Solid oxide fuel cells (SOFCs) are very promising devices for efficient energy conversion to meet the world’s continuously increasing demand of energy. The advantage of fuel flexibility ranging from pure hydrogen to a variety of hydrocarbon fuels and natural gas is one of the most attractive features.\(^1\)\(^-\)\(^3\) Despite all its benefits, SOFC technology is also demanding and a lot of efforts have been made over the past decades to optimize important key factors for commercialization such as durability, manufacturing cost and modularization.\(^4\)\(^-\)\(^7\) The simplest approach to increase long term stability of SOFC systems is to lower the operating temperatures in order to avoid unfavorable side reactions of different components.\(^8\) However, a temperature decrease also lowers the kinetics of processes exhibiting high activation energies, especially the oxygen reduction reaction (ORR). Special attention is therefore put on the search and improvement of cathode materials since the ORR is considered to currently limit the performance of intermediate temperature SOFCs.\(^9\)\(^,\)\(^10\)

Oxides were introduced as cathode materials to substitute expensive noble metals and one prominent example already employed in commercially available SOFCs is La\(_{0.6}\)Sr\(_{0.4}\)MnO\(_3\) (LSM). It offers a high electronic conductivity, acceptable catalytic activity for the oxygen exchange and sufficient chemical stability, but due to its low ionic conductivity it is unattractive for SOFCs operating at intermediate temperatures (400–600\(^\circ\)C). Mixed ionic and electronic conductors (MIECs) of the perovskite-type solid-solution La\(_{1-x}\)Sr\(_x\)CoO\(_3\)-δ can extend the reaction zone from the triple phase boundary (electrode-electrolyte-gas) to the twofold phase boundary due to their excellent ionic conductivity. They also offer high catalytic activity for the oxygen exchange and thus have been in the focus of recent research.\(^11\)\(^,\)\(^12\) For a given Sr concentration, e.g. x = 0.4, the catalytic activity, oxygen vacancy concentration and thus the ionic conductivity increase with the amount of Co on the B-site of the perovskite, though, at the expense of a reduced chemical stability.\(^13\) Furthermore, changes of the electronic structure are observed from semiconductor-like for La\(_{0.6}\)Sr\(_{0.4}\)FeO\(_3\) (LSF64) to metal-like behavior for La\(_{0.6}\)Sr\(_{0.4}\)CoO\(_3\) (LSC64) at SOFC operating conditions.\(^14\) The detailed influence of the B-site metal cation and of the Sr dopant concentration on the electrochemical properties were key aspects of numerous studies,\(^15\)\(^-\)\(^20\) while much less investigations dealt with the effect of alternative A-site dopants.\(^16\)

In this study, the electrochemical properties of well-defined LSC64 and La\(_{0.6}\)Ba\(_{0.4}\)CoO\(_3\) (LBC64) are directly compared with each other. The advantage of comparing these two identically charged dopants is that almost all the chemical and electrochemical differences originate from the different ionic radii of Sr\(^{2+}\) (144 pm) and Ba\(^{2+}\) (161 pm),\(^21\) since both atomic Sr and Ba have a similar valence electron configuration (5s\(^2\); 6s\(^2\)). Nonetheless, the defect structure and thus the MIEC properties differ significantly due to a higher reducibility of the perovskite-type lattice with Ba ions.\(^22\)\(^,\)\(^23\) To the best of the authors’ knowledge, electrochemical investigations of La\(_{1-x}\)Ba\(_x\)CoO\(_3\)-δ (LBC) electrodes have been only performed on porous systems\(^24\)\(^-\)\(^26\) including mixtures of LBC with GDC.\(^27\) These studies already reported comparatively low polarization resistances, but were not able to deconvolute the surface exchange and transport resistances of LBC for geometrical reasons. Therefore, dense thin film model electrodes were used in this work and the catalytic activity for the oxygen exchange could be determined for LSC and LBC over an oxygen partial pressure range of 10\(^{-4}\) to 1 bar O\(_2\) and at temperatures between 450 and 600\(^\circ\)C. The results reveal the superior properties of LBC in terms of catalytic activity for oxygen exchange, in comparison to most state of the art MIECs for intermediate SOFCs.

Experimental

Thin film preparation.—Targets for deposition of LSC thin films by pulsed laser deposition (PLD) were synthesized from powders prepared by Pechini synthesis.\(^28\) La\(_{0.6}\)Sr\(_{0.4}\)CoO\(_3\), BaCoO\(_3\) and BaO powders (all Sigma Aldrich, 99.995\%) were individually dissolved in nitric acid, mixed in appropriate ratios and citric acid (TraceSELECT, 99.9998\%) was added for chelation. A calcination step was performed at 1000\(^\circ\)C, followed by isostatic pressing (\(~150\) MPa) of the powder to a pellet and a sintering procedure at 1200\(^\circ\)C for 12 hours in air, thus yielding a La\(_{0.6}\)Sr\(_{0.4}\)CoO\(_3\)-δ and a La\(_{0.6}\)Ba\(_{0.4}\)CoO\(_3\)-δ target for PLD.

