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Original Article

$Ba_{0.08}Y_{0.04}Co_{2.5}Fe_{0.09}O_{4-\delta}$ cathode deposited on GDC_{10} electrolyte by spray pyrolysis technique

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Abstract

The properties of a thin-film cathode BYCF ($Ba_{0.08}Y_{0.04}Co_{2.5}Fe_{0.09}O_{4-\delta}$) layer prepared by spray pyrolysis between dense electrolyte (GDC_{10}) pellets were studied. This paper presents the method for depositing the cathode material on the electrolyte, as well as its microstructure, electrical conductivity and AC impedance characteristics. The results showed that a layer with 20 µm thickness and high porosity was obtained using the spray pyrolysis technique. The microstructure showed excellent adherence on the electrolyte. The electrical conductivity and AC impedance measurements indicated these properties are a good candidate for cathode material with spray pyrolysis.

Keywords: spray pyrolysis, BYCF cathode, GDC_{10}, BYCF-GDC_{10}

1. Introduction

A Solid Oxide Fuel Cell (SOFC) is an electro-chemical conversion device that produces electricity from oxidising a fuel without CO_2. The advantages of SOFCs include high efficiency, long-term stability, fuel flexibility and low emissions. Thus, SOFCs are promising as a fuel cell that may become the first commercially used fuel cell in the future as it is relatively inexpensive compared to other kinds of fuel cells. Furthermore, the SOFCs operating temperature can be reduced 400-800 ºC from 1000 ºC (Stambouli & Traversa, 2002).

The highly active cathode of solid oxide fuel cells are generally composed of three functional layers: electro-chemically active layers with fine grain size and good interfacial bonding, diffusion layers with large open porosity, and current collecting layers with high-electrical conductivity. The microstructure of the cathode and composition are used to increase electrochemical and mechanical performance. Although traditional wet ceramic processing is capable of fabricating these complex electrodes layer by layer, the total process time and cost are high, leading to repeated coating, drying, and firing (Hui *et al.*, 2007; Patil, 1999).

The spray pyrolysis (SP) technique (Cheng, *et al.* 2017; Kumar, *et al.* 2017) is a simple alternative processing technique used to fabricate graded or multi-layered structures by adjusting the relative flow rates of different feed-stocks and spraying parameters during coating. The ceramic composition is deposited at a high temperature of 800ºC. Functionally-graded cathodes with a thickness of 10-80 µm have been demonstrated by spray pyrolysis. The spraying conditions are ideally selected to deposit five to six layers of cathode, with each layer of approximately 10 µm in thickness. The layers fabricated by PS reveal high porosity and are crack-free. PS exhibits excellent adhesion between interfaces (Princivalle & Djurado, 2008; Suda *et al.*, 2006), which shows very low polarisation resistance. Further, electrical resistivity of the cathode is decreased dramatically at low temperature.

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In this research, we focus on the use of PS to fabricate symmetrical cells BYCF|GDC_{10}|BYCF composite as a cathode for SOFCs. Preliminary work examined the preparation and deposition of the two materials, BYCF (Suklueng, M., Yoong, V. N., Peter, H. I. N. G., & Ming, L. C., 2014) and GDC_{10}. The BYCF cathode composite is deposited on both sides of a GDC_{10} electrolyte pellet. The microstructure, electrical conductivity and electrochemical impedance spectroscopy (EIS) of the deposited layers were studied.

2. Materials and Methods

2.1 Material preparation

The composition BYCF ($Ba_{0.08}Y_{0.04}Co_{2.5}Fe_{0.09}O_{4-\delta}$) was prepared using powders obtained from Sigma Aldrich Laborchemikalian GmbH, with 5% BaO, 3% Fe_2O_3, 2% Y_2O_3 and 90% Co_2O_3 by weight persent. The powder mixture was grinded for 1 hour and then mixed with distilled water including 10 % PVA (Polyvinyl alcohol) by weight %. The mixture was milled with cylindrical alumina balls inserted using a horizontal ball mill machine for 24 hours. The mixture was dried in an oven at 150ºC. After drying, the composition BYCF was grinded for 4 hours to ensure homogeneity of particle sizes. Subsequently, calcination was carried out at 1000ºC with a heating rate of 30ºC/min for 5 hours. The composition was again grinded for 5 hours and sieved with 150 meshes. X-ray powder diffraction (WI-RES-XRD-001, X'Pert MPD, PHILIPS, Netherlands) was conducted to identify the material's crystal structure at an elevated temperature. The module was heated from 40 ºC to 800 ºC at a heating rate of 10ºC/min. 2θ was scanned at the rate of 1.0 s/step with a step size of 0.02º from 10º to 60º. After taking measurements, the temperature was reduced to 40ºC at a cooling rate of 10ºC/min.

