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Ternary titanates as anode materials for solid oxide fuel cells

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Abstract

The electrical properties and phase stability of the titanates $LiTi_2O_4$, $Li_xTi_{3-x}O_5$, $Mg_xTi_{3-x}O_5$, $CrTi_2O_5$, and the niobium-doped compounds $MgTi_2O_5$, Mg_2TiO_4, and $Sm_2Ti_2O_7$ have been studied. High DC-conductivities, using the four-point technique, have been measured in reducing atmospheres (hydrogen) and in the presence of Nb^{5+} dopants at higher oxygen partial pressures. The possible application of these materials as anodes in solid oxide fuel cells is discussed in respect to their electrical and structural properties and redox behaviour.

1. Introduction

The emphasis of this work is to develop suitable materials for anodes in solid oxide fuel cells (SOFC) operating with natural gas. It has been pointed out that the Ni–ZrO_2 cermet anodes which are established for syngas fuels are not stable in hydrocarbon atmospheres [1]. Therefore, alternative materials with good electronic conductivity (>10 S cm^{-1} at 900 °C) at the SOFC operation potential of -1.0 to -0.7 V are desired. According to the Nernst equation this means an oxygen partial pressure range of $\approx 10^{-18}$ to 10^{-13} bar at 900 °C. Additionally, the anode should be able to withstand a locally formed reducing potential caused by carbon formation at the surface. The material should exhibit a comparable thermal expansion coefficient to zirconia and no major phase transition or interface reaction should occur. However, most oxides with high conductivities depending upon the 'mode' of operation are not stable at very low pO_2 values. In addition, high catalytic activity for either total or partial oxidation of methane is desirable.

Mixed valence state (Ti^{3+}/Ti^{4+}) titanates such as the superconducting $LiTi_2O_4$ [2], Mg_2TiO_4–$MgTi_2O_4$ spinel [3, 4], Ti_2O_3–$MgTiO_3$ ilmenite [5, 6] and Ti_3O_5–$MgTi_2O_5$ pseudobrookite-type solid solutions [7, 8], and $CrTi_2O_5$ are among the promising candidate oxides for SOFC anodes; they show high electronic conductivities especially at low pO_2 [8]. Both the structural aspects [8] and the catalytic properties [9, 10] of various titanates have been reported elsewhere. In this work we have concentrated on the redox behaviour and the electrical conductivity of selected titanates depending on the oxygen partial pressure and present some thermal expansion data.

The effect of pO_2 variation and donor-type doping on the electrical conductivity of titanates, *e. g.* rutile-type TiO_2 (see *e.g.* [11–16]) and earth alkaline perovskites (see *e.g.* [17]) has been the subject of several investigations. Generally, there is a region of n-type behaviour which is shifted to higher pO_2 values either with increasing temperature or a small amount of donor-type doping, namely Nb^{5+} and Ta^{5+}. In this case, the compensation of the Nb^{5+} on the Ti^{4+} sites by the creation of an equal amount of Ti^{3+} ions has been described by Verwey's controlled valence model [18]. The present studies are concerned with the effect of doping with Nb^{5+} on the electrical conductivity of the spinel-Mg_2TiO_4, pseudobrookite-$MgTi_2O_5$, and pyrochlore-type $Sm_2Ti_2O_7$.

2. Experimental details

The mixed Ti^{3+}/Ti^{4+} titanates were prepared by solid state reaction of the binary oxides, dried at 700 °C and appropriate amounts of Ti powder at low oxygen partial pressure in an argon atmosphere or hydrogen/nitrogen (1:9) gas mixture. Pseudobrookite-type compounds $Mg_xTi_{3-x}O_5$ [7, 8] were synthesised using MgO (Hopkin & Williams, >99.9%), TiO_2 (Alfa, >99.8%) and Ti (Aldrich, >99.9%) following

$$x\mathrm{MgO} + (2.5-x/2)\mathrm{TiO_2} + (0.5-x/2)\mathrm{Ti} \longrightarrow \mathrm{Mg}_x\mathrm{Ti^{III}}_{2-2x}\mathrm{Ti^{IV}}_{1+x}\mathrm{O}_5$$

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Bars were formed under a pressure of 100 MPa, placed in a molybdenum foil boat and annealed for 15 h in a stream of hydrogen/nitrogen (1:9 mixture) or gettered argon at 1470 °C. The heating and cooling rates were 250 °C h^{-1}. Bars with 70 to 85% of the densities calculated from X-ray diffraction results were obtained. $CrTi_2O_5$ was prepared from Cr_2O_3 (Hopkin & Williams), TiO_2 and Ti.

