Dual-ion Conducting Nanocomposite for Low Temperature Solid Oxide Fuel Cells

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I dedicate this dissertation to my wonderful family.
王晓迪

荣获二〇一一年度国家优秀自费留学生奖学金，特颁此奖，以资鼓励。

CHINA SCHOLARSHIP COUNCIL

Presents the

2011 Chinese Government Award for Outstanding Self-financed Students Abroad

to

Wang Xiaodi

Dr. Liu Jinghui
Secretary-General
China Scholarship Council
Abstract

Solid oxide fuel cells (SOFCs) are considered as one of the most promising power generation technologies due to their high energy conversion efficiency, fuel flexibility and reduced pollution. There is a broad interest in reducing the operating temperature of SOFCs. The key issue to develop low-temperature (300–600 °C) SOFCs (LTSOFCs) is to explore new electrolyte materials. Recently, ceria-based composite electrolytes have been developed as capable alternative electrolyte for LTSOFCs. The ceria-based composite electrolyte has displayed high ionic conductivity and excellent fuel cell performance below 600 °C, which has opened up a new horizon in the LTSOFCs field. In this thesis, we are aiming at exploring nanostructured composite materials for LTSOFCs with superior properties, investigating the detailed conduction mechanism for their enhanced ionic conductivity, and extending more suitable composite system and nanostructure materials.

In the first part, core-shell samarium doped ceria-carbonate nanocomposite (SDC/Na2CO3) was synthesized for the first time. The core-shell nanocomposite was composed of SDC particles smaller than 100 nm coated with amorphous Na2CO3 shell. The nanocomposite has been applied in LTSOFCs with excellent performance. A freeze dry method was used to prepare the SDC/Na2CO3 nanocomposites, aiming to further enhance its phase homogeneity. The ionic conduction behavior of the SDC/Na2CO3 nanocomposite has been studied. The results indicated that H⁺ conductivity in the nanocomposite is predominant over O₂⁻ conductivity with 1-2 orders of magnitude in the temperature range of 200–600 °C, indicating the proton conduction in the nanocomposite mainly accounts for the enhanced total ionic conductivity. The influence of Na2CO3 content to the proton and oxygen ion conductivity in the nanocomposite was also studied.

In the second part, both the proton and oxygen ion conduction mechanisms have been studied. It is suggested that the interface in the nanocomposite electrolyte supplies high conductive path for the proton, while oxygen ions are probably transported by the SDC grain interiors. An empirical “Swing Model” has been proposed as a possible mechanism of superior proton conduction, while oxygen ion conduction is attributed to oxygen vacancies through SDC grain in nanocomposite electrolyte.

In the final part, a novel concept of non-ceria-salt-composites electrolyte, LiAlO2-carbonate composite electrolyte, has been investigated for LTSOFCs. The LiAlO2-carbonate electrolyte exhibits good conductivity and excellent fuel cell performances below 650 °C. The work not only developed a more stable composite material, but also strongly demonstrated that the high ionic conductivity is mainly related to interface effect between oxide and carbonate. As a potential candidate for nanocomposite, uniform quasi-octahedral CeO2 mesocrystals was synthesized in this thesis work as well. The CeO2 mesocrystals shows excellent thermal stability, and display potential for fuel cell applications.
List of Papers

This thesis is based on following publications:


Other work not included:


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

*Int. J. Hydrogen Energ.* **2010**. 35(7). 2580-2585


4) 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

5) Rizwan Raza, Xiaodi Wang, Ying Ma, Xiangrong Liu, Bin Zhu." Improved ceria-carbonate composite electrolytes." 

*Int. J. Hydrogen Energ.* **2010**. 35(7). 2684-2688

6) 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

7) Rizwan Raza, Xiaodi Wang, Ying Ma, Yi Zhong Huang, Bin Zhu." Enhancement of Conductivity in Ceria-Carbonate Nanocomposites for LT SOFCs." 

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


9) 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." 


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


11) 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." 


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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) **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." The X International Conference on Nanostructured Materials (NANO 2010), September 13-17, **2010**, Rome/ Italy


3) **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

4) Ying Ma, **Xiaodi Wang**, Bin Zhu, Mamoun Muhammed "A novel chemical route to synthesize CeO₂ nanowires" (oral) 9th International Conference on Nanostructured Materials, June 2-6, **2008**, Rio de Janeiro/ Brazil

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7) Rizwan Raza, Zhan Gao, Ying Ma, **Xiaodi Wang**, Bin Zhu "Co-doped SDC based nanocomposite electrolytes" (oral) 3rd International Meeting on Developments in Materials, Processes and Applications of Emerging Technologies (MPA-2009), July 21-23, **2009**, Manchester/ United Kingdom
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**Paper 1.** Planning and performing all synthesis work, parts of characterization work, evaluation of the results and writing main parts of the manuscript.

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

**Paper 3.** Developing the idea, performing parts of the literature survey, writing parts of the manuscript.

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

**Paper 5.** Participate in developing the idea, performing parts of the experiments, writing parts of the manuscript.

**Paper 6.** Planning and performing all synthesis and characterization work, evaluation of the results and writing main parts of the manuscript.
### Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ac</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AFC</td>
<td>Alkaline fuel cell</td>
</tr>
<tr>
<td>ASR</td>
<td>Area specific resistance</td>
</tr>
<tr>
<td>dc</td>
<td>Direct current</td>
</tr>
<tr>
<td>DCO</td>
<td>Doped cerium oxide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EMF</td>
<td>Electromotive force</td>
</tr>
<tr>
<td>FC</td>
<td>Fuel cell</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field-emission scanning microscope</td>
</tr>
<tr>
<td>GDC</td>
<td>Gadolinium doped ceria</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>IC</td>
<td>Internal combustion</td>
</tr>
<tr>
<td>LSCF</td>
<td>La$_{1-x}$Sr$<em>x$Co$</em>{1-y}$Fe$<em>y$O$</em>{3-\delta}$</td>
</tr>
<tr>
<td>LSM</td>
<td>La$_{1-x}$Sr$_x$MnO$_3$</td>
</tr>
<tr>
<td>LTOFC</td>
<td>Low-temperature solid oxide fuel cell</td>
</tr>
<tr>
<td>MCFC</td>
<td>Molten carbonate fuel cell</td>
</tr>
<tr>
<td>OCV</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid Fuel Cell</td>
</tr>
<tr>
<td>PEFC</td>
<td>Polymer electrolyte fuel cell</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>SDC</td>
<td>Samarium doped ceria</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
</tr>
<tr>
<td>TEC</td>
<td>Thermal expansion coefficient</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TPB</td>
<td>Triple phase boundary</td>
</tr>
<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>
\( a_x \)  Chemical activity of substance x
\( e^- \)  An electron
\( E \)  EMF (Electromotive force), also Open-circuit voltage (OCV)
\( F \)  Faraday constant, 96485 C \cdot mol^{-1}
\( G \) or \( g \)  Gibbs free energy (or negative thermodynamic potential)
\( h^+ \)  Electronic hole
\( H \)  Enthalpy
\( H^+ \)  Proton in electrolyte
\( I \)  Current
\( i \)  Current density, current per unit area
\( j \)  A complex number with value of \( \sqrt{-1} \)
\( N \)  Avogadro constant, \( 6.002 \times 10^{23} \) mol\(^{-1}\)
\( O^+_O \)  Oxygen ion in the electrolyte
\( P \)  Pressure of gas
\( R \)  Molar or ‘universal’ gas constant, \( 8.314 \) J \( \cdot \) mol\(^{-1}\) \cdot K\(^{-1}\), also electrical resistance
\( S \)  Entropy
\( T \)  Temperature
\( t \)  Time
\( V \)  Voltage
\( V^*_O \)  Oxygen ion vacancy
\( v \)  Flow rate
\( W \)  Work done
\( \sigma \)  Conductivity
\( \eta \)  Efficiency
\( \varphi \)  Phase angle
\( \omega \)  Angular frequency
\( \mu_f \)  Fuel utilization
\( Z' \)  Real parts of the impedance
\( Z^* \)  Imaginary parts of the impedance
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1 Introduction*

Energy is the very lifeblood of today’s society and economy. Our work, leisure, economy, social and physical welfare all depend on the sufficient, uninterrupted supply of energy. Yet we take it for granted – and energy demand continues to grow, year after year. Worldwide demand for energy is growing at an alarming rate. The increased demand is being met largely by reserves of fossil fuel that emit both greenhouse gasses and other pollutants. Those reserves are diminishing and they will become increasingly expensive. To maintain economic prosperity and quality of life, a sustainable energy system is required, which can meet the conflicting demands for increased supply faced to energy security, whilst maintaining cost–competitiveness and reducing climate change. Hydrogen and fuel cells are seen as possible key solutions for the 21st century. On the technology front, hydrogen, as a clean energy carrier, can be produced from any primary energy sources, which represent one of the most promising ways to realize sustainable energy. On the other hand, fuel cells are considered as the most efficient conversion device for converting hydrogen, and possibly other fuels, into electricity. Hydrogen and fuel cells provide integrated “open energy systems” that simultaneously address all of the major energy and environmental issues, and are flexible to be adapted to diverse and intermittent renewable energy sources that will be available in the Europe of 2030.1

1.1 Fuel cell

Fuel cells (FCs) are electrochemical devices which can directly convert chemical energy in fuels (hydrogen) into electricity. A fuel cell is similar as a battery; however, a fuel cell uses externally supplied fuels to generate electricity, while a battery consumes internal fuels. A fuel cell can continuously produce electricity as long as the fuel is supplied; by contrast a battery needs to be recharged or changed once the internal fuel is depleted. Fuel cells are not limited by thermodynamic limitations of heat engines such as the Carnot efficiency (Section 1.1.1.2); therefore, they have much higher efficiency than current thermo-mechanical methods. In addition, because combustion is avoided, fuel cells produce power with minimal pollutant. Therefore, fuel cells are considered as one of the

most promising power generation devices.\textsuperscript{3-6}

A typical fuel cell consists three basic physical parts, which include an electrolyte layer in contact with a porous anode and cathode on either side. Figure 1-1 shows a schematic representation of an individual fuel cell with the reactant/product gases and the ion-conduction flow through the cell. For a typical hydrogen fuel cell the overall reaction is:

\[
H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)
\]  

(1-1)

Although the most common fuel and oxidant are hydrogen and oxygen in a typical fuel cell, Appleby and Foulkes have pointed out that, in theory, any substance capable of chemical oxidation (reduction) can be used as the fuel (oxidant) at the anode (cathode) of a fuel cell.\textsuperscript{7} However, hydrogen is still the main choice of fuel for most applications because of its high reactivity when suitable catalysts are used.

