

Correlation of thermal properties and electrical conductivity of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ material for solid oxide fuel cells

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Abstract A copper-doped ferrite with the chemical composition $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LaSrCuFe) was prepared using the classical ceramics method starting from the oxides. The linear thermal expansion coefficient in air was measured in the temperature range between 550 and 1,250 K to be between 10×10^{-6} and $15 \times 10^{-6} \text{ K}^{-1}$. The electrical conductivity in air was found to be higher than 100 S cm^{-1} for temperatures lower than 1,100 K. A change of oxygen stoichiometry was found above 650 K in an atmosphere of 20 vol% oxygen with argon. This change can be correlated with the electrical conductivity.

Keywords Cathode · Oxygen stoichiometry · Mixed conductor · SOFC · Perovskite

1 Introduction

Solid oxide fuel cells (SOFCs) are commonly operated at temperatures above 700 °C. Lowering the temperature below 700 °C could lead to a longer lifetime of all components needed in a complete SOFC system since thermal and mechanical stresses can be reduced [1]. The cathode is one part of the SOFC system that has to be improved for lowering the operation temperature. It has to provide a sufficiently high catalytic activity for oxygen to provide enough oxygen ions from the oxygen molecules in air for

the transport towards and through the electrolyte [2]. A typical cathode material is strontium doped lanthanum manganite (LSM). However, this material possesses only little oxygen ion conductivity [3]. Thus, the active interface for oxygen conversion and transport is mainly limited to the so-called triple phase boundary (TPB) [4]. Therefore, a certain degree of oxygen ion conduction is wanted to increase the effective surface area for the oxygen molecule-to-ion conversion. Polarization losses can also be reduced by these means [5]. Additionally, the electrical conductivity should be as high as possible to reduce the ohmic losses. Furthermore, the mechanical properties must match those of the other components of a SOFC system [6, 7]. Especially the thermal expansion coefficient (TEC) should be comparable in order to reduce thermal stresses induced mainly during thermal cycling and due to thermal gradients within the SOFC. A commonly used alternative to the standard cathode material LSM is a strontium and cobalt doped lanthanum ferrite (LaSrCoFe, or more popular LSCF) [6, 8].

The LaSrCoFe is a so-called mixed ionic and electronic conductor (MIEC), thus providing electronic and ionic conductivity, while LSM is mainly an electronic conductor [9]. SOFC cells built with LaSrCoFe can therefore provide higher power densities at the same temperature compared to those built with LSM since the effective area for the oxygen catalysis is increased and additional ion conduction paths can be used [10]. Nevertheless, the LSM is a less chemically reactive cathode material compared to LaSrCoFe [11]. This makes LSM more attractive for high temperature applications. However, this issue becomes less important with reducing temperatures since the reaction kinetics is reduced while the oxygen molecule-to-ion conversion e.g. the surface exchange property becomes more important.

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To maintain a high catalytic activity at the reduced temperatures, copper doping instead of cobalt doping of the ferrite is considered. Alifanti et al. [12] examined several strontium and transition metal doped lanthanum ferrites and found the copper doped ferrite showing the highest catalytic activity for the combustion of hydrocarbons among these ferrites. Additionally, Coffey et al. [13] showed that the valence state of copper has a great influence on the electrical properties of the LaSrCuFe.

The aim of this work is to provide more data about LaSrCuFe for the use as cathode material. The focus was set on the thermal expansion coefficient and the stoichiometry change in air.

2 Experimental

2.1 Preparation

Stoichiometric amounts of dried lanthanum oxide (La_2O_3 , Fluka, Germany, 99.98%), dried strontium carbonate (SrCO_3 , Merck, Germany, >99%), iron oxide (Fe_2O_3 , Merck, Germany, pro analysi) and copper oxide (CuO , Merck, Germany, pro analysi) powders were mixed to the final composition of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LaSrCuFe). This powder mixture was homogenized by ball milling for 48 h in ethanol. The dried mixture was calcined at 1,225 K for 12 h. Ball milling was repeated for 72 h to obtain a fine powder. The calcined powder was pressed to bars using small amounts of a binder. The applied pressure was 125 MPa and the bars had the dimensions of approximately $40 \times 5 \times 5 \text{ mm}^3$. The pressed bars were sintered at 1,473 K for 6 h in air. The chemical composition of the calcined powder was checked using optical emission spectroscopy with inductively coupled plasma (ICP/OES) and found to be similar to the weigh-in composition.