The Li_x $Ti_{3-x}O_5$ solid solutions ($Li_xTi^{III}{}_{2-3x}Ti^{IV}{}_{1+2x}O_5$) and $LiTi_2O_4$ were formed at 1180 °C in a hydrogen/nitrogen atmosphere from Li_2TiO_3, TiO_2 and Ti [8].

Li_2TiO_3 was synthesised in air by annealing Li_2CO_3 (BDH, >99.5%) and TiO_2 at temperatures below 800 °C. The use of Li_2TiO_3 in the preparation at low oxygen partial pressures avoids Li_2O evaporation which would occur in a direct synthesis with Li_2CO_3.

The pure and niobium-doped compounds $Sm_2Ti_2O_7$, Mg_2TiO_4 and $MgTi_2O_5$ were prepared in air starting from the binary oxides in two steps with intermediate regrinding each for 24 h at 1200 and 1400 °C. Sm_2O_3 (Aldrich, >99.9%) contained both the cubic and the monoclinic form. Nb_2O_5 (Aldrich, 99.9%) was found to improve the sintering process of the titanates.

The samples were characterised by X-ray powder diffraction (XRD) on a Phillips PW 1710 diffractometer. Unit cell dimensions were calculated by a least squares method (LSUCR) with Si as an internal standard. High temperature XRD experiments were performed on a Siemens K710 generator with Kristalloflex D500 goniometer keeping the specimens under a constant flow of argon. Thermal expansion data were determined from the thermal evolution of the unit cell dimensions and dilatometer measurements.

Four-point DC-conductivities were measured in a dry atmosphere of hydrogen/nitrogen (1:9) providing an oxygen partial pressure of $\approx 10^{-20}$ bar at 1073 K. Contacts between the bars of about $35 \times 6 \times 6$ mm^3 size and platinum wires were made with platinum paste, and a constant current of 100mA was applied. Additionally, the electrical conductivity sigma of some of the samples was measured in dependence on the oxygen partial pressure using H_2/CO_2, CO_2/O_2 gas mixtures. The pO_2 measurement was achieved with a ZrO_2-based oxygen probe with platinum electrodes.

3. Results

3.1. *Ternary lithium oxides*

The main interest in ternary lithium oxides as anode materials in SOFC is focused on their good performance as catalysts in the oxidative coupling of methane to ethane and ethylene, *i.e.* they could be an essential part of an SOFC used as electrochemical reactor. $LiMn_2O_4$ [19], $LiNiO_2$ [20], $LiYO_2$ [21] and Li_2TiO_3 [22] exhibit high conversion rates and selectivities. However, the use as an SOFC anode material introduces more constraints such as thermodynamical stability at 900 °C and high electrical conductivity at low oxygen partial pressures. The latter is not fulfilled for $LiYO_2$ and Li_2TiO_3, the former not for $LiMn_2O_4$ and $LiNiO_2$. $LiNiO_2$ is reduced to nickel metal and Li_2O evaporates. $LiMn_2O_4$ is a mixed conductor (Li^+ ion and electronic) with an overall conductivity of ≈ 10 S cm^{-1} at 1173 K in air [23]. In a hydrogen atmosphere NaCl-structure-type compounds $Li_xMn_{1-x}O$ are formed rapidly. The lithium content of the prepared samples was about 2%, *e.g.* $Li_{0.02}Mn_{0.98}O$ as determined by the weight loss and by lattice parameter calculation ($a = 443.55(6)$ pm for the reduced $LiMn_2O_4$, see $a = 444.50$ pm for MnO and $a = 442.80$ pm for $Li_{0.046}Mn_{0.954}O$ [24]). MnO-based solid solutions are stable between 10^{-8} and 10^{-26} bar pO_2 at 1173 K, but the electrical conductivity is lower than 5 S cm^{-1} and can only slightly be enhanced by impurity doping (see, *e.g.* [25]).

