Structure and Properties of Cathode and Electrolyte for Intermediate Temperature Solid Oxide Fuel Cells (II-SOFCS)

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LIST OF ABBREVIATIONS

SOFCs	Solid Oxide Fuel Cells
IT-SOFCs	Intermediate Temperature Solid Oxide Fuel Cells
LSM	Lanthanum Strontium Manganese Oxide
Ni/YSZ	Nickel/Yttria Stabilized Zirconia
TEC	Thermal Expansion Coefficient
$LaFeO_{3-\delta}$	Lanthanum Iron Oxide
$LaCoO_{3-\delta}$	Lanthanum Cobalt Oxide
YSZ	Yttria Stabilized Zirconia
EDTA	Ethylenediaminetetraacetic acid
XRD	X-ray diffraction
SEM	Scanning Electron Microscopy
SDC	Samarium doped Cerium
BSCF	Barium Strontium Cobalt Iron Oxide
$LaGaO_3$	Lanthanum Gallate Oxide
LSGM	Lanthanum Strontium Gallate Magnesium Oxide
CeO_2	Ceria Oxide
Bi_2O_3	Bismuth Oxide
ZrO_2	Zirconia Oxide
LSC	Lanthanum Strontium Cobalt Oxide
ORR	Oxygen Reduction Reaction
$SrCoO_3$	Strontium Cobalt Oxide
$La_2Zr_2O_7$	Lanthanum Zirconia Oxide
MIEC	Mixed Ionic Electronic Conductor

ASR	Area Specific Resistance
ICDD	The International Centre of Diffraction Data
ICSD	Inorganic Crystal Structure Database
PEM	Polymer Electrolyte Membrane
HT-SOFCs	High Temperature Solid Oxide Fuel Cells

LIST OF SYMBOLS

λ	Wavelength
σ	Conductivity
χ^2	Reduced Chi Square
2θ	Diffraction angle
Z'	Real part of Impedance
$-Z''$	Imaginary part of Impedance

LIST OF EQUATIONS

Struktur dan Sifat Elektrolit dan Elektrod untuk Suhu Pertengahan Sel Oksida Pepejal Bahan Api (IT-SOFCs)

ABSTRAK

Sel bahan api oksida pepejal (SOFCs) adalah peranti yang digunakan untuk menukarkan dari tenaga kimia kepada tenaga elektrik. Objektif utama tesis ini adalah untuk mengakaji stuktur dan sifat-sifat elektrod dan elektrolit yang digunakan dalam aplikasi suhu pertengahan SOFCs. Komposisi bahan positif elektrod (katod) ialah $Ba_{0.5}Sr_{0.5}Co_{0.8-y}Fe_{0.2+y}O_{3-\delta}$ ($0 \geq y \geq 0.8$) yang disintesis dengan menggunakan gabungan kaedah EDTA citrate pengkompleks. Fasa tunggal komposisi ini telah diperolehi selepas dipanaskan pada 900 ℃ selama 15 jam dengan menggunakan kaedah pengisaran terputus-putus. Belauan sinar x menunjukkan semua sampel membentuk larutan pepejal hingga komposisi terakhir dengan menunjukkan struktur simetri kubus dan kumpulan ruang Pm-3m. Selain itu, struktur hablur stabil sehingga apabila disinter sehingga 1100 ℃ di udara. Kemudian, kaedah penyaringan Rietveld dijalankan untuk menegnalpasti perubahan struktur diatas stuktur kubus simetri dengan mengurangkan kandungan kobalt pada $Ba_{0.5}Sr_{0.5}Co_{0.8-y}Fe_{0.2+y}O_{3-\delta.}$ Hasil dari kajian dengan mengurangkan kandungan kobalt parameter kekisi dan sel unit kekisi telah berkurang. Kation Fe kekal pada kedudukan 1b pada koordinat oktahedral. Selain dari itu, bahan elektrolit dengan komposisi $Ce_{0.8}Sm_{0.2}O_{1.9}$ telah disentisis menggunakan kaedah konvensional tidak balas pepejal. Komposisi $Ce_{0.8}Sm_{0.2}O_{1.9}$ yang telah disentisis dibandingkan dengan sampel komesil untuk menentukan struktur hablur, sifat-sifat elektrik dan saiz ira. Hasil dari keputusan tersebut, parameter kekisi dan sel unit kekisi adalah dalam lingkungan yang sama. Walau bagaimanapun, saiz kumin hablur (menggunakan formula Sherrer) dan saiz ira $Ce_{0.8}Sm_{0.2}O_{1.9}$ untuk komersial sampel lebih kecil berbanding sampel yang disintesis, Kekonduksian elektrik pada suhu 600^{o}C untuk komersial sampel dan sampel yang disintesis masing- masing adalah 7 x 10^{-2} and 2 x 10^{-2} Scm^{-1}. Walaupun struktur untk sampel yang disediakan dan komersial adalah sama, namun, sifat-sifat electrik untuk sampel komensial adalah lebih tinggi. Daripada prestasi elektrokimia, setengah sel $Ba_{0.5}Sr_{0.5}Co_{0.4}Fe_{0.6}O_{3-\delta}$ | $Ce_{0.8}Sm_{0.2}O_{1.9}$ | $Ba_{0.5}Sr_{0.5}Co_{0.4}Fe_{0.6}O_{3-\delta}$ daripada katod komposisi $Ba_{0.5}Sr_{0.5}Co_{0.4}Fe_{0.6}O_{3-\delta}$ atau y = 0.4 menunjukkan rintangan tertentu kawasan paling rendah (ASR) mengenai 0.1257 Ωcm2 pada 600 ℃ daripada suhu operasi.

