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An investigation of the oxygen reduction reaction mechanism of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ using patterned thin films

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1. Introduction

Research and development of solid oxide fuel cell (SOFC) cathodes have become more prominent in the last 20 years, partly due to the ability to fabricate increasingly thinner films, which results in a reduction in resistance. A major factor is the downscaling of SOFCs and increased interest in micro-SOFC development allowing a reduction of operating temperatures to 550 °C and lower [1–7]. At lower temperatures the electrodes provide a greater percentage of the voltage loss (polarisation) due to higher activation energy. In the case of cathodes, oxygen reduction is believed to be an electrochemical reaction process which is more difficult to activate at lower temperatures [8]. As a result, the focus of cathode development in recent years was related to investigating the fundamental electrochemical reaction mechanisms.

Lanthanum strontium cobalt iron oxide (LSCF) is a mixed ionic-electronic conducting (MIEC) perovskite (ABO₃) material, most commonly used for cathodes at intermediate temperatures (500-750 °C) [9–11] and has been increased use for potential thin film SOFC applications in recent years [2,12].

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ABSTRACT

Lanthanum strontium cobalt iron oxide ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$) thin films deposited by pulsed laser deposition on single crystal yttria stabilised zirconia (YSZ) substrates were lithographically patterned to produce geometrically well defined micro-cathodes. LSCF cathode designs varying in surface area between 0.038 cm² and 0.267 cm² were electrochemically tested for investigation of the oxygen reduction reaction. A gold current collector geometry was used whilst controlling the LSCF surface area and three-phase boundary lengths. The oxygen surface exchange reaction was identified as the rate limiting step between 400 °C and 500 °C. Below 400 °C, the ASR appeared to be more sensitive to changes at the LSCF surface, possibly due to slower reaction kinetics but the effect of the surface pathway could not be deemed negligible. However, the effect of the microfabrication processing on the oxygen surface exchange properties of the patterned LSCF micro-cathodes cannot be deemed negligible. Degradation in performance scaled inversely with the patterned LSCF feature size.

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Possible oxygen reduction pathways are illustrated in Fig. 1 (adapted from [1,8,13]). Bulk and surface pathways are in competition and occur parallel to each other. Usually one path is faster and determines the overall kinetics. The rate determining/limiting step is the inhibiting step(s) occurring in this serial oxygen reduction pathway. Although the oxygen reduction reaction at LSCF cathodes involves the transport of oxygen ions via the solid state oxygen diffusion path, the oxygen surface exchange reaction has been shown to be rate limiting at temperatures between 425 and 750 °C [10.14.15]. The oxygen surface exchange reaction is a complex process involving many steps such as adsorption of O₂ on the cathode surface and its dissociation into two oxygen atoms. Oxygen is finally incorporated as an oxygen ion (0^{2-}) into a vacancy (V_0^{\bullet}) in the first layer of the mixed conducting electrode with a number of ionisation steps involved in the serial mechanism [10]. The oxygen reduction process is shown in Eq. (1).

$$0_2 + 2V_0^{\bullet} + 4e^{-} = 20^{2-} \tag{1}$$

Few examples of a direct experiment with the potential to separate a surface pathway or TPB mechanism for MIEC materials are demonstrated in the literature [16–19]. Similarly, there is little documentation in the literature for experimental mechanistic studies assessing the direct effect of the electrode geometry on the performance and the consequent rate limiting steps of LSCF cathodes.





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Fig. 1. Schematic diagram illustrating the possible oxygen reduction reaction pathways in a dense MIEC cathode. Bulk and surface pathways are in competition as they occur parallel to each other. Oxygen incorporation at the side walls is also shown. Adapted from [1,8,13].

Mechanistic studies on mixed conducting cathodes reported in the literature utilising micro-patterned thin films often report the electrode area specific resistance (ASR) as a measure of performance [10,13,20]. However it is also possible to deduce important reaction kinetics, such as the oxygen surface exchange rate, k^q directly from the electrochemical measurements [21,22], as reported in this work in order to obtain a measure of the speed at which the rate-limiting step proceeds.

Geometrically well defined (gwd) electrodes are a useful tool for the investigation of fundamental reaction mechanisms. Studies both on the anode [23–27] and on the cathode were carried out in recent years [1,10,14–17,28–32]. A range of gwd electrodes of known TPB length ($l_{\rm TPB}$), bulk diffusion length (film thickness) and surface areas can be tested systematically to correlate these parameters with the area specific resistance (ASR). The following gwd LSCF cathodes were studied in the literature:

Baumann et al. [10] investigated the impedance of 100 nm thick La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃₋₆ circular microelectrodes between 500 °C and 750 °C, deposited by PLD on single crystal YSZ and structured by photolithography and inert gas ion beam etching. Circular microelectrodes with diameters between 20 and 100 µm were produced. The authors conclude that the bulk pathway is dominant for oxygen reduction [10,33], with the oxygen surface exchange reaction contributing greatly to the cathode ASR of approximately 5 Ω cm² at 750 °C.

Prestat et al. [14] investigated the electrochemical reaction mechanism of $La_{0.52}Sr_{0.48}Co_{0.18}Fe_{0.82}O_{3-\delta}$ micro cathodes deposited by PLD on $Ce_{0.9}Gd_{0.1}O_{1.95}$ electrolyte substrates and structured using photolithographic techniques into 3×3 mm² squares. The LSCF micro cathodes varied in thickness between 16 and 766 nm and impedance measurements were made in air between 500 and 700 °C. The authors report that rate determining steps consist of oxygen adsorption, incorporation into the LSCF and bulk diffusion. Bulk diffusion was confirmed by an increase in polarisation resistance

with thickness. In addition, the authors used a combination of state-space modelling and experimental data to determine the oxygen surface exchange rate, k of 2.7×10^{-9} ms⁻¹ at 500 °C.