Lithium titanates such as the spinel $LiTi_2O_4$ [2] or compounds of the pseudobrookite series $Li_xTi_{3-x}O_5$ [8] are thermodynamically stable at pO_2 values lower than 10^{-20} bar at 1173 K. The Li_2O vapour pressure is remarkably low even at higher pO_2 values, due to the formation of ternary titanates such as Li_2TiO_3. The electrical conductivity of some of the $Li_xTi_{3-x}O_5$ phases is shown in Table 1. The stability range of these mixed conductors does not extend at higher pO_2 values. New compounds with slightly higher oxygen contents are formed. The XRD pattern of these lithium titanates could not be indexed yet, but there are similarities with the 'shear structure' Magnéli phases Ti_nO_{2n-1} [26]. For $Li_{0.2}Ti_{2.8}O_5$ the mean linear expansion calculated from the volume increase in the XRD experiment is $6.0(\pm 0.5) \times 10^{-6}$ K^{-1} between 294 and 823 K in an argon atmosphere. The thermal expansion in the *b* and *c*-direction is 10 and 7×10^{-6} K^{-1} respectively. In the

TABLE 1. Electrical conductivity of selected titanates at elevated temperatures in hydrogen/nitrogen (1:9 mixture); for details see [8] and text.

Compound	log σ (σ in $\Omega^{-1} \times cm^{-1}$)	Temperature (K)
$Li_{0.02}Ti_{2.98}O_5$	1.95	973
$Li_{0.5}Ti_{2.5}O_5$	1.58	973
$Mg_{0.2}Ti_{2.8}O_5$	2.19	1073
$Mg_{0.3}Ti_{2.7}O_5$	2.03	1073
$Mg_{0.5}Ti_{2.5}O_5$	1.44	1073
$Mg_{0.8}Ti_{2.2}O_5$	1.12	1073
$Mg_{0.9}Ti_{2.1}O_5$	1.04	1073
$Mg(Ti, Nb)_2O_5$	0.02	1073
$Mg_2(Ti, Nb)O_4$	−1.19	1073
$CrTi_2O_5$	2.24	1073
$Sm_2(Ti, Nb)_2O_7$	−0.25	1073

a-direction only $\approx 4\times10^{-7}$ K^{-1} was determined indicating the anisotropy of Ti^{3+}–Ti^{3+} bondings in the orthorhombic unit cell $a=379.00(5)$, $b=974.5(1)$, $c=995.8(1)$ pm (space group *Cmcm*, 293 K) [8].

Figure 1 presents the electrical conductivity of $LiTi_2O_4$ at 1130 K in dependence on the oxygen partial pressure. According to XRD analysis the sample contained both the high-temperature ramsdellite and the low-temperature spinel phase. The conductivity at higher pO_2 values is not an intrinsic property of $LiTi_2O_4$ because of the segregation of more insulating phases Li_2TiO_3, $Li_4Ti_5O_{12}$ (ramsdellite) and TiO_2 (rutile). There was an indication that the formation of oxidised compounds was enhanced by polarisation effects due to the lithium ion mobility. Finally, the amount of TiO_2 was found to be higher at the anodic side whereas the Li_2TiO_3 concentration was higher at the cathodic side. Polarisation effects have also been observed in DC-conductivity studies of reduced Li_2TiO_3 [5]. After oxidation of $LiTi_2O_4$ to $Li_4Ti_5O_{12}$ and TiO_2 there was an immediate increase of the conductivity of the bar when the pO_2 was decreased again revealing that phase segregation occurs in grain boundaries. Thus, the conductivity data shown in Fig. 1 is mainly governed by the microstructure of the sample, particularly the grain boundary phases involved. Even at low oxygen partial pressure, in the stability range of the spinel $LiTi_2O_4$ grain boundary segregation into lithium-poor and -rich spinels have been reported [27]. The variation of sigma with pO_2 is similar to the observed behaviour of TiO_2 with a p- to n-type transition [28]. However, at pO_2 values higher than $\approx 10^{-12}$ bar sigma is about two orders of magnitude higher than in pure TiO_2. For lithium insertion compounds Li_xTiO_2 the electronic part of the conductivity increases due to the formation of Ti^{3+} ions, *e. g.* 10^{-2} S cm^{-1} for $Li_{0.15}TiO_2$ at 298 K [29]. The unit cell dimensions do not alter significantly with the lithium content [29] so that we could not determine the composition of the rutile phase by XRD studies.

