

Synthesis of Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-δ} composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells

Afzal, Muhammad; Raza, Rizwan; Du, Shangfeng; Lima, Raquel Bohn; Zhu, Bin

DOI:

[10.1016/j.electacta.2015.07.183](https://doi.org/10.1016/j.electacta.2015.07.183)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Afzal, M, Raza, R, Du, S, Lima, RB & Zhu, B 2015, 'Synthesis of Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-δ} composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells', *Electrochimica Acta*, vol. 178, pp. 385-391. <https://doi.org/10.1016/j.electacta.2015.07.183>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

Eligibility for repository: Checked on 21/08/2015

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

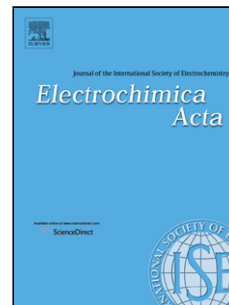
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Accepted Manuscript

Title: Synthesis of $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells

Author: Muhammad Afzal Rizwan Raza Shangfeng Du
Raquel Bohn Lima Bin Zhu



PII: S0013-4686(15)30249-8
DOI: <http://dx.doi.org/doi:10.1016/j.electacta.2015.07.183>
Reference: EA 25465

To appear in: *Electrochimica Acta*

Received date: 12-1-2015
Revised date: 23-7-2015
Accepted date: 31-7-2015

Please cite this article as: Muhammad Afzal, Rizwan Raza, Shangfeng Du, Raquel Bohn Lima, Bin Zhu, Synthesis of $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells, *Electrochimica Acta* <http://dx.doi.org/10.1016/j.electacta.2015.07.183>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Elsevier Editorial System(tm) for Electrochimica Acta
Manuscript Draft

Manuscript Number: SGS15-013R4

Title: Synthesis of Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-δ} composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells

Article Type: Research Paper

Keywords: Composite cathode, perovskite oxide, BCCF37, low temperature, SOFC.

Corresponding Author: Dr. Bin Zhu, PhD

Corresponding Author's Institution: School of Industrial Engineering and Management KTH Royal Institute of Technology

First Author: Muhammad Afzal, PhD Student

Order of Authors: Muhammad Afzal, PhD Student; Rizwan Raza, PhD; Shangfeng Du, PhD; Raquel Bohn Lima, PhD; Bin Zhu, PhD

Abstract: This work reports a new composite Ba_xCa_{1-x}Co_yFe_{1-y}O_{3-δ} (BCCF) cathode material for advanced and low temperature solid oxide fuel cells (SOFCs). The BCCF-based composite material was synthesized by sol gel method and investigated as a catalytic cathode for low temperature (LT) SOFCs. XRD analysis of the as-prepared material revealed the dominating BCCF perovskite structure as the main phase accompanied with cobalt and calcium oxides as the secondary phases resulting into an overall composite structure. Structure and morphology of the sample was observed by Field Emission Scanning Electron Microscope (FE-SEM). In particular, the Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-δ} (BCCF37) showed a maximum conductivity of 143 S cm⁻¹ in air at 550 °C measured by DC 4 probe method. The BCCF at the optimized composition exhibited much higher electrical conductivities than the commercial Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) perovskite cathode material. A maximum power density of 325 mW cm⁻² at 550 °C is achieved for the ceria-carbonate electrolyte fuel cell with BCCF37 as the cathode material.

Dated: 23-07-2015



**KTH Industrial Engineering
and Management**

Dear editor,

A revised manuscript of Synthesis of $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells, is hereby submitted for review again for consideration to be published in "Electrochimica Acta journal". We have carefully considered and addressed reviewers' comments and made corresponding changes and English style revision throughout the paper.

Thank you for consideration!

Sincerely Yours,

Bin Zhu

Bin Zhu, PhD

Head of Fuel cell and Solar cell group in KTH, Sweden

Chair professor in Hubei University appointed by Hubei 100 overseas talent program

Visiting professor in Aalto University, Finland

+46736006613 (mobile) , +4687907403 (Office), email: binzhu@kth.se

Bin Zhu, Associate Professor (Docent)	Visiting Address	Telephone	Telefax
Department of Energy Technology	Brinellvägen 68	Nat. 08-790 7403	+ 46(08)204161
The Royal Institute of Technology		Int. + 46 8-790 7403	email: binzhu@kth.se
S-100 44 Stockholm, Sweden			

Response to reviewers

First of all, we'd like to express our sincere thanks to Reviewers for their efforts made to our manuscript with very good comments for us to improve it again. According to the comments, we have made careful considerations and changes by supplying also in more details and highlighted in the revised manuscript.

Reviewers' comments:

Reviewer #2: Major problems were removed in the revised version of the manuscript. However, several small inconsistencies and mistakes should be eliminated before publication:

Comment # 1: In the abstract we still find the claim on the nanocomposite approach ("...based on nanocomposite approach..."). As accepted by the authors in their reply "As few parts of manuscript were written by coauthors as well so the term nanocomposite material was written due to a mistake". So we have no reason to keep this either in the abstract or in the introduction section as if related to the present results or approach.

Response: “Based on nanocomposite approach” has now been deleted from the abstract. Similarly, in introduction part, such words have also been removed.

Comment # 2: The sentence "There might be another possibility" e.g., the unidentified perovskite composition", which needs future study" seems inadequate in a manuscript. What should be claimed is that irrespective of the exact composition, the presence of a BCCF-related perovskite phase might also provide the observed performance as for other sub-stoichiometric electrode materials with the same structure often used in SOFCs.

Response: Thanks for additional sentence! The sentence "There might be another possibility" e.g., the unidentified perovskite composition", which needs future study", is now deleted from results section and suggested sentence has been added “irrespective of the exact composition, the presence of a BCCF-related perovskite phase might also provide the observed performance as for other sub-stoichiometric electrode materials with the same structure often used in SOFCs.” This sentence is mentioned in the red color in the results section of manuscript.

Comment # 3: Reactions (1), (2) and (3) are so standard that there is no reason to include them.

Response: Yes, according to the comment, we have removed the reactions (1), (2) and (3) from the manuscript.

Comment # 4: In the text we find one reference to "Error! Reference source not found". Please correct this.

Response: Now the reference is written in correct format as JCPDS 75-0426 and is also mentioned in red color in the text. Please follow the link below to find the source.

<http://www.sciencedirect.com/science/article/pii/S1388248111003225>

Comment # 5: The English style needs revision.

Response: The English style is revised throughout the paper.

Synthesis of $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells

Muhammad Afzal^{*a}, Rizwan Raza^b, Shangfeng Du^c, Raquel Bohn Lima^d, Bin Zhu^{*a, e}

^a Department of Energy Technology, Royal Institute of Technology (KTH), 100 44, Stockholm, Sweden

^b Department of Physics, COMSATS Institute of Information Technology, 54000 Lahore, Pakistan

^c School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B152TT, UK

^d *Fibre and Polymer Science*, Chemical Science and Engineering, Royal Institute of Technology (KTH), 10044 Stockholm, Sweden

^e Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Faculty of Physics and Electronic Technology, Hubei University, Wuhan 430062, P.R. China

ABSTRACT

This work reports a new composite $\text{Ba}_x\text{Ca}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (BCCF) cathode material for advanced and low temperature solid oxide fuel cells (SOFCs). The BCCF-based composite material was synthesized by sol gel method and investigated as a catalytic cathode for low temperature (LT) SOFCs. XRD analysis of the as-prepared material revealed the dominating BCCF perovskite structure as the **main phase** accompanied with cobalt and calcium oxides as **the secondary phases resulting into an overall composite structure**. Structure and morphology of the sample was observed by Field Emission Scanning Electron Microscope (FE-SEM). In particular, the $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BCCF37) showed a maximum conductivity of 143 S cm^{-1} in air at $550 \text{ }^\circ\text{C}$ measured by DC 4 probe method. The BCCF at the optimized composition exhibited much higher electrical conductivities than the commercial $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) perovskite cathode material. A maximum power density of 325 mW cm^{-2} at $550 \text{ }^\circ\text{C}$ is achieved for the ceria-carbonate electrolyte fuel cell with BCCF37 as the cathode material.

