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COMPARATIVE PERFORMANCE ASSESSMENT OF NANO-COMPOSITE CATHODE OF LMSO-BSCMF FOR LOW TEMPERATURE SOLID OXIDE FUEL CELL APPLICATIONS

The development of novel cathode materials for low temperature solid oxide fuel cell (SOFC) applications is one of the significant research areas in materials engineering. In the current work, composite cathode materials were prepared by two different modes and the fuel cell performance was assessed using a gadolinium-doped ceria (GDC) electrolyte. Nano-composite cathodes were fabricated using a lanthanum strontium manganite oxide (LSMO) powder of a 50-100 nm particle size and $Ba_{0.5}Sr_{0.5}(Co_{0.2}Mg0.8)_{0.2}Fe_{0.8}O_3$ (BSCMF) powder of a 1 µm particle size. The cathodes were prepared as layered composites and mixed composites. The electrochemical performance of the symmetric cells was investigated by electrochemical impedance spectroscopy (EIS) at the intermediate temperature of 700°C using air atmosphere. The cathode film coating on the electrolyte was sintered at three different temperatures (900, 950 and 1000°C) and the cell performance was assessed at 700°C. Lower polarization resistance (R_P) values were recorded for the cell produced at 900°C. The R_P of the nano-composite cathodes was measured as lower (2.72 Ω-cm^2 for the layered composites and 1.76 Ω-cm^2 for the mixed composites) compared with LSMO. Hence, the results demonstrate the potential of using an LSMO-BSCMF composite in the mixed mode as a cathode for low temperature SOFCs to achieve a lower polarization potential.

Keywords: SOFCs, LSMO, BSCMF, cobalt, magnesium, polarization potential

INTRODUCTION

In recent years, fuel cell based clean energy research has been gaining wide attention due to issues associated with fossil fuels. Fuel cells convert chemical energy to electrical energy without resulting in the pollution usually seen with fossil fuels [1]. Among the available fuels cells, solid oxide fuel cells (SOFCs) are the most attractive because of the flexibility in fuel choice, low-cost electrodes, convenient operating temperatures, and the ease of operating conditions [2]. On the other hand, low temperature SOFCs can simplify the operational conditions and reduce the complexity associated with higher operational temperatures [3]. However, the efficiency of the fuel cell is decreased with the reduced operating temperatures [4].

Recently, the development of ion-doped cathode materials has shown a significant effect on increasing the fuel cell performance, particularly at lower temperatures [4]. $Sm_{0.5}Sr_{0.5}CoO_3$ [5], $LnBa_{0.5}Sr_{0.5}Co_{2-x}Fe_xO_{5+\delta}$ (x = 0, 0.25, 0.5, 0.75 and 1.0) [6], $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ [7], $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [8], Ca_2Fe_2O--$Ce_{0.9}Gd_{0.1}O_{1.95}$ [9] and $(La_{0.6}Sr_{0.4})_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [10] and $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ [11] are a few examples can be found in the reported literature in developing low temperature SOFCs. The BSCF system as cathode material has shown more promising results in the available literature [12, 13]. The presence of more cobalt (Co) in the BSCF cathode material increases the coefficient of thermal expansion (CTE) value, which is not suitable for low temperature SOFCs [14]. Therefore, doping BSCF cathode materials with other ions to enhance the performance of the fuel cell has been adopted, which exhibited better results [15, 16]. Liu et al. [17] improved the oxygen reduction activity (ORR) by doping the B-site of the BSCF cathode with Ce, La, and Pr. From the works of Zeng et al. [18], doping the BSCF cathode with Zn was found to be influential to increase the electrocatalytic activity. The BSCF system was also doped with Mo6+, Nb3+ and Y3+ ions and improved cell performance was demonstrated [19-21]. In our earlier work, doping Mg along with Co was also found to be promising in enhancing the cell performance [22]. On the other hand, developing cathode materials by mixing different material systems, which result in composite cathodes, has also grabbed considerable attention in the research of low temperature SOFCs. For example, Pr_2NiO_4 – $Pr_{0.2}Ce_{0.8}O_{1.9}$ [23], $La_{0.6}Ca_{0.4}Fe_{0.8}Ni_{0.2}O_{3-\delta}$ – YSZ [24], $La_{0.85}Sr_{0.15}MnO_{3-\delta}$ – $Ce_{0.8}Sm_{0.2}O_{1.9}$ [25], $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ – $PrBaCo_2O_{5+\delta}$ [26] and $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$