Xiong et al. [15] deposited dense 50 nm thick nanocrystalline $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ films on nanocrystalline YSZ thin film electrolytes, which were patterned by photolithography. Electrochemical impedance spectroscopy (EIS) was used on circular microelectrodes, 200 µm in diameter, between 425 and 550 °C. The authors also report that the electrochemical resistance of the nanocrystalline 'ultra-thin' LSCF is dominated by the oxygen surface exchange reaction with an associated activation energy of 1.1 eV.

Ryll et al. [29] deposited 140 nm thick $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ thin films by PLD on $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ electrolyte thin films on amorphous silica wafers. The LSCF was structured into 'comb-shaped' patterns by photolithography and etching to produce feature sizes between 20 and 850 µm. Limited electrochemical evaluation of the patterned LSCF films is provided but the authors confirm the feasibility of using such a platform for the measurement of the polarisation resistance of LSCF to characterise electrical conduction and oxygen reduction properties.

In addition to the various LSCF geometries and methods of current collection reported in the literature, the type of electrolyte/substrate used in each study also differs. Table 1 shows an overview of some electrochemically tested patterned LSCF thin films in the literature [10,14,15,20].

Research on oxygen reduction at dense LSCF cathodes has generally been conducted on Co rich compositions such as La_{0.6}Sr_{0.4} Co_{0.8}Fe_{0.2}O_{3- δ} deposited on YSZ or CGO. Although such a composition tends to yield higher electronic and ionic conductivities and lower activation energy for electronic and ionic conduction [34–37] as a result of the increased Co content, a composition of the form La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} was used in this work. This is because its closer thermal expansion coefficient mismatch with YSZ compared to a Co-rich composition might be beneficial to the long-term thermal stability requirements of thin films for micro-SOFCs.

Given that surface diffusion processes gain importance compared to bulk diffusion with decreasing temperature, it seems highly probable that three-phase boundaries become important below a certain temperature range. However, this temperature range remains unknown. It is the aim of this work to determine whether or not the surface path shown in Fig. 1 becomes rate determining in preference to the parallel bulk path of LSCF, rich in Fe, at lower temperatures (350 °C). This will be achieved by quantifying relative differences in performance between LSCF cathodes varying in surface area between 350 °C and 500 °C. Patterned LSCF cathodes of varying geometry have not previously been compared in such a way to determine LSCF reaction kinetics down to 350 °C. Based on oxygen diffusion, D^* and oxygen surface exchange, k^* data obtained by Benson et al. [38] below 600 °C by isotope exchange depth profiling (IEDP) techniques, the characteristic temperature below which oxygen transport is expected to be limited by bulk diffusion for the LSCF thickness of 290 nm used in this study is 417 °C.

Table 1

Overview of the LSCF processing, current collection and cell geometry used in previous studies found in the literature and compared in this work.

| Reference | LSCF composition | LSCF processing | | Electrolyte | Current collection | Cell |
|------------------------|--|----------------------------|--|---|---|-------------|
| | | Deposition | Structuring | | | geometry |
| Beckel et al. [20] | $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3}$ | PLD and spray pyrolysis | Shadow mask | CGO pellet | Pt paste/mesh | 3-electrode |
| Prestat et al. [14] | $La_{0:52}Sr_{0:48}Co_{0:18}Fe_{0:82}O_{3-\delta}$ | PLD | Photolithography and HCl wet etch | CGO pellet | Screen-printed LSCF film | 3-electrode |
| Baumann et al. [10] | $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ | PLD | Photolithography and inert gas ion beam dry etch | Single crystal YSZ | Point contacting via Pt/Ir probe needles (2.5 µm nominal tip radius) | 2-electrode |
| Xiong et al. [15] | La _{0.6} Sr _{0.4} Co _{0.8} Fe _{0.2} O ₃ | Sputter | Photolithography and lift-off | YSZ thin film (on a nanoporous alumina substrate) | Point contacting via Pt-plated tungsten tips | 2-electrode |



Fig. 2. Schematic representation of the cathode design. Adapted from [39] with the permission of the authors.

2. Experimental

LSCF thin films were prepared on (double-sided) epi-polished 9.5 mol% Y-doped 0.5 mm thick, 21 mm × 21 mm yttria stabilised zirconia (YSZ) (100) single crystals in a three-electrode geometry as reported previously in [39]. All La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ thin films (i.e. working, counter and reference electrodes) were deposited at a substrate temperature of 600 °C in 100 mTorr of oxygen with a pulse frequency of 10 Hz and fluence of 2.95 J/cm² (95 mJ laser energy into 1.4×2.3 mm spot size at the target) using a KrF 248 nm excimer laser (Coherent). The films were cooled to room temperature under vacuum conditions (3×10^{-3} mTorr) at 10 °C/min. The target-to-substrate distance was 8.5 cm to ensure a homogeneous film (\pm 5% thickness deviation at 400 nm) over 0.8 cm², which resulted in a deposition rate of approximately 0.06 Å/pulse. All films were 290 nm thick.

LSCF films were patterned within 1 cm^2 area to produce gwd model cathode structures consisting of a series of stripes and gaps using photolithography and etching in a class 1000 cleanroom. LSCF was dry etched using argon ion (Ar⁺) sputtering (Plasmalab 80, Oxford instruments) with an initial base pressure of 9×10^{-5} mbar, an Ar atmosphere of 1.00×10^{-1} mbar, 200 W radio frequency power, and 400 V DC bias, whilst maintaining the substrate at 10 °C.

A photolithography lift-off process was used to structure Au thin films for the current collector (CC) on top of the patterned LSCF. A minimum stripe width of 10 μ m in the Au current collector was obtained. Au was sputtered in an Ar atmosphere of 5×10^{-2} mbar with 60 mA current and deposition rate of 0.46 nm/s yielding 365 nm thick films. The reader is referred to Ref. [39] for more details regarding the fabrication process.

2.1. Cell design

Three-electrode cell geometry was adopted in this work to enable the probing of the working electrode (WE) potential directly. However, it is known that correct electrode positioning is important to reduce electrochemical measurement errors by ensuring that the reference electrode (RE) is at a known potential [20,40–42]. Adler et al. [43] determined by finite element modelling that correct results are generally obtained for a WE to RE separation greater than 3 times the electrolyte thickness. Winkler et al. [42] determined that the WE and counter electrode (CE) misalignment should be less than 10% of the electrolyte thickness. It is assumed that the electrode is at a uniform potential in this work.