Keywords: Composite cathode, perovskite oxide, BCCF37, low temperature, SOFC.

*Corresponding Author: email addresses: binzhu@kth.se, afzalm@kth.se, Tel: +4687907403, Fax: +468204161

1. Introduction

1
2
3 Solid oxide fuel cell (SOFC) is one of the most promising types of fuel cells with a high
4 energy efficiency and multi-fuel operating flexibility [1]. In a typical SOFC as a sustainable
5 energy conversion technology [2], an operating temperature between 800-1000 °C is usually
6 required to control the cathode over-potential but the high temperature (HT) causes
7 mechanical and chemical compatibility issues for a number of materials used for different
8 components in fuel cell systems [3]. Furthermore, at such a high temperature, the cell
9 degradation is fast and excessive maintenance costs are required. All of these together limit
10 the successful commercialization of this technology [4]. To overcome these issues, in recent
11 years, SOFCs operated at a low or intermediate temperature within 500-800°C have attracted
12 much more attention [5]. A lower operating temperature can suppress the degradation of
13 device components and increase the range of material selection, thus enhancing the system
14 durability and reducing the manufacturing cost. However, the decrease in operating
15 temperature also declines the electrode kinetics resulting in an increase in the interfacial
16 polarization resistance for the oxygen reduction reaction (ORR) at the SOFC cathodes. To
17 address these issues, cathode materials with high catalytic activities for ORR as well as good
18 electronic and ionic conductivities at relatively low temperatures are highly favorable.

19
20 Extensive efforts have been devoted to the development of low temperature (300-600°C)
21 SOFCs using ceria-based composite electrolyte materials originated by Zhu's pioneer work,
22 and many new methods have been introduced to develop high performance materials for
23 LTSOFC technology [3]. A key issue in SOFCs is the poor catalytic activity of cathode
24 materials causing slow oxygen reduction and the lower ionic conductivity at low
25 temperatures. Perovskite cathode materials containing cobaltite have been discovered as good
26 candidates as cathode materials in low temperature (LT) or intermediate temperature (IT)
27 SOFCs due to their excellent electrode catalytic functions, high electronic and ionic mixed

28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

conductivities at a relative low temperature. The most commonly used cathode material, lanthanum manganite; LaMnO_3 (LMO) for HT-SOFCs is not practically possible due to its poor catalytic activity and lower ionic conductivity at low temperatures [5].

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (LSCF) perovskite has been reported as cathode material in LTSOFCs but with a low cell performance [6]. $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (BSCF), in particular $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ has also attracted much attention due to its high conductivity as well as a good catalytic activity and oxygen ions transportation [5]. Similarly, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ has also been investigated advantageous for low temperature SOFC operations [8]. Despite of the fact, BSCF has high conductivity and catalytic activity, however, at the high manufacturing and operating temperatures, the diffusion of Sr contaminates the electrolyte thus causing a severe degradation in cell performance [9]- [11]. Furthermore, the high price of Strontium (Sr) with the high content in BSCF also makes it not a real commercialized material. It is extremely important to investigate the economical materials that have an excellent performance in LTSOFCs and also are acceptable for commercialization.

Replacement of Sr by the cheaper Calcium (Ca) being an A-site dopant has been reported as a possible solution [9]. Recently, use of composite materials for electrolytes and perovskite cathode materials has been demonstrated as a practical approach to address the faced challenges for LT and IT (400-700 °C) fuel cells and has attracted huge efforts to develop high performance devices [12].

In this work, we demonstrate $\text{Ba}_x\text{Ca}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (BCCF) ($x = 0.3$; $y = 0.8$) with composite structure prepared by an auto-combustion process as a potential cathode material for LTSOFCs. Calcium is used to replace Strontium at A-site in ABO_3 structure formula for perovskite materials, and some secondary phases are also created in addition to the perovskite main phase to enhance the conductivity. The optimized composition was identified at $x = 0.3$ and $y = 0.8$ and tested in the temperature range of 300-600 °C. The conductivity of the as-

1 prepared material is measured and compared with the commercially available cathode
2 material BSCF and its potential as cathode candidate for LTSOFCs is discussed based on the
3
4 excellent performance achieved in fuel cell tests.
5
6

7 **2. Experimental**

8 **2.1. Materials and preparations**

9
10 Sol gel method was adapted to synthesis the composite $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BCCF37).
11
12 Stoichiometric amounts of the nitrate salts, $\text{Ba}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
13
14 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved into de-ionized water with a molar ratio of Ba:Ca:Co:Fe =
15
16 0.3:0.7:0.8:0.2 to prepare the starting solution. Another appropriate composition
17
18 $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BCCF91) with the molar ratio of Ba:Ca:Co:Fe = 0.9:0.1:0.8:0.2 was
19
20 also prepared in the same way. All chemicals were used as received from Sigma-Aldrich
21
22 (USA) without any further purification.
23
24
25
26
27
28
29
30
31

32 The details for the preparation of both BCCF composites are illustrated in the flow chart
33
34 shown in Fig.1. Solution A of chemical compounds of Ba:Ca in molar ratios 0.3:0.7 for
35
36 BCCF37 and 0.9:0.1 for BCCF91, respectively, and solution B of Co:Fe in molar ratios of
37
38 0.8:0.2 were prepared separately. Solutions A and B are then mixed together to make a 100 ml
39
40 combined aqueous solution C for each composition. After stirring for 30 minutes, an
41
42 appropriate amount (10% by weight) of citric acid was added into solution C and continued
43
44 stirring for 2 hours at 80 °C. As a result, a gel type material was obtained. The auto-
45
46 combustion process was employed by firing the material at 250°C in air for combustion to
47
48 obtain ash like powder material. The ash was then ground and sintered at 1000 °C for 9 hours
49
50 to get the proper composite structure of the material. The heating and the cooling rates were 2
51
52 °C min⁻¹.
53
54
55
56
57
58
59

60 **2.2. Compaction into pellets**

61
62
63
64
65

1 The $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ powder was compacted into pellets with a diameter of 13 mm and
2 2.4 mm in thickness under 300 MPa pressure for 5-10 minutes. The pellets were further
3
4 sintered at 600 °C for 1 hour before testing. Silver paste was coated on both sides of the
5
6 pellets as the current collector for the conductivity measurement. The conductivities of as-
7
8 prepared materials $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and the commercial BSCF
9
10 were measured and compared. The thickness and active area of $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ pellet
11
12 were taken as 2.6 mm and 0.64 cm² respectively with 13 mm diameter under 300 MPa.
13
14
15
16