– $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ [27] composite cathodes have been used in assessing the performance of SOFCs and compared with single phase cathodes, composite cathodes were observed to have better performance. Information on developing composites of lanthanum strontium manganite oxide (LSMO) and $Ba_{0.5}Sr_{0.5}(Co_{0.2}Mg0.8)_{0.2}Fe_{0.8}O_3$ (BSCMF) cathodes for low temperature SOFCs is insufficient in the literature. Therefore, in the current research work, LSMO-BSCMF composite cathodes were prepared in two different modes (layered and mixed) to assess the performance of the fuel cell by using gadolinium-doped ceria (GDC) as the electrolyte.

EXPERIMENTAL DETAILS

$Ba_{0.5}Sr_{0.5}(Co_{0.2}Mg_{0.8})_{0.2}Fe_{0.8}O_3$ powder to produce the cathodes was prepared by using $BaCO_3$, $SrCO_3$, Co_3O_4, Fe_2O_3, and MgO (Merck Ltd & Sigma Aldrich, India) in appropriate amounts. The detailed procedure and the appropriate amounts used to produce the cathode material can be obtained from our earlier work [22]. It was observed that the Co and Mg composition with the 0.2 and 0.8 ratio, respectively, in $Ba_{0.5}Sr_{0.5}(Co_{0.2}Mg_{0.8})_{0.2}Fe_{0.8}O_3$ exhibits better performance compared with the other combinations within the BSCMF system [22]. Lanthanum strontium manganite oxide (LSMO) nano-powder (50-100 nm) was procured (Sigma Aldrich, India) and mixed with the BSCMF powder to produce a nano-composite. The cathode material was prepared by using 50 wt.% of each powder. Ball milling of the powders and subsequent calcinations and filtering of the coarse particles was done to prepare the composite cathode in two different modes. Initially, the layered composite cathode was prepared by depositing LSMO on the doped BSCMF layer. The composite cathode was also produced by mixing both the powders by ball milling for 2 h in Torsion 500 mL containers using water as the media. The LSMO layer was sintered at 1300°C and the BSCMF layer was sintered at 900°C in the layered composite cathode. Gadolinium-doped ceria (GDC) powder (Advanced Materials, India) having a 40 nm particle size was used as the electrolyte to configure the cell. A dense GDC electrolyte disc of the diameter 10 mm and thickness 1 mm was prepared, and a symmetric cell was made by coating the composite cathode on both the sides of GDC electrolyte disc. The thickness of the LSMO, LSMO-BSCF layered and LSMO-BSCF composite cathodes was measured as 40 μm. In order to optimize the sintering temperature of the mixed composite cathode, the film coated on the electrolyte for symmetric cell fabrication was sintered at three different temperatures 900, 950, and 1000°C. The sintered samples were tested for electrochemical performance at 700°C in air atmosphere. Scanning electron microscope (SEM-SU1510, Hitachi) micrographs of the powders and sintered composite cathodes were recorded. The performance of the fuel cell with two different types of composite cathodes was investigated by the electrochemical impedance spectroscopy (EIS) technique based on the symmetric cell configuration. The measurements were made utilising a Solartron SI1260 impedance analyzer. The frequency range employed in the present study is from 1 MHz to 1 Hz. The polarization resistance (R_P) for the cathode symmetric cells was measured at 700°C under the open circuit state.

RESULTS AND DISCUSSION

Porosity plays an important role in the performance of cathodes in SOFCs. As observed in Figure 1a, the LSMO film possesses enough porosity required for gas diffusion through the cathode during functioning of the cell. Compared with the mixed composite cathode, the layered composite cathode has relatively more porosity with well-connected grains (Fig. 1b and c). This might be due to the inappropriate sintering conducted at 900°C for the mixed composite cathode. Usually, LSMO needs a higher temperature (>1300°C) to be sintered. Hence, the mixed composite has poor bonding between the LSMO powder particles. On the other hand, in the layered composite cathode, the layers of LSMO and BSCMF were individually sintered at 1330°C and 900°C, and thus better bonding between the particles was achieved.

