Contact Resistance of Ceramic Interfaces Between Materials Used for Solid Oxide Fuel Cell Applications

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Contact Resistance of Ceramic Interfaces Between Materials Used for Solid Oxide Fuel Cell Applications

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Abstract
Contact resistance of ceramic interfaces between materials used for solid oxide fuel cell applications.

The contact resistance can be divided into two main contributions. The small area of contact between ceramic components results in resistance due to current constriction. Resistive phases or potential barriers at the interface result in an interface contribution to the contact resistance, which may be smaller or larger than the constriction resistance.

The contact resistance between pairs of three different materials were analysed (strontium doped lanthanum manganite, yttria stabilised zirconia and strontium and nickel doped lanthanum cobaltite), and the effects of temperature, atmosphere, polarisation and mechanical load on the contact resistance were investigated.

The investigations revealed that the mechanical load of a ceramic contact has a high influence on the contact resistance, and generally power law dependence between the contact resistance and the mechanical load was found. The influence of the mechanical load on the contact resistance was ascribed to an area effect.

The contact resistance of the investigated materials was dominated by current constriction at high temperatures. The measured contact resistance was comparable to the resistance calculated on basis of the contact areas found by optical and electron microscopy. At low temperatures, the interface contribution to the contact resistance was dominating. The cobaltite interface could be described by one potential barrier at the contact interface, whereas the manganite interfaces required several consecutive potential barriers to model the observed behaviour. The current-voltage behaviour of the YSZ contact interfaces was only weakly non-linear, and could be described by 22±1 barriers in series.

Contact interfaces with sinterable contact layers were also investigated, and the measured contact resistance for these interfaces were more than 10 times less than for the other interfaces.

This thesis is submitted in partial fulfillment of the requirements for obtaining the Ph.D. degree at the Technical University of Denmark at the Department of Chemistry.
**Resume**

Kontaktmodstand mellem keramiske materialer til brug i fastoxid-brændselsceller.

Kontaktmodstanden mellem keramiske enner består af to bidrag. Et lille kontaktareal i keramiske kontakter bidrager til kontaktmodstanden p.g.a. indsnævring af strømvejen. Derudover vil resistive faser eller potentialbarrierer i selve kontaktemrådet også bidrage til kontaktmodstanden. Dette bidrag kan være større end eller mindre end indsnævrings-bidraget.


Kontakter med sintringsaktive kontaktlag blev også undersøgt, og kontaktmodstanden for disse kontakter var mere end 10 gange lavere end for de andre kontakttyper.
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<th>Description</th>
<th>Unit</th>
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<td>Fracture strength equivalent contact area</td>
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<td>Area specific contact resistance</td>
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<td>$Δz$</td>
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1 Introduction

If solid oxide fuel cells (SOFC) are to become economically competitive, the contact resistance in the stacks has to be lowered. Therefore, an understanding of the contact resistance between ceramic components is important. In most SOFC designs, contacts between self-supporting ceramic elements can not be avoided and losses due to contact resistance between the cells and interconnects have been reported [1–3].

High contact resistance between ceramic components consists of two contributions. These include current constriction due to small area of contact and formation of resistive phases between the components. Good individual models for these mechanisms exist, but the combined effect is not well investigated. Potential barriers at the contact interface result in contact resistance. Some resistive phases are potential barriers, which may behave non-Ohmic under certain circumstances. To eliminate the influence of resistive phases formed because of chemical incompatibility between the two materials, contact pairs of identical materials were investigated. Although the contacts used in stacking of SOFC’s are not single material contacts, the contact resistance due to current constriction, resistive phases or potential barriers will still be important.

Two electronic conducting materials (a doped manganite and a doped cobaltite) and one ionic conductor (yttria doped zirconia) were chosen for investigation. The materials were chosen because they are all used in current SOFC-technology. The zirconia and the manganite showed increasing conductivity at increasing temperature, whereas the cobaltite conductivity decreased with increasing temperature.

The Danish Research Academy granted funding for this investigation. My supervisors were:

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¹January 20, 2001

Chapters 2 to 4 of this thesis contain a short introduction to SOFC technology followed by a theoretical description of contact resistance and contact deformation. This part also includes a mathematical description of potential barriers. The experimental procedures are described in chapter 5 and the results are presented in chapters 6 to 10. Chapter 11 discusses these results and the conclusion is in chapter 12.

Søren Koch
31 / 1 2002
2 Fuel cells

Fuel cells have been known for over a century [4]. Originally fuel cells were considered of little practical use, as the power density was low and other power sources were available. Development of the first fuel cells for practical use began in the 1930’s with the alkaline fuel cell design. This fuel cell uses concentrated potassium hydroxide as the electrolyte and was used in the American space programme to power manned space vehicles although now an other type of fuel cell is used [5].

2.1 Principle of operation

Fuel cells operate by combining fuel and oxidiser without direct combustion. This is achieved by placing an electrolyte between two electrodes in contact with the fuel and the oxidiser respectively (figure 2.1). The ideal electrolyte conducts ions, but not electrons (or holes). In order for the fuel (e.g. hydrogen) to combine with the oxidiser (e.g. air) in a fuel cell, the oxygen has to be reduced to oxide ions at the cathode side of the electrolyte so they can travel by ionic conduction through the electrolyte. At the anode side of the electrolyte, the oxygen ions combine with the hydrogen producing water and electrons [6] (in the case of a proton conducting electrolyte, hydrogen ions travel through the electrolyte). The electrons for the oxygen reduction at the cathode side are supplied by the external circuit from the electrons liberated at the anode side by the hydrogen oxidation process as shown in figure 2.1. This results in a dc current through the external circuit. The only difference between solid oxide fuel cells and conventional fuel cells is the solid electrolyte.

![Figure 2.1. Model of the first reported fuel cell. Diluted sulphuric acid was used for electrolyte and platinum was used for electrodes [4].](image)

The potential difference between the electrodes \( E_{\text{cell}} \) depends on the fuels and oxidisers used and on the current density. The open circuit potential is determined by the Nernst equation [7]:

\[
E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q
\]

(2.1)

where \( Q \) is the reaction quotient, \( E_{\text{cell}}^\circ \) is the cell potential under standard conditions, \( R \)
is the gas constant, \( F \) is Faraday’s constant, \( n \) is the number of transferred electrons and \( T \) is the temperature.

If the oxygen partial pressure on the cathode side is constant (e.g. cathode in contact with air) then the cell voltage is dependent on the fuel gas composition as this determines the oxygen partial pressure on the anode side. If a mixture of \( \text{H}_2 \) and \( \text{H}_2\text{O} \) is used, then their concentrations and the equilibrium constant of the reaction

\[
2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}
\]  

(2.2)
determines the cell voltage. As the equilibrium constant can be determined by the Gibbs’ free energy of the reaction [7], the reversible cell voltage of an \( \text{H}_2/\text{H}_2\text{O} \)-air cell becomes [6]:

\[
E^\circ = -\Delta G_{\text{eq.2.2}}^\circ \cdot \frac{4F}{RT} \ln P_{O_{2,c}} + \frac{RT}{4F} \ln \frac{P_{H_2(a)}}{P_{H_2O(a)}}
\]  

(2.3)

If there was no resistive losses and reaction rates were infinite then this equation would determine the cell voltage. Unfortunately this is not the case. Ohmic losses in the electrolyte and electrodes results in a potential drop:

\[
\Delta U = I \cdot R
\]  

(2.4)

In order for electrochemical reactions to occur, an overpotential (\( \eta \) polarisation) at the electrolyte - electrode interface have to exists and depends on the current density [6, 8]. Absorption of reactants, desorption of reaction products and diffusion of reactants and products are mass transport limitations and may reduce cell performance. This ultimately result in an upper limit of the current density [8].

A fourth factor contributing to lowering the output cell voltage is contact resistance between the individual elements of a fuel cell stack. This arises from several factors including constriction resistance due to low relative contact area (refer section 3.1), and resistive phases forming between different components in the fuel cell.

The effective cell voltage obtained is determined by the following equation:

\[
\Delta U_{\text{cell}} = E_{\text{cell}} - (\eta_{\text{polarisation}} + \eta_{\text{mass transport}})
\]

\[
- I \left( R_{\text{electrolyte}} + R_{\text{electrodes}} + R_{\text{contact}} \right)
\]

(2.5)

The first two resistive losses as well as the mass transport overpotential in equation 2.5 are somewhat understood and described [6, 8]. They can be minimised by using the correct combination of electrolyte and electrodes and by controlling the microstructure of the materials. Contact resistance is usually not important in conventional (e.g. liquid electrolyte) fuel cells with noble metal electrodes. In solid oxide fuel cells, however, contact resistance plays a significant role [2, 3] and is not well understood.

### 2.2 Solid oxide fuel cells

Solid oxide fuel cells have been known for more than 60 years and were discovered in 1937 by Bauer and Preis [6, 9] but development of practically usable SOFC’s first began in the beginning of the 1960’s [6].

The advantage of using only solid materials is that they require less maintenance and in general are simpler to operate. Because the solid electrolyte can be made thinner than liquid electrolytes, solid oxide fuel cells can be made more compact.

Another advantage of SOFC’s is that they operate at high temperatures compared to other types of fuel cells, eliminating the need for expensive noble metal catalysts at the electrode-electrolyte interface. The higher temperatures allow the use of waste heat for room heating (for small units) or generation of electricity by steam turbines (for larger plants) [6]. One disadvantage of solid electrolytes is that they are more prone to mechanical failure that can short out individual cells, resulting in direct combustion of the fuel.
and leading to lower efficiency. Another disadvantage is that the materials most suited for electrolytes and electrodes are expensive.

The high temperatures of operation may also be problematic. Rapid start up of a solid oxide fuel cell results in high thermal stresses developing due to large thermal gradients within the fuel cells. This may lead to cracking of the ceramic materials and this always degrades the fuel cell. Some designs of SOFC try to circumvent this problem by using many very small fuel cells that can be heated more rapidly, without risking fracture [10]. The high internal temperatures in SOFC’s are a problem even under static conditions, as the materials connected to the fuel cell stack must be stable at these temperatures, and must be able to handle the thermal gradients between the fuel cell stack and the surroundings.

All these problems have to be overcome if solid oxide fuel cells are to be used in consumer products.

2.3 Components in modern SOFC’s

2.3.1 Electrolyte

Most modern SOFC’s use yttria stabilised zirconia (YSZ) for the electrolyte [3, 6] but other materials have been proposed. Some of these are as doped cerium oxide [6] and LaGaO$_3$ based materials [11–13]. Thin electrolytes are used to lower the ohmic loss as all materials suitable for fuel cells have low ionic conductivities [14–16]. The use of thin electrolytes results in other problems. In order to achieve high fuel efficiency, the electrolyte must be dense and free of cracks. Small pores and cracks might lead to direct combustion of the fuel, resulting in high local temperatures, possibly fast degradation of the cell and loss in electrical efficiency [6].

2.3.2 Electrodes

The most common anode material is a cermet of metallic nickel and YSZ [6, 10, 17]. Nickel has a large mismatch in thermal expansion compared to the YSZ used in the electrolyte preventing the use of an all nickel electrode. The cermet both reduce / prevent thermal mismatch between nickel and the YSZ and produce a large three phase boundary. One problem with the use of cermets, is that the nickel metal tends to sinter over time, thereby reducing the active surface of the electrode [3]. This can be controlled, however, by choosing the right grain size and microstructure of the cermet [6].

Several materials have been proposed for the cathode material. Doped indium oxide was the first non metal used [3, 6]. Later strontium doped lanthanum manganite (LSM) was preferred [18–20] but other oxides have also been proposed [11] as well as composite cathodes [21]. Cathode materials must be stable in oxidising atmospheres at high temperatures. This excludes all but the expensive noble metals and certain oxides.

Thermal expansion is also a matter of concern for cathode materials. The cathode material must have a thermal expansion close to that of the electrolyte over the entire temperature range, as thermal stresses may otherwise lead to cell degradation due to delamination or cracking of electrolyte or electrodes.

