NOVEL HIGHLY TITANIA DOPED YSZ ANODES FOR SOFCs

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ABSTRACT

In the ternary system ZrO2-Y2O3-TiO2 compositions with titania concentrations of 18 mol-% can be dissolved in the cubic fluorite structure. The electrical properties of these compositions close to the high titania, low yttria limit were found to have a predominant ionic conductivity of about 0.01 Scm⁻¹. Substantial electronic conductivity of about 0.2 Scm⁻¹ at 930°C is introduced into the system at oxygen pressures below 10⁻¹⁴ atm. For applications in the SOFC, I-V polarisation studies were performed on anode compositions, screen printed on YSZ electrolytes, using a gold mesh current collector. A low effective contact area of about 20% of the geometrical area suggested that these materials need to be supplemented by a current collecting component. With increasing polarisation of the electrode, the effective contact area decreased due to oxidation of the electrode. However currents, related to the effective contact area were reasonable. By impedance studies the polarisation losses were associated with the electrode and electrolyte resistances, diffusion and charge transfer losses were not very large, perhaps indicating the benefit of an ioniically conducting electrode.

INTRODUCTION

Mixed ionic and electronic conducting oxides show some very attractive characteristics for use as anode materials in solid oxide fuel cells (SOFC). Yttria stabilized zirconias with 1-12 mol% Ti dopant and cubic fluorite structure were considered as promising candidates for SOFC anodes, because they have excellent stability at high temperatures, good compatibility with the YSZ electrolyte, mixed conductivity and might offer high electrocatalytic activity [1,2,3]. A good electrocatalytic activity of such materials is attributed to their good electronic and ionic conductivity, increasing the ability to accelerate the electrode gas reaction. The charge-transfer reaction between lattice oxygen and fuel can then occur over the entire electrode area, whereas in Ni-YSZ cermets this electrode reaction is limited to the three phase contacts between fuel, electrode and electrolyte. However, because of the low electronic conductivity of these doped YSZ compositions with maximum 10 mol% titania additions (~0.02 Scm⁻¹ at 1000°C under fuel cell conditions), these materials by themselves were concluded not to be promising candidates for fuel cell anodes [4].

Investigations of the phase diagram Y₂O₃-ZrO₂-TiO₂ by Feighery et al. [5] revealed that the cubic fluorite structure of YSZ can be retained to much higher titanium contents up to 18 atom%. In this paper, results of investigations of the electrical properties of the most
promising high titania doped compositions with the general formula $Y_xTi_yZr_{1-(x+y)}O_{2-x/2}$ are reported along with polarisation studies on some of these compositions.

**EXPERIMENTAL**

As starting materials TiO$_2$ (Aldrich), Y$_2$O$_3$ (Aldrich) and ZrO$_2$ (Hopkin&Campbell Ltd) powders were used. The samples were synthesised by a solid state reaction between the oxides. The oxides were mixed in the ratios according to the respective formula, ball milled for 1 hr with high speed in ethanol in a zirconia container using zirconia balls and pressed into pellets. The pellets were sintered at 1500°C for 48 hrs in air. Powder X-ray diffraction measurements on the samples were performed to identify their structure, lattice parameter, and phase composition on a Stoe Stadi-P diffractometer. The densities of the pellets were between 75% and 90% that of the theoretical value. Different levels of doping with Titania, which acts as a sintering aid, and varying yttria contents have significant influence on the sintering characteristics and the density of the pellets.

