

UNIVERSITI TEKNOLOGI MARA

**SYNTHESIS AND
CHARACTERIZATION OF
LANTHANUM COBALTITE BASED
CATHODE MATERIAL FOR
POTENTIAL APPLICATION IN
PROTON CONDUCTING FUEL
CELL**

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Thesis submitted in fulfillment
of the requirements for the degree of
Master of Science

Faculty of Applied Sciences

September 2014

ABSTRACT

Proton conducting fuel cell (PCFC) is a device that converts chemical energy directly into electrical energy via electrochemical processes. Currently, one of the targets to boost the commercialization of this device is by lowering the current high operating temperatures (800 – 1000 °C) to intermediate temperatures (IT) (500 – 800 °C). However, at reduced temperatures, the device has performed a high interfacial polarization resistance (R_p) at cathode|electrolyte interface. In this work, strontium-doped lanthanum cobaltite, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSCO64) was chosen as cathode material as it has shown a good performance at IT. The LSCO64 powder was synthesized via polymeric complexing method using metal nitrate salts as precursor material. The calcined LSCO64 powder was transformed to cathode slurries which have been prepared using four different electrode binders namely ethyl cellulose (EC), polyvinyl alcohol (PVA), polyvinyl butyral (PVB) and polyvinyl pyrrolidone (PVP). These slurries were separately painted on pellet surfaces of yttrium-doped barium cerate-zirconate, $\text{BaCe}_{0.54}\text{Zr}_{0.36}\text{Y}_{0.1}\text{O}_{2.95}$ (BCZY64) electrolyte to produce half-cell of LSCO64|BCZY64|LSCO64. The obtained powders and fabricated half-cells were respectively characterized by employing Thermogravimetric Analysis (TGA), Fourier Transform Infrared (FTIR) Spectroscopy, X-ray Diffractometry (XRD), Scanning Electron Microscopy/Electron Dispersive X-ray Spectrometry (SEM/EDS) and Electrochemical Impedance Spectroscopy (EIS). The TGA results showed the lowest total weight loss, W_{TL} (~86%) and the lowest thermal decomposition temperature, T_{td} (600 °C) were recorded at heating rates of 5 °C min⁻¹ and 2 °C min⁻¹, accordingly. The XRD and SEM analysis revealed that a single perovskite phase of LSCO64 with small particle size (~130 – 260 nm), respectively was obtained at calcination temperature of 800 °C with heating/cooling rate of 5 °C min⁻¹. The presence or absence of carbonyl compounds at ~1600 cm⁻¹ and ~860 cm⁻¹ and metal-oxide (M-O) bond at 700 – 400 cm⁻¹ after heat treatment was proven by the FTIR. SEM micrographs at cross-sectional view of the prepared cells with different electrode binders showed there were three areas corresponding to the LSCO64, BCZY64 and LSCO64|BCZY64 interface with or without crack and/or hole. Among all the electrode binders, only PVP has aided to form a good contact between the LSCO64 and BCZY64 with no formation of crack and/or hole at LSCO64|BCZY64 interface region. The elemental atomic percentage of elements at the interface region of the cell prepared with the PVP such as lanthanum, La (3.16%), barium, Ba (9.52%) and cerium, Ce (6.02%) was detected by EDS. The EIS results showed the R_p values in terms of area specific resistance (ASR) decreased as temperatures increased from 400 °C to 800 °C. A relatively low R_p of 0.48 Ω cm² at 700 °C indicates that the LSCO64 is a promising cathode material for the PCFC at intermediate temperatures.

ACKNOWLEDGEMENT

In the name of Allah S.W.T. The Most Gracious and Most Merciful.

Assalamualaikum W.B.T.

Alhamdulillah and thanks to God because of His bless, I finally succeed to complete the given task in a proper and an organize manner. I offer my sincerest gratitude to my beloved and helpful supervisor and co-supervisor, Dr. Nafisah Osman and Assoc. Prof. Dr. Hj Mohd Azlan Mohd Ishak, respectively who have been everything I could ask for in an advisor. Their guidance, encouragement, patience, knowledge and enthusiasm for research have truly helped me make it this far. Thank you for opening my eyes to the world of research in academia by giving me a huge opportunity to conduct a research on “Synthesis and Characterization of Lanthanum Cobaltite Based Cathode Material for Potential Application in Proton Conducting Fuel Cell”. Thank you also for allowing me the space to work on my own way.

In my daily work, I have been blessed with friendly, helpful and cheerful group of friends. I appreciate all of them especially my laboratory-mates who work in Material Science Laboratory of Universiti Teknologi MARA (UiTM) Perlis for all their time and support throughout the duration of my study. My heartfelt thank also goes to all laboratory staffs of UiTM Perlis, UiTM Shah Alam and Universiti Malaysia Perlis (UniMAP) for allowing me to use the instruments and facilities provided in their laboratories.

Besides that, I would like to thank UiTM especially the Research Management Institute (RMI) and Faculty of Applied Sciences for providing me financial support to conduct my research (Dana Kecemerlangan RMI/ST/Dana 5/3/Dst (461/2011)) and to attend few international conferences. My deepest thank also goes to the Ministry of Education (MOE) of Malaysia for the Research Acculturation Collaborative Effort (RACE) grant.

I would also want to give my special respect and appreciation to my adored family members who are always love, care and support me. They are the precious people in my life who have brought me up to this level. In addition, thank you too to all the people around and the parties who have involved in this research neither directly nor indirectly. Without them, this thesis would not have materialized.

Thank you very much!

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF STUDY

Intermediate temperature (500 – 800 °C) solid oxide fuel cell (IT-SOFC) is deemed to be one of the most promising future clean power generations as it offers low or zero pollutant emission, high energy conversion efficiency (~80%) and excellent fuel flexibility. In comparison to the high temperature (800 – 1000 °C) SOFC, IT-SOFC including proton conducting fuel cell (PCFC) has a variety of advantages. It shortens time taken for startup/shutdown, extends operation lifetime and minimizes thermal and sealing degradation. Besides that, it also broadens materials selection and able to solve other materials problems in a cost-effective manner. Unfortunately, by reducing the operating temperatures (from high to intermediate temperatures), interfacial polarization resistance (R_p) at electrode|electrolyte interface (particularly at cathode|electrolyte site) increases and become the main factor that limiting and affecting the IT-SOFC performance.

In order to overcome the increment of the R_p , several solutions have been attempted such as the used of mixed ionic-electronic conductor (MIEC) based on perovskite-type oxide materials that able to work at intermediate temperature range (Sunarso et al., 2008; Shao, Tao, Wang, Xu, & Wang, 2009; Tao et al., 2009) and optimize the synthesis parameters in producing the required materials (Tao, Shao, Wang, & Wang, 2008; Nityanand, Nalin, Rajkumar, & Chandra, 2011; Shao, Zhou, & Zhu, 2012). In addition, selection of additives to optimize cathode structure and cathode contact on electrolyte at cathode|electrolyte interface (cell fabrication technique) could also help to decrease the R_p (Qiang et al., 2009).

Currently, ceramic MIEC perovskite-type oxide materials with formula of $\text{Ln}_{1-x}\text{A}_x\text{MO}_{3-\delta}$ (Ln = La, Sm, Nd; A = Ca, Sr, Ba; M = Co, Fe, Ni) are widely used as cathode materials for IT-SOFC to replace conventional lanthanum strontium manganite, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM) cathode materials. The LSM which usually works