Commercial GDC_{10} (10% gadolinium doped ceria) powders (Fuel Cell Materials, USA) with a surface area of 10-14 m^2/g and particle size of 0.1-0.4 µm were pressed to form 15 mm diameter and 0.9 mm thick pellets. These dense electrolyte pellets were then sintered at 1400ºC for 5 hours at a heating rate of 30ºC/min.

2.2 Preparation of symmetrical cells

The experimental set-up to deposit thin layer of BYCF on electrolyte pellet, using the spray pyrolysis technique, is shown in Figure 1. The spray gun was operated at 120 psi air pressure and the nozzle was set up at a height of 20 cm with a 16 cm spraying diameter. The pellet was placed on a stainless steel substrate. The temperature was increased to 450ºC, which resulted in a crack-free thin layer. For the purpose of thermal expansion matching, the spray precursor solution was made of the prepared BYCF doped 20% GDC_{10} by weight % and mixed with distilled water in 50:50 vol %. The solution was ball milled for 24 hours and then sprayed on the GDC_{10} pellet for 10 seconds. This pellet with BYCF doped 20% GDC_{10} deposited (half cell) was then sintered at 1100ºC. After sintering, BYCF doped 20% GDC_{10} was again deposited on the other side of the pellet, which became a symmetrical cell and was again sintered at 1100ºC.

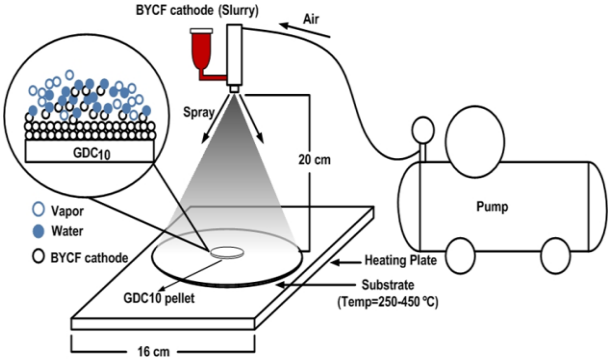

Figure 1. Principle of the spray pyrolysis process.

2.3 Microstructure characterization

The spray pyrolysis thin layer microstructure co-sintered at 1100ºC was studied by SEM (Oxford Instrument, Model: 7378). Figure 2 shows SEM micrographs of the fractured surface of the BYCF (x7520) and BYCF-GDC_{10} interface (x993). The microstructure showed a highly porous cathode and dense electrolyte (97% > theoretical density). As seen in Figure 2b, the cathode had good bonding and continuous contact with the dense electrolyte pellet. The adhesion of the cathode to electrolyte was excellent, which suggested similar thermal expansion between the two materials. The thickness of the deposited BYCF was found to be 20 µm.

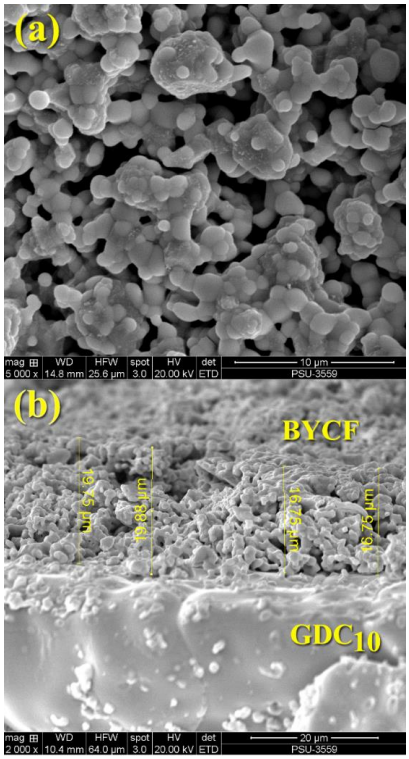

Figure 2. SEM micrographs: (a) fractured surface of BYCF+20% GDC_{10} and (b) BYCF-GDC_{10} interfaces.