2.3.3 Interconnect

Typical interconnect materials include dense (mostly perovskite type) oxides (CoCr$_2$O$_4$, LaCrO$_3$ or YCrO$_3$ [3, 6]) or metals which are often coated to prevent oxidation or reaction with the other materials [22, 23]. Oxides are used at high temperatures as metals tends to become unstable above approximately 900°C [6]. At lower temperatures, metals are used, as they are cheaper than the oxides.
### 2.3.4 Geometries of fuel cells

At present, two main fuel cell geometries are used. One is a tubular design where the electrolyte is supported by a porous tube of the cathode or anode material (Westinghouse sealless tubular design or segmented-cell-in-series [6, 24]). The other design is the flat plate design which is more compact, but more problematic in terms of gas manifolding [6]. Other designs also exist, but most of these are derivations of the main types described here. Figure 2.2 shows the most important of the currently used SOFC designs.

![Different SOFC designs](image)

*Figure 2.2. Different SOFC designs [6].*

### 2.3.5 Power generation

Modern SOFC stacks have been reported to generate up to approximately 300 mW/cm$^2$ for the Westinghouse tubular cells [25] and similar power generation for flat plate SOFC’s has been reported [6]. In spite of the relative high power generation reported, SOFC’s still have some problems. Typically they degrade over time [6], resulting in lower power generation after a few thousand hours of use [6].

Reproducibility is a second problem. In a fuel cell stack, all the cells involved have to have good performance, as one bad cell in a series connected stack might render the whole stack useless. If SOFC’s are to be used by the industry, better performance and durability have to be obtained.
3 Theoretical description of metal and ceramic contacts

The properties of metallic contacts have been investigated during the last 100 years [26]. One of the earlier investigations performed by Hertz was on elastic deformation in point contacts [26]. Most of the research so far has been conducted on metals, as metallic contacts have the largest practical use in consumer products such as relays and switches in modern electronic equipment [27].

In the following sections the concepts of constriction resistance (also called spreading resistance) [28], resistance heating (often also called Ohmic heating or Joule heat) and contact deformation in response to changes in pressure will be addressed based on analytical derivations assuming ideal materials and geometries.

3.1 Constriction resistance

When a contact between two nominally parallel planes is established, the area of contact is much smaller than the geometric area [29]. If the resistance in a contact is only due to the reduced contact area, it can be shown that the resistance $R_{\text{full contact}}$ is proportional to the resistivity $\rho$ (or inversely proportional to the conductivity $\kappa$) and inversely proportional to the diameter $d$ of the contact (assuming only one circular contact point) [27].

$$R_{\text{full contact}} = \frac{\rho}{d} = \frac{1}{\kappa d} \quad (3.1)$$

This formula is often used in a slightly different form [30]. Typically only one side of a contact contributes with spreading resistance in contacting experiments. In the field of electrochemistry this is sometimes referred to as Newman’s formula [30, 31]:

$$R_{\text{half contact}} = \frac{\rho}{2d} = \frac{1}{4 \kappa r} \quad (3.2)$$

where $\kappa$ is the conductivity and $r$ is the radius of the contact point. If more than one contact point exists the rule for parallel-coupled resistors have to be used [32]. For $m$ equal contact points, with a large distance between the points, the combined resistance is:

$$\frac{1}{R_m} = m \frac{1}{R_{\text{contact}}} \quad (3.3)$$

$$R_m = \frac{1}{4 \kappa r m} \quad (3.4)$$

If the exact number of contacts is unknown, the area of contact is difficult to determine from a measurement of the contact resistance over the interface. It is possible to vary the number of contacts and the size of the individual contacts to get the observed resistance, and no unique solution exists [27]. Only in the cases where the number of contact points is known is it possible to utilise equation 3.4 to calculate the area of contact.

3.2 Load influence on contact resistance

A contact between two surfaces consists in general of a number of discrete individual contact points. In the following sections, the load behaviour of idealised point contacts is examined. It is assumed that only one side of the contact is contributing to the contact resistance, that the materials behave ohmic and that the conductivity of the materials is independent of the pressure.

The effect of load ($P$) on a contact depends upon the deformation mechanism. If the deformation is elastic, the expected relation between contact resistance and normal load (perpendicular to the contact surface) is [27, 29, 33]:

$$R_{\text{contact}}^3 \propto \frac{1}{P} \iff R_{\text{contact}} \propto P^{-\frac{1}{3}} \quad (3.5)$$
When plastic deformation occurs the relation is [33]:

\[ R_{\text{contact}} \propto \frac{1}{P} \iff R_{\text{contact}} \propto P^{-\frac{1}{2}} \quad (3.6) \]

If a spherical indenter is pressed against a plane surface of the same material and all deformation is elastic, the radius of contact \((r)\) is [33]:

\[ r = \sqrt[3]{\frac{3PnR_s}{8E}} \quad (3.7) \]

where \(P\) is the load normal to the plane, \(E\) is Young’s modulus, \(R_s\) is the radius of curvature of the spherical indenter and \(n\) is a numerical constant ranging between 3 and 4 depending on Poisson’s ratio [33].

Most materials have a Poisson’s ratio of 0.3 [34], inserting this in equation 3.7 results in [35]:

\[ r = 1.109 \left( \frac{PR_s}{E} \right)^{\frac{1}{3}} \quad (3.8) \]

The area \(A\) of a contact consisting of a sphere on a plane is found by using the radius found in equation 3.8:

\[ A = \pi r^2 = \pi 1.230 \left( \frac{PR_s}{E} \right)^{\frac{2}{3}} \quad (3.9) \]

If the resistance is localised at the contact interface, the resistance scales inversely with the area of contact. The localisation of the contact resistance may be due to resistive phases (e.g. surface oxides on metals) or potential barriers at the interface. In the case of a layer with a conductivity of \(\kappa\) and a thickness \(\delta\), the resistance is [32]:

\[ R = \frac{\delta}{\kappa A} \quad (3.10) \]

If the area of contact is determined by a Hertz-type mechanism and the resistance scales with the area of contact as equation 3.10 (e.g. surface resistive phases or potential barriers at the interface), then the resistance scales with the applied load as:

\[ R \propto P^{-\frac{1}{3}} \quad (3.11) \]

If contact resistance arises from constriction resistance (section 3.1), the contribution from the plane below the contact has to be included. The combined contact resistance is found by substituting the Herz-radius found in equation 3.7 into equation 3.2. This gives equation 3.12 which is in agreement with equation 3.5.

\[ R = \frac{1}{4\kappa 1.109 \sqrt[3]{\frac{P R_s}{E}}} \quad (3.12) \]

### 3.2.1 Corrections for the spherical part of the model contact

In all the previous calculations it has been assumed that only the semi-infinite medium below the indenting sphere contributes with resistance. If the resistance of the sphere has to be included, it would lie somewhere between that of a cylinder, with height equal to the radius of the sphere and radius equal to the radius of contact (found from equation 3.8), and that of a semi-infinite space (spreading resistance according to equation 3.2). The ratio between the resistance found by the cylinder-model and that found by the spreading resistance is:

\[ \frac{R_{\text{cylinder}}}{R_{\text{Newman}}} = \frac{4}{1.109\pi} \sqrt[3]{\frac{E}{P}} \approx 1 \quad (3.13) \]
This is not a constant value as it depends on the load. Most ceramic materials have Young’s modulus between $100 \cdot 10^9 \ Pa$ and $400 \cdot 10^9 \ Pa$ [34] and loads as small as $200 \ mN$ over an area of one square micron corresponds to a pressure of $200 \cdot 10^9 \ Pa$, thus the variation is not large considering that the cubic root helps to lessen any difference.

It is therefore safe to assume that the resistance of the whole contact, consisting of a sphere on a plane, is twice as big as equation 3.12 predicts.

Similar precautions do not have to be included for the model where resistive phases at the interface dominates the contact resistance (equation 3.11), as the resistance is assumed to be within the contact interface without any contribution from the bulk material.

### 3.2.2 Multi-point contacts

In the previous sections the contact resistance was assumed to be due to one contact point deforming by changes in the contact pressure.

If the contact is modeled as a number of identical contact points, then the behaviour is different. As the combined resistance of a parallel-coupling of identical resistors is inversely proportional to the number ($m$) of resistors, then the resistance should scale with the applied load in the following way:

$$ R_{\text{multi}} = \frac{1}{4kr} \frac{1}{m} $$

(3.14)

For a situation in which the contact point radius is constant, the area of contact for $m$ equal points is:

$$ A = m \pi r^2 $$

(3.15)

$$ m = \frac{A}{\pi r^2} $$

(3.16)

Inserting this in equation 3.14 and reducing gives:

$$ R_{\text{multi}} = \frac{r \pi}{4kr A} $$

(3.17)

If this model is to be used, an independent method for contact area determination has to be utilised.

### 3.2.3 Fracture strength equivalence

The Hertz model can not be used if the deformation mechanism is brittle fracture and another method for determination of the contact area is necessary. One method is to utilise equation 3.14 [18, 20, 30] if the number of contact points is known and there is no surface resistive phases [27]. Another method is to determine the area of contact after testing by inspection.

The local contact pressure can not exceed the compressive fracture strength of the materials given a low confining pressure. The area of contact must therefore exceed the fracture strength equivalent area, $A_{\text{FSE}}$:

$$ P = \sigma_{\text{fracture}} A_{\text{FSE}} $$

(3.18)

where $\sigma_{\text{fracture}}$ is the compressive fracture strength of the material.

This model, combined with the model for constriction resistance (equation 3.14) result in two laws for contact resistance load behaviour. First, if the number of contact points is constant, the individual points must grow in order to support the load, resulting in:

$$ R \propto P^{-\frac{1}{2}} $$

(3.19)

In the case where the individual points do not change, the increased load must be supported by creation of more contact points resulting in:

$$ R \propto P^{-1} $$

(3.20)
3.2.4 Conclusion

Two models of indentation by a sphere describe the load-variance of a single contact point, and they differ in the exponent on the load (refer equation 3.11 and 3.12). The correction needed for the spherical part of the model contact is small and can be approximated by doubling the spreading resistance contribution from the plane below the contact.

The previous models for the load-dependence of ceramic and metallic contacts are all power-law functions. The expected load exponents for each model are listed in table 3.1.

<table>
<thead>
<tr>
<th>Load model</th>
<th>Resistance model</th>
<th>Expected load exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Hertz sphere</td>
<td>constriction</td>
<td>1/3 [29]</td>
</tr>
<tr>
<td></td>
<td>resistive phase</td>
<td>2/3 (equation 3.11)</td>
</tr>
<tr>
<td>Fracture strength</td>
<td>constriction, constant n</td>
<td>1/2 (equation 3.19)</td>
</tr>
<tr>
<td>equivalent area</td>
<td>constriction, constant r</td>
<td>1 (equation 3.20)</td>
</tr>
<tr>
<td></td>
<td>resistive phase</td>
<td>1 (equation 3.10)</td>
</tr>
<tr>
<td>Plastic deformation, metals</td>
<td></td>
<td>1/2 [29, 33]</td>
</tr>
</tbody>
</table>

In real contacts, the observed behaviour will be somewhere in between the behaviour of the different models described above, as more contact points are formed upon increasing load at the same time as already formed contacts increase in size.

3.3 Ceramic materials

Ceramic materials differ from metals in a number of ways. Ceramics consist of ionically bonded atoms (although some covalence occurs), and therefore the electrical conductivity is lower than for metals. Most metals deform easily by plastic deformation when subjected to stress whereas ceramic materials are much more brittle and ceramic materials have higher melting points than most metals.