17 **2.3. X-ray diffraction of as-prepared cathode**

18
19
20
21 A number of studies for mixed perovskite conductors have reported the existence of
22
23 secondary phases but mostly have been left unidentified [15]. Most of the cathode materials in
24
25 SOFCs are composite in nature because no single material can fulfill every requirement for
26
27 fuel cell activities [18]. Composite cathodes provide high catalytic property; activation of the
28
29 reaction sites takes place due to the addition of ionic conductors in the material structure for
30
31 improvement in oxide ion transportation [19]. The phase structure of sintered as-prepared
32
33 BCCF37 was examined at room temperature by X-ray diffractometer using Cu-K α radiation
34
35 at 45 kV and 35 mA.
36
37
38
39

40 **2.4. Thermogravimetric Analysis**

41
42
43 Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA 851°
44
45 (Greifense, Switzerland) from 30 to 1100 °C with a heating rate of 10 °C min⁻¹ and a constant
46
47 air flow (50 ml min⁻¹).
48
49
50

51 **2.5. Fourier Transform Infrared Spectroscopy (FTIR)**

52
53
54
55 Fourier transform infrared spectroscopy (FTIR) analysis was performed on a Mid-infrared
56
57 spectra Perkin-Elmer Spectrum 2000 FTIR spectrometer (Waltham, MA, USA) equipped with
58
59 an ATR system, Spectra MKII Golden Gate (Creekstone Ridge, GA, USA). The region
60
61
62
63
64
65

1 between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans was recorded. The
2 software Spectrum (Molecular Spectroscopy) version 3.02.01 (Perkin Elmer Instrument) was
3
4 used to process the spectra.
5
6

7 **2.6. FE-SEM characterization**

8
9
10 Microstructures analysis of the as prepared BCCF37 and BCCF91 samples was studied with a
11 field emission scanning electron microscope (FE-SEM, JEOL 7000F) operating at 20 kV.
12
13
14
15

16 **2.7. Conductivity measurements**

17
18 The resistance R in ohms of the samples was measured in air atmosphere as a function of
19
20 temperature from room temperature to 550 °C by DC 4 probe technique. The heating rate of
21
22 the tubular furnace was 5 °C min^{-1} . Data for electrical conductivity was taken after equal
23
24 intervals of 50 °C.
25
26
27
28

29 **2.8. Fuel cell fabrication and testing**

30
31 The as-prepared BCCF37 powder was mixed with sodium carbonate-samarium doped ceria
32
33 (NSDC) at a volume ratio of 1:1 and calcined at 600 °C for 2 hours. The resulting material
34
35 was further used as the cathode component in fuel cell devices and tested in the “Fuel Cell
36
37 Rig” for I-V measurements.
38
39
40
41
42

43
44 The fuel cell devices with 3-layers assembly consisting of anode, electrolyte and cathode were
45
46 fabricated. Nickel foam was used as a substrate and current collector before anode layer then
47
48 NiO (nickel oxide) was spread homogeneously as anode layer which was prepared by the heat
49
50 treatment of nickel carbonate basic at 700 °C, a thin layer of NSDC (samarium doped ceria)
51
52 was used as an electrolyte prepared according to the literature [20]. The ratio between
53
54 samarium (Sm) and cerium (Ce) was considered 1: 4 (20%: 80%) for this electrolyte. 0.02
55
56 mole of cerium nitrate $\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ (Sigma Aldrich, USA) was prepared in 0.5L distilled
57
58
59
60
61
62
63
64
65

1 water and stirred for 2 minutes at a frequency of 800 rev/min at 80 °C. 0.005 mole of

2 $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, USA) was added into the cerium nitrate solution and

3
4 continued stirring with the same speed for further 30 minutes to get samarium doped ceria

5
6 (SDC) solution to be used in all samples.

7
8
9 Solution of sodium carbonate (Na_2CO_3) was added drop wise into the SDC solution and was

10
11 stirred for 2 minutes. The molar ratio between SDC and Na_2CO_3 was taken 1:2. After stirring

12
13 for 30 minutes, the solution was filtered to get precipitates. The wet precipitates were dried

14
15 in an oven at 150°C for 2 hours. Then the powdered precipitates were sintered in a furnace

16
17 at 800°C for 4 hours. After sintering, the nanocomposite of the electrolyte was obtained

18
19 which was grinded for further use. BCCF37 as cathode material was spread over the

20
21 electrolyte surface. Cathode was painted with silver paste as the current collector. These three

22
23 components of fuel cells, with electrolyte sandwiched between the anode and the cathode

24
25 were assembled layer by layer. This structure with anode supported was uniaxial pressed

26
27 under a pressure of 250 MPa with a diameter of 13 mm and about 1 mm in thickness

28
29 consisting of 0.60 mm anode, 0.15 mm electrolyte and 0.25 mm cathode. The fabricated fuel

30
31 cells with an active area of 0.64 cm² were tested between 500 to 600 °C. Hydrogen and air

32
33 were used at the anode and the cathode side, respectively, with a flow rate of ca. 110 ml min⁻¹

34
35 at 1 atm.

36 37 38 39 40 41 42 43 44 45 **3. Results and discussion**

46 47 48 **3.1. XRD analysis of BCCF37 material**

49
50
51 Fig. 2 shows XRD pattern of the synthesized BCCF37 material. By comparing this pattern

52
53 with the perovskite material peaks of BSCF, it is obvious that the perovskite is the main

54
55 phase, dominating in the pattern with the diffraction peaks at $2\theta = 21^\circ, 30^\circ, 38^\circ, 50^\circ,$

56
57
58
59
60
61
62
63
64
65 $56^\circ, 65^\circ, 74^\circ$ and 78° . These peaks observed are identified as barium iron oxide as JCPDS 75-

0426. In addition, some traces of cobalt oxide are observed at diffraction angles 27.5° , 33° , 33.5° , 52.2° , 52.7° , 64.5° , 65.4° , 68.8° , and calcium oxide also exists besides the perovskite phase at 26° , 31° , 48° , 58° , 61.5° , 73.5° . The analysis indicates that as-prepared BCCF37 is actually the composite-type material due to cobalt and calcium oxides present as secondary phases. The presence of the secondary phases additional to the perovskite phase turns the material into its composite nature, which enhances the properties of the BCCF37 material with higher conductivity and cell performance which is in agreement with the composite type materials for intermediate temperatures fuel cells [12]. Since the observed cobalt oxide and calcium oxides peaks co-exist with the perovskite phase, therefore the enhancement may be due to the composite effect. Irrespective of the exact composition, the presence of a BCCF-related perovskite phase might also provide the observed performance as for other sub-stoichiometric electrode materials with the same structure often used in SOFCs. The average sizes of the crystallite of each phase are calculated from each phase peaks. The grain size of the cubic perovskite, cubic calcium oxide and tetragonal cobalt oxide are 36, 42 and 39 nm, respectively, which is comparable to the reported work [8].