2.4 Electrical conductivity

The conductivity of the pellet was measured using the four-probe dc technique (Mitsubishi, LORESTA-GX). Platinum (Pt) electrodes were used as probes. Pt paste was printed in between the Pt electrode and the pellet. All electrodes were pressed on the pellet to ensure good contact between electrode and pellet. Then, the pellet with Pt electrode was placed in an in-house made furnace and heated from 40ºC to 800ºC at a heating rate of 10ºC/min. Conductivity was measured at 20ºC/step.

2.5 Electrochemical characterization of the symmetrical cell

Polarisation and ohmic resistance were investigated by means of electrochemical impedance spectroscopy using a symmetrical cell. For impedance measurement and Nyquist plots, impedance spectroscopy was carried out using an Analogue Device EVAL-AD5933/34EBZ impedance analyser at the frequency range of 1 Hz - 1 MHz at 1Vrms signal amplitude over temperatures of 800°C to 30°C with 50°C steps. The pellet was held in a purpose-built sample holder, as seen in Figure 3, then fitted within our in-house build furnace. For measurements, 30ml/minute air as oxidant was applied. The AC current output was measured with excitation potentials of 50 mV over a frequency range of 0.1 Hz to 1 MHz at a temperature range from 550 to 800ºC and a heating rate of 10ºC/min.

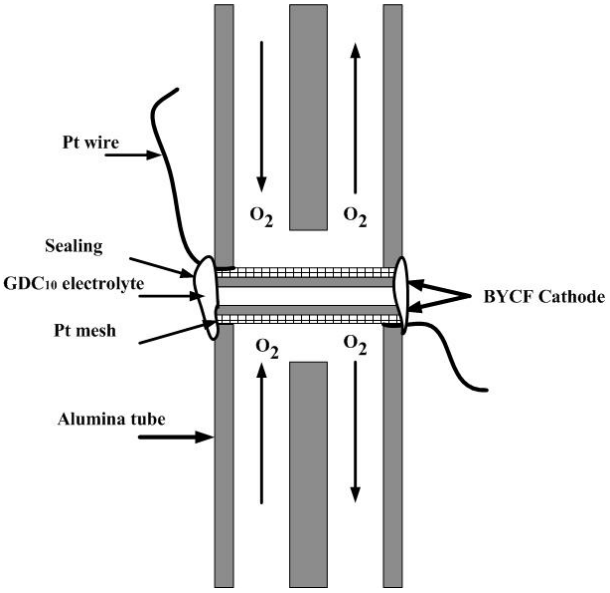

Figure 3. Sample holder for AC impedance spectroscopy measurement.

3. Results and Discussion

3.1 Crystallography

The X-ray diffraction pattern of $Ba_{0.08}Y_{0.04}Co_{2.5}Fe_{0.09}O_{4-\delta}$ at room temperature is shown in Figure 4. It can be seen that there are peaks corresponding to $Ba_{0.95}FeY_{0.05}O_{2.81}$ (barium iron yttrium oxide), $Fe_{0.98}O$ (iron oxide), $BaCo_2Fe_{16}O_{27}$ (barium cobalt iron oxide) and $Ba_2Co_2Fe_{12}O_{22}$ (barium cobalt iron oxide). These are the four major composites that can be decomposed to form the perovskite phase. $Ba_{0.95}FeY_{0.05}O_{2.81}$ compound exhibited cubic crystal system as reported for similar compositions (Liu *et al.*, 2011). As mentioned in (Liu *et al.*, 2011). a cubic system contributed to an increase in both electrical and oxygen conductivity. This suggests that the electrical conductivity was mainly contributed by $Ba_{0.95}FeY_{0.05}O_{2.81}$ composition. $Fe_{0.98}O$ and $BaCo_2Fe_{16}O_{27}$ showed a hexagonal structure. $Ba_2Co_2Fe_{12}O_{22}$ is Y-type ferrites with a rhombohedral crystal system. The electrical conductivity of ferrites was due to two possible conduction mechanisms, namely n-type electron conduction and p-type holes conduction. The electrons produce polarisation by local displacement in the opposite way to the electric field, while the holes produce polarisation by local displacement in the way of the external electric field *(Tang et al.*, 2015).

Figure 5 shows the XRD pattern of the composites at elevated temperatures. The XRD pattern reveals a very strong cobalt oxalate as the major phase, which was contributed by $BaCo_2Fe_{16}O_{27}$ and $Ba_2Co_2Fe_{12}O_{22}$. Upon heating at 700-800ºC, the $Ba_2Co_2Fe_{12}O_{22}$ phase in the range of 20-30º for 2 theta (degree) disappeared, showing weak diffrac-tion reflections and indicating some disorder in the crystalline or amorphous structure, which may affect the electrical properties of the cathode.

