Synthesis and characterization of $Sm_{0.5}Ba_{0.5}MnO_{3-\delta}$ as anode materials for solid oxide fuel cells

A. M. Abdalla*, N. Radenahmad, M. S. Abu Bakar, Pg M .I. Petra, and A. K. Azad.

Universiti Brunei Darussalam, Faculty of Integrated Technologies, JalanTunku Link, Gadong BE 1410, Brunei Darussalam.

*Email: 14h8851@ubd.edu.bn, Phone: +6738626040

Abstract. The material performance is a crucial issue in the current fuel cell technology, and for this reason we present this new series of Samarium family which can be used as electrode giving a high performance in a particular application. $Sm_{0.5}Ba_{0.5}MnO_{3-\delta}$ was prepared by solid state reaction method and characterized by using X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Rietveld analysis of XRD data shows that the material has an Orthorhombic crystal structure with cell parameter ***a = 3.883(1) Å b = 3.8742(5) Å c = 7.762(4) Å***, in the Pmmm space group. TGA analyses shows that the materials is going to decrease by 0.32%.The density of the materials was calculated from structural refinement and found to be 8.372 gm/cm^3.

1. Introduction

Despite the continuous development of energy resource including fossil fuels, extensive efforts still paid to different types of fuel cell technologies, which mainly depending on electrochemical reactions to get high power density [1-6], and (used in versatile applications at different scales such as; transportation, remote power sources, structure, military use, remote villages, and aerospace). Moreover global warming problem requires essential findings with reliable solutions that come with the enhancement of environmental issues. The solid oxide fuel cells (SOFCs) in the last 20 years gave a noticeable achievements and exponentially increased attention because of the various advantages such as, easy in processing and manufacturing, operates at higher temperatures, handling more convenient hydrocarbon fuels , no reforming catalysts are required, and high power density can be obtained [7,8]. Typically, working with SOFCs materials requires the full understanding of the occurred reactions, specifically, the electrochemical reactions, in addition to the full characterization of the material, microstructure starting from the microscopic level [9, 10].

Anode supported fuel cell consumes more than 95% of the total amount of the material and it is very important to obtain good ohmic resistance[11,12].Cell manufacturing techniques mainly depend on the easy processing and minimization of the interfacial reactions between the electrolyte and the

electrode materials [13,14]. The state-of-the-art Ni/YSZ cermet anodes are usually made of the commercial NiO and YSZ powders, are in homogenized by milling and mechanical mixing. Many literatures reported that performance and electric properties of Ni/YSZ cermet anodes are critically dependent on both distribution of Ni and YSZ phases and the microstructure [1,15]. However, Ni particles aggregate and reduce the porosity of an anode by eliminating the triple-phase boundary (TPB) required for cell operation, thereby decreasing cell performance.ABO_3 perovskite material aimed for use in fuel cells to avoid the high temperature sintering and to exhibit high electrical conductivity at elevated temperature. This can be achieved by substitution of either A or B sites with acceptor-or donor-type cations [16]. Recent research reported that samarium oxide Sm_2O_3 is a good catalyst with high activation energies[17-19]. Doping of Ce in $SmFeO_3$ results in a noticeable stability, and good modification of the material characteristics [20]. Samarium doped materials [21] shows that the conversion of the Sm^{+3} to Sm^{+2} species can happen at same time with the oxidation of the other doped material, so the possibility of such modifications open up the way for more research to use samarium based material as an electrode in SOFCs.

Form the pervious investigations done by literature and the good properties of Sm, a new series of Sm family was prepared and investigated as anode material. New samarium based materials $Sm_{0.5}Ba_{0.5}MnO_{3-\delta}$ was prepared by solid state reaction method at 1400 ° C then was characterized by X-ray diffraction (XRD), and thermogravimetic analysis (TGA).

2. Experimental

$Sm_{0.5}Ba_{0.5}MnO_{3-\delta}$ (SBMO) was prepared by solid state reaction method. The material SBMO anode was obtained by calcinations of the single pervoskite $Sm_{0.5}Ba_{0.5}MnO_3$ in air from 800 °C to 1400 °C within 25 total sintering hours through three stages. The initial structural characterization of the SBMoxide was performed by XRD, SIEMENS Diffraktometer D5000 Kristalloflex, Cu K-Alpha1, 40 kV, 30 mA (Chalmers, Sweden). In addition to TGA Simultaneous thermal analysis - NETZSCH STA 409 PC Luxx, run under N2 in 20 ml/min (Chalmers, Sweden), was performed at 1000C°. Finally for the density measurements, it was calculated using both experimental method based on Archimedes and theoretical method from structural refinement.