The three-electrode design used in this work is shown in Fig. 2 (adapted from [39]) from the top in (a) and in cross section in (b). The LSCF WE and CE (shown in grey) are symmetric to each other $(\pm 20 \,\mu\text{m})$. The WE consists of connected stripes varying in width between 20 and 130 µm and varying in stripe-to-stripe separation between 20.5 and 130 µm. A limit of 20 µm stripe width and separation was imposed based on previous fabrication-related studies seen for LSCF [10,14,44] and due to photolithographic alignment tolerances. The total number of stripes (and therefore l_{TPB}) in the design remained constant. However, additional l_{TPB} due to roughened stripe edges resulting from the dry etching process was observed for smaller stripe widths. Increasing the stripe width and separation in this way served to increase the effective surface diffusion length and total area. The symmetric (LSCF) CE was an unpatterned square of 1 cm² in size. A summary of the cathode geometries is shown in Table 2. The effective LSCF surface area is the surface area of LSCF exposed to the atmosphere and not covered by the current collector (CC,

Table 2

Summary of geometrically well defined patterns and LSCF thickness used in this work. The electrode geometry was determined by SEM-image analysis techniques.

| Sample | LSCF stripe/gap width [µm] | ^a Effective LSCF surface area [cm ²] | LSCF <i>l</i> _{TPB} [m/cm ²] | LSCF thickness [nm] | Au stripe/gap width [µm] | Au <i>l</i> _{TPB} [m/cm ²] | LSCF/YSZ Interfacial area [cm ²] |
|--------|-------------------------------|--|--|------------------------|-----------------------------|--|--|
| 1 2 | 130/20.5 50/100 | 0.267 0.097 | 1.051 1.181 | 290 290 | 65/85.5 25/125 | 0.921 0.925 | 0.999 0.654 |
| 3 | 20/130 | 0.038 | 1.777 | 290 | 10/140 | 0.927 | 0.532 |

^a Effective LSCF surface area is the LSCF surface area not covered by Au and exposed to the atmosphere.

defined below). The LSCF/YSZ interfacial area is the LSCF imprint on the YSZ electrolyte.

A circular LSCF RE of 2 mm diameter was separated from the working electrode by a distance of 3.5 cm. The electrode placement adopted is experimentally convenient since it allows the exposure of the RE and WE to the same gas composition.

Gold CC stripes were patterned centrally along each previously fabricated LSCF WE stripe with half the LSCF stripe width and also over the LSCF outer-frame and electrical pickup contacts (Fig. 2), reducing the initial LSCF surface area. A summary of the CC geometry for each micro-cathode is shown in Table 2. Uniaxially pressed flattened Pt wires of 0.25 mm in diameter were fixed to electrical contact pads on the WE using Pt paste. A uniaxially pressed flattened Pt mesh was fixed to the CE using Pt paste.

Alignment of WE and CE was enabled using a combination of alignment marks fabricated on either side of the transparent YSZ substrate. The WE and CC (shown in grey and yellow, respectively in Fig. 2) were aligned to within 5 µm, on the same side of the YSZ substrate.

2.2. Electrochemical impedance testing

Electrochemical measurements were conducted using a Solartron Model 1260 Frequency Response/Impedance Analyser (FRA) to apply sinusoidal waves between the frequencies of 1 MHz and 0.01 Hz when combined with Solartron Model 1287 Electrochemical Interface, which provided potentiostatic AC conditions. Data acquisition was controlled using ZPlot® 3.0 and analysed using ZView® 3.0. AC measurements were conducted as a function of temperature during cooling from 500 °C to 350 °C in flowing O₂. All samples were subjected to the same temperature cycle. A summary of the impedance spectroscopic measuring conditions is shown in Table 3.

The equivalent circuit shown in Fig. 3 was adopted in order to best fit impedance spectra in this work. General constant phase elements (CPE), Q with impedance Z_Q [10] were used rather than capacitors to account for the depression of semi-circular impedance arcs. The impedance, Z_Q is given by Eq. (2).

$$Z_{Q} = \frac{1}{Q(j\omega)^{n}}$$
(2)

where ω is the angular frequency, *n* is a fitting constant between 0 and 1 related to the depression of the impedance arc (a value of 1 corresponds to an ideal semi-circle) and $j = \sqrt{-1}$. The capacitance, *C* was transformed from CPE values according to [16,45], using Eq. (3).

$$C = \frac{(RQ)^{\frac{1}{n}}}{R} \tag{3}$$

where *R* is the absolute resistance of the impedance arc.

Table 3

Summary of impedance spectroscopy measuring conditions. In general, the greater the integration time/cycles the more accurate the result but the longer the measurement time. E.g. A measurement at 0.01 Hz will take 1/ 0.01 s \times 5 = 500 s.

| Parameter | Value |
|--------------------------------------|----------|
| O ₂ flow [ml/min] | 33.3 |
| Frequency range [Hz] | 10°-0.01 |
| AC amplitude [mV] | 10 |
| Max. potentiostat current [mA] | 20 |
| Integration cycles ^a | 5 |
| Interval [steps/decade] | 10 |
| Temperature range [°C] | 350-500 |
| Heating/cooling ate [°C/min] | 3 |
| Time per measurement [min] | 40 |
| Temperature equilibration time [min] | 30 |

^a Number of cycles at a particular frequency over which data is collected.



Fig. 3. Equivalent circuit adopted for the LSCF electrode on single crystal YSZ electrolyte (O_2 /electrode/YSZ). $R_{\rm HF}$ represents the finite YSZ electrolyte resistance with capacitance $C_{\rm HF}$. $R_{\rm MF}$ and $R_{\rm LF}$ represent resistances due to LSCF electrode processes at medium frequency and at low frequency with corresponding constant phase elements $Q_{\rm MF}$ and $Q_{\rm LF}$.

