NEW MIXED CONDUCTING OXIDES FOR SOFC ANODES

J.T.S. Irvine, S. Tao, A.J. Feighery and T.D. McColm
University of St Andrews, School of Chemistry, St Andrews KY16 9ST, Scotland, UK

ABSTRACT

In this study we have attempted to combine electronic and ionic functionality in single phase materials, with the aim of developing improved single phase or composite fuel electrode materials. In both the detailed studies, we have started with oxide ion-conducting solids and substituted to induce electronic conductivity. On introducing titania into fluorite zirconia, it was found that combined stabilisation with both yttria and scandia gave improved properties over either scandia or yttria stabilised materials. At 900°C oxygen ion conductivities in excess of 0.01Scm⁻¹ and electronic conductivities in excess of 0.1Scm⁻¹ were achieved in 86% dense samples. Focusing on perovskite gallate electrolyte-based systems, a new galloniobate with an ordered perovskite structure has been prepared and characterised. The air conductivity of the undoped Sr₂GaNbO₆ indicates that doping will be required to induce sufficient oxide ion conductivity for utilisation in an SOFC, as for lanthanum gallate. Reasonable electronic conductivity was induced on reduction. Both sets of materials show promise as fuel electrodes, especially if considered as constituents of composite electrodes.

INTRODUCTION

Fuel cells offer a means of electrochemical conversion of hydrogen or hydrocarbon fuels (such as methane) to produce electricity. The solid oxide fuel cell (SOFC) is an all-ceramic device operating at high temperatures. The current development of SOFC is mainly based on the yttria-stabilised zirconia (YSZ) electrolyte, because it exhibits good thermal and chemical stability, high oxide-ion conductivity and mechanical strength at high temperature, i.e. 900-1000°C (1). Interest is also focusing on higher conductivity electrolytes such as lanthanum gallate for use at lower temperatures, e.g. 600°C. The most commonly used anode materials for SOFCs are Ni/electrolyte cerments, which exhibit disadvantages, such as low tolerance to sulphur (2) and carbon deposition (3) when using hydrocarbon fuels and poor stability on redox cycling. In this study, we have sought alternative fuel electrode materials, looking to achieve good mixed oxide ionic/electronic conductivity under fuel conditions. Mixed conduction under fuel conditions is very important because this allows the electrochemical reactions to occur over the entire electrode-fuel interface as opposed to the reaction at solely electrolyte, electrode and fuel three phase boundary (TPB), as in the present cermet materials (4,5). Such mixed conductivity effectively catalyses the fuel...
oxidation. These mixed conductors will be utilised either as single phase electrodes or, more likely, along with a current collecting component as composite electrodes.

The introduction of early transition metal oxides, e.g. TiO₂, into zirconia solid solutions for use as anode materials is a very promising strategy. Such materials display reasonable electrochemical activity that is comparable to ceria doped with 40% Gd (6). The phase diagram and conduction behaviour of Y₂O₃-ZrO₂-TiO₂ ternary system have been investigated in previous reports (7,8). In order to further optimise the ionic conductivity, scandium was introduced to the system because the size of the Sc³⁺ dopant is much closer to Zr⁴⁺ than Y³⁺ ions. This results in Sc-stabilised ZrO₂ (ScSZ) exhibiting much higher ionic conductivity than YSZ (9,10). Therefore, in this work, the ionic and electronic conductivities of samples in the Y₂O₃-Sc₂O₃-ZrO₂-TiO₂ system have been studied. The possible factors that may affect the mixed conduction are also discussed.

An alternative electrolyte with considerable promise is the perovskite lanthanum gallate (11-14). Following a parallel approach to that for the fluorite system, we have attempted to introduce electronic functionality into the lanthanum gallate type structure by doping with niobium. Herein, we report on the conduction properties of the new phase Sr₂GaNbO₆.

**EXPERIMENTAL**

For the zirconia system, samples were weighed, mixed with acetone and ball-milled in zirconia containers with zirconia balls. After drying and removing of acetone, the mixtures were pressed into pellets (13mm diameter × 2mm thick) at a pressure of 2000 kg cm⁻². The pellets were calcined at 1000°C for 1 hour, sintered at 1500°C for at least 48 hours, and then air quenched to room temperature from 1200°C. The relative densities for the sintered samples are in the range of 82-92%. The samples used for d.c. measurement were prepared by crushing the 1500°C pellets, grinding, pressing again to form a pellet, calcining at 1300°C for 4 hours. The relative density of as-prepared pellets is 66%. The galloniobates were prepared by grinding reagents in a mortar and pestle before solid state reaction at 1350°C for 24 hours.