A variety of fuel cells are in different stages of development. Classified by the type of electrolyte used in the cells, the current fuel cells include polymer electrolyte fuel cell (PEFC) or 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).\textsuperscript{8} PEMFC uses a proton exchange membrane as electrolyte and operates under room temperature; AFC uses aqueous alkaline solution as electrolyte and operates under 80 °C; PAFC uses molten phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) as electrolyte and operates in a temperature range of 150-200 °C; MCFC uses molten alkaline carbonate as electrolyte and operates in a temperature range of 600-650 °C; while SOFC uses a solid oxide material as
electrolyte and typically operate above 600 °C. By far, solid oxide fuel cell attracts much research interest throughout the world for its potential market competitiveness, including highest efficiency, fuel-flexibility, low price, long life expectancy, etc.⁹⁻¹²

1.1.1 Thermodynamic description of fuel cell

1.1.1.1 Open circuit potential

In a fuel cell, the change in the Gibbs free energy of formation, \( \Delta G_f \), illustrates the energy release. This change is the difference between the Gibbs free energy of the products and the Gibbs free energy of the inputs or reactants.¹³

\[
\Delta G_f = G_f \text{ of products} - G_f \text{ of reactants}
\]  \hspace{1cm} (1-2)

To make comparisons easier, it is convenient to consider these quantities in their ‘per mole’ form. These are indicated by “\( \bar{\text{-}} \)” over the lower case letter, for example, \( \bar{g}_f \) is the molar specific Gibbs free energy of formation for water. Consider the basic reaction for the hydrogen/oxygen fuel cell, equation (1-1), we have

\[
\Delta \bar{g}_f = (\bar{g}_f)_{H_2,O} - (\bar{g}_f)_{H_2} - (\bar{g}_f)_{O_2}
\]  \hspace{1cm} (1-3)

However, the Gibbs free energy of formation is not constant; it changes with temperature and state (liquid or gas). If the process is ‘reversible’, the Gibbs free energy is converted into electrical energy (In practice, some is also released as heat.). We will use this to find the reversible open-circuit voltage (OCV) of a fuel cell. If \( E \) is the voltage of the fuel cell, then the electrical work done moving this charge round the circuit is

\[
\text{Electrical work done} = \text{charge} \times \text{voltage} = -2F \times E
\]  \hspace{1cm} (1-4)

where \( F \) is Faraday constant.

If the system is reversible (or has no losses), then the electrical work done is equal to the Gibbs free energy released, \( \Delta \bar{g}_f \). So

\[
\Delta \bar{g}_f = -2F \times E
\]  \hspace{1cm} (1-5)

Thus

\[
E = \frac{-\Delta \bar{g}_f}{2F}
\]  \hspace{1cm} (1-6)

This fundamental equation gives the electromotive force (EMF) or reversible open circuit voltage (OCV) of the hydrogen fuel cell.

In fact, the Gibbs free energy changes in a chemical reaction vary with temperature. Equally important, though more complex, are the changes in Gibbs free energy with reactant pressure and concentration.

Consider a general reaction such as
The Gibbs free energy change can be written as a function of activity,

\[
\Delta g_f = \Delta g_f^0 - RT \ln \frac{a_i^f \cdot a_k^k}{a_i^m}
\]  

where \( \Delta g_f^0 \) is the change in molar Gibbs free energy of formation at standard pressure, \( R \) is the universal gas constant: \( R = 8.314 \, J \, K^{-1} \, mol^{-1} \), \( T \) is the absolute temperature, \( a \) is the chemical activity for the relevant species, \( a_x = \gamma_x c_x \), where \( \gamma_x \) is the activity coefficient of species \( X \) (Since activity coefficients tend to unity at low concentrations, activities are frequently replaced by simple concentrations.).

In the case of the hydrogen fuel cell reaction, equation (1-1), the equation becomes

\[
\frac{1}{2} \, 2H_2 + \frac{1}{2} \, O_2 = \ln \frac{a_{H_2}^0 \cdot a_{O_2}^0}{a_{H_2O}^0}
\]

To see how this equation affects voltage, we can substitute it into equation (1-6) and obtain

\[
E = -\frac{\Delta g_f^0}{2F} + \frac{RT}{2F} \ln \frac{a_{H_2}^0 \cdot a_{O_2}^0}{a_{H_2O}^0} = E^0 + \frac{RT}{2F} \ln \frac{a_{H_2}^0 \cdot a_{O_2}^0}{a_{H_2O}^0}
\]

which is the general form of the Nernst equation, where \( E^0 \) is the EMF at standard pressure.

The Nernst potential, \( E \), gives the open circuit cell potential (ideal equilibrium potential). This potential sets the upper limit or maximum performance achievable by a fuel cell. The Nernst equation provides a relationship between the ideal standard potential \( (E^0) \) for the cell reaction and the ideal equilibrium potential \( (E) \) at other partial pressures of reactants and products. For the overall cell reaction, the cell potential increases with an

![Figure 1-2 – Open circuit potential of a H2/O2 fuel cell as a function of temperature.](image)
increase in the partial pressure (concentration) of reactants and a decrease in the partial pressure of products. For example, for the hydrogen reaction, the ideal cell potential at a given temperature can be increased by operating at higher reactant pressures, and improvements in fuel cell performance have, in fact, been observed at higher pressures. Moreover, the open circuit potential of a fuel cell is also strongly influenced by the operating temperature, based on the Nernst equation. (1-10). Figure 1-2 gives the relationship between \( E \) and the operating temperature. The figure shows the potential of higher temperature cells and the ideal potential corresponds to a reaction where the water product is in a gaseous state (i.e., \( E^0 \) is 1.18 V).

### 1.1.1.2 Efficiency

Conventionally, chemical (fuel) energy is first converted to heat, which is then converted to mechanical energy. The mechanical energy can then be converted to electrical energy. For the thermal to mechanical conversion, a heat engine is typically used. Carnot showed that the maximum efficiency of such an engine is limited by the ratio of the absolute temperatures at which heat is rejected and absorbed, respectively, which is as following:

\[
\eta_{\text{carnot}} = \frac{T_1 - T_2}{T_1}
\]  

(1-11)

where \( T_1 \) is the maximum heat engine temperature and \( T_2 \) is the temperature at which the heated fluid is released. Although the calculated maximum efficiency of the heat engine can reach over 70%, in a current internal combustion (IC) engine, the efficiency is less than 30% due to significant thermal loss (~60%) and friction work (~10%).\(^{14}\) Thus, the typical overall energy efficiency of current IC engine-powered cars is less than 15%.\(^{15}\)

Fuel cell efficiency cannot be analyzed correctly as a thermodynamic system using the Carnot efficiency. Unlike many electrical power generating systems it is not obvious what

\[ \text{Figure 1-3 – Basic Fuel Cell Inputs and Outputs.} \]
form of energy is being converted into electricity in a fuel cell. The inputs and outputs of
the basic fuel cell are shown in Figure 1-3. Fuel cells convert chemical energy directly into
electrical energy. In the ideal case of a fuel cell, the change in Gibbs free energy, $\Delta G$, of
the reaction is available as useful electric energy at the temperature of the conversion. The
maximum efficiency, $\eta_T$, is defined as electrical energy produced compared with the
formation enthalpy change ($\Delta H_{298}^0$), which is determined by intrinsic fuel properties:

$$\eta_T = \frac{\Delta G(T, P)}{\Delta H_{298}^0}$$  \hspace{1cm} (1-12)

where $\Delta G(T, P)$ is the Gibbs free energy of formation at a given temperature and pressure,
$\Delta H_{298}^0$ is the standard enthalpy of formation of the chemical reaction.

For a hydrogen and oxygen reaction (Equation (1-1)), the maximum efficiency limits
of fuel cell using H$_2$ as fuel is:

$$\eta_{H_2} = \frac{\Delta G(T, P)}{\Delta H^0} = \frac{G_{H_2O(l)}(T) - G_{H_2}(T) - \frac{1}{2}G_{O_2}(T)}{H^0_{H_2O(l)} - H^0_{H_2} - \frac{1}{2}H^0_{O_2}}$$  \hspace{1cm} (1-13)

where the product water is in liquid form. At standard conditions of 25 °C (298K) and 1
atmosphere, the free energy available of useful work is 237.1 kJ/mole, and the formation
enthalpy of a hydrogen/oxygen reaction is 285.8 kJ/mole. Thus, the thermal efficiency of

Figure 1-4 – Maximum theoretical fuel cell efficiencies with various fuels at standard pressure, with
reference to higher heating value (HHV) at room temperature (25 °C). For CH$_4$ and C$_8$H$_{18}$, the efficiencies
are calculated based on the process of reformation of the hydrocarbons and oxidation of H$_2$, CO fuels. Carnot
efficiency, which limits the maximum efficiency of IC engines, is shown for comparison with a 25°C exhaust
temperature.
an ideal fuel cell operating reversibly on pure hydrogen and oxygen at standard conditions is:

\[ \eta = \frac{237.1}{285.8} \times 100\% = 83\% \]  

(1-14)

For some hydrocarbon fuels, the thermal efficiency determined by equation (1-14) is over 100% at low temperature, such like the efficiency of CH\(_4\) below 300 °C (Figure 1-4). This can be simply explained from the definition of the thermodynamic efficiency. According to the definition of Gibbs free energy:

\[ G = H - TS \]  

(1-15)

where \( S \) is entropy, the equation (1-12) can be restated by:

\[ \eta_T = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T\Delta S}{\Delta H} = 1 - T \frac{\Delta S}{\Delta H} \]  

(1-16)

Since the enthalpy of formation of most hydrocarbon fuels are negative, if the entropy of the formation is positive (\( \Delta S > 0 \)), a theoretical thermal efficiency over 100% is possible.

### 1.1.1.2.1 Overall fuel cell efficiency

Overall fuel cell efficiency (\( \eta \)) is obtained by multiplying three primary efficiencies:

\[ \eta = \eta_t \times \eta_v \times \eta_f \]  

(1-17)

where \( \eta_t \), \( \eta_v \), and \( \eta_f \) are thermodynamic efficiency, voltage efficiency and fuel utilization efficiency, respectively.

The voltage efficiency (\( \eta_v \)) reflects irreversible polarization losses in actual operation, including ohmic, activation, and concentration polarizations (1-19). This efficiency is defined as the ratio of the actual operational voltage of the fuel cell (\( V \)) to the thermodynamic reversible voltage (or ideal voltage, \( E_{\text{ideal}} \)).

\[ \eta_v = \frac{V}{E_{\text{ideal}}} = \frac{E_0 - \Delta V_{\text{ohm}} - \Delta V_{\text{act}} - \Delta V_{\text{con}}}{E_{\text{ideal}}} \]  

(1-18)

where \( E_0 \) is the open circuit voltage (OCV). \( \Delta V_{\text{ohm}} \), \( \Delta V_{\text{act}} \) and \( \Delta V_{\text{con}} \) are the voltage drops due to ohmic, activation and concentration polarization losses, respectively (see Figure 1-5).

In principle the OCV should be the same as \( E_{\text{ideal}} \), however, in many practical cases the measured OCV is less than the ideal voltage due to several reasons, such as leaky gas seals; open pores/micro-cracks and internal electronic current leakage in electrolyte.

Ohmic polarization (\( \Delta V_{\text{ohm}} \)) corresponds to resistances of electron flow in electrodes and ion flow in the electrolyte. Most ohmic polarization is attributed to ionic resistance in the electrolyte. \( \Delta V_{\text{ohm}} \) is frequently expressed as
In terms of current density \( i \) in \( A/cm^2 \) and area specific resistance (ASR in \( \Omega \cdot cm^2 \)). Therefore, thicker electrolytes, and lower ionic conductivity of the electrolyte, cause greater ohmic polarization loss.

Activation polarization \( \Delta V_{act} \) are losses caused by reaction kinetics at cathode (oxygen reduction reactions) and anode (fuel oxidation). These reactions typically occur at triple phase boundaries (TPBs) where the electronic, ionic, and gaseous phases meet. Thus, \( \Delta V_{act} \) strongly depends on TPB density.

Concentration polarization \( \Delta V_{con} \) is caused by mass transport limitations (fuel in anode and oxidant in cathode) within the porous electrode microstructure. In anode-supported SOFC structures, most of \( \Delta V_{con} \) occurs in the anode bulk due to the spatial depletion of fuel at high current operation and/or high tortuosity and low porosity in the relatively thickest portion of the cell. Thus, tailoring porosity of the anode and control of fuel flow rate are important to mitigate concentration polarization.