The LSC and LBC thin films were deposited onto (100) oriented yttria stabilized zirconia (YSZ, 9.5 mol\% Y\(_2\)O\(_3\), Crystrac GmbH, Germany) single crystals with a thickness of 0.5 mm and a size of 5 × 5 mm\(^2\) or 10 × 10 mm\(^2\). Epipolished substrates were used to prepare symmetrical samples with nominally identical thin films on both sides of the YSZ for impedance measurements. Ablation of the target material was carried out by a KrF\(^*\) (λ = 248 nm) excimer laser (Lambda COMPexPro 201F) operated at a pulse repetition rate of 5 Hz, a pulse duration of 50 ns and a laser fluence of approximately 1.5 J·cm\(^{-2}\) at the target. The atmosphere was set to 4 · 10\(^{-7}\) mbar oxygen partial pressure and the substrate was heated to a surface temperature of 600\(^\circ\)C. By applying 9,150 laser pulses to the LSC and 8,175 laser pulses to the LBC target, thin films of approx. 300 nm thickness were grown on the substrate (substrate to target distance = 6 cm). After deposition, the sample was cooled in the deposition atmosphere at a cooling rate of 12\(^\circ\)C · min\(^{-1}\). The substrate was flipped and the PLD procedure was again repeated for the back side. Prior to the impedance measurements, the 5 × 5 mm\(^2\) samples were broken into pieces of about 1.5 × 1.5 mm\(^2\) to minimize the influence of electronic sheet...
resistance, see also EIS – Initial measurements and equivalent circuit model section. It is noteworthy that the sample surface was never exposed to “cleaning” treatments after deposition in order to avoid any reactions and contamination from solvents including H₂O.  

**Structural characterization.**—The PLD target material was analyzed in Bragg Brentano geometry by a X’Pert Powder (PANalytical) diffractometer. A thin film diffraction pattern was obtained using a DB-Discover instrument (Bruker AXS) in parallel beam geometry equipped with a general area detector diffraction system (GADDS). Secondary electron microscopy was performed on a FEI Quanta 200 field emission gun scanning electron microscope equipped with an Everhart-Thornley detector.

**Electrochemical measurements.**—All annealing and impedance experiments were performed in a cleaned quartz tube which was evacuated and refilled several times with the desired high purity N₂ (ALPHAGAZ 1 > 99.999 mol% nitrogen)/O₂ (ALPHAGAZ 1 > 99.998 mol% oxygen) mixture before the sample was uniformly heated in a tube furnace. The symmetrical samples (thin film – YSZ – thin film) were sandwiched between two platinum foils for impedance measurements. The electronic connection in the sample holder consisted of Pt wires and a non-encapsulated type S thermoelement was used for temperature measurement. No materials other than Pt, quartz and the sample itself were heated during impedance measurement and annealing. All these precautions were taken in order to obtain electrochemical measurements that do not suffer from any cathode poisoning. It took approximately 45 minutes to heat the sample to the desired temperature (thermal equilibration), then the different impedance measurements were performed. The impedance was measured by a Novocontrol Alpha A High Performance Frequency Analyzer in the frequency range from 10⁶ to a minimum of 5 · 10⁻³ Hz with a resolution of five points per decade and an alternating voltage of 10 mV (rms) applied between the two thin film electrodes.

In-plane resistivity measurements of the thin films were also performed in a quartz tube. Four platinum needles were placed on top of the thin film in the corners of a 10 × 10 mm² sample as close as possible to the sample boundary to meet the prerequisites of the van der Pauw method. The quartz apparatus was uniformly heated in a tube furnace and temperature was measured by means of an encapsulated type S thermoelement positioned adjacent to the sample. A mixture of high purity N₂/O₂ was used to realize an oxygen partial pressure of 1 atm under standard conditions (298.15 K, 1 atm) can be calculated from literature. Both values are close to 60° - the value for a cubic crystal structure. Generally, changes in the crystal structure symmetry of the ABO₃ perovskite family can be explained by Goldschmidt’s tolerance factor t₀. For LBC (t₀ ~1.00) an almost ideal cubic structure is found in contrast to the more rhombohedrally distorted LSC₆₄ (t₀ ~0.98), calculated with ionic radii from. The pseudo cubic lattice parameter derived from the polycrystalline target diffraction patterns for LSC (aₚ = 3.838 ± 0.003 Å) and LBC (aₚ = 3.889 ± 0.002 Å) agree well with literature values.

