Chapter 12 - Session B15
Cathodes: State-of-the-art & novel materials

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Chapter 12 - Session B15
Cathodes: State-of-the-art & novel materials

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Oxygen Exchange on Real Electrode Surfaces; experimentally-guided computational insight

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Abstract

The exchange of oxygen across the gas/solid interface is a process of crucial importance in the application of mixed conducting perovskites as air electrodes in SOECs and SOFCs. We have used a model system that displays an outer surface layer equivalent to that of a practical air electrode to provide important insights into this critical process. Density Functional Theory (DFT) and Low Energy Ion Scattering (LEIS) spectroscopy were applied to study the mechanisms of oxygen dissociation on the SrO-terminated surfaces of strontium titanate (SrTiO$_3$) and iron-doped strontium titanate (SrTi$_{1-x}$Fe$_x$O$_{3-δ}$). Our study reveals that while O$_2$ dissociation is not favored on the stoichiometric SrO-terminated perovskite surface, oxygen vacancies can act as active sites and catalyze the O-O bond cleavage. Electron transfer from lattice oxygen atoms to the O$_2$ molecule, mediated by the subsurface transition metal cations, plays an important role in the resulting formation of surface superoxo species. The O$_2$ molecule dissociates to produce oxygen ions, which are incorporated into the perovskite lattice, and highly active oxygen radicals on the perovskite surface, which further recombine to O$_2$ molecules. Whereas most theoretical studies have focused on the transition metal terminated surfaces (e.g. the TiO$_2$), which is assumed to be more catalytically active, our focus on the SrO terminated surface (figure 1), is driven by experimental observation using LEIS spectroscopy. This revealed that the surface of SrTiO$_3$ after high temperature heat treatment, as for many Sr containing air electrode materials, is SrO-terminated. Given the similarity in the composition of the surface exposed to the gas phase, we expect our results on STO to correspond directly to the mechanism of oxygen exchange in real solid oxide electrodes.

Figure 1 Active species on the (001) SrO terminated surface
Introduction

There is a current drive to lower the operating temperature of SOFCs (<650°C) to achieve cost reduction and increase durability to meet commercial targets. Unfortunately, the performance of SOFCs in this temperature regime can be limited by the decreased activity of the mixed conducting cathode at low temperatures. The majority of the mixed conducting materials used practically as air electrodes in both SOFCs and SOECs are perovskite oxides such as LaCoO$_3$ that have been heavily substituted on the La$^{3+}$ site by the lower valent Sr$^{2+}$ cation. A critical part of the cathode process is the dissociation of the oxygen molecule at the surface of the ceramic electrode and the subsequent exchange of oxygen atoms across the gas/solid interface. Clearly, gaining an understanding of this process will aid in the design and selection of materials for low temperature operation.

There have been many attempts to unravel oxygen exchange and determine the individual atomistic steps involved, however no clear picture has emerged, especially as the surface termination of the ceramic phase was unknown and had to be assumed. Recently it is becoming recognised that at the temperatures and conditions of operation these materials are dominated by the segregation of the Sr to the outermost surface. Thus we have initiated a program combining experiment and simulation to try to determine the role of the surface termination and surface defects on oxygen exchange, starting with a model perovskite system and moving towards more realistic systems. These results present the first stage in this process.

1. Scientific Approach

In this study we have combined low energy ion scattering (LEIS) spectroscopy with density functional theory (DFT) calculations to elucidate the surface reactivity of real electrode materials. All measurements and calculations were performed for iron doped SrTiO$_3$ as a model material.

2. Experiments/Calculations/Simulations

Low Energy Ion-Scattering

Surface characterisation was performed by means of Low-Energy Ion Scattering (LEIS) (Qtac, LEIS spectrometer, Ion-ToF GmbH, Germany), which probes the outermost atomic single layer of the surface. A noble gas ion beam with an energy between 1-8 keV is rastered over a large area (typically 1 mm$^2$) in order to minimise surface damage during the analysis. In the present work, 3 keV He$^+$ and 6 keV Ne$^+$ primary ions were used, which provide information on the lighter and heavier atoms present at the surface, respectively. The primary ion beam is directed towards the surface at normal incidence, and ions backscattered through an angle of 145 degrees due to collisions with the surface atoms are collected from the whole azimuth. The elemental composition of the surface is then determined by analysing the kinetic energy distribution of these backscattered ions, according to the kinematics of the scattering event. The surface coverage for each surface species is directly proportional to the peak areas in the LEIS surface spectrum. Additionally, the near-surface distribution of the elements can be analysed by depth profiling analysis in a dual beam mode by alternating the analysis and sputtering beams. In this case, a second ion beam of Ar$^+$ at 500 eV incident at an angle of 59 degrees is used to sputter the material between analysis cycles. The sputtered area is larger than the analysed region to avoid crater-edge effects due to the Gaussian beam profile (sputtered area = 1.3 x 1.3 mm$^2$).
In this work, the surface and near-surface composition of a (100) SrTiO$_3$ single crystal (STO) was analysed by LEIS. The single crystal was cleaned in aqua regia solution (1 mL of 70% HNO$_3$ and 3 mL of 70% HCl) at room temperature for 10 min and then annealed for 2 h at 1000 °C in pO$_2$ = 1 atm. The STO surface was further cleaned after introduction into the LEIS spectrometer to remove adsorbed moisture and organic organic surface contamination by oxidation with a flux of reactive atomic oxygen at room temperature. This surface oxidation is necessary due to the extreme surface specificity of the LEIS technique; the presence of these adsorbates after atmospheric exposure would otherwise hinder the detection of the surface atoms of the ceramic.

**Density Functional Theory Calculations**

The calculations in this study were performed with the plane wave density functional theory (DFT) implemented in the Vienna ab initio Simulation Package (VASP)\(^4\). The Perdew–Burke–Ernzerhof exchange-correlation functional (PBE) was employed using projector augmented wave pseudo potentials. We have used the graphical visualization package VESTA to analyze and visualize the computed DFT electron density distribution. The bulk SrTiO$_3$ crystal lattice was optimized with 400 eV cutoff energy and 4 x 4 x 4 k-points sampling. Spin polarized calculations were performed throughout the study for all investigated systems. The surface model was constructed after cleavage of the bulk SrTiO$_3$ at the crystal plane with (001) Miller indexes and vacuum slab of 12 Å. The thickness of the vacuum layer was sufficient to avoid the physical interaction between neighboring supercells. The top surfaces are SrO terminated and the bottom surface are TiO$_2$ terminated. All chemical reactions in this study occur on the SrO terminated surface in agreement with the experimental observations. The slabs contain 8 layers. The coordinates of the atoms in the bottom 4 layers are fixed and the atoms in the top 4 layers are fully relaxed. The AO layers are the top, 3\(^{rd}\), 5\(^{th}\) and 7\(^{th}\) layers. The BO$_2$ layers are the 2\(^{nd}\), 4\(^{th}\), 6\(^{th}\) and 8\(^{th}\) layers. Three surface models are considered: a 1 x 1 surface unit cell of SrTiO$_3$, a 1 x 1 surface unit cell of SrTi$_{0.75}$Fe$_{0.25}$O$_{3-\delta}$, where the iron atoms are located in the 4\(^{rd}\) and 6\(^{th}\) layers beneath the surface and the surface is characterized with a single oxygen vacancy (shown in Figure 1), and a 2 x 1 surface unit cell of SrTi$_{0.75}$Fe$_{0.25}$O$_{3-\delta}$, where the iron atoms are located in the 4\(^{rd}\) and 6\(^{th}\) layers beneath the surface and the surface is characterized with two oxygen vacancies. The position of the iron atoms is selected far from the surface in order to have minimal effect on the surface reactions. One of the iron atoms is within the layers with fixed coordinates and the second iron atom is in the layers with fully relaxed coordinates. The 1 x 1 surfaces are modeled with 4 x 4 x 1 k-point sampling and the 2 x 1 surfaces are modeled by 2 x 4 x 1 k-point sampling. Bader population analysis was performed to determine the atomic charges. Activation barriers for various reaction mechanisms were obtained using the nudged elastic band method (NEB) combined with the climbing nudged elastic band method (cNEB). In the process of NEB calculations five images were used between the starting and ending geometries.

![Figure 1. Model of the SrTi$_{0.75}$Fe$_{0.25}$O$_{3-\delta}$ with surface oxygen vacancy.](image-url)
3. Results

Low Energy Ion-Scattering

LEIS analysis of the (001) STO single crystal surface after the aqua regia etching and 1000°C annealing treatment revealed that the outer surface is not the expected TiO$_2$ termination and is mainly SrO-terminated. Figure 2 shows a comparison of the surface composition of the first atomic layer and the bulk of the single crystal obtained with 3 keV He$^+$ primary beam. At the outer surface (Figure 1, black solid line), two main peaks were identified at scattering energies of ~1180 and 2540 eV (high energy onsets), corresponding to $^{16}$O and Sr atoms at the surface, respectively. A small Na surface impurity was also identified at 1580 eV, but was only present at the outer surface and removed by the first sputtering cycle. The comparison with the bulk composition of the STO single crystal (Figure 1, blue dotted line) highlights the clear absence of Ti at the outer surface (theoretical scattering energy at 2212 eV). At the position where a strong Ti signal is obtained for the bulk spectrum, the spectrum for the unsputtered outer surface shows a step in the signal background, indicating that the Ti species are not present at the first atomic layer, but in the sub-surface layers. Although the aqua regia etching and subsequent high temperature annealing is commonly applied to obtaining nominally single TiO$_2$-terminated, atomically-flat, STO surfaces, our results reveal that, at the limits of detection of the technique, the outer surface is in fact SrO-terminated.

Figure 2. LEIS spectra obtained by 3 keV He$^+$ analysis of the (001) SrTiO$_3$ single crystal after etching and annealing at high temperature. Solid line: Elemental composition of the outermost surface, dotted line: elemental composition of the bulk of the STO single crystal after sputtering with 500 eV Ar$^+$.

