$_3$ nanocomposite

The Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ (SDC) and Ce$_{0.8}$Ca$_{0.2}$O$_{2-\delta}$ (CDC) sample were synthesized via coprecipitation method using sodium carbonate and ammonium oxalate as the precipitant, respectively. The stock solution was first made by dissolving stoichiometric amount of cation salt in distilled water. Aqueous solutions of precipitant (Na$_2$CO$_3$ or (NH$_4$)$_2$C$_2$O$_4$) with specific concentration were also prepared. In a typical synthetic procedure, 50 mL mixed salt solution was dripped at a speed of 5 mL min$^{-1}$ into 150 mL precipitant solution under vigorous stirring at room temperature to form a white precipitate. The resultant suspension, after homogenizing for 1 h, was filtered via suction filtration. The precipitate cake was washed repeatedly with distilled water, followed by drying at 80 °C to obtain precursor.

The doped ceria/Na$_2$CO$_3$ nanocomposites with Na$_2$CO$_3$ weight content of 20% were prepared by either a wet mixing method or dry mixing method. After the mixing step, the sample was subject to a calcination step under certain temperature. More detailed fabrication process for each sample was described in published papers.$^{112,113}$

2.1.2 Thermal stability test of core-shell SDC/Na$_2$CO$_3$ nanocomposite

The SDC/Na$_2$CO$_3$ composite sample was then annealed at 600 °C and 700 °C for 2 h and 24 h for the thermal stability test, as well as pure SDC sample for comparison. Crystallite sizes, particle sizes and surface areas of the above annealed samples were calculated or measured by XRD, SEM, and BET respectively, to compare the thermal stability of Na$_2$CO$_3$ coated and uncoated SDC sample.

2.2 Control synthesis of hierarchically structured cerium oxides

2.2.1 Synthesis of ceria nanowires

Briefly, stoichiometric amounts of Ce(NO$_3$)$_3$·6H$_2$O were dissolved in deionized water to obtain a 0.2 M Ce(NO$_3$)$_3$ stock solution; similarly citric acid solution (0.6 M) was prepared. Then, equal volumes of Ce(NO$_3$)$_3$ and citric acid solutions were mixed in a beaker, adjusting the pH value to 2.0 by the addition of 5 M NaOH solution. Then the beaker was sealed and heated to 90 °C in an oven. After 24 h reaction, white deposit was
formed in the beaker. The deposit was collected by centrifugation and washed by water and ethanol for several times, and dried at 120 °C in vacuum oven overnight. This precursor was then calcined at 300 °C for 3 h to obtain the CeO₂ nanowires.

2.2.2 Synthesis of ceria mesoporous microspheres

For synthesis of hierarchically structured CeO₂ microspheres, the mixed solution of Ce(NO₃)₃ and citric acid with the pH equals 2.0, were transferred to microwave process vials and heated to 105 °C for 1 h by a Biotage® Initiator microwave reactor. After reaction, precursor deposit was collected, washed, dried and calcined at 400 °C for 3 h to get the CeO₂ microspheres sample.

2.3 SDC nanowires based nanocomposite

The SDC nanowires were synthesized by the same method as described in Section 2.2.1 for ceria nanowires, while the initial cation solution was prepared by dissolving stoichiometric amounts of Ce(NO₃)₃·6H₂O and Sm(NO₃)₃·6H₂O in deionized water to obtain a 0.2 M solution (total moles of cations per liter of solution). The SDC nanowires/Na₂CO₃ nanocomposite was prepared by a wet mixing method. As-prepared SDC sample was mixed with Na₂CO₃ solution (2 M) under vigorous stirring with Na₂CO₃ weight ratio of 20 wt%. The mixture slurry was dried at 80 °C in air for 24 h, annealed at 600 °C in air for 2 h and immediately cooled to room temperature to form the SDC nanowires/Na₂CO₃ composite.

2.4 Mesoporous CuO-Ce₀.₈Sm₀.₂O₂-δ composite anode

Stoichiometric amounts of Ce(NO₃)₃·6H₂O and Sm(NO₃)₃·6H₂O were dissolved in deionized water to obtain a 0.3 M solution (total moles of lanthanide ion per liter of solution); similarly Cu(NO₃)₃ solution (0.3 M) and citric acid solution (0.9 M) was also prepared. Same volume amount of the above three solutions were mixed in a beaker to obtain a clear mixture with ratio of La³⁺ (Ce³⁺ + Sm³⁺): Cu²⁺: Citric acid = 1:1:3. Adjust the pH value of the mixed solution to 2.0 by dropwise addition of 5 M NaOH solution. Then certain amount of as-prepared mixed solution was taken into a microwave vial. Seal the vial and heat it to 105 °C in the Biotage® Initiator microwave synthesizer. After 40 min reaction, some deposit was formed in the microwave vial. The deposit was collected, washed and dried at 120 °C in vacuum oven overnight. This precursor was then calcined at 400 °C for 3 h to obtain the CuO-SDC sample.