2.2 Characterization

The X-ray diffraction (XRD) measurement was carried out on the calcined powder using a Siemens D500 diffractometer in the angular range of 2Θ between 20° and 70° using $\text{Cu-K}\alpha$ radiation.

The electrical conductivity measurements were carried out using a Solartron 1260 impedance spectrometer and a four-point setup. The recorded frequency range was from 1 Hz to 100 kHz with an applied monitored constant AC voltage of 10 mV. Sintered bars were used for these measurements and the surfaces were ground with P1200 grinding paper before usage to avoid surface effects. Platinum paste was applied to connect the working and the voltage sensing electrodes. The paste was sintered at 1,273 K for 12 h prior to the measurements. The temperature range examined was

between 1,250 and 666 K. The temperature was kept constant until at least three subsequent impedance measurements showed similar values.

The impedance spectra showed in general only a resistive component, as can be seen for the nearly constant value of phase and impedance over a large frequency range in Fig. 1. Therefore, the impedance values obtained in the frequency range from 1 Hz up to 1 kHz were averaged to a single value. This value was used to calculate the specific electrical conductivity that includes the geometry of the samples and the distances of the voltage sensing electrodes.

The thermal expansion coefficient (TEC) was measured using a Netzsch ED 402 differential dilatometer. Two sintered bars were cut to 20 mm length for this measurement. The samples were measured from room temperature to 1,323 K with a heating rate of 3 K/min. The measurements of the TEC were carried out in air and a nitrogen atmosphere with an oxygen partial pressure of 10^{-5} bar. Two thermal expansion coefficients were considered, the technical and the true. The definitions of the different TECs are given in Table 1 [14–17].

Differential thermal analysis with simultaneous thermogravimetry (DTA/TG) was carried out using a Netzsch DTA 449 device in the temperature range between 673 and 1,323 K and a heating rate of ± 5 K/min. Calcined powder was used and the first cooling was carried out in air. The

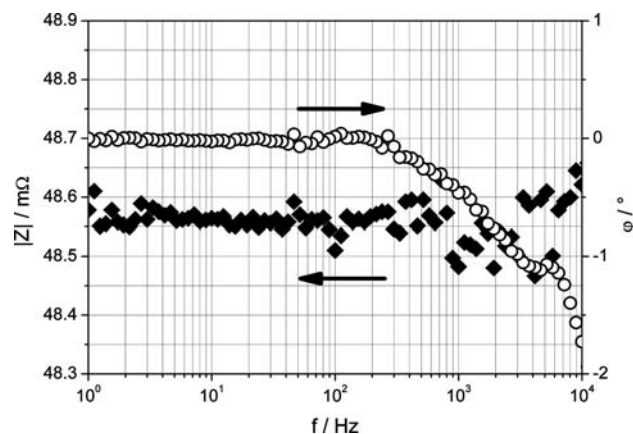


Fig. 1 Typical impedance spectra of LaSrCuFe

Table 1 Definition of the different thermal expansion coefficient (TEC) according to [14–17]

Type of TEC	Definition
Technical/average	$\alpha = 1/L_0 [(L_1 - L_0)/(T_1 - T_0)] = (1/L_0) (\Delta L/\Delta T)$
Instantaneous	$\alpha_I = (1/L_0) (L_2 - L_1)/(T_2 - T_1)$
True	$\alpha_T = (1/L) dL/dT$

T (actual) temperature of sample, L (actual) length of sample, L_0 length at reference temperature T_0 , L_1 length at temperature T_1 , L_2 length at temperature T_2

gas supply was then switched to nitrogen and two subsequent thermo cycles were carried out.