3. Results and Discussion

3.1. Structural analysis

The XRD powder diffraction patterns of the $Sm_{0.5}Ba_{0.5}MnO_3$ (SBMO) material was obtained from sintered pellet as shown in Fig. 1. The rietveld analysis of XRD data in Fig.2 shown that the material has main phase of crystal structure of orthorhombic crystal structure, and fig 3 shows the 3D crystal structure and the atoms arrangement, also the cell parameter in this structure are, a = 3.883(1) Å, b =

3.8742(5) Å, c = 7.762(4) Å, $\alpha = \beta = \gamma = 90^{o}$, in the Pmmm space group and very small phase of hexagonal crystal structure with cell parameters a = 5.6593(3)Å, b = 4.67012(1)Å, α = β = 90°, and γ = 120° in the R-3m space group for the $Sm_{0.5}Ba_{0.5}MnO_3$. Sengodan et al. [13] has analyzed the layered perovskite $PrBaMn_2O_{5+d}$ and showed very good performance as anode materials. However their structure refinement was a mixture of cubic and hexagonal phases. Due to splitting of some major peaks in our diffraction pattern, we got orthorhombic and hexagonal phase which converged in a very good χ^2 value (χ^2 = 0.515). This suggests that the perovskite structure is well developed after the certain calcinations process with elevated temperatures [20].Corresponding data (2θ, D_{hkl}, and h, k, l values) for this sample is presented in Tables 1–2

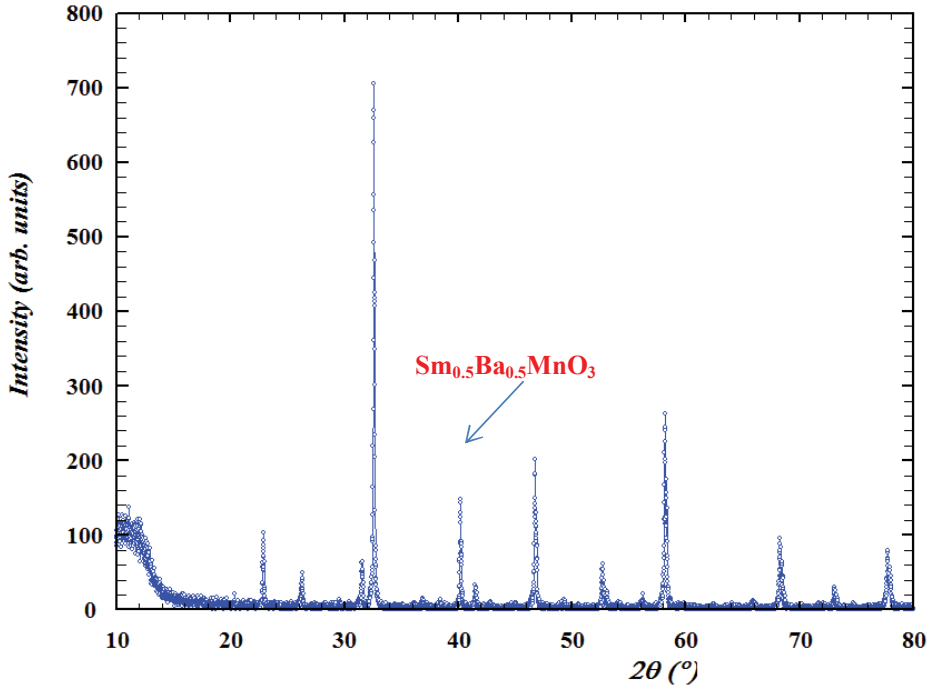

Figure 1. The X-ray diffraction (XRD) patterns show, Sm0.5Ba0.5MnO3 layered SBMO, by SIEMENS Diffraktometer D5000 Kristalloflex (Cu Kα radiation, 40 kV, 30 mA). Sm0.5Ba0.5MnO3was calcinated in air from 800 C° to 1400 C° for 25 hrs.

