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SYNTHESIS OF NEW Mn/Ti CONTAINING PERVOSKITES AND EXAMINATION OF THEIR POTENTIALS FOR USE AS SOLID OXIDE FUEL CELL ELECTRODES

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ABSTRACT

A series of new Mn/Ti containing perovskites, $La_{1-x}Mn_xMn_{1-x}Ti_xO_{3-\delta}$ were synthesized for investigation of their potential for use as solid oxide fuel cell electrodes, particularly anodes. Single-phase samples could be achieved for x ≤ 0.4. Above this level, $La_2Ti_2O_7$ impurities were found. Conductivity measurements showed electronic conductivity up to a maximum of 12 S cm^{-1}at 650°C in air. While the samples were shown to be stable in both air and 5% H_2S, the conductivities in the latter were significantly lower (≈0.4 S cm^{-1}), which would be an issue for potential anode application.

KEYWORDS: Solid oxide fuel cell; anode; perovskite; titanate; manganate

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INTRODUCTION

The requirement to reduce fuel usage and carbon emissions has driven considerable research into fuel cells. In terms of stationary power applications, solid oxide fuel cells (SOFCs) have attracted considerable interest due to their high efficiencies and fuel flexibility. In terms of the anode, the most widely used system has been Ni dispersed into a matrix of electrolyte material[1, 2].While demonstrating for the most part excellent performance, this cermet anode is not without its problems, in particular a tendency for coking at elevated temperatures, and sulphur poisoning when using hydrocarbon fuels, such as natural gas. Consequently, there has been considerable interest in the development of new anode materials as outlined in recent review articles[3, 4]. In particular, mixed metal oxides that are redox stable are attracting growing interest, driven by the expectation that they will be less susceptible to the coking or sulphur-poisoning problems associated with Ni[5–12]. In this respect, perovskite systems have attracted considerable interest including Ti-, Cr/Mn- and Mo-based systems [3, 4, 11, 12]. Titanate systems, based around $SrTiO_3$, were the first perovskite systems to be investigated. Undoped $SrTiO_3$ was found to be difficult to reduce, even at the high-operating temperatures of an SOFC, leading to low electronic conductivity. However, through doping on either the Sr or Ti sites, samples with conductivities up to 10 S cm^{-1} were obtained[8, 10], with further improvements possible via prereduction at temperatures up to 750°C[11-15]. However, while respectable electronic conduction can be achieved, these systems struggle with relatively low oxide ion conductivity, in part due to the lack of oxide ion vacancies in the material. In order to improve the conducting properties, we have synthesized a series of mixed Mn/Ti-based perovskites. The starting point of the series examined is $LaMnO_3$, a traditional SOFC cathode material when doped with Sr. In order to create a potentially redox stable material capable of being used as a SOFC anode, we have examined partial substitution of Ti^{4+} in place of Mn^{3+}, with charge balance achieved through introduction of Mn^{2+} on the La^{3+} site, which results into the composition of $(La_{1-x}Mn_x)\ Mn_{1-x}Ti_xO_3$. An attempt has been made to introduce manganese to improve the oxide ion conductivity over most titanates, while theTi^{4+} remains present to increase redox stability, and provide an N-type electronic contribution under reducing conditions. The results reported are based on the synthesis of samples in this series by investigating their conductivities in air and 5% H_2S environment.

METHODS AND MATERIALS

High-purity La_2NO_3, $SrNO_3$, $MnNO_3$ and $TiNO_3$ were used to prepare the samples using sol gel citrate method. A stoichiometric mixture of nitrates was mixed with citric acid and ethanol and stirred magnetically at 80°C for 3h to obtain a homogenous solution which was further heated in a pressure vessel at about 130°C for 12 hrs and subsequently kept at 350°C for 3h. The dried powder was then calcined from 450 to 750°C, in order to improve the crystallinity of the powder. To improve the sensitivity and selectivity, nitrates were added to the reaction mixture in the proper ratio. Fig 1 shows the flow chart for the synthesis of nanocrystalline samples. These were crushed to desired mesh size and the pellets were prepared for the conductivity measurements using the 4 probe dc method in both air and 5% H_2S atmosphere. Further XRD study was also carried out on samples to confirm redox stability.