A better sensitivity for the heavier cation species can be achieved by analysis using 6 keV Ne$^+$ primary ions. Figure 3 shows the LEIS spectra at different depths from the initial surface, after sputtering by a low energy Ar$^+$ beam during depth profiling analysis. Here, the outer surface (solid black line) again shows the absence of Ti atoms with a full coverage of SrO. After a first sputtering cycle, a peak at ~1180 eV assigned to the Ti atoms at the sub-surface is observed (red solid line spectrum in Figure 2, corresponding to an approximate depth of 0.04 nm, i.e. after removal of a single atomic layer). Additionally, the Sr peak also increases in the subsurface, due to the sputtering of the Na impurity, and partial reduction by preferential sputtering of oxygen by the Ar$^+$ beam.
Figure 3. LEIS partial spectra obtained for the first 2nm of the (001) STO single crystal using 6 keV Ne⁺ beam for the analysis and 500V Ar⁺ for the sputtering. The estimated depth was obtained from the sputter rate calibration on the STO single crystal measured by laser interferometry.

Although these results are in contradiction with the expected TiO₂-single surface termination, they are in agreement with previous reports on perovskite materials after annealing at high temperatures. For instance, an AO-termination (with A = aliovalent dopant and alkaline-earth cations) was found for different perovskite and perovskite-related oxides after annealing in O₂ at 1000°C. Furthermore, previous studies on STO surfaces revealed that the high temperature annealing used after the surface etching can promote Sr segregation, leading to a partial SrO surface coverage, and this partial surface coverage can be increased to obtain a complete SrO coverage by exposing the surface to air. Since the analysis of our STO single crystal was not performed immediately after the etching and thermal annealing, the obtained composition of the surface was predominantly SrO-terminated.

Figure 4. LEIS depth profile for the STO single crystal. Dotted lines indicated the bulk composition obtained for the plateau signals of the cationic species.
The distribution of cations in the near-surface (first 5 nm) region of the STO single crystal is shown in the LEIS depth profile in Figure 4. The very low coverage of the transition metal at the outer surface, rapidly increasing with sputtering, again indicates an SrO surface termination due to the segregation of the Sr cations towards the surface. The cation signals reach a plateau at about 5 nm depth, which is assumed to indicate the bulk composition has been reached.

**Density Functional Theory Calculations**

Our DFT calculations suggest that the SrO terminated STO surface cannot dissociate the oxygen. No electron transfer is observed between the perovskite surface and the adsorbed oxygen molecule. Thus, our efforts were directed towards the Fe doped STO with surface oxygen vacancies as the model is shown in Figure 1. We have investigated the oxygen vacancy migration between the surface and subsurface layers, as well as, the oxygen vacancy migration within the top SrO layer. The results are summarized in Figure 5.

The results show that oxygen vacancy is stabilized within the surface layer with 0.15 eV and the activation barrier for subsurface to surface migration is 0.44 eV. The activation barrier for vacancy migration within the surface layer is two times higher, 0.98 eV. The reason for the higher barrier for the surface migration compared to subsurface to surface migrations is due to the complete cleavage of the Ti-O bonds. The Ti-O bonds play important role for the stabilization of the O-species. An important conclusion is that oxygen vacancy clustering is energetically favored on the surface. The reason is geometry relaxation of the Ti-O-Ti bond angle in vicinity of surface oxygen vacancies. In the case of STO that bond angle is 168°. A single oxygen vacancy degreases this angle to 156°. A second oxygen vacancy further decreases the angle to 136°. The optimal valence angle for the oxygen atoms is similar to the water molecule, 107°. Thus, oxygen vacancy clustering stabilizes the oxygen valence bonds and lowers the slab energy.
In the gas phase, the oxygen molecule is stable in its triplet ground state with two unpaired electrons occupying degenerate π-molecular orbitals with an orthogonal spatial distribution. Any dissociation of the oxygen molecule progresses through its activated states, i.e., singlet oxygen, superoxo state \((O_2^-)\), or peroxo state \((O_2^2-)\). Such activation requires significant interaction with the catalytic surface and possible electron transfer. The activated states of the oxygen molecule are characterized by different spin states and bond lengths. The superoxo state has a radical character and an O-O bond of 1.3~1.4 Å, while the peroxo state is singlet and is characterized with an O-O bond length of 1.4~1.6 Å.

We investigate the interaction of the oxygen molecule with a surface vacancy as it is shown in Figure 6. From the geometry we can conclude that the O-O bond has been activated as it is elongated to 1.47 Å, however, an oxygen atom has not been yet incorporated into the lattice as the O-Ti distance is 2.21 Å. The O-O bond length elongation suggests that electron density if transferred from the surface to the oxygen molecule is activated to its peroxo state. We have performed Bader population analysis, which shows identical charges of -0.65 electrons at each O-atom, or -1.3 electrons for the total \(O_2\) molecule. The geometry and charge analyses suggest that the \(O_2\) molecule was activated to its peroxo state. Electron density is donated from the \(d_{z^2}\) orbital of the Ti-atom underneath the vacancy to the π* orbital of \(O_2\). Additionally, electron density redistribution occurs in the \(O_2\) molecule as electron density is transferred from the O-O internuclear region to the π* orbitals. The π* orbitals of \(O_2\) are the result of out-of-phase combination between the oxygen 2p atomic orbitals, and are characterized by an antibonding interaction, with their occupancy leading to O-O bond elongation.

![Figure 6. Orbital diagram of the oxygen molecule. Geometry of an oxygen molecule within a surface vacancy. Electron density difference resulting from interaction of an oxygen molecule and a surface vacancy.](image)

**Figure 6.** Orbital diagram of the oxygen molecule. Geometry of an oxygen molecule within a surface vacancy. Electron density difference resulting from interaction of an oxygen molecule and a surface vacancy.

**Figure 7.** Oxygen dissociation on Fe doped STO with a surface oxygen vacancy. A: Dissociation over a single vacancy. B: Dissociation over a vacancy cluster.
The O\textsubscript{2} dissociation is shown in Figure 7. Figure 7 A shows oxygen dissociation over a surface vacancy and Figure 7 B shows oxygen dissociation over a vacancy cluster. Over a single surface vacancy, the dissociation proceeds with a barrier of 1.023 eV and is endothermic by 1.00 eV. The high energy of the resulting product, i.e., the oxygen atom incorporated into the lattice and the adsorbed O-atom on the surface is due to the small electron transfer from the surface to the adsorbed O-atom and its high spin state. The Bader analysis reveals that the charge of the surface oxygen in the product is -0.7 e\textsuperscript{-}. One of the oxygen atoms from the adsorbed O\textsubscript{2} molecule is fully incorporated in the lattice. The high energy of the product is due to the highly unstable remaining oxygen atom on the surface. Figure 7 B shows the mechanism of O\textsubscript{2} dissociation and oxygen vacancy incorporation catalyzed by two neighboring oxygen vacancy sites. The oxygen molecule splits over a Sr-Sr bridge site and the activation barrier was estimated to be 0.5 eV. The reaction proceeds further as the second oxygen atom fills the second lattice oxygen vacancy leading to vacancy free AO-terminated perovskite surface. The energy of the product (Figure 7 B) relative to the energy of the starting structure is -2.38 eV. The reaction is strongly exothermic and the equilibrium is shifted towards O\textsubscript{2} dissociation and oxygen atoms incorporation into the surface vacancies. The activation barrier of the O\textsubscript{2} dissociation is lower compared to the O-atom surface migration, which would make the later the rate-determining step for the proposed reaction mechanism.

Conclusions

Our LEIS study has shown that SrTiO\textsubscript{3}, annealed at 1000°C terminates in an SrO surface and thus provides a good model for the Sr substituted mixed conductors used as SOFC/SOEC air electrodes. It further reveals that while O\textsubscript{2} dissociation is not favored on the stoichiometric SrO-terminated SrTiO\textsubscript{3} perovskite surface, oxygen vacancies can act as active sites and catalyze the O-O bond cleavage. Electron transfer from lattice oxygen atoms to the O\textsubscript{2} molecule, mediated by the subsurface transition metal cations, plays an important role in the resulting formation of surface superoxo species. The O\textsubscript{2} molecule dissociates to produce oxygen ions, which are incorporated into the perovskite lattice, and highly active oxygen radicals on the perovskite surface, which further recombine to O\textsubscript{2} molecules. We believe that this first result is one that has a more general applicability to all SrO terminated surfaces of perovskite mixed conducting electrodes and underlines the importance that surface vacancies play in the oxygen exchange process.

References

High-Performance Cathode/Electrolyte Interfaces for SOFC

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Abstract

High-performance solid oxide fuel cells (SOFC) mostly utilize the mixed conducting cathode La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-δ}$ (LSCF). The drawback of LSCF however lies in the formation of an ion-blocking layer of Strontiumzirconate (SrZrO$_3$ - SZO) when it is directly applied on Y$_2$O$_3$ stabilized ZrO$_2$ electrolyte (YSZ). This secondary phase reaction can in practise be prevented by inserting a dense Gd-doped Ceria (GDC) between LSCF and YSZ [1,2,3]. Commonly, the GDC interlayer is screen printed and correct density is assured by subsequent sintering. This high temperature treatment however causes a low ionic conducting GDC-YSZ interdiffusion phase (ID) [4, 5]. The correct balance between GDC-density and GDC-YSZ interdiffusion is crucial for achieving highly functional GDC interlayers.

In this study, the characteristics of LSCF/GDC/YSZ interfaces were substantially modified by a variation in GDC sintering temperature [6]. Evidently, the nature of the GDC barrier layer depends strongly on sintering temperature and alterations of the area specific resistance of the cathodic polarization over two orders of magnitude (~6-7 mΩ⋅cm$^2$ to ~7 Ω⋅cm$^2$ at 800 °C) were measured [7,8,9].

Our findings confirm a complex heterogeneous cathode/electrolyte interface consisting of primary phases (LSCF, GDC and YSZ) and secondary phases (SZO and ID). Still, in technical relevant processes secondary phases inherently appear and their detrimental impact which overshadows every high-performing material property points to the necessity of understanding the interplay between chemical composition, processing and microstructure for individual cell concepts.