Fitting with this simple model mostly resulted in fitting errors of less than approximately 10%. Therefore, no advanced equivalent circuit models such as discussed in Baumann et al. [10] and Jamnik et al. [46], were used in this study.

After electrochemical measurements were made, the samples were characterised by scanning electron microscopy (SEM, LEO 1530). A working distance of 6-8 mm, 5 kV accelerating voltage and an aperture size of 30 μ m were used.

3. Results and discussion

3.1. LSCF pattern and microstructure

Characterisation of as-deposited LSCF thin films, as-fabricated LSCF patterned thin films and LSCF thin films post-annealed in air was reported previously in Ref. [39]. A typical as-fabricated image of the patterned LSCF micro-cathode stripes is shown in Fig. 4. The image shows 130 µm wide LSCF stripes on which 65 µm wide Au stripes are deposited. The YSZ substrate is shown as 20.5 µm wide stripes between LSCF stripes. A typical SEM image of the as-deposited LSCF microstructure is shown in Fig. 5 (a). Triangular-like grains, corresponding to the top of individual columns are prominent in the as-deposited LSCF microstructure with an average grain size of 60 nm. After electrochemical measurement, grain sizes are between 55 nm and 60 nm. Compared to the as-deposited thin film, the grains appear rounded after electrochemical measurement (Fig. 5 (b)). There is less contrast difference between the grains of the as-deposited LSCF film.

All cathodes in this study were subjected to the same processing and experimental conditions. Grain sizes were always between 55 nm and 60 nm and there are no major differences in the microstructure or surface morphology between the cathodes.

3.2. Electrochemical impedance spectroscopy (EIS) measurements

The EIS spectrum for micro-cathodes of different effective LSCF surface areas at 500 °C is shown in Fig. 6, between 0.01 and 10⁶ Hz. A response at high frequency, HF, medium frequency, MF and at low frequency, LF was observed between 350 °C and 500 °C. Fitting of



Fig. 4. Optical microscope image of LSCF micro-cathode stripes; 130 μm LSCF stripe width, 20.5 μm LSCF stripe separation and 65 μm Au stripe width.



Fig. 5. SEM micrographs taken at 150,000 and 100,000 times magnification of the typical LSCF surface microstructure are shown in (a) as-deposited and (b) after EIS testing, respectively.

the electrode response is represented by solid lines. The LF arcs dominate in the main plot. HF impedance arcs are shown as inset, with a small impedance MF electrode response and the associated peak frequencies. A negative offset of the HF arc can be seen in the inset of Fig. 6, the origin of which is discussed in Appendix A.

The area specific resistance, ASR, is calculated from the resistance from impedance measurements multiplied by the electrode area. The electrode area here is called the LSCF/YSZ interfacial area which is the imprint of the LSCF on the YSZ. In contrast to the LSCF/YSZ interfacial area, the effective LSCF surface area is the LSCF surface area which is not covered by Au and is freely exposed to the atmosphere. It will be discussed in the text where the analysis of EIS measurements is performed by normalisation of the ASR to the effective LSCF surface area, which is exposed to O_2 .



Fig. 6. Nyquist plot of cathodes with different effective LSCF surface areas measured at 500 °C. The MF response is shown inset.

3.2.1. High frequency response

It can be seen in Fig. 6 that the HF arc for each cell (approximately 10^5 to 10^6 Hz) is clearly very similar and terminates between 25 and 45 Ω . The temperature dependence of the HF response shows Arrhenius-type behaviour. The average activation energy of $0.96 \pm$ 0.08 eV is in close agreement with the value of 0.94 ± 0.03 eV determined by Baumann et al. [10] and 1.1 eV determined in Refs. [47,48] for the HF contributions. The capacitance of order 10^{-8} - 10^{-9} F is also at least 5 orders of magnitude smaller than any other impedance arc measured. It is therefore reasonable to assign the HF response to the bulk resistance of YSZ, R_{YSZ} i.e. the resistance to bulk ionic transport of 0^{2-} through single crystal YSZ. The measured capacitances are larger than expected for a bulk contribution. However, since single crystal YSZ substrates were used, the capacitances cannot be attributed to a grain boundary effect. Stray capacitances from the leads connected to the electronics may be responsible for the higher capacitance.

3.2.2. Medium frequency response

The temperature dependence of the impedance response at MF, R_i is shown in Fig. 7 for three micro-cathodes of different effective LSCF surface areas. The depressed MF arcs were fitted with n values between 0.6 and 0.7. The absolute values of the resistance at MF are all <10 Ω cm² at 500 °C and contribute very little to the total ASR. In fact, at 500 °C, this resistance contributes <4% of the total absolute resistance in the case of the cathode with largest effective LSCF surface area (0.267 cm²). The average activation energy was found to be 1.11 ± 0.06 eV.

A similar feature was observed at MF by Baumann et al. [10] and Xiong et al. [15] who used LSCF electrodes with a composition rich in Co i.e. 0.8:0.2 (Co:Fe) on YSZ. The literature values for R_i are lower than the values reported here. However, when extrapolating the data of Baumann et al. [10] to the same temperature range as studied here, the resistance values correspond. The resistance values of Xiong et al. [15] are lower compared to the data in this study which could be due to the nanocrystalline thin film YSZ electrolyte used by the authors. The activation energies in the literature (1.55 eV [10] and 1.34 eV [15]) are slightly higher than those found in this study. Different current collection methods might be a reason for the differences. It is therefore likely that the MF feature observed in this work is associated with an interfacial resistance i.e. a charge



Fig. 7. Arrhenius plot of R_i (based on the LSCF/YSZ interfacial area) for micro-cathodes of different effective LSCF surface areas in this study, with the corresponding E_A values shown. Data from Baumann et al. [10], utilising 100 nm thick electrodes produced by PLD and Xiong et al. [15], utilising 50 nm thick electrodes produced by sputtering (SPT) is shown for comparison.

double-layer effect, R_i relating to the ionic transfer resistance at the electrode/electrolyte interface.