The measurement of the stoichiometry change was carried out using a Mettler-Toledo UMT5 balance device. This device is capable of measuring masses up to 5 g with a resolution up to 100 ng. Since the balance is of asymmetric design, zero correction and mass correction using a highly compacted and pure alumina reference sample was carried out on the measurement data before calculating the stoichiometry change. The stoichiometry change was calculated assuming an ideal perovskite structure ($ABO_{3-\delta}$, $\delta = 0$) of the LaSrCuFe and therefore a negligible amount of oxygen vacancies at room temperature and atmospheric condition. Since the A sites of the perovskite are occupied by the trivalent lanthanum ions (La^{3+}) and the bivalent strontium ions (Sr^{2+}), the electric charge of the B site of the perovskite has to be compensated by the copper and iron ions to fulfil the total electrical cation charge of +6 of the perovskite unit cell. This is accomplished by assuming mixed valence states of the iron (Fe^{3+} , Fe^{4+}) and the copper cations (Cu^{2+} , Cu^{3+}). Although trivalent copper ions are not common in chemistry, they can exist in certain solids and especially perovskite structures [18–20]. However, trivalent copper or tetravalent iron can only exist at high oxygen partial pressures and low temperature. A partial reduction to the next lower oxidation state is compensated by the release of oxygen out of the perovskite, forming an oxygen vacancy, the so-called change of oxygen stoichiometry ($\Delta\delta$). Sufficient high changes of δ can therefore be detected by a weight change of the sample. A low heating rate to $\pm 0.625\text{ K min}^{-1}$ and a ‘reversed’ thermo cycle, e.g. starting at high to low temperature, was used to measure the samples in a nearly equilibrated state.

3 Results and discussion

3.1 X-ray diffraction pattern (XRD)

The calcined LaSrCuFe material shows two phases according to Fig. 2. The dominant lines can be assigned to a perovskite structure, which is similar to that of a strontium doped lanthanum ferrite. However, La_2CuO_4 was identified as the secondary phase. This phase was identified for similar chemical compositions by Coffey and co-workers [13, 21]. The formation of the secondary phase may be due to the classical ceramics method which provides a lower homogeneity of the starting materials before calcination than a wet chemical synthesis [12, 13, 22]. However, Park et al. [23] found a correlation between reducing conditions and amount of secondary phases for the classical ceramic method. This might be an indication

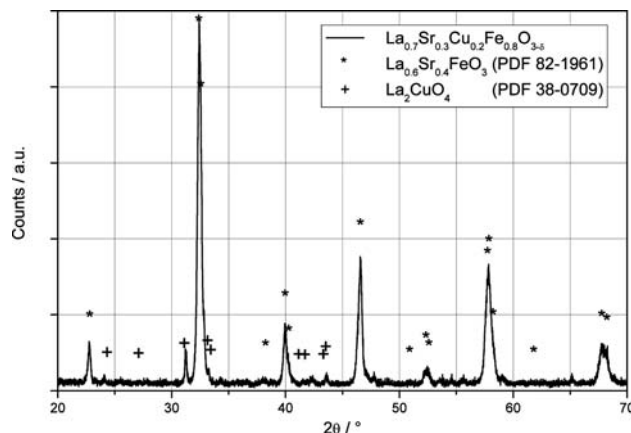


Fig. 2 XRD pattern of the calcined LaSrCuFe powder

that this kind of material should be sintered in an oxygen-enriched atmosphere.

3.2 Thermal expansion coefficient (TEC)

The technical TEC of the LaSrCuFe is in the range between 8×10^{-6} and $15 \times 10^{-6}\text{ K}^{-1}$ which is in good agreement with Rieke et al. [21]. The TEC curve can be split in three parts according to Fig. 3. In the first part up to 725 K there is an increase of the TEC up to approximately $12 \times 10^{-6}\text{ K}^{-1}$. In the second part between 725 and 1,250 K the TEC increases nearly linear with temperature. In the third part above 1,250 K, a decrease in TEC with temperature becomes apparent. The reason for this cannot be explained using the TEC curve solely.

The true TEC (α_{true}) as shown in Fig. 4 derived directly from the elongation data shows the three areas more clearly. The α_{true} had to be smoothed by using 15 point adjacent averaging since the scatter due to noise superimposes the trend. A linear increase of α_{true} with reciprocal temperature can be found in the Arrhenius-like plot in the

