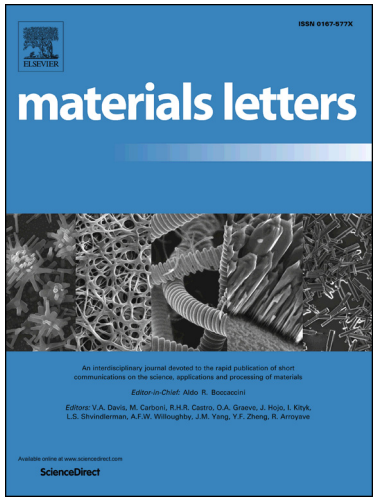

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Novel Layered Perovskite $SmBaMn_2O_{5+\delta}$ for SOFCs Anode Material

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Abstract

$SmBaMn_2O_{5+\delta}$ (SBMO), a novel layered perovskite compound with samarium based material (Sm^{+3}) as rare earth doped in A-site was synthesized and processed by using dry chemistry method (solid state solution). Structural characterization of SBMO has been investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). While, thermal and electrochemical testing were done by using thermogravimetric analysis (TGA) and current voltage measurements. The Rietveld analysis of XRD data shows that SBMO was crystallized in the orthorhombic structure with the Pmmm space group. The surface morphology images showed a porous structure which indicates that this material can be used as a potential electrode in solid oxide fuel cells (SOFCs). TGA result showed the mass loss of 0.022% for $SmBaMn_2O_{5+\delta}$ which is very small and indicates that the material is very stable. DC conductivity and performance test were done at RT in air atmosphere. The performance tests have done at 800 °C and 750 °C and the maximum power density was found to be 0.4 W/cm^2 at 800 °C.

Keywords: Layered pervoskite; structural analysis; power density measurements, SOFCs anode.

1. Introduction

Nowadays, SOFCs are considered the most promising energy conversion devices and its efficiency is to get the highest performance through electrochemical reactions [1-2]. SOFCs have versatile applications in energy sector like; transportation, remote power sources, military use, remote villages, aerospace and smart portable electronic devices. The anode of SOFC is the most important due to its

involvement with the fuel. Therefore, anode supported fuel cell depletes huge percetage of the total utilized materials (around 95% or more) as anode and essentially required a good ohmic resistance in the cell [3-5]. The cell fabrication methods are mainly depend on: firstly, easy processing and secondly, minimization of the interfacial reactions between the dense electrolyte and the porous electrode materials [6,7]. The state-of-the-art anode material is Ni/YSZ cermet which are usually made of the commercial NiO and YSZ powders. They are homogenized by sonication method, ball milling and mechanical mixing. Therefore, their electrochemical properties are critically rely on both allocations of Ni and YSZ phases inside the microstructure [8]. However, Ni particles aggregate and reduce the porosity percentage of the anode through the elimination of triple-phase boundary (TPB) required for cell operation. But its effects on cell performance is negative and always decreases the value of the performance. Most well-known types of perovskite materials $ABO_{3-\delta}$ and $A_2B_2O_{5+\delta}$ are aimed to use in SOFC anodes, and are essentially needed to overcome high temperature sintering and to exhibit high electrical conductivity at elevated temperature. Hence, this achievements requires different types of elements either A or B sites with acceptor-or donor-type cations [9]. Samarium oxide Sm_2O_3 has been reported as a good catalyst with low activation energies [10,11]. Accordingly, samarium doped materials [12] has also showed that the conversion of the Sm^{+3} to Sm^{+2} species can occurs at same time with the oxidation of the other doped materials. Hence, the possibility of this enhancement through research can results in the use of samarium based material doped with other elements as an electrode in SOFCs.

2. Experimental

The materail $SmBaMn_2O_{5+\delta}$ (SBMO) was prepared by solid state reaction method. Stoichiometric amount of Sm_2O_3, $BaCO_3$ and Mn_2O_3 were mixed together with ethanol and in a roller type ball mill for 24 hours. The formed powder was dried and calcined at 800 °C for 8 hours. The collected powder was then mixed in an agate mortar pestle, pelletised and fired at 1200 °C and finally sintered at 1400 °C for 12 hours. The heating and cooling rate was 5 °C/min. Afterwards the structural characterization were performed by X-ray diffraction. The XRD data were collected using a

SIEMENS Diffraktometer (D5000 Kristalloflex, $\lambda = 1.5406$ Å) in the range of $10^{o} \leq 2\theta \leq 80^{\circ}$ with the step size of 0.01. The SEM images were collected on the pellet surface using a JSM-7610F (SEM) and the TGA analysis were made using the ASTM E1131. A dc conductivity jig of 4-terminals (Van der Pauw, an in house built dc conductivity jig) was used to measure the dc conductivity of the material and was done in air at 850 °C. Cell performance tests were measured at 800 °C and 750 °C.