2.5 Characterization

The materials at the different processing steps are characterized by different means of characterization.

Thermodynamic modelling was performed by Medusa software to simulate aqueous
solution reaction.

Powder X-ray diffraction (XRD) patterns of the samples were collected on a Philips X’pert pro super Diffractometer with Cu Kα radiation (λ=1.5418 Å). The average crystallite size, D, can be evaluated from the peak broadening of the diffraction pattern, based on the following Scherrer’s equation.

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]

Where β is the pure diffraction line width, full width at half maximum, expressed in radians in terms of 2θ at angle θ, and λ is the X-ray wavelength.

A Zeiss Ultra 55 digital field emission scanning microscope (FE-SEM) equipped with energy-dispersed X-rays analysis (EDX) was used to examine the morphology, size distribution and elemental composition of samples. The specimen was prepared by dripping nanoparticle suspension in ethanol or acetone onto aluminum sample holder followed by drying in a vacuum oven at 70 °C overnight. To view the inner texture of the sample and perform the phase identification, transmission electron microscopy (TEM), selective area electron diffraction (SAED), high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) analysis were performed on a JEOL JEM-2100F field-emission microscope using an accelerating voltage of 200 kV. The specimen for TEM imaging was prepared by dropping the suspension of nanoparticles on a carbon-coated 200 mesh copper grid, followed by drying the sample under ambient conditions.

The precursor samples were subjected to thermogravimetric analysis (TGA) to study the thermal decomposition process, with a heating rate of 10 °C min⁻¹ in synthetic air using TA TGA Q500. The differential scanning calorimetry (DSC) analyses were carried out using TA DSC Q2000 to investigate thermal behavior of samples, at a heating rate of 10 °C min⁻¹ in synthetic air atmosphere.

Fourier-transform infrared spectroscopic (FT-IR) spectra (500–5000 cm⁻¹ with a resolution of 0.4 cm⁻¹) of the samples were obtained on a Nicolet Avatar 360 E.S.P. spectrophotometer. Surface areas of samples were determined using the Brunauer–Emmett–Teller (BET) method from the low-temperature adsorption of nitrogen, performed at −196 °C after degassed at 350 °C for 12 h.

2.6 Single cell fabrication and electrochemical measurement

2.6.1 Conductivity measurement

2.6.1.1 Electrochemical impedance spectroscopy

For conductivity measurement, the composite electrolyte powder was uniaxially
pressed at 300 MPa to form a 13 mm diameter green pellets by a manual hydraulic press. The green pellets were then sintered at 600 °C in air for 1 h. After sintering, both sides of the disks were grounded and polished to obtain the desired thickness and to produce faces that were flat and parallel to one another. Then, silver paste was applied as electrode onto both sides of the pellets and heated at 600 °C for 40 min. Conductivity of samples was measured by electrochemical impedance spectroscopy (EIS) in the temperature range between 300 and 600 °C, using a two-electrode configuration. The measurements were conducted in the frequency range from 5 Hz to 13 MHz using a computerized HP 4192A LF Impedance Analyzer with an applied signal of 20 mV. A K-type thermocouple was positioned adjacent to the sample in order to monitor sample temperature.

2.6.1.2 Four-Probe D.C. technique

The setup of d.c. conductivity measurement is shown in Fig. 2-1. Platinum paste was applied on both surfaces of electrolyte pellets as electrodes, followed by firing at 700 °C for 30 min. The four-probe setup consists of aligned platinum ring electrodes on both sides of pellet as current probes, while a pair of aligned Pt points placed at the center of Pt rings work as voltage probes, as shown in the cell sketch in Fig. 2-1. The distance of voltage probes and current probes is about 1 mm. Two copper rings were employed as both current collectors and mechanical support for voltage probes, connecting with sample holder and electrolyte pellet by platinum paste. Two platinum wire leads were connected to each current probe through the ceramic tube in the copper ring at both sides of the pellet. The exposed part of sample was sealed by Pyrex® glass powder. Anode gas (5% H₂, 95% N₂) or cathode gas (synthetic air, 21% O₂, 79% N₂) were supplied continuously on both sides.

Fig. 2-1  A schematic illustration of setup applied for d.c. conductivity measurement, and the four-probe electrodes design. The bottom view of electrolyte pellet is the same as the top view.
of the electrolyte to determine proton and oxygen ion conductivity. A typical excitation of 1 mA was applied from EG&G 366 current source. The potential drop across the sample was measured using a HP 3478A digital multimeter.