Structure and Properties of Electrolyte and Electrode Materials for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs)

ABSTRACT

Solid oxide fuel cell (SOFCs) is a device that used to convert from chemical energy to electrical energy. The aim of this thesis is to evaluate the correlation of structure and properties of electrode and electrolyte materials that were used for IT-SOFCs. The positive electrode (cathode) materials with the composition of $Ba_{0.5}Sr_{0.5}Co_{0.8-y}Fe_{0.2+y}O_{3-\delta}$ ($0 \geq y \geq 0.8$) were prepared using combined EDTA citrate complexing method. Phase pure samples were obtained after the samples were heated at 900°C for 15 hours with intermittence grindings. X-ray diffraction (XRD) showed that all samples were formed full solid solution between both end-members with a cubic symmetry and the space group of Pm-3m. Furthermore, the crystal structure remained stable after heated up to 1100°C in air. Then, Rietveld refinements were performed to evaluate structural changes on the crystal symmetry by reducing cobalt contents in $Ba_{0.5}Sr_{0.5}Co_{0.8-y}Fe_{0.2+y}O_{3-\delta}$. Results indicated that reducing Co contents decreased the lattice parameters and unit cell volume. Fe cation was remained at the 1b-site with the octahedral coordination. On the other hand, electrolyte material with the composition of $Ce_{0.8}Sm_{0.2}O_{1.9}$ was prepared using conventional solid-state synthesis route. The prepared $Ce_{0.8}Sm_{0.2}O_{1.9}$ was compared with the commercial sample to determine their structure, electrical properties, and grain size. Results show that the lattice parameters and unit cell volume of the prepared and commercial $Ce_{0.8}Sm_{0.2}O_{1.9}$ were similar within errors. But crystallite size (using Scherrer's formula) and grain size (SEM micrograph) of the commercial $Ce_{0.8}Sm_{0.2}O_{1.9}$ were relatively smaller than the prepared sample. Furthermore, the measured electrical conductivities of commercial and prepared $Ce_{0.8}Sm_{0.2}O_{1.9}$ were 7×10^{-2} and 2×10^{-2} Scm^{-1}at 600°C, respectively. The structure of commercial and prepared $Ce_{0.8}Sm_{0.2}O_{1.9}$ are similar, however, electrical properties of commercial $Ce_{0.8}Sm_{0.2}O_{1.9}$ is relatively much better than prepared $Ce_{0.8}Sm_{0.2}O_{1.9}$. On the other hand, the electrochemical performance of in-house prepared half-cell $Ba_{0.5}Sr_{0.5}Co_{0.4}Fe_{0.6}O_{3-\delta}$ | $Ce_{0.8}Sm_{0.2}O_{1.9}$ | $Ba_{0.5}Sr_{0.5}Co_{0.4}Fe_{0.6}O_{3-\delta}$ shows the lowest Area Specific Resistance (ASR) about 0.1257 Ωcm^2 at 600°C.