3. Results and Discussion

3.1 Structural analysis

Figure 1 shows the Rietveld refinment analysis of the XRD data of $SmBaMn_2O_{5+\delta}$ by using Fullprof software [13] and the schematic 3D crystal structure has been shown in the insert. The XRD pattern was indexed by using the TREOR90 [14] and SPUDS software [15] was used to obtain the atomic positions. The main phase of SBMO exhibits an orthorhombic crystal structure with the Pmmm space group; while a tiny hexagonal phase (less than 5% of the main phase) of Sm_2O_3 was observed in the R-3c space group. Rietveld refinement converged in a very good χ^2 (= 1.25). The cell parameters and cell volume are shown in Table 1. The structure was confirmed as layered perovskite-type. A substantial reflection broadening was observed in the XRD pattern which reflects micro-strain broadening because of compositional non-uniformity, which can be observed clearly from the G-Fourier analysis. Williamson - Hall calculations also showed high strain broadening effect in this material. It is interesting to see that the unit cell dimension and volume differs from simple perovskite, while the composition was made in the layered perovskite form. This difference is mainly due to the oxygen occupancy in the cell [5,17].

3.2 Microstructural analysis

The morophological images indicate that this material have an accepted porosity percentage and crystallinity which makes it an appropriate selection as electrode for SOFCs applications. The percentage of porosity could be increased further through addition of pore-formers. This morphology gives an excellent stability and reversibility of oxygen storage-related process. Figure 2(a-c) shows the SEM images of SBMO.

3.3 TGA measurement

TGA of SBMO was done in air with a portion of coulometric titrated in order to evaluate the absolute oxygen content. There was a very small percentage of mass loss started from room temperature to 200 ^{o}C. The initial mass loss might be related to the evaporation of moisture from the sample. After 200 °C the mass gradually losses and continued until 1000 °C because of the formation of oxygen vacancies as shown in Fig 3. The total mass loss is about 0.022%. The total mass loss is mainly due to the oxygen loss from the structure.

3.4 Performance test

3.4.1 Electrical conductivity

The DC conductivity of the sample was calculated according to Uhilr equation (1) [18]:

$$\sigma = \frac{d}{R * t * L_{av}} \quad (1)$$

Where d is the spacing between the attached wires, t is the bar thickness and L_{av} is the effective length during the measurements. SBMO exhibits good electrical conductivity of 8 S/cm at 850 °C in air. The obtained high value of electrical conductivity is due to the rapid reactions of the doped elements especially of Mn^{+3} which have high stability with oxygen species.

3.4.2 Power density

Single cell of $SmBaMn_2O_5$/YSZ/$La_{0.75}Sr_{0.25}MnO_3$ was prepared with an attachment of Pt current collector and fixed on the testing jig (see fig 4) with aremco ceramic paste. Then the whole setup was placed in a dual chamber SOFC. The measurements were done at 800 °C and 750 °C using air in the cathode side and 5% H_2/Ar in the anode side with the flow rate of 100 ml/S. The obtained results is shown in Fig 4 represents a high power density of 0.4 W/cm^2 at 800 °C under the testing atmosphere and it decreases with the decrease in temperature.

Conclusions

The SBMO layered perovskite was successfully synthesized by solid state reaction method. According to our characterizations, this material shows high conductivity in air (about 8 S/cm at 850 °C). The power density was also very promising (0.40 W/cm^2). The structural analyses were done for investigating the space group and cell parameters. Careful analysis of the peak splitting, we have found the correct space group and accurate structural parameters. In the performance test, this material showed promising results to be used as SOFC anode which is electrochemically very stable.

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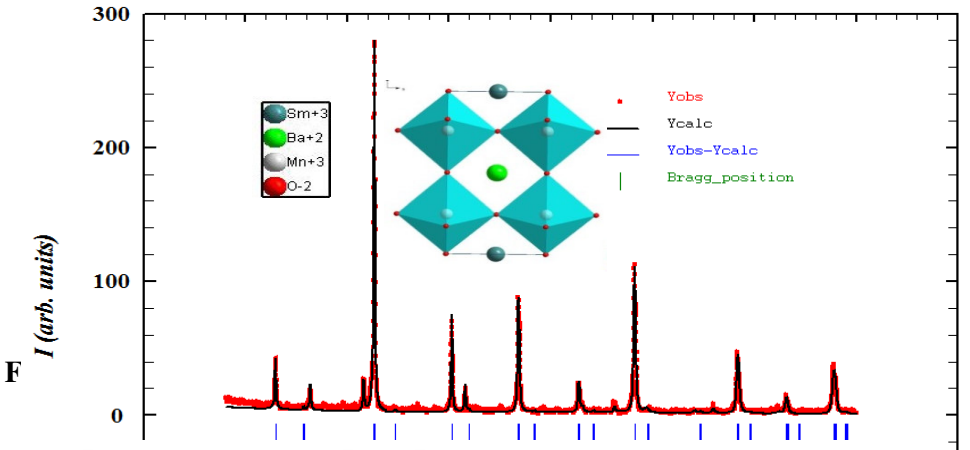