The thin film samples show the actual thin film growth relative to the (100) YSZ-plane. Therefore, both patterns are dominated by the intense (00l) peaks of the substrate. Again, no other peaks besides the substrate or the thin film peaks are found, indicating a sufficiently phase-pure deposition. Furthermore, it can be seen that both films grow preferentially in (100) and (110) direction on the substrate. Due to the

**Figure 1.** SEM images of LSC (l.h.s.) and LBC (r.h.s.) thin films. Cross sections are shown on the top and the surface on the bottom.

**Figure 2.** XRD pattern of LSC₆₄ and LBC₆₄ PLD target and thin film deposited on YSZ.
small amount of thin film peaks, the out-of-plane lattice parameters for LSC ($a_{pc} = 3.83 \pm 0.01$ Å) and LBC ($a_{pc} = 3.90 \pm 0.01$ Å) can be only given with limited accuracy.

**EIS – Initial measurements and equivalent circuit model.**—First, electrochemical impedance spectroscopy was used to measure the response of freshly deposited LSC and LBC thin films at $604 \pm 2$ °C in synthetic air and 0.21 bar oxygen partial pressure ($pO_2$). Nyquist plots normalized to the projected electrode surface area are shown in Fig. 3a for LSC and Fig. 3b for LBC, a comparison between the two materials is made in Fig. 3c after subtraction of the high frequency intercept. Qualitatively, both materials show a very similar Nyquist plot. The high-frequency intercept ($>25$ kHz) on the x-axis can be predominantly attributed to the oxide ion conduction in the electrolyte.

In addition, the high frequency intercept is slightly higher for the LBC sample, probably because of its smaller electronic conductivity compared to LSC (see Van der Pauw – electronic conductivity section), which may cause an additional sheet resistance. This additional high frequency resistance amounts to 13 – 18% of the total high frequency intercept and might indicate a slightly smaller active surface area for the LBC sample. However, compared to other effects found in this study, these differences are of minor importance and were thus not considered for the calculation of the resistive and capacitive values presented in this work. The electrode impedance is determined by a small shoulder at medium frequencies (25 kHz–1 kHz) and a pronounced low frequency (1 kHz–0.1 Hz) semicircle. It is generally agreed that the oxygen exchange resistance dominates the overall electrode impedance for thin films of the La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ perovskite family. Therefore, the resistive contribution of the low frequency semicircle is associated with the oxygen exchange reaction at the surface, which is also supported by its time, temperature and pressure dependency shown in the following sections. Accordingly, the surface exchange resistance can already be approximated from the impedance spectra without any detailed fit model.

A surface exchange resistance ($R_{surf}$) of $\sim 0.5 \Omega \text{cm}^2$ is found for the freshly deposited LSC thin film, which is in good agreement with literature values reported for similarly prepared thin films. This indicates that, compared to other materials, already LSC thin films show excellent kinetics for the oxygen reduction reaction at 600 °C; other values are: Ba$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ $\sim 3 \Omega \text{cm}^2$, SrFeO$_{3-\delta}$ $\sim 9 \Omega \text{cm}^2$, Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ $\sim 14 \Omega \text{cm}^2$, La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ $\sim 70 \Omega \text{cm}^2$, SrTi$_{0.95}$Fe$_{0.05}$O$_{3-\delta}$ $\sim 85 \Omega \text{cm}^2$, La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ $\sim 130 \Omega \text{cm}^2$. Freshly deposited LBC, however, shows an even lower surface exchange resistance than LSC; impressively small $\sim 0.17 \Omega \text{cm}^2$ can be estimated, see Fig. 5. This is certainly among the lowest oxygen surface exchange resistances reported so far for dense perovskite-type materials and to the best of our knowledge also the first value reported for the oxygen exchange kinetics of dense LBC thin films.

One of the major challenges in impedance spectroscopy is the quantitative evaluation of spectra in order to extract physically meaningful quantities. In general, impedance analysis is performed using equivalent circuits that consist of a network of resistors and capacitors. For a detailed analysis of the electrode impedance in Fig. 3 two different equivalent circuit models, see Fig. 4, were employed to fit the data; CPE denotes constant phase elements.
It can be seen in Figs. 3a and 3b that both models describe the measured data quite well but an excellent agreement between the equivalent circuit and the experimental data does not necessarily confirm the validity of any model. For a physical interpretation it is important to check whether the values of the fitting parameters are reasonable and show the expected dependencies on temperature, oxygen partial pressure and geometrical variations.

Baumann et al.\textsuperscript{11} already approached this issue for La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3} (LSCF) thin films and derived the equivalent circuit shown in Fig. 4a from a general description of mixed ionic-electronic conductors proposed in Ref. 47 under the assumptions of a very high ionic and electronic conductivity i.e. the oxygen incorporation into the electrolyte $1/2O_2 + 2e^- \rightarrow O^{2-}$ is limited by the surface exchange and electrode-electrolyte interface transfer. In this model $R_b$ represents the ionic bulk conductivity of the electrolyte, $R_{int,ion}$ the oxygen transfer between electrode and electrolyte and $R_s$ the surface exchange resistance. The capacitors were replaced by constant phase elements, where

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

is the impedance of the constant phase element and the capacitance is calculated by

$$C = (R^{1-n} \cdot Q)^{\frac{1}{n}}$$

For $n = 1$ the impedance of the constant phase element corresponds to the impedance of an ideal capacitor. $C_{int,con}$ represents the double layer capacitance expected at the interface between electrode and electrolyte due to the blockage of electronic charge carriers and $C_{chem}$ the chemical capacitance of the thin film.

