Impedance Study on NiO-BaCe$_{0.54}$Zr$_{0.36}$Y$_{0.1}$O$_{2.95}$ Composite Anode for Proton-Conducting Fuel Cell.

S M Senari$^1$, N Osman$^2$ and A M M Jani$^3$

$^1$ Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
$^2$ Faculty of Applied Sciences, Universiti Teknologi MARA, 02600 Arau, Perlis, Malaysia
$^3$ Faculty of Applied Sciences, Universiti Teknologi MARA, 35400 Tapah, Perak, Malaysia

fisha@perlis.uitm.edu.my

Abstract. A composite anode of NiO-BaCe$_{0.54}$Zr$_{0.36}$Y$_{0.1}$O$_{2.95}$ (NiO-BCZY) has been proposed as a suitable anode material for the application in a proton-conducting fuel cell (PCFC). A single anode supported cell with the structure of NiO-BCZY|BCZY|La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ (LSCF) was fabricated by a dry-pressing assisted with spin-coating technique. The cell was sintered in air at 1400°C for 3 hours with a heating rate of 10°C/min. Complex impedance measurements were conducted in H$_2$:N$_2$ (10%:90%) as the fuel and air as the oxidant after the cell was reduced in H$_2$:N$_2$ (10%:90%) for 7 hours. The typical impedance pattern of the single cell was resolved using an equivalent circuit consisting two parallel RQ elements connecting in series. The cell showed an overall resistance of 17.34 to 69.53 Ω cm$^2$ at a temperature ranging from 550 and 700°C. The SEM cross-sectional view of the single cell after impedance measurement showed a good adhesion between the three layers with characteristic dense electrolyte layer and a unique porous electrode. The experimental results indicated that NiO-BaCe$_{0.54}$Zr$_{0.36}$Y$_{0.1}$O$_{2.95}$ is a suitable candidate for anode material for the PCFC application.

1. Introduction
During past several years, solid oxide fuel cell (SOFC) becomes one of the clean energy generation systems that give a great impact to the research world. It can directly convert the chemical energy from fuel such as hydrogen and ethanol to the electrical energy effectively. Besides, it is one type of fuel cell which consists of a solid electrolyte and offers high energy conversion with minimum emissions, simple and environmental safety. The net conversion efficiencies reached as high as 70% had been recognized in the SOFC/gas turbine hybrid system which offers efficient electricity generation [1]. Unfortunately, when it comes to the commercial application, there are still some limitations such as expensive system, high operating temperature, poor stability and easily sulfur-poisoned in the longtime run [2,3]. Nowadays, the urgent demand for board commercialization focused on reducing the working temperature to intermediate/lower temperatures which can benefit both fabrication and stability.

Proton conducting fuel cell (PCFC) has a unique property of proton conductor from the anode to the cathode, while producing water at the cathode side which avoids fuel dilution problems compared to the conventional oxygen-ion conducting electrolytes [4]. This factor extends practical applications and leads to an important increase in overall cell efficiency. In addition, PCFC potentially lowering the cost and enhancing the durability and reliability of SOFC systems due to the lower activation
energy and relatively high proton conductivity at intermediate temperatures attainable from proton conducting oxides enables reduced operating temperature PCFC.

Among the different types of solid-state proton conductors, the most extensively studied materials are simple perovskite structured ABO3-based proton conductors. A stable and effective perovskite type barium cerate with co-doping of yttrium and zirconium (BCZY) was developed by Zuo et al. Its exhibited both adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of conditions relevant to fuel cell operation [5]. BaCe0.54Zr0.36Y0.1O2.95 has been proven for good electrolyte and showed the best performance among other composition of BCZY [6] and the most promising anode for PCFCs is Ni-BCZY [7]. Nickel is still the best choice for PCFC anode due to its high electrical conductivity, high catalytic activities and low cost. In this work, the combination of Ni and BaCe0.54Zr0.36Y0.1O2.95 based material to form composite anode of NiO-BCZY is expected to enhance the fuel oxidation at the PCFC anode. In all cases, a thin electrolyte layer is needed to reduce the resistance losses and to yield improved cell performance at reduced operating temperatures. So, in order to get a thin layer of electrolyte, anode-supported cells fabricated by a dry-pressing assisted spin coating technique have been chosen. In this study, the microstructure and electrochemical performance of the cell were examined.

