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Mixed Ionic and Electronic Conduction in Mn/Mo Doped Gadolinium Titanate

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Abstract

Recent work has shown that $Gd_2(Ti_{1-x}MO_x)_2O_7$ *(Mo doped GT) exhibits high levels of mixed conduction under reducing atmospheres, making it suitable as an anode in a solid oxide fuel cell. It decomposes at high* P_{O_2}, *however. We have succeeded in extending the stability limits of the GT–Mo to higher* P_{O_2} *with the addition of Mn. Our earlier studies on* $Gd_2((Mo_yMn_{1-y})_xTi_{1-x})_2O_7$ *(GMMT) as a function of* P_{O_2}, *T, and composition utilizing impedance spectroscopy and X-ray diffraction are extended to include the joint effects of variations in x and y on the conductivity and stability of the material in cathodic environments. Defect models explaining the dependence of the partial conductivities on oxygen partial pressure, temperature and composition are also presented. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

Solid oxide fuel cell materials have gained a great deal of attention in recent years due to the fuel cell's environmentally friendly operation and high electrical efficiency. The pyrochlore, $Gd_2Ti_2O_7$ (GT), is a promising material for incorporation in solid oxide fuel cells (SOFC). Ca doped GT, in particular, is attractive as an electrolyte material due to its high ionic conductivity and low electronic conductivity.[1] Mo doped GT has been shown to have a very high mixed ionic and electronic conductivity (MIEC) under reducing conditions, making it suitable as an anode material.[2]

If a pyrochlore material could be found that exhibits high MIEC under cathodic conditions, a monolithic fuel cell constructed entirely from pyrochlore materials could be constructed.[3] In such a cell, each different region of the cell (anode, electrolyte and cathode) is composed of materials of the same phase doped appropriately to provide the required conduction properties. Monolithic cells have a significant advantage in mechanical, thermal and chemical stability.[4] This paper focuses on the search for a stable MIEC pyrochlore under cathodic conditions.

The starting material for this work is Mo doped GT, $Gd_2(Mo_xTi_{1-x})_2O_7$. As demonstrated previously,[2] for high values of x under reducing conditions, this material exhibits high electronic conductivity ($\sigma_e \geq 10^{1\cdot5}$ at 1000°C) while maintaining a reasonable ionic conductivity ($\sigma_i \geq 10^{-1}$ at 1000°C). However, the material decomposes at higher partial pressures of oxygen. This decomposition was attributed to a sharp increase in oxygen interstitial concentrations due to Mo shifting valence from Mo^{+4} to Mo^{+6}.

Previously we reported conductivity and stability data for $Gd_2(Mo_{1/3}Mn_{2/3})_xTi_{1-x})_2O_7$ (GMMT) as a function of x.[5] All compositions were stable in air (up to $x=0\cdot2$). The conductivity was found to be primarily electronic with a value of about 10^{-1} S/cm in air (for $x=0\cdot2$). This was significantly higher than the highest value achieved previously with a stable Mo doped GT composition (Mo dopant value of 10%) in air of about 10^{-2} S/cm. The addition of Mn as a co-dopant was shown to stabilize the Mo valence. The Mn shifts its valence from Mn^{4+} to Mn^{3+}, thereby compensating the valence shift in Mo from +4 to +6. The ratio Mo/Mn was kept to 1/2 at first to provide full charge compensation for the valence shift in the Mo. According to the defect theory presented in Ref.5 (see Fig. 1), it should be possible to raise the overall conduction level by increasing the Mo/Mn ratio. In this work,

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we examine the results of the importance of this ratio in governing the overall conduction level.

Two-probe AC impedance is used to extract values for the bulk conductivity. These measurements were performed as a function partial pressure of oxygen (P_{O_2}), and temperature. The stability of the materials was monitored by X-ray powder diffraction. The conductivity results were then compared against a defect model for the system to aid in establishing the microscopic conduction mechanisms.