One may suggest the same equivalent circuit for our La\textsubscript{0.6}Sr\textsubscript{0.4}CoO\textsubscript{3} (LSC64) and La\textsubscript{0.6}Ba\textsubscript{0.4}CoO\textsubscript{3} (LBC64) thin films, since they also show an excellent mixed conductivity and are limited by the surface exchange reaction. However, inconsistencies with this model are found in the medium frequency regime (small shoulder), since the extracted values for an interfacial double layer capacitance

$$C_{int,con}$$

are too large. Baumann\textsuperscript{11} calculated a $C_{int,con}$ of $\sim 100 \mu F/cm^2$ for LSC thin films at 500 $^\circ$C, while in our case much larger values are deduced from the model in Fig. 4a (LSC $\sim 2500 \mu F/cm^2$, LBC $\sim 10000 \mu F/cm^2$ for the two thin films at 510 $^\circ$C). Yang et al.\textsuperscript{48} also measured similarly high capacitances in the medium frequency range on La\textsubscript{0.5}Sr\textsubscript{0.5}CoO\textsubscript{3} thin films. Assuming a capacitor thickness as small as the interatomic distance of the two cation layers in an elementary cell ($d = 1.9 $ Å), a relative permittivity $\epsilon_r$ can be calculated by

$$\epsilon_r = \frac{C_{int,con}}{A} \frac{d}{\epsilon_0}$$

with $\epsilon_0 (= 8.85 \times 10^{-12} F/m)$ being the vacuum permittivity, and A the interfacial area. This model would deliver relative permittivity values of $\approx 430$ (LSC) and $\approx 2100$ (LBC). Such large $\epsilon_r$ values are hardly conceivable while the value of $\approx 21$ for LSCF, calculated using $C_{chem}$ from Ref. 11, is still in a realistic range. Therefore, we suggest that the high capacitance obtained at medium frequencies in this work represents stoichiometric changes and thus also reflects a chemical capacitance. Hence, it is not appropriate to use the Baumann model (Fig. 4a), since a second chemical capacitance would rather be in series and not in parallel to the $R_s[CPE_{chem}]$ element. Quantities discussed in this work are thus extracted by the modified equivalent circuit shown in Fig. 4b. The exact mechanisms behind $CPE_{chem}$ and $R_s$ are unknown and the circuit is considered as approximation of a more complex one; values could only be determined with limited accuracy, since the overall electrode impedance is strongly dominated by the large arc, i.e. by $CPE_{chem}$ and $R_s$. Exponential fitting parameters of $n \sim 0.7$ for the $R_s[CPE_{chem}]$ and $n > 0.92$ for the $R_s[CPE_{chem}]$ element were determined throughout this work.

**EIS - Time dependent measurements.**—Electrochemical impedance spectroscopy was used to investigate changes of the electrochemical performance for as-deposited LSC and LBC thin film electrodes at 604 $^\circ$C and 0.21 bar pO\textsubscript{2} over annealing time. Impedance spectra were measured continuously in an interval of $\sim 5$ minutes for 15 hours. Nyquist plots normalized to the projected electrode surface area are shown in Fig. 5a for LSC and Fig. 5b for LBC thin films after the given annealing times. The points represent measured data and the straight line the fit according to the model shown in Fig. 4b.

Figs. 6a and 6b summarize the resistive and capacitive changes during 15 hours of annealing. The oxygen surface exchange resistance $R_s$ increases continuously from 0.5 2cm\textsuperscript{2} to 4.2 2cm\textsuperscript{2} for LSC and 0.15 2cm\textsuperscript{2} to 1 2cm\textsuperscript{2} for LBC within 15 hours of annealing time at 600 $^\circ$C. The degradation of the electrochemical exchange kinetics of LSC and related materials was often reported and mostly connected to cation stoichiometry changes at or close to the surface.\textsuperscript{40-51} Especially, the presence of certain atmospheric trace gases such as SO\textsubscript{2}, CO\textsubscript{2} or H\textsubscript{2}O\textsubscript{2-} as well as Si or Cr sources in the vicinity of perovskite samples in wet atmosphere are known to decrease the electrode performance by formation of Sr rich phases on the surface.\textsuperscript{55,56} Even though similar degradation mechanisms may affect thin film...
electrodes as well as macroscopic electrodes we generally found that degradation rates are faster for thin films. However, special care was attributed to avoiding any contaminations of the atmosphere during the annealing procedure, see Electrochemical measurements section. For similarly prepared LSC thin films we already showed by low-energy ion sputtering and on-line inductively coupled plasma mass spectrometry\(^1\) that degradation during annealing (in the same setup) is not necessarily connected to severe cation stoichiometry changes at the surface. It is beyond the scope of this paper to clarify reasons of the changes measured here but they have to be kept in mind when analyzing activation energies (EIS - Temperature dependent measurements section).