The thermal expansion for $LiTi_2O_4$ derived from XRD data is 15.6×10^{-6} K^{-1} in the range of 293 to 1073 K [30].

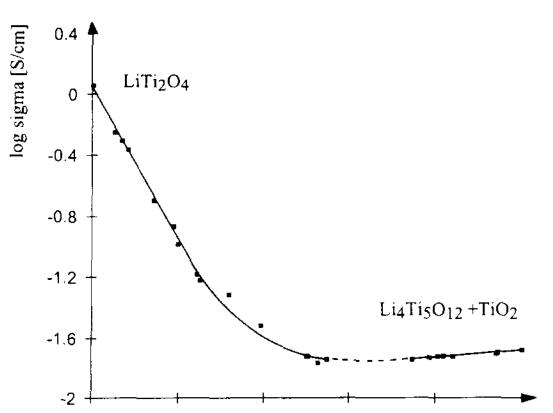

Fig. 1. Electrical conductivity of $LiTi_2O_4$ as a function of the oxygen partial pressure at 1130 K.

3.2. $Mg_xTi_{3-x}O_5$ series and $CrTi_2O_5$

The structural properties and the electrical conductivity of the pseudobrookite series $Mg_xTi_{3-x}O_5$ [7, 8] and V_3O_5-structure-type $CrTi_2O_5$ [8, 31] have previously been reported. Electrical conductivity data of some of the compounds obtained under reducing conditions are shown in Table 1. These small polaron conductors are stable at very low pO_2, but their stability range at higher pO_2 values has not been reported previously. Figure 2 illustrates the redox behaviour of selected compounds at elevated temperatures. In their stability region the compounds show slightly n-type behaviour which has also been demonstrated by thermoelectric power measurements at low temperatures [7]. None of the materials is stable at a pO_2 higher than 10^{-17} bar, but Mg^{2+} (and Ti^{4+}) in the solid solutions $Mg_xTi_{3-x}O_5$ stabilise the pseudobrookite structure against oxidation compared with pure Ti_3O_5. Ti_3O_5 is oxidised at 1173 K and 10^{-23} bar pO_2 [11] to the 'shear-type' structures described by Anderson *et al.* [26] and finally to TiO_2 at $pO_2\approx10^{-20}$ bar [11, 13]. In order to achieve equilibrium conditions near the phase boundary region, annealing for several days was necessary. TiO_2 as a