2 Experimental

Powders of $Gd_2((Mo_{2/3}Mn_{1/3})_xTi_{1-x})_2O_7$ (Mo/Mn = 2) were made via a citric acid based liquid organic preparation route[6] for the composition $x = 0{\cdot}1$. Disk shaped samples (average area of 0·3 cm^2 and length of 0·2 cm) were first pressed uniaxially at 5000 psi ($3{\cdot}45\times10^7$ Pa) for 15 min. They were then isostatically pressed at 40000 psi ($2{\cdot}76\times10^8$ Pa) for 10 min and sintered at 1250°C for 16 h under an atmosphere of 50% CO/50% CO_2 gas. Upon completion of the sintering, the samples were quenched from this temperature with continued gas flow. It should be noted that these sintering conditions are significantly different from the ones used in Ref. 5 (which were sintered in air at 1500°C). The conditions were changed to correct observed Mo losses in the samples during sintering. Electrodes were prepared by applying layers of Pt paste and firing at 1000°C for 20–30 min.

AC impedance scans were performed with a Solartron 1260 frequency response analyzer. Measurements were made from 1 MHz to 0·1 Hz. Scans were made under the conditions 600°C $\leq$ 1000°C and 10^{-25} atm $\leq P_{O_2} \leq$ 1 atm. Fitting of the AC impedance data was performed with the commercially available 'Zview' software program from Scribner Associates, Inc. Stability investigations were performed by X-ray powder diffraction.

3 Results

The conductivity of $Gd_2(Mo_{2/3}Mn_{1/3})_{0{\cdot}1}Ti_{1-x})_2O_7$ (Mo/Mn = 2) is shown in Fig. 2 as a function of P_{O_2} and T. The plots show that the conductivity is P_{O_2} independent under oxidizing environments. The conductivity then increases roughly 1/2 an order of magnitude and reaches a second plateau under reducing conditions. Under extremely reducing conditions, the conductivity again begins to increase as P_{O_2} is decreased.

The conductivity of the Mo/Mn = 2 sample is compared to previous conductivity data taken on a Mo/Mn = 1/2 sample[5] at 900°C in Fig. 3. The Mo/Mn = 2 sample has a noticeably higher conductivity and a significantly different P_{O_2} dependence than the Mo/Mn = 1/2 sample. The Mo/Mn = 1/2 sample exhibits no plateau under reducing conditions. The activation energies of conduction in the two samples in oxidizing environments (air) were calculated to be 0·62 eV for the Mo/Mn = 2, and 0·57 eV for the Mo/Mn = 1/2.

X-ray analysis taken of the Mo/Mn = 2 pellet immediately after sintering in reducing conditions indicate a fully pyrochlore phase. Scans were also performed on the pellet after quenching from air at 800°C after conductivity measurements were performed. These also indicated a fully pyrochlore phase.

4 Discussion

As predicted (Fig. 1), raising the Mo/Mn ratio does lead to higher conductivity in GMMT. While the

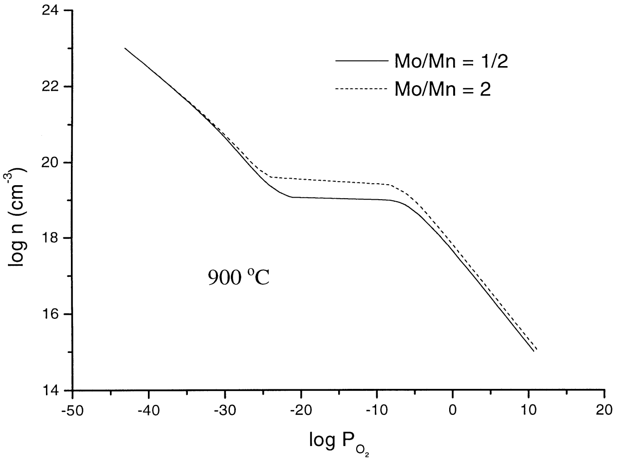

Fig. 1. The electron concentration of GMMT at 900°C with Mo/Mn = 1/2 and Mo/Mn = 2 is shown plotted against P_{O_2}. This plot was generated using the methods developed in. Ref. 7.