\(C_{\text{chem}}\) decreases within the first 5 hours from 1050 F cm\(^{-3}\) to 950 F cm\(^{-3}\) for LSC and from 2300 F cm\(^{-3}\) to 2000 F cm\(^{-3}\) for LBC. This minor variation may be due to morphological changes of the thin film since the samples were only shortly at such temperatures during deposition (20 minutes). The higher \(C_{\text{chem}}\) values for LBC reflects its ability to undergo larger stoichiometric changes upon polarization in comparison to LSC. For \(C_x\), measured at medium frequencies, very high values in the order of 4 to 7 mF/cm\(^2\) were obtained. Neither \(C_x\) nor \(R_x\) show substantial changes with annealing time for both materials; \(R_x\) is 1–2 orders of magnitude smaller than \(R_s\) at the start of the measurement. For both materials \(R_s\) remains the same and is close to the expected value assuming a YSZ ionic conductivity of 4.75 \(\cdot\) 10\(^{-3}\) S/cm at 600°C.

**EIS - Temperature dependent measurements.**—Freshly deposited LSC and LBC thin films were thermally equilibrated in synthetic air at 604°C for 1 h and then measured between 604°C and 463°C with intervals of 22–24°C. A total of 8 temperature cycles (each consisting of 1 heating and 1 cooling subcycle) was measured for both materials with each temperature cycle taking approx. 8 hours. Representative Nyquist plots at different temperatures during the first temperature cycle are shown in Fig. 7. A very good agreement between equivalent circuit fit (solid line) and measured data (points) is found over the whole temperature range. The general shape of the impedance spectra at medium and low frequencies does not change at lower temperatures. However, at higher frequencies (> 10 kHz) the onset of a semicircle is observed, which represents the ionic resistance of the YSZ electrolyte in parallel to its geometrical capacitance. This part of the spectra was not visible at 604°C, because of the higher bulk relaxation frequency which is proportional to the ionic conductivity. The higher \(R_s\) value found for the LBC sample may be again attributed to a sheet resistance and thus slightly decreased active area of the electrode. Arrhenius plots of the resistances and capacitances extracted from the first temperature cycle together with their activation energies are shown in Fig. 8. For all quantities, except \(C_x\) of LBC, an Arrhenius-type behavior could be determined. The activation energies obtained for 1/\(R_b\), for example, are 1.02 ± 0.01 eV for LSC and 1.04 ± 0.01 eV for LBC, and agree well with literature values reported for the ionic bulk conductivity of 9.5 mol% YSZ single crystals, 1.07 ± 0.06 eV.\(^{11,48,57,58}\)

The activation energy of the oxygen surface exchange is 1.26 ± 0.02 eV for LSC and 1.19 ± 0.11 eV for LBC, calculated from all data of the first temperature cycle. However, as already mentioned in EIS - Time dependent measurements section degradation occurs, leading to an increase of the surface exchange resistance with annealing time also during the temperature cycles, see Fig. 9a. The increase of the absolute values is accompanied by a continuous increase of the
activation energy with number of temperature cycles, as can be seen in Fig. 9b. The activation energy calculated from the last (8th) temperature cycle amounts to 1.33 ± 0.04 eV for LSC and 1.33 ± 0.02 eV for LBC. The surface exchange resistance continuously increases during the temperature cycles. Therefore, the activation energy is shifted to lower values when calculated from a heating subcycle only and to higher values when calculated from a cooling subcycle. The averaged activation energies are shown in Fig. 9b by a polynomial approximation.

For both materials a similar pre-exponential factor of the Arrhenius equation, $5 \cdot 10^{-8} \pm 2 \cdot 10^{-8} \Omega \text{cm}^2$ for LSC and $4 \cdot 10^{-8} \pm 3 \cdot 10^{-8} \Omega \text{cm}^2$ for LBC, is found. Hence, the different oxygen exchange kinetics of the two materials can be mainly attributed to the different activation energies. Moreover, the pre-exponential factor changes by less than 10% during the course of the 8 temperature cycles. This factor includes the high temperature limit of the number of sites participating in the rate limiting step of the oxygen exchange reaction. Even without exact knowledge of the nature of those sites it is reasonable to conclude from this constancy that only a small fraction of possible reaction sites becomes deactivated during the course of the measurements. Thus, mainly the change of the activation energy causes degradation. This change may reflect a homogenous and continuous variation of the chemical environment of active surface sites.