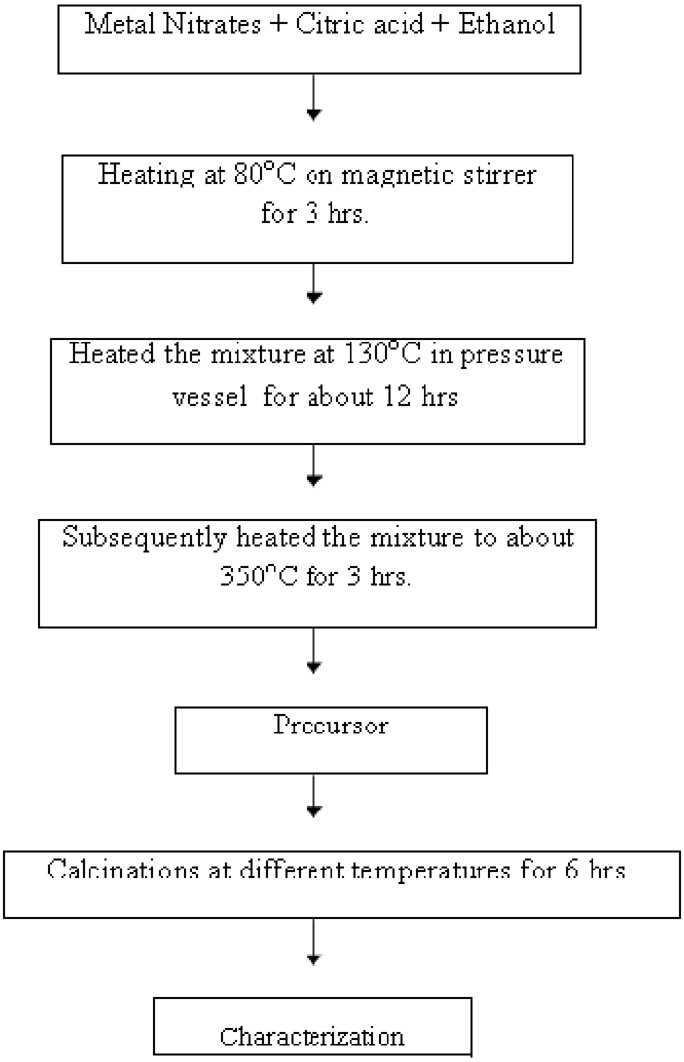

Figure 1
Flow chart for the preparation of nanomaterial

RESULTS AND DISCUSSION

Following the synthesis conditions outlined above, XRD showed single-phase samples for x ≤ 0.4, with $La_2Ti_2O_7$ impurities observed for higher Ti levels. Conductivity measurements were therefore performed on the following samples, $La_{0.6}MnTi_{0.4}O_3$ (x=0.4), $La_{0.7}MnTi_{0.3}O_3$ (x=0.3) and $La_{0.8}MnTi_{0.2}O_3$ (x=0.2). Initially, measurements were made in air and these results showed semiconducting behavior with conductivities in the range of 1.6–12.5 S cm^{-1}at 650°C, with the conductivities being lowest for samples with higher Ti content as shown in Figure 2. In addition, the activation energy values showed rising trend across the series as the Ti content (x) increased, Ea =59.5, 49.2 and 46.5 $kJmol^{-1}$ for x = 0.4, 0.3 and 0.2, respectively (Figure 3). The decrease in conductivity in air with increasing Ti content is to be expected as manganate perovskites have higher conductivities than their titanate counterparts in oxidizing conditions.

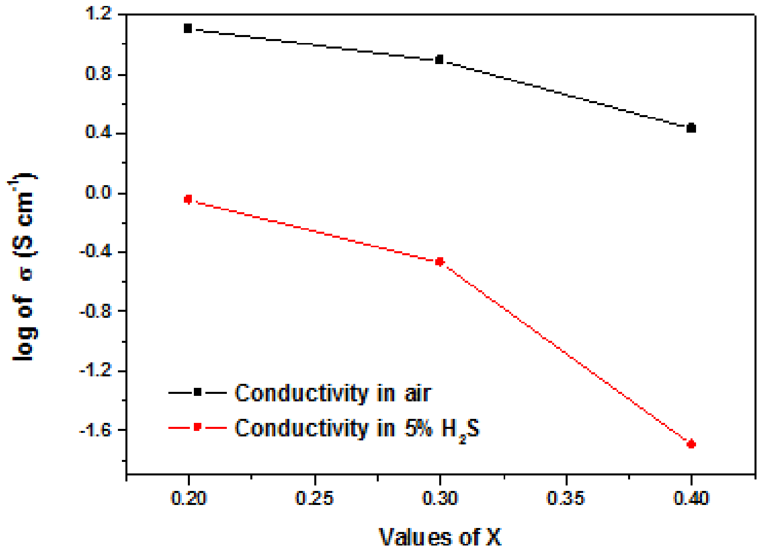

Figure 2
Variation in the Conductivities of the series $La_{1-x}Mn_x$ $Mn_{1-x}Ti_xO_{3-\delta}$ in air and 5% H_2S at 650°C.