2.6.2 Fuel cell fabrication and performance test

The single cells were fabricated by anode, electrolyte and cathode materials using the co-pressing process. In a typical process, equal volume of electrolyte material and commercial NiO powder were first mixed to prepare anode material. The cathode powder was composed of lithiated NiO (50 vol.%) mixed with electrolyte (50 vol.%). Then, the anode, electrolyte and cathode were uniaxially pressed into a pellet with diameter of 13 mm at a pressure of 300 MPa and then sintered at 600 °C for 30 min in air. Finally, both anode and cathode surfaces were painted by silver paste as current collectors for fuel cell measurements. In the fuel cell test procedure, a stainless steel sample holder was used to test the cell at 450 to 600 °C, as shown in Fig. 2-2. The effective working area of the pellet was 0.64 cm². Hydrogen and synthetic air were used as fuel and oxidant respectively. The gas flow rates were controlled in the range of 80 to 120 mL min⁻¹ at 1 atm pressure.
3 Results and Discussion*

3.1 Core-shell doped ceria/Na$_2$CO$_3$ nanocomposite electrolyte

Currently the fabrication of nanostructured composite electrolyte material with enhanced properties is still a challenge and will lead to a new research direction in LTSoFCs field, since it will not only improve the performance of composite electrolyte but also contribute to the study of enhanced conduction mechanism. So in this section, the fabrication and investigation of nanocomposite based on 3D doped ceria nanoparticles is the main focus. First, in section 3.1.1, the preparation and evaluation of SDC/Na$_2$CO$_3$ nanocomposite will be elucidated. Thereafter, synthesis and properties of calcium doped ceria (CDC) based nanocomposite will be studied in section 3.1.2. CDC was selected as the main phase of the nanocomposite from viewpoint of both material performance and economical aspects. The thermal stability study of SDC/Na$_2$CO$_3$ nanocomposite will be demonstrated in section 3.1.3, in order to prove that these materials are promising for long-term SOFCs operation.

3.1.1 Core-shell SDC/Na$_2$CO$_3$ nanocomposite (Paper VI)

The fabrication of core-shell nanocomposite materials consisting of SDC core and amorphous Na$_2$CO$_3$ shell in nano-scale has been conducted for the first time. XRD pattern of as-prepared SDC/Na$_2$CO$_3$ nanocomposite shows that all the peaks could be indexed to the cubic fluorite-type structure CeO$_2$ (JCPDS 34-0394). But no peak has been observed associating with Na$_2$CO$_3$, though the content of Na$_2$CO$_3$ is 20%, which indicates that Na$_2$CO$_3$ exists as amorphous phase in the nanocomposite. SEM characterization (Fig. 3-1a) reveals that the nanocomposite consists of particles smaller than 100 nm and show faceted and occasionally irregular shape. Further TEM analysis clearly illustrates that nanocomposite has a core-shell structure and SDC nanoparticles are surrounded by a uniform amorphous Na$_2$CO$_3$ layer of 4-6 nm thickness. HRTEM image (Fig. 3-1b) further displays the microstructure. The dominant lattice fringes are seen clearly in the core; the distance between parallel fringes is equal to the spacing of the {111} planes in SDC. No lattice fringe can be observed in Na$_2$CO$_3$ shell layer which further confirms that Na$_2$CO$_3$ is

* This part of the thesis provides a comprehensive summary of the enclosed papers.
amorphous. Simultaneously the interface between core and shell is also clearly observed.

The SDC/Na$_2$CO$_3$ nanocomposite electrolyte exhibits greatly enhanced conductivity compared to pure SDC. From DSC analysis and conductivity measurement results, it is concluded that the significantly enhanced conductivity of nanocomposite results from a new interfacial conduction mechanism beyond bulk conduction effects. Compared with single phase electrolyte, composite electrolyte contains a high density of interface regions between the two constituent phases. The interface supplies high conductivity pathway for ionic conduction, which have the capacity to increase mobile ion concentration than that of the bulk. The conductivity of nanocomposite electrolyte is presumably dominated by interfacial ionic conduction rather than bulk conduction, which results in low activation energy and high ionic conductivity.

Finally, single cells using the core-shell SDC/Na$_2$CO$_3$ nanocomposite as electrolyte obtained good performance, with the $P_{\text{max}}$ of 0.8 W cm$^{-2}$ at 550 °C. Compared with the thin-film SDC single cell reported by Shao et al., the SDC/Na$_2$CO$_3$ nanocomposite fuel cells show better performances at 450-550 °C, indicating that the nanocomposite electrolyte has great potential value for low-temperature SOFC technology.

