Bi$_2$O$_3$ AS A SINTERING AID FOR La(Sr)MnO$_3$ CATHODE MATERIAL FOR SOFC

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ABSTRACT

Sr-doped lanthanum manganite [La(Sr)MnO$_3$] has been prepared by two different routes namely (1) solid state route and (2) citrate-gel route. The powder prepared through citrate-gel route is relatively finer than that prepared through solid state route. Sintering characteristics of the powders have been studied by measuring density and porosity. Bi$_2$O$_3$ is found to be an effective sintering aid for La(Sr)MnO$_3$. Measurement of electrical conductivity and thermal expansion coefficient at elevated temperatures indicate that Bi$_2$O$_3$ addition does not have any adverse effect on these properties so far as SOFC application is concerned.

1. INTRODUCTION

Sr-doped lanthanum manganite [La(Sr)MnO$_3$] is known to be a very promising cathode material for SOFCs based on stabilized zirconia electrolyte (1). A nominal composition of La$_{0.84}$ Sr$_{0.16}$ MnO$_3$ is normally used in the present generation SOFCs for its high electrical conductivity as well as thermal and chemical stability at the working temperature and also because of its compatibility with the zirconia electrolyte. Conventionally the compound is prepared by solid state reaction of metal oxides or carbonates at high temperatures. However in recent years various other techniques, primarily the solution chemistry routes, have also been reported (2-5). The material is normally sintered at a temperature above 1400°C to get a dense product (6-9). In an earlier investigation (10) Bi$_2$O$_3$ was tried as a sintering aid with the powder prepared by solid state route. However, no significant effect was reported.

In this investigation, La$_{0.84}$ Sr$_{0.16}$ MnO$_3$ has been prepared by conventional solid state route as well as citrate-gel route. The effect of addition of small amounts
of Bi$_2$O$_3$ on the sintering behaviour of these powders have been studied in detail. In order to check the suitability of the material as a cathode, its electrical conductivity and thermal expansion have also been measured at elevated temperatures.

2. EXPERIMENTAL

The solid state powders were prepared by reaction of oxides and carbonates at a high temperature as described by several investigators (6-8). The raw materials used were La$_2$O$_3$, Mn$_2$O$_3$ (prepared from decomposition of (CH$_3$COO)$_2$Mn, 4H$_2$O) and SrCO$_3$. After thorough mixing they were calcined at 1050°C for 6 h followed by grinding in a planetary mill (Fritsch, Model P4). The preparation of the powder by the citrate-gel technique follows the principle adopted by Baythoun and Sale (3) and Blank et al. (11) but with certain differences. In the present investigation, the starting materials were La(NO$_3$)$_3$, (CH$_3$COO)$_2$Mn, 4 H$_2$O and Sr(NO$_3$)$_2$. To the mixed aqueous solution of these salts, required amount of citric acid was added and the solution was slowly heated on a hot plate (keeping a constant temperature of 80°C) with continuous stirring until initially a viscous gel was formed which on further heating became dry and finally burnt with glowing flame. The ash, thus obtained, was calcined at 800°C to obtain a very fine and phase-pure powder. The powder after calcination was mixed thoroughly with varying amounts of Bi$_2$O$_3$ (1-10 wt.%) and pressed into small pellets at a pressure of 226 MPa. These pellets were sintered in air at different temperatures up to a maximum of 1425°C normally for 6h. X-ray diffraction studies were made using Cu-K$_\alpha$ radiation (Philips - PW 1730) and particle size distribution was analysed by SediGraph - 5100. Bulk density of the sintered material was measured by liquid displacement method using toluene and porosity was measured by mercury porosimeter (Quanta Chrome, USA). Fracture surface of the sintered specimens were observed in SEM. Electrical conductivity was measured by four probe technique (12) and thermal expansion was measured by a recording dilatometer (Shimadzu DT- 30).