The fuel utilization efficiency \( \eta_f \) is defined as the ratio of the fuel used by the fuel cell to total fuel input. When fuel cells generate current, \( i \), and fuel input supplied with the rate of \( v_f \) (mole/sec), the fuel utilization efficiency \( \eta_f \) is:

\[
\eta_f = \frac{i/ nF}{v_f} \quad (1-20)
\]

Combining equation (1-19) (1-21) into (1-18), the overall fuel cell efficiency can be written as
Thus, overall fuel cell efficiency can be maximized by decreasing temperature and minimizing fuel reforming processes. High OCV, approaching theoretical, is essential by using highly dense and low leakage current electrolytes. In addition, the polarization losses can be minimized by increasing electrolyte conductivity and decreasing its thickness (ohmic polarization), increasing electrode TPB density and specific reactivity (activation polarization), as well as high porosity with continuity of conducting phases (concentration polarization).

1.2 Solid oxide fuel cell

Solid oxide fuel cells (SOFCs) are a class of fuel cell characterized by the use of a solid oxide material as the electrolyte, which traditionally acts as an oxygen ions conductor. The development of solid electrolyte fuel cells started with the work of F. Haber, who first patented a solid electrolyte fuel cell in 1905. 17 Swiss scientist Emil Baur and his colleague H. Preis experimented with solid oxide electrolytes in the late 1930s, using such materials as zirconium, yttrium, cerium, lanthanum, and tungsten. As early as 1937, Bauer and Preiss used zirconia ceramics for the first time in fuel cells and fabricated the first tubular SOFC.18

1.2.1 Benefits of SOFCs

Recently, there is a growing interest in developing solid oxide fuel cells, due to their benefits. Solid oxide fuel cell has been considered as an important candidate for future fuel cell application. SOFCs operate at very high temperature, typically between 800 and 1000 °C. At this temperature, SOFCs do not require expensive platinum catalyst material, as is currently necessary for lower temperature fuel cells such as PEMFCs,6 and are not vulnerable to carbon monoxide catalyst poisoning.

Because of this high operating temperature, light hydrocarbon fuels, such as methane, propane and butane can be internally reformed within the anode. For example, methanol

\[
CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad [\Delta H = 49.7 \text{ kJ mol}^{-1}]
\]  (1-22)

SOFCs can also be fueled by externally reforming heavier hydrocarbons, such as gasoline, diesel or biofuels. Such reformates are mixtures of hydrogen, carbon monoxide, carbon dioxide, steam and methane, formed by reacting the hydrocarbon fuels with air or steam in a device upstream of the SOFC anode. 19-21

SOFC power systems can increase efficiency by using the heat given off by the exothermic electrochemical oxidation within the fuel cell for endothermic steam reforming process. Internal reforming also leads to a large decrease in the balance of plant costs in...
designing a full system.\textsuperscript{22,23}

Solid oxide fuel cells have a wide variety of applications, which can be used as from auxiliary power units in vehicles to stationary power generation with outputs from 100 W to 2 MW.\textsuperscript{24,25} In 2009, Australian company, Ceramic Fuel Cells Ltd successfully achieved an efficiency of a SOFC device up to the previously theoretical mark of 60\%.\textsuperscript{26} The higher operating temperature make SOFCs suitable candidates for application with heat engine energy recovery devices or combined heat and power, which further increases overall fuel efficiency.

1.2.2 Cell components

The major components of an individual SOFC cell include a porous anode, an electrolyte, and a porous cathode.\textsuperscript{27,28} Fuel cell stacks contain an electrical interconnect, which links individual cells together in series or parallel. The electrolyte is made from a ceramic such as yttria-stabilized zirconia (YSZ) and normally functions as a conductor of oxide ions. The operation of traditional solid oxide fuel cell is straightforward, as shown in Figure 1-6. In a SOFC, oxygen atoms are reduced on the porous cathode surface by electrons. The oxygen ions diffuse through the electrolyte to the fuel rich and porous anode, where they react with the fuel (hydrogen) and give off electrons to an external circuit. Thus, the final products of SOFC are electricity, heat and water.

Typically, The reactions at the cathode and anode can be expressed using Kröger-Vink Notation as follows, where $\text{V}_\text{O}^-$ is the oxygen ion vacancy and $\text{O}_\text{O}^-$ is the oxygen ion in the electrolyte:\textsuperscript{13}

Cathode Reaction:

\begin{align*}
\text{O}_2 + 2\text{H}_2 &\rightarrow 2\text{H}_2\text{O} + 4\text{e}^- \\
\text{H}_2 &\rightarrow 2\text{H}^+ + 2\text{e}^- \\
\text{O}_2 &\rightarrow 2\text{O}^-
\end{align*}
\[ \frac{1}{2}O_2(g) + 2e' + V_{o}^{\prime\prime} \rightarrow O_0^{\prime} \quad (1-23) \]

Anode Reaction:

\[ H_2(g) + O_0^{\prime} \rightarrow H_2O (g) + V_{o}^{\prime\prime} + 2e' \quad (1-24) \]

So the overall reaction can be expressed as:

\[ H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O (g) \quad (1-25) \]

1.2.2.1 Electrolyte Materials

The electrolyte is the most principal component of a 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 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 reactants cross-over; low cost and environmentally benign.

Currently fluorite structure materials, such as zirconia-based oxides, ceria-based oxides and perovskite LaGaO₃ based materials are generally used as oxygen ion conductors for SOFC. Figure 1-7 shows the specific oxygen ion conductivity of different solid oxide electrolytes varies with temperature. Today, yttrium stabilized zirconia (3, 8 or 10% yttria, abbreviated to YSZ) is the most common electrolyte for SOFC. YSZ provides high conductivity at temperatures above 800 °C while exhibiting negligible electronic conductivity at these temperatures. In addition, fully stabilized zirconia offers

![Figure 1-7 – Specific ion conductivities of selected solid oxide electrolytes.](image-url)
Introduction

matching secondary requirements such as chemical stability with the other SOFC components or durability and good high-temperature mechanical properties. However, the major disadvantage of YSZ is its very high operation temperature (> 800 °C). Doped cerium oxide (DCO), also with a fluorite structure, is considered as a promising electrolyte for low temperature SOFC. Gadolinium-doped ceria is even more conductive, but is partially reduced in hydrogen at temperatures above 600°C; the formation of Ce ions generates electron holes make ceria electronically conductive, thus short-circuiting the cell. A substantially more conductive material that is stable in air and hydrogen was discovered by Goodenough. 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 even on a thick electrolyte.

Proton-conducting oxides are also possible electrolytes for SOFCs. Since the proton is the smallest positive ion, its mobility is high and good ionic conductivity may be obtained at low temperature in certain materials. Proton conductivity in oxide electrolytes at high temperatures was first found by Iwahara et al. using BaCeO₃-based compositions, with high conductivity obtained by doping BaCeO₃ with rare earth cations on the Ce sites. However, proton conductivity in doped BaCeO₃ is still smaller than oxygen ion conductivity in LaGaO₃ or SDC and the chemical stability of BaCeO₃, particularly in CO₂, is poor. While these electrolytes are still in the very early stages of development, such proton conductors might eventually overcome some of the limitations of cells as oxygen ion conductors.

1.2.2.2 Anode

The role of an anode in SOFC is the electro-oxidation of fuel by catalyzing the reaction, and facilitating fuel access and product removal. Therefore, the requirements for SOFC anode materials are good chemical and mechanical stability in reducing environment; high ionic and electronic conductivity; porous structure and good chemical and thermal compatibility with electrolyte and interconnect materials; high surface oxygen exchange kinetics and good catalytic properties for the anode reactions etc.

The traditional anode of SOFCs is a cermet made of metallic nickel and solid electrolyte skeleton, such as Ni-Yttria stabilized zirconia (Ni-YSZ), Ni-Samarium doped ceria (Ni-SDC). The electrolyte serves to inhibit sintering of the metal particles and provides a TEC comparable to that of the electrolyte. The anode should have a high porosity (e.g., 20–40%) that allows mass transport of reactant and product gases. The conductivity of the anode depends on its microstructure, in particular the size and particle size distribution of the solid electrolyte and nickel particles, and the connectivity of the nickel particles in the cermet. There is growing interest in developing ceramic anodes as alternatives to cermets. Recently, lanthanum-substituted strontium titanate (La-SrTiO₃)
with nominal oxygen over-stoichiometry has been studied and shown to have high electronic conductivity and methane oxidation catalytic activity.\(^{49}\)

### 1.2.2.3 Cathode

In SOFCs, the cathode functions as the site for the electrochemical reduction of oxygen. To realize this function, the cathode must have: high electronic and ionic conductivity; a matched TEC and chemical compatibility with the electrolyte and interconnect materials; adequate porosity to allow gaseous oxygen to readily diffuse through the cathode to the cathode/electrolyte interface; stability under an oxidizing atmosphere; and high catalytic activity for the oxygen reduction reaction.\(^{50-52}\)

Numerous doped oxides have been studied as cathode materials for SOFC. Strontium-doped lanthanum manganite (LSM), \(\text{La}_{1-x}\text{Sr}_x\text{MnO}_3\) is the most commonly used cathode material for YSZ based SOFC.\(^{53,54}\) Another perovskite material that has been extensively studied as a cathode material for SOFC is doped lanthanum cobaltite, \(\text{LaCoO}_3\).\(^{55}\) The conductivity can be increased by substituting cations on the lanthanum and cobalt site. \(\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}\) (LSCF), for example, has been identified as promising materials in terms of both ionic and electronic conductivity.\(^{56}\) 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 \([\text{(Sm, Sr)}\text{CoO}_3, (\text{Ba, Sr})(\text{Co, Fe})\text{O}_{3-\delta}]\), layered perovskite-related structures \(\text{(La}_{n+1}\text{Ni}_n\text{O}_{3n+1})\) and double perovskites \((\text{GdBaCoO}_{2+\delta})\), all of which have shown encouraging performance at lower temperatures.\(^{57}\)

### 1.2.3 The relevance of the temperature for SOFCs

In order to attain reasonable power density, current state-of-the-art SOFC systems are normally operated in the temperature regime of 800 to 1000°C, typified by developers such as Siemens Westinghouse and Rolls-Royce.\(^{29}\) However, its high operating temperature has limited the development and deployment of this conventional technology, which is resulting in higher systems costs and performance degradation rates, as well as slow start-up and shutdown cycles, the latter dramatically limiting applicability in portable power and transportation markets.\(^{16}\) Currently, SOFCs cannot be accepted by commercial applications. Researches have shifted their interest to low-temperature SOFCs (LTSOFCs) which is operating at a temperature range of 300–600 °C.

LTSOFCs can further reduce system cost due to wider material choices for interconnects and compressive nonglass/ceramic seals, as well as reduced balance of plant (BOP) costs.\(^{58}\) Moreover, below 600 °C, both radiative heat transfer (Stefan-Boltzmann) and sintering rates exponentially drop off, thus reducing insulation costs and primary performance degradation mechanisms, respectively.\(^{16}\) At even lower temperatures (\(\leq 350 ^\circ \text{C}\)), cheap stamped stainless steel interconnects, elastomeric/ polymeric seals (e.g.,
Kapton), and off-the-shelf BOP are possible.

