UNIVERSITI TEKNOLOGI MARA

SYNTHESIS AND CHARACTERIZATION OF CERATE-ZIRCONATE CERAMIC POWDER PREPARED BY SUPERCRITICAL FLUIDS, SOL-GEL AND SOL-GEL ASSISTED SUPERCRITICAL FLUIDS METHODS: A COMPARISON STUDY

NAJWA 'ADNI IBARAHIM

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

Faculty of Applied Sciences

August 2017

ABSTRACT

In this study, the $BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$ (BCZY) powder was synthesized by a high pressure – high temperature (HP-HT) batch wise reactor system using supercritical fluids (SCFs) method. The sample was subjected to the sub-, super- and post-critical conditions in the reactor and treated with ethanol as a reaction media. As a comparison, the BCZY powder was also prepared via a sol-gel (SG) and sol-gel assisted supercritical fluids (SGSCFs) methods. All the reaction products from these methods were dried at 200 – 325 °C and then calcined at 1100 °C for 10 h. The resulting powders were characterized by Thermogravimetric Analyzer/Differential Scanning Calorimeter (TGA/DSC), Fourier Transform Infrared (FTIR) Spectroscopy, X-Ray Diffractometer (XRD), Particle Size Analyzer (PSA), Density Analysis and Scanning Electron Microscopy (SEM). For samples prepared with SCFs method, TGA thermogram of the dried powders showed three stages of weight loss which corroborated by four or five exothermic peaks as shown in derivative thermogravimetric (DTG) signal. A complete thermal decomposition for all of the samples was accomplished at ~977 °C for 2 h. The samples prepared at post-critical condition showed the lowest weight loss compared to others. At calcination temperature of 1100 °C, the remaining carbonate species was found in the samples as proven by the FTIR analysis. The calcined samples did not exhibit any crystalline peak associated to BCZY compound (JCPDS card 89-2485) due to secondary phases of $BaZrO_3$, $BaCeO_3$, BaO and CeO_2 were detected in the XRD spectrum. Particle size of the calcined powders was in the range of 0.5 to 1.5 μm as measured by PSA. From the six samples prepared by SCFs method, the optimum result was found for the one prepared at P = 11 MPa and T = 300 °C. This sample was denoted as S2 and its properties were compared to those prepared by SG (denoted as S1) and SGSCFs (denoted as S3). TGA result showed that the thermal decomposition temperature for S2 was higher than S1 and S3. The traces of carbonate residue and secondary phase were observed for both S2 and S3 powder due to the incomplete combustion of intermediate compounds. However, S1 shown highly crystalline powder and its XRD peaks were matched to the standard BCZY compound (JCPDS card 89-2485). All the major peaks can be indexed to the index miller of (110), (111), (200), (210), (220) and (310). The particle size was in the range of 0.2 to 0.5 μm for the first group of agglomerate and 0.7 to 0.8 μm for the second group of agglomerate. S1 showed the highest powder density with 99 % dense compared to S1 (95 %) and S2 (93 %). In terms of morphology as observed by SEM, the powder of S1 was in spherical shape, S2 was in cubic-like shape and S3 showed a mixture of spherical and rod-like shape. Since the BCZY powder produced using SG method have shown high phase purity and high quality of grain properties it is recommended that the powder are used as electrolyte material for electrochemical devices.

ACKNOWLEDGEMENT

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

Alhamdulillah and many thanks to Allah for His bless, I finally finished the long awaited journey. Many thanks to both of my .parents En. Ibarahim Ismail and Pn. . for their prayers, patience and financial support. Not forgetting to my siblings Najwa Nadhirah, Muhammad Najmi, and Najwa Khairani.

I offer my sincerest gratitude to my beloved supervisor and co-supervisor, Assoc. Prof. Dr. Nafisah Osman and Assoc. Prof. Dr. Hj Mohd Azlan Mohd Ishak, respectively who have been everything I could ask for in an advisor. Many thanks to Dr. Nafisah Osman for her patience, guidance, enthusiasm and giving me the huge opportunity to be a part of research group in Solid-State Ionic field.

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 (60/2011)) and to attend few international conferences. My deepest thank also goes to the Ministry of Higher Education (MOE) of Malaysia for the Research Articulation Grant Scheme (RAGS) and Exploratory Research Grant Scheme (ERGS).

My heartfelt thanks to my laboratory-mates who work in Material Science Laboratory of Universiti Teknologi MARA (UiTM) Perlis for all their time and support; Syafkeena, Syazana, Abdullah, Nabilah, Ana, and my postgraduate working team Syafinaz, Rifhan, Iziana, Syaza, Syikin, Anis, Asma, Anjila, Kak Aein, Yani, Ain and many more. Last but not least, to my pillar support Muhamad Hanif.

My deepest appreciation also to UiTM Perlis, UiTM Shah Alam and Universiti Malaysia Perlis (UniMAP) for instrumentation and facilities provided in their laboratories. In addition, thank you to all the people who have involved in this research neither directly nor indirectly. This Master journey taught me that you can not change the world with your study alone but you can change yourself to be better.

Thank you.

TABLE OF CONTENTS

CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND OF STUDY

State of the art proton-conducting ceramics are one of the promising materials for future energy and environment preservation. The electrolyte based on proton conductor for example barium zirconate oxide ($BaZrO_3$) is widely been used in solid oxide fuel cells (SOFCs) that are couple with lanthanum strontium cobalt oxide ($La_{1-x}Sr_xCoO_3$) for the cathode and nickle-cermets for the anode [1]. The electrolyte has to be stable under oxidizing atmosphere prevailing at the cathode and under reducing atmosphere at the anode. By doping with divalent or trivalent oxides oxygen vacancies are created which give rise to protonic conductivity.

A study on the nature and use of high temperature proton (H^+) conductor perovskite based was started by Iwahara et al. (1981) for the past 36 years [2]. Up to now, these high proton conductors proved their potential as an electrolyte and have been numerously exploited in applications such as fuel cells, sensors and hydrogen separation. The well-known ceramic perovskite-type oxides (PTOs) that being employed are $SrZrO_3$, $SrCeO_3$, $BaCeO_3$, $BaZrO_3$, and $CaZrO_3$; due to their good protonic or proton conduction in atmosphere containing hydrogen and/or water vapour at elevated temperatures [6–9]. The required properties of the electrolyte depend on their application. For the application of sensors, the electrolyte needs to exhibit high chemical and mechanical properties. Work by Iwahara et al. (1995) reported that doped $CaZrO_3$ was used as electrolyte material in hydrogen sensor for molten metal owing to its good mechanical and chemical stability [7]. On the other hand, for proton conducting fuel cell (PCFC) the electrolyte needs to have good mechanical and chemical stability as well as high ionic conductivity ($> 10^{-1}$ Scm^{-1} at 800 °C).

It is common to believe that the electrolyte has to be pure ionic conductors. Electrolyte conductor based on cerate for example $BaCeO_3$ is an interesting candidate of SOFCs due to its high ionic conductivity. However, cerates are not stable