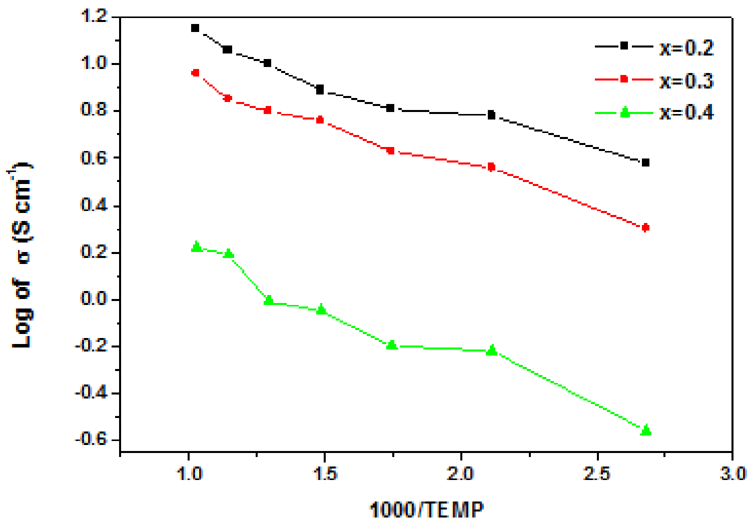

Figure 3
Graph of Log_{10} Conductivity vs. 1000/T for the series $La_{1-x}Mn_x$ $Mn_{1-x}Ti_xO_{3-\delta}$ in air.

The conductivities were then measured under 5% H_2S.Samples were heated in this atmosphere up to 750°C and held for 1 h before making measurements on cooling. The data showed that the conductivities of all three samples suddenly decreases by several orders of magnitude, to be in the range of 0.015–0.4 S cm^{-1}. As before, the lowest conductivities were observed for the samples with the higher Ti content. The activation energies displayed the similar trend once again, rising as 'x' increases, with Ea = 188.0, 154.3 and 114.8 kJmol^{-1} for x =0.4, 0.3 and 0.2, respectively (Figure 4). Thus, in addition to the lower conductivities, the activation energies are considerably higher especially for the high Ti content samples. The samples were analyzed by XRD after the conductivity measurement, which confirmed that no decomposition had occurred. However, while the samples show positive redox stability.

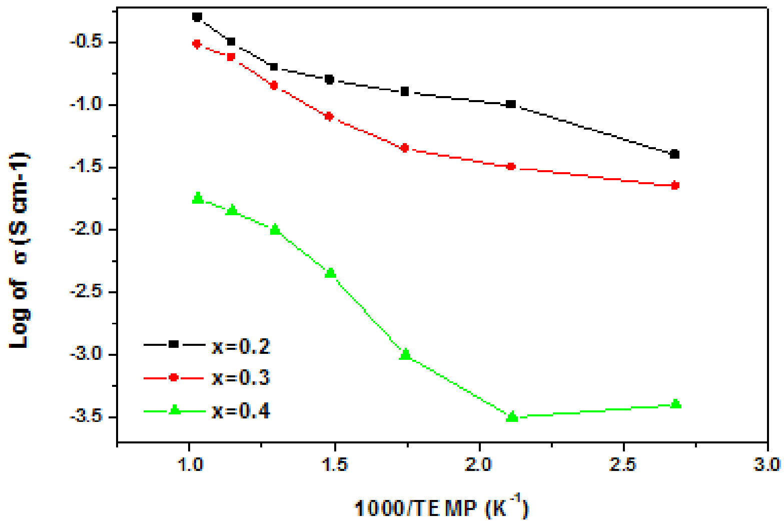

Figure 4
Graph of Log_{10} conductivity vs. 1000/T for the series $La_{1-x}Mn_x\ Mn_{1-x}Ti_xO_{3-\delta}$ in 5% H_2S.

CONCLUSION

A new series of perovskite systems, $La_{1-x}Mn_xMn_{1-x}Ti_xO_{3-\delta}$ ($x \leq 0.4$), synthesized during this work are found to be stable under both the cathode and anode SOFC operating conditions. While reasonable magnitudes of conductivities were observed in air, which decreases substantially in reducing environments.

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