Another reason to reduce operating temperature is to maximize the theoretical efficiency. In contrast to the Carnot cycle temperature dependence of IC engines, theoretical fuel cell efficiency increases with decreasing temperature, as described in equation (1-22) and illustrated in Figure 1-4. For example, the maximum theoretical efficiency of an SOFC using CO as a fuel increases from 63% at 900 °C to 81% at 350 °C. At first glance, this would imply that PEMFCs are more efficient than SOFCs because of their lower operating temperature. However, from an overall system efficiency perspective, PEMFCs have a lower efficiency due to the use of H₂ as fuel. The vast majority of all H₂ produced today comes from hydrocarbon resources (typically CH₄), which requires additional external processes, each step having a thermodynamic penalty that decreases the overall system efficiency. Moreover, PEMFCs cannot take advantage of the higher theoretical fuel cell efficiency of CO over H₂ at lower temperature (Figure 1-4) because CO is a poison for PEMFCs rather than a fuel for SOFCs. The second reason that lower temperature does not necessarily result in higher system efficiency is that all of the major cell polarization losses are thermally activated. Thus, the difference between attained efficiency and theoretical efficiency increases as temperature is lowered.

Lower temperature operation also affords more rapid start-up and shut-down, reduced corrosion rate of metallic components, improved durability (sintering and component inter-diffusion is accelerated at higher temperatures), more robust construction through the use of compressive seals and metallic interconnects as well as the advantage of greatly simplified system requirements.

### 1.2.4 Development of LTSOFCs

Low temperature fuel cells (LTSOFCs) have many advantages. However, there is a major challenge technically. As the operating temperature decreases, the ionic conductivity of the traditional electrolyte (YSZ) decreases exponentially and the ohmic loss of electrolyte becomes considerable. When temperature is lowered from 800 to 400 °C, the ionic conductivity is reduced by nearly three orders of magnitude. As applied for SOFCs, the minimum requirement of ionic conductivity is 10⁻¹ S/cm. The traditional electrolyte material (YSZ) cannot fit this request. Until now two main strategies are under investigation to reduce the operation temperature, while still attaining sufficient low resistance of electrolyte. First, the dimensional thickness of the electrolyte can be reduced, so reducing the area specific resistance of the fuel cell. Second, exploring new electrolyte material with high ionic conductivity can bring about the same result at lower temperatures. In the following section, we give an effective strategy to develop electrolyte materials for LTSOFC.
1.3 Composite ionic conductors as electrolyte for LTSOFC

In recent years, a novel category of SOFCs electrolyte materials have been developed in order to develop functional electrolytes for LTSOFC applications, which were named as ceria-based dual-phase composite electrolytes. These materials consist of two-phases; host phase (ceria-based oxide) and second phase (various salt, proton conductor, etc.). Many efforts have been made on the investigation of various ceria-based composite ceramics, such as samarium doped ceria (SDC), incorporated with salts or hydrates. The ceria–based composite electrolyte has displayed high ionic conductivity of $10^{-2}$~$1 \text{ S cm}^{-1}$ and excellent fuel cell performance of 300–1100 mW cm$^{-2}$ at 400–600 °C, which increased about one to two magnitudes on conductivity compared to conventional single-phase electrolyte, like YSZ, GDC, etc. Development on ceria–based composite electrolyte has opened up a new horizon in the LTSOFCs research field.

1.3.1 State-of-the-art development of ceria based composite

Composite electrolytes are basically physical mixtures consisting of two or more solid phases that possess different ionic conductivity properties. Composite materials usually show enhanced conductivity, but the effects are not simply additive; rather they are synergistic in the sense that the overall conductivity is significantly higher than in both of the constituent phases. The conductivity enhancement, the so-called composite effect, is suggested to be due to high ionic conductivity in the interface region between components. Therefore, the initial idea to fabricate composite is to obtain more interface region for high ionic conduction pathway. The research work on ceria-based composite in last decade mainly focused on extensive fuel cell performance test based on various ceria-based composite ceramics, such as samarium doped ceria (SDC), gadolinium doped ceria (GDC) and yttrium doped ceria (YDC) etc. incorporated with different salts and hydrates, such as chlorides, fluorites, carbonates, sulphates and hydrates. Based on these extensive results, it has been approved that ceria-carbonate composite obtained the best performance, therefore becoming the research highlight of this decade.

In recent studies on ceria based composite, the host phase, i.e. ceria-based oxide still focused on various rare earth doped or co-doped ceria, including $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC), $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC), $\text{Ce}_{0.8}\text{Gd}_{0.05}\text{Y}_{0.15}\text{O}_{1.9}$ (GYDC), $\text{Ce}_{0.8}\text{Sm}_{0.2-x}\text{Ca}_{x}\text{O}_{2-\delta}$ (CSDC), $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Nd}_{0.1}\text{O}_{1.9}$ (SNDC), $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{Ca}_{0.2}\text{O}_{2-\delta}$ (CSDC) etc.; while the second carbonate phase is among single $\text{Na}_2\text{CO}_3$ salt, binary Li–Na, Li-K, Na-K carbonate eutectic, or ternary Li–Na–K carbonate mixture. The doped ceria oxides were synthesized by several different chemical methods, e.g. oxalate co-precipitation, carbonate co-precipitation, sol-gel method, glycine nitrate combustion method, etc. Then the mixture of doped ceria and carbonates was ground and sintered for conductivity measurement or fuel cell performance test. Table 1-1 summarizes the conductivity and
relevant fuel cell performances of various composite electrolytes reported by different groups worldwide, as compared to the conductivity of single phase SDC in the similar temperature range. From data in Table 1-1 we can see that most of the groups obtained fairly good fuel cell performance using the composite electrolyte, which is much better than the conventional SOFCs with single phase solid oxide electrolyte in IT or LT region. However, the conductivity values of composite electrolytes differ a lot as measured by these groups, which is due to different measurement techniques or setups used.

### 1.3.2 Ionic conduction mechanism in composite electrolyte

Earlier, ceria-based composites as promising alternative electrolyte materials for LT-SOFC was suggested in 2001. In later reports, Zhu and his colleagues demonstrated that enhanced ionic conductivity can be achieved in the ceria-based composite systems, resulting in superior fuel cell performances, as reviewed in reference. This composite approach was designed and fabricated based on the utilization of the interface as express path for ionic conduction. When ceria-based composites electrolyte was developed for SOFC, the dual or hybrid H⁺ and O²⁻ conduction was discovered at the same time, by the phenomenon that water was detected from both gas outlets when testing a single cell made

<table>
<thead>
<tr>
<th>Doped Ceria</th>
<th>Salt</th>
<th>Conductivity (S cm⁻¹)</th>
<th>Fuel cell Performance (mW cm⁻²)</th>
<th>T (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₀.₈Gd₀.₂O₁.₉ (GYDC)</td>
<td>40 wt. % of Li/Na₂CO₃ (52/48, mol.% )</td>
<td>3×10⁻⁴ - 0.4</td>
<td>150-670</td>
<td>400-650</td>
<td>83</td>
</tr>
<tr>
<td>Ce₀.₈Sm₀.₂O₁.₉ (SDC)</td>
<td>30 wt. % of Li/Na/K₂CO₃ (43.5/31.5/25, mol.% )</td>
<td>0.05-0.07</td>
<td>100-720</td>
<td>500-650</td>
<td>84</td>
</tr>
<tr>
<td>Ce₀.₈Sm₀.₂O₁.₉ (SDC)</td>
<td>30 wt. % of Li/Na₂CO₃ (50/50, mol.% )</td>
<td>0.1-0.16</td>
<td>300-1700</td>
<td>500-650</td>
<td>85</td>
</tr>
<tr>
<td>Ce₀.₈Sm₀.₂O₁.₉ (SDC)</td>
<td>20 wt. % of Li/Na₂CO₃ (50/50, mol.% )</td>
<td>0.071-0.093</td>
<td>450-600</td>
<td>500-600</td>
<td>86</td>
</tr>
<tr>
<td>Ce₀.₈Sm₀.₂O₁.₉ (SDC)</td>
<td>20 wt. % of Li/K₂CO₃ (50/05, mol.% )</td>
<td>0.067-0.092</td>
<td>300-550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce₀.₈Sm₀.₂O₁.₉ (SDC)</td>
<td>20 wt. % of Na/K₂CO₃ (50/05, mol.% )</td>
<td>0.044-0.083</td>
<td>270-550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce₀.₈Sm₀.₂O₁.₉ (SDC)</td>
<td>20 wt. % of Li/Na₂CO₃ (53/47, mol.% )</td>
<td>3.7×10⁻³-0.029</td>
<td>432-817</td>
<td>450-600</td>
<td>87</td>
</tr>
<tr>
<td>Ce₀.₈Sm₀.₂₂Ca₀.₀₈O₂₋δ (CSDC)</td>
<td>Na₂CO₃</td>
<td>0.1-0.3</td>
<td>200-980</td>
<td>350-560</td>
<td>88</td>
</tr>
<tr>
<td>Ce₀.₈Sm₀.₂O₁.₉ (SDC)</td>
<td>20 wt. % of Li/Na₂CO₃ (52/48, mol.% )</td>
<td>7×10⁻³-0.5</td>
<td>46-590</td>
<td>450-600</td>
<td>89</td>
</tr>
<tr>
<td>Ce₀.₈Gd₀.₂O₁.₉ (GDC)</td>
<td>25 wt. % of Li/Na₂CO₃ (53/47, mol.% )</td>
<td>5×10⁻⁴-0.175</td>
<td>45-92</td>
<td>450-550</td>
<td>90</td>
</tr>
<tr>
<td>Ce₀.₈Sm₀.₂O₁.₉ (SDC)</td>
<td>No salt</td>
<td>10⁻⁶ -0.03</td>
<td>240-650</td>
<td></td>
<td>91</td>
</tr>
</tbody>
</table>
by the composites electrolyte. With increased works done by researchers worldwide, the dual-ion conduction mechanism was unveiled gradually. In the beginning, Zhu figured out that the O– conduction in ceria phase was determined by the oxygen ion vacancies (mechanism) in the ceria lattice, while the H+ conduction may have formed in the carbonate through temporal bonding, $\text{H}^+\text{CO}_3^- \rightarrow \text{HCO}_3^-$ mechanism. Later on, he found that the ion conduction at interface region, i.e. interfacial conduction, plays a key role for hybrid H+ and O2– conduction, which demonstrated a distinct composite effect. Up to now the interfacial conduction mechanism is widely recognized in the ceria-based composites research field, although more detailed mechanism still needs to be investigated.

However, though hybrid H+ and O2– conduction was recognized, there are many contradictory results regarding to the contribution of each charge carriers to the overall conduction. For instance, it was considered in some earlier report that the oxygen ion conduction is predominant over the proton conduction. Different to the above studies, Huang et al. claimed that the SDC-carbonate composites are mainly proton conductors, by the evidence that the majority of water was observed at the cathode side during fuel cell operation. Taking into account these contradictory results, many works have been done by several groups. Di et al. studied the effect of water vapor on EMF and found that unlike that of cells based on pure oxygen ionic conductor or pure protonic conductor, the open circuit voltage of the SDC–carbonate based fuel cell decreases with an increase in water content of either anodic or cathodic inlet gas, indicating the electrolyte is a co-ionic ($\text{H}^+/\text{O}^{2–}$) conductor, which oxygen ionic conductivity dominates.

### 1.4 Motivation and objectives

For composite electrolyte, the size of host particles will undoubtedly influence the volume of interface region, which will further affect the ionic conductivity of the composite electrolytes. If we consider from nanoscience viewpoint, when composite meets “nano”, there will be an enormous ionic conductivity enhancement, since the interfacial effect is dominant in overall transport in nanocrystalline composite samples. However, the fabrication of nanostructured composite electrolyte with enhanced ionic conduction and desired properties is still a challenge, which will not only improve composite electrolyte performance but also contribute to the study of conductivity mechanism.

