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研究課題名（和文）Improvement of fuel cell electrolytes by strain engineering

研究課題名（英文）Improvement of fuel cell electrolytes by strain engineering

研究代表者

ハリントン　ジョージ（Harrington, George）

九州大学・次世代燃料電池産学連携研究センター・助教

研究者番号：２０７５３７１８

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研究成果の概要（和文）：　燃料電池で使われている電解質材料の中をイオンが移動する際の電気抵抗が、燃料電池の性能低下の主要因の一つである。この電解質材料（本研究では酸化物）の中でイオンを動きやすくする革新的な材料設計コンセプトとして、結晶構造（結晶格子）を膨張・収縮させることに、George Harrington特任助教が本科研費事業で取り組む。一つは、イオン半径が異なる異種イオン（ドーパント）を結晶中に溶かし込んで結晶格子を制御する方法である。もう一つは、結晶構造のミスマッチを利用して、電解質結晶に機械的な応力を原子レベルで加えることを試みる。

研究成果の概要（英文）：The interplay of defect-defect interaction and strain on the ionic conductivity were investigated in rare-earth substituted ceria. By thermally annealing high quality epitaxial films fabricated by pulsed laser deposition, the strain was systematically varied, whilst avoiding any influence from interfacial or grain boundary effects. The work focused upon three different substituents, La, Gd, and Yb, whereby the defect-association in rare earth substituted ceria could be varied. It was shown that the activation energy increased with increasing in-plane biaxial strain. Furthermore, it was demonstrated that the change in the activation energy for Yb-substituted CeO_2 is around three times that for Gd or La substitutions for the same applied strain, indicating the important role played by defect association.

研究分野：Materials Science and Engineering

キーワード：SOFCs　Thin films　Strain　Ceramic　Ionic Conductors

１．研究開始当初の背景

Solid oxide fuel cells (SOFCs) are receiving widespread attention as a highly efficient, fuel flexible means to generate power with reduced emissions and potential for combined heat and power generation. The predominant barrier to widespread commercialization of SOFCs is the material durability issues associated with sustained use at the high operating temperatures of 800-1000˚C. There are two possible approaches to overcoming this:

1. Lower the operating temperature.
2. Create more stable materials operating at the same temperature.

Recently there has been emerging interest in nanoscale thin film devices such as micro-SOFCs as well as other low temperature electrochemical devices such as memristors. For example, commercial electrolyte materials such as $Y_xZr_{1-x}O_{2-d}$(YSZ) and $Gd_xCe_{1-x}O_{2-d}$ (CGO) have shown tantalizing enhancements in the conductivity of up to three orders of magnitude when grown in confined systems such as thin films. Strain and dislocations are often thought to be the predominant cause due to changes in the migration enthalpy (ΔH_M), however the exact mechanisms are not well understood and the chemical structure of the interfaces and dislocations of these systems have not yet been studied in detail.

Defect association (ΔH_A) between dopants cations and oxygen vacancies is known to have vast influence on the barrier for ionic transport, due the localized strain fields surrounding dopants with varying ionic radii to that of the host lattice. While this has been well studied experimentally in bulk materials, as yet no studies have addressed the possible interplay between the defect association and externally applied strain. However, recently Rushton and Croneos have calculated that for doped-CeO2 solid solutions under tensile strain the radii of the optimum dopant varies compared to the unstrained bulk.

Furthermore, much of the work so far on the effects of strain on the transport properties have focused on the so-called 'optimised' ionic conductors, such as commercial electrolytes Y-stabilised ZrO_2 or Gd- or Sm-doped CeO_2. Very little attention has been payed to the 'non-optimised' electrolytes where the defect-defect interactions are much more significant. However, as the defect association limits the conductivity for these materials a much larger enhancement in the transport properties (or a less significant reduction) due to strain may be possible.

２．研究の目的

The purpose of this research was to induce faster transport and slower degradation in doped-ceria systems by understanding the interplay between interfacial lattice strain and dopant ionic radii, paying particular attention to the 'non-optimised' electrolytes. This will yield design consideration for the integration of strained materials into electrochemical devices such as solid oxide fuel cells (SOFCs) and memristors with higher efficiency and decreased degradation rates.

３．研究の方法

We have fabricated both 'optimised' and 'non-optimised' doped-CeO_2 films by pulsed laser deposition on MgO substrates. The dopants used were La, Gd, and Yb, which represent an ionic radii mismatch with the host Ce lattice of 19.6%, 8.6%, and 1.5% respectively. Epitaxy was maintained using a double $BaZrO_3$ and $SrTiO_3$ buffer layer resulting in films free from grain boundaries. The thickness of the films was kept constant and the strain varied by thermal annealing (from 600°C to 1000°C) to relax the intrinsic strain occurring during growth. Crucially, this means that the strain in these materials can be tailored and the conductivity measured without complications due to grain boundary effects or changes in the volume fraction of the interface and surface.