Most mechanical analysis of ceramic - ceramic contacts have been made using indentation tests [36, 37]. These usually found brittle fracture in the contact area, but in some cases a small plastic deformation may occur [37]. Numerical simulations of the behaviour of small-scale contacts have been performed, and attempts have been made to predict the behaviour of the contact points with respect to brittle fracture and quasi-plastic deformation [38, 39]. Quasi-plastic deformation is characterised by non-elastic deformation by small scale fractures and cracks, each with only a small offset. If quasi-plastic deformation occurs, it is dominated by a zone of microcracks in the material [39]. Only in the case of a high isostatic pressure does ceramic materials deform plastically [37]. However, the use of small spherical indentors may in some cases delay brittle fracture of the materials, and small scale plastic deformation may be found [40].

Several authors have investigated contact resistance in LSM. Theoretical work on the influence of inhomogeneous contacts on the impedance spectra obtained from these contacts have been investigated by Fleig and Maier [31, 41] who found an extra semicircle in the impedance spectra due to the inhomogeneity. Load behaviour of LSM contacts have not been investigated so deeply, but in general the resistance decrease with increasing load [18, 42].
3.4 Resistance heating

Due to the higher yield strength and low toughness, ceramic materials cannot deform plastically to achieve a contact area equal to the geometric area of the contact. If the contact points were melted and resolidified again, better contact performance would be expected. This is observed for metals where resistance heating of the individual contact points causes melting, which reduces the contact resistance [27].

3.4.1 Modeling of heating in metallic contacts

Jones [27] investigated resistance heating in metals and found that the maximum temperature \( T_{\text{max}} \) in a metal contact can be calculated using equation 3.21 and is not influenced to a significant degree by radiation loss from the surface of the metal [27].

\[
\frac{U^2}{4} = 2 \int_{T_{\text{ambient}}}^{T_{\text{max}}} \frac{\lambda}{\kappa} dT
\]  

(3.21)

In equation 3.21 \( \lambda \) is the thermal conductivity, \( \kappa \) is the electrical conductivity, \( U \) is the potential across the contact and \( T_{\text{ambient}} \) is the ambient temperature. In order to solve the integral the Weidemann-Franz law that applies for metals is used [27]:

\[
\frac{\lambda}{\kappa} = LT
\]  

(3.22)

where \( L \) is the Lorenz constant: \( L = 2.45 \cdot 10^{-8} \frac{\text{W} \cdot \text{O} \cdot \text{s}}{\text{K}^2} \) [43] (experimental values range from \( 1.4 \cdot 10^{-8} \) to \( 8.8 \cdot 10^{-8} \) depending on the materials [44] so it is not a universal constant as stated in [43]). When equation 3.22 is substituted into equation 3.21 and the integral is solved the relation between temperature and applied potential is found:

\[
T_{\text{max}}^2 - T_{\text{ambient}}^2 = \frac{U^2}{4L}
\]  

(3.23)

Contacts in metals often heat to a considerable degree. This helps to improve the contact properties of metals, as the contact actually ‘welds’ together and negligible contact resistance is usually observed for metals. The initial high contact resistance resulting in high contact potentials cause the welding of the contact. This melts enough metal to allow larger contact areas to be formed and as these allow larger currents to pass, the contact potential is lowered below what is necessary to melt the metal and the contact solidify again [27].

3.4.2 Resistance heating in ceramics

Typical ceramics do not have metallic conductivity in which electrons can be described as freely moving in the lattice. Although LSM is a good conductor with an electronic conductivity of approximately 160 S/cm at 1000°C [45], the mechanism of conduction is that of a small polaron semiconductor where the conduction electrons are bound to individual atoms, but can jump from atom to atom with a low activation energy. As the Weidemann-Franz law depends upon freely moving electrons with a mean velocity (determined from gas theory) [43], this law does not apply for LSM and the integral in equation 3.21 is more difficult to solve as the temperature dependence of the conductivity of heat and electricity has to be known.

To establish if resistance heating plays any role in ceramic contacts Hendriksen & Østergård [46] investigated temperature effects in LSM-YSZ half-cells to establish if electrical heating effects could account for improved cell performance at high current densities. They found that sample temperatures increased up to 10°C above bulk temperatures for current densities in the order of 1 to 3 A/cm² and concluded that resistance heating is not responsible for improved cell performance at high current densities.

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Contact heating in ceramics were investigated by numerical simulations (refer appendix A). The model calculations lead to the conclusion that, for SOFC-stacks with contact point distances below 100 µm, resistance heating in the contact points should not be observed. Resistance heating of the contact points will only arise when defect contact surfaces between individual SOFC-elements are present and will be evident by a contact resistance exceeding 0.2 Ωcm².
4 Potential barrier theory

In most materials the current-voltage characteristics are linear i.e. ohmic. For some interfaces, a distinct non-linearity is observed. Several physical models exist that explain non-linear current-voltage behaviour. One model is the potential barrier model.

The following sections describe various different potential barrier models and their steady state current-voltage dependency is derived. First the simple symmetrical barrier is described, followed by a description of the classical Schottky barrier in section 4.2.1.

The next sections involve barriers with more than one crest. Finally complex barriers are discussed. The current-voltage behaviour for equal consecutive barriers is addressed (section 4.4.2) as well as for multiple barriers with varying height (section 4.4.3).

In this chapter the positive current direction is defined toward the right. A positive polarisation is defined as the case where the left side of the barrier is at a higher potential than the right side.

It is assumed that the polarisation of the barriers is small compared to the barrier height, i.e. the average electron energy outside the barriers is less than the energy needed to cross the barrier. It is also assumed for all the described models that the attempt frequency of the charge carriers is independent of temperature and polarisation of the barriers.

4.1 Physical formation of potential barriers

The simplest way of forming a potential barrier is by placing two pieces of metal close to each other in a vacuum. It requires energy to extract electrons from metals [32]. This effectively creates a square potential barrier with barrier height equal to the work function of the metals [32]. This effect was used in the old vacuum tube diodes where electrodes at different temperatures resulted in rectifying properties [47]. Another way to create a potential barrier is by placing an insulator between two conductors. The potential barrier is created as electrons have to be promoted to the conduction band of the insulator for current to pass [48].

For semiconductors in contact with a metal, another type of potential barrier is observed. Due to the difference in Fermi levels between the two materials, electrons are transferred from one to the other. This creates space charges, which in return are responsible for the formation of the classical Schottky barrier (refer section 4.2.1) [48].

Termination of semiconductor crystals leads to the formation of surface energy states [48]. These surface states capture some of the charge carriers, resulting in the creation of space charges in the surface of the crystal. Therefore, potential barriers are always present in the surfaces of band type semiconductors [48]. Small polaron semiconductors are expected to show similar edge effects.

Termination of an ionic structure breaks the symmetry, leading to rearrangement at the surface layers and resulting in dipole moments and space charges [49]. Non-stoichiometric materials may also create space charges at the surface of the crystals by concentration of charged defects at the surface [50]. The presence of space charges in the surface region of the crystals result in potential barriers and either rearrangement of the ionic species or by concentration of charged defects creates space charges in the surface of the crystals.

Grain boundaries in polycrystalline semiconductors also create potential barriers as surface states in the grain boundaries capture charge carriers [48].

4.2 Simple barriers

The simplest potential barrier is a symmetrical barrier as shown in figure 4.1. This barrier is characterised by the barrier height $E_a$ and width $l$. In order for electrons to pass the barrier they either have to tunnel through the barrier or climb it by thermal activation [48]. If the width of the barrier is large enough, tunnelling does not play any significant role.
This leaves thermal activation as the main mechanism for electron transport across the barrier. In the following sections, thermal activation is assumed to be the only means of electron transfer across potential barriers.

Figure 4.1. Simple symmetrical potential barrier. The potential distribution before (black) and after (grey) an external potential has been applied. $\Delta U$ is the external polarisation of the barrier when current passes the barrier.

Electron energies in non-degenerate semiconductors follow the Boltzmann distribution [48] and the fraction $f$ of the electrons that carry enough energy to climb a barrier with height $E_a$ is [51]:

$$f = \frac{1}{kT} \int_{E_a}^{\infty} \exp \left(\frac{-E}{kT}\right) dE = \exp \left(\frac{-E_a}{kT}\right)$$ (4.1)

The current across a barrier in any direction is dependent on the barrier height observed in that direction. Applying a potential $\Delta U$ to a barrier effectively changes the barrier height observed from the two sides of the barrier (figure 4.1). The barrier height is:

$$E_{a,\text{effective}} = E_a \pm \frac{\Delta U}{2}$$ (4.2)

depending on which side the barrier is observed from.

When a potential barrier is subjected to a potential difference ($\Delta U$), non-linearity is observed in the current response. This results from the difference in the two opposite currents passing the barrier. The positive current when calculating $E_a$ in J/mol and changing $\frac{1}{kT}$ to $\frac{1}{RT}$ is:

$$I_+ = N_0 \cdot K \exp \left(-\frac{E_a + \frac{\Delta UF}{2}}{RT}\right)$$ (4.3)

where $K$ is a constant containing the geometry and the attempt frequency of the charge carriers. $N_0$ is the charge carrier concentration.

Similarly the negative current is:

$$I_- = -N_0 \cdot K \exp \left(-\frac{E_a - \frac{\Delta UF}{2}}{RT}\right)$$ (4.4)

Combining equation 4.3 and 4.4 results in:

$$I = I_+ + I_-$$ (4.5)

$$I = N_0 \cdot K \exp \left(-\frac{E_a + \frac{\Delta UF}{2}}{RT}\right) - N_0 \cdot K \exp \left(-\frac{E_a - \frac{\Delta UF}{2}}{RT}\right)$$ (4.6)

$$I = N_0 \cdot K \exp \left(-\frac{E_a}{RT}\right) \left(\exp \left(\frac{\Delta UF}{2RT}\right) - \exp \left(-\frac{\Delta UF}{2RT}\right)\right)$$ (4.7)

The second exponential term in the product is the source of the non-linearity observed in figure 4.2. At large positive potentials the term $\exp \left(\frac{-\Delta UF}{2RT}\right)$ approaches zero and the current is dominated by the other exponential term. A similar effect dominates at large negative potentials.
Figure 4.2. Current dependence of polarisation of a simple symmetrical potential barrier.

At high temperatures, the non-linearity at small potentials disappears. This is due to the increase of the denominators in equation 4.7. The exponential function can be expanded in a Taylor series [52]:

$$\exp x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$  \hspace{1cm} (4.8)

By discarding all the higher order terms in the Taylor-series (third order and above), equation 4.7 becomes:

$$I = N_0 \cdot K \exp \left( -\frac{E_a}{RT} \right) \cdot \left( 1 + \frac{\Delta U F}{2RT} + \frac{(\Delta U F)^2}{8R^2T^2} - 1 - \frac{\Delta U F}{2RT} - \frac{(\Delta U F)^2}{8R^2T^2} \right)$$  \hspace{1cm} (4.9)

$$I = N_0 \cdot K \exp \left( -\frac{E_a}{RT} \cdot \frac{\Delta U F}{RT} \right)$$  \hspace{1cm} (4.10)

This results in ohmic behaviour as long as $RT$ is larger than $\Delta U F$ (within 5 % accuracy) as the higher order terms of equation 4.8 are insignificant below this polarisation. The linear range is defined as the polarisation where the deviation of the current is less than 5% of that of a true linear response. At higher temperatures a linear response should be observed with higher potential differences than at lower temperatures. At 1000 °C the linear potential range is ±0.1 V and at room temperatures it is ±0.02 V.

Another feature of the simple potential barrier is that increasing the temperature increases the conductivity. The improved conductivity arises from the first exponential term in equation 4.7 where increased temperature leads to higher average electron energy and hence more electrons with enough energy to climb the barrier.

### 4.2.1 The Schottky barrier

When a semiconductor is placed in contact with a metal, differences in the Fermi levels of the two materials result in a charge transfer across the interface [48]. This results in the formation of space charges close to the contact. These space charges build up a potential barrier, which the charge carriers must either climb by thermal activation or tunnel through [48]. A space charge will theoretically also reside in the metal, but as
metals have high conductivity (and hence low Debye length) the space charges reside on the surface of the metal, and can safely be ignored [8, 48].