However, for LSC and most other MIECs it is still under debate, which elementary step is rate limiting during the oxygen incorporation i.e. adsorption, dissociation, charge transfer. Hence, it is also difficult to find a more detailed explanation for the degradation. Regardless of the drifting activation energy, it has to be emphasized that both, LSC and LBC, show very low activation energies for the oxygen incorporation compared to other MIEC perovskite-type materials. This makes both of them and especially LBC due to its low absolute polarization resistance highly attractive for the use in intermediate-temperature SOFCs.

For the unknown interfacial process, represented by $R_x$, an activation energy of 1.51 ± 0.11 eV for LSC and 1.34 ± 0.02 eV for LBC was calculated. As already discussed in Electrochemical measurements section, Baumann et al. assigned this resistive contribution to the transfer of $O^2-$ ions across the electrode/electrolyte boundary and determined an activation energy of 1.55 ± 0.05 eV for $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3-\delta$ thin films. Yang et al. assumed a similar reaction mechanism for the medium frequency range and obtained an activation energy of 1.6 eV for $La_{0.5}Sr_{0.5}CoO_3-\delta$ thin films. A more detailed discussion of this minor part to the overall polarization resistance is beyond the scope of this paper.

Fig. 8b shows the activation energies of $C_{\text{chem}}$ for LSC (0.31 ± 0.01 eV) and LBC (0.12 ± 0.01 eV). $C_{\text{chem}}$ is proportional to $\partial \delta / \partial \mu_O$. 

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**Figure 8.** Arrhenius plots of the (a) resistive and (b) capacitive quantities of LSC64 and LBC64 thin films at 0.21 bar $pO_2$ measured during the first cooling (■) and heating (□) subcycle. The activation energies determined from these data are also given.

**Figure 9.** (a) Arrhenius plot of the surface exchange resistance of LSC64 and LBC64 thin films at 0.21 bar $pO_2$. For each thin film 8 temperature cycles (cooling and heating) were performed within 62 hours. (b) The activation energies of $1/R_x$ calculated from each subcycle of (a) and a polynomial approximation is shown (solid line).
with $\mu_0$ being the chemical potential of oxygen in the electrode. Thus, a positive activation energy is in accordance with data obtained by coulometric titration\textsuperscript{59} and thermogravimetry\textsuperscript{60} for polycrystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ bulk samples respectively. A detailed discussion of $C_{\text{chem}}$ and a comparison to literature values is given in EIS – $pO_2$ dependent measurements section. For LBC a clear trend of the temperature dependence of $C_\text{L}$ could not be observed. However, for the LSC thin films an activation energy of $0.20 \pm 0.02$ eV was determined. The positive activation energy again highlights the difference to the interfacial capacitance reported in Ref. 11 for $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ thin films, the latter is negatively thermally activated by $-0.15 \pm 0.05$ eV.

**EIS – $pO_2$ dependent measurements.**—Subsequent to the time dependent measurements, see EIS - Time dependent measurements section, EIS analysis was performed on both materials at constant temperature (604 °C) but different atmospheres. The ratio of the $O_2/N_2$ gas mixture was changed using mass flow controllers to vary the oxygen partial pressure ($pO_2$) between 1 and $2 \times 10^{-4}$ bar $pO_2$. A $pO_2$ cycle from 0.21 to $2 \times 10^{-4}$ and back to 1 bar $pO_2$ was recorded for both materials within 10 hours. Qualitatively, degradation slowed down at lower oxygen partial pressures and therefore values obtained during the decreasing and increasing $pO_2$ subcycle are in good accordance. In Fig. 10 Nyquist plots are shown for the whole oxygen partial pressure range and both materials. It can be seen that the fit becomes less detailed discussion of $C_{\text{chem}}$ and a comparison to literature values is given in EIS – $pO_2$ dependent measurements section. For LBC a clear trend of the temperature dependence of $C_\text{L}$ could not be observed. However, for the LSC thin films an activation energy of $0.20 \pm 0.02$ eV was determined. The positive activation energy again highlights the difference to the interfacial capacitance reported in Ref. 11 for $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ thin films, the latter is negatively thermally activated by $-0.15 \pm 0.05$ eV.

Figure 10. Nyquist plots displaying the dependence of the LSC64 and LBC64 thin film impedance on $pO_2$ at 600 °C. Data points represent measured values and the solid line the corresponding fit according to the model presented in Fig 4b. The insets show the medium-low frequency (25 kHz–100 Hz) range for both materials. For a better overview, only a limited selection of graphs is displayed in the inset of (a).