４．研究成果

The out-of-plane and in-plane strain in the films was characterised in detail using X-ray diffraction and Raman spectroscopy. Fig. 1 shows the peak position of the (004) peak of the RE:CeO_2 films as a function of heat treatment and dopant type. Clearly the lattice parameters could be systematically controlled in the films. The microstructure evaluated by high-resolution transmission electron microscopy (Fig. 2). This demonstrated the high-quality epitaxial nature of the films. Impedance spectroscopy measurements

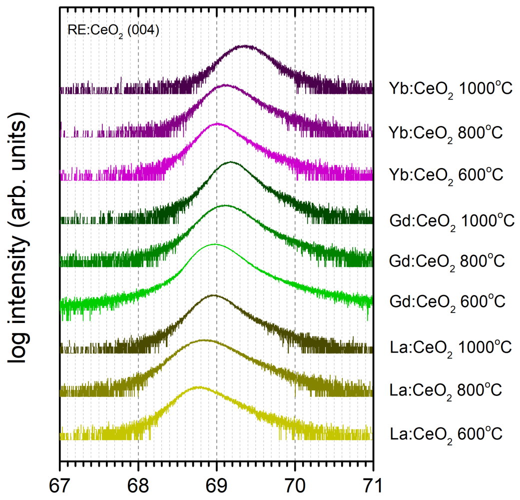

Figure 1 – Shift in the (004) peak position in XRD out-of-plane spectra demonstrating the change in lattice parameter of the films.

showed that the conductivity of the relaxed films was in excellent agreement with bulk rare earth substituted CeO_2. With increasing in-plane compressive strain, the conductivity of the films was reduced and the activation energy increased, as shown in Fig. 3.

Through this careful experimental design, we systematically varied the strain in substituted-ceria films without complications due to grain boundaries or interface effects. This has allowed us to

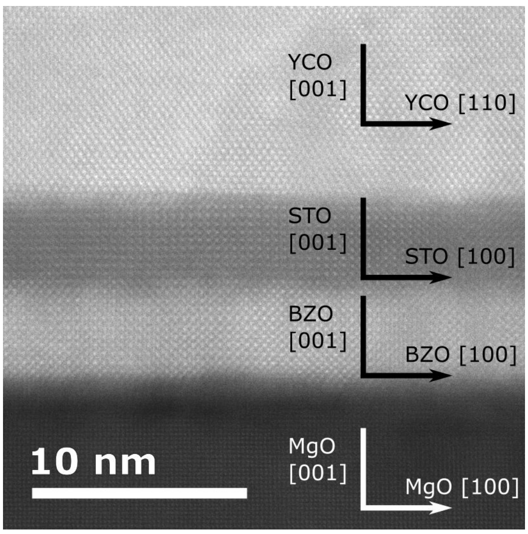

Figure 2 – High resolution high-angle annular dark field scanning transmission electron microscopy image of the interface of a film. The epitaxial relationship can be clearly seen.

measure the effect of lattice strain on the activation energy, which is excellent quantitative agreement with previous computation and experimental results. These findings provide a much sought-after quantitative consensus on the effects of strain on ionic transport, which has eluded the field for many years.

We have also demonstrated that the change in activation energy due to strain is three times higher for Yb-substituted ceria compared with Gd-substituted ceria (Fig 3). This demonstrates that a much larger change in conductivity can be observed for

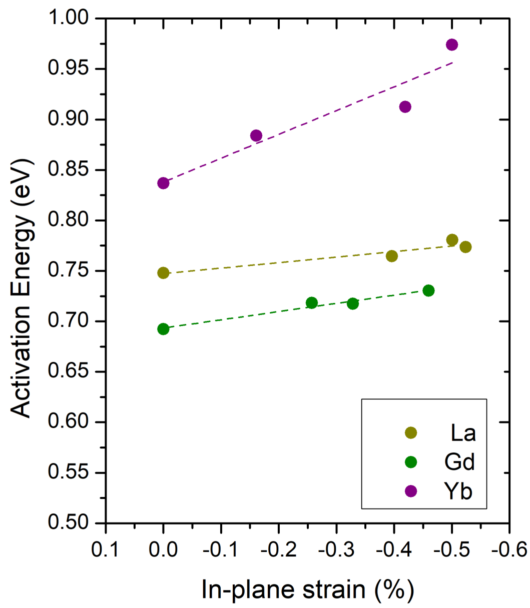

Figure 3 – Activation energy of the films as a function of in-plane lattice strain. Yb-CeO_2 is more sensitive to strain than Gd- or La-CeO_2.

materials where the defect-defect interactions are stronger. So far the interplay of defect association and lattice strain on conductivity has been almost entirely overlooked, however our results presented here indicate that it plays a significant role.

Our studies have important practical implications for electrochemical devices operating at reduced or ambient temperatures where the modification in ionic transport due to strain becomes substantial. They emphasize that the effects of the species and concentration of substitutional cations plays a particularly important role for strain modified conductivity that has, to date, been overlooked. We have demonstrated that much larger changes in the transport properties may be possible by selecting materials where there is a larger contribution of defect-defect interactions on the conductivity. Furthermore, this work provides new information on the effects of defect association which occurs in all extrinsic ionically conducting materials.

５．主な発表論文等

（研究代表者、研究分担者及び連携研究者には下線）

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〔雑誌論文〕（計　3　件）

〔学会発表〕（計　8　件）

〔図書〕（計　1　件）

〔産業財産権〕

○出願状況（計　　件）

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〔その他〕
ホームページ等
https://scholar.google.co.uk/citations?user=ZlNz7k8AAAAJ&hl=en

６．研究組織

(1)研究代表者
George Harrington
Kyushu University, Center for Co-Evolutional Social Systems
Assistant Professor
&
MIT, Department of Materials Science and Engineering
Research Affiliate

研究者番号：20753718

(2)研究分担者
(　　　)

研究者番号：

(3)連携研究者
(　　　)

研究者番号：

(4)研究協力者

Harry Tuller
MIT, Department of Materials Science and Engineering
Professor

Nicola Perry
I2CNER, Kyushu University
Assistant Professor

Lixin Sun
MIT, Department of Nuclear Science and

Engineering
PhD Student

Bilge Yildiz
MIT, Department of Nuclear Science and Engineering
Professor