2. Experimental

2.1 Material Preparation and Powder Synthesis.
Precursors used for the electrolyte, anode and cathode were metal nitrate salts. Powder samples of BaCe0.54Zr0.36Y0.1O2.95 (BCZY) compound were prepared by a sol-gel method as reported elsewhere [8]. Pure BCZY compound was finally obtained after calcination at 1100°C for 10 h in air. A stoichiometric amounts of Ba(NO3)2 (99%, ACROS), Ce(NO3)3.6H2O (99.5%, ACROS), Zr(NO3)2O.xH2O (99.5%, ACROS), Y(NO3)3.5H2O (99.9%, Aldrich) and Ni(NO3)2.6H2O (99%, ACROS) were used as starting materials for anode preparation. The nitrate salts were dissolved in deionized water. As a complexing agent, citric acid was then added to the solution with molar ratios of soluble metal ions: citric acid of 1:1.5. Ammonium hydroxide, NH4OH (25%, HmbG) was added to the solution to adjust the pH value around 7. The resulting solution was slowly evaporated on a hot plate at 120°C. During the process, the browning gas (known as NOx) was released and a dark brown gel obtained. The gel was dried at 325°C in a furnace to yield black flakes. Then the sample was calcined at 1100°C with heating a rate of 10°C min⁻¹ for 6 h to produce NiO-BCZY powders. LSCF cathode powder was synthesized by a sol-gel method as well [9].

2.2 Fabrication of Single Cell.
A button cell with a configuration of porous NiO-BCZY anode supported |BCZY electrolyte| LSCF cathode was fabricated by a dry-pressing assisted spin-coating technique. The NiO-BCZY powder was formed into disc pellet with a diameter of 13mm at a pressure 74 MPa. Then loose BCZY powder was uniformly distributed onto the anode substrate, co-pressed at 221 MPa and co-sintered at two-step sintering profile to obtain a dense BCZY electrolyte layer. Fine LSCF powder was mixed thoroughly together with an ethylcellulose-terpineol binder, to prepare the cathode slurry. The cathode slurry was then spin-coated on the BCZY electrolyte layer and was sintered at 950°C for 2 h in an air to form a tri-layer cell NiO-BCZY|BCZY|LSCF. Finally, Pt paste was painted onto the cathode layer as a current collector.

2.3 Characterization and Electrochemical Measurement.
The microstructure of the anode-supported single cell was investigated by a benchtop scanning electron microscope. The electrochemical impedance of the single cell was measured from 500-700°C at 50°C intervals by a lab-designed electrochemical system, with H2:N2 (10%:90%) as the fuel and stagnant air as the oxidant after the cell were reduced in H2:N2 (10%:90%) for 7 hours. The electrochemical impedance spectra were measured by ZIVE SP2 Electrochemical Workstation (ZIVELAB WonATech) connected to a personal computer. ZIVE® Smart Manager™ software was
used for data acquisitions and analysis. The impedance spectra were obtained in the frequency range of 1 MHz to 0.1 Hz with ten steps per decade and signal amplitude of 10mV. The impedance spectra obtained were analyzed using ZMAN software.

3. Results and Discussion
Figure 1 presents the typical scanning electron microscopy (SEM) images of (a) cross-section view of the single cell and (b) higher magnification image of an interface of anode and electrolyte. Good adhesion is obtained between the three layers of cathode, electrolyte and anode. A dense electrolyte is observed in Figure 1(d), indicating that dry-pressing is as an effective way to fabricate dense electrolyte layer. Both the anode and cathode have the porous microstructure and no delaminations are found at the interfaces between electrodes and electrolyte.

![Figure 1. SEM image of (a) cross-section view of single cell, (b) higher magnification image of interface of anode and electrolyte, (c) anode surface and (d) electrolyte surface.](image-url)

Electrochemical impedance analysis was performed for the anode-supported single cell by the lab-designed electrochemical system. Figure 2 shows the impedance spectra of the anode-supported single cell and the equivalent circuit (inset) used to separate all the responses. The typical impedance pattern of the anode-supported single cell was resolved using an equivalent circuit consisting two parallel RQ elements connecting in series. The intercept with the real axis at high frequencies represents the resistance of electrolyte (ohmic resistance), whereas the difference between the high-frequency and low-frequency intercepts with the real axis represents the sum of the electrode polarization resistances.
of the cell. The total cell resistances which represent the polarization and ohmic resistances as a function of the temperature were shown in Figure 3. Both the polarization and ohmic resistances decrease as the temperature increase, while the polarization resistances decrease more rapidly, typically from 56.00 Ω cm$^2$ at 550°C to 7.77 Ω cm$^2$ at 700°C. The values of ohmic resistances for the anode-supported single cell at 550, 600, 650 and 700°C were 13.53, 12.01, 10.95 and 9.57 Ωcm$^2$ respectively. It should be noted that the values of polarization resistances and ohmic resistances are higher than values in previously reported work [10,11]. The high ohmic resistance might be contributed from the different fabrication technique as well as the thickness of the electrolyte layer. The thicker electrolyte layer gives a higher ohmic resistance. These results of fuel cell tests could be enhanced by further investigation on the thickness of electrolyte and the fabrication technique. Anyhow, these results confirmed the functionality of proton conducting cermet anodes NiO–BCZY.