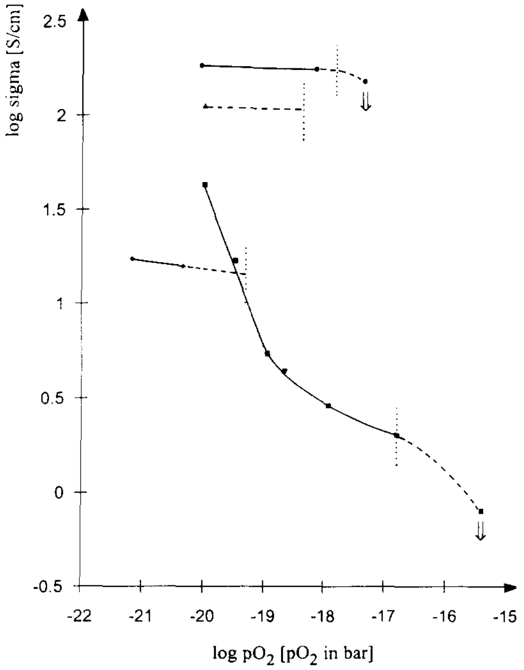

Fig. 2. Electrical conductivity of $Mg_{0.8}Ti_2O_5$ (◆, 1103 K), $Mg_{0.5}Ti_{2.5}O_5$ (■, 1163 K), $Mg_{0.3}Ti_{2.7}O_5$ (Δ, 1173 K), and $CrTi_2O_5$ (●, 1227 K) as a function of pO_2; dotted lines (⋮) are phase stability borders; arrows indicate non-equilibrium data.

second phase and magnesium richer pseudobrookites were formed firstly. The change in composition of the pseudobrookites was determined from the unit cell dimensions given in [7, 8]. Finally, the complete oxidation products TiO_2 and $MgTi_2O_5$ were formed according to the TiO_2–MgO phase diagram [32]. Compared with the pseudobrookites, spinel-type $Mg_{1+x}Ti_{2-x}O_4$ compounds are less stable at higher pO_2, particularly on the Ti^{3+}-rich side. The existence of the spinel $MgTi_2O_4$ has even been called into question [4].

The thermal expansion of the spinel Mg_2TiO_4 which is $11.0(\pm 0.4) \times 10^{-6}$ K^{-1} in the range of 293 to 1293 K has been determined from XRD data in air [33]. The pseudobrookite-type compound $Mg_{0.3}Ti_{2.7}O_5$ exhibits a mean thermal expansion of $10.4(\pm 0.5) \times 10^{-6}$ K^{-1} at temperatures from 290 to 716 K. For $CrTi_2O_5$ a mean value of $9.0(+1.0) \times 10^{-6}$ K^{-1} was obtained between 291 and 598 K. The results of the former compound were determined from dilatometer, those of the latter one by XRD measurements, both in an argon atmosphere.

3.3. Mg(Ti, Nb)$_2$O$_5$, Mg$_2$(Ti, Nb)O$_4$ and Sm$_2$(Ti, Nb)$_2$O$_7$ systems

The reduction of the insulating titanates $MgTi_2O_5$, Mg_2TiO_4 and $Sm_2Ti_2O_7$ was examined in hydrogen/nitrogen (1:9) mixtures at elevated temperatures. Impurity doping with Nb^{5+} favours the formation of semiconducting phases at higher pO_2 values than in the pure compounds. The niobium content in the systems $Mg(Ti, Nb)_2O_5$, $Mg_2(Ti, Nb)O_4$ and $Sm_2(Ti, Nb)_2O_7$ was chosen in a way that the total cation to anion ratio of the sample did not alter, *i.e.* there were second phases formed in air.

Niobium doping of the pseudobrookite $MgTi_2O_5$ ($a = 374.8(1)$, $b = 973.3(3)$ and $c = 1000.2(2)$ pm) leads to cation deficient pseudobrookites $MgTi_{2-5x/4}Nb_xO_5$ and $x/4$ TiO_2 in air. For a compound with $x = 0.05$ the lattice dimensions were $a = 374.60(7)$, $b = 974.7(1)$ and $c = 999.4(1)$ pm, but the changes are too small to be interpreted. Even in pure $MgTi_2O_5$ the lattice dimensions alter strongly with the amount of quenched order–disorder transitions [32]. Under reducing conditions a single-phase semiconducting pseudobrookite ($a = 375.0(1)$, $b = 975.2(4)$ and $c = 1000.3(3)$ pm for $x = 0.05$) was formed at 1150 K. At 1470 K magnesium-poorer, black pseudobrookites ($a = 3.764(1)$, $b = 9.773(2)$ and $c = 9.995(2)$ for $x = 0.05$) and ilmenite $MgTiO_3$ were present. Increasing a and b lattice constants with the Ti^{3+} content have been reported for the $Mg_xTi_{3-x}O_5$ solid solution as well [7, 8]. Further increasing of the temperature leads to ilmenite-type phases described in [6], such as $Mg_{0.67}Ti_{1.33}O_3$ for pure $MgTi_2O_5$.