3. RESULTS AND DISCUSSION

a) X-ray Diffraction Study

X-ray diffraction patterns reveal no detectable change in phase purity of the samples with the addition of...
different amounts of Bi$_2$O$_3$. The material remains single phase throughout the composition range. It crystallizes with the perovskite type structure in R3C space group. The XRD spectra of two representative samples with 10 wt.% Bi$_2$O$_3$ and without Bi$_2$O$_3$ are shown in Fig.1 and hexagonal-rhombohedral unit cell dimensions, as obtained by using computer programme POWD, and presented in Table I, are similar to those obtained by Hammouche et al.(13) for Sr-doped LaMnO$_3$ in the region of low Sr concentration. Since no additional phase containing Bi$_2$C$_3$ has been detected by XRD it is evident that Bi$_2$O$_3$ has entered into the lattice of La$_{0.84}$Sr$_{0.16}$MnO$_3$.

b) Particle Size Distribution

Cumulative mass percent finer vs equivalent spherical diameter of the initial powders prepared by two different routes are shown in Fig. 2. Average median diameter obtained in citrate-gel route is 1.14µm which is much lower than that obtained in case of solid state route (2.16µm). It may be observed that in citrate-gel powder 46% particles are in submicron range as compared to only 12% for the solid state powder.

c) Sintering Study

The effect of Bi$_2$O$_3$ as well as that of powder preparation technique on the sintered density is clearly evident from the results presented in Fig.3 in which the percentage theoretical density of the sintered pellets is plotted against Bi$_2$O$_3$ content for different temperatures of sintering used for the two types of powders prepared in this investigation. For each of the temperatures and bismuth oxide contents the extent of sintering is considerably better in case of citrate-gel derived powder. This is expected not only because of the finer particle size but also possibly due to greater reactivity of this powder. However, the effect of temperature on the sintered density is more or less similar for both the powders. In general, the density increases in a regular manner with increasing temperature. The effect of bismuth oxide, on the other hand is quite different in the two cases. For the solid state powder, the sintered density increases steadily with the wt.% bismuth oxide added, resulting in a near straight line behaviour. In case of citrate-gel derived powder, on the other hand, most of the density increment takes place with the smallest amount of bismuth oxide added in this investigation (1 wt.%). Further addition of the sintering aid does not change the density so much particularly for higher sintering temperatures. This is an interesting observation in the sense that bismuth oxide appears to be a
more effective sintering aid when the particle size of the starting powder is finer and it is more reactive.

The effect of sintering temperature on densification is more distinctly seen in Fig. 4. The observed S shaped curves are typical of any sintering study. The effectiveness of bismuth oxide as the sintering aid is also very clearly demonstrated in this figure. In the absence of Bi$_2$O$_3$ the densification increases gradually with increasing temperature. Negligible sintering takes place below 1100°C and around 80% densification occurs at a sintering temperature of 1275°C. But with addition of just 1 wt.% Bi$_2$O$_3$, there is a sudden increase in density between 1050 and 1100°C, thereafter it increases rather gradually till about 1275°C. 10 wt.% Bi$_2$O$_3$ addition is still more effective in enhancing the sintering rate particularly at lower temperatures. In this case the densification starts from a very low temperature (below 1000°C) and a maximum densification of 87% is achieved at a temperature as low as 1125°C. Further increase of temperature does not have much effect on densification. It may be once again emphasized at this stage that such a distinct advantage of bismuth oxide as the sintering aid has not been observed in case of conventionally prepared (solid state route) lanthanum manganite powder.

In accordance with the density data presented above, the open porosity as measured by mercury porosimeter decreases quite significantly with addition of Bi$_2$O$_3$ (Fig. 5). In absence of Bi$_2$O$_3$ the porosity is around 12% which decreases to around 1% with 10 wt.% of the additive.

The effectiveness of Bi$_2$O$_3$ as a sintering aid is also evident from the SEM fractographs of the sintered specimens presented in Fig. 6. A progressive change in microstructure with Bi$_2$O$_3$ content is clearly visible. As expected, more and more dense microstructure is formed with increasing Bi$_2$O$_3$ content. A fully dense clean microstructure with beautifully developed grains is formed with the highest amount of Bi$_2$O$_3$. No grain boundary phase appears to be formed during sintering. This also corroborates our conclusion from the X-ray diffraction study. Therefore, liquid phase sintering does not appear to be the mechanism for enhanced sintering in this system. Solid state sintering with increased point defect concentration resulting from solid solution effect may be the cause of enhanced sintering. More detailed investigation is however, necessary in this direction.
d) Electrical Conductivity and Thermal Expansion Behaviour