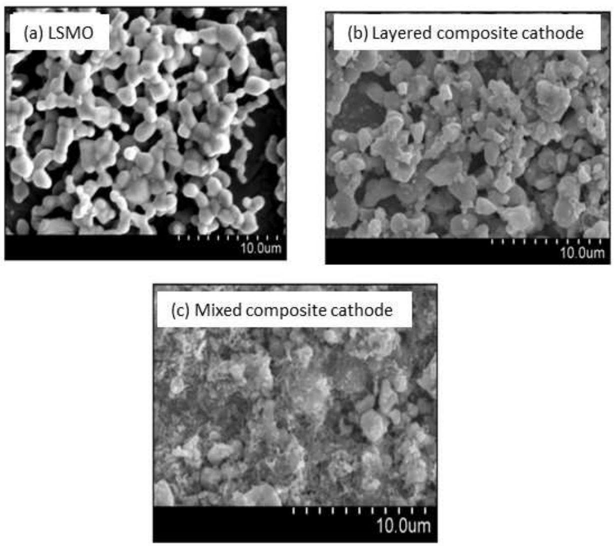

Fig. 1. SEM micrographs of cathode materials: a) LSMO cathode film sintered at 1330°C, b) layered composite cathode and c) mixed composite cathode

Figure 2 presents the microstructure of the sintered cathode (mixed composite cathode) at different temperatures (900, 950 and 1000°C). As seen from the micrographs, with the increased temperature, segregation of the cathode at some places can be observed. This observation suggests the development of a more resistive phase at the interface with an increased sintering temperature, which may contribute to an increase the ohmic resistance. The comparison of the impedance spectra of the cells of the mixed composite cathode at 700°C is presented in Figure 3. The semicircles in the plot represent the electrochemical phenomena involved at the characteristic frequency ranges. As observed from the impedance plot, with the increase in temperature there is an increase in the R_P value for the whole frequency range, indicating a reduction in porosity and the number of triple phase boundaries (TPBs).

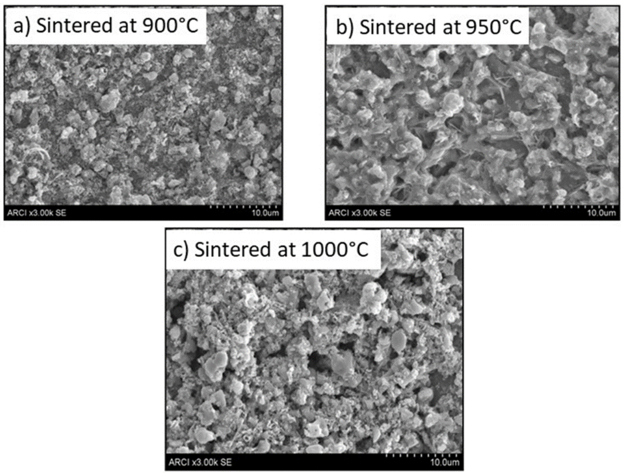

Fig. 2. SEM micrographs of sintered mixed composite cathodes sintered at: a) 900°C, b) 950°C and c) 1000°C

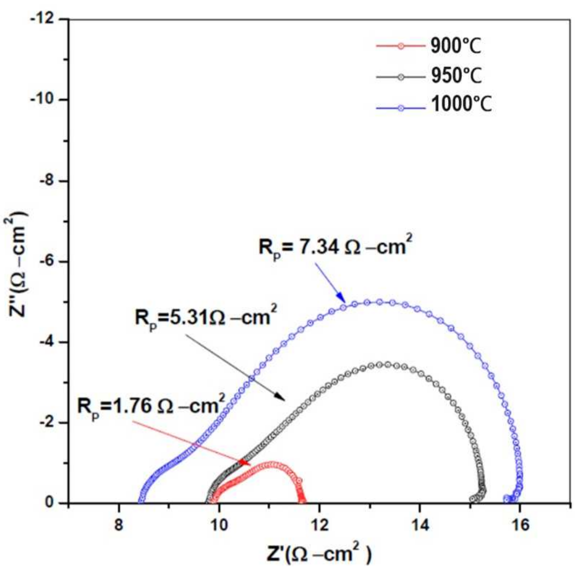

Fig. 3. Impedance spectra of cells with mixed composite cathodes produced at 900, 950 and 1000°C sintering temperatures

From the EIS data, lower R_P values demonstrate the detrimental effect on the performance of the cell with the increased sintering temperature when preparing the cathodes from the mixed composite of the LMSO--BSCMF powders. Therefore, the mixed composite cathode sintered at 900°C was selected to compare with the performance of the fuel cell with the layered composite cathode.