CHAPTER 1

INTRODUCTION

1.1 Solid Oxide Fuel Cells (SOFCs)

There is an increasing electrical energy demand over the world to power all electrical devices. The major demand mainly used for construction, stationary power sources and transportations sector (Abas et al., 2015). Fossil fuel from natural resources is a main resource used to generate electricity. However, fossil fuel is non-renewable and not sustainable energy resources. Therefore, alternative energy resources have been intensively investigated to replace the usage of natural resources.

Solid oxide fuel cell (SOFCs) is one of the alternatives of clean and sustainable energy resources to generate electricity. SOFCs is used to generate electricity from chemical reaction between hydrogen (H_2) and oxygen (O_2) gas (Dupuis, 2011). SOFC offers high efficiency energy conversion (about 60 to 80%) and very low environmental impact to ensure future clean energy generation (Shao et al., 2012). Furthermore, SOFC is exhibited the highest specific power (in $W.kg^{-1}$) and power density (in $W.cm\text{-}^{3}$) at operating temperature of $650^{o}C$ compared to other alternative energy conversion devices such as combustion engines, PEM fuel cells, photovoltaic cells, electromagnetic generator and thermoelectric generator as shown in Figure 1.1. Thus, SOFC is considered as the most promising electrical power generation device for sustainable energy resource.

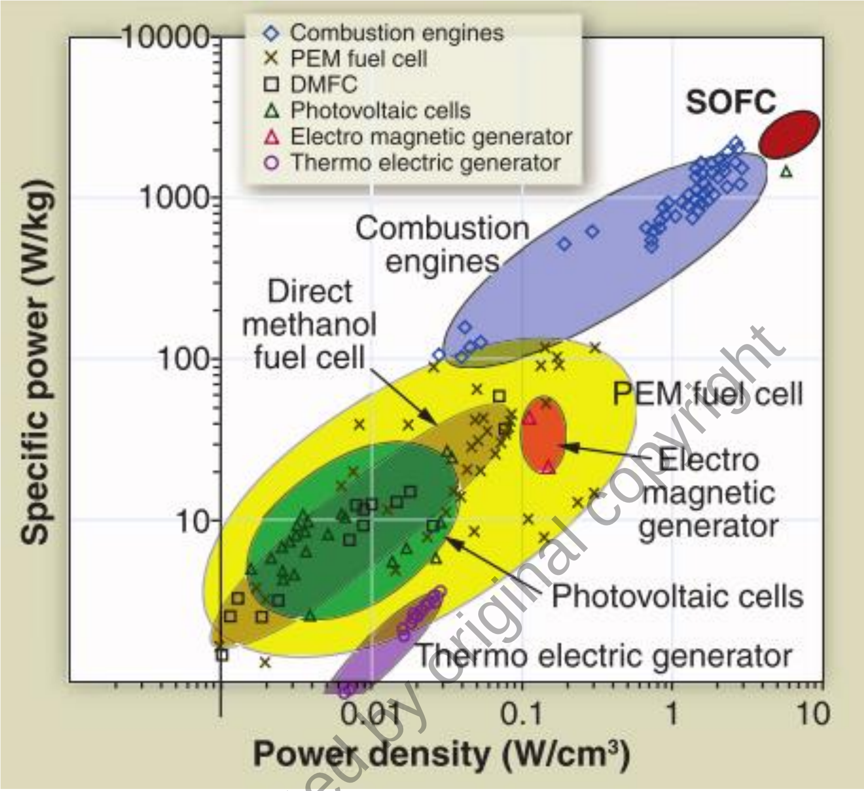

Figure 1.1: The specific power of energy conversion device as a function of power density at 650^{o}C (Wachsman & Lee, 2011).