In this thesis, we are aiming at developing a novel nanocomposite approach to design and fabricate ceria-based composite electrolytes for LT SOFC. First, core–shell nanocomposite consisting of SDC nanoparticles and amorphous Na2CO3 shell were fabricated and applied as electrolyte in low-temperature SOFC. It is concluded that the homogeneity of nanocomposite, especially the homogeneous distribution of Na2CO3 plays an important role on the property of nanocomposite. Therefore, a new freeze drying method was employed to synthesis SDC/Na2CO3 nanocomposites with homogeneous
phase distribution.

Second, the ionic conduction behavior and conduction mechanism of the nanocomposite have been studied in this thesis. Since there are many contradictory results regarding to the contribution of each charge carriers to the overall conduction in the literature, a more systematic examination has to be established. In this thesis, a four-probe d.c. technique was employed to study the conduction behavior of proton and oxygen ion in SDC/Na$_2$CO$_3$ nanocomposite electrolyte. Based on these results, the conduction mechanism for proton and oxygen ion conduction was proposed.

The third part of the thesis aims to extend the composite strategy to a wider range and explore more nanostructured functional materials. LiAlO$_2$ was used to instead of doped-ceria and to prepare non-ceria-based composites as electrolyte. Besides, new uniform nanostructured ceria mesocrystal was synthesized as well, which shows potential competence for further LTSOFC application.
2 Experimental

2.1 Material preparation

2.1.1 Synthesis of SDC/Na$_2$CO$_3$ nanocomposite

The Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ (SDC) sample was synthesized via coprecipitation method using sodium carbonate as the precipitant. All the chemicals are used as received without further purification. The stock solution was made by dissolving the cerium nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, 99.9%, Chempur, Karlsruhe, Germany) and samarium nitrate hexahydrate (Sm(NO$_3$)$_3$·6H$_2$O, 99.9%, Sigma-Aldrich) in distilled water with a molar ratio of Ce$^{3+}$:Sm$^{3+}$ = 4:1, and the total concentration of cation (Ce$^{3+}$ and Sm$^{3+}$) was 0.5 M. Aqueous solutions of sodium carbonate (Na$_2$CO$_3$, 99.5%, Merck) with a concentration of 0.5 M were used as the precipitant. In a typical procedure, 50 ml mixed salt solution was added at a rate 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. The precipitate cake was washed repeatedly with distilled water to obtain the SDC precursor.

Based on SDC precursor, the SDC/Na$_2$CO$_3$ nanocomposite was prepared by two different mixing methods, which are a wet mixing method and new freeze drying method. For wet mixing method, as-prepared SDC precursor was mixed with Na$_2$CO$_3$ solution (2 mol L$^{-1}$) under vigorous stirring with weight ratio of SDC: Na$_2$CO$_3$ = 4:1. The slurry mixture was dried at 80 °C in air for 24 h, calcined at 700 °C in air for 1h and immediately cooled to room temperature to form SDC/Na$_2$CO$_3$ composite with Na$_2$CO$_3$ weight content of 20%. For freeze drying method, first, the prepared SDC precursor was mixed with saturated Na$_2$CO$_3$ solution in a cylindrical container under vigorous stirring with SDC: Na$_2$CO$_3$ weight ratio of 95:5, 90:10, 85:15 and 80:20, respectively. Secondly, the slurry mixture was introduced into the freeze dryer (Ilsin, Model TFD5503), after frozen in the sealed container immersed in liquid nitrogen. The freeze drying process was carried out at a vacuum of ca. 5 mTorr and a temperature of -55 °C for about 72 h, until most of the water solvent was eliminated by sublimation. The resulting dried mixture was grounded and calcined at 600 °C in air and immediately cooled to room temperature to form SDC/Na$_2$CO$_3$ nanocomposite with different content of Na$_2$CO$_3$. 
2.1.2 Synthesis of LiAlO₂/carbonate composite electrolyte

Commercial LiAlO₂ powder and various contents (20, 30, 40, 50 wt%) of binary carbonates (62 mol% Li₂CO₃ and 38 mol% Na₂CO₃) were mixed. The mixtures were grounded and sintered at 680°C for one hour. The composite anode and cathode were the same materials, which composed of NiO and CuO mixed with the electrolyte (volume ratio: 1:1).

2.1.3 Synthesis of Quasi-octahedral CeO₂ mesocrystals

In a typical synthesis, 5 mmol of the cerium nitrate (Ce(NO₃)₃·6H₂O) was dissolved in 100 mL 1-octanol under stirring until a homogeneous colourless solution was obtained. The mixture was refluxed at 150°C. The colour of the mixture changed initially to yellow during reflux. A precipitate started to form after 5 minutes with the evolution of a brown gas (NO₂). Upon completion of gas evolution, the mixture was centrifuged and washed with ethanol 3 times to remove excess solvent and unreacted cerium precursor. The product was dried at 120°C overnight for further characterization.

2.2 Materials Characterization

The materials at the different processing steps are characterized by different techniques. Powder X-ray diffraction (XRD) patterns of the samples were collected of a Philips X’pert pro super Diffractometer with Cu Kα radiation (λ=1.5418 Å). A Zeiss Ultra 55 digital field emission scanning microscope (FE-SEM) was used to examine the morphology, size distribution of each sample, as well as energy dispersive X-ray (EDX) elemental mapping. The specimen was prepared by dripping the 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), high-resolution transmission electron microscopy (HRTEM) 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 onto a carbon-coated 200 mesh copper grid, followed by drying the sample under ambient conditions. 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.

2.3 Electrochemical characterization

2.3.1 Ionic conductivity of SOFCs

2.3.1.1 Electrochemical impedance spectroscopy

The EIS technique in general involves the measurement of current through a solid electrolyte cell when a sinusoidal voltage of low amplitude is applied. For a linear
system, the magnitude of the response is directly related to the electrical stimulus for any
given frequency. Hence, in a linear system, the applied potential is given by:

\[ E(t) = \Delta E \exp(j\omega t) \]  

(2-1)

The current output of the system is also sinusoidal and has the same angular frequency
\( \omega \), but differences in amplitude and phase from the voltage signal may occur depending on
the elements in the circuit which can be represented by:

\[ I(t) = \Delta I \exp(j\omega t + \phi) \]  

(2-2)

where \( \phi \) is the phase angle, \( \Delta E \) is the amplitude of the voltage and \( \Delta I \) the amplitude
of the current signal. For a pure resistor, the phase shift is zero.

As Ohm's law holds true in time or frequency domain, the impedance of a circuit
consisting of resistors, capacitors and/or inductors is the ratio of the voltage signal divided
by the current flowing through the circuit. The impedance of the circuit \( Z(\omega) \) at any
frequency \( \omega \), can be represented in both polar and Cartesian form both consisting of the
magnitude \( Z \) and the phase angle \( \phi \).

\[ Z(\omega) = \frac{E(t)}{I(t)} = Z \exp(-j\omega) = Z \cos \phi - jZ \sin \phi = Z' - jZ'' \]  

(2-3)

where \( j \) is a complex number with value of \( \sqrt{-1} \), \( Z' \) and \( Z'' \) are real and imaginary parts of
the impedance.

In this work, electrochemical impedance spectroscopy analysis were performed in air
atmospheres, using either a computerized Hewlitt-Packard HP4274A or HP4192 LCR-
meter. The measured frequency range covers from 1Hz to 1MHz with an applied signal of
50 mV. The temperature is manually controlled in a range of 200 to 650 °C.

2.3.1.2 Four-Probe D.C. technique

The setup of d.c. conductivity measurement is shown in Figure 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 Figure 2-1. The distance
of voltage probes and current probes is about 1mm. 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 of the electrolyte to determine proton and oxygen ion conductivity.
A block diagram of the measurement setup is shown in Figure 2-2. The equipment consists of a constant current source, digital voltmeters, temperature monitor, temperature controller and desktop computer. The constant current source is a EG&G 366 potentiostat. The supplied current is controlled manually. All the current settings used for conductivity

Figure 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.

Figure 2-2 – Scheme diagram of the four-probe d.c. conductivity measurement apparatus.
measurements are recalibrated and the values corresponding to a given setting are read from a HP 3478A multimeter within the computer program. These values are only slightly different (within ± 0.1%) from those on the settings in the constant current source. The voltage drop across the potential probes is measured with a RadioShack 22-168 programmable electrometer. The meter used for monitoring voltage can be controlled remotely through an RS232C interface. The temperature is detected by a PicoTC-08 thermocouple data logger, and the thermocouple is attached to the sample holder to ensure the temperature of sample is controlled. The furnace is controlled by a Velleman K8056 relay. Temperature monitor cooperates with furnace controller and both are operated via a RS232C interface. Since heating temperature lag between the temperature sample and furnace, the temperature of sample holder is controlled within a range of ±3 °C at given setting. Type T thermocouples are used for measuring and controlling the temperature. All the equipment is interfaced to desktop computer and operated by the homemade software developed by Labview. The raw data is displayed on the screen and stored in a file. Upon completion of an experiment the data is processed and may be displayed on the screen in graphical form, printed and plotted.

2.3.2 Electronic conductivity of SOFCs

The ion blocking method (sometimes also referred to as the dc polarization or the Wagner asymmetric polarization cell method) pioneered by Hebb and Wagner is the most extensively used method for determining very low electronic conductivity of ionic solids and has been detailed by a number of authors. The cell arrangements employed in this technique are as follows:

\[(-) \text{cation reversible electrode/ mixed conductor/ ion blocking electrode (+)} \quad (2-4)\]

or;

\[(-) \text{ion-blocking electrode/ mixed conductor/ anion reversible electrode (+)} \quad (2-5)\]

The method involves application of a small dc voltage signal to the solid ionic conductor placed between a reversible electrode and an inert electrode, which blocks the flow of ions (termed the ion blocking electrode). The reversible electrode has a known chemical potential and the applied dc voltage generates a chemical potential gradient across the solid material. Under steady state conditions no ionic current flows due to the presence of the ion blocking electrode. The residual current is carried only by the electrons or holes.

The ion blocking cell employed for the measurement is shown in Figure 2-3. Electrolyte material was pressed into a pellet with 13 mm diameter and 1.5 mm thickness, Pt paste (homemade) was painted on the both surfaces of the sample pellet and fired at 600 °C in air. The sample with Pt electrodes was attached to a stainless steel holder using a
Experimental

2.3.3 Discharge performance of SOFCs

In a typical experiment, the anode was composed of NiO mixed with the electrolyte and the cathode was based on mixture of lithiated NiO and the electrolyte. The anode, nanocomposite electrolyte and cathode materials were uniaxially pressed at 250 MPa to form a sandwich structure by a pressing procedure. Finally, both anode and cathode surfaces were painted by silver paste as current collectors for fuel cell measurements. The fuel cell with an active area of $0.64 \text{ cm}^2$ was tested at 450 to 580 °C, where hydrogen and 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.