The ASR values (based on the LSCF/YSZ interfacial area) of R_i for the three cathodes measured in this work are separated by a maximum of half an order of magnitude, with no significant correlation in ASR with the micro-cathode effective LSCF surface area. This strengthens the case made for such ionic transfer resistance, since after normalising to the interfacial area the LSCF/ YSZ interfaces are nominally equal. Therefore, one expects no ASR correlation with effective LSCF surface area and similar R_i values.

The associated capacitance at MF, C_i , is almost temperature independent for all cathodes and provides a good indication that little change (degradation) occurred at the LSCF/YSZ interface. The area specific capacitance (based on the LSCF/YSZ interfacial area) at 500 °C for the cathode of largest effective LSCF surface area (0.267 cm²) of $4.3 \pm 0.3 \times 10^{-5}$ F cm⁻² is at the upper end of typical capacitances arising due to the electrode/electrolyte interface [49]. However, the capacitance of the MF feature is largest for the cathode of smallest effective LSCF surface area (0.038 cm²) i.e. $1.9 \pm 0.1 \times 10^{-3}$ F cm⁻² at 500 °C, which also has the smallest LSCF/YSZ interfacial area. This indicates a shift to lower peak frequencies with decreasing LSCF/YSZ interfacial area.

Hence, the MF arc is attributed to the LSCF/YSZ interfacial resistance. It is not considered as a significant polarisation step in the oxygen reduction reaction. Similarly, Prestat et al. [14] determined charge transfer at the LSCF/CGO interface not to be rate-determining.

3.2.3. Low frequency response

The temperature dependence of the ASR, $R_{s,(int)}$ (based on the LSCF/YSZ interfacial area) determined from EIS measurements at LF for all three micro-cathodes is shown in Fig. 8 (a). The absolute resistance of the LF arc is considerably larger than the absolute resistance of the MF arc in Fig. 6. The LF arcs were fitted with *n* values >0.9 and are considerably less depressed than the MF arcs. However, less ideal semicircles were fitted at higher temperatures due to the extended measurement time at lower frequencies, which resulted in slightly elongated arcs. Such data points are measurement artefacts and are not believed to be indicative of an additional process. Activation energies, E_A in this work are between 0.67 eV and 1.34 eV with an average E_A of 0.85 \pm 0.1 eV (Fig. 8 (a)). This is 22% and 35% lower than the activation energies found by Xiong et al. [15] and Baumann et al. [10], respectively. In both these studies the LF arc was also the dominating electrode response and was attributed to the oxygen surface exchange reaction. Extrapolated ASR values of the results from these literature studies are within the same range as the three cathodes measured in this work, particularly below 450 °C. The LF impedance arc is therefore likely due to the oxygen surface exchange reaction, $R_{s,(int)}$ i.e. a surface resistance and indicates that resistance associated with ionic conduction through the LSCF bulk can be assumed negligible in the micro-cathode geometries used.

A clear dependence of the LF electrode response on the effective LSCF surface area (the LSCF surface area exposed to O_2 and not covered by Au) exists when the absolute resistance is considered in the Nyquist plot of Fig. 6. The absolute resistance decreases as the effective LSCF surface area increases. However, when the resistance is normalised to the LSCF/YSZ interfacial area (the area of LSCF in contact with the YSZ), the ASR of the two cathodes of largest effective LSCF surface area i.e. 0.097 cm^2 and 0.267 cm^2 is almost indistinguishable, in Fig. 8 (a). The cathode of smallest effective LSCF surface area i.e. 0.038 cm^2 is considerably larger in contrast. This result is because the LSCF/YSZ interfacial area that is used to define the 'technological' ASR differs in this study from the effective LSCF surface area, which excludes the areas not covered with Au. We therefore plot the ASR associated with the surface resistance, based on the effective LSCF surface area, i.e. $R_{s,(eff)}$, in Fig. 8 (b), since this is the



Fig. 8. Arrhenius plot of the ASR (based on the interfacial area) associated with the LF response, $R_{s,(int)}$ (a) and based on the effective LSCF surface area, $R_{s,(eff)}$ in (b), with the corresponding E_A values shown. Data from Baumann et al. [10] and Xiong et al. [15] is shown for comparison. 'SPT' refers to sputtering.

area over which oxygen exchange is considered to take place. The ASR associated with the surface resistance, $R_{s,(eff)}$ will be based on the effective LSCF surface area from this point.

Since the effective LSCF surface area is less than the LSCF/YSZ interfacial area, $R_{s,(eff)}$ displayed in Fig. 8 (b) is now less than $R_{s,(int)}$ in Fig. 8 (a). In addition, the difference in ASR between the cathodes in this work in Fig. 8 (b) has decreased and the values are more comparable to the ASR measured by Xiong et al. [15]. The extrapolated ASR of measurements by Baumann et al. [10] is now approximately one order of magnitude larger in comparison. This can be related to differences in the micro-/nanostructure of the LSCF thin film, according to Plonczak et al. [5]. To further investigate the influence of the effective LSCF surface area on $R_{s,(eff)}$, $R_{s,(eff)}$ is plotted as a function of the effective LSCF surface area at different temperatures, for each cathode, in Fig. 9. The influence of the effective LSCF surface area on $R_{s,(eff)}$ is not pronounced at 500 °C, with similar values obtained for all cathodes. However, as the temperature is reduced to 350 °C, the difference in $R_{s,(eff)}$ between the cathodes increases, with increased scatter in the data points. The error bars in Fig. 9 are due to the equivalent circuit fitting process. The ASR of the cathode with the smallest effective LSCF surface area (0.038 cm^2) increases more at *lower* temperatures relative to the two cathodes of larger effective LSCF surface area, in Fig. 9. Once



Fig. 9. Surface resistance, $R_{s,(eff)}$ (based on the effective LSCF surface area) plotted as a function of effective LSCF surface area, between 345 and 503 ± 1 °C.

correcting for the difference in effective LSCF surface area, $R_{s,(eff)}$ should be similar for each cathode (displaying a horizontal line connecting the data points) if the bulk path remains dominant and if no change in the electrode kinetics occurs. However, the performance of nominally identical samples was not directly compared in this study, which may explain the scatter in $R_{s,(eff)}$ in Fig. 9. It is clear from Fig. 9 however, that the scatter in $R_{s,(eff)}$ occurs for the cathode with the smallest LSCF stripe width of 20 µm and effective LSCF area of 0.038 cm².