Figure 4.3. The electron energy ($U(x)$), the electric field ($E(x)$) and the charge distribution ($\rho(x)$) in the classical Schottky barrier. $l_0$ is the length over which the space charge in the semiconductor is distributed. All curves are for a no-current situation for an $n$-type semiconductor. The charge on the metal is numerically equal to the one on the semiconductor, although spatially it is much less extended (modified from [48], figure 2.1).

In the classical Schottky barrier, the space charge ($Q$) in the semiconductor is assumed to be uniformly distributed with a charge density ($\rho$) from the interface to some length ($l_0$) (figure 4.3 c). It is assumed that the charge everywhere else is zero.

The electrical field (as seen from the interior of the semiconductor) will rise linearly with distance towards the contact as the electric field in the bulk of the semiconductor is
zero (figure 4.3 b). The electric field \( E(x) \) as seen from the semiconductor is:

\[
E(x) = \begin{cases} 
\frac{Q \cdot (l_0 - x)}{l_0 \epsilon} & \text{for } 0 \leq x \leq l_0 \\
0 & \text{elsewhere}
\end{cases}
\] (4.11)

\[
E(x) = 0 \text{ elsewhere} \quad (4.12)
\]

Using this electric field in the basic formulas for calculating one dimensional potentials [32], the potential distribution is:

\[
U = -Edx \quad (4.13)
\]

\[
Edx = \frac{(l_0 - x)Q}{l_0 \epsilon} dx \quad (4.14)
\]

\[
U_x - U_{l_0} = \int_{l_0}^{x} \frac{(l_0 - x)Q}{l_0 \epsilon} dx \quad (4.15)
\]

\[
U_x - U_{l_0} = \frac{Q}{\epsilon} \left( \frac{x^2}{2l_0} + \frac{l_0}{2} - x \right) \quad (4.16)
\]

This is a parabolic function of \( x \) in agreement with Heinisch [48]. The result of this charge distribution is the formation of a potential barrier at the contact.

As the Schottky barrier is asymmetric (figure 4.3a), it behaves differently than the simple barrier described in section 4.2. The Schottky barrier is in itself rectifying, that is, current passes much easier in one direction than in the other. From the metal side, the barrier height is more or less independent of applied potential. From the semiconductor side however, the effective barrier height changes with applied potential [48]. The result is that the Schottky barrier is only conductive in one direction (although a small reverse current is observed). Metal-semiconductor contacts have a breakdown potential where an extreme increase in the current is observed due to the dielectric decomposition of the semiconductor material at the interface [48].

### 4.3 Double barriers

A number of real contact barriers are well described by either the simple barrier or the Schottky barrier [48], other systems behave inconsistently with the simple models discussed earlier. One example is the LSM-LSM contact interface investigated in this work.

In the following sections the density of states inside the more complex barriers are assumed to be large enough so that adding or subtracting electrons do not change the energy levels.

#### 4.3.1 Two barriers in series

In a system with transition states as barriers, the presence of an external potential field would shift the energy levels in the barriers relative to each other [8].

If the potential drop across the barrier is assumed to influence the energy profile across two identical barriers as shown in figure 4.4 and the energy levels of the barrier crests are shifted equally an amount, \( x \), from their initial values, then the exchange currents across the individual barriers are:

\[
I_{1+} = N_0 K \exp \left( -\frac{E_a}{R T} \right) \exp \left( -\frac{-xF + \frac{\Delta U F}{R T}}{R T} \right) \quad (4.17)
\]

\[
I_{1-} = -N_0 K \exp \left( -\frac{E_a}{R T} \right) \exp \left( -\frac{-xF}{R T} \right) \quad (4.18)
\]

\[
I_1 = N_0 K \exp \left( -\frac{E_a}{R T} \right) \left( \exp \left( -\frac{-xF + \frac{\Delta U F}{R T}}{R T} \right) - \exp \left( -\frac{-xF}{R T} \right) \right) \quad (4.19)
\]
Figure 4.4. Energy diagram for two identical barriers, which are assumed to be independent of each other. The crests of the barriers are increased or lowered $x$ by the external potential difference.

\[ I_{2+} = N_0 K \exp \left( \frac{-E_a}{RT} \right) \exp \left( \frac{xF}{RT} \right) \] (4.20)

\[ I_{2-} = -N_0 K \exp \left( \frac{-E_a}{RT} \right) \exp \left( \frac{xF - \Delta UF}{RT} \right) \] (4.21)

\[ I_2 = N_0 K \exp \left( \frac{-E_a}{RT} \right) \left( \exp \left( \frac{xF}{RT} \right) - \exp \left( \frac{xF - \Delta UF}{RT} \right) \right) \] (4.22)

For steady state to exist, the two currents $I_1$ and $I_2$ must be equal:

\[ I_1 = I_2 \] (4.23)

\[ \exp \left( \frac{-xF + \Delta UF}{RT} \right) - \exp \left( \frac{-xF}{RT} \right) = \exp \left( \frac{xF}{RT} \right) - \exp \left( \frac{xF - \Delta UF}{RT} \right) \] (4.24)

\[ x = \frac{\Delta U}{4} \] (4.25)

This shows that the energy levels at the top of the barriers have to change by one quarter of the applied potential. This is in effect to say that the barriers share the potential and only experience half the potential difference (for a detailed derivation from equation 4.24 to equation 4.25 see appendix B).

The current passing the barriers is:

\[ I_1 = N_0 K \exp \left( \frac{-E_a}{RT} \right) \left( \exp \left( \frac{\Delta UF}{4RT} \right) - \exp \left( -\frac{\Delta UF}{4RT} \right) \right) \] (4.26)

When comparing equation 4.26 with equation 4.7 it is observed that the only difference between them is a factor two in the denominator in the potential dependent exponential terms. This shows that two potential barriers in series share the potential difference.

### 4.3.2 Barrier with a valley

Figure 4.5 shows a barrier with a valley where the energy level in the valley is kept constant and where the crests of the two sides of the barrier is fixed to each other and to the energy in the valley. The number of electrons in the valley must be low enough to allow equilibrium with the electrons outside the barrier. For the valley to be in equilibrium, the exchange current across half the barrier (one crest) must be equal.

\[ I_+ = N_0 K \exp \left( \frac{-E_a}{RT} \right) \] (4.27)

\[ I_- = N_0 K \exp \left( \frac{-E_a + E}{RT} \right) \] (4.28)
As it is assumed that the attempt frequency is constant and equal in both directions, the charge carrier concentration in the valley has to be:

\[ N = N_0 \exp \left( -\frac{E}{RT} \right) \]  

(4.29)

The potential distribution across the two halves of the barrier has to change and \( \alpha \) designates the amount of the applied potential that the left side of the barrier experiences (as shown in figure 4.5).

\[ I_1 = N_0 K \exp \left( -\frac{E_a}{RT} \right) \exp \left( \alpha \Delta UF \right) \frac{\exp}{RT} \]  

(4.30)

\[ I_2 = N_0 K \exp \left( -\frac{E_a}{RT} \right) \exp \left( -\frac{(1 - \alpha) \Delta UF}{RT} \right) \]  

(4.31)

\[ I_1 = N_0 K \exp \left( -\frac{E_a}{RT} \right) \left( \exp \left( \frac{\alpha \Delta UF}{RT} \right) - 1 \right) \]  

(4.32)

\[ I_2 = N_0 K \exp \left( -\frac{E_a}{RT} \right) \exp \left( -\frac{(1 - \alpha) \Delta UF}{RT} \right) \]  

(4.33)

\[ I_2 = N_0 K \exp \left( -\frac{E_a}{RT} \right) \exp \left( -\frac{(1 - \alpha) \Delta UF}{RT} \right) \]  

(4.34)

\[ I = N_0 K \exp \left( -\frac{E_a}{RT} \right) \frac{1 - \exp \left( -\frac{\Delta UF}{RT} \right)}{1 + \exp \left( -\frac{\Delta UF}{RT} \right)} \]  

(4.35)

\[ I = N_0 K \exp \left( -\frac{E_a}{RT} \right) \frac{1 - \exp \left( -\frac{\Delta UF}{RT} \right)}{1 + \exp \left( -\frac{\Delta UF}{RT} \right)} \]  

(4.36)

\[ I = N_0 K \exp \left( -\frac{E_a}{RT} \right) \frac{1 - \exp \left( -\frac{\Delta UF}{RT} \right)}{1 + \exp \left( -\frac{\Delta UF}{RT} \right)} \]  

(4.37)

If steady state is assumed, \( I_1 \) is equal to \( I_2 \). Solving the resultant equation for \( \alpha \) results in:

\[ \alpha = \frac{RT}{\Delta UF} \ln \left( \frac{2}{1 + \exp \left( -\frac{\Delta UF}{RT} \right)} \right) \]  

(4.36)

Inserting this in equation 4.32 results in:

\[ I = N_0 K \exp \left( -\frac{E_a}{RT} \right) \frac{1 - \exp \left( -\frac{\Delta UF}{RT} \right)}{1 + \exp \left( -\frac{\Delta UF}{RT} \right)} \]  

(4.37)

The behaviour of a barrier with a constant energy valley is shown in figure 4.6. It is found that the current approaches a constant value for large potentials. This is due to the fact that the current across the barrier is limited by the exchange currents ‘out’ of the valley (for complete derivation of equation 4.37, refer appendix C). The energy level of the valley does not influence the final current-voltage response (equation 4.37), therefore the response to changes in polarisation of a barrier with a valley as the one shown in figure 4.5 is independent on the valley energy as long as it is bellow the energy of the barrier crests.
4.3.3 Barriers with different height

Two identical barriers in series share the potential evenly as shown in section 4.3.1. If a height difference exists, they share an external potential unevenly. A new variable, \( \alpha \), describing how the barriers share the applied polarisation has to be included (\( \alpha \Delta U \) for one of the barriers and \( (1 - \alpha) \Delta U \) for the other). The exchange currents across two barriers with activation energy \( E_a \) and \( E_b \) are then:

\[
I_{a+} = N_0 K \exp \left( \frac{-E_a}{RT} \right) \exp \frac{\alpha \Delta U F}{2RT} \\
I_{a-} = -N_0 K \exp \left( \frac{-E_a}{RT} \right) \exp \frac{-\alpha \Delta U F}{2RT} \\
I_{b+} = N_0 K \exp \left( \frac{-E_b}{RT} \right) \exp \frac{(1 - \alpha) \Delta U F}{2RT} \\
I_{b-} = -N_0 K \exp \left( \frac{-E_b}{RT} \right) \exp \frac{-(1 - \alpha) \Delta U F}{2RT}
\]

The current across each barrier is thus:

\[
I_a = N_0 K \exp \left( \frac{-E_a}{RT} \right) \left( \exp \frac{\alpha \Delta U F}{2RT} - \exp \frac{-\alpha \Delta U F}{2RT} \right) \\
I_b = N_0 K \exp \left( \frac{-E_b}{RT} \right) \left( \exp \frac{(1 - \alpha) \Delta U F}{2RT} - \exp \frac{-(1 - \alpha) \Delta U F}{2RT} \right)
\]

As steady state is assumed, the two currents \( I_a \) and \( I_b \) must be equal:

\[
\exp \left( \frac{-E_a}{RT} \right) \left( \exp \frac{\alpha \Delta U F}{2RT} - \exp \frac{-\alpha \Delta U F}{2RT} \right) = \exp \left( \frac{-E_b}{RT} \right) \left( \exp \frac{(1 - \alpha) \Delta U F}{2RT} - \exp \frac{-(1 - \alpha) \Delta U F}{2RT} \right)
\]

Solving this equation for \( \alpha \) gives (for complete derivation refer appendix D):

\[
\alpha = \frac{RT}{\Delta UF} \ln \left( \frac{\exp \left( \frac{E_a}{RT} \right) \exp \frac{\alpha \Delta U F}{2RT} + \exp \frac{E_b}{RT} \exp \frac{\alpha \Delta U F}{2RT}}{\exp \frac{E_a}{RT} + \exp \frac{E_b}{RT} \exp \frac{(1 - \alpha) \Delta U F}{2RT}} \right) + \frac{1}{2}
\]

From equation 4.46 it is then found that it is only in the case of \( E_a = E_b \) that \( \alpha \) is equal to one half. \( \alpha \) shows a small dependency upon the external polarisation as shown in figure 4.7. This causes the two barriers to display properties somewhere between the properties of a single barrier and the behaviour of two equal barriers. Figure 4.8 shows a numerical fit for the behaviour of two non-identical barriers modelled as \( x \) identical barriers and the difference is small.