The setup of fuel cell performance measurement is showed in Figure 2-4. The electronic equipment consists of load controller, digital voltmeters, digital current meter, temperature monitor, temperature controller and desktop computer. The computer software has been written to control all the main instrument functions and data acquisition and manipulation by Labview. The raw data is displayed on the screen and stored in a file. On completion of an experiment the data is processed and may be displayed on the screen in graphical form, printed and plotted. The load consists 7 constant resistors which are in range of 4.7 Ω to 0.2 Ω, are controlled by programmed Labview software. The supplied different loads are decided by inserting different resistors into the parallel circuit. Current is read from a HP 3478A multimeter within the computer program. The voltage across the load is measured with a RadioShack 22-168 programmable electrometer. The meters used for monitoring current and voltage can be controlled remotely through GPIB and RS232C interface. The temperature is detected and controlled by the same setup used in four-probe d.c. technique.

![Figure 2-4 – Scheme diagram of single cell performance (I-V) measurement.](image)
3 Core-shell SDC/ Na$_2$CO$_3$ nanocomposite

Ceria-salt-composites have been developed as functional electrolytes for the application of IT/ LTSOFCs more than 10 years. The previous research work emphasized more on the SOFC performance test rather than elaborate structure fabrication, so the detailed conduction mechanism of composite materials is still not clear. On the other hand, considering the interface conductivity effect, nanostructured material can have more interface region which will further improve the composite electrolyte performance. In this section, core-shell nanocomposite materials consist of SDC core and amorphous Na$_2$CO$_3$ shell was fabricated, and the nanocomposite have been used for further charge carrier behavior and conductivity mechanism study. Two different mixing methods have been employed to synthesis SDC/Na$_2$CO$_3$ nanocomposite.

3.1 Core-shell SDC/Na$_2$CO$_3$ nanocomposite - Wet mixing synthesis

Composite material is basically physical mixtures consisting two phases different materials. There are several mixing methods to synthesis composite materials, such as dry mixing and wet mixing. Wet mixing is a facile and more effective to fabricate homogenous composite. In this section, wet mixing method has been used to obtain core-shell SDC/Na$_2$CO$_3$ nanocomposite.

3.1.1 Morphological and structural characterization

Novel core-shell amorphous Na$_2$CO$_3$@SDC (Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$) nanocomposite was successfully synthesized for the first time by a simple coprecipitation synthesis and a wet mixing method. The nanocomposite consists of particles smaller than 100 nm and show faceted and occasionally irregular shape. The nanocomposite has a core-shell structure; SDC nanoparticles are surrounded by a uniform Na$_2$CO$_3$ thin layer of 4~6 nm. Further characterizations show that the core is single crystalline SDC, while the shell is amorphous Na$_2$CO$_3$ (Figure 3-1). Three evidences confirmed that the Na$_2$CO$_3$ shell is in the amorphous state. (1) In XRD pattern, there is no peak which can be observed corresponding to Na$_2$CO$_3$, even if the content of Na$_2$CO$_3$ in the composite reaches a 20%. (2) In HRTEM image, no lattice fringe can be observed in Na$_2$CO$_3$ shell layer. (3) A widen endothermic process in a range of 200 to 300 °C can be clearly observed in the DSC trace. However, within this temperature range, SDC or crystalline Na$_2$CO$_3$ does not exhibit any thermal transition, so the thermal response could be corresponding to the soften process and glass
transition of amorphous Na$_2$CO$_3$. The amorphous Na$_2$CO$_3$ plays an important role in forming interface region with SDC; more details will be discussed in section 3.2.

3.1.2 Ionic Conductivity

Electrical conductivity of a solid electrolyte at different temperature is, in general, the most important factor to be used to evaluate its property. Two conductivity measurement methods were employed in this work.

3.1.2.1 A.C. Conductivity

Temperature dependence of a.c. conductivity for SDC/Na$_2$CO$_3$ nanocomposite electrolyte, as well as that of pure SDC is shown in Figure 3-2, which are measured by the electrochemical impedance spectroscopy (EIS) method. The a.c. conductivity of the
nanocomposite electrolyte reaches over 0.1 S cm\(^{-1}\) above 300 °C, and the result is several orders of magnitude higher than that of pure SDC. Although EIS is not very suitable for this salt contained composite system, which will be discussed in section 3.1.2.2, the EIS conductivity still provides valuable information to confirm the composite effect. The remarkable conductivity of the SDC/Na\(_2\)CO\(_3\) nanocomposite electrolyte cannot result from either SDC or Na\(_2\)CO\(_3\) phase based on conventional ionic conduction bulk mechanism, since individual SDC and Na\(_2\)CO\(_3\) is nearly an insulator at around 300 °C. The conductivity enhancement from nanocomposite to bulk materials could be due to interface plays as superionic pathway.

3.1.2.2 D.C. conductivity

In SOFC field, EIS is extensively used to determine the conductivity of all types of solid electrolytes. However, despite its versatility, EIS is not very suitable for studying composite systems, where multiple mobile charge carriers will contribute to the overall measured conductivity, e.g. O\(^{2-}\), H\(^+\), Na\(^+\), and CO\(_3^{2-}\).\(^{83}\) Hence the contribution of the specific ions of interest in SOFC operation, i.e. O\(^{2-}\) and H\(^+\), cannot be distinguished from contributions of other ions (Na\(^+\) or CO\(_3^{2-}\)) when studied by EIS. Whereas d.c. conductivity measurement, on the other hand, gives an unequivocal conductivity measure of mobile ions under different gas atmosphere. In the d.c. measurement, only ions associated with fuels (O\(_2\)-O\(^{2-}\) and H\(_2\)-H\(^+\)) can contribute to the measured conductivity, while other ions are blocked in a “static status”. Furthermore, from a practical point of view, d.c. measurements are more close to the actual application regime of SOFCs. The d.c. measurement can be a good alternative to determine the contribution of each charge carrier (O\(^{2-}\) and H\(^+\)) in the

![Figure 3-3](image-url) - Conductivity of SDC/Na\(_2\)CO\(_3\) nanocomposite electrolyte obtained from d.c. measurement (the sum of proton conductivity and oxygen ion conductivity), a.c. impedance spectroscopy, and derived from fuel cell I-V curve.\(^{118}\) (Reprinted with permission. Copyright © 2010 Elsevier B.V.)
SDC/Na$_2$CO$_3$ nanocomposite system.

Different total conductivity results obtained from three techniques are compared in Figure 3-3. It is seen that the conductivity measured by d.c. technique, which is the sum of the proton conductivity and oxygen ion conductivity, is much closer to that derived from the slope of fuel cell I-V curve representing the actual fuel cell performance. However, the conductivity data measured by EIS show much higher values, which is because of the contributions from other ions, such as Na$^+$, CO$_3^{2-}$.

Figure 3-4 displays the temperature dependence of proton and oxygen ion conductivities of SDC/Na$_2$CO$_3$ nanocomposite electrolyte determined by d.c. measurements. The results show that proton conductivity $\sigma_{H^+}$ of nanocomposite electrolyte is much higher than oxygen ion conductivity $\sigma_{O^2-}$ with 1-2 orders of magnitude in the temperature range of 200–600 °C. For example, at 600 °C $\sigma_{H^+}$ is approximately 0.06 S/cm while $\sigma_{O^2-}$ is 0.005 S/cm.

These results demonstrate that proton conduction mainly accounts for the enhanced ionic conductivity in the nanocomposite electrolyte. The interface introduced by carbonate in the SDC/Na$_2$CO$_3$ nanocomposite enhances the protons conduction, while it seems not to have a clear effect on the oxygen ions transportation. It can be hypothesized that the interface introduced by carbonate as inclusion acts as pathway for proton transport, on the other hand, oxygen ion path is expected to be the grains of SDC.

3.1.3 Fuel cell performance and durability

Based on the high conductivity, high fuel cell performance can thus be expected. I-V and I-P characteristics of a single cell using as-prepared core-shell SDC/Na$_2$CO$_3$
nanocomposite as electrolyte at various temperature are shown in Figure 3-5. Under prerequisite of sufficient open circuit voltage of 1.0 V, the maximum power density of 0.8 W cm\(^{-2}\) has been achieved at 550 °C. Compared with the thin-film SDC single cell reported by Shao et al.,\(^{120}\) the core- shell SDC/Na\(_2\)CO\(_3\) nanocomposite fuel cells show better performance at 450-550 °C, indicating that the nanocomposite electrolyte has great potential value for low-temperature SOFC technology.

The durability of SDC/Na\(_2\)CO\(_3\) nanocomposite as electrolyte is also tested as well and is displayed in Figure 3-6. During the initial operation period, the fuel cell exhibited a minimum performance; within 50 min operation, the performance of the cell increases gradually and then a relatively steady output was delivered, due to the activation of the
electrode catalysts and interfaces between the electrodes and electrolyte. Then the cell was operated constantly at 550 °C for more than 12 h; despite a slight degradation after 12 h operation, an average power density output of 0.62 W cm$^{-2}$ was delivered. The notable durability verified not only thermal stability of the SDC/Na$_2$CO$_3$ nanocomposite but also its potential for low-temperature SOFCs applications.

3.2 Core-shell SDC/Na$_2$CO$_3$ nanocomposite – Freeze drying synthesis

As the conclusion of previous work, interface region of nanocomposite electrolyte plays the important role in enhancing ionic conductivity. The volume of interface area directly determines the composite electrolyte performance. As the interface region can only formed between carbonate and SDC particle, a homogeneous distribution of Na$_2$CO$_3$ is required, aiming to obtain more interface region and further enhance composite performance. Freeze drying technique can effectively prevent the salt phase nucleation and crystal growth, which has been advocated as a chemical process capable of producing pure, chemical homogeneous and ultrafine powders. It involves the preparation of an aqueous or non-aqueous solution, followed by rapid freezing of the solution and subsequent sublimation of the solvent under high vacuum. The technique has been applied to produce a wide spectrum of ceramic materials such as hematite, lead magnesium niobate, and lithium manganese oxide, etc., and its ability in controlling the chemical homogeneity

![Figure 3-7 – EDX mapping of the SDC9010 sample.](image)

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has been verified. Therefore, the freeze drying technique is suitable for the fabrication of SDC/Na$_2$CO$_3$ nanocomposite with highly homogeneous distribution of Na$_2$CO$_3$ phase. In the section, a new freeze drying technique was employed to fabricate SDC/Na$_2$CO$_3$ highly homogeneous nanocomposites and content effects of Na$_2$CO$_3$ phase in composite are studied as well.

### 3.2.1 Homogeneity of carbonate distribution

The homogeneity of carbonate distribution in SDC/Na$_2$CO$_3$ nanocomposites synthesized by freeze drying technique is confirmed by energy dispersive X-ray (EDX) mapping. Figure 3-7 shows the EDX mapping results of the SDC9010 sample as an example. Figure 3-7(a) is a regular SEM image, while the other images (Figure 3-7(b-d)) represent EDX mapping of Na, Ce and Sm elements, respectively. The arbitrary gray scale is proportional to the element's concentration. It can be clearly seen that both SDC and Na$_2$CO$_3$ phases are uniformly distributed over the composite sample, which confirms the homogeneity control of the nanocomposite by freeze drying technique.

### 3.2.2 Effect of Na$_2$CO$_3$ phase content

As the secondary phase in composite electrolyte, Na$_2$CO$_3$ performs several crucial functions in SDC/Na$_2$CO$_3$ nanocomposite: 1) the ionic conductivity of the electrolyte was significantly enhanced by adding carbonate as inclusions; 2) the thermal stability of the nanostructure was improved; 3) the electronic conductivity of SDC was suppressed effectively by the introduction of carbonate, as evidenced from the open-circuit voltage (OCV) of cells based on the SDC-carbonate electrolyte which was significantly higher than typical SDC single cells. In addition, the softening of amorphous Na$_2$CO$_3$ could improve densification of solid electrolyte layer to prevent any gas leakage. The content of Na$_2$CO$_3$ directly influences the performance of composite electrolyte. Based on the series of SDC/Na$_2$CO$_3$ nanocomposite samples, the effects of Na$_2$CO$_3$ phase content on material morphology, proton conductivity, oxygen ion conductivity and fuel cell performance have been studied.