The oxygen surface exchange resistance exhibits a power law behavior $R_s \sim (pO_2)^m$ for $pO_2 < 5 \times 10^{-2}$ bar. For both materials, exponents $m$ between $-0.65$ to $-0.68$ are found. At higher pressures the $pO_2$ dependence becomes very weak. This is most probably not caused by a change of the rate limiting step to ionic transport; a change of the impedance shape from a semicircle to a Warburg element is not observed and the exponential fitting parameter $n$ of the CPE elements was $>0.98$ at 1 bar $pO_2$. The very similar $pO_2$ dependence of $R_s$ for LSC and LBC again support the assumption that the oxygen reduction mechanism and rate limiting step are the same and only differ in their activation energy. However, a detailed mechanistic interpretation of the $pO_2$ dependence is far from trivial since $pO_2$ not only affects the concentration of adsorbed species but also all defect concentrations in the MIEC. Such a defect chemical analysis is beyond the scope of this work. $R_s$ exhibits large fitting errors of approx. 30–80% for both materials and does not show a clear dependence on the oxygen partial pressure. Also the step change of $R_s$ in Fig. 9a between $1 \times 10^{-2}$ and $2 \times 10^{-2}$ bar $pO_2$ for LSC most probably originates from fit inaccuracies.

Fig. 10b shows that $C_{\text{chem}}$ and $C_\text{L}$ of both materials decrease with increasing oxygen partial pressure, which supports the assumption of $C_\text{L}$ also being a chemical capacitance (of the interface). $C_{\text{chem}}$ of LBC is larger than for LSC over the measured partial pressure range but the difference decreases toward lower $pO_2$. The larger $C_{\text{chem}}$ of LBC indicates that the material is more ready for stoichiometry changes, i.e. is easier to reduce compared to LSC. This may be due to the fact that the larger ionic radius of Ba leads to an increased lattice parameter, as shown in Structural characterization section, and thereby offers more space to form oxygen vacancies and reduced (larger) B cations.\textsuperscript{61} A similar observation was made on $\text{Ba}_x\text{Sr}_{1-x}\text{Ti}_{1-y}\text{Fe}_y\text{O}_{3.3}$ bulk samples using thermogravimetry to analyze the oxygen vacancy concentration.\textsuperscript{22,23} It was found that the non-stoichiometry curve is shifted to higher $pO_2$ for LBC and higher amounts of Ba. In analogy, we may assume that the LBC-$C_{\text{chem}}$ curve in Fig. 11b is shifted compared to LSC by about 3–4 orders of magnitude in $pO_2$ and thus that LBC has a higher vacancy concentration due a lower vacancy formation enthalpy. Unfortunately, $C_{\text{chem}}$ cannot be used to directly determine the concentration of oxygen vacancies, which are the minority charge carriers in the measured $pO_2$ range, since we do not fulfill the prerequisites of a dilute system to apply the corresponding simplified equations.\textsuperscript{47}
Nonetheless, we may compare the measured chemical capacitances of LSC with those expected from non-stoichiometry data of bulk samples. The chemical capacitance is given by

\[
C_{\text{chem}} = \frac{4 \cdot F^2 \cdot d \cdot (3 - \delta)}{V_M \cdot \mu_{\alpha}} \quad [4]
\]

with F being the Faraday constant (96485 C·mol\(^{-1}\)) and \(V_M\) denoting the molar volume of LSC64 (39.12 cm\(^3\)·mol\(^{-1}\)). The non-stoichiometry data from Lankhorst et al.,\(^{62}\) Kawada et al.,\(^{15}\) and Kuhn et al.\(^{64}\) for bulk samples were numerically evaluated in terms of Eq. 4. The resulting \(C_{\text{chem}}\) values are plotted in Fig. 12 together with \(C_{\text{chem}}\) values directly obtained from the impedance measurements in our study but also from measurements on thin films by Kawada\(^{23}\) and Yang\(^{48}\) (open symbols). The asterisk (\(*\)) denotes that data had to be extrapolated, \(d\) is the thickness of the thin films. A dashed line is drawn as guide to the eye.

**Figure 11.** Dependence of the (a) resistive and (b) capacitive quantities of LSC64 and LBC64 thin films on pO\(_2\) at 600°C. Power laws according to \(R_x \sim (\text{pO}_2)^{\eta}\) are highlighted together with their linear fit (solid lines) in (a). The solid lines in (b) represent a guide to the eye.