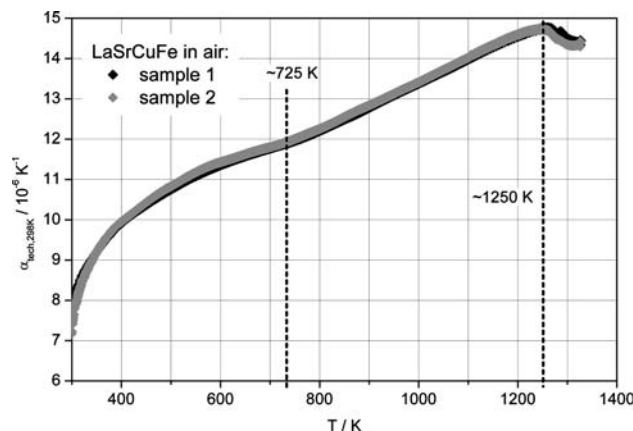


Fig. 3 Technical thermal expansion coefficient in air of sintered LaSrCuFe

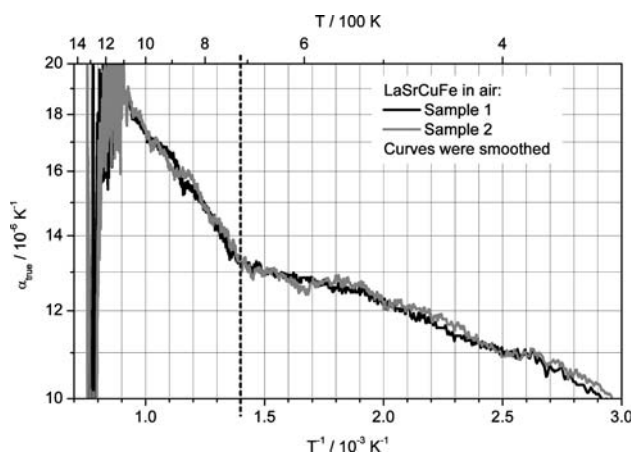


Fig. 4 True thermal expansion coefficient of the sintered LaSrCuFe in air. Curves were smoothed with 15 point adjacent averaging to reduce scattering due to noise

temperature range between 725 and 1,175 K. This indicates a thermally activated process in this temperature range.

Beside the measurements in air, the sample was heated in a nitrogen atmosphere. The material apparently did not decompose, although it was heated up to 1,325 K during the measurement. It can be suggested that the material annealed in air atmosphere undergoes at least two structural changes during heating in the nitrogen atmosphere as can be seen in Fig. 5. A repeated heating in nitrogen atmosphere does not give any indication of a phase transition. Moreover, the TEC of the sample reduced in nitrogen is lower at high temperatures than that of the sample oxidized in air for temperatures above 800 K. This may demonstrate the influence of chemical expansion, similar to that investigated for strontium doped lanthanum cobaltite (LaSrCo) [24]. Nevertheless, the TEC can exceed more than +20% of the value for the oxidized state of the LaSrCuFe during the reducing step. This might be due to

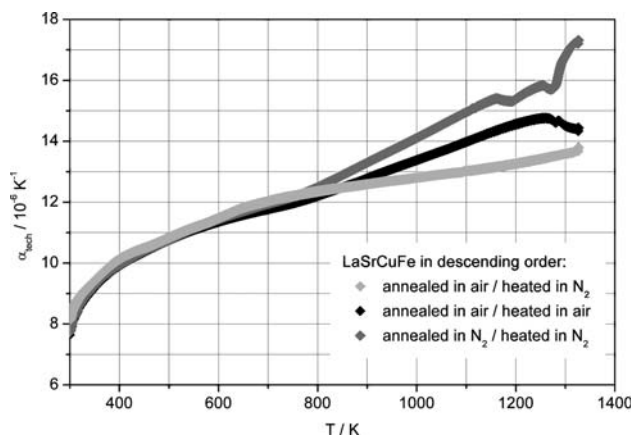


Fig. 5 Technical thermal expansion coefficient of LaSrCuFe in air and nitrogen atmosphere

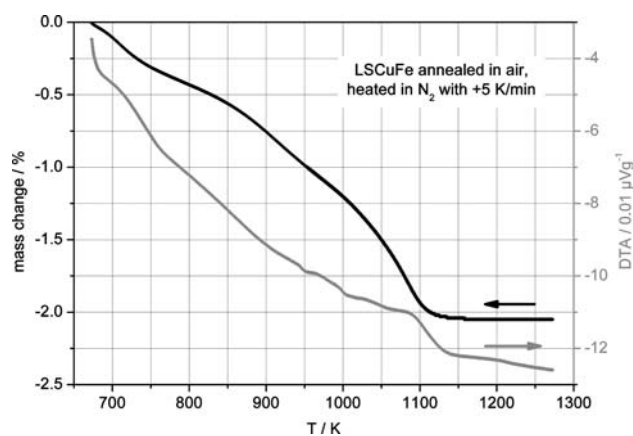


Fig. 6 DTA/TG of sintered LaSrCuFe annealed in air heated in nitrogen

the formation of oxygen vacancies during reducing and should be considered when designing an application with this material.