Phase purity and unit cell lattice parameters were determined by a Stoe Stadi-P X-ray diffractometer (10-85° 2θ, step size 0.02° 2θ, CuKα radiation) using silicon as an external calibration standard. For a.c. impedance measurements, a Schlumberger Solartron 1260 Frequency Response Analyser coupled with a 1287 Electrochemical Interface controlled by Z-plot electrochemical impedance software was used over the frequency range 1MHz to 100mHz. Measurements were performed in 50°C steps in air and 5%H₂ in Ar, between 600 and 900°C on as-sintered pellets coated with porous Pt electrodes at both sides. The pH₂O of the gases used is about 8.4x10⁻⁴atm. The samples were reduced overnight in 5% H₂ at 900°C (pO₂ ~ 10⁻²²atm) before measuring the total conductivities in 5%H₂ in Ar. The d.c. conductivity was measured by a conventional four-terminal method using a Keithley 220 Programmable Current Source to control current and a Schlumberger Solartron 7150 Digital Multimeter to measure the voltage. Thermogravimetric analyses were performed using a Rheometrics 1000M TGA.
RESULTS AND DISCUSSION

Yttria-Scandia-Zirconia-Titania

The composition in the ternary Y$_2$O$_3$-ZrO$_2$-TiO$_2$ system offering the best compromise to optimise ionic and electronic conductivity is Y$_{0.16}$Zr$_{0.66}$Ti$_{0.18}$O$_{1.92}$. As this composition is right on the limit of the cubic fluorite phase field (8), our attention has focused on the composition Y$_{0.7}$Zr$_{0.62}$Ti$_{0.18}$O$_{1.9}$. In this study we report on the replacement of part or all of the yttria in this composition by scandia. Pure cubic phases were obtained for all the compositions in the range (Sc$_x$Y$_{1-x}$)$_{2}$Zr$_{0.62}$Ti$_{0.18}$O$_{1.9}$. The solubility limit of titanium in the cubic fluorite regime of the Sc-Y-Zr-Ti-O system is about 18mol% in the Sc-rich area and 20mol% in Y-rich area, thus mixed doping of scandium and yttrium expands a little the solubility limit of titanium in zirconia. Single phase fluorite samples were obtained for Sc$_{0.1}$Y$_{0.9}$Zr$_{0.62}$Ti$_{0.18}$O$_{1.9}$ and Sc$_{0.05}$Y$_{0.15}$Zr$_{0.62}$Ti$_{0.18}$O$_{1.9}$, see figure 1. The relation between lattice parameter and Sc content in cubic Sc$_x$Y$_{0.2-x}$Ti$_{0.18}$O$_{1.9}$ is shown in Fig. 2. The lattice parameter $a$ decreases with increasing amounts of scandium in the solid solution when yttrium is substituted by the smaller scandium. This change is almost linear with Sc-content except for the half-substituted sample Sc$_{0.1}$Y$_{0.9}$Zr$_{0.62}$Ti$_{0.18}$O$_{1.9}$, in which sub-lattice order might play an important role.

![Fig. 1 XRD pattern of Sc$_{0.1}$Y$_{0.9}$Zr$_{0.62}$Ti$_{0.18}$O$_{1.9}$](image1)

![Fig. 2 Dependence of $a$ upon composition in Sc$_x$Y$_{0.2-x}$Zr$_{0.62}$Ti$_{0.18}$O$_{1.9}$](image2)

Fig. 3 shows the variation in ionic conductivity of (Sc$_x$Y$_{1-x}$)$_{2}$Zr$_{0.62}$Ti$_{0.18}$O$_{1.9}$ samples with different Sc/Y ratios. Conductivity is enhanced with increasing amounts of scandium in the system because the size of the scandium ions is much closer to that of Zr$^{4+}$ ions than Y$^{3+}$, facilitating oxygen ion transport (9,10). The ionic conductivity of Sc$_{0.05}$Y$_{0.15}$Zr$_{0.62}$Ti$_{0.18}$O$_{1.9}$ is slightly lower than for Sc-free Y$_{0.2}$Zr$_{0.62}$Ti$_{0.18}$O$_{1.9}$. Short range order may account for this drop. With increasing amounts of scandium, the ionic size effect becomes dominant resulting in enhancement of conductivity. The yttrium-free sample Sc$_{0.2}$Zr$_{0.62}$Ti$_{0.18}$O$_{1.9}$ exhibits the highest ionic conductivity. The conduction activation energies are close to 1.2eV for all samples as might be expected the concentrated defect regime of the cubic zirconia fluorites.