3.2. TGA Analysis of BCCF37

Thermogravimetric analysis (TGA) was widely used to investigate the decomposition of the as-prepared material. Fig. 3 shows the TGA profiles of BCCF37 in air atmosphere performed with a heating rate of $10^\circ\text{C}/\text{min}$. The weight of BCCF37 can be observed as decreased gradually with increase in temperature. However, weight loss below 200°C is due to the emission of adsorbed water molecules, the initial loss and subsequent gain of weight are clearly caused by evolution of oxygen and adsorption of CO_2 , respectively. The second weight loss is mainly due to the CO_2 emission from the oxides. Continued heating from ~ 400 to 1100°C resulted in a steady weight loss, ranging from 0.8% to 4.5%. According to the literature, the mixed Ba and Ca perovskite oxides adsorb CO_2 easily but other perovskite

1 oxides excluding either Ba or Ca cannot adsorb significantly [9],[21]. From TGA results,
2 actually a slight weight increases at temperatures between 450-620°C. This may be due to
3 adsorption and interaction of CO₂ molecules with the as-prepared material; it causes the
4 formation of some carbonates due to reaction kinetics of CaO-CO₂ [22]. The carbonate phases
5 as secondary phases show even better property of the material in electrolytes, which have
6 been extensively studied in various ceria-carbonate composite electrolytes for low and
7 intermediate SOFCs, typically such a work is reported by Zhu et al [23], the barium and
8 calcium carbonate composites with the ceria create an excellent material property and the fuel
9 cell performance. In case of cathode material BCCF37, carbonate phases are not identified in
10 XRD pattern because material was sintered at 1000 °C therefore no carbonates remained at
11 such high temperature and material was converted into its oxide phase. So it means that CO₂
12 adsorbed at lower temperatures is automatically emitted from as-prepared BCCF37 material at
13 high temperatures during sintering process as observed in TGA analysis and secondary phases
14 of CaO and CoO were identified therefore is considered that these CaO and CoO phases have
15 contributed to the perovskite phase for enhanced conductivity of BCCF37 and overall cell
16 performance.

39 3.3. FTIR Analysis

40 The FTIR spectrum of BCCF37 is shown in Fig. 4. IR shows that CO₂ band is due to the
41 adsorption of CO₂ from air atmosphere which is agreed with the above TGA results. The
42 analysis further confirms that the as-prepared material is a composite type. In the FTIR
43 spectrum, three peaks at 1430, 857 and 695 cm⁻¹ can be assigned to the vibrational band of
44 the carbonic acid radical [9]. The peaks located at 692 and 857 cm⁻¹ (barium carbonate), and
45 712 and 872 cm⁻¹ (calcium carbonate) correspond to the in-plane bending modes of CO₃⁻²,
46 and the strong peaks at 1444 cm⁻¹ (barium carbonate) and 1432 cm⁻¹ (calcium carbonate) are
47 the C–O stretching mode of carbonate [24]. It should be noted that from the TGA and FTIR
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 analysis, though there is such possibility to form carbonate phases in air CO₂-containing
2 atmosphere at lower temperatures, which are converted into oxide phases at high temperature
3
4 (1000°C) therefore could not be detected by XRD.
5
6
7
8
9

10 **3.4. Microstructure analysis of the as-prepared BCCF37**

11
12 The sintered BCCF37 cathode material is examined by SEM analysis to investigate the
13 microstructure as shown in Fig. 5a-c. The particle size varies in a certain range from 80 nm to
14
15 200 nm and the agglomeration of the particles can be widely observed. According to the
16
17 literature, porosity level increases with Ca content that tends to cause agglomeration giving
18
19 rise to the coarsening in the morphology **Error! Reference source not found.** Hence the
20
21 composite material particles have been observed in the shape of clusters due to nano-particles
22
23 agglomeration. It is demonstrated that the conductivity can be improved by decreasing the
24
25 particles size with NANOCOFC approach [25]5, [26] which can be realized by carefully
26
27 adjusting the synthesizing method. For the composition BCCF91, Fig. 5d shows its SEM
28
29 image. Morphology of this composition shows that particle size varies in a range of 200-500
30
31 nm, particles distribution is uniform only in a certain region. It has been observed that
32
33 BCCF37 has better conductivity due to smaller particle size as compared to BCCF91.
34
35
36
37
38
39
40
41
42

43 **3.5. Conductivity Measurement**

44
45 The conductivities of the BCCF37, BCCF91 and the commercial BSCF samples were
46
47 measured by DC 4 probe method and the conductivity results versus 1000/T are plotted in
48
49 Fig. 6. The conductivity increases rapidly with temperature. BCCF37 shows the highest
50
51 electronic conductivity of 143 S cm⁻¹ at 550°C. BCCF91 and BSCF show the maximum
52
53 conductivity of 25 and 33 S cm⁻¹ at 550 °C. Although the as-prepared BCCF based material
54
55 has mixed conductivity (both electronic and ionic), the measured value is referred to as
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

electronic because it is dominant over ionic conductivity. The later measurements, with two probe method did not show too much difference and also the two-probe results can be easily repeated. Comparison of both BCCF compositions and the commercial BSCF shows that BCCF37 has the better conductivity than that of BCCF91 and commercially available BSCF. This indicates that BCCF37 is very useful for LTSOFCs operated between 500-600°C. This is a novel material and is expected to have higher conductivity by using other better methods for preparation e.g. co-precipitation. It has also been observed that BCCF37 has no distinct material degradation during the conductivity and fuel cell testing which shows that the material is thermally and electrically useful. This demonstrates the high potential of BCCF37 as the candidate for cathode materials in LTSOFC applications

3.6. Fuel Cell Performance

Three-component configuration SOFC was fabricated with the anode (NiO-NSDC), electrolyte (NSDC) and cathode (BCCF37-NSDC) using as-prepared BCCF37 composite cathode. Fig. 7 displays the obtained I-V (current density-voltage) and I-P (current density-power density) curves tested at 550 °C. A maximum power density of 325 mW cm⁻² is achieved at 550°C. Composite anode provided the catalytic activity to hydrogen oxidation, uniform distribution of ions and electrons for promoting the electrode electrochemical reactions, and the electrolyte provides conduction as well as transportation of oxide ions to realize the electricity generation.

Fuel cell was operated with uniform performance for ten hours in the Lab. The BCCF37-based cathode in the cell operation shows a very good catalytic activity. In addition, by changing the composition of the mixed anode and cathode, the fuel cell performance can still be improved.

1 The electrochemistry of cell reactions occurring in the low temperatures conventional SOFC
2 using as-prepared material for the cathode is in line with our earlier work [27]. It can be
3
4 expected with even better performance by controlling the size of the particles. In addition, by
5
6 changing the composition of the mixed anode and cathode, the fuel cell performance can still
7
8 be improved. The ionic conductivity of the electrolyte material allows oxide ions to travel
9
10 through the electrolyte to complete the fuel cell redox reactions and electricity generation.
11
12
13
14

15 **4. Conclusion**

16
17
18 $Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF37) based material was prepared by a sol-gel method followed
19
20 by an auto-combustion process. The as-prepared materials showed the composite feature with
21
22 more than **one phase** included, where *perovskite was the dominated phase in the structure*
23
24 *accompanied with trace of oxide phases, i.e. calcium and cobalt oxides as secondary phases.*
25
26
27

28 BCCF37 displayed a conductivity of 143 S cm^{-1} at $550 \text{ }^\circ\text{C}$ which was much higher than 25 S
29
30 cm^{-1} of the $Ba_{0.9}Ca_{0.1}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF91) and 33 S cm^{-1} in case of the commercial BSCF
31
32 cathode materials. A maximum power density of 325 mW cm^{-2} was achieved for the LT-
33
34 SOFC operated at 550°C using the as-prepared BCCF37 material as the cathode. The results
35
36 achieved from this work have demonstrated the new opportunity to use novel BCCF37
37
38 composite materials for the high performance LT-SOFCs. In particular, considering the high
39
40 conductivity, we may expect even higher fuel cell performances by the continuous
41
42 improvement of fuel cell technologies with other compatible materials and combinations in
43
44 anode and electrolyte components.
45
46
47
48
49
50