3.3 Effect of change to nitrogen atmosphere

The TEC measurements showed at least two abnormalities for the samples annealed in air and measured in nitrogen atmosphere. A DTA/TG measurement was carried out under the same conditions to clarify the reasons.

The result of this measurement is shown in Fig. 6. The LaSrCuFe loses up to approximately 2% of its mass upon heating. At about 1,125 K, this is accompanied with a change in the DTA signal. This can be related to the first change in TEC during heating. Since a changed DTA signal may reflect a different heat capacity, this can support the assumption of a phase transition.

The second abnormality in TEC starting even below 1,273 K does not have any apparent influences on the DTA/TG measurements.

3.4 Oxygen stoichiometry change

The oxygen stoichiometry measurements carried out shows three distinct areas as can be seen in Fig. 7. The first area up to 670 K shows no significant change of oxygen stoichiometry ($\Delta\delta$). The second area in the temperature range between 750 and 1,250 K shows a nearly linear increasing non-stoichiometry with temperature. At about 1,250 K a significant change in oxygen stoichiometry appears. In the third area above 1,300 K again a nearly linear increase of non-stoichiometry with temperature appears.

The low temperature transition appears between 575 and 825 K. A hysteresis in oxygen stoichiometry is apparent in that temperature range. Since a bulk sample was used for the measurement instead of powder, surface activity and

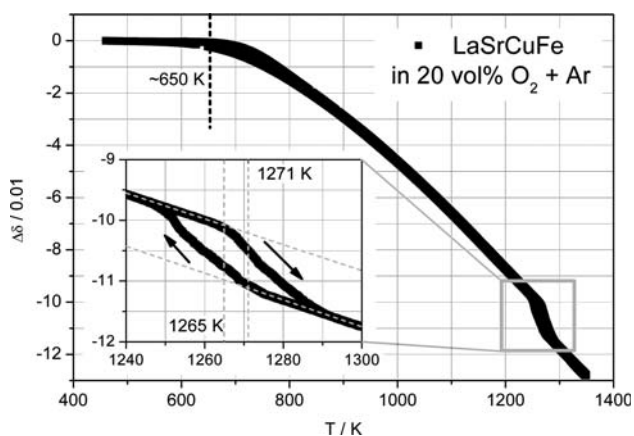


Fig. 7 The stoichiometry change of LaSrCuFe in air with a heating rate to $\pm 0.625 \text{ K min}^{-1}$

diffusion effects as well as internal mechanical strains might delay the oxygen uptake to its equilibrium state during cooling despite the low cooling rate of 0.625 K min^{-1} . On the other hand, the oxygen stoichiometry seems to be in equilibrium at low temperature since no positive oxygen stoichiometry change, e.g. indicated by a mass increase, is observed upon heating.

The high temperature transition appears between 1,250 and 1,290 K. In the work of Park et al. [23], a similar behaviour was found when the oxygen partial pressure was changed instead of temperature. It is interesting to note, that this transition takes place at an oxygen stoichiometry change of $\Delta\delta = -0.1$. If a perovskite structure with a negligible amount of oxygen vacancies is assumed as reference state at low temperature, e.g. the oxygen stoichiometry amounts to exactly 3, this may reflect the complete reduction of the copper from a trivalent to divalent state.

Since a fully occupied oxygen sublattice of the perovskite is therefore required, the valence sum of the cations needs to be +6. Since the A sites are occupied by fixed valence ions (La and Sr) the mean valence state thereof amounts to $0.7 \times (+3) + 0.3 \times (+2) = +2.7$. Therefore, the mean valence state of the B sites needs to be +3.3 to fulfil charge neutrality. Since both cations, the Fe and the Cu, can have different valence states, several combinations can be considered. For the iron, only the Fe(III) and Fe(IV) ions were considered, since those were the most likely ones and reported by Patrakeeve et al. [25] for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ compounds. For the copper cation, the situation is more complicated. Three different valence states can be considered: Cu(I), Cu(II) and Cu(III). Yu et al. investigated $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5-\delta}$ perovskites [26] and showed that a $\text{La}_{0.7}\text{Sr}_{0.3}\text{CuO}_{2.5-\delta}$ possesses up to 19.6% of Cu(III) ions at atmospheric condition. Therefore, only Cu(II) and Cu(III) ions were considered. The two possible boundary conditions (options) for the valence states are given in Table 2.