A SOFCs consist of two porous electrodes; anode (as negative electrode), cathode (as positive electrode) and separated by highly dense solid electrolyte. During the chemical conversion process, hydrocarbon was used as a fuel to supply H_2 gas to anode while air was used to supply O_2 gas to cathode. At the anode, oxidation process occurs and H_2 was converted to H^+ ions and released electrons. The electrons were flowed to the external circuit and move to cathode. The reduction process was occurred when O_2 from air reacted with the flux of electrons at the cathode to produce O^{2-} ions. Then, the O^{2-} ions were diffused through electrolyte toward the anode. In the mean time, O^{2-} ions at the anode were reacted with H^+ ions to produce H_2O as a by-product. Therefore, continuous oxidation and reduction processes at the both anode and cathode, respectively, resulting electricity was generated (Mahato et al., 2015). Figure 1.2 shows a schematic diagram of SOFCs. The electrochemical reaction occurred at the anode and cathode as shown in equation (1.1) and (1.2), respectively.

Anode: $2H_2\ (g) + 2O^{2-} \rightarrow 2H_2O + 4e^-$ (1.1)

Cathode: $O_2\ (g) + 4e^- \rightarrow 2O^{2-}$ (1.2)

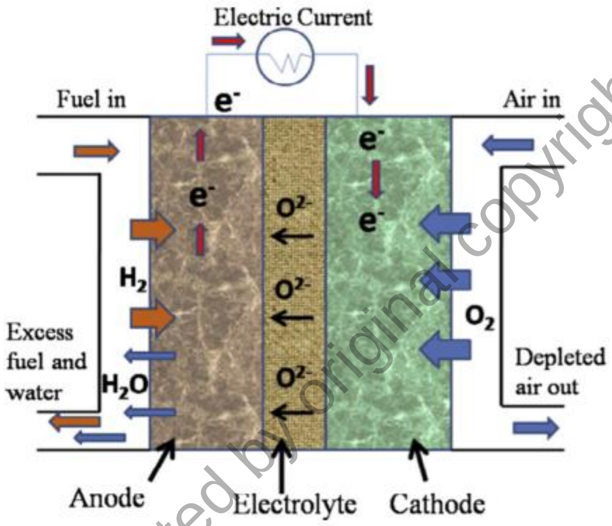

Figure 1.2: The schematic diagram of SOFCs (Mahato et al., 2015).

Conventional SOFCs are operated at high temperature between 800 and 1000°C. The high operating temperature is necessary for conventional SOFCs to improve kinetic reactions of the electrode and to reduce ohmic drop at the electrolyte (Zhou et al., 2009). However, several problems occurred at the high operation temperature such as interface-reactions problem between electrode and electrolyte, materials compatibility, possibility of crack formation of cells due to thermal expansion coefficient (TEC) mismatch and high cost (Ahmadrezaei et al., 2013). Thus, these problems had led to the development of the new type of SOFCs that able to operate at relatively lower temperature (between 500 and 700^{o}C) compared to conventional SOFCs (HT-SOFCs) known as the Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs).

IT-SOFCs are offers several advantages such as the reduction of energy consumptions, lowering the operation and setup cost, improved materials compatibility of components, enhancing the durability and reliability at long-term operation, and more widely selection of materials could be used (Huang et al, 2012):

1.2 Properties of SOFCs components

1.2.1 Electrolyte

Electrolyte is a medium for diffusion of oxygen ions from cathode as a positive electrode to anode as a negative electrode. Electrolyte should only allow oxygen ions diffuse from cathode to anode but electrically resistive. Therefore, electrolyte materials must exhibit excellent ionic conductivity, chemical resistant, and high thermal stability at the operating temperature. Yttria stabilized zirconia (YSZ) is an example of conventional electrolyte used for SOFC. YSZ has high ionic conductivity, excellent chemical resistivity and thermal stability at an operation temperature of about 1000^{o}C. There are seven general criteria of solid electrolyte could be used in SOFCs, such as the following (Mahato et al. 2015):

1. Easy to fabricate and have small thickness, L and large area, A.
2. Has ionic conductivity in range of 10^{-3} to 10^{-1}Scm^{-1} at operating temperature.
3. Have chemical stability or inert in oxidizing or reducing atmosphere.
4. Low cost of materials and fabrication.
5. Long-term stability at operating temperature.
6. Match TEC with electrode and interconnector.
7. High long-term reliability (high strength and high durability).