Substitution of Ti^{4+} with equal amounts of Nb^{5+} in the spinel Mg_2TiO_4 with inverse cation distribution ($a = 844.01(8)$ pm, see 844.04(3) pm [32] results in the formation of cation-deficient spinels and $MgTiO_3$ as second-phase according to, $Mg_{2-x/4}Ti_{1-5x/4}Nb_xO_{4-x/4}$ $+ x/4$ $MgTiO_3$. The cubic lattice parameter of the spinel phase for $x = 0.05$ remained unchanged under different conditions, $a = 845.24(8)$ (air), $a = 845.05(7)$ (1150 K, H_2/N_2) and $a = 845.16(10)$ pm (1470 K, H_2/N_2). The increase of the unit cell in the Nb^{5+}-substituted compounds can be an effect of the cation vacancies created and the ionic radii involved (Ti^{4+}, 74.5; Ti^{3+}, 81; Nb^{5+}, 78 pm in octahedral coordination [34]). The composition of the spinel is almost independent on pO_2, since increasing lattice constants have been reported for Ti^{3+}-rich spinels [3, 4] and the amount of the ilmenite phase did not alter as well.

The evolution of the electrical conductivity with temperature of $Mg(Ti, Nb)_2O_5$ and $Mg_2(Ti, Nb)O_4$, both with $x_{Nb} = 0.05$, was fitted by using the adiabatic small polaron model [35, 36] like in the $Mg_xTi_{3-x}O_5$ series [8]. As shown in Fig. 3 the Arrhenius curves log (sigma × T) versus $1/T$ exhibit high activation energies for both compounds in a hydrogen/nitrogen atmosphere. Both the fluctuation of the potential due to the statistical distribution of the cations with different charges on crystallographically equivalent positions and localised electrons caused by low Ti^{3+} concentrations have been attributed to high activation barriers [4, 7]. The changes

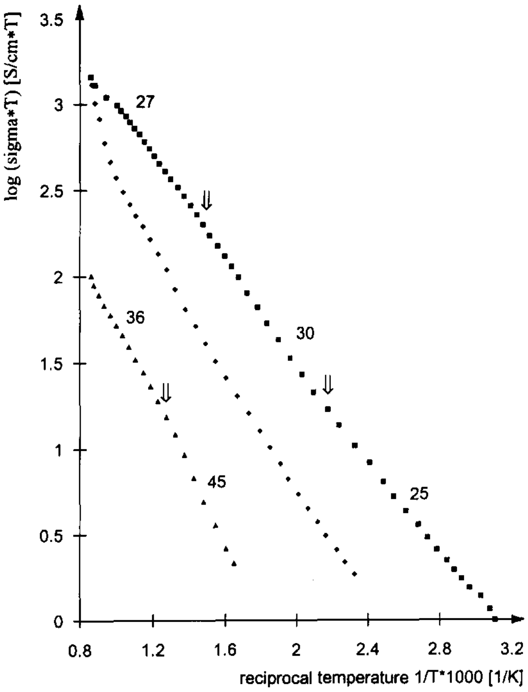

Fig. 3. Arrhenius plot log ($\sigma \times T$) versus $1/T$ for $Mg(Ti, Nb)_2O_5$ (■), $Mg_2(Ti, Nb)O_4$ (♦) and $Sm_2(Ti, Nb)_2O_7$ (▲); numbers, activation energy [kJ mol^{-1}]; arrows indicate change in activation energy.

in activation energy are probably caused by order–disorder transitions which are reported for the undoped compounds at these temperatures [32] and in addition variations of the carrier concentration. As a consequence of the high stability of Ti^{4+} in the spinel compounds, revealed by the XRD studies, the electrical conductivity is more than one order of magnitude lower than in the pseudobrookite-type $Mg(Ti, Nb)_2O_5$.