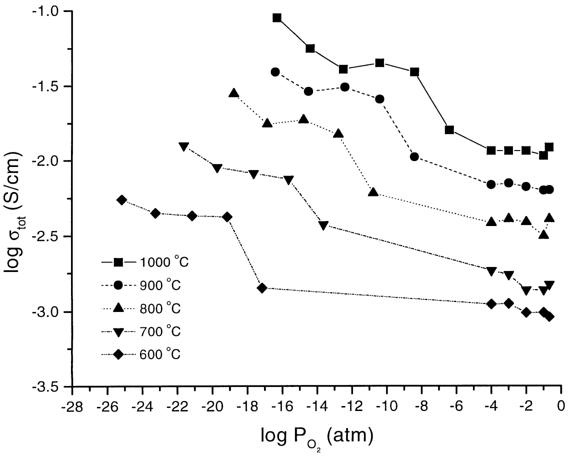

Fig. 2. The total conductivity of GMMT with Mo/Mn = 2 is shown versus P_{O_2} and T. The plots have two plateaus, one under oxidizing conditions and one at more reducing conditions.

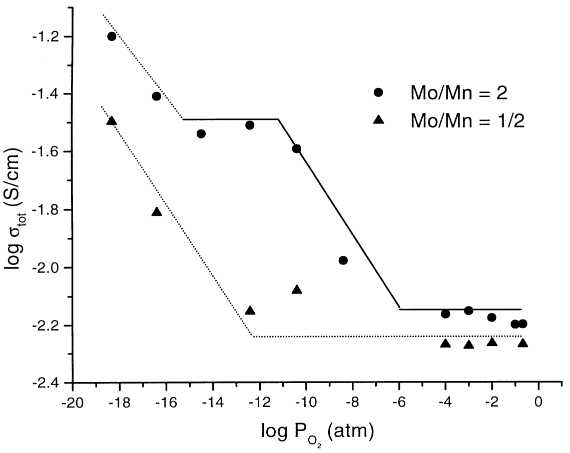

Fig. 3. The total conductivity of Mo/Mn = 2 is compared against that of Mo/Mn = 1/2 at 900°C versus P_{O_2}. Note the absence of a second plateau under reducing conditions for the Mo/Mn = 1/2 line.

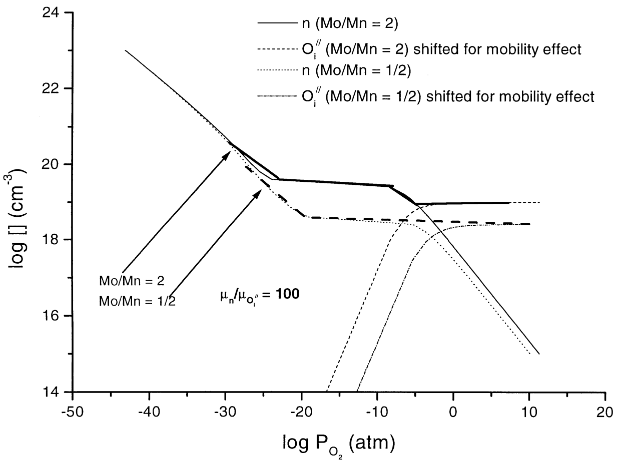

Fig. 4. Plot of various defect concentrations in GMMT with both Mo/Mn = 2 and Mo/Mn = 1/2 at 1000°C. The electron concentration (*n*) and oxygen interstitials corrected for the shown mobility ratio are shown. The bold lines indicate the dependence of the total conductivity given this mobility assumption. The conductivity in this model is controlled by oxygen interstitals at high P_{O_2} and electrons at lower P_{O_2}