The influence of the LSCF stripe width on the ASR associated with the surface resistance, $R_{s,(eff)}$ follows the same trend as the surface area as seen in Fig. 9 because the stripe width is a measure of the effective LSCF surface area. The stripe width is effectively the surface pathway, shown in Fig. 1. However, due to the large scatter in data the surface pathway cannot necessarily be deemed negligible in the oxygen reduction reaction process, particularly below ~400 °C. The effect of l_{TPB} used in this study is not so pronounced because the similar l_{TPB} of the micro-cathodes did not result in similar impedance spectra when the effective LSCF surface area was changed. The surface area dependence of the dominating LF arc in the (as-measured) impedance data (Fig. 6) strengthens the case for a rate limiting surface resistance, $R_{s,(eff)}$. If the LF arc is due to a dominant surface diffusion process i.e. the surface pathway, one expects the size of the LF arc to scale with the stripe width, i.e. the opposite of what is displayed in Fig. 6. Hence the effective LSCF surface area is the important parameter. Below 400 °C, $R_{s,(eff)}$ seems to be more sensitive to changes at the LSCF surface due to slower reaction kinetics. However, no conclusion can be made on the reaction mechanism between 350 °C and 400 °C. Likewise, the ratio of LSCF l_{TPB} to LSCF surface area required for a change in mechanism to occur over a given temperature range, for a given LSCF thickness, remains an open question.

The area-specific capacitances (based on the effective LSCF surface area) associated with the LF feature are of the order 10^{-2} to 10^{-1} F cm⁻². The absolute values are also larger than the typical values of approximately 10^{-4} F due to electrode reactions [49]. A negative activation energy is evident for each micro-cathode i.e. the capacitance increases with increasing temperature, which is consistent with equivalent capacitance measurements of the LF feature made by Baumann et al. [10]. However a reduced (average) E_A of -0.18 ± 0.1 eV was determined in this work with Co/Fe ratio of 0.2:0.8 compared to $E_A = -0.3$ eV with the Co/Fe ratio of 0.8:0.2 in the study of Baumann et al. [10]. Assuming this capacitance is also a chemical capacitance, C_{chem} , the difference is likely because of the different composition used in this work. For a variation in oxygen partial pressure, an increase in C_{chem} is described as an increase of the "readiness" of the material to undergo stoichiometric changes [10,46].

A summary of resistive and capacitive quantities and associated activation energies as determined via equivalent circuit fitting of data measured using EIS is shown in Table 4.

Impedance measurements were taken twice at the same temperature at different times of the (measurement) thermal cycle; at ~400 °C during heating to the maximum temperature and repeated at ~400 °C during cooling, approximately 4 h later. An increase in the electrode ASR, particularly the LF arc was observed for all cathodes. The degradation was larger for smaller LSCF feature sizes/ stripe widths. An increase in $R_{s.(eff)}$ of approximately 40%, 75% and 110% was observed for LSCF stripe widths of 130 µm, 50 µm and 20 µm, respectively. The increased resistance is indicative of a change in the surface reaction. The change in the microstructure shown in Fig. 5 may be responsible for the degradation observed, the effect of which appears to be more pronounced with smaller LSCF feature sizes. The degradation is consistent with the observation made by Baumann et al. [10], where an increase in resistance of the LF arc with time at the higher temperature of 750 °C is reported. The

Table 4

Summary of separate resistive and capacitive values measured at 500 °C. Values for each component are provided in order of decreasing effective LSCF surface area of the cathodes.

| | | 1 (500.80) | 24 |
|-------------------------------|--|--|---------------------------------|
| Equivalent circuit element | Physical interpretation | Area specific value (500 °C): | "Average activation energy (eV) |
| R _{YSZ} ^b | YSZ electrolyte (O ^{2 –} conductivity). | 57.4 (\pm 0.2) Ω | 0.96 ± 0.08 |
| | | 41.9 $(\pm 0.1) \Omega$ | |
| | | 38.1 (\pm 0.1) Ω | |
| R_i^c | LSCF/YSZ interfacial resistance due to ion transfer. | 7.1 (\pm 0.2) Ω cm ² | 1.11 ± 0.06 |
| | | $3.8 (\pm 0.1) \Omega \text{ cm}^2$ | |
| | | 9.1 (\pm 0.2) Ω cm ² | |
| $R_{s,(eff)}^{d}$ | Oxygen surface exchange reaction resistance at LSCF surface. | 47.9 (\pm 0.7) Ω cm ² | 0.85 ± 0.1 |
| | | 24.0 (\pm 0.7) Ω cm ² | |
| | | 29.3 (± 0.7) Ω cm ² | |
| Ci | LSCF/YSZ interfacial capacitance. | 4.3 $(\pm 0.3) \times 10^{-5} \mathrm{F cm^{-2}}$ | 0.03 ± 0.2 |
| | | $3.4~(\pm 0.2) \times 10^{-4} \mathrm{F}\mathrm{cm}^{-2}$ | |
| | | $1.9~(\pm 0.1) \times 10^{-3} \mathrm{F}\mathrm{cm}^{-2}$ | |
| C _{chem} | 'Chemical' capacitance of LSCF electrode bulk. | $4.0~(\pm 0.1) \times 10^{-2} \mathrm{F}\mathrm{cm}^{-2}$ | -0.18 ± 0.1 |
| | | $1.42 \ (\pm 0.02) \times 10^{-1} \ \mathrm{F} \ \mathrm{cm}^{-2}$ | |
| | | $1.74~(\pm 0.05) \times 10^{-1} \mathrm{F}\mathrm{cm}^{-2}$ | |

^a Averaged over all cathodes.

^b For 21×21 mm YSZ substrate.

^c ASR based on LSCF/YSZ interfacial area.