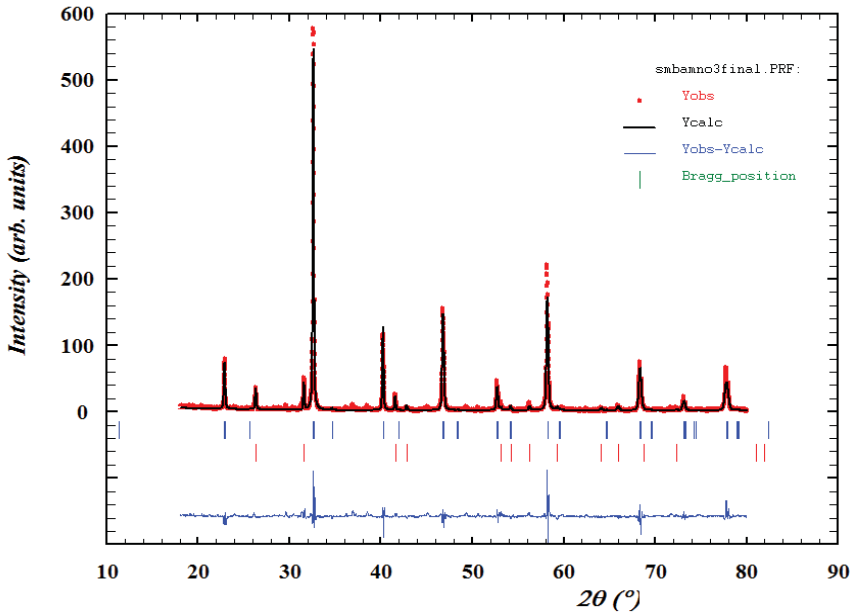

Figure.2 Rietveld refinement profile of $Sm_{0.5}Ba_{0.5}MnO_3$

Table1. Refinement results for the orthorhombic phase.

Serial No	*2Θ*	*Dhkl*	*h*	*k*	*l*
1	22.91	3.8775	0	0	1
2	32.63	2.7418	0	1	1
3	40.26	2.2387	1	1	1
4	46.82	1.9387	0	0	2
5	52.75	1.7341	0	1	2
6	58.23	1.5830	1	1	2
7	68.37	1.3709	0	2	2
8	73.08	1.2925	0	0	3
9	73.16	1.2925	2	1	2
10	7783	1.2262	1	0	3

Table 2. Refinement results from the hexagonal phase.

Serial No	*2Θ*	*Dhkl*	*h*	*k*	*l*
1	26.30	3.3848	1	0	1
2	31.576	2.8328	1	1	0

3	41.52	2.1724	0	2	1
4	42.82	2.1104	0	1	2
5	53.06	1.7239	2	1	1
6	65.88	1.4164	2	2	0

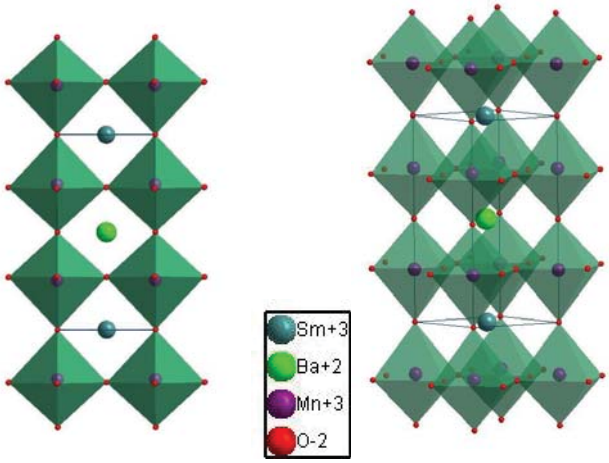

Figure.3 Schematic 3D-crystal structure of $SMBO_3$

3.2. Thermogravimetric analysis (TGA)

TGA of SBM oxide was carried out in air atmosphere with a portion of coulometric titrated sample to estimate the absolute oxygen content. Due to the heating in air, no weight loss happened from 20 - 640 ^{o}C under the ramp heating process, and the weight loss started after 640 ^{o}C, and lasted until 1000 ^{o}C as shown in Fig.4.