For impedance measurements in air a Solartron 1260 impedance analyser was used over the frequency range 10 MHz to 100mHz. Measurements were performed on the as prepared pellets, which were coated with an organo-platinum paste on each face. The platinum electrodes on the pellets were first dried at 120°C for 30 minutes and then fired at 1000°C for 1 hour. The samples with a density between 70 and 90% of theoretical density, were mounted in a compression jig with Pt wire electrodes. For the jig a temperature dependent resistance correction had been determined. The conductivity jig was fixed in a horizontal tube furnace and the a.c. impedance measurements were made in 50 degree steps in air between 400 and 1000°C. The electrical conductivity was measured in the oxygen partial pressure range from 0.21 atm to 1x10$^{-22}$ atm at 930°C by DC techniques. The low oxygen pressures were obtained by flowing hydrogen into the apparatus. The actual oxygen partial pressure was measured by a zirconia sensor. Polarisation studies were performed using 4-electrode geometry. The working electrode (2 cm$^2$) was screen printed onto a 300μm thick electrolyte, made from 8 mol% yttria-stabilised zirconia with small amounts of alumina-addition (CeramTec AG). Contact was made with this electrode via a gold mesh. A Pt counter electrode was applied to the opposite face of the electrolyte plate and a Pt reference electrode was applied to each face of the electrolyte, Figure 1. A series of measurements were performed at increasing currents, with both dc and ac measurements being taken at each current level.

![Figure 1](image-url)

**Figure 1.** Schematic cross sectional view of the cell used for polarisation measurements. WE = working electrode (anode), CE = counter electrode (Pt), RE1 and RE2 = reference electrodes.
RESULTS AND DISCUSSION

Stability of the $Y_xTi_yZr_{1-(x+y)}O_{2-x/2}$ System

Investigations about the system $Y_2O_3$-$TiO_2$-$ZrO_2$, in which the extent of the cubic fluorite region was determined, have been published elsewhere by Feighery et al. [5]. Different compositions near the edge of the single phase fluorite region with the highest possible titania content have been investigated to maximise the electrical conductivity for application as SOFC anode materials (Figure 2). Although the phase equilibria were determined for samples prepared in air at 1500, the data are believed to pertain well to experiments performed at 1000°C in fuel gas. The extent of the fluorite system in air at equilibrium at 1000°C may well be slightly less than that at 1500°C; however the extent of solid solution would be expected to be more extensive at low oxygen partial pressures. In any case, the system is very refractory and would only be expected to transform significantly over a period of months at 1000°C or less.

![Figure 2. Phase diagram of the system $ZrO_2$-$Y_2O_3$-$TiO_2$ at 1500°C, shaded region corresponds to single phase, cubic fluorite region. The compositions investigated as possible electrode materials are marked with large open circles.](image)

The Ionic Conductivity of Cubic Titania Doped YSZ in Air

The temperature dependence of the conductivity of the $Y_xTi_yZr_{1-(x+y)}O_{2-x/2}$ fluorite solid solution samples (YZT) with high Ti content (18 atom-%) and close to the low Y limit (15 atom-%) in air has been previously reported [6]. Arrhenius conductivity plots show straight lines, indicating that there is not a change in the activation energy $E_a$ within the temperature region of study. For these compositions the ionic conductivity decreases with the yttria content. The reason for this decrease is believed to be the same as for highly
yttria doped YSZ. The ionic conductivity in YSZ decreases with Y-content above 8 mol% Y2O3, because of the formation of dopant-oxygen vacancy clusters. This is related to the greater likelihood for trapping oxygen vacancies by the formation of associates between the oxygen vacancies and the dopant cation [7]. An EXAFS study of 10 mol% YSZ by Catlow et al. [8] indicated that the oxygen vacancies must be preferentially sited adjacent to the Zr4+ ion and not to the Y3+ ion. A change in activation energy Ea for a dopant concentration below 20 atom% yttrium between 550 and 650°C was reported, which has been attributed to the dissociation of defect clusters [9,10].

In the system Y2O3-TiO2-ZrO2 this change in Ea was not observed, which may be due to stronger dopant-vacancy interaction. Only a small increase of the activation energy Ea from about 1.15 eV (for compositions with Y<20atom%) to 1.25 (for Y=25 atom%) was observed as the Y-content was increased, which may be due to the tendency of the small Ti atoms to relieve lattice strain and so reduce activation energy. The magnitude of ionic conductivity of the titania doped samples is about one order of magnitude lower than 8mol%YSZ [2]. This has been attributed to a stronger association of the oxygen vacancies with the small Ti4+ ions [11] or by a tetragonal short range order in the cubic fluorite structure [3]; however, it should be noted that the conductivity values are very similar to those for samples with similar Yz/v, V0’ contents in the absence of Ti. As has been reported previously [12] it seems clear that the Yttrium concentration and hence degree of clustering is the dominant factor determining ionic conductivity.