Two barriers with different height may be modelled as \( x \) identical barriers, where \( x \) is between 1 and 2. The important observation here is that an integer number of non-identical barriers can be modelled as a non-integer number of identical barriers.

4.4 Complex barriers

4.4.1 Single barrier with variable height

Experimental data for LSM contact surfaces show a current-voltage behaviour inconsistent with a simple barrier (refer chapter 10). If a potential barrier with variable height is used to model those results, the barrier height dependence of the applied potential is:

\[
E_a(U) = E_0 - RT \ln \frac{\sinh \frac{\alpha \Delta U F}{2RT}}{\sinh \frac{\Delta UF}{2RT}}
\]

(for derivation of equation 4.47 refer appendix E).
4.4.2 Consecutive potential barriers

If \( n \) identical potential barriers are placed in series, they also share an applied external potential difference. This was shown for the \( n = 2 \) case in section 4.3.1. If the barriers are independent and steady state is assumed, the effective potential drop experienced by each barrier is \( \frac{\Delta U}{n} \). The current response to changes in total applied potential across the barriers is [53].

\[
I = N_0 K \exp \frac{-E_a}{kT} \left( \exp \frac{\Delta U F}{2RTn} - \exp \frac{-\Delta UF}{2RTn} \right) \tag{4.48}
\]

Equation 4.48 can be derived by inserting \( \Delta U/n \) in stead of \( \Delta U \) in equation 4.3 and 4.4, as each barrier is assumed to be independent of the others. The difference between equation 4.48 and the current-voltage behaviour for a single barrier (equation 4.7) is the \( n \) in the denominator. Therefore, consecutive potential barriers behave similar to single...
barriers, except that the non-linearity in the current-voltage response is less than for the single barrier case.

If the barriers have unequal heights, the \( n \) value would be between one and the number of barriers depending on the height difference (same effect as the two barrier system with different barrier heights discussed in section 4.3.3).

Depending on the polarisation, temperature and the number of barriers, a strong non-linear current-voltage behaviour, as well as a linear behaviour can be observed. Linear response is expected if \( n \) is large or if the temperature is high as shown in figure 4.9. If the temperature is low and \( n \) is small, then strong non-linearity will be observed.

![Figure 4.9. Current response to changing polarisation calculated from equation 4.48. Curves are shown for different values of \( n \cdot T \). The barrier height is 0.5 eV and \( K \) is set to 1.10^{-4} \text{A}.](image)

If a large number of potential barriers are placed in series, the current-voltage response would be be linear as long as the polarisation is not very large as the polarisation of the individual barriers would be within the linear range. This is the reason for ohmic behaviour of ionic conductors, where the ions reside in potential wells and move only by thermally activated jumps to nearby sites.

### 4.4.3 Multiple barriers with different heights

Multiple barriers with varying heights also share an applied potential, however, the potential drop across each barrier is no longer equal. If current passes a large number of barriers, the exchange currents across the individual barriers must be equal for steady state to be observed.

\[
I_{1+} + I_{1-} = I_{2+} + I_{2-} = I_{3+} + I_{3-} = \ldots = I_{m+} + I_{m-}
\]  

(4.49)

In order to simplify the above condition, the following model describes the case where one barrier has higher activation energy than the rest \((E_a > E_b)\):

\[
E_{a,m} = E_a \quad \text{for } m = 1 \\
E_{a,m} = E_b \quad \text{for } m > 1
\]

(4.50)

(4.51)

The current across a barrier subjected to an external potential \( \Delta U_1 \) is (refer equation 4.7):  

\[
I = N_0 2K \exp \frac{-E_a}{RT} \sinh \frac{\Delta U_1 F}{2RT}
\]

(4.52)
\[
\Delta U_1 = \frac{2RT}{F} \text{asinh}\left(\frac{I}{2N_0K \exp \frac{E_a}{RT}}\right)
\]  
(4.53)

The combined potential \((U_m)\) across \(m\) identical barriers with activation energy \(E_b\) is then:

\[
U_m = \frac{2mRT}{F} \text{asinh}\left(\frac{I}{2N_0K \exp \frac{E_b}{RT}}\right)
\]  
(4.54)

The total potential across the barriers is:

\[
U = \frac{2RT}{F} \left( \text{asinh}\left(\frac{I}{2N_0K \exp \frac{E_a}{RT}}\right) + m \text{asinh}\left(\frac{I}{2N_0K \exp \frac{E_b}{RT}}\right) \right)
\]  
(4.55)

Analysis of this formula shows that at small potentials, the behaviour is the same as that for single barrier as long as the difference in activation energy is more than a factor of two. At larger potentials the influence from the other potential barriers is more pronounced.

### 4.5 Summary

It is possible to mathematically describe ideal potential barriers and the current-voltage dependency can be calculated. Real barriers are more complex to analyse. Real barriers may not have simple barrier profiles and may to some extent be asymmetrical. The actual barrier profile is less important, however, as the current is only influenced by the height of the barrier [48].

Some potential barriers posses rectifying properties, whereas others do not. It is only asymmetric barriers which may show non-symmetrical current-voltage behaviour [48].

Multiple barriers in series share the applied potential difference if the barrier crests are not locked to each other (i.e. the energy of the barriers change with applied potential as in the two barrier case; refer section 4.3.1). The current-voltage response for multiple barriers in series is the same as that of a single barrier where the barrier only experiences a fraction of the external potential difference (figure 4.8). This is also the case for non-identical barriers, only here the effective potential is not a simple fraction depending on the number of barriers and it is possible to model an integer number of non-identical barriers as a non-integer number of identical barriers.

Some potential barriers owe their existence to differences in Fermi levels in the materials on each side [48]. Other barriers result from termination of crystals and both band-type and small polaron-type semiconductors create barriers at crystal surfaces and grain boundaries [48].
5 Experimental

5.1 Analytical methods

Several analytical methods were used in the analysis of the contact resistance. The most important was DC resistance measurements. All the electrical analyses were performed using the contactometer, which allowed precise measurements of the electrical contact resistance with respect to changes in load, temperature, atmosphere and contact polarisation.

The samples were investigated by scanning electron microscopy, both before and after experiments and by optical microscopy. Atomic force microscopy was used for high-resolution surface measurements.

5.1.1 Contactometer

Precise measurements of the contact resistance between two ceramic components require a high degree of control of external parameters: temperature, atmospheric composition, contact load and contact potential. A special instrument (the contactometer) for analysing contact phenomena was built at Risø National Laboratory. A schematic view of the instrument is shown in figure 5.1. The contactometer allowed precise control and in situ change of the contact load on the interface under investigation. Contact interfaces could be investigated at temperatures up to 1200°C in various atmospheres. Changes in sample height were measured by a linear voltage differential transformer (LVDT) with a precision of ±1 µm at room temperature and ±4 µm at 1000°C. The sample and reference position each has its own load arrangement and is connected to each other with an LVTD sensor as shown in figure B.

The increased uncertainty of the LVDT sensor at elevated temperatures is due to the long (approximately 80 cm) load rods, which heats unevenly. This uncertainty was only important for time periods longer than 10 minutes due to the heat capacity of the load rods. For shorter time intervals the uncertainty of the LVDT sensor was in the order of 2 µm even at elevated temperatures.

In order to measure the pure contact resistance without interference of the bulk materials, a 6-point measurement system was used (figure 5.2). By measuring two potential differences across the contact interface and knowing the geometry of the samples, it was possible to exclude the bulk resistance effects from the measurements. The temperature was measured at six points within the quartz-glass tube (figure 5.1), two close to the sample, two close to the reference and two in the sample chamber.

Two oxygen sensors were attached to the contactometer. One internal, which was only operative at constant furnace temperatures of 700°C and above and one external, which monitored the exhaust gas. Small leakages in the gas system resulted in slightly higher oxygen partial pressures measured by the external oxygen sensor compared to the internal.

5.1.2 Scanning electron microscopy

The samples were analysed using a high vacuum SEM (JEOL-840 equipped with an Noran Voyager energy dispersive spectrometer) as well as a low vacuum SEM (JEOL-5310LV). For analysis of the YSZ samples, an environmental SEM was used (Electro Scan E-3 equipped with a Kevek spectrometer). The acceleration potential used was between 10 and 20 kV. Secondary electron images of the contact interfaces were acquired both before and after testing.
5.1.3 Optical analysis

Optical microscopy were made partly by conventional microscopy (Leitz Aristomet) and partly by laser scanning microscopy using a UBM laser scanning microscope (at Ferroperm Piezoceramics A/S) in non-contacting optical surface measurement mode. This
resulted in three-dimensional maps of the analysed surfaces. The resolution of the laser microscope was 2 \( \mu \text{m} \) horizontally and 0.01 \( \mu \text{m} \) vertically.

### 5.1.4 Atomic force microscopy

The high-resolution analyses of the ceramic surfaces were performed with an atomic force microscope (Burleigh Metris 2000). Surface images were obtained down to a point to point resolution of 40 nm horizontally. The images were obtained using contact mode microscopy.

### 5.2 Sample preparation

Three different materials were used in the investigation: Strontium doped lanthanum manganite (LSM), yttrium doped zirconia (YSZ) and strontium and nickel doped lanthanum cobaltite (LSCN).

#### 5.2.1 Strontium doped lanthanum manganite

Samples of the cathode material LSM \( \text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_{1.1}\text{O}_3 \) (Haldor Topsøe A/S batch #132) were prepared using the following method:

1. Powder of LSM was ball milled in acetone with \( \text{ZrO}_2 \) milling elements for 20 hours (10 g LSM to 100 ml acetone).
2. Evaporation of the acetone.
3. The dry powder was mixed in a 5% water based solution of PVA (batch MV 115000) to a viscous mass (1-1.5 ml PVA solution to 5 g material).
4. The paste was smeared on a glass plate and allowed to dry for 24 hours.
5. The dry paste was then crushed in an agate mortar to a particle size less than 200 \( \mu \text{m} \).

Three different types of samples were prepared from the powder:

- A: 'As-pressed' samples, that were pressed and sintered (figure 5.3).
- B: 'Polished' samples that were pressed, sintered, polished (1 \( \mu \text{m} \) diamond paste) and subsequently annealed at 1000°C in air for three days.
- C: 'Pyramid' samples. After pressing, between 30 and 85 500 \( \mu \text{m} \) high pyramids (1 mm base) were made on the contact surface prior to sintering (figure 5.3).

All samples were uniaxially pressed at approximately 800 GPa for 2 minutes followed by sintering at 1350°C using the sintering program shown in figure 5.4. The program was obtained from Inger Grethe Krogh Andersen at Syddansk Universitet, Odense, Denmark.

The final density of the sintered LSM pellets was 6.21 g/cm\(^3\), which corresponds to 95% of the theoretical density of LSM \( (\rho = 6.57 \text{ g/cm}^3) \) [45, 54]). Grooves were machined on the sides of the samples in order for the platinum potential probes to be firmly positioned. Similarly, at the bottom of the samples a groove was machined for the current leads (figure 5.2).