The name, weight ratio and calculated volume ratio of each composite samples is given in Table 3-1. The volume ratio of each component is calculated from the density of

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Weight ratio SDC: Na$_2$CO$_3$</th>
<th>Volume ratio SDC: Na$_2$CO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDC9505</td>
<td>95:5</td>
<td>87:13</td>
</tr>
<tr>
<td>SDC9010</td>
<td>90:10</td>
<td>76:24</td>
</tr>
<tr>
<td>SDC8515</td>
<td>85:15</td>
<td>67:33</td>
</tr>
<tr>
<td>SDC8020</td>
<td>80:20</td>
<td>59:41</td>
</tr>
</tbody>
</table>
pure components at room temperature.

### 3.2.2.1 Effect on proton conductivity

The most important function of Na$_2$CO$_3$ phase is to form interface region with SDC. As concluded in Section 3.1.2.2, interface region mainly enhances proton conduction, thus the Na$_2$CO$_3$ content in composite will significantly influence the proton conductivity. Proton conductivity as a function of Na$_2$CO$_3$ volume fraction for different SDC/Na$_2$CO$_3$ nanocomposite samples was studied, as shown in Figure 3-8. It is observed that proton conductivity first increases with the increase of Na$_2$CO$_3$ volume fraction (to 24 %), then decreases with the continued increase Na$_2$CO$_3$ volume fraction. The SDC9010 sample shows the highest proton conductivity as compared to other nanocomposite samples, which means the optimized volume fraction of Na$_2$CO$_3$ in the nanocomposite is 24 % corresponding to weight fraction of 10%. This result is not in agreement with the previous studies reported by A. Bodén.\textsuperscript{126} In their study, it is concluded that the conductivity continuously increases with increasing the carbonate content based on the EIS measurement. As we discussed before, when using EIS technique, all mobile charge carriers including O$^2-$, H$^+$, especially Na$^+$, Li$^+$ and CO$_3^{2-}$ can contribute to the total measured conductivity. This may be the reason that the conductivity of composite continuously increases with increasing the carbonate contents in their study.

### 3.2.2.2 Effect on oxygen ion conductivity

On the other hand, Na$_2$CO$_3$ content effect on oxygen ion conductivity shows in different way compared with effect on proton conductivity. From the oxygen ion...
conductivity curve (Figure 3-9), it can be clearly seen that the oxygen ion conductivity deceases with the increasing of Na$_2$CO$_3$ volume fraction in the nanocomposite. This can be attributed to the conduction barrier effect of Na$_2$CO$_3$ phase; since the oxygen ion conduction is through the SDC phase, the dispersion of Na$_2$CO$_3$ phase in the nanocomposite blocks the oxygen ion conduction pathway. The more Na$_2$CO$_3$ phase dispersed in the nanocomposite, the more serious conduction barrier for oxygen ion.

3.2.2.3 Effect on fuel cell performance

To compare the fuel cell performances of the series of SDC/Na$_2$CO$_3$ nanocomposite samples, the current-voltage characteristics and corresponding power densities of the cells

![Figure 3-9](image_url) – The oxygen ion conductivity for a series of SDC/Na$_2$CO$_3$ nanocomposite samples at different temperatures determined by the four-probe d.c. measurements. (Reprinted with permission. Copyright © 2011 Hydrogen Energy Publications, LLC.)

![Figure 3-10](image_url) – The current-voltage characteristics and corresponding power densities of the cells made of each nanocomposite sample at 550 °C. (Reprinted with permission. Copyright © 2011 Hydrogen Energy Publications, LLC.)
made of each nanocomposite sample at 550 °C are illustrated in Figure 3-10. The fuel cells using SDC9505, SDC9010, SDC8515 and SDC8020 as electrolyte materials have delivered maximum power densities ($P_{\text{max}}$) of 514, 833, 729 and 613 mW cm$^{-2}$ at 550 °C, respectively. The results reveal once more that the optimized volume fraction of Na$_2$CO$_3$ in the nanocomposite is 24% corresponding to weight fraction of 10%. The fuel cell performances for each nanocomposite sample match well with the measured proton conductivity as a function of Na$_2$CO$_3$ volume fraction, where the SDC9010 sample exhibits the best proton conduction performance, demonstrating the optimized interface area in this nanocomposite system.
4 Ionic conduction mechanism in nanocomposite electrolyte

The ionic conduction mechanism in nanocomposite electrolyte has been studied simultaneously as the composite materials were invented. However, up to now, the exact mechanism remains unclear. The major bottleneck for mechanism study is that it lacks an effective method to determine the ionic conduction behaviors of composite materials. In this thesis, proton and oxygen ion conductivity of SDC/Na$_2$CO$_3$ nanocomposite electrolyte has been carefully investigated by employing a four-probe d.c. technique (Section 3.1.2.2). Based on the conductivity data, it is possible to identify the conduction pathways for proton and oxygen ion in the nanocomposite and further study conduction mechanism.

4.1 Simultaneous dual ion conduction in composite electrolyte

Based on H$^+$ and O$_2^-$ conduction data analysis (Figure 3-4), it is clearly demonstrated that the interface introduced by carbonate acts as pathway for proton transport. On the other side, the interface does not have any effect on the oxygen ions transportation, whose

Figure 4-1 – (a) A schematic illustration of dual H$^+$//O$_2^-$ conduction pathways: the protons are transported by the interface in the SDC/Na$_2$CO$_3$ nanocomposite, while oxygen ion conduction is through the grains of SDC, (b) comparison of conventional oxygen ion conductor and SDC/Na$_2$CO$_3$ nanocomposite as electrolyte for SOFCs.\(^{18}\) (Reprinted with permission. Copyright © 2010 Elsevier B.V.)
path is expected to be the grains of SDC.

From the above, the electrode reactions of SDC/Na$_2$CO$_3$ nanocomposite SOFCs during operation of the fuel cell can be expressed as:

Anode reactions:

\[ H_2 \rightarrow 2H^+ + 2e^- \]  \hspace{1cm} (4-1)
\[ O^+_0 + H_2 \rightarrow V_{o}^{**} + H_2O + 2e^- \]  \hspace{1cm} (4-2)

Cathode reactions:

\[ \frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O \]  \hspace{1cm} (4-3)
\[ \frac{1}{2} O_2 + V_{o}^{**} + 2e^- \rightarrow O^*_o \]  \hspace{1cm} (4-4)

where $H^+$, $V_o^{**}$, $O^*_o$, $e^-$ denote a proton, an oxygen vacancy, a lattice oxide ion and an electron, respectively. Thus, different to conventional electrolytes in SOFCs, SDC/Na$_2$CO$_3$ nanocomposite electrolyte possesses the unique simultaneous H$^+$/O$_2^-$ dual ion conduction property. Figure 4-1 gives a schematic illustration of the dual ion conduction, where the protons are transported in the interface region of the composite, while the oxygen ions are conducted through the SDC grains. The dual ion conduction of protons and oxygen ions not only enhances the total ionic conductivity, but also promotes reactions at both electrodes, resulting in improved fuel cell output, as shown in Figure 4-1b.

4.2 Oxygen ion conduction mechanism

In d.c. conduction curves (Figure 4-2), oxygen ion exhibits a simple conduction
behavior, which shows nearly a linear curve. The activation energy calculated for this result is 0.896 eV. This value is comparable to the value obtained for doped nanostructured ceria electrolytes reported by Bellino et al\textsuperscript{127}, see Figure 4-2. Therefore, it is suggested that the oxygen ion conduction mechanism in the composite electrolyte may be the same as that of conventional bulk doped ceria electrolyte materials. The conduction mechanism of bulk doped ceria is clear now which may also be applied for oxygen ion in composite material. Thanks to the oxygen vacancy in the doped ceria, the oxygen ion can transfer though the oxygen vacancy. In our composite case, oxygen ion can go through the SDC grain, as shown in Figure 4-1 (a). From the comparison (Figure 4-2), we also found that the oxygen ion conductivity of our composite materials is a bit lower than the conventional doped ceria materials; this is because in our composite system we have sodium carbonate as the second phase cover the SDC particle, and sodium carbonate is oxygen ion insulator, therefore, we have an oxygen ion transfer barrier at interface region.

### 4.3 Proton conduction mechanism

Based on the above discussion, it can be accepted that proton transport through the interface region in the composite materials. On the other hand, until now, there is no direct work reporting the proton conduction mechanism at the interface of the composite material. However, we still can provide some insights from literature, such as following.

1. It is widely accepted that hydrogen bond is involved in almost all proton conduction processes.\textsuperscript{128,129}

2. Long-range proton transport also requires rapid bond breaking and forming processes, which are expected to occur only in meta-stable hydrogen bonded systems.\textsuperscript{128}

![H⁺ Concentration Gradient](image)  

**Figure 4-3 – “Swing Model” pathway for proton conduction in SDC/Na₂CO₃ nanocomposite.**\textsuperscript{118} (Reprinted with permission. Copyright © 2010 Elsevier B.V.)
3. Proton conduction was also reported in the grain boundary of nanostructured oxides, i.e. doped ceria\textsuperscript{130,131} and YSZ\textsuperscript{131-133.}

Based on these insights, we propose an empirical “Swing Model” to interpret the proton conduction mechanism in the composite system. As illustrated in Figure 4-3, when protons approach the composite electrolyte from anode, it can form meta-stable hydrogen bonds with oxygen ions from both SDC surface and CO\textsubscript{3}\textsuperscript{-} group. When the operating temperature is above the glass transition temperature of amorphous carbonate phase, the bending and stretching vibration of C-O bonds are enhanced, as well as the mobility and rotation of CO\textsubscript{3}\textsuperscript{-} group. These enhanced movements facilitate rapid breaking and forming of hydrogen bonds in the interface region, leading to effective long-range proton transportation driven by proton concentration gradient. In this process, carbonate serves as a “bridge” for protons to move from one hydrogen bond to another.
5 Other type of composite electrolyte and potential nanostructure material

5.1 LiAlO$_2$/carbonate composite electrolyte

So far, the composite electrolyte materials developments for SOFC applications are still in the initial stage, and most of them are the ceria-based composites. It is necessary to explore new type of functional materials for either pure scientific interest to extend the composite electrolyte research for LT-SOFCs or for better performances in applications. It is well known that LiAlO$_2$ and carbonate system is the state of the art electrolyte material for molten carbonate fuel cells (MCFCs). From two-phase composite material perspective, this system may also be a promising composite electrolyte. In this system, LiAlO$_2$ is very stable at both anode and cathode sides, thus it was expected that the LiAlO$_2$ system would also be more stable than the ceria composite electrolyte. In addition, the LiAlO$_2$ system is the type of non-ceria composite electrolyte. Studies on the electrochemical performances of these materials at SOFCs environment will not only improve the durability of composite materials, but will also give an open view to understand the ion transport mechanisms in different composite systems.

5.1.1 Material Characterization

![Figure 5-1 – The XRD Pattern of as-prepared LiAlO$_2$]
The LiAlO₂/carbonate composite electrolyte was synthesized by a simple physical mixture method, using product. The crystal structure of the commercial LiAlO₂ is confirmed as typical $\gamma$-type LiAlO₂ (JCPDS 73-1338) by XRD (Figure 5-1). The a.c. conductivities of LiAlO₂ based composite electrolytes vary from $10^{-5}$ to $10^{-1}$ S cm$^{-1}$ in the temperature range of 400–650 °C which were obtained from EIS measurement.