51 **Acknowledgements**

52
53
54
55 This work was supported by European Commission through FP7 TriSOFC project, (Contract
56
57 No. TRISOFC-03042012), the Swedish Research Council (VR, Contract No. 621-2011-4983)
58
59 and the Swedish Agency for Innovation Systems (VINNOVA, Contract No. P36545-1). The
60
61
62
63
64
65

1 leading author would like to thank Professor Peter Lund in Aalto University Finland and
2 Associate Professor Muhammet Toprak at KTH for their valuable discussions, suggestions
3 and cooperation during working in their labs.
4
5

6 **References**

- 7
8
9 [1] J. Schoonman, *Solid State Ionics* 157 (2003) 319-326.
10
11 [2] A. G. Olabi, *Energy* 77 (2014) 1-5.
12
13 [3] B. Zhu, *J. Power Sources* 114 (2003) 1-9.
14
15 [4] B. C. H. Steele, *Solid State Ionics* 94 (1997) 239-248.
16
17 [5] N.Q.Minh, T. Takahashi, Elsevier Amsterdam (1995).
18
19 [6] D. Ding, M. Gong, C. Xu, N. Baxter, Y. Li, J. Zondlo, K. Gerdes, X. Liu, *J. Power Sources*
20
21 196 (2011) 2551–2557.
22
23 [7] M. Shah, P. W. Voorhees, S. A. Barnett, *Solid State Ionics* 187 (2011) 64-67.
24
25 [8] M. S. Toprak, M. Darab, G. E. Syvertsen, M. Muhammed, *Inter. J. Hydrogen Energy* 35
26
27 (2010) 9448-9454.
28
29 [9] P. Ciambelli, S. Cimino, L. Lissi, M. Faticanti, G. Minelli, I. Pettiti, P. Porta, *Appl. Catal. B*
30
31 33 (2001) 191-193.
32
33 [10] F. Tietz , A. Mai , D. Stöver, *Solid State Ionics* 179 (2008) 1507-1509.
34
35 [11] E. Bucher , W. Sitte , F. Klauser , E. Bertel, *Solid State Ionics* 191 (2011) 61-67.
36
37 [12] X. Chen, Z. Tao, G. Hou, N. Xu, Q. Zhang, *Electrochimica Acta* 165 (2015) 142-148.
38
39 [13] L. Zhang, R. Lan, S. Tao, *Inter. J. Hydrogen Energy* 38 (2013) 16546-16551.
40
41 [14] L. Zhang, R. Lan, A. Kraft, S. Tao, *Electrochem. Comm.* 13 (2011) 582-585.
42
43 [15] N. Ortiz-Vitoriano, I. R. de Larramendi, S. N. Cook, M. Burriel, A. Aguadero, J. A.
44
45 Kilner, T. Rojo, *Adv. Funct. Mater.* 23 (2013) 5131-5139.
46
47 [16] H. Ming-Hao, M. V. Madhava Rao, T. Dah-Shyang, *Materials Chemistry and Physics*
48
49 101 (2007) 297-302.
50
51 [17] T. Nagai, W. Ito, *Solid State Ionics* 259 (2014) 21-28.
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
- [18] M. Mogensen, N. M. Sammes, G. A. Tompsett, *Solid State Ionics* 129 (2000) 63-94.
- [19] C. Sun, R. Hui, J. Roller, J. *Solid State Electrochem.* 14 (2009) 1125-1144.
- [20] Y. Zhao, X. Ding-Bang, H. Qin, F. Gao, H. Inui, B. Zhu, *Inter. J. Hydrogen Energy* 37 (2012) 19351-19356.
- [21] K. Nomura, Y. Ujihira, T. Hayakawa, K. Takehira, *Appl. Catal.* 137 (1996) 25–36.
- [22] A. Biasin, C. U. Segre, G. Salviulo, F. Zorzi, M. Strumendo, *Chemical Engineering Science* 127 (2015) 13-24.
- [23] B. Zhu, X. Liu, P. Zhou, X. Yang, Z. Zhu, W. Zhu, *Electrochem. Comm.* 3 (2001) 566-571.
- [24] H. Patra, S. K. Rault, S. K. Pratihari, S. Bhattacharya, *Powder Technology* 209 (2011) 98-104.
- [25] B. Zhu, X. Liu, Z. Zhu, R. Ljungberg, *Inter. J. Hydrogen Energy* 33 (2008) 3385-3392.
- [26] B. Zhu, P. Lund, R. Raza, J. Patakangas, H. Qiu-An, L. Fan, M. Singh, *Nano Energy* 2 (2013) 1179-1185.
- [27] B. Zhu, R. Raza, H. Qin, L. Fan, *J. Power Sources* 196 (2011) 6362–6365.

List of figures

Fig. 1. Sol gel synthesis process for BCCF

Fig. 2. XRD pattern for sample BCCF37

Fig. 3. Thermogravimetric analysis (TGA) curve of BCCF37 material

Fig. 4. FTIR spectra of the BCCF37 material

Fig. 5. Fe-SEM images for samples BCCF37 (a, b and c) and BCCF91 (d)