1.2.2 Anode

Anode is a negative electrode in SOFCs. A porous anode should be electrically conductive to facilitate oxidation process for conversion of H_2 from fuel to H^+ ions and electrons. Thus, enables electrons to flow from the reaction site to the current collector. Thus, a conventional anode of SOFCs is made up by cermet which is the combination of ceramic and metallic materials. Ni/YSZ is a common anode materials used in SOFCs. The criteria of an anode are (Taroco, et al. 2009):

1. High mixed ionic and electronic conductivity about 1000 Scm^{-1}.
2. TEC values are matches those of the adjoining components (electrolyte).
3. High chemical stability under a reducing atmosphere.
4. Large triple phase boundary.
5. High electrochemical or catalytic activity for the oxidation of the selected fuel gas.
6. High porosity (20 - 40 %) adequate for the fuel supply.

1.2.3 Cathode

Cathode is a positive electrode in SOFCs. A porous cathode should be electrically conductive to facilitate a flux of electrons from anode through external circuit to react with oxygen gas. Therefore, reduction process of O_2 to O^{-2} ions could be accelerated. Lanthanum strontium manganese oxide (LSM) is an example of conventional cathode material that was used at high temperature operations of SOFCs. Generally, the requirement for SOFCs cathode are listed as follows (Sun et al., 2009):

1. High electronic conductivity (approximately above 100 Scm^{-1} under oxidizing atmosphere).

2. Should have adequate porosity (approximately 30 to 40%) to diffuse gaseous oxygen.
3. Thermal expansion coefficient (TEC) similar between an electrolyte and interconnector.
4. Stable in oxidizing environment.
5. Large triple phase boundary for electrochemical reaction of electron, oxygen ions and gas.
6. Easily fabricated and relatively low cost.

1.3 Problems Statement

High temperature SOFCs (HT-SOFCs) that is operated at about 800 to 1000^{o}C introduces a several drawbacks to cell components and also limited of trials selection. Thus, IT-SOFCs was developed to ensure the promising future clean of power generation. IT-SOFC offers very low carbon emissions, highly efficient (~80 %) and excellent fuel flexibility compared to the HT-SOFCs. Furthermore, IT-SOFCs also has a variety of advantages such as shortens time taken for start-up/shutdown, extended operation lifetime and minimizes thermal and sealing degradations (Zhao et al., 2009).

The composition of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was reported as excellent cathode materials for IT-SOFCs compared to $La_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (Ahmadrezaei et al., 2013). However, high~~er~~ amount of cobalt content in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ had raised to an environmental issue, high cost, structural instability and high thermal expansion coefficient (Chen et al., 2007). Thus, different concentrations of cobalt contents in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ were investigated in this project.

On the other hand, $Ce_{0.2}Sm_{0.8}O_{1.9}$ was reported as the best candidate for electrolyte materials to be used in IT-SOFCs. However, preparation of $Ce_{0.2}Sm_{0.8}O_{1.9}$ commonly involved complex wet methods such as sol-gel and combustion methods (Hui et al., 2007). Thus, we attempted to simplify the synthesis method by using conventional solid-state synthesis route. After that, a comparison between commercial and in-house prepared SDC was performed to evaluate their properties. Then, electrochemical performance of half-cell between $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}|Ce_{0.2}Sm_{0.8}O_{1.9}|Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ were evaluated.

1.4 Objectives

The objectives of this study are:

i. To synthesise and characterise electrolyte and positive electrode (cathode) materials for IT-SOFCs component.

ii. To determine crystallographic properties of $Ce_{0.8}Sm_{0.2}O_{1.9}$ as an electrolyte and $Ba_{0.5}Sr_{0.5}Co_{0.8-y}Fe_{0.2+y}O_{3-\delta}$ ($0 \geq y \geq 0.8$) as a cathode.

iii. To evaluate the electrical and electrochemical properties of electrolyte ($Ce_{0.8}Sm_{0.2}O_{1.9}$) and half cells of BSCF|SDC|BSCF, respectively.