### 3.1.2 CDC/Na$_2$CO$_3$ nanocomposite (Paper III)

In order to develop more efficient electrolyte based on the nanocomposite approach, we considered calcium doped ceria (CDC) as a good candidate since it shows comparable high conductivity as SDC and calcium is much less expensive. In this study, CDC nanomaterial was prepared by oxalate co-precipitation, and resultant CDC/Na$_2$CO$_3$ nanocomposite was obtained by dry mixing method. TGA coupled with FT-IR analysis determines the calcination temperature of oxalate precursor to be 650 °C, in order to get pure CDC phase. XRD pattern of CDC confirms a cubic fluorite-type structure. As a comparison, CDC/Na$_2$CO$_3$ composite exhibits the same fluorite-type structure with broader
peak widths due to smaller particle size. However, there is no peak associated with Na$_2$CO$_3$, indicating that Na$_2$CO$_3$ exists as amorphous phase, which demonstrates the same phenomenon as SDC/Na$_2$CO$_3$ nanocomposite. SEM images clearly illustrate that the CDC/Na$_2$CO$_3$ nanocomposite consists of CDC particles smaller than 100 nm, and these CDC particles are evenly covered with homogeneous Na$_2$CO$_3$ coatings. Besides, the CDC/Na$_2$CO$_3$ composite exhibits a good nanostructure with grain-boundary can be easily distinguished, while high temperature calcination of CDC sample leads to severe agglomeration and grain growth.

In this paper, we used a novel four-probe d.c. method to determine the proton and oxygen ion conductivity of the CDC/Na$_2$CO$_3$ nanocomposite. Fig. 3-2(a) displays the conductivity of the CDC/Na$_2$CO$_3$ nanocomposite, which is much higher than pure CDC. The significantly enhanced conductivity of CDC/Na$_2$CO$_3$ electrolyte demonstrates a distinct composite effect, which can be ascribed to interfacial interaction. The plot of proton conductivity (\(\sigma_{\text{H}^+}\)) and oxygen ion conductivity (\(\sigma_{\text{O}^2-}\)) of CDC/Na$_2$CO$_3$ nanocomposite (Fig. 3-2b) show that \(\sigma_{\text{H}^+}\) is higher than \(\sigma_{\text{O}^2-}\) with 1-2 orders of magnitude at 200-600 °C, which resembles the conductivity curves of SDC/Na$_2$CO$_3$ nanocomposite. The \(\sigma_{\text{H}^+}\) curve shows a change of the slope at around 400 °C, corresponding to activation energy of 0.475 eV above 400 °C and 1.059 eV below 400 °C. The transition of activation energy was explained to be due to the glass transition of carbonate. On the other hand, the oxygen ion conductivity has a nearly constant slope corresponding to activation energy of 0.949 eV.

Thus, the novel CDC/Na$_2$CO$_3$ nanocomposite electrolyte possesses the unique H$^+/O^{2-}$ dual ion conduction property, different to conventional electrolytes in SOFCs. From Fig. 3-2 it is clearly demonstrated that the interface in the CDC/Na$_2$CO$_3$ nanocomposite

Fig. 3-2 (a) Overall conductivity comparison of pure CDC oxygen ion conductor and CDC/Na$_2$CO$_3$ nanocomposite electrolyte. (b) Proton and oxygen ion conductivity of CDC/Na$_2$CO$_3$ nanocomposite electrolyte measured by four-probe d.c. technique. (Reprinted with permission from ref 112. Copyright © 2011, Elsevier)
RESULTS AND DISCUSSION

considerably boosts proton conduction, whilst oxygen ions are most probably transported within CDC phase. The dual ion conduction of protons and oxygen ions not only enhances the total ionic conductivity, but also promotes reactions at both electrodes, thus the fuel cell output based on nanocomposite electrolyte is improved. The transport of proton in the interface was explained by a “Swing Model” in our previous work.118

CDC-based nanocomposite shows a slightly lower conductivity values because of the lower $\sigma_H^\sigma$, compared to the ionic conductivity of SDC/Na$_2$CO$_3$ nanocomposite.118 This can be explained by the “Swing Model”. In CDC/Na$_2$CO$_3$ composite electrolyte, the Ca$^{2+}$ forms weaker O-Ca bond than Sm$^{3+}$,119 and O from O-Ca will form stronger hydrogen bond as the acceptor in hydrogen bond. Then, the hydrogen bond formed between proton and oxygen ions from CDC surface is stronger than that formed with oxygen ions from CO$_3^{2-}$ group. The meta-hydrogen bond may be dragged by CDC surface, leading to slower breaking and forming, which further results in lower conductivity. At any rate, the total ionic conductivity of CDC/Na$_2$CO$_3$ composite is still high enough for SOFCs application. Therefore, CDC/Na$_2$CO$_3$ nanocomposite can be regarded as an alternative potential electrolyte material for LTSoFCs.

3.1.3 Thermal stability study (Paper II)

As a nanostructured material, the core-shell doped ceria/Na$_2$CO$_3$ nanocomposite may have the deficiency on maintaining its unique structure under elevated temperature. Therefore, in order to develop long-term SOFCs performance, the thermal stability and operation durability of the nanocomposite needs to be investigated. The thermal stability of the SDC/Na$_2$CO$_3$ nanocomposite was studied by annealing the sample at various temperatures, while pure SDC sample was annealed as a reference as well. The characterization results show that SDC/Na$_2$CO$_3$ nanocomposite remarkably maintains its

![Fig. 3-3 Durability test of a single cell based on SDC/Na$_2$CO$_3$ nanocomposite electrolyte. (Reprinted with permission from ref120. Copyright © 2011, Elsevier)
crystallite size, surface area as measured by BET, microstructure and morphology after high temperature annealing, due to significant diffusion barrier effect\(^{121}\) of amorphous Na\(_2\)CO\(_3\), which demonstrates a notable thermal stability. Furthermore, the TGA measurement shows that Na\(_2\)CO\(_3\) phase exists steadily in the nanocomposite within the LTSoFCs operation range (400-600 °C).