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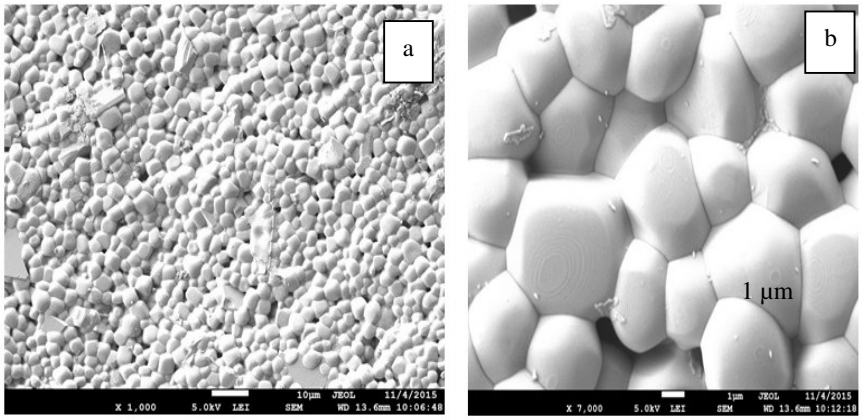


Fig. 2 SEM mic enlarge view of the pores in SBMO structure and c) Single cell of SBMO/YSZ/LSM.

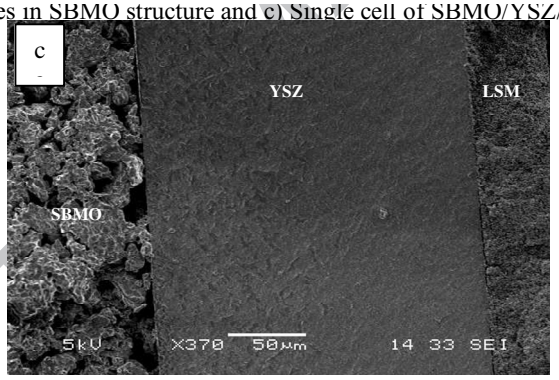
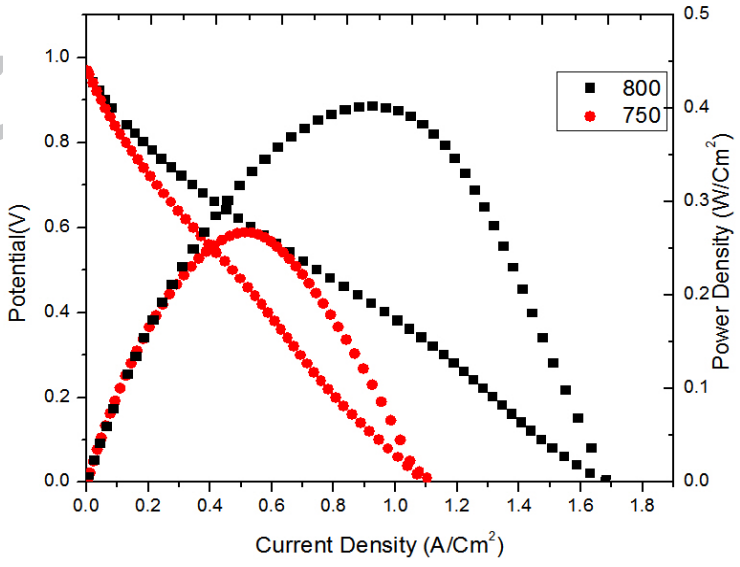


Fig 3. Thermogravimetric analysis of $SmBaMn_2O_5$.



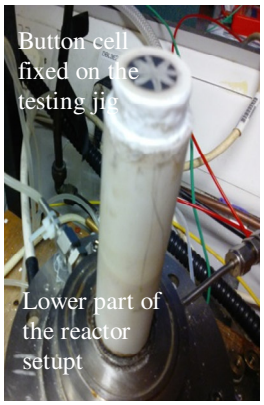


Fig 4. Performance of $SmBaMn_2O_5$ at 800 °C.

Table 1. Cell parameters of the tested materials.

Chemical composition	Phase structure	Space group	a (Å) α(°)=β(°=γ(°)=90	b (Å) γ(°)=120	c (Å)	V (Å^3)
$SmBaMn_2O_5$	Orthorhombic Hexagonal	Pmmm R-3c	***3.877(9)*** ***5.6589(7)***	***3.8704(3)***	***7.7556(5)*** ***4.6685(1)***	116.405(6) 149.504(1)
$BaSmMn_2O_5$*	Tetragonal	P4/nmm	5.5963(1)		7.7105(1)	241.48(1)

* Data from the reference [16]

Highlights

- $SmBaMn_2O_{5+d}$ layered Perovskite for SOFCs anode materials.
- SBMO crystallize in the orthorhombic symmetry in the (Pmmm S.G).
- High DC electrical conductivity of 8 Scm^{-1} at 850 °C.
- $SmBaMn_2O_{5+\delta}$ Power density was found 0.4 Wcm^{-2}.