Remark: Only the abstract is available, because the authors chose to publish elsewhere. Please see Presentations on www.EFCF.com/LIB or contact the authors directly.
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Synthesis through electrospinning of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ceramic fibers for IT-SOFC electrodes

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Abstract

We synthesize $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) fibers through the electrospinning method. This technique applies high voltage to induce the formation of a liquid charged flow, which is then ejected with evaporation of the solvent and simultaneous formation of solidified, continuous, ultra-thin fibers. The formation of nanofibers is a function of the operating parameters, i.e. the rotation speed of the support, the solution feeding rate, and the operating voltage, which are investigated in this work. The results indicate that a rotation speed of 750 rpm, a solution feeding rate of 0.5 ml/h, and an operating voltage of 17 kV allow to obtain fiber diameter in the range 500 nm – 1500 nm, with linear and one-directionally oriented fibers. Since the fibers must undergo heat treatment, their behavior during the calcination processes is investigated as well through TGA. The results show exothermic peaks which we interpret as solvent evaporation and perovskite structure formation, and suggest to perform calcination slowly in the temperature range 250-550 °C. The final goal of this research is to couple the experimental results described here to a previously developed theoretical model, in order to gain a better understanding of the fundamental electrochemistry of the processes occurring in fibrous electrodes for IT-SOFC applications.

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Effect of microstructural parameters on a performant SOFC cathode: Modelling vs Experiments

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Abstract

The present study concerns the influence of the micro/nano-structural properties of LSCF (La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$) and 60:40 vol.% LSCF/CGO (Ce$_{0.9}$Gd$_{0.1}$O$_{2-δ}$) composite cathode films on their electrochemical behavior. Electrostatic spray deposition technique is used to deposit 10 μm-thick functional films as shown in Figure 1. Contrary to expectations, pure LSCF has a better response compared to the composite. It presents an Area Specific Resistance (ASR) value as low as 0.021 and 0.068 Ω cm$^2$ at 650 °C and 600 °C respectively, which to the best of our knowledge is one of the lowest reported values to date for LSCF-6428 composition in OCV condition.$^1$ To better comprehend the complex relationships between material properties, processing, micro/nano structure and electrode performances, a simplified geometry representing the porous columns of the electrodes is modelled by 3D finite element (FEM).$^2$ Electrode performance is computed as a function of real microstructural parameters obtained from 3D FIB/SEM technique. On the other hand, ASR is calculated by a simple volume-averaged analytical model (1D-ALS model)$^3$ within an assumed macrohomogeneous geometry. The computed ASRs with these two relatively simple models are compared to experimental results and the relevancy of such models for columnar microstructures is discussed.

Figure 1 Microstructural characterization of the films a-c) LSCF, e-g) 60/40 vol.% LSCF/CGO composite films viewed by SEM. 3D reconstructed images by FIB/SEM technique of (d) LSCF and (h) 60:40 LSCF/CGO composite.

1. Çelikbilek, O., Jauffres, D., Siebert E., Dessemond, L., Burriel, M., Martin, C.L., Djurado, E.,(2016), to be submitted

Remark: Only the abstract is available, because the authors chose to publish elsewhere. Please see Presentations on www.EFCF.com/LIB or contact the authors directly.
Quantifying the surface exchange coefficient of cathode materials in ambient atmospheres

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Abstract

Isotopic exchange has been used for over 30 years to quantify the effective surface exchange, $k^*$, and self-diffusion, $D^*$, coefficients of SOFC materials. Typically, however, the nominal exchange environment in the literature is pure, dry oxygen, which is not representative of realistic SOFC operating conditions. A novel two step exchange process, “back-exchange”, has been developed to overcome this limitation. The first step is a conventional exchange in pure, dry $^{18}\text{O}_2$, but the second step can be in any environment with the same $p\text{O}_2$. A new analytical expression was found for the special case of back-exchange in which the parameters $k^*$ and $D^*$ were constant across the two exchanges. However, in order to fit the data obtained from exposing the sample to ambient conditions in the second step, a 1-dimensional, Crank-Nicholson type, finite-difference simulation was constructed.

Fitting the data from two experiments against the simulation suggested a 2× increase in the value of $k^*$ in the ambient environment compared to pure dry $^{18}\text{O}_2$. The analytical solutions, simulations and fitting procedures, as well as a host of data analysis tool, have been packaged by the author into a MatLab application called TraceX, which is freely available upon request. The results of this study highlights the significance of the back-exchange technique, but further work must be done to determine the origin of the observed augmentation in surface exchange.
Introduction

The effective surface exchange, $k^*$, and self-diffusion coefficient, $D^*$, of oxygen conducting materials has been the focus of much academic and industrial interest due to their relevance in a wide range of applications, such as in fuel cells and oxygen sensors. Isotopic Exchange Depth Profiling (IEDP) as a means of quantifying $k^*$ and $D^*$ of oxygen conducting materials was first described by Kilner et al. in 1984 [1]. The technique has since been greatly refined to allow not only for the investigation of a wider range of materials, but also to study the relationship between multiple material properties.

The cost of high purity oxygen-$^{18}$ is significant and as such it is common to reclaim the gas used during each experiment. Thus, the use of enriched multi-component gas mixtures, which are needed to model typical operating conditions for many common applications, is precluded. In addition, the literature contains multiple examples of disagreement on the values of $D^*$ and $k^*$ for many widely studied materials, such as the mixed conductor La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF6428) [2]. This may be the result of trace gasses present during the exchange, which are not always reported. Alternatively, it could be caused by variations in the measurement of the duration, temperature and pressure of the exchange anneal.

This study proposes an extension to the IEDP technique through the use of multiple exchange steps, combined with simulation derived profiles in order to extract material parameters. This allows the effect of gas composition on the materials to be investigated, without the use of expensive isotopically enriched multi-component gasses.

High diffusivity materials, such as those used for SOFC electrodes, are difficult to analyse using the conventional depth profiling approach as, for reasonable anneal durations (i.e. not so short as to incur large errors from furnace ramping), the profile generated would be very deep. This means that to capture a proportion of the profile sufficient for curve fitting, the sputtering time would become impractically long. To overcome this limitation, Chater et al. proposed a line-scanning approach where, following exchange, the sample is cut normal to the exchange surface and then a SIMS raster image is taken of a region spanning a much greater depth than is available to conventional IEDP [3].

A further innovation in the quantification of $D^*$ and $k^*$ was the parallel detection of secondary ions using a Time-of-Flight Secondary Ion Mass Spectrometer (ToF-SIMS) [4]. Not only does this approach allow for the oxygen isotopes to be detected in parallel, so that the images require no alignment in post-processing, but it can also be used to quantify the varying stoichiometry in the near surface region, which may locally affect the diffusivity.

Water only IEDP experiments, which similarly do not represent in operando conditions, have previously been performed on materials similar to LSCF6428 using water labelled with oxygen-$^{18}$ and, in some cases, an order of magnitude difference in surface exchange was observed [5] compared to oxygen only experiments. In the study described in this paper, the sample was exposed to ambient air, which is expected to comprise of a host of oxygen containing species (e.g. CO$_2$, H$_2$O).

Alternative isotope labelling techniques exist besides IEDP. Horita et al. developed a polarization driven exchange, where a sample is exposed to a range of cathodic overpotentials in an enriched environment and then analysed in-depth using SIMS [6]. The Isothermal Isotope Exchange (IIE) approach described by Armstrong et al. passes oxygen through powder samples in a continuous flow reactor [7]. By introducing well defined
pulses of labelled oxygen into the system and measuring, as a function of time, the outflow using a mass spectrometer, it is possible to extract the surface exchange coefficient of the materials. Labelled carbon dioxide was used by Kleiminger et al. to investigate the performance of solid oxide electrolyser [8], although $D^*$ and $k^*$ could not be extracted directly due to the complexity of modelling a complete electrolyser cell.

The electrical conductivity relaxation (ECR) technique [9] employed by Lane et al. does not require isotopes and measures the transient electrical response of a sample when exposed to a change in surface oxygen partial pressure. These ECR results can be converted using the “thermodynamic factor” and so ultimately, each of the various methods described above should yield comparable results when treated appropriately, however variations in measured values persist [2].

1. Scientific Approach

In order to extract $D^*$ and $k^*$ from the IEDP data the exchanging material is typically modelled as a one dimensional (1D), semi-infinite system with diffusion in the bulk and an exchange boundary at the surface, as defined in the following system of linear equations,

\[
\begin{align*}
\frac{\partial C'}{\partial t} &= D^* \frac{\partial^2 C'}{\partial x^2} \quad \text{on } x \geq 0, t > 0, \\
C'\big|_{t=0} &= 0 \quad \forall x \geq 0, \\
C'\big|_{x=0} &= 1 + \frac{D^*}{k^*} \frac{\partial C'}{\partial x} \bigg|_{x=0} \quad \forall t > 0, \\
\lim_{x \to \infty} C'(t, x) &= 0 \quad \forall t > 0.
\end{align*}
\] (1)

where, $x$ is the depth from the exchange surface; $t$ is the exchange time; $C'$ is the normalised isotopic fraction, given by eq. 2; and $C_{gas}$ and $C_{bg}$ are the isotopic fractions of the exchange gas and the natural abundance respectively.

\[
C'(t, x) = \frac{C(t, x) - C_{bg}}{C_{gas} - C_{bg}}
\] (2)

The solution to this system, $C'_{\text{Crank}}$, often referred to as “Crank’s solution” [10], is shown in eq. 3.

\[
C'_{\text{Crank}} = \text{erfc} \left\{ \frac{x}{2\sqrt{D^*}\phi} \right\} - \exp \left\{ \frac{k^* x}{D^*} + \frac{k^* \phi}{D^*} \right\} \text{erfc} \left\{ \frac{x}{2\sqrt{D^*}\phi} + \frac{k^* \sqrt{\phi}}{D^*} \right\}
\] (3)

Notice that in this solution the time variable, $t$, has been replaced by the effective time, $\phi$, which is necessary due to the unavoidable ramping of the exchange furnace up to the required temperature. The effective exchange durations were calculated using thermocouple time series, based on the method proposed by Killoran [11], as suggested in a similar study by De Souza [12].

