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**Conductivity and Microstructural Characterisation of
Doped Zirconia-Ceria and Lanthanum Gallate
Electrolytes for the Intermediate-Temperature,
Solid Oxide Fuel Cell**

by

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Declaration

I declare, to the best of my knowledge, that no material contained in this thesis has been previously written or published by another person, except where reference is made in the text. I declare that none of this work has been previously accepted for the award to the candidate of any other degree or diploma. Where work is based on joint research or publications the relative contributions of the respective workers or authors is disclosed.

Justin Andrew Kimpton

Publications

The following papers were published from research completed for this thesis.

J. Kimpton, T.H. Randle, J. Drennan and G. Auchterlonie, "An investigation of the microstructural/electrical conductivity relationship in In_2O_3 -substituted LSGM," *Mater. Res. Bull.* 36 (2001) 639-649.

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J. Kimpton, T.H. Randle and J. Drennan, "Conductivity/microstructure study of a pyrochlore-type ordered phase in the compound $\text{Zr}_{0.75}\text{Ce}_{0.08}\text{Nd}_{0.17}\text{O}_{1.92}$," *Solid State Ionics* 154-155C (2002) 473-480.

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Abstract

Lowering the operating temperature of the high-temperature, solid oxide fuel cell (SOFC) improves both the thermodynamic efficiency and the lifetime of this energy efficient technology. Unfortunately the rate of oxygen-ion transport through the solid electrolyte is temperature dependent, and materials previously employed as electrolytes in the high-temperature SOFC perform poorly at intermediate temperatures. Therefore new oxygen-ion conductors with enhanced ionic conductivity at intermediate temperatures are required. The bulk of the existing literature on high-temperature SOFCs has focussed on zirconia-based binary systems as electrolytes, due to their high ionic conductivity and negligible electronic conductivity. Only select compositions within the zirconia-scandia system have demonstrated acceptable ionic conductivity levels at intermediate temperatures; however unstable phase assemblage and the high economic cost of scandia are clear disadvantages. Ceria-based binary systems have demonstrated improved oxygen-ion conductivity at intermediate temperature compared to many zirconia systems, however significant levels of n-type electronic conductivity are observed at low oxygen partial pressures. Consequently it was thought unlikely that significant increases in ionic conductivity would be found in existing zirconia- and ceria-based binary systems, therefore another approach was required in an attempt to improve the performance of these established fluorite systems.

The fluorite systems $Zr_{0.75}Ce_{0.08}M_{0.17}O_{1.92}$ ($M = Nd, Sm, Gd, Dy, Ho, Y, Er, Yb, Sc$) were prepared and investigated as possible, intermediate-temperature SOFC electrolytes in an attempt to combine the higher conductivity found in the ceria systems with the low electronic conductivity observed in the zirconia systems. Also it was anticipated that systems containing dopants not previously observed to confer high ionic conductivity in either zirconia- and ceria-based binary systems, might exhibit enhanced ionic conductivity with expansion of the zirconia lattice resulting from the addition of ceria. All the as-fired $Zr_{0.75}Ce_{0.08}M_{0.17}O_{1.92}$ compositions possessed the face-centred cubic structure and lattice parameter measurements revealed the anticipated unit cell enlargement as the size of the dopant cation increased. No unusual microstructural parameters were identified that could be expected to interfere with the ionic transport properties in the as-fired compositions. The electrical conductivity was found to be

influenced by the dopant-ion radius, the presence of ceria, low oxygen partial pressures and, in some compositions, the formation of poorly conducting, ordered-pyrochlore microdomains dispersed amongst the cubic defect-fluorite matrix.

In a second approach to the formulation of new oxygen-ion conductors suitable for the intermediate-temperature SOFC, compounds possessing structures other than the fluorite structure were considered. An examination of the literature for oxides having the pyrochlore, scheelite and perovskite structures showed that the Sr^{+2} - and Mg^{+2} -doped LaGaO_3 perovskites (LSGM) possessed ionic conductivity equal to the highest conducting, zirconia and ceria binary compounds. Therefore the perovskite systems $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{(0.8-x)}\text{In}_x\text{Mg}_{0.2}\text{O}_{2.85}$ ($X = 0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8$) (I-LSGM) were prepared and examined, the objective being to favourably influence structural parameters believed responsible for optimal ionic conductivity, namely the unit cell symmetry and volume.

It was found that In^{+3} systematically substituted for Ga^{+3} on to the B-site of LSGM at least up to the $X = 0.4$ composition. While In^{+3} was found to replace the Ga^{+3} as expected, Mg^{+2} , which occupies the same crystallographic site, was also replaced by In^{+3} . Up to the $X = 0.2$ composition, at least two trace level secondary phases were observed to form along with the bulk I-LSGM phase. For I-LSGM compositions with $X > 0.2$, significantly larger concentrations of the secondary phases were identified. Evidence of a strontium-rich, high-temperature liquid phase was observed also near the grain boundaries on as-sintered and thermally etched surfaces in LSGM and I-LSGM compositions. It is believed that the observed, high sintered density in the complex, doped- LaGaO_3 systems is due to the formation of this high-temperature liquid phase. Increasing levels of diffuse scatter and superstructure formation were observed in electron diffraction patterns in the I-LSGM bulk phase (up to $X = 0.2$), indicating a possible decrease in vacancy concentration and reduced, localised unit cell symmetry. The electrical conductivity in the I-LSGM compositions was believed to be influenced by the distortion of the oxygen-ion conduction path, a reduction in vacancy concentration, formation of stronger dopant-vacancy associates at low temperature and the presence of ordered structures. In addition, phase instability, in the form of subtle ordering in specific crystalline planes, was observed to influence the electrical conductivity as a function of time at intermediate temperatures.