Fig. 3-3 shows the durability test result of cell based on SDC/Na\(_2\)CO\(_3\) nanocomposite as electrolyte. During the initial 50 min operation period, the performance of the cell increases gradually and then a relatively steady output was delivered. The cell was operated constantly at 550 °C for more than 12 h corresponding to the constant current density of 1 A cm\(^{-2}\); despite a slight degradation after 12 h operation, an average power density output of 0.62 W cm\(^{-2}\) was delivered during the whole operation process. This high performance at low temperature depends mainly on the high ionic conductivity of the composite electrolyte, which is realized by the interfacial dual ion conduction of the nanocomposite materials. In conclusion, the notable durability not only verified thermal stability of the SDC/Na\(_2\)CO\(_3\) nanocomposite, but also demonstrated that nanocomposite approach is an effective and practical approach to develop new electrolyte materials for long-term SOFCs technology.

### 3.2 Shape-tunable synthesis of ceria and their application in LTSoFC

In this part of thesis, we explicitly use the nanoscience tetrahedron (section 1.1.1) as a guideline to develop novel electrolyte and electrode materials for LTSoFC. First, in section 3.2.1, we demonstrate a novel template-, surfactant-free synthetic route for the controlled synthesis of cerium oxide with tunable nanowire and mesoporous sphere morphologies. Considering the unique structure of 1D nanowire, it is expected that these nanowires may achieve higher ionic conductivity compared to their nanoparticles analogues as electrolyte material, due to their longer continuous grain-boundary/interface from high aspect ratio. Therefore, samarium doped cerium (SDC) nanowires were synthesized and applied as electrolyte materials for LTSoFC, as shown in section 3.2.2. Similarly, the mesoporous spherical morphology is a potential structure for anode materials of SOFC, which can facilitate gas diffusion and enlarge the triple-phase boundary (TPB) regions. Thus the fabrication and investigation of CuO-SDC mesoporous spheres as composite anode of SOFC will be elucidated in section 3.2.3.

#### 3.2.1 Controlled synthesis of hierarchically structured ceria (Paper IV)

Hierarchically structured metal oxides have two or more levels of structure. Their nano-sized building blocks provide a high surface area, a high surface-to-bulk ratio, and functional surface groups, which are promising candidates for practical catalysts, optical devices, electrochemical devices and sorbent for water treatment.\(^{122-125}\)
In this work, we developed a novel template-, surfactant-free synthetic route for the controlled synthesis of hierarchically structured CeO$_2$ with nanowires and mesoporous spheres morphologies. Fig. 3-4 gives a schematic illustration of controlled synthetic processes. The synthetic route was designed by utilizing the chelate formation between cerium ion and various carboxylates forms of citric acid. By adjusting the reaction temperature, cerium citrate (CeCit) complex with nanowires morphology and cerium itaconate (CeIta) with microspherical shape can be prepared as precursors. After calcinations of precursors, cerium oxides with nanowire and mesoporous sphere morphologies are obtained accordingly, where the shape is inherited from the precursor. The formation mechanism of the CeCit precursor nanowires is explained to be due to highly anisotropic structure of CeCit. While a possible oriented aggregation formation mechanism is proposed for the formation of cerium itaconate spheres. The above proposed synthetic strategy has been approved by characterization results of the precursors (SEM, FT-IR, TGA, etc.), and the formation mechanism of nanowire and microsphere morphologies has been well elucidated, which can be found in attached paper IV with more detailed investigations.

Fig. 3-5 shows part of the morphology characterizations of ceria nanowire and mesoporous spheres. The diameter of individual ceria nanowire is between 100 nm to 200 nm. HRTEM micrograph shows the texture of a single nanowire as poly-crystalline with recognizable boundaries or voids, and the average crystallite size is calculated as 7±1 nm. The selected area electron diffraction (SAED) pattern recorded on a single nanowire verifies the poly-crystalline nature, which displays a set of continuous rings (inset of Fig. 3-5b). SEM images of ceria microspheres (Fig. 3-5c) indicate that the surface is comprised of many small particles, and the pores on the surface are less than 50 nm in diameter,
demonstrating a clear hierarchical mesoporous structure. The further magnified image (Fig. 3-5d) shows that the nanoparticles constructing the surface are 20–50 nm in size and many mesopores exist in the interstice among them. The formation of the mesoporous structure can be attributed to the thermal decomposition of the organic compounds precursor.