In the case of the back-exchange, an analytical solution has not previous been reported in the literature, but is shown for the first time here, $C'_{\text{BE}}$, for the special case where the
material’s exchange parameters in the second step \((k^*_{2} \text{ and } D^*_{2})\) are equal to those found in the first step \((k^*_{1} \text{ and } D^*_{1})\).

\[
C_{BE}' = \cdots \left( \text{erfc} \left\{ \frac{x}{2\sqrt{D^*(\phi_1 + \phi_2)}} \right\} - \exp \left\{ \frac{k^*_{1}x}{D^*_{1}} + \frac{k^*_{2}(\phi_1 + \phi_2)}{D^*_{1}} \right\} \text{erfc} \left\{ \frac{x}{2\sqrt{D^*(\phi_1 + \phi_2)}} + k^*_{1}\sqrt{\frac{\phi_1}{D^*_{1}}} \right\} 
\right) 
- \left( \text{erfc} \left\{ \frac{x}{2\sqrt{D^*\phi_2}} \right\} - \exp \left\{ \frac{k^*_{1}x}{D^*_{2}} + \frac{k^*_{2}\phi_2}{D^*_{2}} \right\} \text{erfc} \left\{ \frac{x}{2\sqrt{D^*\phi_2}} + k^*_{2}\sqrt{\frac{\phi_2}{D^*_{2}}} \right\} \right) \right)
\]

Or in its more compact form,

\[
C_{BE}' = C_{Crank}'(\phi_1 + \phi_2, x) - C_{Crank}'(\phi_2, x)
\]

Where \(\phi_1\) and \(\phi_2\) are the effective anneal times of the first and second exchanges respectively. However, the experiments described in the following section could not be fitted with this analytical expression, suggesting a change in the exchange parameters resulting from the change in gas composition. As such, a Crank-Nicolson [13] type 1D, finite-difference simulation was constructed, which allowed the exchange parameters to be varied between the two steps.

Using these models, a non-linear, least squares optimisation algorithm, \textit{fminsearch}, was implemented in MatLab to fit profiles to the IEDP data [14]. The analytical solutions, simulations and fitting procedures, as well as a host of data analysis tool, have been packaged by the author into a MatLab application called \textit{TraceX}, which is being made freely available upon request.

2. Experiments

In this study, ToF-SIMS has been used to quantify the isotopic fraction, as a function of distance from the surface, to analyse the effect of exchanging samples in air compared to pure dry oxygen. The protocol described by DeSouza \textit{et al.} for oxygen isotopic exchange in dense ceramic pellets [12] was used as the basis for the following experiments. LCSF6428 powder was pressed into cuboid pellets with dimensions \(2 \times 2 \times 5\) mm and then sintered at 1250 C for 8 hours (using a heating rate of 300 C/hour). The dimensions of the pellets allowed the IEDP profile to be modelled as a 1D system only if the expected depth of \(x' = 2\) (where \(C' < 0.005\) for all \(k^*\)) was < \(c. 250\) µm, which informed the proposed anneal time. The normalised depth, \(x'\), is defined as

\[
x' = \frac{x}{2\sqrt{D^*\phi_{tot}}}
\]

where \(\phi_{tot}\) can be taken as the total duration of all exchanges in the experiment; and \(D^*\), which is necessarily an approximation before the experiment has been performed, is taken as the upper bound of similar values available in the literature.

The pellets were then ground and polished to a mirror finish on one face using sequentially finer grades of polishing media. P800 grade (\(c. 22\) µm particle size), P1200 (\(c. 15\) µm particle size) and P2400 (\(c. 10\) µm particle size) silicon carbide paper lubricated by water were used. Following this, the sample was polished using water based diamond
suspending with particle sizes of 6 µm, 3 µm, 1 µm and 0.25 µm sequentially. This procedure was important for ensuring not only that the surface was suitably flat for SIMS analysis, but also that the mechanical damage induced by each step was removed by the following step. Before the first exchange, each pellet was annealed at the desired experimental temperature and oxygen partial pressure in research grade 99.999% pure, dry oxygen. By doing so, chemical equilibrium was established, ensuring the oxygen vacancy concentration of the sample was uniform and known before the following exchanges. To provide a sufficiently large region with a constant oxygen non-stoichiometry, the pre-anneal time is calculated to be approximately ten times that of the first exchange. Ensuring the dryness and oxygen purity of the pre-anneal step and the first exchange were important for accurately determining the effect of the atmosphere in the back-exchange.

All experiments were performed in an ultra-high-vacuum, bakeable exchange apparatus fabricated from stainless components and sealed with “conflat” flanges. A turbomolecular pump (backed by a dry membrane pump to reduce the chance of back-streamed oil vapour) was used before each experimental step to evacuate the chamber to a pressure of < 4×10⁻⁷ mbar. The $^{18}$O₂ enriched oxygen for the exchanges was derived from a 5 Å molecular sieve reservoir, which ensured that the gas was dry to c. 1 ppb water. The samples were not re-polished between exchanges.

Two samples were prepared in the above manner, which were then simultaneous heated to a nominal temperature of 650 C and exposed to an atmosphere of pure, dry isotopically enriched oxygen, for a period of 90 minutes. After this, sample A was removed from the furnace, whereas sample B was subjected to a second exchange anneal for a further 45 minutes, again at c. 650 C, but now in an environment of ambient air.

3. Results

The effective anneal duration were calculated to be 83 minutes for the first exchange and 53 minutes for the second exchange, both at an effective temperature of 656 C. Figure 1 shows the ToF-SIMS line-scan profiles superimposed onto the isotopic fraction data from the analysis area observed in sample A and B respectively.

![Figure 1: ToF-SIMS line-scan profiles superimposed onto the isotopic fraction data from](image-url)
the analysis area observed in sample A and B respectively

Figure 2 contains plots of the normalised isotopic fraction profiles against normalised depth for samples A and B respectively, as well as the fitted model profiles used to extract the exchange parameters. Figure 2(b) also contains the profile, based on the analytical back-exchange solution, that would result in the case where the exchange parameters did not change between the two anneals.

Figure 2: Plots of the normalized isotopic fraction profiles against normalised depth for samples A and B respectively. 2(b) also contains the profile, based on the analytical back-exchange solution, that would result in the case where the exchange parameters did not change between the two anneals.

Table 1 contains the exchange parameters extracted from the two data sets, which highlight both the validity of the technique, due to the consistency of $D^*$ and $k^*$ between experiments, as well as the utility of the technique as shown by effective surface exchange double when sample b was exchanged in air. Both of these fits had an $R^2$ value of better than 0.99, when calculated in the domain $0 < x' < 2$, as recommended in [15].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k^*_1 / 10^{-9}$ m s$^{-1}$</th>
<th>$D^*_1 / 10^{-13}$ m$^2$s$^{-1}$</th>
<th>$k^*_2 / 10^{-9}$ m s$^{-1}$</th>
<th>$D^*_2 / 10^{-13}$ m$^2$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>3.49</td>
<td>1.92</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sample B</td>
<td>3.84</td>
<td>1.85</td>
<td>7.11</td>
<td>1.85</td>
</tr>
</tbody>
</table>

4. Conclusions

A novel isotopic exchange technique has been developed to quantify the effect of contaminants on the surface exchange coefficient of oxygen conducting ceramics. This “back-exchange” approach allows the effect of any gas (ideally with the same $pO_2$) to be investigated using the same apparatus, where previously long saturation anneals or costly enriched multi-gas mixtures were required. The method involves a two-step exchange process, followed by line-scan SIMS imaging of the isotopic fraction.
The analytical solution to the back-exchange system was derived for the special case where the exchange variables, \( D^* \) and \( k^* \), are uniform across all exchanges. For a back-exchange in which the gas environment was different for each exchange, a Crank-Nicholson type finite-difference simulation had to be used to fit the data, which allowed each of the variables to be floated independently.

This work found that ambient air had caused a c. 2× increase in the value of \( k^* \) compared to pure, dry \( \text{O}_2 \), which demonstrates the significance of the technique. Although, the back-exchange approach can be extended to any atmosphere with the same \( p\text{O}_2 \) as that of the first exchange step, the asymptotic behavior of the profiles when \( k^* \) varies significantly from \( k^*_1 \) cause the uncertainty to become large and asymmetric. Further work must be done to isolate the effect of each gas component in air to establish the cause of the augmented exchange.

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SOFC Cathode Degradation Studies Using Impedance Spectroscopy Genetic Programming

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Abstract

In this technical contribution, we will present electrochemical impedance spectra of LSM/YSZ/Pt cells tested in different environment atmospheres and their analysis results by an Impedance Spectroscopy Genetic Programming technique. Electrochemical spectra under the different cathode ambient environments (dry air only, 3% H2O/air, and 3%H2O/air with Cr vapor) have been measured during 100-hour tests. A novel impedance spectroscopy Genetic Programming technique has been utilized for the analyses of these electrochemical impedance spectra. The best model for each typical impedance spectrum has been generated by this technique. EIS spectra of the Tests C and D (absence and presence of chromium getters) show opposite trends of semi-arc at low frequency range. Both distribution function of relaxation times (DFRTs) of the Tests B and C show a peak at log τ range of -10 to -9, indicating both water and chromium attribute to an increase of resistance. The presence of getters in the cathode gas stream has effectively improved the electrochemical performance by lowering the resistance.
Introduction

Electrical performance degradation has been a challenge to a long term operation of solid oxide fuel cell (SOFCs) power systems [1]. Some degradation factors are structural and thermo-chemical instability, materials migration and densification, solid-solid and solid gas interactions with the component materials at the cell and stack level such as cathode, electrolyte, and anode, interconnect and gas seal [2]. Cell degradation due to minor impurities (H$_2$O, CO$_2$, Cr vapor, Si, and SO$_2$) in the air stream has been reported [3-5]. Water in air aggregates the corrosion and oxidation of chromium containing alloys, which leads to higher chromium vapor in the wet air stream than in dry air [6]. Degradation of cathodes becomes a major contributor for overall SOFC performance degradation [7].