Fig. 6. Conductivity vs temperature for samples BCCF37, BCCF91 and BSCF

Fig. 7. Fuel cell performance

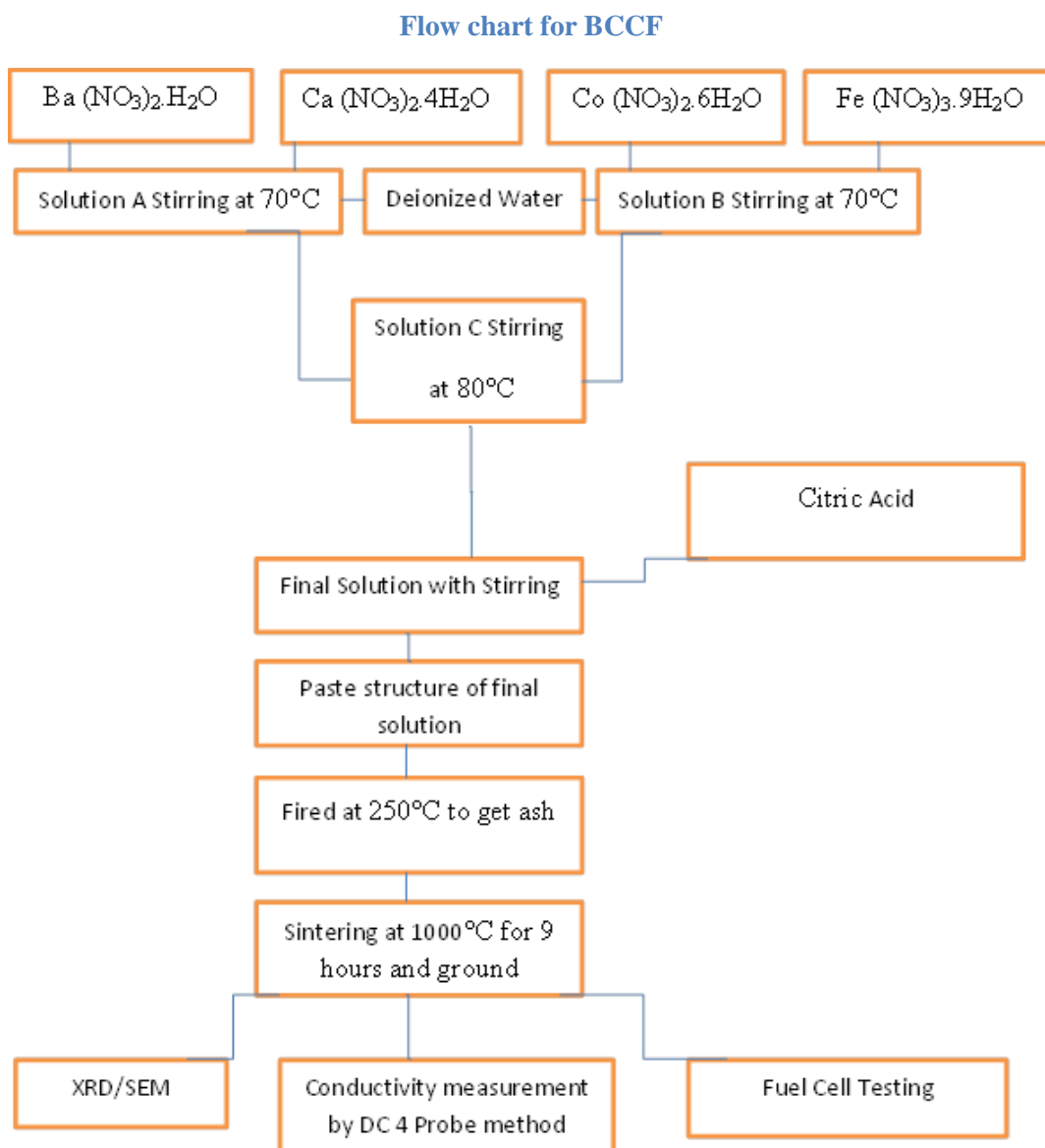
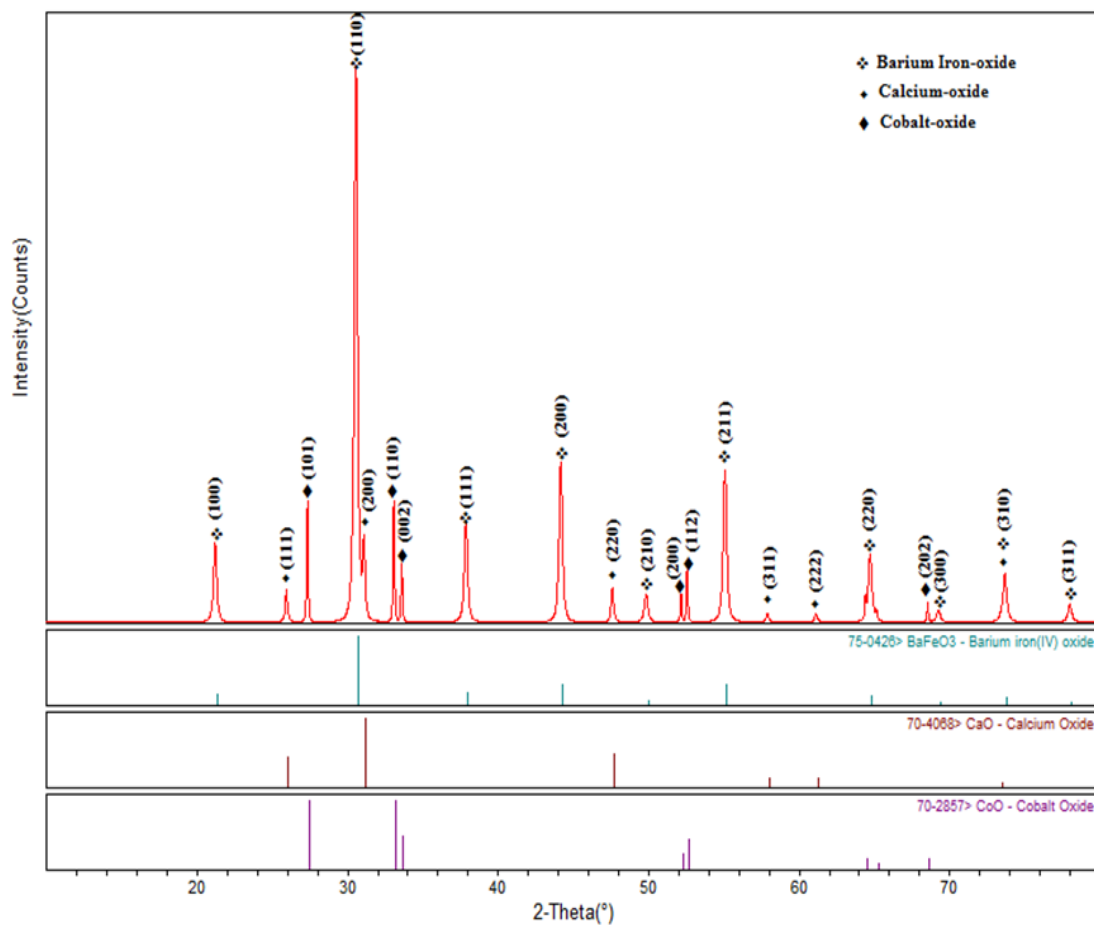


Fig. 1. Sol gel synthesis process for BCCF



Barium iron oxide, particle size (36 nm), Cubic structure

Calcium oxide, particle size (42 nm), Cubic structure

Cobalt oxide, particle size (39 nm), Tetragonal structure

Fig. 2. XRD Pattern for Sample $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BCCF37)