Finally, the adsorption ability of the hierarchically structured CeO$_2$ nanowires and mesoporous microspheres was tested by adsorptive removal of As(V) ions from simulated wastewater. The maximum adsorption capacities of as-prepared CeO$_2$ nanowires and mesoporous microspheres were found to be 8.0 and 21.4 mg g$^{-1}$, respectively. Compared to previous reports, the As(V) adsorption capacity 21.4 mg g$^{-1}$ of our mesoporous spherical CeO$_2$ is so far the highest among all the reports on using ceria for water treatment. The notable performance for water treatment is related to the unique hierarchical structure and high surface area of synthesized ceria samples.

3.2.2 SDC nanowires based nanocomposite electrolyte (Paper I)

This work reported for the first time on the use of 1D nanomaterials in SOFCs
application, since their longer continuous grain-boundary/interface due to high aspect ratio implies higher ionic conductivity compared to nanoparticles. This work overcame two obstacles that prevent the use of 1D nanomaterials in SOFCs: 1) we developed a template-, surfactant-free method which can produce large quantities of SDC nanowires at low costs, while it is rather difficult, costly and time consuming to accomplish by conventional techniques like template electrodeposition; 2) we prepared “nanocomposite” of SDC where Na₂CO₃ was introduced as secondary phase to hinder the grain growth of SDC nanostructures, resulting in stabilized utilization of nanowires at high operation temperature.

The SDC nanowires were prepared by homogeneous precipitation of lanthanide citrate complex in aqueous solutions as precursor followed by calcination. The XRD pattern of SDC nanowires confirms the cubic fluorite-type structure CeO₂ with a lattice constant of 5.434 Å. The lattice expansion of SDC, compared with pure CeO₂, confirms that the Sm³⁺ ions have been doped into the crystal lattice of CeO₂. The average crystallite size of SDC nanowires calculated by Scherrer’s equation is ~7 nm. SEM analyses indicated that length of nanowires is more than 10 µm and the diameter ranges from 100 nm to 200 nm. The average crystallite size of SDC nanowires is calculated as 7±1 nm from several HRTEM micrographs, which matches well with that calculated from XRD. The SAED pattern recorded on a single nanowire verifies the poly-crystalline nature. To stabilize SDC nanowires at elevated temperature, Na₂CO₃ of 20 wt% content was added to the SDC nanowires, followed by annealing at 600 °C.

A single fuel cell was fabricated using as-synthesized SDC nanowires/Na₂CO₃ nanocomposite as electrolyte. SEM image of as-fabricated single cell (Fig. 3-6a) shows that the electrolyte layer of the SDC nanowires/Na₂CO₃ nanocomposite is about 200 µm thick and appears to be fully dense, while the anode and cathode layer displays distinctly porous structure. As shown in Fig. 3-6 (b), the electrolyte layer is comprised of dense

![Cross section SEM image of a single cell based on SDC nanowires/Na₂CO₃ nanocomposite electrolyte and (b) a closer view of the electrolyte layer.](image)
clusters of almost parallel SDC nanowires, indicating that the nanostructure of SDC nanowires has been well-preserved even after annealing, co-pressing under pressure and sintering. Moreover, the softening effect of amorphous Na₂CO₃ under fuel cell operation temperature could further enhance densification of electrolyte layer.

The fabricated single cell delivered maximum power densities (P_max) of 160, 316, 417 and 522 mW cm⁻² at 450, 500, 550 and 600 °C, respectively, which is much better than the single cell based on the state-of-the-art Gd-doped ceria (GDC) electrolyte of similar thickness (P_max of 130 mW cm⁻² at 550 °C, 220 mW cm⁻² at 600 °C). The mechanism of the better performance can be ascribed to enhanced ionic conductivity of nanocomposite by interfacial conduction. The interface supplies enlarged pathway for ionic conduction, which have the capacity to increase mobile ion concentration than that of the bulk. However, the grain-boundary/interface of the SDC nanowires determined by their structure needs to be further optimized by aligning these nanowires, since they are now randomly assembled. This may explain the slightly lower performance of the SDC nanowires/Na₂CO₃ electrolyte as compared to the previous core-shell SDC/Na₂CO₃ nanocomposite. Anyway, the notable performances of the SDC nanowires/Na₂CO₃ composite electrolyte verify that that nanocomposite is an effective way to design promising electrolyte materials for low-temperature SOFCs.

3.2.3 Mesoporous CuO-Ce₀.₈Sm₀.₂O₂₋δ composite anode (Paper V)

As stated in section 1.4, to explore compatible active anode with sufficient low polarizations is another way to develop LTSOFC. Mesoporous metal oxides can be considered as a potential category of materials for anode of SOFC, since the porosity of the anode cermet can serve two functions. First, it allows easy gas diffusion into the anode microstructure; second, triple-phase boundary (TPB) regions are enlarged by increasing the number of interfaces between electronic conductor, ionic conductor and the gaseous reactants. Therefore, in this work, we report the synthesis and characterization of mesoporous CuO-SDC microspheres with superior phase homogeneity as anode materials for SOFCs by a novel microwave synthesis.