Electrochemical impedance spectroscopy (EIS) is an effective tool for the analysis of the electrical response of electrode materials and interfaces. There are several different approaches for analyzing EIS. “Direct” equivalent circuit solutions are the most common approach for EIS analysis, by which the experimental data are compared to a prediction of a given equivalent circuit [8-10]. The parameters of each circuit elements are attributed to a certain process and they can be calculated from the given equivalent circuit. Equivalent circuits may suffer from several problems, including non-uniqueness, overlap of features and insufficient bandwidth. For a complex system such as real SOFC, the number of circuit elements grows and the latter problems become more severe. The underlying physical phenomena are related to relaxation times. Recently, another approach, named Impedance Spectroscopy Genetic Programming (ISGP) has been developed to find the distribution function of relaxation times (DFRT) [11]. The DFRT has the form of a peak or several peaks, which can be related to different processes. Tsur’s group has reported the DFRTs of the samples such as solid oxide electrolytes and supercapacitors by this ISGP approach [12-14].

In this study, we have recorded the EIS of the cathodes exposure to different ambient environments (dry air only, 3% H$_2$O/air, and 3%H$_2$O/air with Cr vapor) for 0-100 hours. These EIS spectra of the cathodes were analyzed by the ISGP approach. The analysis results are presented in this proceeding.

1. Scientific Approach

1.1. EIS Measurement

The procedures for the cell fabrication and electrical testing have been described in previous studies [15, 16]. LSM ink was screen-printed on one side of YSZ electrolyte (Fuel Cell Materials) and Pt paste was applied on the other side to fabricate LSM/YSZ/Pt half-cells. The LSM electrodes have a diameter of 1.0 cm with a thickness of about 15 µm. Platinum mesh and wires (Alfa Aesar) and platinum paste (Engelhard) were used as electrode materials. Table 1 shows the schematic of the experimental set up for EIS measurement at different cathode gas environments. As-fabricated LSM/YSZ/Pt cells were loaded in an alumina reactor. The cathode gases (150 cm$^3$/min) were introduced to the cells by a mass flow controller. The three platinum electrodes (anode, cathode, and reference) of the cell were connected to the leads of a potentiostat. The as-assembled setup was heated in a vertical furnace to the testing temperature (1123 K) with a ramp rate of 3 K/min. The voltage was applied between the cathode and reference electrode.
Table 1. EIS measurement conditions for the LSM cathodes exposure to different cathode gas stream

<table>
<thead>
<tr>
<th></th>
<th>Test A</th>
<th>Test B</th>
<th>Test C</th>
<th>Test D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>1123</td>
<td>1123</td>
<td>1123</td>
<td>1123</td>
</tr>
<tr>
<td>Cathode Atmosphere</td>
<td>dry air</td>
<td>3% H₂O/air, no Cr</td>
<td>3% H₂O/air, Cr vapor</td>
<td>3% H₂O/air, Cr vapor</td>
</tr>
<tr>
<td>Bias (V)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Cr Getter</td>
<td>No getter</td>
<td>No getter</td>
<td>No getter</td>
<td>Getter</td>
</tr>
<tr>
<td>Test time (h)</td>
<td>1-100</td>
<td>1-100</td>
<td>1-100</td>
<td>1-100</td>
</tr>
</tbody>
</table>

EIS measurements have been performed at three different cathode gas environments. First, a base line experiment of the LSM/YSZ/Pt half-cell A in dry air at a flow rate of 150 cm³/min at 1123 K was performed. The second experiment was conducted on the half-cell B exposure to 3% H₂O/air at a flow rate of 150 cm³/min at 1123 K. The third experiment was performed in absence of getter (which serves as a trap for Cr impurities) and in presence a Cr source and 3% H₂O/air at a flow rate of 150 cm³/min at 1123 K to compare the EIS spectra in different gas environments. The fourth experiment was performed in presence of getter and the Cr source at the same conditions as the third experiment. The real-time EIS were recorded by a multi-channel potentiostat at an interval of 1 h. A bias was applied between the cathode and the reference electrode. The EIS measurements were conducted in the frequency range of 0.5 Hz to 200 kHz with 15mV sinus amplitude.

1.2. Impedance Spectroscopy Genetic Programming

The EIS analysis procedures by the ISGP approach have been described in previous studies [17]. In this work, an updated version of the ISGP was employed for the EIS analysis. The ISGP program was operated using the MATLAB (version R2015b) software. The ISGP approach includes a population of candidate models to an optimization problem that evolves towards a better solution over generations. The proposed models in the population are assigned with parameter values that generate its best possible fit. Two sets of data (taken at identical conditions) can be entered to avoid over-fitting. The first step for the ISGP analysis is checking the validity of the impedance data by Kramers-Kronig (K-K) transforms to find distorted points due to experimental artifacts. A filter may be introduced if necessary to rank the results close to the high or low frequency limits. The second step is normalizing the impedance data by the maximum value of real Z (Re Z) to fulfill threshold requirements of the program. Then, the ISGP code begins running up to a given criterion (number of generations with no improvement, chosen by the user) and then the resulting model is analyzed.
2. Results and Discussions

The purpose of this study is to investigate the mechanisms of chromium poisoning on the LSM cathode. For the comparisons of the effects of air impurities, the impedances of the LSM cathodes in dry air and 3% H₂O/air have been measured first as blank conditions. Experimental impedance spectra of the LSM cathodes exposure to various atmospheres have been taken each hour during these 100-hour tests. All the impedance spectra shown in Figures 1-4 are normalized by Rmax in the ISGP analysis. Several known distribution functions, including Gaussian (G), Lorentzian (L), Hyperbolic Secant (H), Kirkwood-Fuoss (B) and Cole-Cole (C), have been used in the EIS analysis.

Figure 1 shows the impedance spectra and DFRT of the LSM cathode exposure to dry air at 1123 K for 100 hours. After finished 64 generations, the best model was achieved with a compatibility of 0.904:  L ([1.0338], u1=[-3.2983], [0.26981]) + D ([0.96459], u1=[-4.2648], [0.09]). The first number in each function represents its height, the second its central position and the third its width, where for pseudo-delta (D) the width is fixed at 0.09. Two peaks have shown at -4.2648 and -3.2983 of log τ (µ 1).

Figure 2 shows the impedance spectra and DFRT of the LSM cathode exposure to 3% H₂O/air with Cr vapor and getter at 1123 K for 100 hours. After finished 87 generations, the best model was achieved with a compatibility of 0.91: G ([0.40879], u1=[-2.9954], [0.545]) + Y ([3.5184], u1=[-9.5002], [0.09]) + D ([0.21848], u1=[-1.6331], [0.09]). Compared to the DFRT of the test A, additional peaks has been observed at -9.5002 of log τ and other two peaks has shifted to higher values (-2.9954 and -1.6331).

The chromium poisoning on the LSM cathode with time was shown in the EIS spectra and DFRT (Figure 3). With chromium deposition on the LSM cathode, the Rmax values of the LSM cathode for 1 h, 10 h, and 100 h increased accordingly from 5.0 Ω, 10.6 to 1.75 Ω.
Ω, to 16.7 Ω, respectively. The impedance part of Im Z increased with more chromium deposition. The second semi-arc at low frequency gradually disappeared. The resulting DFRTs have a good compatibility (0.94-0.97) and the best models of DFRT for 1 h, 10 h, and 100 h are listed below:

1 h: S ([0.20309], u1[-0.27658], [1.0337]) + Y ([0.94603], u1[-9.0024], [0.09]) + S ([0.33058], u1[-2.9252], [0.3847])
10 h: S ([0.41949], u1[-2.7141], [0.42381]) + Y ([0.2711], u1[-9.0007], [0.09]) + L ([0.19789], u1[-0.4546], [0.99927])
100 h: L ([0.15473], u1[-0.076722], [1.4461]) + G ([0.22975], u1[-2.1909], [1.0372]) + D ([1.4285], u1[-2.1622], [0.09])

Figure 3. The impedance spectra (left) and DFRT (right) of the LSM cathode exposure to 3% H₂O/air with Cr vapor in the absence of a getter at 1123 K for 1-100 hours. The Rmax values for 1 h, 10 h, and 100 h are 5.0 Ω, 10.6 Ω, and 16.7 Ω, respectively.

The effect of chromium getter on the LSM cathode with time was shown in the EIS spectra and DFRT (Figure 4). With a getter trapping chromium vapor gettering the cathode gas stream, due to cathodic activation, the Rmax values of the LSM cathode for 1 h, 10 h, and 100 h decreased accordingly from 9.8 Ω, 4.6 Ω, to 4.3 Ω, respectively. The impedance part of Im Z increased with more chromium deposition. The second semi-arc at low frequency gradually grew larger. The resulting DFRTs have a good compatibility (0.91-0.97) and the best models of DFRT for 1 h, 10 h, and 100 h are listed below:

1 h: G ([0.52321], u1[-2.9318], [0.65023]) + D ([0.72965], u1[-0.090299], [0.09]) + L ([0.25696], u1[-0.99996], [1.0346])
10 h: D ([0.74828], u1[-3.463], [0.09]) + S ([0.50823], u1[-3.0563], [0.48583]) + D ([0.66278], u1[-0.41203], [0.09])
100 h: L ([0.53707], u1[-2.2861], [0.29066]) + S ([0.49201], u1[-3.9268], [0.3324]) + D ([0.71816], u1[-0.5582], [0.09])
Figure 4. The impedance spectra (left) and DFRT (right) of the LSM cathode exposure to 3% H₂O/air with Cr vapor in the presence of a getter at 1123 K for 1-100 hours. The Rmax values for 1 h, 10 h, and 100 h are 9.8 Ω, 4.6 Ω, and 3.3 Ω, respectively.