8 as-pressed samples was made, of these 7 was used in experiments. 4 polished samples were made and of these 2 was used for the contact experiments and the other 2 was used for the experiments with sinterable contact layers, where they were polished and annealed between the two experiments (see section 5.3.6). 2 pyramid samples were manufactured.
5.2.2 Yttria stabilised zirconia

Samples of yttria stabilised zirconia (YSZ) were prepared by the following means: Powder of 8YSZ (8 mol % yttria doped zirconia obtained from TOSOH, TZ8Y) was uniaxially pressed at approximately 25 MPa for 15 seconds and then isostatically pressed at approximately 325 MPa for 30 seconds.

The resulting cylindrical samples were then machined into two types of samples:

- A: 'As-pressed' samples: Cylindrical samples which were machined before sintering to get a plane surface.
- C: 'Pyramid' sample: Sample with 18 to 25 pyramids that were 0.3 mm high. The pyramids were fabricated using the same method as for the LSM pyramid samples.

Sintering of the YSZ samples followed a program with the temperature profile shown in figure 5.5.
After sintering, grooves were machined at the side and bottom of the samples so potential and current probes could be mounted (figure 5.2).

The density of the sintered samples was 5.94 g/cm$^3$ which corresponds to 99% of the theoretical density of TZ8Y ($\rho = 5.95$ g/cm$^3$ [16]).

10 as-pressed and 1 pyramid sample was made of YSZ.

### 5.2.3 Strontium and nickel doped lanthanum cobaltite

Samples of strontium and nickel doped lanthanum cobaltite ($\text{La}_{0.69}\text{Sr}_{0.30}\text{Co}_{0.9}\text{Ni}_{0.1}\text{O}_3$) were prepared by the following means:

The powder was prepared by the glycine/nitrate pyrolysis technique where nitrate solutions of the metal ions are mixed with glycine and heated to ignition. The resulting powder was divided in two parts: one was calcined in air for 2 hours at 900°C and the other was left untreated.

The two powders were mixed after calcination and ball milled for 30 minutes.

The powder was then pressed into cylindrical samples by uniaxial pressing at 50 MPa for 30 seconds followed by isostatic pressing at 325 MPa for two minutes. The samples were then sintered in air at 1250°C for 2 hours with increasing and decreasing temperature ramps of 100°C.

X-ray powder diffraction showed an almost uniform material with a rhombohedral unit cell (parameters shown in table 5.1). The calculated X-ray density of the material was 6.75 g/cm$^3$ (assuming stoichiometry and six formula units in each unit cell). The density of the sintered samples was 6.33 g/cm$^3$, which corresponds to 94% of the calculated X-ray density.

After sintering, grooves for the potential and current probes were cut in the samples to ensure precise positioning of the probes. Only 2 as-pressed samples were made of this material (type A).
5.3 Contact experiments

Two samples were placed on top of each other and the contact resistance was measured as a function of temperature, polarisation, atmospheric composition and contact load. Experiments with pyramid samples (type C) involved contacting a pyramid sample with an as-pressed sample (type A). Maximum load was 2000 g/cm² (geometric area).

In order to test the behaviour of newly created contact interfaces as well as ageing-effects, contacts of two types were made:

- Type I: Fresh contacts created by lifting the top sample and then lowering it again. This could be done in situ in the furnace at elevated temperatures.
- Type II: Aged contacts, which were investigated after 1 to 3 days under load (200 g/cm²). The experiments are performed without lifting the top sample.

Contacts were only classified as ‘fresh’ as long as the time between the formation of the contact and the measurement did not exceed one hour.

LSM contacts were tested at room temperature, 200°C, 400°C, 600°C, 800°C and 1000°C.

For the YSZ contacts, experiments were performed at 600°C, 700°C, 800°C, 900°C and 1000°C, as the conductivity below 600°C was too low. The LSCN samples were tested at room temperature, 200°C, 400°C, 600°C, 800°C and 1000°C.

At all the above mentioned temperatures, load experiments, as well as potential sweep and ageing experiments were performed.

5.3.1 Potential sweep experiments

The polarisation influence on the contact resistance was measured by linear potential sweep methods with sweep rates ranging from 0.1 to 0.8 V/min. Each potential sweep measurement consisted of at least two complete polarisation cycles. The YSZ samples were tested at polarisations up to 2 V, whereas the cobaltite was tested at currents below 500 mA/cm². The LSM was tested at currents up to 200 mA/cm². The contact load for the plane samples (as-pressed and polished) during the potential sweep measurements was approximately 200 g/cm² and for the pyramid samples it was approximately 100 g/cm².

Data were logged at 5-second intervals and polarisation sweeps were made both on fresh and aged contacts at all the investigated temperatures.

5.3.2 Load sweep experiments

The load experiments were performed by measuring the contact resistance at different contact loads. Each measurement was performed after the contact had equilibrated for 4 seconds at each load. Each load-unload run with approximately 50 measurements took about 10 minutes and when possible three subsequent load-unload runs were made. The time interval between each measurement in a load sweep sequence was between 8 to 10 seconds.

The pyramid samples (type C) were only tested up to 1000 g/cm² in order to prevent cracking that might render the sample useless.

Fresh contacts were investigated in the range 0 to 2000 g/cm² whereas aged contacts were analysed in the load range 200 g/cm² to 2000 g/cm². 9 sample pairs was investigated; 3 LSM sample pairs, 5 YSZ sample pairs and 1 LSCN sample pair.

5.3.3 Ageing experiments

A number of sample pairs (7 pairs of which 3 was LSM, 3 was YSZ and 1 was LSCN) were tested for change in the contact resistance during the course of time. The ageing
experiments involved making a fresh contact and then measuring the contact resistance every 15 minutes for one to seven days (usually 3 days).

The contact load was kept constant at 200 g/cm\(^2\) (geometric area) during the experiments.

### 5.3.4 Temperature experiments

The contact resistance was measured while the temperatures was changed. These measurements were performed with constant contact load (approximately 200 g/cm\(^2\)) and constant temperature ramps. The rate of the temperature change was between 15 and 100 °C/h but for most experiments the temperature rates was between 25 and 50 °C/h. 10 contact pairs was investigated of these 4 was of LSM, 5 was of YSZ and 1 was of LSCN.

### 5.3.5 Experiments at different atmospheres

A Contact pair of LSM (type A) was heated in different atmospheres: air (0.08% H\(_2\)O), dry nitrogen (5 ppm H\(_2\)O) and wet nitrogen (0.2% H\(_2\)O and 3% H\(_2\)O). The oxygen partial pressure in the nitrogen atmospheres was between 2.3·10\(^{-3}\) and 3.0·10\(^{-3}\) atm. measured by the external oxygen sensor on the contactometer (section 5.1.1). The relatively high oxygen partial pressure in the nitrogen was most likely due to gas leakage in the contactometer.

During the experiments with different atmospheres the maximum polarisation of the contact was 0.2 V and a current limit of 0.1 A was used.

In order to ensure that the contact surfaces were in equilibrium with the chosen atmosphere, the samples were annealed in the same atmosphere as the test atmosphere. This was performed before the contact was created. The annealing was performed at 600 °C for 2 hours.

Each experiment started at room temperature with the formation of a fresh contact, then the furnace was engaged and the contact resistance was measured with 15 minutes intervals. At 800 °C the contact rested for 4 hours before the temperature was lowered again. The samples were heated at a rate of 25 °C/h and cooled at a rate of 50 °C/h.

One sample pair of LSM was used for these experiments, and these samples had not previously been used in any experiments.

### 5.3.6 Experiments with technological applicable contact layers

Two experiments involving technological contact interface materials were made. These interfaces were designed to be able to deform in order to achieve a high contact area.

One of these experiments included a contact layer of an LSM tape (unsintered LSM powder in an organic binder) between polished LSM samples (type B). As the LSM tape (Risø LSM#TC438) was sinterable, no load-sweep experiment was made. This contact was named a type D contact.

The contact layer was heated to 600 °C, 750 °C, 850 °C and 900 °C and the contact resistance was measured every 15 minutes. At each of the above temperatures, the contact layer was held at constant temperature for approximately 24 hours. This was done to investigate how the contact resistance of the layer depended on the temperature, as well as on the elapsed time.

The other technological experiment (called type E) included a contact layer made of small (1 mm diameter and 1 mm high) unsintered cylindrical LSM pellets in a hexagonal pattern with 1 mm between the cylinders (figure 5.6). The contact layer had polished LSM samples (type B) on each side. The LSM contact layer was obtained from IRD A/S (LSM-00-14/1 produced from LSM batch #132 powder from Haldor Topsøe A/S).

A schematic comparison between the two types of contact layers is shown in figure 5.6 and the temperature profile used for the cylindrical contact layer is shown in figure 5.7.
Figure 5.6. Schematic view of the two types of technological contact layers investigated. The height of the LSM tape was approximately 100 µm whereas the height of the soft LSM cylinders in the cylindrical contact layer was approximately 1 mm. The upper solid LSM is shown transparent.

Figure 5.7. Temperature profile used in the contact experiment with a sinterable contact layer consisting of small cylinders.

After approximately 50 hours the temperature had to be brought back to room temperature in order to fix a short circuit between two of the potential probes. After repairing the potential probes, the temperature was brought back to 850°C and the experiment continued. After 6 days at this temperature, thermal cycling experiments were performed (decreasing the temperature to room temperature and increasing it to 850°C again). A load sweep experiment to investigate the mechanical stability were performed after 16 days. This experiment was performed at 850°C.
5.4 Summary of the experiments

The different materials were all analysed for current-voltage response and contact resistance dependence on load and temperature. The LSM and LSCN were analysed at room temperature, 200°C, 400°C, 600°C, 800°C and 1000°C whereas the YSZ was only analysed at 600°C, 700°C, 800°C, 900°C and 1000°C.

The LSM and YSZ samples were also analysed for the time dependence of the contact resistance after formation of a fresh contact (ageing experiments).

Optical and SEM microscopy of the contact interfaces were performed before and after the samples had been tested. All the sample types were investigated and one polished and two as-pressed LSM samples were also analysed by AFM and laser scanning microscopy.

Table 5.2 is a summary of the surface analysis performed on the different sample types and table 5.3 is a listing of the different experiments performed on the different contact pairs.

Table 5.2. Summary of the different analysis performed on the different sample types divided according to contact pairs used.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>LSM</th>
<th>YSZ</th>
<th>LSCN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>SEM</td>
<td>X</td>
<td>X</td>
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</tr>
<tr>
<td>Optical</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Laser</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>AFM</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3. Summary of the different experiments performed on the different sample types divided according to contact pairs (where multiple contact pairs were investigated subscripts are used).

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample</th>
<th>Potential sweeps</th>
<th>Load sweeps</th>
<th>Ageing</th>
<th>Temperature Change</th>
<th>Atmospheric composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM</td>
<td>A1</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>A2</td>
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<td>C1</td>
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<td>C2</td>
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<tr>
<td>LSCN</td>
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</tbody>
</table>

LSM Contact pair C 2 was used in a no-current experiment and was investigated with SEM and optical microscopy for changes in the contact interface during the experiment. The results from YSZ contact pairs A 2 and A 3 were discarded as the contact resistance for these contacts were above 1 MΩ at all the investigated temperatures.

The following chapters present the results of the surface analysis and the electrical measurements. Each chapter is divided according to material in the order: LSM, YSZ and LSCN. The only exception to this is chapter 6, where the laser scanning microscopy data of the LSM samples are presented last.
6 Results of the surface analysis

Changes in the surface structure of the ceramic contact interfaces were expected during the experiments. In order to determine if changes had taken place, most of the samples were examined by SEM before and after the experiments. Atomic force microscopy, laser scanning microscopy, and Optical laser profile analysis was used to determine the surface morphology of some of the samples.

6.1 Surface structures of the LSM samples

The as-pressed and polished LSM samples (type A and B) generally showed little change after the experiments, whereas the pyramid (type C) LSM samples showed considerable changes at the points of contact. SEM and optical analyses were used to determine the contact area. Based on this, comparison between the contact resistance expected by constriction resistance and the measured contact resistance could be made.