Fig. 3-7 shows the X-ray diffraction patterns of the resultant CuO-SDC sample. All the peaks detected were ascribed to the cubic fluorite-type structure SDC (JCPDS No. 34-0394) and monoclinic tenorite structure CuO (JCPDS No. 48-1548). The calculated crystallite size of SDC is 12.7 nm and the size of CuO is 14.9 nm. It is noted that the CuO crystallite size is slightly bigger than that of SDC, indicating that the coarsening of CuO particles takes place more quickly than SDC with the increase of temperature. SEM observation of the product (Fig. 3-7b) indicates that the CuO-SDC composite spheres possess porous surfaces that consist of many small the pores and particles, and the size of pores are around 50 nm in diameter, demonstrating a clear mesoporous structure. EDX
mapping demonstrates that both SDC and CuO phases are uniformly distributed over the composite sample, which confirms the phase homogeneity in the composite anode. The phase homogeneity of SDC and CuO, together with mesoporous structure, ensures a large area of triple-phase boundary (TPB) region in the anode part for hydrogen oxidation reaction.

Single fuel cells were fabricated using the mesoporous CuO-SDC composite as anode, and SDC/Na$_2$CO$_3$ nanocomposite were used as electrolyte materials.\textsuperscript{113} The maximum power densities ($P_{\text{max}}$) of 198, 285 and 408 mW cm$^{-2}$ have been achieved for the fuel cell at 500, 550 and 600 °C, respectively. From the viewpoint of catalytic property for hydrogen oxidation, Cu is inert compared to Ni, which results in a lower I-V performance compared to the cell with a NiO-SDC anode, as studied previously.\textsuperscript{113} However, compared to the cell using CuO-SDC prepared by conventional solid-state method, the SOFC using our mesoporous CuO-SDC composite as anode shows much better performance ($P_{\text{max}}$ of 127, 192, 290 mW cm$^{-2}$ at 500, 550 and 600 °C) This performance improvement can be attributed to the mesoporous structure and phase homogeneity of SDC and CuO in anode materials, which ensures a large area of TPB region for hydrogen oxidation reaction.
Conclusions

In conclusion, nanocomposite approach has been successfully applied to design and develop electrolyte and anode materials with enhanced properties for low-temperature SOFC in this thesis.

In the first part, SDC and CDC were synthesized by coprecipitation method as the core materials, and novel SDC/Na$_2$CO$_3$ and CDC/Na$_2$CO$_3$ nanocomposite was fabricated and applied for LTSONFC. The core-shell SDC/Na$_2$CO$_3$ nanocomposite consists of SDC particles smaller than 100 nm coated with amorphous Na$_2$CO$_3$ shell of 4–6 nm in thickness. The prepared core-shell SDC/Na$_2$CO$_3$ nanocomposite shows high ionic conductivity above 300 °C, and the conductivity reaches over 0.1 S cm$^{-1}$. Such high conductive nanocomposite electrolyte has been applied in low temperature solid oxide fuel cells, and displays an excellent performance with output power density of 0.8 W cm$^{-2}$ at 550 °C. To develop more efficient composite electrolyte, CDC was selected as the main phase of the nanocomposite from viewpoint of both material performance and economical aspects. The proton and oxygen ion conductivity of CDC/Na$_2$CO$_3$ nanocomposite has been determined by the four-probe d.c. measurement, which proved that the doped ceria/Na$_2$CO$_3$ nanocomposite electrolyte possesses the unique simultaneous H$^+$/O$_2^-$ conduction property. SDC/Na$_2$CO$_3$ nanocomposite can remarkably maintain its crystallite size, BET-surface area, microstructure and morphology after high temperature annealing, due to significant diffusion barrier effect of amorphous Na$_2$CO$_3$, demonstrating a notable thermal stability. The high performances, together with notable thermal stability, make the doped ceria/Na$_2$CO$_3$ nanocomposite as a potential electrolyte material for long-term SOFCs that operate at 500-600 °C.

In the second part of the thesis, hierarchically structured CeO$_2$ with nanowires and mesoporous microspheres morphologies has been controlled synthesized by a template-, surfactant-free chemical synthetic route, by adjusting the reaction temperature. Microscopy analyses revealed that the synthesized CeO$_2$ nanowires are poly-crystalline, with diameter ranging from 100 to 200 nm and the length up to 10 μm. While the size of as-prepared ceria spheres is in the range of 2–5 μm and the surface of the ceria microspheres is comprised of many small particles and the pores on the surface are less than 50 nm in diameter, indicating a hierarchical mesoporous structure. Moreover, doping with specific elements, SDC nanowires and SDC-CuO mesoporous microspheres were prepared and
used for electrolyte and anode materials, respectively. The single fuel cell based on SDC nanowires/Na$_2$CO$_3$ has been fabricated and the maximum power densities of 417 and 522 mW cm$^{-2}$ at 550 and 600 °C were achieved, demonstrating a great potential for low-temperature SOFC applications. In mesoporous CuO-SDC composite anode, both SDC and CuO phases are uniformly distributed over the nanocomposite anode, which ensures a large area of triple-phase boundary region in the anode part for hydrogen oxidation reaction. When the mesoporous CuO-SDC composite anode were used to fabricate single cell, the maximum power densities of 285 and 408 mW cm$^{-2}$ at 550 and 600 °C have been delivered, which is much better than conventional CuO-SDC anode prepared by solid state method.
Future work