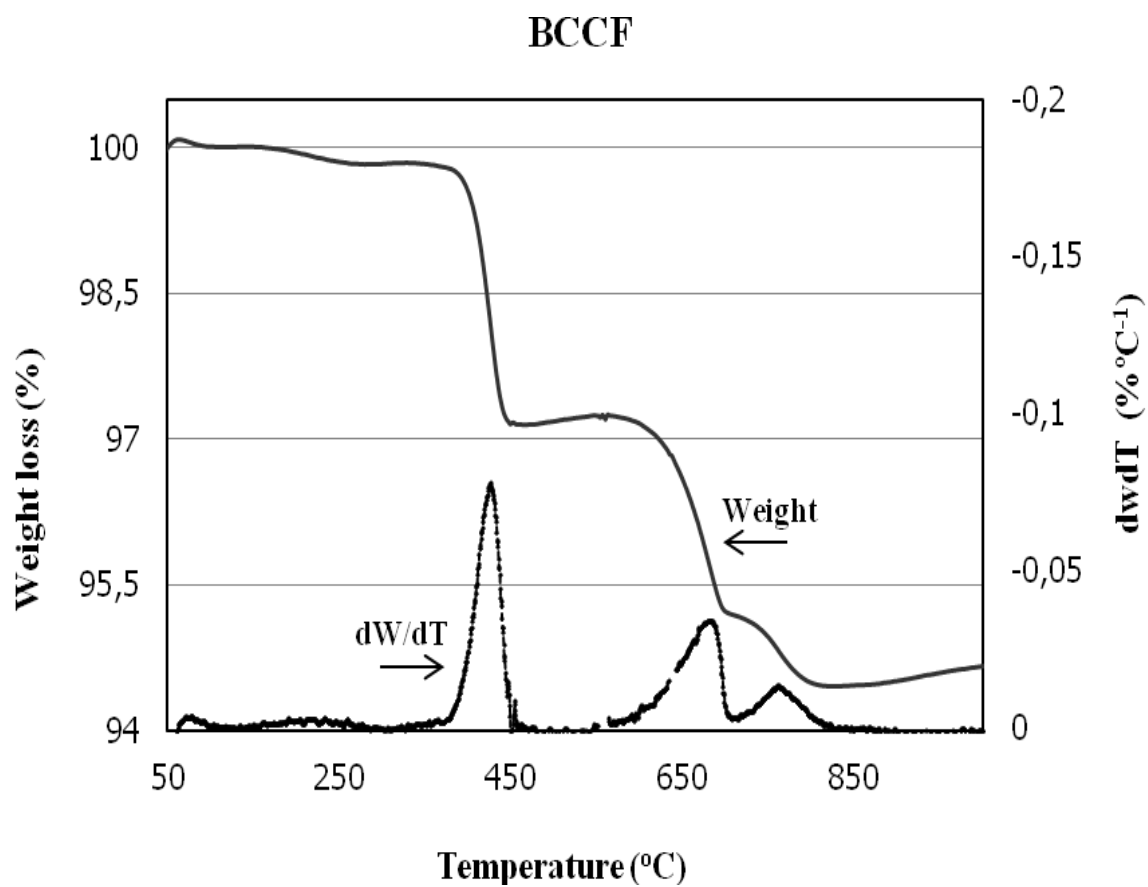


Fig. 3. Thermogravimetric analysis (TGA) curve of BCCF37 material

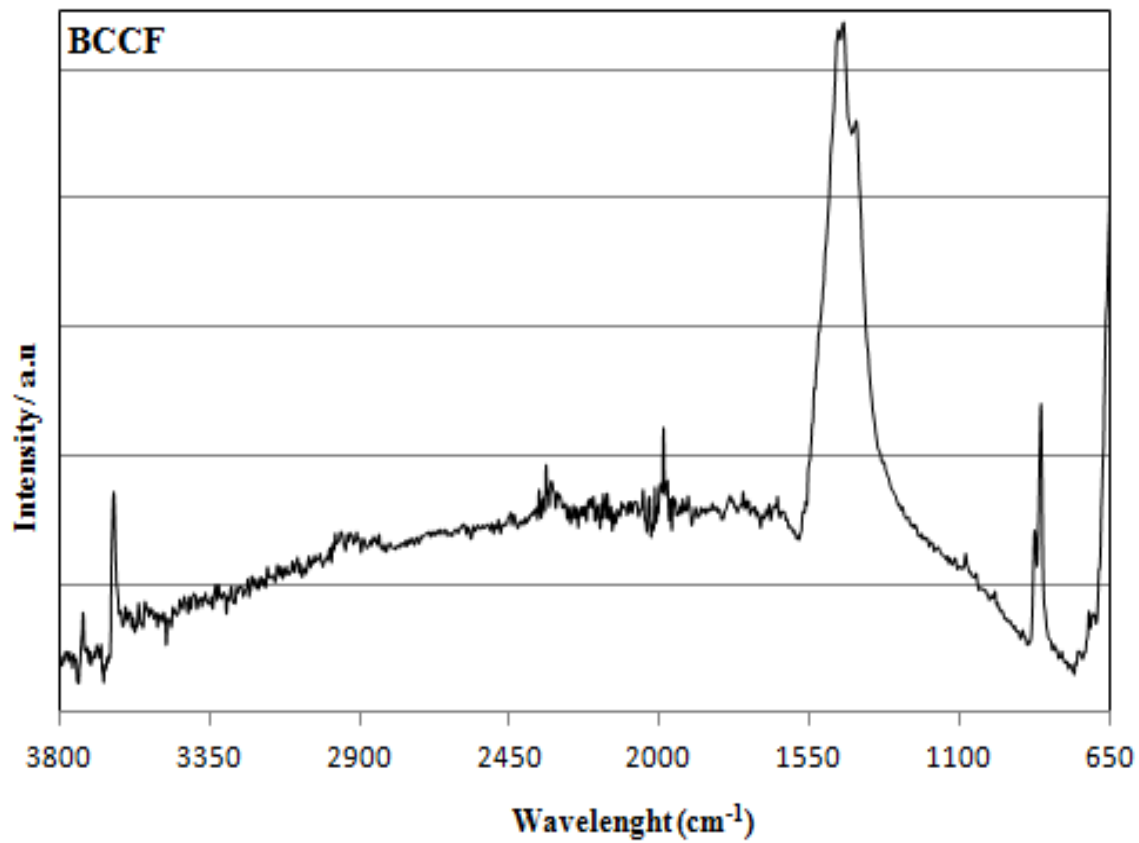


Fig. 4. FTIR spectra of the BCCF37 material

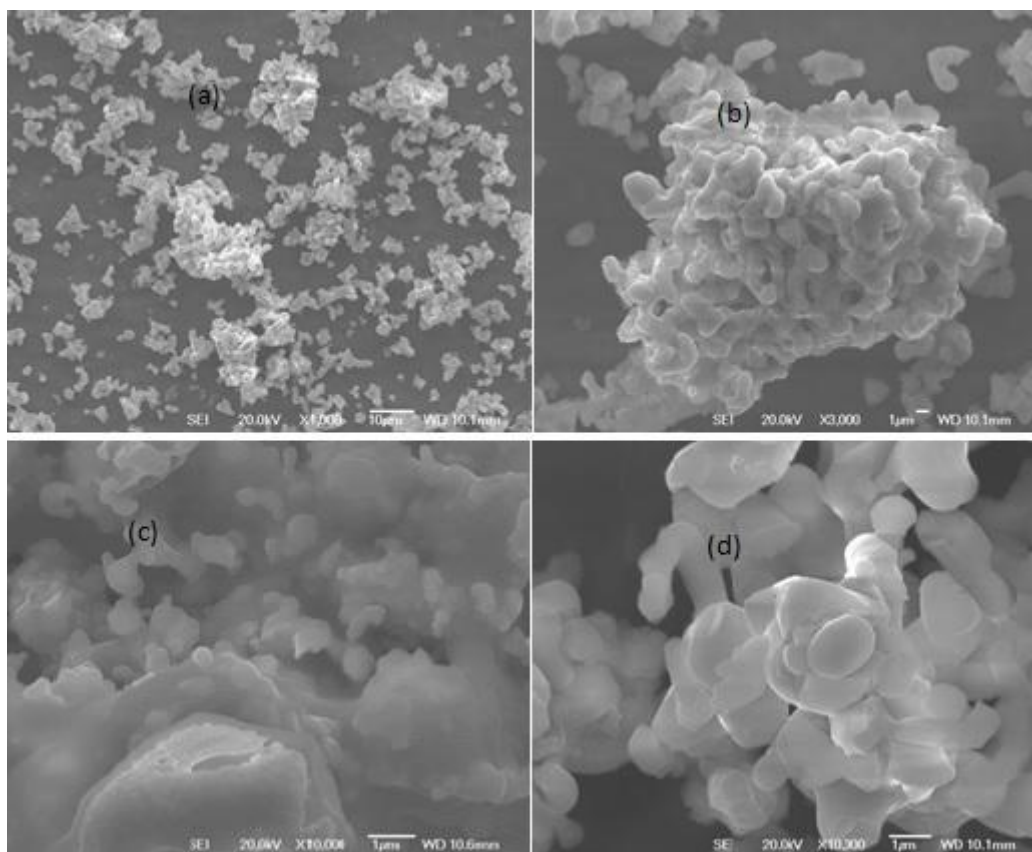


Fig. 5. FE-SEM images for sample BCCF37 (a, b and c) and 2nd composition of the sample BCCF91 (d)