Table 2 Boundaries for the cation valences of Cu and Fe for the LaSrCuFe material

Option	Copper (total 0.2)		Iron (total 0.8)	
	Cu(II)	Cu(III)	Fe(III)	Fe(IV)
1	–	0.2	0.5	0.3
2	0.2	–	0.3	0.5

Park et al. [23] propose that the predominant cation being reduced would be Fe(IV) rather than Cu(III). From the $\Delta\delta$ measurements, it seems to be opposite way, since the transition appears at a $\Delta\delta$ value of -0.1 and not of -0.15 as it is expected for the Fe(III)/Fe(IV) transition. Mössbauer spectroscopy, electron spin resonance measurements (ESR) or other techniques are required for at least one reference state to clarify this discrepancy. However, the temperature of this transition could be determined to $1,268 \pm 5 \text{ K}$ by averaging the onset temperature from the heating and cooling curve.

The following strong increase of oxygen non-stoichiometry with temperature above 1,300 K might be explained by a structural rearrangement of the lattice and thus changing the local charges. Additionally such a phase transition changes the TEC, which is in good agreement with the findings mentioned above. Another possibility is the formation of a liquid phase as reported by Coffey et al. [13] although we did not find any obvious evidence for that.

3.5 Electrical conductivity

The specific electrical conductivity (σ_{spec}) shown in Fig. 8 is in agreement with the data published by Coffey et al. [13], although our conductivity values are smaller. A reason for this might be the higher amount of the secondary phase found for our samples. We also used a different method for the measurement. Coffey et al. used the

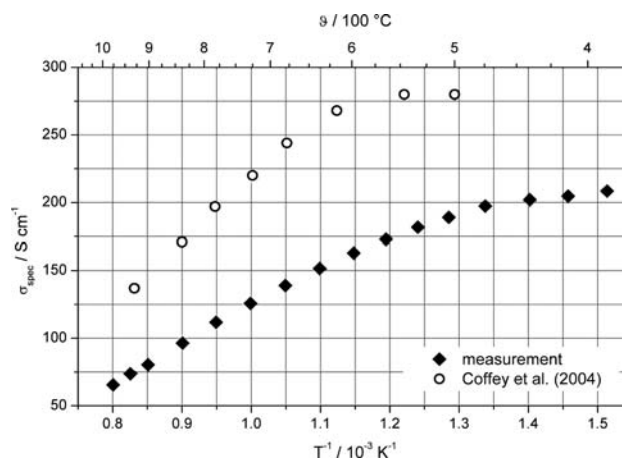


Fig. 8 Specific electrical conductivity of sintered LaSrCuFe in air

DC-impedance and changed the temperature with a constant heating rate. We used the steady state value of impedance measurements obtained for a specific temperature and averaged the impedance for a range of frequency values.

3.6 Correlation

The data obtained from the TEC, conductivity and oxygen stoichiometry change measurements are shown together in Fig. 9. It is apparent that all measurements correlate. Below 670 K the conductivity data were not measured, but from the work of Park et al. [23] one can estimate the electrical conductivity values at lower temperatures. It is expected that the electrical conductivity will increase slightly with increasing temperature, indicating predominantly electronic conductivity. Additionally, the true TEC and the oxygen stoichiometry are nearly constant for temperatures below 670 K.

