Synthesis and characterization of Sm$_{0.5}$Ba$_{0.5}$MnO$_{3-\delta}$ as anode materials for solid oxide fuel cells

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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 g/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$_2$O$_3$ 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 1000°C. 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 =
3.874(5) Å, c = 7.762(4) Å, \( \alpha = \beta = \gamma = 90^\circ \), 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, \( \alpha = \beta = 90^\circ \), and \( \gamma = 120^\circ \) 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\(_2\)O\(_{5+d}\) 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 \( \chi^2 \) value (\( \chi^2 = 0.515 \)). This suggests that the perovskite structure is well developed after the certain calcinations process with elevated temperatures [20]. Corresponding data (2\( \theta \), \( D_{hkl} \), and \( h, k, l \) values) for this sample is presented in Tables 1–2.
Figure 2. Rietveld refinement profile of Sm$_{0.5}$Ba$_{0.5}$MnO$_3$.

**Table 1.** Refinement results for the orthorhombic phase.

| Serial No | $2\theta$ | 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 | $2\theta$ | Dhkl  | h  | k  | l  |
|-----------|----------|-------|----|----|----|
| 1         | 26.30    | 3.3848| 1  | 0  | 1  |
| 2         | 31.576   | 2.8328| 1  | 1  | 0  |
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 °C under the ramp heating process, and the weight loss started after 640 °C, and lasted until 1000 °C as shown in Fig.4.

Figure 3 Schematic 3D-crystal structure of SMBO$_3$

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 °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:

\[
\rho = \frac{Z \times F_{\text{w}}}{V \times N_{\text{a}}}
\]

Where: \(\rho\) is the density, \(Z\) is the number of atoms in unit cell, \(F_{\text{w}}\) is the Atomic Weight [kg mol\(^{-1}\)], \(V\) is the Volume of unit cell \([\text{m}^3]\), and \(N_{\text{a}}\) is the Avogadro’s number \([\text{atoms mol}^{-1}\])

According to actual measurements from Archimedes theory, the \(\text{Sm}_{0.5}\text{Ba}_{0.5}\text{MnO}_3\) 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\(_2\)S 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, \(\text{Sm}_{0.5}\text{Ba}_{0.5}\text{MnO}_3-\delta\) (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 (\(\text{Mn}^{4+}/\text{Mn}^{3+}/\text{Mn}^{2+}\)) 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 electrical conductivity, 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.

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6. References

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