Figure 4 presents the comparison of the impedance spectra of the cells with two different cathodes, i.e. the mixed composite cathode and the layered composite cathode. From the impedance spectra of the symmetric cells, it was observed that the polarization resistance (R_P) of the nano-composite cathodes was lower (layered composite R_P = 2.72 Ω-cm^2, mixed composite R_P = = 1.76 Ω-cm^2) compared with LSMO (23.88 Ω-cm^2). Polarization resistance mainly depends on the triple phase boundaries in the material. When the composite is made by mixing fine-sized powders, the triple phase boundaries are increased within the confined area to convert oxygen molecules to ions. Hence, the LSMO--BSCF mixed composite exhibited lower polarization resistance. The significant decrease in the polarization resistance for both the composites strongly suggests that the nano-composite cathodes can provide a greater number of triple phase boundaries for oxygen reduction compared to that of single phase LSMO.

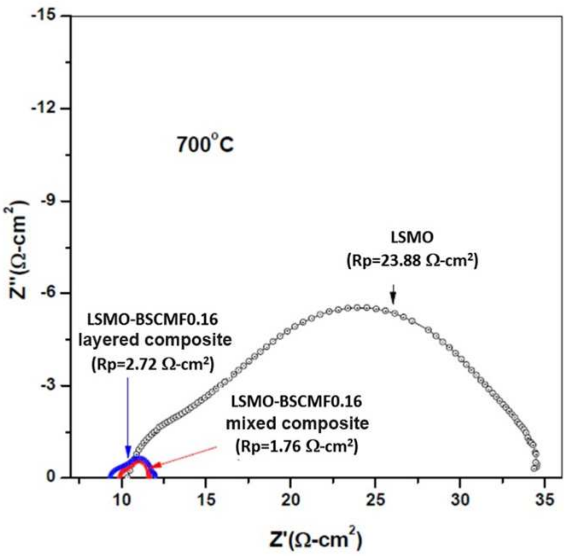

Fig. 4. Impedance spectra of nano-composite cathode compared with LSMO cathode

The R_P value of the layered composite cathode is measured as higher (2.72 Ω-cm^2) compared with the R_P value of the mixed composite (1.76 Ω-cm^2). This may be owing to the thickness of the nano-composite cathode films. The thickness of the cathode film in the layered composite was greater compared to the mixed composite. Since the layered composite needed to be coated with the electrolyte (GDC) on both sides, the thickness of the cathode film was higher compared with the mixed composite. Thus, from the results it is understood that developing a composite cathode using LSMO and BSCMF materials can be a promising strategy to enhance the performance of low temperature SOFCs. Compared with the layered configuration, producing composites by mixing both the LMSO and BSCMF powders to produce the cathode material was found to be effective in decreasing the polarization resistance in improving the performance of low temperature SOFCs.

CONCLUSIONS

In the current work, two different cathode materials (LMSO and ion-doped BSCMF) were used to produce composite cathodes in two different configurations (layered and mixed). By using gadolinium-doped ceria as the electrolyte, symmetric cells were fabricated, and the cell performance was assessed by measuring the polarization resistance (R_P) at 700°C. Furthermore, while sintering the cathode powders, different temperatures (900, 950 and 1000°C) were adopted to produce the mixed composite cathode. From the impedance spectroscopy, a lower R_P value (1.76 Ω-cm^2) was observed for the cathode produced at 900°C. Compared with the monolithic LMSO cathode (23.88 Ω-cm^2), the composite cathodes exhibited lower R_P values, which indicates the promising role of producing the cathodes by using composite powders. Furthermore, the mixed mode of configuration was observed with a lower R_P (1.76 Ω-cm^2) compared with the layered configuration of the composite (2.72 Ω-cm^2). The results demonstrate the potential of combining LMSO and ion-doped BSCMF cathode materials to yield combined benefits and to improve the performance of low temperature SOFCs.

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