**Total Electrical Conductivity at Different Oxygen Partial Pressures**

In Figure 3, the dependence of the total conductivity $\sigma_T$ on oxygen partial pressure at 930°C is given for the sample Y0.2Ti0.18Zr0.62O1.9. The electronic contribution $\sigma_e$ has been calculated according to the equation $\sigma_e=\sigma_T-\sigma_i$, assuming that the concentration of oxygen vacancies is effectively constant over the investigated $pO_2$ range and that the value for $\sigma_T$ gives the value of the ionic conductivity $\sigma_i$ at high $pO_2$. The electronic contribution of the conductivity $\sigma_e$ for the re-oxidation range between $10^{-14}$-$10^{-20}$ atm is shown in Fig. 3 as open circles, fitted to a straight dotted line. The calculated slope for this log($\sigma_e$) vs. log($pO_2$) plot and the plots for all other measured samples follow a $pO_2^{-1/4}$ dependence in the $pO_2$ range from $10^{-13}$ to $10^{-20}$ atm. Substantial electronic conductivity is introduced into the system at oxygen partial pressures below $10^{-13}$ atm via reduction of Ti4+ ions to Ti3+. The hysteresis between the reduction and oxidation curve in Fig 3 is related to the relatively high density of the sample (80% theoretical density), which did not allow this sample to reach equilibrium (complete reduction or reoxidation), at each measured point. The points obtained on reoxidation between oxygen partial pressures of $10^{-20}$ atm and $10^{-13}$ atm and from $10^{-3}$ atm to $10^{-1}$ atm are the most reliable as the reoxidation occured @20 times more slowly than the initial reduction. It is always difficult to attain equilibrium in the region $10^{-10}$-$10^{-5}$ atm. due to the extremely low concentration of active species available in the gas phase.
Figure 3. The conductivity dependence of $Y_{0.2}Ti_{0.18}Zr_{0.62}O_1.9$ upon oxygen partial pressure.

Figure 4 shows the dependence of the electronic and the ionic conductivity on yttrium content of a number of compositions in the YZT system. The electronic conductivity at low $pO_2$ is higher for all compositions containing 18 atom% titania, because $\sigma_e$ increases with the concentration of Ti$^{4+}$/Ti$^{3+}$ sites. The ionic conductivity decreases slightly with higher titania content of 18 atom%, whereas $\sigma_i$ is reduced significantly with yttrium content.

Figure 4. Dependence of ionic conductivity $\sigma_i$ (filled symbols) and electronic conductivity $\sigma_e$ (open symbols) upon yttrium content in different $Y_xTi_yZr_{1-(x+y)}O_{2-x/2-y}$ compositions. The samples are either $y=15$ atom% titanium, squares or $y=18$ atom% titanium, circles.
Results from DC polarisation measurements for single cells with an $\text{Y}_0.2\text{T}_0.15\text{Z}_{0.65}\text{O}_{1.9}$ anode composition (with $y=0.15$ and 0.18) are presented in figure 5. Following from these experiments it appears that electrodes containing 18 atom % Ti achieve a higher performance than electrodes containing 15 atom% Ti. In the shown voltage-current characteristics the currents are related to the contact (or active) electrode area, calculated from impedance measurements at each current step. The actual cell voltage of the cell with a $\text{Y}_0.2\text{T}_{0.18}\text{Z}_{0.62}\text{O}_{1.9}$-anode drops from open circuit voltage of about 1.1 V at OCV ($I=0$) to 0V at a current density of about 0.1 A/cm$^2$, if the current is related to the total geometrical area of the cell (not shown in Fig. 5).