Compared to the EIS spectra and DFRTs in absence (Figure 3) and presence (Figure 4) of a chromium getter, the Tests C and D show opposite trends of semi-arc at low frequency range. Both DFRTs of Tests B and C show leaks at log τ range of -10 to -9, indicating both water and chromium attribute to an increase of resistance. Each peak of the DFRTs may be related to a certain process, which is shown in Figures 3 and 4. Further analyses and interpretation of the DFRT are underway to develop the mechanisms of chromium poisoning on the LSM cathodes.

3. Conclusions
We have recorded electrochemical spectra under the different cathode ambient environments (dry air only, 3% H₂O/air, and 3% H₂O/air with Cr vapor) for 0-100 hours. A novel impedance spectroscopy Genetic Programming technique has been utilized for EIS analysis. The best model for each typical impedance spectrum has been generated by this technique. EIS spectra of the Tests C and D (absence and presence of chromium getters) show opposite trends of semi-arc at low frequency range. Both DFRTs of the Tests B and C show leaks at log τ range of -10 to -9, indicating both water and chromium attribute to an increase of resistance.

Acknowledgements
We acknowledge the financial support of Ed Satell Foundation and the US Department of Energy and National Energy Technological Laboratory under federal grant DE-FE 0023385. We thank the Center for Clean Energy Engineering, University of Connecticut for providing the instrument and facilities for the testing.
References

B1507 (see B1503)
High-throughput screening of SOFC cathode materials

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Abstract

Lanthanum and strontium manganites, cobaltites and ferrites (LSM, LSC and LSF, respectively) have been extensively used as oxygen electrodes in solid oxide fuel cells (SOFCs) [1]. None of them provide all the requirements for operating by themselves as cathodic material due to issues related with low ionic conductivity, low stability and/or incompatibility with the rest of constitutive SOFC materials. One of the approaches followed to overcome these inconveniences has been the combination among them, aiming to obtain mixed properties. A successful example of this strategy is the LSCF which presents mixed conductivity at intermediate temperature [1] and nowadays is commonly used as cathode in IT-SOFCs. However, when LSCF is employed a protective layer is needed to screen the YSZ electrolyte due to the reactivity between them. Following this approach, in this work a high-throughput methodology is employed for the preparation of a LSM, LSC and LSF ternary compositional map. Combinatorial Pulsed Laser Deposition is a very efficient procedure that allows the fabrication of multiple samples with different compositions in a single experiment [2]. Previous works showed the benefits of this method applied to a LSM + LSC binary system [3]. In this case in which a ternary system is studied, additional features are expected due to the likely natural trend of different stoichiometric samples to give rise to a variety of structures, properties or even phases. Initially, the simulation of the deposition process will allow us to determine the best configuration to obtain the largest compositional distribution throughout the wafer area. Besides, prediction of thickness and composition gradient is anticipated. In this initial stage of the work, assessments of phase purity, thin film stability and morphology and, compositional map generation are shown.

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Chromium Poisoning of Non-Manganiferous Cathode Materials for Solid Oxide Fuel Cells

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Abstract

Chromium poisoning accompanied with cathode degradation has been identified as a major cause for reduced SOFC stack/component lifetimes. In-depth knowledge of the mechanisms has been obtained for the (La,Sr)MnO$_3$ based cathode materials. It was long thought, that the (La,Sr)(Co,Fe)O$_3$ based cathodes materials were less susceptible to chromium poisoning, because of other mechanisms, i.e. mainly the formation of SrCrO$_4$. Recently, however, similar poisoning effects as seen for LSM have been observed for LSCF as well, urging us to perform another in-depth analysis of the mechanisms of chromium poisoning in non-manganiferous cathode materials.

In this initial study standard anode substrate cells with (La,Sr)(Co,Fe)O$_3$ cathodes were characterized via current-voltage measurements and impedance spectroscopy at various conditions (e.g. current density, temperature). In a next step anode supported cells were manufactured using these cathode materials and characterized via impedance spectroscopy at various conditions (e.g. current density, temperature, oxygen partial pressure and humidity) in the presence and absence of chromium sources. The impedance spectra recorded for a non-chromium exposed sample revealed multiple time constants depending on the operating temperature. A charge-transfer process could be identified based on the temperature dependence.

First current-voltage measurements performed on a chrome source exposed sample revealed already directly after cell reduction a decreased cell performance. Additional long-term tests and variations in the operating parameters however have to give more detailed information.

Remarks:

At the time of completion of these proceedings the planned experiments with "various (La,Sr)(Co,Fe)O$_3$ cathode materials with different stoichiometries", "various conditions (e.g., [...] oxygen partial pressure and humidity)", "3-probe setup", "long-term tests (> 3000 h)", were delayed. Therefore only first initial results could be presented in the extended abstract. Additional results of running experiments are shown on the poster during the European Fuel Cell Forum 2016.

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B1510 (Abstract only, published elsewhere)

Development of LCFCN system perovskites as interconnect and cathode materials for SOFCs

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Abstract

Over the past few decades solid oxide fuel cells (SOFCs) have attracted much attention due to their huge potential for clean power generation in stationary, portable, transport applications and also our increasing need for sustainable energy resources. The purpose of this research is to develop an interconnect and cathode material for use in SOFCs which demonstrates desired properties of high electrical conductivity, excellent chemical stability at high temperatures, desirable thermal expansion characteristics and which can be easily manufactured by sintering in conditions acceptable with other cell components.

This research is important because there are a few shortcomings in the materials that are currently being used as cathodes and interconnects in the SOFCs. In this study, five different perovskite oxides comprising of lanthanum in combination with chromium, iron, cobalt and nickel oxides powders (LaCr_{0.7}Co_{0.1}Fe_{0.1}Ni_{0.1}O_{3}, LaCo_{0.7}Cr_{0.1}Fe_{0.1}Ni_{0.1}O_{3}, LaFe_{0.7}Cr_{0.1}Co_{0.1}Ni_{0.1}O_{3}, LaNi_{0.7}Cr_{0.1}Co_{0.1}Fe_{0.1}O_{3}, and LaCr_{0.25}Co_{0.25}Fe_{0.25}Ni_{0.25}O_{3}) were synthesized through Pechini method. Obtained powders were characterized by X-ray diffraction (XRD) to observe crystal structure and microstructure. XRD results show that all materials are single phase few with rhombohedral and few with orthorhombic crystal structure. Powders feature with nano particle size through TEM micrographs. The resulting powders were then sintered at a temperature of 1400°C in air. Properties of sintered samples, including relative density, mechanical properties, and electrical conductivity from room temperature to 800°C were studied and evaluated. The material which has the desired properties is considered and elemental modifications can be done to it for application in practical purposes.

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Evaluation of cathode performance in co-sintered inert substrate-supported SOFC

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Abstract

The demand for energy-efficient power production is expected to grow throughout the coming years. Therefore, interest in SOFC-based combined heat and power systems is constantly rising. Hence, improvement of their lifetime as well as cost reduction are crucial factors to make them attractive for the market. The aim of this work is to evaluate the degree of maturity of cost-effective cells. The cell is mechanically supported by an inert porous oxide layer on the air side made of cheap silicate. The low sintering temperature of this support enables a one-step co-sintering process of the entire cell at temperatures between 1100°C and 1400°C.

In this contribution, we present the current status of cathode performances in this nascent cell concept. The performance of a traditional LSM-YSZ cathode on a silicate support is investigated by means of electrochemical impedance spectroscopy (EIS) at 750°C on a symmetrical cell geometry. A polarization resistance (Rp) of 2.82 Ω·cm² is measured in stagnant air. For comparison, an Rp of 1.95 Ω·cm² is measured for an electrolyte supported cell sintered under identical conditions.

The formation of secondary phases in the cathode layer due to interaction with the silicate is identified as a reason for the high Rp in inert substrate-supported cells and possible solutions for performance improvement are under development. Although co-sintered inert substrate-supported SOFCs are at an early stage of development, and further work is required for their optimization, our first results are promising when the advantages in terms of cost and lifetime of the new concept are taken into account.

Fig. 1: Cross-section of inert substrate-supported cathode in a half-cell
1. Introduction

The solid oxide fuel cell is a promising technology for micro combine heat and power systems (µ-CHP), which can yield a total efficiency higher than 80 % and reduce CO$_2$ emissions [1]. Currently, the main limitations for a market entry for µ-CHP are high costs and limited lifetime.

In this contribution, we report on an innovative full ceramic concept, which is promising in terms of lifetime and production cost and therefore very attractive for the next generation of µ-CHP. The concept is based on the introduction of an inert ceramic support, on which the functional layers are applied via screen printing and co-sintered in a single step process.

The ceramic support is a porous silicate, nominally composed of Zn, Mg and Si. The cells and the support are co-sintered at a temperature higher than 1100°C but low enough to avoid formation of insulating phases such as lanthanum zirconate [2]. This design presents several advantages. First, the single-step co-sintering and the cheap mechanical support strongly reduce the manufacturing costs. Then a longer lifetime in comparison to that of state of the art planar cells can theoretically be achieved, as no metallic interconnector is required. Consequently, the risks of corrosion and chromium poisoning in the cathode, the most significant degradation mechanisms in SOFC, are avoided [3].

On the other hand, in the new concept, co-sintering implies some restrictions on microstructural optimization of the cathode, as the co-sintering temperature is higher than the one of the state of the art electrodes. This can result in a coarser microstructure and in a significant interaction between neighboring functional layers. Notably, elements from the support like Si, Zn, Mg can migrate into the cathode during co-sintering. Poisoning of cathodes due to chromium or silicon have widely been reported [4,5], whereas to the best of our knowledge the effects of Zn or Mg on cathode performance has not been investigated. Therefore, for the optimization of the inert substrate-supported concept the investigation of the effect of co-sintering and of the silicate substrate on the electrochemical performance of a LSM-8YSZ cathode is highly interesting.