740 Electrochemical Society Proceedings Volume 2001-16
Under reducing conditions, i.e., 5% H₂ flow (p(O₂) ~ 10⁻²² at 900°C), these titania doped fluorites exhibited small polaron type behaviour with activation energies of about 0.25 eV or less. The relation between electronic conductivity and composition of (ScₓY₁₋ₓ)₀₂ₓZr₀.₆₂Ti₀.₈₀O₁₉ samples is shown in Fig. 4. Mixed Sc/Y doped samples exhibit higher electronic conductivity than solely Sc or Y doped samples when x = 0 or 0.2. The deviation seems to be at the Sc-rich end and this may well relate to the strong tendency of Sc-rich zirconias to anion order. Perhaps some short range order causes a deviation from the local cubic structure that reduces conductivity. The highest electronic conductivity, 1.36 x 10⁻¹⁸ S/cm, was observed for Sc₀.₁₅Y₀.₀₅Zr₀.₆₂Ti₀.₁₈O₁₉ at 900°C among the (ScₓY₁₋ₓ)₀₂ₓZr₀.₆₂Ti₀.₈₀O₁₉ samples. Considering both ionic and electronic conductivities, Sc₀.₁₅Y₀.₀₅Zr₀.₆₂Ti₀.₁₈O₁₉ seems to be a promising SOFC anode material offering close to the highest electronic and ionic conductivities among the tested samples. The densities of the studied samples were all ~85% of theoretical; however, no correction factor has been applied. The reported values are, therefore, underestimates of the true value of bulk conductivities. Correcting by multiplying by theoretical density and dividing by observed density will give a reasonable estimate of the conductivity for samples of density > 80% (15), so conductivity values should be increased @ 18%.

The conductivity dependence of Sc₀.₁₅Y₀.₀₅Zr₀.₆₂Ti₀.₁₈O₁₉ upon p(O₂) was measured by the four-terminal d.c. method and compared to data for Y₀.₂₀Zr₀.₆₂Ti₀.₁₈O₁₉, figure 5. The relative density of both samples was 65%, which facilitated gas equilibration during the measurement and in fact is of direct relevance to porous electrode geometries. This means; however, that the conductivities measured are lower than those measured by a.c. methods for samples with relative densities of 86%. Correcting to 100% density as performed for the 86% dense sample will underestimate the conductivity of a 66% dense sample (15). P(O₂) measurements on porous samples are best used to obtain the ionic and electronic domains and to determine p(O₂) dependences, they are not appropriate for accurate grain conductivity determinations; however the comparison between Y and Y/Sc samples is fully valid as the densities are the same. For both compositions ionic conduction is dominant from 1 to 10⁻¹⁰ atm.
FIG. 5 Dependence of dc conductivity of $\text{Sc}_{0.15}\text{Y}_{0.85}\text{Zr}_{0.62}\text{Ti}_{0.18}\text{O}_{1.9}$ and $\text{Y}_{0.20}\text{Zr}_{0.62}\text{Ti}_{0.18}\text{O}_{1.9}$ upon $p(\text{O}_2)$ at 900°C, both samples 65% of theoretical density.

The total conductivity increases significantly below $10^{-10}$ atm. After correcting for the ionic contribution, the slope of logarithm of electronic conductivity against logarithm of $p(\text{O}_2)$ from $10^{-15} \sim 10^{-18}$ atm is quite close to $-1/4$, for both compositions, as expected for a defect electronic conductor. The Sc-containing sample clearly exhibits both higher ionic and electronic conductivities.