The values of electrical conductivity ($\sigma$) and thermal expansion co-efficient (TEC) for the specimens sintered at 1200°C for 6 h. with different percentages of Bi$_2$O$_3$ are presented in Table II. It may be seen that these results are comparable to those reported earlier (5,10,13) for Sr-doped LaMnO$_3$ without Bi$_2$O$_3$ addition. With the increase of Bi$_2$O$_3$ content electrical conductivity at 950°C increases gradually but there is negligible change in thermal expansion coefficient. The increase of electrical conductivity with Bi$_2$O$_3$ may be attributed to the increase of density ($d$) of the material as reported earlier (10). As Bi$_2$O$_3$ addition does not have any adverse effect on these crucial properties, it is likely to be a prospective sintering aid for the SOFC cathode material.

4. CONCLUSIONS

Bi$_2$O$_3$ is found to be a very effective sintering aid for La$_{0.84}$Sr$_{0.16}$MnO$_3$ particularly when the starting powder is prepared by citrate-gel route. Addition of Bi$_2$O$_3$ does not appear to form any additional phase after sintering. The enhancement in sintering is possibly due to the solid solution of Bi$_2$O$_3$ with strontium-doped lanthanum manganite which increases the concentration of point defects in the lattice. Bi$_2$O$_3$ addition does not have any adverse effect on the electrical conductivity and thermal expansion behaviour of the cathode material.

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Table I: Lattice parameters of La$_{0.84}$Sr$_{0.16}$MnO$_3$ with and without Bi$_2$O$_3$

|                | No Bi$_2$O$_3$                                      | 10 wt.% Bi$_2$O$_3$                                |
|----------------|----------------------------------------------------|---------------------------------------------------|
| $a_h$          | 5.5170 Å                                           | 5.5234 Å                                         |
| $c_h$          | 13.3617 Å                                          | 13.3717 Å                                        |
| $V$            | 352.21 Å$^3$                                       | 353.29 Å$^3$                                     |
| $M(10)^*$      | 44.5                                               | $= 19.7$                                         |

* Figure of merit

Table II: Effect of Bi$_2$O$_3$ Content on the Electrical Conductivity and Thermal Expansion Coefficient of La$_{0.84}$Sr$_{0.16}$MnO$_3$ Sintered at 1200°C for 6 h.

| Bi$_2$O$_3$ Content ( Wt.% ) | Electrical Conductivity at 950°C ( S/cm ) | Thermal Expansion Coeff. at 1000°C ( x 10$^{-6}$/°C ) |
|------------------------------|-------------------------------------------|--------------------------------------------------------|
| 0                            | 127                                       | 11.22                                                  |
| 1                            | 149                                       | 11.26                                                  |
| 5                            | 153                                       | 11.44                                                  |
| 10                           | 171                                       | 11.61                                                  |
Fig. 1. X-ray powder diffraction patterns for La$_{0.84}$Sr$_{0.16}$MnO$_3$ (a) without Bi$_2$O$_3$ (b) with 10 wt.% Bi$_2$O$_3$.

Fig. 2. Cumulative mass percent finer vs. diameter for La$_{0.84}$Sr$_{0.16}$MnO$_3$ for powders prepared in citrate gel route (solid line) and solid state route (dashed line).
Fig. 3. Effect of Bi$_2$O$_3$ content on the densification of La$_{0.84}$Sr$_{0.16}$MnO$_3$ at different temperatures (sintering time 6 h) solid lines are for citrate-gel powder and dashed lines for solid state powder.

Fig. 4. Effect of sintering temperature on densification of the specimens prepared in citrate-gel method (sintering time 6 h).

Fig. 5. Variation of apparent porosity with Bi$_2$O$_3$ content in the specimens prepared by citrate-gel route and sintered at 1200°C for 6 h.
Fig. 6 SEM photographs of fractured surfaces of the specimens containing different percentages of Bi$_2$O$_3$ (a) 0 (b) 1 (c) 5 (d) 10 (all samples sintered at 1200°C for 6h).