Pyrochlore-type $Sm_2Ti_2O_7$ is stable against reduction in hydrogen at 1470 K. The sample remained white and the cubic lattice constant did not alter, $a = 1022.6(2)$ in air and $a = 1022.9(1)$ in highly reducing condition (see $a = 1023.2(5)$, space group $Fd\bar{3}m$ [10]). $Sm_2Ti_2O_7$ is an insulator in air [37]. Samples of the section $Sm_2Ti_2O_7$–$SmNbO_4$ (19.5:1, 4.5:1, 2:1) contained both end member compounds when prepared in air at 1670 K. The variation of the lattice parameter of the pyrochlore phase with the composition of the sample, *e.g.* $a = 1026.7(2)$ for a 2:1 mixture of $Sm_2Ti_2O_7$ and $SmNbO_4$, reveals the solubility of niobium in the pyrochlore structure. The thermal expansion of the pyrochlore phase $6.4(\pm 0.1) \times 10^{-6}$ K^{-1} was linear from 293 to 1273 K indicating that the homogeneity range is only slightly dependent on the temperature. It should be noted that a compound $Sm_2Nb_2O_7$ could not be synthesised so far at different pO_2 conditions [38]. In contrast to the pure $Sm_2Ti_2O_7$, the niobium-doped compounds were black after annealing in a reducing atmosphere at 1470 K. The unit cell dimensions of the pyrochlore phase were similar to those of the air-treated compounds, but the homogeneity range was enlarged, $\approx Sm_2Ti_{1.9}Nb_{0.1}O_7$. The semiconducting behaviour of the 2:1 mixture is shown in Fig. 3. A linear fit of the electrical conductivity data could not be achieved using various models, probably because of the two phase nature of the sample. Low oxygen defect concentrations associated with low oxygen conductivities have been reported for $Sm_2Ti_2O_7$ [10, 37]. Acceptor-type doping with trivalent metal ions enhances the ionic conductivity [10], while our results show increasing electronic conductivity with donor-type doping.

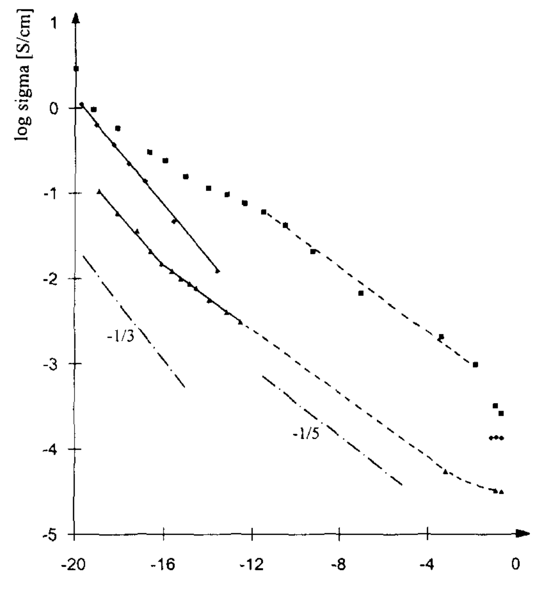

Fig. 4. Electrical conductivity of $Mg(Ti, Nb)_2O_5$ (■), $Mg_2(Ti, Nb)O_4$ (▲) and $Sm_2(Ti, Nb)_2O_7$ (◆) at 1150 K as a function of pO_2; for interpretation of the slope, see text.

Figure 4 reveals the n-type conductivity of niobium-substituted $MgTi_2O_5$, Mg_2TiO_4 and $Sm_2Ti_2O_7$ in a wide pO_2 range. The conductivity of $Mg(Ti, Nb)_2O_5$ at $pO_2 > 10^{-12}$ bar is approximately proportional to $pO_2^{-1/5}$. At lower oxygen partial pressures no uniform regime has been observed. The conductivity of the niobium-doped spinel Mg_2TiO_4 exhibits again a $pO_2^{-1/5}$ regime at $pO_2 > 10^{-16}$ bar and a proportionality of approximately $pO_2^{-1/3}$ under highly reducing conditions. In the case of niobium-substituted $Sm_2Ti_2O_7$ a variation of log σ with $pO_2^{-1/3}$ has been found at low pO_2, but this regime is not extended to higher pO_2 values.