2. Experiments

**Materials** – In this study we investigated symmetrical cathode-cells composed of the following materials: (i) cathode conductive layer: (La$_{0.8}$Sr$_{0.2}$)$_{0.98}$MnO$_3$ (LSM); (ii) cathode functional layer: LSM-8YSZ (8YSZ: Y$_{0.16}$Zr$_{0.84}$O$_2$) composite with volume ratio 50/50; (iii) electrolyte: 8YSZ. In addition, platinum paste was applied on the cell surface to improve current collection and electrical contact.

**Cell preparation** – For the herein reported investigations two cell geometries were considered:

1. Co-sintered electrolyte supported cells (ESC) (Fig2a) were prepared via screen-printing of the cathode functional and conducting layers on both sides of a green 8YSZ tape, followed by a co-sintering process. The functional and conducting layers had a final thickness of 25 µm and 50 µm respectively, whereas the electrolyte had a thickness of approximately 150 µm.

2. Co-sintered inert substrate-supported cells (ISC) (Fig2b) were prepared via screen printing of the functional and conducting layers (cathode/electrolyte/cathode) on a green silicate support. Since the electrolyte does not have any support function, its thickness was reduced to 15 µm. Finally, to achieve a full symmetry, a plate of silicate coated with fresh LSM-ink was pressed on the upper cathode layer. The cells were then co-sintered.
ESC were used as benchmark for the assessment of the new inert layer-supported concept, in terms of cathode performances.

**Characterization** – The cells were characterized via electrochemical impedance spectroscopy (EIS) using a Solartron SI 1260 frequency response analyzer (FRA) at frequencies ranging from 1 MHz to 10 mHz. Impedance spectra were acquired at 750 °C in stagnant ambient air. The measured value of the polarization resistance of the symmetrical cells is divided by two in order to obtain the value of a single cathode.

![Cross section of a) an electrolyte-supported cell, b) an inert substrate-supported cell](image)

**Fig. 2: Cross section of a) an electrolyte-supported cell, b) an inert substrate-supported cell**

Microstructural analyses were carried out through scanning electron microscopy (SEM) on polished cross-sections sputtered with Pt/Pd using a Zeiss Supra 55VP. Elemental distribution was analyzed through energy dispersive X-ray spectroscopy (EDX) with an Oxford Instruments INCA Energy detector. Furthermore, Raman spectroscopy was used for phase analysis. Spectra were acquired with confocal LabRAM Aramis using a 633 nm HeNe Laser. Elemental analysis of raw material were carried out by induced-coupled plasma- mass spectrometry (ICP-MS) with an ICP-QQQ 880 from Agilent.

### 3. Results

Nyquist plots of impedance spectra of the ESC and ISC acquired at 750 °C after a stabilization of 2.5 hours are reported in Fig. 3. The measured value of the polarization resistance of the symmetrical cells is divided by two in order to obtain the polarization resistance of a single cathode.

The Rp of the ISC and ESC cathodes are respectively 2.82 Ω·cm² and 1.95 Ω·cm². The higher Rp in comparison with that of an optimized cathode [6,7] could be ascribed to a non-optimized microstructure [8].

The Rp of the ISC cathode is approximately 1,5 times larger than the Rp of the ESC cathode. Considering that the two cells have the same cathode material and were processed in the same way, this difference can be due to the following factors: (i) oxygen transport limitation through the porous support; (ii) microstructural variation or (iii) a decrease in the catalytic activity of the functional layer during the co-sintering.
Fig. 3: Nyquist plot of an ESC and an ISC symmetrical cell recorded at 750 °C in stagnant air.

The first hypothesis can be discarded; notably, mass transport limitation in the gas phase within the silicate substrate could be estimated using the dusty gas model [9], from which a contribution of 32 mΩ·cm² was calculated. This value is two orders of magnitude lower than $R_p$ and thus negligible.

The porosity of the cathode functional layer are 34% and 33% for the ESC and ISC, respectively. The difference is small but a microstructural change cannot be discarded.

The last hypothesis, namely the decrease of the catalytic activity during co-sintering, is supported by the Fig. 4, a secondary phase is observed in considerable amounts in the cathode of the ISC. EDX analysis reveals a clear signal that could be ascribed either to sodium or to zinc.

The presence of these elements in the raw cathode material is excluded by ICP-MS analysis of raw LSM powder. Therefore, the additional element, responsible for the formation of the new phase must diffuse into the cathode during the sintering process.

Fig. 4: EDX mapping of the Zn signal in an ISC cathode. A zinc or sodium-rich secondary phase is observed.
Raman spectroscopy offers the possibility to identify the secondary phase. Five intense peak at 304.7-, 326.4-, 480-, and 681.3 cm\(^{-1}\) are observed in the Raman spectrum acquired on the new phase. Their positions are in agreement with a spectrum of ZnMn\(_2\)O\(_4\) with a spinel structure [10]. On the other hand, the presence of sodium in the spinel is excluded due to its ionic radius which would not fit in the spinel lattice [11]. Based on the above investigations, we can conclude that the initial cathode performance of the ISC is affected by co-sintering with the inert support. Notably, Zn evaporates or diffuses from the support into the cathode and reacts with LSM to form a zinc manganite spinel.

### 4. Conclusion

Cathode performance of co-sintered inert substrate-supported SOFC cells have been investigated by means of electrochemical impedance spectroscopy in two cell geometries. Co-sintering at high temperatures lead to decrease of performance and a higher polarization resistance compared to literature values. ESC cells had lower performances than state-of-the-art cells. The silicate support increases the polarization resistance by a factor 1.5. The effect is explained by a cathode poisoning, due to Zn-evaporation and/or diffusion during co-sintering.

### References


Thermodynamic aspects of Cr poisoning for LSCF cathodes

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Abstract

Cr-poisoning of solid oxide fuel cell (SOFC) cathodes in stacks with metallic interconnects is a serious issue for degradation and long term operation. During operation, gaseous Cr-species, which consist of CrOx(OH)y and/or CrOx, evaporate from the Cr2O3-containing scale of ferritic interconnect. The evaporated Cr-species deposit on the surface of and inside LSCF cathode as SrCrO4 and/or Cr2O3. The formed secondary phases result in degradation of the cathode material and subsequent loss in electrical conductivity.

Thermodynamic aspects of cathode Cr-poisoning are studied. The effect of different influence factors (temperature, oxygen partial pressure, water vapor partial pressure) on the equilibrium vapor pressures of different possible gaseous Cr-species over Cr2O3(s) is assessed numerically using FactSage and discussed. The subsequent deposition of gaseous Cr-species is analyzed by thermodynamic calculations in terms of: 1) deposition of evaporated Cr-species directly as Cr2O3(s) and 2) reaction between evaporated Cr-species and SrO in cathode material.

From the calculation, the hexavalent Cr-species such as CrO3(g) and CrO2(OH)2(g), are the dominating gaseous Cr-species evaporating in dry and humid conditions, respectively. The partial pressure of CrO3 depends stronger on temperature than CrO2(OH)2. During the Cr-species deposition, the thermodynamic activity of SrO in the cathode material is a decisive factor for the secondary phase formation.

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 Optimization of GDC interlayer against SrZrO₃ formation in LSCF/GDC/YSZ triplets

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Abstract

Gadolinia-doped ceria (GDC) thin films were prepared using pulsed laser deposition in order to study its stability as an interlayer against SrZrO₃ formation in La₀.₆Sr₀.₄Co₀.₆Fe₀.₄O₃₋₅ (LSCF)/GDC/yttria-stabilized zirconia (YSZ) triplets. Dense GDC interlayer was utilized to minimize the complexity arising from a porous interlayer. The GDC films were pre-annealed at 1000°C to 1400°C for 1 h to 10 h in air. The as-grown GDC interlayer showed nanocolumnar microstructure. At low temperature (1000°C), GDC did not fully densify; instead, microcracking and nanoporosity arising from nanocolumnar microstructure became pronounced. At high temperature (1400°C), crack formation and grain boundaries were minimized. However, pore formation became severe. The LSCF cathode layer was screen printed on top of these differently annealed GDC/YSZ couples and fired at 1080°C for 3.5 h in air. We find that the high density of microcracks, as well as severe pore formation in GDC, is detrimental to preventing SrZrO₃ (SZO) formation in LSCF/GDC/YSZ triplets. To avoid this problem, we implemented a multi-step heat profile consisting of annealing at 1400°C for 1.5 h followed by 1000°C for 10 h in air. We obtained an interlayer with reduced pores and microcracks preventing the severe SZO formation at the GDC/YSZ interface. On the other hand, SIMS analysis revealed that the heat treatment of GDC interlayers led to enhanced Zr mobility indicating the possible formation of a small amount of SZO phase at the LSCF/GDC interface. Hence, a delicate trade-off optimization of PLD-grown GDC interlayer is necessary for preventing the severe SZO formation across the interfaces.
Introduction

In solid oxide fuel cells (SOFCs), degradation due to the reactivity of its major components are the main limiting factors for its development. In particular, Lanthanum strontium cobalt iron oxide (LSCF) cathode in conjunction with state-of-the-art yttria-stabilized zirconia (YSZ) electrolyte generates secondary phases across the interfaces such as SrZrO3 (SZO) with low oxide ion conductivity during fabrication and cell operation (1-2). In order to remedy this problem, a diffusion barrier such as gadolinia-doped ceria (GDC) is inserted between LSCF cathode and YSZ electrolyte (3-5). However, this is not a problem-free approach, and different aspects have been reported about using GDC barrier layer (3-5).