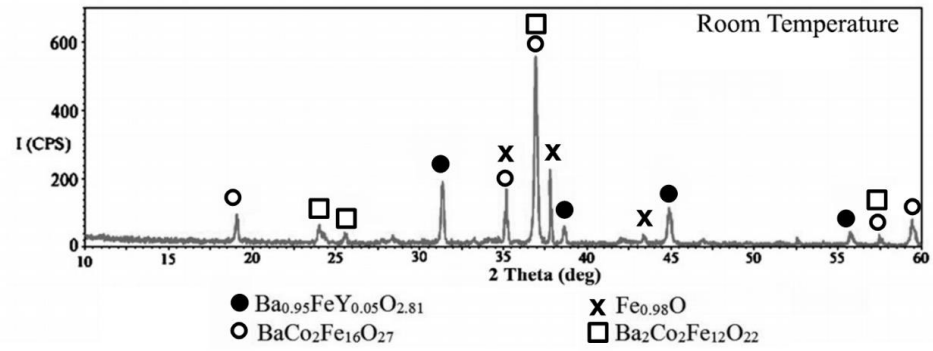

Figure 4. XRD pattern for $Ba_{0.08}Y_{0.04}Co_{2.5}Fe_{0.09}O_{4-\delta}$ at room temperature.

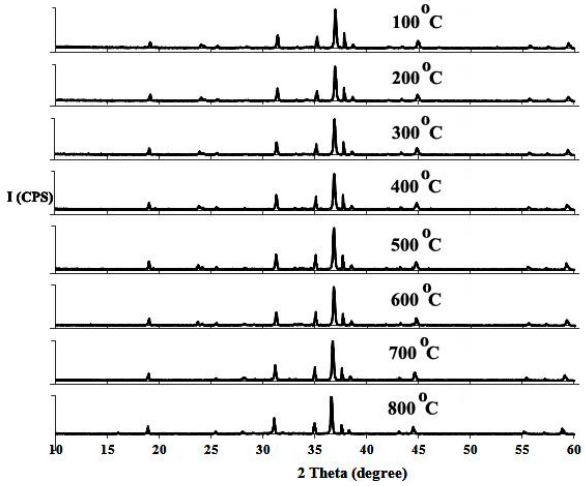

Figure 5. XRD patterns of $Ba_{0.08}Y_{0.04}Co_{2.5}Fe_{0.09}O_{4-\delta}$ at elevated temperatures.

3.2 DC conductivity

The temperature dependence of electrical conductivity for BYCF is shown in Figure 6. It is clearly seen that the relationship between conductivity and temperature is non-linear. Its conductivity increased slightly until 600ºC and then increased dramatically at 800ºC. Also, the activation energy was gradually increased from 37.394 kJ/mol at 300ºC to 95.007 kJ/mol at 450ºC and then decreased slightly from 73.160 kJ/mol at 660ºC. After that, the activation energy increased enthusiastically from 312.330 kJ/mol at 800ºC. The deposition of spray pyrolysis can produced the thin film and high porosity for the cathode that produced low resistivity and low activation energy (Uekita *et al.*, 1982) These properties brilliantly generate electricity for fuel cells.

3.3 AC impedance

The experimental impedance spectra measured for the cells at 650-770ºC in air is shown in Figure 7. The non-intercept on the real axis at high frequencies corresponds to the ohmic resistance (R_o) of the cell involved in the contribution of the electrolyte. Irrespective of the symmetric cell configuration, an increase in operating temperature, from 650 to 770ºC, tends to shift the position of the arc towards high frequency, thereby minimising the contribution of ohmic resistance on the overall cell. From the figure, it is clearly seen that ohmic resistance decreased as the operating temperature increased. A similar characteristic is observed in (Mukhopadhyay *et al.*, 2013), where the overall decrease in cell resistance is caused primarily by acceleration in oxygen reduction reaction of the cathode at higher temperature. Ohmic resistance as low as 4.15 Ωcm^2 was observed at an operating temperature of 770ºC.

The segment between low and high frequency cut-offs on the real impedance axis was used to study the polarisation resistances (R_p) of the cells. According to (Mukhopadhyay *et al.*, 2013), polarisation resistance corresponds to the sum of the polarisation resistances of the two electrodes of the cell. The lowest R_p was 1.01 Ωcm^2 at 770ºC. Therefore, the thin film from the spray pyrolysis technique adhered well between the cathode and electrolyte as well as can reduce AC impedance (Kim *et al.*, 2017) and high ionic conductivity.