There are mainly two parts of the work that need further investigation, regarding to further improvement of composite electrolyte and electrodes materials for LTSOFC.

To improve performance of nanocomposite electrolyte, firstly, further work will pay more attention on nano effect of nanocomposite, which will be mainly focused on how size and morphology of host particle (SDC) affects the properties of nanocomposite. Some new nanostructured doped ceria materials can be employed for nanocomposite electrolyte, i.e. different mesocrystals, different morphology 3D and 1D particles. Furthermore, thin film technique may be used to fabricate composite electrolyte pallets, which will reduce the resistance and enhance the power density output. To study the interfacial conduction mechanism of, some modeling simulation will be established based on current experimental results and theoretical calculation will be conducted as well as deep work on new composite systems (non-ceria composite). The work will not only reveal the fundamental conduction mechanism, but also help optimizing the material design and architecture.

To develop better electrode materials, first, the detailed electrochemical analyses of the mesoporous CuO-SDC anode needs to be further investigated, such EIS measurement for interfacial polarizations. Then from viewpoint of composition and morphology, some new anode and cathode materials can be explored and studied to optimize the performance of doped ceria/Na₂CO₃ nanocomposite electrolyte. Besides, the current electrochemical measurement techniques need to be customized to apply for the electrochemistry test of the composite materials and resultant cells.
Acknowledgements

First and foremost, I would like to express profound gratitude to my supervisor, Prof. Mamoun Muhammed, for giving me the opportunity to join the Functional Materials Division in KTH, and for his invaluable support, encouragement, supervision and useful suggestions throughout this research work. His continuous guidance enabled me to carry out my work successfully.

Zillions of thanks to my co-supervisor, Dr. Bin Zhu, for all his professional guidance and supervision on research work and enormous help in my life. Without him, I would not have had chance to study in Sweden. I admire his great passion on scientific research, and I wish him a great success in the scientific career and best of the best for all his family.

I would like to thank Dr. Song Li, Dr. Rizwan Raza, Liangdong Fan, my research partners from Department of Energy Technology, KTH, for the pleasant, effective and productive cooperation. Now many of them have left Sweden, I wish Dr. Li and Rizwan a great success on their career in their home country.

Millions of thanks to Asso. Prof. Muhammet S. Toprak and Dr. Shanghua Li for their tremendous help, discussion, incredible patience and continuous encouragement. I wish them the best for their future profession. I am extremely grateful to Muhammet and Abhi for the thorough linguistic check of the thesis. Thanks to Sylvan, Andrea, Fei, Yichen, Terrance, Salam, Carmen, Sverker, Mohsin, Hans, Wubeshet, Mazher, Robina, Marta, Nader, Mohsen, all the current and previous members in FNM. I will always remember the joyful time I spent with them in FNM and I wish them all the best, both for their research and for their lives.

I would like to thank dearest Per-Arne and Kestin Sandmark for hosting me in Djursholm for nearly five years. This was indeed the most memorable days of my life. Great thanks to my dearest friends in Sweden: Jia Mi, Geng Tian and their son; Shanghua Li, Jing Chen and their kids; Jian Qin, Chuanmin and their daughter; Abhilash, Shilpa and their daughter; Zhipeng Chen and Xuan Wang; Fei Ye and Min Tian; Yichen Zhao and Dandan Wei; Hongwei Wang and Yueshi Wu; Liang Ding, Fang Chen and their son; Zhiying Liu and Botao Shao; Shun Yu; Jia Li; Jun Luo; Fei Song. I will always remember the happy times we spent together. My life in Sweden would not have been the same without their friendship.

我要特别感谢我在国内哈尔滨工程大学的同事朋友，张密林，景晓燕，刘金胜，
I would like to deeply thank my parents, my sister and my brother, whose constant care and concern helped me to go through all these years. Special thanks to my parents-in-law, who went through so many difficulties to come to Sweden and help me take care of my daughter. I am so grateful for their unconditional love and support.

Finally, I owe my deepest gratitude to my sweetest family: my husband Xiaodi Wang and my little angel Beier Isabella Wang. Xiaodi is my research partner on my work and soul mate in life. He has been a true and great supporter and has unconditionally loved me during all my good and bad times. Beier is the best gift I got from above and now she is the source of all my hope and happiness. I dedicate this work to my sweetest family.
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