6.1.1 Surface structures before experiments

All the as-pressed and pyramid samples (type A and C) showed rounded crystals and equilibrium grain boundaries were found in all samples. Figure 6.1 shows the typical surface structure observed on the as-pressed samples. These samples generally showed 'long-range hills' on the surface of the samples as shown in figure 6.1. The polished samples did not show these structures, which were most likely due to irregularities in the pressing tools.

As expected, the polished LSM samples (type B) showed lower relief than the as-pressed samples (type A). SEM images taken before annealing revealed a plane surface which was scratched and porous. Images taken after annealing showed evidence of mass transport, as grain boundaries were visible as small grooves (see figure 6.2).

Figure 6.1. SEM image of the surface of an as-pressed LSM sample (type A) showing long range structures (horizontal ridges with 20 µm between crests) from the pressing of the sample.
Figure 6.2. SEM images of the surface of a polished sample (type B). (A) before and (B) after annealing at 1000°C for four hours in air. Before annealing no grain boundaries were found. After annealing the grain boundaries are visible as small grooves.

6.1.2 Atomic force microscopy of LSM

An as-pressed and a polished LSM sample (type A and B) were examined by AFM. There was a clear difference in the surface morphology of the two sample types. The polished samples showed a tile pattern with relative plane crystal surfaces and grain boundary grooves. Figure 6.3 shows a typical example of a polished surface imaged in the AFM. The dark spots are holes, with a depth greater than 0.5 µm as it was not possible to precisely determine the depth of all the holes due to the small diameter of the holes.

Figure 6.4 shows an as-pressed LSM sample (type A). The surface of these samples was rough compared to the polished surfaces (type B). The individual grains were more rounded with a relatively high relief of approximately 4 µm compared to approximately 0.5 µm for the polished samples.
Figure 6.3. AFM image of a polished and annealed sample (type B) showing clear grain boundaries.

Figure 6.4. AFM image of an as-pressed LSM sample (type A).
6.1.3 LSM contact area determination after experiments

After the experiments, no clear contact area could be identified for the as-pressed and polished samples (type A and B). For the pyramid samples, however, the maximum area of contact achieved during an experiment could be determined. An experiment was performed to determine if any change in the pyramids may be due to the loading only. In this experiment the pyramid tips were loaded for three days at room temperature. A distinct cracking of the pyramid tops was found on the pyramids that had been subjected to load (200 g/cm², geometric area). Figure 6.5 shows several cracks and fractures along the rim of the contact area after the sample had been under load. The small bright grains in figure 6.5 are most likely pieces of the LSM sample placed on top during the experiment. All changes in the contact interface are results of mechanical effects as this experiment was without electrical connections.

![Figure 6.5. Tip of LSM pyramid before (A) and after (B) 72 hours at room temperature in contact with a LSM covered YSZ plate pressed against the tip with a load of 200 g/cm².](image)

Similar changes were seen on samples that had been annealed under mechanical load at a temperature of 800°C. At this temperature the cracking was observed in the form of a porous contact area with a low grain size as shown in figure 6.6 and 6.7. EDX analysis
of the contact areas showed impurities within the cracks. The impurity elements observed were: sodium, potassium, chlorine, aluminium and silicium.

Figure 6.6. SEM images of a pyramid tip (type C). Image A is taken before the experiment, and image B was taken after three days at 800°C under a load of 200 g/cm². The estimated contact area is outlined in white.

Figure 6.7. Porosity on the tip of a LSM pyramid sample that was under a mechanical load of 220 g/cm² for three days at 800°C.

Using images of pyramid samples taken before and after the experiments, the maximum contact area could be determined. For the pyramid sample (LSM type C) that had been kept at 800°C for three days at a load of 200 g/cm², the contact area was found to be $2.4 \times 10^{-4}$ cm² with an estimated uncertainty of 10%. Out of 82 pyramids, 36 had been in contact. The contact resistance at 800°C due to constriction was calculated to be 0.14 $\Omega$cm². This was achieved using equation 3.14 and correcting for the pyramid geometry. The measured contact resistance at 800°C was 0.495 $\Omega$cm².

6.2 Surface structures on the YSZ samples.

The as-pressed YSZ samples (type A) showed rough surfaces. Figure 6.8 is an SEM image of an as-pressed YSZ sample. The grain size of the bulk YSZ was approximately 4 $\mu$m (measured in fractures and holes as shown in figure 6.9), while for the surface of the YSZ no clear grain boundaries could be observed. Long grooves were seen on the
YSZ surfaces. These grooves probably result from the machining before sintering.

![SEM image of the surface of a YSZ sample (type A). The long grooves are a result of the machining before sintering.](image)

EDX analysis of the YSZ samples did not show any presence of impurities at the surface, only yttrium, zirconium and hafnium (which are present in commercially available zirconia [55]) were found.

### 6.2.1 YSZ contact area determination after experiments

After tests, certain pyramid tips had developed flat areas at their apex. The size of the individual contact areas varied between 50 and 3200 $\mu m^2$. The main part of one of these is shown in figure 6.9.

Figure 6.10 shows the apex of a YSZ pyramid before and after testing revealing the flat contact area after the experiment. The contact areas were smooth and flat in comparison to the surrounding YSZ surface (figure 6.10). Out of 31 pyramids, 14 were found to have been in contact. The maximum area of contact was determined to be $8 \cdot 10^{-5} \text{ cm}^2$ corresponding to a relative contact area of 0.007%.

Using equation 3.14 and the measured contact areas (and assuming circular contact areas), the calculated contact resistance arising only from constriction resistance was 200 $\Omega \text{ cm}^2$ at 1000°C. The measured contact resistance at 1000°C was 586 $\Omega \text{ cm}^2$.

### 6.3 Surface structures on the LSCN samples

The crystals at the surface of the as pressed LSCN samples were smooth. Figure 6.11 shows a typical LSCN surface as viewed with the SEM. The surface has undulating grain boundaries and minor porosity. The grain size was generally between five and ten microns but larger and smaller grains were observed.

The LSCN samples appeared dense, as only minor porosity were observed in the surface.

#### 6.3.1 Changes in the surface structure of the LSCN samples after experiments

Most of the surface of the LSCN samples did not show any sign of changes during the experiments. A few small areas where were found where the surface structure had changed.
Figure 6.9. SEM image of the tip of an YSZ pyramid. The rough surface in the left side of the image is similar to the surfaces observed on the as-pressed YSZ samples (figure 6.8). The flat area in the center is assumed to be the contact area formed during the contact experiments.

Figure 6.10. SEM image of the tip of a YSZ pyramid (sample type C) viewed before (A) and after experiment (B). The estimated area of contact is outlined in figure B.

These areas were assumed to be the actual areas of contact and figure 6.12 shows one of these areas where the smooth LSCN surface was replaced by a more rough surface structure.

EDX measurements of these contact areas showed traces of aluminium, phosphorus, sodium, potassium and chlorine. On the surface of the LSCN samples (outside the contact areas) a few grains of segregated material were observed. Figure 6.13 show some of these grains, which showed a increased content of nickel and strontium compared to the other grains on the surface. The segregate grains had a rough surface compared to the LSCN grains and were generally smaller with a diameter less than five microns.

6.4 Contact area determination for sinterable contact layers

It was possible to determine the contact area for the technological experiment involving a green LSM tape (type D). After the experiment, the samples were pulled apart and the
contact area was measured by analysing optical microscopy images. Figure 6.14 shows the contact interface after the experiment. It was observed that only 40% of the area had been in contact during the experiment and several areas were observed from which the LSM tape had disappeared (dark grey areas without porosity in figure 6.14). The resistance of the layer was calculated to be 3.6Ω/cm². This was calculated using a conductivity of 20.3 S/cm (determined by in-plane measurements of a LSM tape heated to 850 °C ) and equation 3.10.

For the cylindrical contact layer, the small cylinders that was still between the pellets and was not tilted was assumed to have been in contact during the experiment. The area of contact was determined to be 20% of the geometrical area (the area of the underlying pellet). The resistance of the layer was calculated to be 7.4mΩcm² assuming a conductivity of 54 S/cm [56] for the porous LSM and using equation 3.10.
Figure 6.13. SEM image of segregates on an LSCN sample (type A).

Figure 6.14. Composite optical micrograph of the sinterable contact interface (LSM type D) after the experiment.

6.5 Optical profile analysis

Two types (as-pressed and polished) of LSM samples were investigated by laser scanning microscopy. The laser scanning microscope was not able to analyse the pyramid samples (type C) due to the geometry.

Figure 6.15 shows sections of the resulting 3-dimensional surface maps obtained. The
polished sample showed a smooth surface with small height differences as opposed to the as-pressed sample which was rougher.

**Figure 6.15.** A: Surface height of an as-pressed sample (type A). B: Surface height of a polished sample (type B).

The 3-dimensional maps were used to calculate the contact area at different indentations, and the indentation/area distribution for the different surface geometries are shown in figure 6.16 and 6.17. The indentation/area distribution for a pyramid sample, based on an ideal pyramid surface was calculated,

\[ A = 4z^2 \tan \theta \]

where \( z \) is the indentation, and \( \theta \) is half the opening angle of the pyramid (\( \theta = 45^\circ \)). The pyramid samples achieve 100% contact area at an indentation (\( \Delta z \)) of 500 \( \mu \)m.

To be able to compare the measurements, the data was normalised so that the indentation/area curves cross each other at a relative contact area of 0.01%. This value was chosen as the contact areas measured by electron microscopy were within this order of magnitude.

**Figure 6.16.** Relative contact area versus indentation depth (\( \Delta z \)) for the different surface morphologies. The data for the pyramid samples are based on calculations on a perfect pyramid. The other surfaces are based on statistical analysis of 1 mm x 1 mm scan data of the relevant samples.

Figures 6.16 and 6.17 show that the contact area versus indentation for the as-pressed and polished samples differ little compared to the pyramid samples. The difference is that the polished samples (type B) achieve 95% contact area after an indentation of only 3 \( \mu \)m whereas the as-pressed sample (type A), due to circular medium to large-scale (20 \( \mu \)m to 0.5 mm between crests) hill structures left over from pressing, first achieve full contact area (95%) after 16 \( \mu \)m. A cross section of one of the large hills is shown in figure 6.18. Another difference between the polished and as-pressed samples is the steeper
increase in contact area for the as-pressed sample in the beginning (as seen in figure 6.17). This is perhaps because the indentation of the as-pressed sample was dominated by a circular hill for the first few µm. Another possibility is the influence of small amounts of impurities or dust on the surface of the polished sample, which could account for the 'tail' at low indentations.

![Graph showing relative change and indentation depth]

**Figure 6.17. Subsection of figure 6.16.**

![Graph showing surface height along a 1 mm line]

**Figure 6.18. Surface height of an as-pressed LSM sample (type A) along a 1 mm line. The large hill is a result of the pressing of the sample.**

The laser scanning data were also analysed using fast fourier transformation analysis (FFT). The 2-dimensional scan data were analysed in the x and y directions for each line individually. The resultant spectra were then stacked (added) to increase the signal to noise ratio.

The figures 6.19 and 6.20 show the cumulative Fourier spectra for a polished and an as-pressed sample.

A clear distinction between the two surfaces were observed in the Fourier spectra. The polished sample showed no dominating wavelengths (figure 6.20), whereas the as-pressed sample was dominated by wavelengths above 0.1 mm (figure 6.19).
Figure 6.19. Cumulative Fourier spectra for an as-pressed sample (type A). The green and blue lines represent scans at right angles to each other and each line represents 500 stacked scan lines.

Figure 6.20. Cumulative Fourier spectra for a polished sample (type B). The green and blue lines represent scans at right angles to each other and each line represents stacked data for 500 scan lines.
7 Ageing effects on the contact resistance

The contact resistance changed after formation of a contact. When a fresh contact was created, the contact resistance was generally higher than after several days under load.