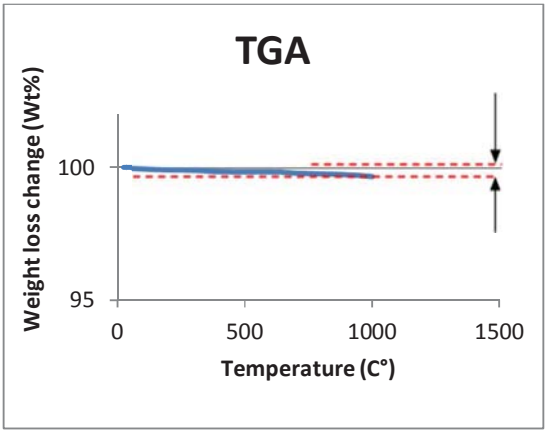

Figure.4 TGA analysis during heating process. Weight loss after 600 oC by 0.32 wt %.

A TGA analysis shows that the material is going to decrease by percentage 0.32% in heating and 0.26% in cooling stages. Apparently, the layered SBMO shows only a slight decrease or increase in weight compared to the initial weight. The analysis shows that the weight of the present material was decreased. The weight loss in the layered SBMO attributes to, the oxygen vacancy formation or decrease in oxygen content. The magnitude of weight loss by percentage after 600 ^{o}C was 0.32 wt % in heating process, and after cooling, it shows a slight weight gain for layered SBMO during cooling process and this may be due to the reoxidation of the layered SBMO sample, and it based on the delay time.

3.3. Density measurement

The density of the material was measured using both structural refinement and Archimedes theory. For structural refinement formula is:

$$\rho = \frac{Z*F_w}{V*N_a} \quad (1)$$

Where: ρ is the density, Z is the number of atoms in unit cell, F_w is the Atomic Weight [kg mol^{-1}], V is the Volume of unit cell [m^3], and N_a is the Avogadro's number [atoms mol^{-1}].

According to actual measurements from Archimedes theory, the $Sm_{0.5}Ba_{0.5}MnO_3$ shows the actual density of 6.0255 gm/cm^3. From the structural refinement the density was found to be 8.372 gm/cm^3, where the relatively percentage was about 71.98%, where it seems the particles steadily getting smaller and change in shape [21] and this suggests that SBMO oxide will show high percentages of porosity and make it as a good anode material used in SOFCs. However, high electrochemical performances tolerating carbon coking and H_2S poisons [15] depend on the B-site cations and high electrical conductivity of the pervoskite [20]. This new redox-stable mixed oxide-ion electron conductors (MIEC) anode consists of an A-site layered double and single perovskite structure, $Sm_{0.5}Ba_{0.5}MnO_{3-\delta}$ (SBMO), for hydrocarbon fuel operation. The selection of this material relied on some basic factors. Firstly, the chemical and thermal stability under fuel electrode conditions along with the A- site ordering layered SBMO [15,24]; Secondly, the oxygen kinetics and, the highest conductivity. Hence mixed-valence transition metal cations ($Mn^{+4}/Mn^{+3}/Mn^{+2}$) is supported by the layered SBMO pervoskite structure, and this results in an enhancement of the electrical conductivity and maintain a large oxygen voids content and can promote the oxygen migration in the perovskite lattices, which in terms contribute to the fast oxygen ion diffusion[21,25-28]; Third, the extremely good and active catalytic hydrogen and hydrocarbon oxidation perovskite oxides of first row transition metals containing Mn, Co and Fe-rich perovskite provide high activity in hydrocarbon oxidation[25,29,30]. Finally non-phase change and conductivity increases with regard to the addition of barium (Ba) doing with Sm and Mn [31-33].Furthermore, the existence of $BaMnO_3$ in this

compound makes it a highly active and carbon tolerant anode, and also work as a good material can be used for solid oxide fuel cells.