4. Discussion

The defect chemistry of niobium-doped oxides can only be interpreted using simplifying assumptions, in particular that the deviation from stoichiometric composition is high enough to neglect intrinsic defect and electronic equilibria [13, 18]. The defect chemistry of donor-doped Mg_2TiO_4 and $MgTi_2O_5$ is probably similar to the mechanism suggested in donor-doped TiO_2 [13, 15]. The proportionality of log σ to $pO_2^{-1/5}$ at higher pO_2 as shown in Fig. 4 can be attributed to tetravalent ionised titanium interstitials according to,

$$2O_O + Ti_{Ti} \longleftrightarrow O_2 + Ti_i^{\bullet\bullet\bullet\bullet} + 4\,e'$$

(for details see, *e. g.* [13]).

It has also been shown that a slope of $-1/3$ can arise in the presence of both tetravalent ionised titanium interstitials and double ionised oxygen vacancies if the concentration of the oxygen vacancies dominates [13]. In the donor-type doped titanates presented here, this occurs only at highly reducing conditions (see Fig. 4).

However, the scope of our studies is mainly concerned with the practical aspects of the materials presented and their use as anodes in SOFC. The electrical conductivity of MnO-based compounds like $Li_xMn_{1-x}O$ is too low to be used as SOFC anodes. $LiTi_2O_4$ and $Li_xTi_{3-x}O_5$ compounds are only stable at highly reducing conditions, and their thermal expansion is not compatible to ZrO_2 which is about 10×10^{-6} K^{-1} between 273 and 1273 K depending on the content of substituting metal ions [39]. Furthermore, polarisation effects, the possibility of Li^+ diffusion into the electrolyte and interface reaction to $LiYO_2$ and Li_2ZrO_3 restrict their application to temperatures lower than currently employed in SOFC systems (900 to 1000 °C) despite their qualities as partial oxidation catalysts for methane. Mixed valence Ti^{3+}/Ti^{4+} pseudobrookites $Mg_xTi_{3-x}O_5$ exhibit the desired electronic conductivities, but they are not stable against oxidation to insulating phases occurring at $pO_2 > 10^{-17}$ bar and 1170 K. The thermal expansion data of the magnesium titanates is comparable to zirconia, warranting further studies as alternative anode. Donor-type doping of the insulating compounds $MgTi_2O_5$, Mg_2TiO_4 and $Sm_2Ti_2O_7$ improves their electrical conductivity, but the values are at least two orders of magnitude lower than in the Ti^{3+}-rich $Mg_xTi_{3-x}O_5$ series.

Catalytic studies on the n-type semiconducting titanates revealed increasing activity for total oxidation of methane in the sequence $CrTi_2O_5$, $Sm_2Ti_2O_7$ (pure) < $MgTi_2O_5$ (Nb-doped) < $Sm_2Ti_2O_7$ (Nb-doped) [9]. The catalytic activity for partial oxidation was low confirming the suggestion of Dubois and Cameron [40] that partial oxidation catalysts are p-type semiconductors.

The following strategies for further anode development can be derived from the results presented so far.

(1) Mixed niobium, magnesium pseudobrookites could reveal an extended stability range at higher pO_2 even for the highly conducting Ti^{3+}-rich compounds. In addition, the electronic conductivity of the oxidation products $MgTi_2O_5$ and TiO_2 would be increased by donor-type doping which has been shown, leading to a better conductivity in a wider pO_2 range. It is referred that niobium can be incorporated into Ti_3O_5 with the pseudobrookite structure [41]. The oxygen surface exchange and diffusion constants of the pseudobrookites have not been investigated so far. The option of adding a good oxygen conductor, *e. g.* the zirconia electrolyte by itself, to the anode in order to create a large three-phase boundary (fuel–gas/anode/electrolyte) has been described earlier [42].

(2) Alternatively, the single-phase mixed oxygen ion and electronic conductors can be used as anodes. Future work could be concerned with semiconducting, quarternary pyrochlores, such as $Sm_2Ti_{2-x}Mo_xO_{7-y}$ which have recently been synthesised in a reducing atmosphere [43].

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