![Figure 2. Impedance spectra of the anode-supported single cell under open circuit condition at 550-700°C.](image-url)
Figure 3. The total cell resistances, polarization resistances, and ohmic resistances (Rohm) obtained from the impedance spectra at different temperatures.

4. Conclusion
In this study, NiO-BCZY composite was fabricated and applied as an anode in PCFC with BCZY as the electrolyte. With a structure of NiO-BCZY|BCZY|LSCF, an excellent adhesion was obtained between the three layers with individual dense electrolyte layer and a unique porous electrode. The typical impedance pattern of the single cell was resolved using an equivalent circuit consisting two parallel RQ elements connecting in series. An increase in operating temperature from 550 to 700°C, results in the polarization resistance of the single cell decreasing from 56.00 to 7.77 Ωcm². The results indicate the NiO-BCZY composite to be a promising candidate anode for PCFC.

Acknowledgements
The authors would like to thank the Minister of Higher Education for the FRGS 1/2017 funding and Universiti Teknologi MARA for the facilities support.

References
[1] Shao Z P and Haile S M 2004 A High-Performance Cathode for The Next Generation of Solid Oxide Fuel Cells, Nat. 431 170-3
[2] Lee J G, Park J H and Shul Y G 2014 Tailoring Gadolinium-Doped Ceria-Based Solid Oxide Fuel Cells to Achieve 2 W cm⁻² at 550 °C, Nat. Commun. 5 4045
[3] Steele B C H and Heinzel A 2001 Materials for Fuel-Cell Technologies, Nature 414 345–352
[4] Wang S, Zhang L, Yang Z, Fang S, Brinkman K and Chen F 2012 Two-step Co-Sintering Method to Fabricate Anode-Supported Ba₃Ca₁.18Nb₁.82O₉-δ Proton-Conducting Solid Oxide Fuel Cell, J. Power Sources 215 221-6
[5] Zuo C, Lee T H, Dorris S E, Balachandran U, and Liu M 2006 Composite Ni-Ba(Zr₀.₁Ce₀.₇Y₀.₂)O₃ Membrane for Hydrogen Separation. J. Power Sources 159(2) 1291–5
[6] Othman N W, Osman N, Ramli A and Saffian D S 2016 Microstructure and Electrical Characterization of Ba(Ce,Zr)O₃ Solid Solution prepared by a TSS Method J.Solid St Sci. & Technol. Lett. 17(1) 61-6
[7] Lim D K, Kim J H, Chavan A U, Lee T R, Yoo Y S and Song S J 2016 Performance of Proton-conducting Ceramic-electrolyte Fuel Cell with BZCY40 electrolyte and BSCF5582 cathode Ceram. Int. 42 (3) 3776–3785

[8] Abdullah N A, Osman N, Hasan S and Hassan O H 2012 Chelating Agents Role on Thermal Characteristics and Phase Formation of Modified Cerate-Zirconate via Sol-gel Synthesis Route, Int. J. Electrochem. Sci. 7 9401–9

[9] Ismail I, Osman N and Md Jani A.M 2016 Tailoring The Microstructure of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-α} Cathode Material: The Role of Dispersing Agent. J. Sol-Gel Sci. Technol. 1–8

[10] Liu M, Gao J, Liu X and Meng G 2011. High Performance of Anode Supported BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} (BCZY) Electrolyte Cell for IT-SOFC. Int. J. Hydrog. Energy. 36 13741-5

[11] Yuan R H, He W, Zhang C, Ni M and Leung M K H 2017 Cobalt Free SrFe_{0.95}Nb_{0.05}O_{3-δ} Cathode Material for Proton-Conducting Solid Oxide Fuel Cells with BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} Electrolyte Mater. Lett. 200 75-8