^d ASR based on effective LSCF surface area.

degradation of cathode materials containing Sr is of particular interest [50,51] since a reduction in Sr content is correlated with a reduced electrochemical performance [50]. Sr is believed to segregate to the surface and inhibit oxygen exchange [52,53]. EIS measurements in this work were performed in a flow of O₂, in an unsealed furnace. It is known that the humidification of the oxidant affects the long term stability of LSCF due to changes to the surface cation composition, resulting in a greater decrease in oxygen surface exchange kinetics with time than in dry atmospheres [51,54].

3.3. Limiting oxygen surface exchange kinetics

Using isotope exchange depth profiling (IEDP) data obtained by Benson et al. [38] for the diffusion coefficient, D^* and surface exchange coefficient, k^* of LSCF of the same composition used in this study, the characteristic thickness, $L_c = D^*/k^*$ was calculated as a function of temperature. A limitation in oxygen reduction kinetics due to solid state diffusion of oxygen is not expected at temperatures >417 °C due to the electrode thickness of 290 nm. Bulk diffusion of oxygen ions above this temperature is expected to remain facile compared to the oxygen surface exchange reaction. In IEDP measurements of LSCF, Benson et al. [38] measured almost parallel D^* and k^* temperature profiles, i.e. equal activation energy, E_A , above about 600 °C. Below this temperature, there was a decrease in the activation energy E_A of k^* , which is attributed to a possible change in mechanism.

However, the LF impedance arc was found to depend on the effective LSCF surface area below 417 °C in this work, but the influence of the surface pathway could not be determined below 400 °C. The oxygen surface exchange rate constant from tracer experiments, k^* , is close to the oxygen surface exchange rate from electrical experiments, k^q , for some MIEC perovskite materials [21,22]. To investigate this, k^q was calculated using the EIS results in this study by applying Eq. (4) [21,22].

$$R_{s,(eff)} = \frac{k_B T}{4e^2 c_0 k^q} \tag{4}$$

where k_B is the Boltzmann constant, *T* is the temperature, *e* is the elementary charge and c_0 is the concentration of lattice oxygen. This equation predicts the 'area specific' cathode resistance due to the surface exchange process ($R_{s.(eff)}$) with negligible charge transfer at the LSCF/YSZ interface [55]. Fig. 10 compares values of k^q from



Fig. 10. Comparison between: k^q calculated from $R_{s.(eff)}$ obtained via EIS on micro cathodes in this work. k^q , calculated from values of the surface resistance in references [10] (Baumann et al.) and [15] (Xiong et al.) by applying Eq. (4) and by a numerical optimisation process in [14] (Prestat et al.) is represented by solid symbols. k^* , determined from isotope exchange depth profiling experiments in references [38] (Benson et al. Po2 = 1000 mbar) and [56] (Steele et al.) is represented by open symbols.

this work with k^* determined from IEDP techniques as a function of *T* in [38] and [56] (porous LSCF), k^q calculated from surface resistance values of patterned LSCF cathodes in the literature [10,15] and by a numerical optimisation process in [14]. Note, a value of $c_0 = 5.2 \times 10^{22} \text{ cm}^{-3}$ was used for the calculation of k^q in Fig. 10, assuming 3 oxygen atoms per unit cell and a pseudo-cubic lattice constant of $3.87 \times 10^{-8} \text{ cm}$ [57] for La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ}.

Absolute values of the oxygen surface exchange rate, k^q determined from EIS measurements in this work varied by an order of magnitude. The smallest values of k^q were obtained for the micro-cathode of smallest effective LSCF surface area (0.038 cm²), with the smallest feature size of 20 µm. However, the values of k^q associated with micro-cathodes of larger effective LSCF surface area (0.267 cm² and 0.097 cm²) are very similar between 350 °C and 500 °C. The difference in k^q between the two micro-cathodes of largest effective LSCF surface area (0.267 cm² and 0.097 cm²) respectively) and the micro-cathode with the least effective LSCF surface area (0.038 cm²) increases as the temperature is decreased. This is because the activation energy, E_A of k^q of the micro-cathode of smallest effective LSCF surface area is approximately double the E_A of the two micro-cathodes with larger effective LSCF surface area.

The values of the oxygen surface exchange rate determined via an electrical method, i.e. k^q on cathodes with effective LSCF surface area of 0.267 cm^2 and 0.097 cm^2 in this work, are in good agreement with those determined via 'tracer' experiments on bulk LSCF (i.e. sintered ceramics) of the same composition in [38], in slightly different P_{O_2} , i.e. k^* . Extrapolated values of k^q from Baumann et al. [10] and Xiong et al. [15] are lower, which may be due to the Co-rich composition used in each case and the different PLD and sputtering conditions used, respectively. However, k^q is three times less than the LSCF thin films (86–766 nm) prepared by PLD and of a similar composition, determined by Prestat et al. at 500 °C in [14]. Differences in k are indicative of a modified surface composition (which may be a function of the deposition process and/or sample preparation e.g. bulk sintered ceramics), of which k is extremely sensitive. k is influenced by many parameters; particularly the surface composition and differences between actual area and geometric area due to the microstructure e.g. a surface roughness effect and nanopores. The activation energy of k^q for all LSCF cathodes in this work varies considerably compared to values of k^q adapted from measurements of $R_{s.(eff)}$ made by Baumann et al. [10] and Xiong et al. [15]. A possible explanation for the scatter in the activation energies in this work is the multiple processing steps leading to the final patterned microcathodes. If the processing steps affect the surface of the patterned LSCF micro-cathodes in an unknown way and affect the resulting oxygen surface exchange properties, it is plausible to expect the greatest impact to the micro-cathode with the smallest effective LSCF surface area i.e. stripe width. The smaller the feature size, the more likely it will be to modify a larger proportion of the LSCF surface area from the as-deposited state during processing. This might also lead to greater degradation in performance with time and thus may explain the reduction of the oxygen surface exchange rate observed for the cathode with the smallest stripe width and effective LSCF surface area.