4. Conclusions

Usually, thin films used for deposition in SOFC technology need strong connections between the cathode and electrolyte, as well as high porosity and low resistivity. However, the deposition also needs to be cost effective and have an easy procedure for fabrication. The spray pyrolysis technique in the current study used an air pump for injecting the slurry (50vol% BYCF doped GDC_{10}+50vol% distilled water) and spraying on the sample (GDC_{10} electrolyte) to put on the hot plate (200-450ºC). The spray is coated on the sample and evaporates the water, which means only the thin film BYCF is deposited on the sample. Spray pyrolysis is employed to deposit BYCF cathodes on GDC_{10} electrolytes. The microstructure of the deposited BYCF showed excellent adherence on the electrolyte. It also exhibited high porosity for cathode thicknesses under 20µm. Conductivity is decreased dramatically at 91.11-1252 Scm^2 at 660-800 ºC, respectively. Low AC impedance, R_p =1.01Ωcm^2 and R_o=4.15 Ωcm^2, was observed at 770ºC. Therefore, the BYCF cathode using the spray pyrolysis technique incorporates potential for fabricating thin layer SOFC cathodes.

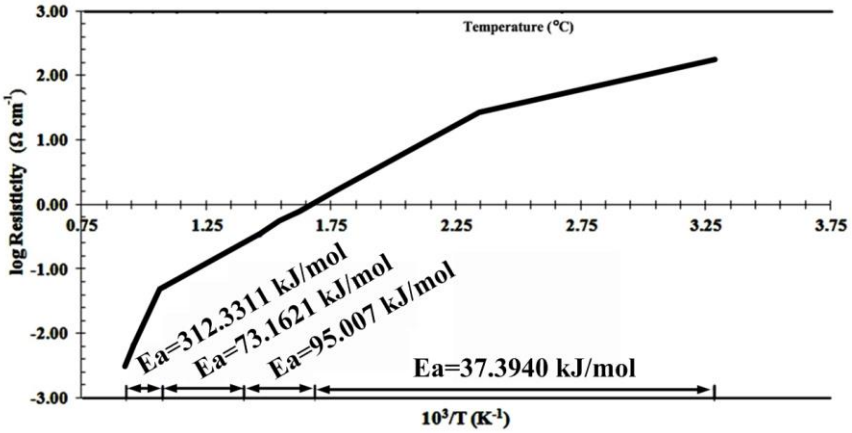

Figure 6. Electrical conductivity of the $Ba_{0.08}Y_{0.04}Co_{2.5}Fe_{0.09}O_{4-\delta}$ composite at different temperatures.

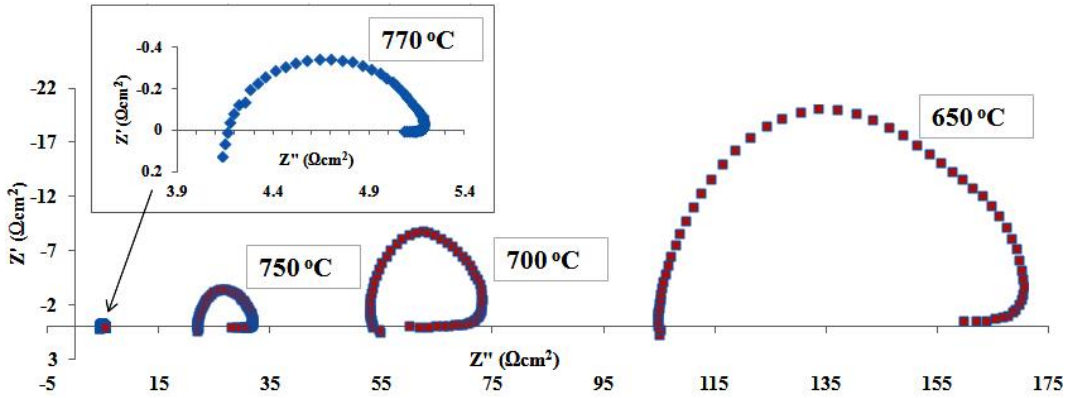

Figure 7. AC impedances spectra of symmetrical cells (BYCF|GDC_{10}|BYCF) at temperature 650, 700, 750 and 770 °C.

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