conductivity is raised by nearly 1/2 an order of magnitude at intermediate and low $P_{O_2} < 10^{-5}$ atm), the effect is more limited under the oxidizing regime of interest. As explained in. Ref. 5 the conductivity is thought to be primarily electronic. At intermediate P_2 the dopant sites in the band gap control the conductivity level by thermal ionization of electrons to the conduction band. Mn lies lower in the band gap than Mo. For Mo/Mn = 1/2 in this regime, the Mo^{+6}, is fully compensated by Mn^{+3}. All electrons in the conduction band are excited from the lower Mn level. By raising the Mn/Mo ratio to 2, more electrons are trapped in the MO level since there is no longer enough Mn to fully compensate the charge shift. The Fermi level moves closer to the conduction band edge thereby raising the concentration of electrons in the conduction band. Removing Mn eventually leads to the case of pure Mo doped GT. In this case, the Mo charge shift to +6 is compensated by oxygen interstitial instead of Mn, which leads to decomposition of the material for high MO concentrations.

The other feature of Fig. 3 is the differing conductivity trends with P_{O_2} for the Mo/Mn = 1/2 and Mo/Mn = 2 samples. The Mo/Mn = 2 material exhibits two plateaus while the Mo/Mn = 1/2 material exhibits only one broad plateau. Figure 4 shows the dependence of selected defects plotted versus P_{O_2} for both samples based on a modeling program developed in. Ref. 7 The electron concentrations are shown as well as the oxygen insterstials concentration shifted to account for the mobility differential, assuming that the electron mobility is 100× higher than that of the interstitials. The total conductivity is then shown across all P_{O_2} by the bold lines. In the scenario pictured in Fig. 4, the oxygen interstitials actually control conduction under oxidizing conditions. The electrons then dominate as the material passes into reducing conditions ($P_{O_2} < 10^{-10}$ atm). This shift in mechanism leads to the plateau in the Mo/Mn = 2 sample. The Mo/Mn = 1/2 sample shows no plateau as the conduction level of the two regimes happen to be nearly equal. This model is also consistent with other Mo/Mn = 1/2 compositions shown in Ref. 5.

It might be reasonable to propose that the plateaus shown in the Mo/Mn = 2 sample were due to phase changes in the sample. However, X-ray analysis on the sample both after sintering and quenching in reducing atmosphere and after quenching from 800°C in air showed a fully pyrochlore phase.

While the model in Fig. 4 matches well with the actual experimental data shown in Fig. 3, the model requires additional supporting evidence. Concentration cell measurements are planned to confirm the presence of ionic interstitial conduction at high P_{O_2}. Other factors need to be ruled out as well. As mentioned in Experimental, the two samples were sintered under significantly different conditions. The Mo/Mn = 2 sample was sintered at 1250°C under reducing conditions to avoid observed Mo loss during sintering. The Mo/Mn = 1/2 sample, on the other hand, was sintered at 1500°C in air. The differing conduction behaviors maybe due to Mo loss in the Mo/Mn = 1/2 sample. Experiments are under way to reproduce the Mo/Mn = 1/2 data with samples sintered in the same manner as the Mo/Mn = 2 sample.

5 Conclusions

Previous work on the system $Gd_2(Mo_{1/3}Mn_{2/3})_x Ti_{1-x})_2O_7$ (GMMT) was extended to include varying Mo/Mn dopant ratio. An increasing overall conductivity value was predicted for increasing Mo/Mn based on an defect chemical model. Conductivity values for GMMT ($x=0{\cdot}1$) with Mo/Mn = 1/2 and Mo/Mn = 2 as a function of P_{O_2} and T were compared. Analyses of both were performed based on the theoretical defect model. While the Mo/Mn = 2 did show an enhanced conduction value, P_{O_2} dependencies of the conductivities were quite different. These observations could be explained on the basis of a conduction model where oxygen interstitials are dominant at high P_{O_2} followed by a shift to electron dominated conduction at lower P_{O_2}. Future work will concentrate on confirming these conduction mechanisms, especially the presence of oxygen interstitial conduction at high P_{O_2}. Specimens with increased values of x will be analyzed in an effort to raise the conductivity to even higher values.

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