4. Conclusion

The proper selection of SOFCs materials mainly depends on the characterization and the performance that can give in a specific application, so the synthesis of this new material makes it able to fit with the requirements needed for SOFCs. Optimum characterization and reliable analysis of material $Sm_{0.5}Ba_{0.5}MnO_3$, it might help to draw the specifications of the used SOFCs material after measuring the power density in single cell test measurements. According the characterizations performed here, it gave a good agreement with the literature results, and this indicates that this material after making a full characterization as a new A- site single pervoskite may show asuperior SOFC anode performance according to the electrochemical stability. It is expected that this single A-site and also double A- site layered SBMO anodes should give higher electricalconductivity, in addition to an excellent redox and coking tolerance and sulphur tolerance, and this will make this new series of layered SBMO oxides as a promising ceramic anode materials for SOFCs.

5. Acknowledgment

The author A.M.Abdalla is grateful to the Universiti Brunei Darussalam for providing him Graduate Research Scholarship to do PhD. We also acknowledge the help from the Centre for Advanced Materials and Energy Sciences (CAMES) for their help.

6. References

[1] San P J and Sie C 2004 A review of anode materials development in solid oxide fuel cells *J. Material .Sci* **39** 4405– 4439

[2] Nigel P B 2007 Materials Engineering for Solid Oxide Fuel Cell Technology *J.Mater. Sci. Forum* **539** 20–27

[3] Neelima M, Amitava B, Alka G, Shobit O and Kantesh B 2015 Progress in material selection for solid oxide fuel cell technology: A review" *J.Progress in Materials Science* **72** 141-337

[4] Zhu W and Deevi S 2003 A review on the status of anode materials for solid oxide fuel cells *J.Mater. Sci* **362** 228–239

[5] Z Shao,W Zhou and Z Zhu 2012 Advanced synthesis of materials for intermediate-temperature solid oxide fuel cells *J.Progress in Materials Science* **57** 804-874.

[6] Jan R, and Wolfgang G B, 2008 Trends in catalytic activity for SOFC anode materials *J. Solid State Ionics* **178** 1694–1700

[7] Norbert H M, Frank T, Sven U, Hans P B, and Detlev S 2010 Materials and manufacturing technologies for solid oxide fuel cells *J. Mater. Sci* **45** 3109–3135

[8] Ghosh A, Abul K A, and John T S I 2011 Study of Ga Doped LSCM as an Anode for SOFC *J.ECS Transac.* **35** 1337-1343

[9] Abul K A, Jung H K and John T S I 2014 Structural,electrochemical and magnetic characterization of the layered-type $PrBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ perovskite *J.Solid State Chem* **213** 268–274

[10] Abul K A and John T S I, 2008 Location of Deuterium Positions in the Proton-Conducting Perovskite $BaCe_{0.4}Zr_{0.4}Sc_{0.2}O_{2.x}$ D_2O by Neutron Powder Diffraction *J.Chem. Mater* **21** 215-222

[11] Frank T, Hans P B and Detlev S 2006 10 years of Materials Research for Solid Oxide Fuel Cells At Forschungszentrum Jülich *J. Electroceramics* **17** 701–707

[12] Shabana P S S, Andanastuti M and Mahendra R S 2015 A review of anode materials development in solid oxide fuel cells *J.Renewable and Sustainable Energy Reviews* **51** 1–8

[13] Sivaprakash S, Sihyuk C, Areum J, Tae H S, Young W J, Hu Y J, Jeeyoung S, John T S I and Guntae K 2014 Layered oxygen-deficient double perovskite as an e cient and stable anode for direct hydrocarbon solid oxide fuel cells *J.Nature Materials* **4166** 1–5

[14] Abul K A, Jung H K and John T S I 2011 Structure–property relationship in layered perovskite cathode $LnBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ (Ln= Pr, Nd) for solid oxide fuel cells *J.Power Sources*, **196** 7333-7337

[15] Abul K A and John T S Irvine 2011 Characterization of $YSr_2Fe_3O_{8-\delta}$ as electrode materials for SOFC *J.Solid State Ionics* **192** 225-228

[16] Hirota K, Hatta H, Yoshinaka M I M and Yamaguchi O 2003 Formation, densification, and electrical conductivity of air-sinterable $(Sm_{1-x}Ca_x)CrO_3$ *J.Mater. Sci. Eng* B **8** 3431–3435

[17] Tolstopyatova A A, Chuan Y C and Gorshkova L S 1964 Catalytic properties of samarium with respect to the dehydrogrogenation and dehydration of alcohols and the dehydrogenation of tetralin *J.of Russien Bulltein* **4** 7–10