![IV curve for a single $\text{Y}_0.2\text{T}_0.15\text{Z}_{0.65}\text{O}_{1.9}$/YSZ-Al$_2$O$_3$/Pt cell measured in 5% H$_2$: 95% Ar with a flow rate of 150 ml/min$^{-1}$. The current density is related to the "active" electrode area. — characteristic for $\text{Y}_0.2\text{T}_{0.15}\text{Z}_{0.65}\text{O}_{1.9}$, and ♦ for $\text{Y}_0.2\text{T}_{0.18}\text{Z}_{0.62}\text{O}_{1.9}$](image)

Curve 2 reveals, that the "active" area (or contact area) performs well in the electrochemical oxidation of hydrogen. The ratio of the apparent contact area to physical contact area, which is about 20% at OCV, decreases with potential (figure 6), indicating that the electrode becomes oxidised and less conductive with increasing polarisation losses. The impedance spectra also show that for this fluorite composition ohmic losses due to the poor conductivity of the electrode exceed or, at the highest potential losses, are equal to the overpotential losses due to electrochemical phenomenon such as charge transfer and diffusion. This indicates that the high ionic conductivity of this electrode facilitates the fuel oxidation processes.

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CONCLUSIONS

In the system TiO$_2$-Y$_2$O$_3$-ZrO$_2$ electronic conductivities of about 0.2 Scm$^{-1}$ with a simultaneous ionic conductivity of 0.01 Scm$^{-1}$ can be achieved on 18 mol% titania doped samples at 930°C and 10$^{-20}$ atm. The stability of highly Ti-doped YSZ should be investigated under long-term fuel cell condition, i.e. at 800-1000°C in fuel gas. Highly titania doped YSZ compositions show a good mixed conductivity and may be considered as the ceramic component in cermet structures for the anode. Currents, corrected for effective contact area, e.g. 400 mAcm$^{-2}$ at 500mV, were promising; however the effective contact area was only of the order of 20%. With increasing polarisation of the electrode, the effective contact area decreased due to oxidation of the electrode. Impedance studies showed that most of the polarisation losses were associated with the electrode and electrolyte resistances; diffusion and charge transfer losses were not very large, perhaps indicating the benefit of an ionically conducting electrode.

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REFERENCES

1. S. S. Liou and W. L. Worrell, *Appl. Physics A*, 49, 25 (1989).
2. H. Naito and H. Arashi, *Solid State Ionics*, 53-56, 436 (1992).
3. L. S. M. Traqueia, T. Pagnier and F. M. B. Marques, *J. Euro. Ceram. Soc.*, 17, 1019 (1997).
4. T. Lindegaard, C. Clausen, M. Mogenson, *Proc. 14th Int. Mat. Sci.: High Temp. Electrochem. Behaviour of Fast Ion and mixed conductors*, eds. F. W. Poulsen, J. J. Bentzen, T. Jacobsen, E. Skou and M. Ostergard, RisØ Nat. Lab., Denmark, (1993).
5. A. Feighery, D. Fagg, J. Irvine, A. Kaiser *J. Solid State Chem.*, 1999, in press.
6. A. Kaiser, A.J. Feighery and J.T.S. Irvine, *Ionics*, 1999, in press.
7. J. A. Kilner, C. D. Waters, *Solid State Ionics*, 6, 253 (1982).
8. C.R.A. Catlow, A.V. Chadwick, G. N. Greaves, and L.M. Morony, *J. Am. Ceram. Soc.*, 69, 272 (1986).
9. S.P.S. Badwal, *J. Mat. Sci.*, 19, 1767 (1984).
10. I.R. Gibson, J. Irvine, *J. Mat. Chem.*, 6, 1985 (1996).
11. P. Li, I-W. Chen, J.E. Penner-Hahn, *J. Am. Ceram. Soc.*, 77, 118 (1994).
12. J.T.S. Irvine, I.R. Gibson and D.P. Fagg, *Ionics*, 1, 279 (1995).