### 5.1.2 Fuel cell performance

The synthesized composite material was fabricated into a single cell and tested. Performance of the fuel cells with LiAlO₂/carbonate composite as electrolyte is presented in Figure 5-2. The open circuit voltages (OCV) almost reach 1.0 V. This indicates that these composite electrolytes can form a relative gas-tight electrolyte membrane to avoid gas crossover, since the carbonates in the composite electrolyte soften at operation temperature and expanded or fill everywhere if pores exist in the electrolyte. The maximum output power density reaches 466 mW/cm$^2$, when the carbonate content is 40%.

![Figure 5-2](image)

**Figure 5-2** – Fuel cell performance of the single cell with LiAlO₂/carbonate composite electrolyte at 650 °C, where the carbonate content is 40% wt.

![Figure 5-3](image)

**Figure 5-3** – Discharging curves for the fuel cells with various electrolytes at 650 °C using the electrolyte with 40% carbonate.
wt. The discharge performance of as-fabricated fuel cell is studied as well. Figure 5-3 shows the discharging curves of the fuel cells at 650 °C using LiAlO$_2$/carbonate composite electrolyte with carbonate content of 40%. At the beginning of the discharge curves, some polarization is observed, but after about 5 min the cells display a constant output under the average current density of 130~140 mA/cm$^2$. The tests were kept for about 30 min with a discharging plateau. The stable high current output implies a good ionic transport and conduction. It can be concluded that the fuel cell with LiAlO$_2$-carbonate composite electrolyte can exhibit excellent electrochemical performances at the H$_2$ /air environment, and display a strong potential for fuel cell applications.

### 5.2 Quasi-octahedral CeO$_2$ mesocrystals

Until today, the ceria based composite electrolyte materials are still the most important candidate for LTSOFC application, due to its high performance. As the host phase in ceria based composite electrolyte materials, doped CeO$_2$ not only form interfacial region with carbonate, but also is the framework to determine the composite microstructure while carbonate phase is soften under operating temperature. The microstructure of ceria particle directly influents the whole composite performance. When we are considering the ionic pathway in the interface of composite electrolyte, it is clear that more interfacial region leads higher composite performance. Nanotechnology can achieve this target by nanosize effect. Recently, some new composite electrolyte with unique nanostructures, i.e. core-shell SDC/Na$_2$CO$_3$ nanocomposite (Chapter 3) and SDC nanowires based nanocomposite$^{92}$ were designed by the novel nanocomposite approach. However, different nanostructured ceria materials are still a challenge for composite electrolyte development. In this section, we describe the synthesis of quasi-octahedral ceria mesocrystals with nanocrystalline building blocks from a facile surfactant-free nonaqueous system. The

![Figure 5-4 – (a) SEM images of as-prepared CeO$_2$ quasi-octahedrons (b)TEM image of as-prepared CeO$_2$ quasi-octahedral mesocrystals with corresponding indexed SAED pattern of an isolated mesocrystal in the inset. Scale Bar: 100 nm.](image-url)
unusual nanostructured ceria material will have strongly potential for future composite electrolyte applications.

### 5.2.1 Material Characterization

SEM image reveals that the synthesised CeO₂ particle consists of well-dispersed quasi-octahedrons, with an average diameter of 77±6 nm, which is shown in Figure 5-4a. Carefully looking at each particle (inset of Figure 5-4a), a quite regular octahedron structure with sharp facets and edges can be clearly distinguished. TEM image displays further details of the nanostructure of CeO₂ mesocrystals. Figure 5-4b shows that the mesocrystals are well-dispersed and exhibit a uniform size and morphology. Their morphologies are similar to rhombus, which is the projection of octahedron in 2-D under TEM observation. The texture of mesocrystals is observed to be built up of numerous small primary crystals with recognizable boundaries or voids between the component subunits. The selected area electron diffraction (SAED) pattern (inset of Figure 5-4b) indicates that the whole assembly of mesocrystal behave as a single crystal.

### 5.2.2 Growth mechanism

S. Seal et al. performed a detailed investigation to explain the self-assembly of ceria, which gives a strong foundation to the formation of ceria mesocrystal/superstructure. Based on these reports, we hypothesize the formation of hierarchically assembled mesocrystals to be a multistage process. In the first stage, primary ceria nanocrystals nucleate. A complex, Ce(NO₃)₃·nC₈H₁₇OH, is formed when Ce(NO₃)₃·H₂O dissolves in 1-octanol. Ce(NO₃)₃·nC₈H₁₇OH decomposes when the temperature reaches 150 °C, accompanied by the formation (nucleation and growth) of primary ceria nanocrystals. In the second stage, the ceria crystals are capped by long C-chain molecules forming oxide-organic hybrid. In the third stage, the primary hybrid ceria-octanoate building blocks grow.

![SEM image of CeO₂ mesocrystals calcined at 550 °C for 3h.](Reprinted with permission. Copyright © 2011, Springer Science+Business Media B.V.)
to secondary and tertiary octahedral mesocrystal through oriented assembly. When two building blocks come together, the capillary forces between them facilitate the solvent removal and strengthen the agglomerate through van der Waals forces $^{141}$. In this stage, face-specific interactions between the building blocks lead to directed self-assembly of oriented nanocrystals and eventually mesocrystal formation.

### 5.2.3 Thermal stability

Ceria are always subjected to high temperature when applied to fuel cell or catalysis. Therefore, thermal stability is a very important property for ceria materials. Thermal stability was investigated by calcination of the as-prepared product through heating at 550 °C for 3 hours in air. Figure 5-5 shows the SEM image of calcined product, which reveals that the size and morphology of calcined powder were identical to as-prepared product, no noticeable variations can be observed and mesocrystals are still well-dispersed.
Conclusion

In this work, we introduced a new composite electrolyte concept, and successfully used it for LTSOFCs. Nanotechnology was employed to improve composite material. It has been accepted that the new composite concept especially nanocomposite concept will become a new strategy for future fuel cell development.

Firstly, nanotechnology has been successfully applied to engineer the composite material. Novel core-shell amorphous SDC/Na₂CO₃ nanocomposite was synthesized by two mixing techniques, wet mixing and freeze dry mixing. The host particle sizes synthesized by both of methods are smaller than 100 nm. As-prepared core-shell SDC/Na₂CO₃ 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 of 0.8 W cm⁻² at 550 °C. Core-shell SDC/Na₂CO₃ nanocomposites with homogeneous distribution of Na₂CO₃ phase have been successfully synthesized by a new freeze drying. It can be clearly seen out that both SDC and Na₂CO₃ phases are uniformly distributed over the nanocomposite sample, and the fuel cell performance has been improved as well. Both the proton and oxygen ion conduction behavior has been determined by the four-probe d.c. conductivity measurement, which proved that the SDC/Na₂CO₃ nanocomposite electrolyte possesses the unique simultaneous H⁺/O₂⁻ conduction property. The measurements reveal that the proton conductivity in SDC/Na₂CO₃ nanocomposite electrolyte is 1-2 orders of magnitude higher than oxygen ion conductivity in the temperature range of 200-600 °C, which confirms that proton conduction mainly accounts for the significantly enhanced total ionic conductivity, resulting in an excellent fuel cell performance.

Secondly, ionic conduction mechanisms in nanocomposite electrolyte material have been suggested as well, based on proton and oxygen ion conduction behavior study via d.c. conductivity measurement. It is concluded that the interface introduced by adding sodium carbonate phase supplies high conductive paths for proton transport, whilst oxygen ions are most probably transported within SDC phase. An empirical “Swing Model” has been proposed for the mechanism of superior proton conduction.

Thirdly, aiming to develop new composite materials, a novel non-ceria-based ceramic composite has been successfully prepared and applied for LTSOFCs as electrolyte. The
new ceramic fuel cell using LiAlO$_2$-carbonate composites can exhibit excellent fuel cell performance when hydrogen and air were used as fuel and oxidant. The maximum output power density reached to 466 mW/cm$^2$ at 650 °C. Since the air was used as an oxidant, the contribution of CO$_3^{2-}$ ion transport can be neglected. This work strongly demonstrates that the high conductivity of oxide/ carbonate composite is mainly related to the interface effect between oxide and carbonate.

Fourthly, aiming to extend different nanostructures of ceria particle, well-dispersed cerium(IV) oxide mesocrystals was synthesized in this thesis work. The sample synthesis approach holds promise in large-scale preparation of CeO$_2$ mesocrystal for a wide range of applications, especially for LTSOFC. Based on careful structural investigation, we proposed that the mesostructure was formed by directed self-assembly of primary nanocrystals. The size and morphology was retained after calcination at 550 °C, revealing high thermal stability. The thermal stable ceria mesocrystals will be potential candidate for nanocomposite electrolyte applications.
Future work

In the future, there are mainly two parts of work need to be investigated, regarding to further improving performance of composite electrolyte and deep studying interfacial conductivity mechanism of composite conductor.

To improve performance of composite electrolyte, firstly, further work will pay more attention on nano effect of nanocomposite by nanotechnology, 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 will be employed for nanocomposite electrolyte, i.e. different mesocrystals, different morphology 3D and 1D particles. Furthermore, thin film technique will be used to fabricate composite electrolyte pallets, which will reduce the resistance and enhance the power density output.

To study interfacial conduction mechanism, some modeling simulation will be established based on current experimental results and theoretical calculation will be conducted as well as deep on the composite systems. The work will not only reveal the fundamental conduction mechanism, but also help optimizing the material design and architecture.
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References

17. Haber, F., Moser, A. Z Elektrochem. 1905. 11(36). 593
References

24 Acres, G. *J Power Sources*. 2001. 100(1-2). 60
25 Dell, R. M., Rand, D. *J Power Sources* 2001, 100 1-2. 2
32 Fergus, J. W. *J. Power Sources*. 2006. 162(1). 30
35 Inaba, H., Tagawa, H. *Solid State Ionics*. 1996. 83(1,2). 1
37 Feng, M., Goodenough, J. B., Huang, K., Milliken, C. *J Power Sources*. 1996. 63(1). 47
44 Goodenough, J. B., Huang, Y. *J Power Sources*. 2007. 173(1). 1
67 Zhu, B. *Key Eng Mater*. 2005. 280-283. 413
81 Tuller, H. L. *Solid State Ionics*. 2000. 131(1,2). 143
References

84 Xia, C., Li, Y., Tian, Y., Liu, Q., Zhao, Y., Jia, L., Li, Y. J Power Sources. 2009. 188(1). 156
86 Huang, J., Gao, Z., Mao, Z. Int J Hydrogen Energ. 2010. 35(9). 4270
104 Li, S., Sun, J. Int J Hydrogen Energ. 2010. 35(7). 2980
110 Zhu, B. *J. Power Sources*. 2003. 114(1). 1
114 Wagner, C. Z. *Elektrochem*. 1956. 60. 3
116 Mizusaki, J., Fueki, K. *Solid State Ionics*. 1982. 6(1). 85
125 Le Mercier, T., Gaubicher, J., Bermejo, E., Chabre, Y., Quarton, M. *J Mater Chem*. 1999. 9(2). 567
129 Kreuer, K. *Chem Mater*. 1996. 8(3). 610
135 Kuchibhatla, S. V. N. T., Karakoti, A. S., Seal, S. Nanotechnology. 2007. 18. 75303
141 Manoharan, V. N., Pine, D. J. Mrs Bull. 2004. 29. 91