**Figure 12.** Dependence of the chemical capacitance on pO\(_2\) at 600°C for LSC64 and LSC55, respectively. Data determined from \(\delta(\text{pO}_2)\) slopes of thermogravimetry and coulometric titration measurements by Lankhorst,\(^{62}\) Kawada/Mizusaki\(^{20,63}\) and Kuhn\(^{64}\) on bulk samples (solid line) are shown together with data extracted from impedance measurements on thin films by Kawada\(^{23}\) and Yang\(^{48}\) (open symbols). The asterisk (\(*\)) denotes that data had to be extrapolated. \(d\) is the thickness of the thin films. A dashed line is drawn as guide to the eye.

\[\sigma_{\text{con}} = \frac{\text{conductivity measured in thin films}}{\text{conductivity of bulk material}}\]

**Van der Pauw – electronic conductivity.**—Resistivity measurements using the van der Pauw method\(^{35}\) were performed on LSC and LBC thin films at 0.21 bar pO\(_2\) and different temperatures (80–600°C). This technique is able to determine the thin film resistivity irrespective of the contact placement and the shape of the sample (as long as point contacts are at the periphery of the specimen). To ensure that the YSZ substrate does not influence the thin film conductivity measurement, the conductivity of YSZ obtained during the impedance measurement is far above any conceivable ionic conductivity. The samples were equilibrated at 600°C, 4.75 \cdot 10^{-3} S/cm, is used to compare sheet resistances of substrate and film. From \(R_{\text{sheet}} = \frac{1}{\sigma_{\text{eon}}} \cdot \frac{d}{\pi r^2}\), with \(d\) being the thickness, the measured sheet resistance of the thin film is in the 1% range of the substrate sheet resistance and thus a substrate effect can be safely neglected.

The temperature dependent electronic conductivity resulting after one hour thermal equilibration at 600°C is shown in Fig. 13 for both materials. LSC is known to be primarily electron conducting under these conditions and also LBC thin films revealed conductivity values far above any conceivable ionic conductivity. The samples were equilibrated for 1 hour at 600°C before several temperature cycles were started. In Fig. 13a it can be seen that for both materials a conductivity maximum is found (LSC \(\sigma_{\text{con}} = 1028\) S/cm at 382 ± 8°C, LBC 839 S/cm at 442 ± 5°C). At higher temperatures, \(\sigma_{\text{con}}\) decreases as one would expect for metallic conductivity. The maximum of \(\sigma_{\text{con}}\) for LSC is observed close to the phase transition temperature of \(\sim 390°C\) for bulk samples, where the crystal lattice changes from the low temperature rhombohedral into a cubic structure. However, for bulk LSC64 samples the maximum of \(\sigma_{\text{con}}\) was found to be close to 0°C.

In Fig. 13b additional measurements from Ding et al.\(^{65}\) and Mizusaki et al.\(^{15}\) on LSC64 and LSC73 bulk samples, respectively, are plotted together with LSC64 thin film measurements conducted by Joo et al.\(^{66}\) While the thin film data of Joo and our work correspond well, a difference of about 40% is found between thin film and bulk samples. This could again be caused by defect chemical differences between bulk and thin film but might also be due to the columnar microstructure of our thin films, since the grain boundaries may have a higher resistivity. The somewhat smaller electronic conductivity of LSC was already mentioned in EIS – Initial measurements and...
equivalent circuit model section as the possible cause of an increased high frequency intercept. However, above 400°C the conductivity is still far beyond that of most SOFC cathode materials such as La$_{1-x}$Sr$_x$MnO$_3$ and La$_{1-x}$Sr$_x$FeO$_3$, and sufficient for excellent cathodes. Hence, we conclude that based on its superior oxygen exchange activity LBC is a highly promising material for porous cathodes in intermediate temperature SOFCs.

Conclusions

This work revealed the extraordinarily high catalytic activity of dense La$_{0.6}$Ba$_{0.4}$CoO$_3$–δ (LBC) thin film model electrodes for the oxygen surface exchange. A comparative study with La$_{0.6}$Sr$_{0.4}$CoO$_3$–δ (LSC) thin films showed that the oxygen incorporation of both perovskite-type material is limited by the oxygen surface exchange reaction in the temperature range of 450–600°C. The surface exchange resistance $R_s$ in synthetic air, already known to be very low for LSC (0.5–0.7 Ωcm$^2$ at 604°C, 17–18 Ωcm$^2$ at 463°C) is even lower for LBC (0.15–0.22 Ωcm$^2$ at 604°C, 5.8–6 Ωcm$^2$ at 463°C). Furthermore, a very low activation energy of $R_s$ was found for both materials (LSC 1.26 ± 0.11 eV, LBC 1.19 ± 0.11 eV) in the temperature range relevant for intermediate temperature SOFC applications. A very similar oxygen partial pressure dependency of the surface exchange resistance was found for both materials and together with other similarities this suggests the same oxygen incorporation mechanism. Differences and variations of $R_s$ are mainly caused by changes of the activation energy. The larger chemical capacitance of LBC is attributed to an increased reducibility of the perovskite lattice caused by the introduction of the larger Ba ion in comparison to Sr. Chemical capacitances of LSC films are close to those expected from bulk defect chemical data. The temperature dependence of the electronic conductivity revealed a maximum for LSC $\sigma_{\text{eon}} = 1028$ S/cm at 382 ± 8°C and LBC 839 S/cm at 442 ± 5°C. At all relevant temperatures, conductivity values are by far sufficient for application in SOFCs.

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