However, the associated E_A of the micro-cathodes with effective LSCF surface area 0.267 cm² and 0.097 cm² is in very good agreement with that determined by Benson et al. (with the same composition) within the specified error of 0.07–0.08 eV, which indicates a similar oxygen transport process within the temperature range. This is particularly relevant since the (reduced) low temperature dependence of k^* reported in [38] is thus confirmed in this study. This illustrates the suitability of using thin film gwd cathodes to yield information regarding the surface exchange coefficient, k^q .

As mentioned, k^q is found to limit the oxygen reduction process between 400 °C and 500 °C in this work and it is therefore beneficial to increase the surface area by using a porous structure. In this case the Adler, Lane, and Steele, or 'ALS' model [58] governed by Eq. (5) can be applied.

$$R_{\rm chem} = \left(\frac{RT}{2F^2}\right) \sqrt{\frac{\tau}{(1-\varepsilon)\frac{D^*}{f}C_0^2 ak^*}}$$
(5)

where *R*, *T*, and *F* take their usual meaning, R_{chem} is the ASR due to chemical contributions from the electrode impedance, τ and ε are tortuosity and porosity that can be estimated from SEM observation and D^* is the tracer diffusion coefficient. Eq. (5) can be applied to estimate the internal surface area required of a porous La_{0.6}Sr_{0.4}Co_{0.2} $Fe_{0.8}O_{3-\delta}$ cathode of typical footprint of $1\ cm \times 1\ cm$ and $1\ \mu m$ thickness to achieve an acceptably low ASR of 0.5 Ω cm² at 500 °C; assuming similar exchange kinetics deduced in this work. Estimates of porosity and tortuosity are $\varepsilon = 0.4$ (40%) and $\tau = 1.5$, respectively, a value of the Bardeen–Herring correlation factor, f = 0.69 is assumed for perovskite-type oxides [38,59], $k^q \approx k^* = 6.24 \times 10^{-8} \text{ cm s}^{-1}$ and $D^* = 8.86 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ (from [38]). A total internal surface area of $12.3 \times 10^3 \text{ cm}^2$ (i.e. internal surface area/volume ratio, $a \sim 10^8 \text{ cm}^{-1}$) is required for the porous structure of the aforementioned dimensions to achieve an ASR of 0.5 Ω cm² at 500 °C. Such a large internal surface area cannot be attained from porous cathodes of this thickness. For a realistic internal surface area of 1.2 cm² (with a volume of 6×10^{-5} cm³ for $\varepsilon = 0.4$ such that $a = 20,000 \text{ cm}^{-1}$), the required k^* is $6.4 \times 10^{-4} \text{ cm s}^{-1}$, some 4 orders of magnitude greater than currently achieved. Therefore, from the perspective of increasing the cathode internal area, a thicker porous cathode with grains as small as possible is required.

4. Conclusions

The oxygen reduction reaction at thin film La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3 – δ} cathodes was investigated using electrochemical impedance spectroscopy to determine the resistance of patterned micro-cathodes of different geometries. Micro cathodes with effective LSCF surface area of 0.038 cm², 0.097 cm² and 0.267 cm² were analysed in this study between 350 and 500 °C. This temperature range is lower than usually measured in the literature.

Two electrode responses were identified: (i) an interfacial resistance i.e. a charge double-layer effect, R_i relating to the ionic transfer resistance at the LSCF/YSZ interface and (ii) a surface resistance, R_{s.(eff)} associated with the oxygen surface exchange reaction. Absolute values of R_i contributed less than 10% of the total electrode resistance and therefore the oxygen surface exchange reaction was determined to be the dominating resistive process for patterned thin film LSCF micro-cathodes in the study. The reduction in size of the LF impedance arcs with increasing effective LSCF surface area at lower temperatures is related to the increased reaction area for direct oxygen exchange to take place. The bulk pathway was found to be dominant above 400 °C in this work because the ASR did not show a dependence on the LSCF stripe width. However, the relative importance of the surface pathway could not be deemed negligible due to increased scatter in the ASR below 400 °C. In addition, below 400 °C, the ASR seems to be more sensitive to changes at the LSCF surface, possibly due to slower reaction kinetics. The effect of the microfabrication processing on the oxygen surface exchange properties of the patterned LSCF micro-cathodes cannot be deemed negligible. Further work is required to investigate the performance of nominally identical micro-cathodes.

Electrochemical measurements of the resistance associated with the oxygen surface exchange reaction enabled the determination of the oxygen surface exchange rate constant, k^q . Comparing the range of k values determined in this work with available literature data indicates that it is the surface state/composition of the LSCF that largely determines the resulting reaction kinetics. Degradation in the performance of the LSCF cathodes was observed, characterised by an increase in area specific resistance associated with the oxygen surface exchange reaction. Degradation in performance scaled inversely with the patterned LSCF feature size with a maximum increase in $R_{s,(eff)}$ of 110% occurring over 4 h, for the micro-cathode with the smallest LSCF stripe width (20 µm) and effective surface area (0.038 cm²). This indicates changes at the LSCF surface that acts to reduce efficient oxygen exchange from taking place, which may be related to changes in the LSCF microstructure and the microfabrication processing. Further work is required to investigate changes to the LSCF surface layer over time and as a function of oxygen partial pressure.

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Appendix A. Negative HF offset

Regardless of the micro-cathode geometry, all samples exhibited a HF offset in the negative x-axis (Z') direction when samples were measured with a 3-electrode set-up (see Fig. A.1). If a two electrode set up was used for the measurements, an offset of approximately 45 Ω from the origin in the x-direction is found. This offset is comparable to the diameter of the HF arc in the 3 electrode setup. Hence the measurement setup is believed to be the reason for the negative offset. Similar observations are reported in the literature [60,61] and are related to different actual potentials of the working and the reference electrode due to misalignment of the working and the counter electrode. The maximum misalignment in this study was 20 µm; the reference electrode was always a fixed distance from the working electrode.



Fig. A.1. Impedance spectra shown between ~1 Hz-1 MHz and ~0.1 Hz-1 MHz for halfcells measured in a 3-electrode (0.267 cm²) and 2-electrode (preliminary test sample) setups, respectively.

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