Between 670 and 1,270 K, the oxygen stoichiometry decreases with increasing temperature. This indicates the formation of more oxygen vacancies. However, the increasing true TEC indicates that these formed vacancies or unoccupied oxygen cation sites use more volume than an occupied anion site. Additionally, the electrical conductivity decreases with increasing oxygen non-stoichiometry, e.g. the formation of oxygen vacancies lowers the electrical conductivity. However, the drop of conductivity with temperature is so strong, that it may not be explained solely by the formation of additional oxygen vacancies. Since the TEC increases additionally in this temperature range, an additional effect of the crystallographic structure is supposed which might be induced by the change of valence of some cations. Since a small polaron conduction mechanism is most likely for this material [13, 27], effects changing the unit cell parameters and, therefore, changing the

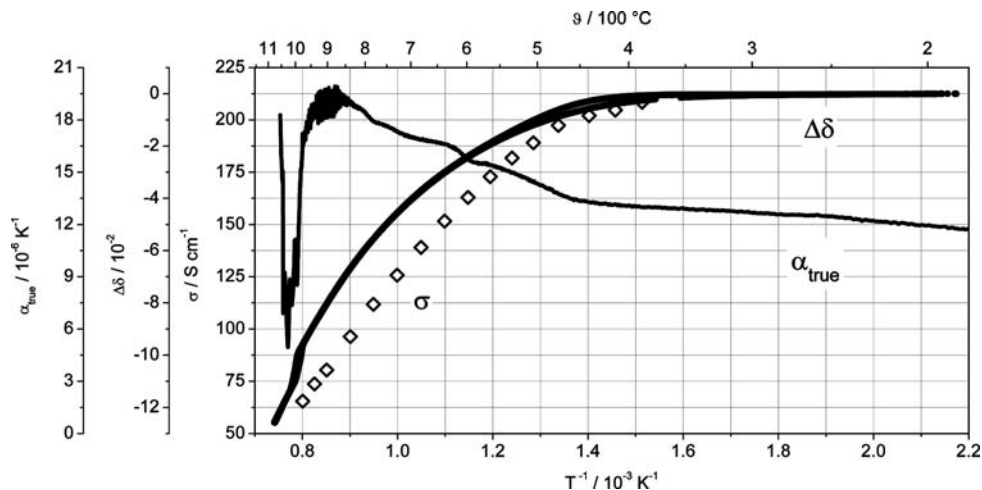
bonding conditions may have a strong effect on the electrical conductivity.

4 Summary

A copper and strontium doped lanthanum ferrite (LaSrCuFe) with the chemical composition to $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ was examined in order to evaluate its possible use as cathode material for SOFCs. The material was nearly single phase after sintering at 1,473 K for 6 h in air and shows a perovskite structure. It is stable in air up to 1,225 K, e.g. under these conditions the material does not show any major phase change. The maximum electrical conductivity in air was obtained at about 670 K and amounts to about 200 S cm^{-1} . This electrical conductivity drops with further increasing temperatures. This is accompanied by a mass loss due to a reversible oxygen release. At $1,267 \pm 5 \text{ K}$ in air a structural or phase change appears according to the stoichiometry change measurements. The stoichiometry change related to room temperature amounts to $\Delta\delta = -0.1$ at this temperature and the electrical conductivity drops to roughly one-third of the maximum value measured at 670 K. The true thermal expansion coefficient, which is nearly constant for temperatures below 670 K, decreases nearly linear with the reciprocal temperature from $12 \times 10^{-6} \text{ K}^{-1}$ up to $19 \times 10^{-6} \text{ K}^{-1}$ at 1,175 K. This is believed to be due to the oxygen release. The phase change itself shows a hysteresis. The temperature window amounts to about 40 K even at a low heating rate of $\pm 0.625 \text{ K min}^{-1}$. The technical thermal expansion coefficient (TEC) of the LaSrCuFe amounts to $11 \times 10^{-6} \text{ K}^{-1}$ at 673 K and increases to $15 \times 10^{-6} \text{ K}^{-1}$ at 1,225 K.

When the sample annealed in air is heated in nitrogen atmosphere, the transition temperature is lowered to about 1,100 K according to the DTA/TG results. Above this

Fig. 9 Correlation between electrical conductivity, oxygen stoichiometry change and true TEC



temperature, no more oxygen is released from the LaSrCuFe. If heated further, another phase transition is apparent according to the TEC measurements at about 1,275 K. An overall maximum value for the technical TEC of $17.5 \times 10^{-6} \text{ K}^{-1}$ was measured at this temperature.

However, when the LaSrCuFe material is annealed and measured in a nitrogen atmosphere, no phase transitions were apparent.

Therefore, the LaSrCuFe might be a suitable cathode material for SOFC operated below 1,075 K. If this temperature condition is met, the material shows an electrical conductivity higher than 100 Scm^{-1} and a moderate value for the TEC.

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