GDC interlayers fabricated by the screen-printing technique is characterized by high residual porosity, anisotropic pores and pore clusters originating from the constrained sintering due to the presence of rigid substrates (3). These microstructural features act as fast diffusion pathways for cation migration from the cathode to the electrolyte. Specifically, Sr can be transported via gaseous phase during cell fabrication and operation leading to the formation of SZO at the GDC/YSZ interface (2-3). The severe SZO formation contributed to the drastic degradation of cell performance. Physical vapor deposition such as pulsed laser deposition (PLD) is an ideal method of fabricating dense and epitaxial GDC barrier layers on YSZ substrates (6-7). These features of the interlayer grown by PLD minimizes the complexity of diffusion through the gas phase across the layers. Knibbe, et al., showed that the grain boundaries of a dense epitaxial GDC interlayer deposited by PLD facilitate Sr diffusion (8). Wang et al., demonstrated using thermal annealing and polarization that the cathode preparation above 1000ºC, leads to significant Sr diffusion allowing complete formation of SZO across the interfaces even with the use of a dense PLD-grown GDC interlayer (9-10). These results demonstrate that although PLD method is ideal for producing dense GDC interlayer, SZO formation is still difficult to mitigate. To our knowledge, no report thus far on the optimization of dense GDC interlayers grown by PLD against SZO formation. Furthermore, the fundamental understanding of how heat processes influence SZO formation is vital in improving GDC barrier functionality for enhanced cell stability and performance.

1. Scientific Approach

In this work, we fabricated dense GDC barrier by PLD technique and implemented series of heat treatments to determine the microstructural properties of dense GDC that affect its stability against the SrZrO3 formation. The first part of the paper is devoted to the fabrication and characterization of the GDC/YSZ diffusion couples in contact with LSCF cathode. The second part of the work is focused on the cation diffusion process across the interfaces elucidated by performing secondary ion mass spectroscopy (SIMS).

2. Experimental details

The GDC interlayer was prepared on 8 mol % Y2O3-stabilized ZrO2 (8YSZ) polycrystalline substrates using pulsed laser deposition (PLD) utilizing a sintered target of Gd0.1O-Ce0.9O1.95 and a KrF excimer laser source (λ= 248 nm, Comprex Pro 102F, Coherent Technologies). The film deposition was carried out using the following conditions: 750°C substrate temperature, 200 mJ laser energy per pulse, 10 Hz repetition rate, 5 Pa oxygen partial pressure. After the deposition, the films were allowed to cool in the chamber under the same oxygen partial pressure. Three types of heat treatment were performed to investigate their effect on the microstructure of PLD-grown GDC interlayer and correlate it
to the suppression of SZO formation. The annealing of GDC films was performed in air using a conventional box furnace as follows: (sample B) 1000°C for 2 h, (sample C) 1400°C for 5 h and (sample D) 1400°C for 1.5 h with subsequent annealing at 1000°C for 10 h. A cooling rate of 27°C/min was used for the multi-step process. The LSCF cathode layer was then screen printed on top of these differently annealed GDC/YSZ couples and fired at 1080°C for 3.5 h in air. LSCF was also prepared on top of as-grown GDC as a reference (sample A). Table 1 shows the summary of analyzed samples with their respective GDC interlayer processing condition. The microstructure and composition of the samples were examined using scanning electron microscopy coupled (SEM) with energy-dispersive x-ray spectroscopy and wavelength-dispersive spectroscopy (WDS). To elucidate the cation diffusion process across the layers elemental depth profiling using secondary ion mass spectrometry (SIMS) was performed. In addition, we estimated the apparent diffusivity of Zr in GDC using the SIMS depth profiles. The apparent bulk diffusion coefficient was determined by using the solution proposed by Crank (11):

\[
\frac{X - X_o}{X_s - X_o} = 1 - \text{erf} \left( \frac{z}{2\sqrt{Dt}} \right) \quad (1)
\]

where \(X_o\) is the intensity at the background \((X_o=0)\), \(X_o\) is the intensity at the surface \((z=0)\), \(X\) is the normalized intensity of the secondary ion given by \(I(M^{16}O)/I(M^{18}O)\), \(z\) is the depth and \(t\) is the annealing time. From the tail of the profile, the Whipple-Le Claire model was used to determine the grain boundary diffusion coefficient,

\[
\alpha D_{gb} = -0.66 \left( \frac{\partial \ln X}{\partial \ln z} \right)^{5/3} \left( 4D_b \right)^{1/2} \quad (2)
\]

**Table 1.** Analyzed LSCF/GDC/YSZ triplets with their respective GDC interlayer

<table>
<thead>
<tr>
<th>Sample</th>
<th>GDC</th>
<th>LSCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>---</td>
<td>1080°C/ 3.5 h</td>
</tr>
<tr>
<td>B</td>
<td>1000°C/ 2h</td>
<td>1080°C/ 3.5 h</td>
</tr>
<tr>
<td>C</td>
<td>1400°C/ 5h</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1400°C/1.5 +1000°C/10h</td>
<td></td>
</tr>
</tbody>
</table>

3. Results and Discussion

Representative SEM back-scattered electron images of GDC interlayer before and after LSCF cathode fabrication are shown in Figure 1. Figure 1b shows accumulation of secondary phase on both LSCF/GDC and GDC/YSZ interfaces after fabricating LSCF cathode on the as-grown GDC interlayer (sample A, Fig. 1a and b). When LSCF is prepared on GDC interlayer annealed at 1000°C for 2h (sample B, Fig. 1c and d), the secondary phases are not only found in the interfaces but also in the inner region of the GDC interlayer (dashed rectangles) as shown in Fig. 1d. The apparent densification of GDC after LSCF cathode fabrication can be due to the possible diffusion of Co and Fe along the grain boundaries which is well known to enhance the sinterability of cerium oxide (3). When LSCF is prepared on GDC fired at 1400°C for 5 h (sample C, Fig. 1e and f), secondary phases formed at the LSCF/GDC interface as shown in Fig. 1f. Pores, particularly at the GDC/YSZ interface became more apparent indicating migration of cations across this interface (indicated by circle). On the other hand, after LSCF cathode preparation on GDC interlayer fired using multi-step heat treatment (sample D, Fig. 1g and h), we can observe a homogeneous interlayer devoid of secondary phase formation.
across the interfaces. The significant differences in the secondary phase formation after LSCF fabrication can be related from the preparation condition of PLD-grown GDC interlayer, which consequently affects the interfacial property of cathode and electrolyte.

Figure 2 shows the SEM-EDS cross-sectional composition mapping of LSCF/GDC/YSZ triplets with (a) as-grown- Sample A, and (b) multi-step annealed GDC interlayer- Sample D. Without heat treatment of GDC interlayer, severe SZO formation at the GDC/YSZ interface is observed as shown in Fig. 2a. The cracks and pores in GDC provide a faster diffusion for Sr to reach YSZ electrolyte. As shown in Fig. 1, these microstructural features are only minimized at high sintering temperature. Hence, we infer that SZO is same secondary phase formed for GDC annealed at 1000ºC for 2h (Sample C). On the other hand, annealing at 1400ºC densify and minimize the cracks and grain boundaries in the PLD-grown GDC interlayers. Reducing the annealing time at 1400ºC and rapid cooling to 1000ºC were shown to reduce porosity. Although not all pores were entirely eliminated, upon second annealing at 1000ºC for 10 h, the interlayer of sample D shows a remarkable improvement over the interlayer which was annealed using only one-step annealing (sample C). SEM-EDS also shows no apparent SZO formation at the GDC/YSZ interface for this type of interlayer as shown in Fig. 2b. This result clearly shows that the multistep heat treatment produces a structurally restrictive GDC interlayer for Sr diffusion towards YSZ.
To further clarify the cation diffusion across the interfaces, we performed SIMS elemental depth profiling of the GDC/YSZ couples. Figure 3 shows the typical SIMS depth profile of as-grown and multi-step annealed GDC interlayer. Zr intensity broadens towards the inner part of the interlayer indicating initial diffusion via the surface of the nanocolumns of the as-grown GDC. After multi-step annealing, Zr intensity marginally increases towards GDC indicating that grain boundaries of GDC are filled with Zr. In addition, we estimated the apparent diffusivity of Zr in GDC using the SIMS depth profiles. The estimated grain diffusivity of Zr ($D_{gb}$) in PLD-grown GDC interlayer is five orders of magnitude higher than the apparent bulk diffusivity ($D_{gb}$ = $7.27 \times 10^{-7}$ cm$^2$ s$^{-1}$, $D_{bulk}$ = $5.13 \times 10^{-12}$ cm$^2$ s$^{-1}$). The Zr apparent bulk diffusivity in PLD grown GDC interlayer is also three orders of magnitude faster than in polycrystalline sintered CeO$_x$/ScSZ diffusion couple (12). Upon cathode sintering, the Sr from the adjacent LSCF may react with the Zr in GDC indicating the possible formation of a small amount of SZO phase at LSCF/GDC interface although this was not detected by SEM-EDS results. Hence, improving the functionality of GDC interlayer against SZO formation is a trade-off between suppressing severe Sr diffusion in YSZ and Zr migration towards GDC. Further details will be discussed during the presentation.

4. Summary

GDC thin films were prepared using PLD to study its stability as an interlayer in LSCF/GDC/YSZ triplets. A series of heat treatments was performed to determine the effects of the microstructural features of the PLD-grown GDC interlayers in SZO formation. Based on our results, a combination of fast high-temperature sintering and prolonged annealing at low-temperature minimized grain boundaries, pores and cracks on PLD-grown GDC interlayers. This heat treatment procedure led to the improved functionality of the PLD-grown GDC interlayers against Sr diffusion towards YSZ suppressing severe formation of SZO at the GDC/YSZ interface. SIMS analysis revealed that the PLD-grown GDC interlayers showed enhanced Zr mobility indicating the possible formation of a small amount of SZO phase at the LSCF/GDC interface. This result shows that a delicate trade-off optimization of PLD-grown GDC interlayer is necessary for preventing the severe SZO formation across the interfaces. The formation of SZO at the LSCF/GDC interface with a
PLD-grown GDC interlayer is in contrast to SZO formation at GDC/YSZ interface typical in SOFC. Hence, further studies are underway examining the evolution and microstructure of SZO at the LSCF/GDC interface under accelerated tests to clarify its effects on the electrochemical properties of LSCF/GDC/YSZ triplets.

References