**Strontium Galloniobate**

Sr$_2$GaNbO$_6$ was synthesised in an effort to develop a new material that combines the ionic functionality of lanthanum gallate with the electronic functionality of strontium niobate. Quite possibly such a material might consist of interspersed gallium and niobium layers. Initial inspection of the powder X-ray pattern of this new material indicated a perovskite unit cell but with a number of additional peaks, figure 6a. The appearance of perovskite supercell spots, at similar d-spacings to these additional peaks in the electron diffraction pattern, indicated that this was in fact an ordered perovskite, probably with a doubling of the unit cell. After reduction in hydrogen at 1000°C for 24 hours, this phase demonstrated a significant shrinkage, figure 7. The pseudo-cubic primitive unit cell edge decreased from 3.95 to 3.83 Å (i.e as determined for the primitive cubic peaks). As the supercell peaks moved in accord with the perovskite subcell, it was demonstrated that this was a single phase, ordered perovskite. Further work is underway to determine the nature of this ordering. Thermogravimetry in oxidising and reducing conditions indicated that this reduction was associated with the loss of around 0.2 weight %, or 0.05 oxygens per Sr$_2$GaNbO$_6$ formula unit.
In air, Sr$_2$GaNbO$_6$$_8$ exhibited a conductivity value at 1000°C of only $5 \times 10^{-15}$Scm$^{-1}$, whereas after reduction this conductivity increased to $10^{-14}$Scm$^{-1}$, figure 8. In both cases, the electronic contribution appeared to dominate, i.e. ionic transport numbers were less than 1, $t_e < 1$. The bulk activation energy for conduction in air was 1.16eV and that under reducing conditions 0.87eV. Further investigations are underway to improve these conductivity values by chemical substitution.

**Figure 7** Comparison between powder X-ray diffraction patterns of Sr$_2$GaNbO$_6$$_8$ before (a) and after reduction (b).
CONCLUSIONS

The titania-zirconia systems containing scandia provide a significant enhancement of electrical properties over those not containing scandia. Although the lateral conductivity of such materials may not be sufficient to use as an electrode on its own, such materials do offer considerable promise for use in Ni or Cu cerments. The galloniobates in the stoichiometric composition Sr$_2$GaNbO$_{6.8}$ offer fairly poor conductivity in air. As for LaGaO$_3$, it is anticipated that appropriate doping may significantly improve this. Such materials may also find their best application in cermet electrodes. Testing as fuel electrodes is underway for all these materials.

ACKNOWLEDGMENTS

We thank EPSRC (UK), the Royal Society of Edinburgh and NEDO (Project 99EA2: ‘Zero Emission Power Generation Using an All-Perovskite Solid Oxide Fuel Cell’ for support.
REFERENCES

1. N. Q. Minh, *J. Am. Ceram. Soc.* **76**, 563 (1993).
2. N. S. Jacobson and W. L. Worrell, *Proc. High Temp. Mater.* **2**, 217 (1983).
3. B. C. H. Steele, I. Kelly, H. Middleton, and R. Rudkin, *Solid State Ionics* **28-30**, 1547 (1988).
4. J. T. S. Irvine, D. P. Fagg, J. Labrincha, and F. M. B. Marques, *Catal. Today* **38**, 467 (1997).
5. S. W. Tao, Q. Y. Wu, D. K. Peng, and G. Y. Meng, *J. Appl. Electrochem.* **30**, 153 (2000).
6. A. Kaiser, A. J. Feighery, P. Holtappels, J. L. Bradley, and J. T. S. Irvine, *Solid State Ionics*, submitted
7. A. Kaiser, A. J. Feighery, D. P. Fagg, and J. T. S. Irvine, *Ionics* **4**, 215 (1998).
8. A. J. Feighery, J. T. S. Irvine, D. P. Fagg, and A. Kaiser, *J. Solid State Chem.* **143**, 273 (1999).
9. S. P. S. Badwal and J. Drennan, *Solid State Ionics* **63-56**, 769 (1992).
10. O. Yamamoto, Y. Arati, Y. Takeda, N. Imanishi, Y. Mizutani, M. Kawai, and Y. Nakamura, *Solid State Ionics* **79**, 137 (1995).
11. T. Ishihara, H. Matsuda and Y. Takita, *J. Am. Chem. Soc.* **116**, 3801 (1994).
12. T. Ishihara, H. Matsuda and Y. Takita, *Solid State Ionics* **79**, 147 (1995).
13. M. Feng, J.B. Goodenough, K. Huang, and C. Milliken; *J. Power Sources* **63**, 47 (1996).
14. T. Ishihara, H. Minami, H. Matsuda, H. Nishiguchi, and Y. Takita; *Chem. Commun.* 929 (1996).
15. A.J. Feighery, PhD thesis, University of St Andrews (1997)