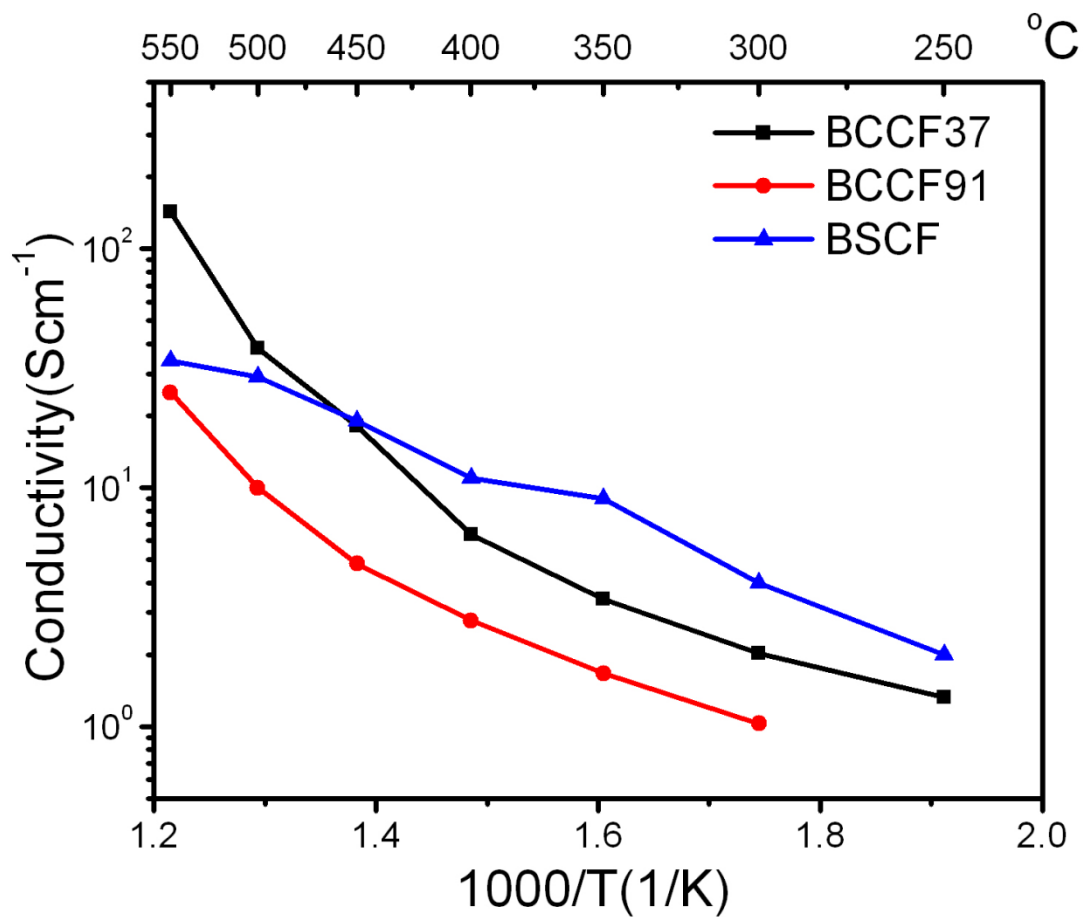


Fig. 6. Conductivity vs temperature for samples BCCF37, BCCF91 and BSCF

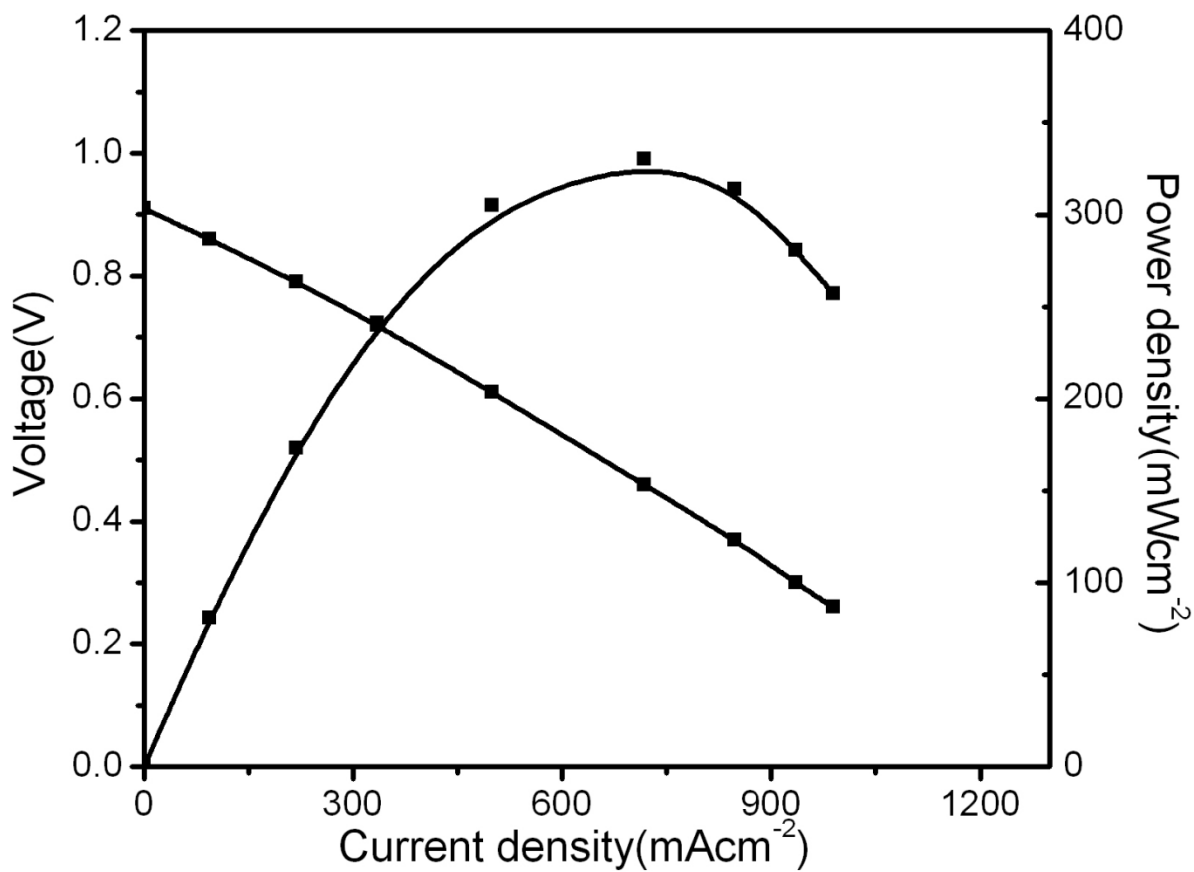


Fig. 7. Fuel cell performance