[18] Hussein M A G, Buttrey D J, DeSanto P, Abd-Elgaber A A Roshdy H and Myhoub A Y Z, 2003 Formation and characterization of samarium oxide generated from different precursors *J.Acta thermomechanica* **402** 27–36

[19] Wei L, Yanyi L, Bin L, Taylor D S, Xi W and Wei P 2010 Ceria (Sm3+, Nd3+) carbonates composite electrolytes with high electrical conductivity at low temperature *J.Composits. Sci. Technol* **70** 181–185

[20] Syed M B and Javier B G 2011 Surface and redox chemistry of $Sm_{0.95}Ce_{0.05}Fe_{1-x}Ni_xO_{3-\delta}$ perovskites *J.Solid State Ionics* **194** 33–40

[21] Rada S, Pascuta P, Rada M and Culea E 2011 Effects of samarium (III) oxide content on structural investigations of the samarium–vanadate–tellurate glasses and glass ceramics *J.Non. Cryst. Solids* **357** 3405–3409

[22] Yarong W, Toshiyuk M, Ji-Guang L and Yoshiyuk Y 2011 Low-temperature fabrication and electrical property of 10 mol% Sm_2O_3-doped CeO_2 ceramics *J.Sci. Technol. Adv. Mater* **4** 229–238

[23] Dengjie C, Ran R, Kun Z, Jun W and Zongping S 2009 Intermediate-temperature electrochemical performance of a polycrystalline $PrBaCo_2O_{5+\delta}$ cathode on samarium-doped ceria electrolyte *J.Power Sources* **188** 96–105

[24] Trukhanov S V, Trukhanov A V Szymczak H, Szymczak R and Baran M 2006 Thermal stability of A-site ordered $PrBaMn_2O_6$ manganites *J.Phys. Chem. Solids* **67** 675–681

[25] Mónica V S, Aracely M, Tulio M, Rosana Z D, Gustavo A L, Matias D A, Célia F M, Paola G M and Gilles H G 2014 Barium-modified NiO–YSZ/NiO–GDC cermet as new anode material for solid oxide fuel cells (SOFC) *J.Solid State Ionics* **261** 36–44

[26] Taskin A A, Lavrov A N, and Ando Y 2007 Fast oxygen diffusion in A-site ordered perovskites *J.Prog. Solid State Chem* **35** 481–490

[27] Khakpour Z, Yuzbashi A, Maghsodipour A and Ahmadi K 2012 Electrical conductivity of Sm-doped CeO2 electrolyte produced by two-step sintering *J. Solid State Ionics* **227** 80–85.

[28] Tanapol C, Manop P, Nattawut C and Bussarin K 2013 Fabrication of Samarium Doped Ceria Electrolyte on Rough Glass Substrate with High Electrical Conductivity by Electrostatic Spray Deposition for Intermediate Temperature Solid Oxide Fuel Cells *J. Energy Procedia* **34** 471–478

[29] Ran R, Wu X, Weng D and Fan J 2013 Oxygen storage capacity and structural properties of Ni-doped LaMnO3 perovskites *J. Alloys Compd* **577** 288–294.

[30] Nemanja D, Adrien V, Jing-Li L, Karl T Chuang, Rob H and Alan R S 2010 Correlation of Fuel Cell Anode Electrocatalytic and ex situ Catalytic Activity of Perovskites $La_{0.75}Sr_{0.25}Cr_{0.5}X_{0.5}O_{3-\delta}$ (X = Ti, Mn, Fe, Co) *J.Chem. Mater* **22** 957–965

[31] Meng L, Bin H, San P J, Jian P, Bo C and Li J2014 $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ as highly active and carbon tolerant anode for direct hydrocarbon solid oxide fuel cells *Int. J. Hydrogen Energy* **39** 15975–15981

[32] Lay E, Dessemond L and Gauthier G 2013 Ba-substituted LSCM anodes for solid oxide fuel cells *J.Power Sources* **221** 149–156

[33] James J, Sankar M, Kumar S S and Nair K V 2004 Preparation and properties of $Ba_{2-x}Sr_xSmTaO_6$ (x=0–2): a group of new perovskite materials *J.Mater. Chem. Phys* **83** 328–333