7.1 LSM contact ageing

Contact ageing was investigated for all the LSM sample types. Figure 7.1 shows the area specific contact resistance (ASR) at different temperatures. Generally the contact resistance decreased after formation of the contact. Exceptions were found at 200°C, where the contact resistance was not stable and showed no clear trend (two experiments were performed at this temperature, and both showed similar behaviour), and at 600°C, where the contact resistance increased slightly over time (figure 7.1). Due to the unstable contact resistance at 200°C, no experiments were performed at this temperature for as-pressed and pyramid samples (type A and C).

Figure 7.1. Change in area specific contact resistance for a polished LSM contact interface. The contact resistance is normalised by multiplying with the electrical conductivity

The as-pressed samples (type A) showed a similar anomaly at 600°C, although the increase in resistance was small as shown in table 7.1 and figure 7.2. The pyramid samples (type C) showed a small decrease in contact resistance after contact formation at all investigated temperatures. The relative changes in the contact resistance for the three sample types are shown in table 7.1.

7.1.1 LSM contact deformation

At 800°C the change in contact resistance for the pyramid contacts (type C) was accompanied by a change in the sample height as shown in figure 7.3. Although the LVDT sensor (section 5.1.1) had a resolution of only 2 μm at this temperature, it was possible to measure the decrease in sample height. The total change in sample height was 10 μm and the displacement followed the law for primary creep with $m = 0.5$ [57]

$$
\varepsilon = \beta \varepsilon^m
$$

(7.1)

where $\varepsilon$ is the creep, $\beta$ is a constant, and $m$ is a constant between 0.03 and 1 depending on material, stress and temperature [57].
Figure 7.2. Comparison of the change in area specific contact resistance at 600°C for the different LSM surface morphologies. Note that the contact resistance for the polished samples (type B) is higher than the resistance for the other sample types.

Table 7.1. Relative contact resistance change for LSM contacts after 18 hours under load (200 g/cm²).

<table>
<thead>
<tr>
<th>Sample type</th>
<th>T / °C</th>
<th>ΔASR / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-pressed</td>
<td>25</td>
<td>-3.5</td>
</tr>
<tr>
<td>(A)</td>
<td>400</td>
<td>-8.7</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>-43.0</td>
</tr>
<tr>
<td>Polished</td>
<td>25</td>
<td>-16.6</td>
</tr>
<tr>
<td>(B)</td>
<td>200</td>
<td>-6.2</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>-9.6</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>-47.6</td>
</tr>
<tr>
<td>Pyramid</td>
<td>25</td>
<td>-15.2</td>
</tr>
<tr>
<td>(C)</td>
<td>400</td>
<td>-0.9</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>-0.8</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>-28.8</td>
</tr>
</tbody>
</table>

A linear relation between the square root of time and the displacement was found (figure 7.3). Changes in sample height were not observed for the as-pressed and polished samples (type A and B).

7.2 Effect of sinterable LSM contact layers on contact resistance

The contact resistance measured for the sinterable contact layers was smaller than the contact resistance measured for all the other LSM experiments. The area specific contact resistance at 850°C was measured to be 5 mΩcm² for the soft layer (type D, section 5.3.6) and 15 mΩcm² for the cylindrical contact layer (type E, section 5.3.6). Figures 7.4 and 7.5 shows the contact resistance for the two sinterable layers (type D and E) at different temperatures. Both experiments were characterised by an extremely high initial contact resistance, but at temperatures around 600°C the area specific contact resistance had dropped below 1 Ωcm² for both contact layer types.

No variation in contact resistance with changing load was observed for these experiments, and the contact interface for the cylindrical contact layer was thermally stable, as
Figure 7.3. Decrease in sample height ($\Delta z$) and area specific contact resistance (ASR) versus the square root of time at 800°C for pyramid contacts (LSM type C).

Figure 7.4. Contact resistance for a sinterable LSM layer (type D) at different temperatures.

two thermal cycles did not increase the contact resistance more than 3%.

LSM contacts without sinterable contact layers (type A, B and C) showed a much higher contact resistance than contacts with a deformable layer. Resistances measured for the three different LSM surface morphologies are reported in table 7.2.

7.2.1 Change in contact layer height

For the cylindrical contact layer (type E), a decrease in the height of the contact layer of 80 $\mu$m was measured as shown in figure 7.5. Most of the change in layer height observed was between 800°C and 950°C. This decrease in contact layer height was accompanied by a reduction of the contact resistance of 80% (between 800°C and 950°C). This should be compared to the significant decrease in contact resistance observed at lower temperatures. From room temperature to 500°C the contact resistance dropped by more than three
Table 7.2. Lowest area specific contact resistances achieved for different surface morphologies.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Lowest area specific contact resistance at 800°C / mΩcm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-pressed (A)</td>
<td>381</td>
</tr>
<tr>
<td>Polished (B)</td>
<td>160</td>
</tr>
<tr>
<td>Pyramid (C)</td>
<td>495</td>
</tr>
<tr>
<td>Sinterable contact (D)</td>
<td>5</td>
</tr>
<tr>
<td>Cylindrical contact layer (E)</td>
<td>15</td>
</tr>
</tbody>
</table>

orders of magnitude.

Figure 7.5. Change in contact layer height and contact resistance for an LSM contact layer consisting of small cylindrical contact points (type E).

The cylindrical contact layer (type E) continued to decrease in height while the temperature was kept at 950°C. During this time the height decreased 20 µm the small increase in layer height observed in figure 7.5 at t = 1.4 was assumed to be due to external noise and not an actual increase in layer height. During the time the contact was held at 950°C, the contact resistance decreased from 26 to 15 mΩcm².

7.3 YSZ contact ageing

Only two of the experiments involving as-pressed YSZ samples resulted in a contact resistance below 1 MΩ. For these samples, the contact resistance decreased after formation of the contact interface (figure shows the typical response 7.6). This was observed at temperatures above 600°C. At 600°C, a slight increase in the contact resistance over time after the formation of the contact was observed for one of the samples as shown in figure 7.7. For the other sample no change was observed. Figure 7.8 shows the area specific contact resistance for the pyramid YSZ sample (type C) at 800 and 1000°C. This sample showed only small changes in contact resistance at 800°C whereas a significant decrease in the contact resistance over time was observed at 1000°C.
Figure 7.6. Change in area specific contact resistance for an as-pressed YSZ contact interface at 800°C.

Figure 7.7. Change in area specific contact resistance for as-pressed and pyramid YSZ contact interfaces at 600°C.

7.4 LSCN contact ageing

The LSCN contact showed a decrease in the contact resistance at 800°C. At room temperature, a small increase in the contact resistance over time was found. Figure 7.9 show the change in contact resistance at room temperature and at 800°C.
Figure 7.8. Change in area specific contact resistance for a pyramid YSZ contact interface at 800 and 1000°C. Note the different scales.

Figure 7.9. Change in area specific contact resistance for an as-pressed LSCN contact interface at room temperature and at 800°C. Note the different scales.
8 Temperature effect on contact resistance

Increasing the temperature of a contact interface had the effect, that the contact resistance decreased. This was observed for all the investigated materials.

8.1 Temperature effect on LSM contacts interfaces

The contact resistance of LSM contact pairs was highly temperature dependent as shown in figure 8.1 and a large difference in the contact resistance between the heating and the cooling ramps was observed. The apparent activation energy for the contact interface was higher during heating than after the samples had been at high temperatures (above 600°C). This is observed as the difference in the slopes of the heating and cooling curves in the Arrhenius plot (figure 8.1).

![Figure 8.1. Contact resistance dependence on temperature for as-pressed LSM samples (type A) in air (0.08% H₂O). The rate of temperature change was 25°C/h for the increasing temperature ramp and 50°C/h for the decreasing ramp.](image)

Different surface morphologies resulted in different apparent activation energies, both for heating and subsequent cooling. The largest activation energy was observed for the polished samples (type B) and the lowest was observed for the pyramid samples (type C). The activation energies for the different surface types are shown in table 8.1.

During cooling, the pyramid samples (type C) showed an apparent activation energy close to that observed for bulk LSM above 200°C (table 8.1). The as-pressed samples (type A) showed an activation energy close to that of the bulk, whereas the polished samples (type B) had an activation energy higher than the bulk above 200°C (table 8.1).

It should be noted that after the heat treatment, the low contact resistance after heating was permanent until the contact was broken.
Table 8.1. Activation energies for different temperatures and surface morphologies (all data are from LSM in air with 0.08% H₂O and all samples had been heated to 800°C). The activation energy for bulk LSM is shown for comparison.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Increasing temperature</th>
<th>Decreasing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T / °C</td>
<td>Eₐ / eV</td>
</tr>
<tr>
<td>As-pressed (A)</td>
<td>100 to 200</td>
<td>0.15 ±0.01</td>
</tr>
<tr>
<td></td>
<td>500 to 600</td>
<td>0.23 ±0.01</td>
</tr>
<tr>
<td>Polished (B)</td>
<td>100 to 200</td>
<td>0.23 ±0.01</td>
</tr>
<tr>
<td></td>
<td>500 to 600</td>
<td>0.34 ±0.01</td>
</tr>
<tr>
<td>Pyramids (C)</td>
<td>100 to 200</td>
<td>0.19 ±0.005</td>
</tr>
<tr>
<td></td>
<td>500 to 600</td>
<td>0.13 ±0.005</td>
</tr>
<tr>
<td>Bulk LSM</td>
<td>100 to 200</td>
<td>0.15 ±0.01</td>
</tr>
<tr>
<td>Sinterable contact (D)</td>
<td>100 to 200</td>
<td>0.15 ±0.01</td>
</tr>
<tr>
<td></td>
<td>500 to 600</td>
<td>0.11 ±0.01</td>
</tr>
<tr>
<td>Sinterable contact (E)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

8.1.1 Atmospheric influence on LSM contact resistance

The influence of the atmosphere on the contact resistance was examined for the LSM contact interfaces. During heating, no difference in the activation energy between samples in air and nitrogen was observed and all samples showed similar conductivity-temperature behaviour as that shown in figure 8.1.

The activation energy between 800°C and 200°C did not show any dependence on the atmospheric composition. As shown in figure 8.3, after annealing at 800°C for 4 hours, a difference in the low-temperature (100°C < T < 200°C) activation energy was observed between the air experiments and the experiments in nitrogen. The water content did not influence the activation energy for the LSM significantly. The bulk LSM activation energy did not show any dependence on the atmosphere within the oxygen and water partial pressures investigated and the room temperature current-voltage response was not influenced to a significant degree by the oxygen or water partial pressure as shown in table 8.2.
Figure 8.3. Change in low temperature ($100^\circ C < T < 200^\circ C$) activation energy for as-pressed LSM contact resistance in different atmospheres. The values are all determined on decreasing temperature ramps.

Table 8.2. Number ($n$) of potential barriers between as-pressed LSM surfaces at room temperature in different atmospheres

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>$n$ ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air (0.08% H$_2$O)</td>
<td>4.4±0.2</td>
</tr>
<tr>
<td>N$_2$ (5 ppm H$_2$O)</td>
<td>4.4±0.2</td>
</tr>
<tr>
<td>N$_2$ (0.2% H$_2$O)</td>
<td>3.9±0.2</td>
</tr>
<tr>
<td>N$_2$ (3% H$_2$O)</td>
<td>4.6±0.2</td>
</tr>
</tbody>
</table>

8.2 Temperature effect on YSZ contact interfaces

As shown in figure 8.4, increasing the temperature of YSZ contacts yields a significant decrease in contact resistance. A reduction in the contact resistance over time was observed at 1000$^\circ$C. In figure 8.4 this is represented by the jump from the lower to the upper curve.

The activation energy in the YSZ contact interfaces was higher during heating of the contact than during cooling as shown in table 8.3.

Table 8.3. Activation energies for different temperatures and YSZ surface morphologies. The activation energy for bulk YSZ is shown for comparison.

| Sample type               | Increasing temperature | Decreasing temperature | |
|---------------------------|------------------------|------------------------|
|                           | $T / ^\circ C$ | $E_a / eV$ | $T / ^\circ C$ | $E_a / eV$ | |
| As-pressed (A)            | 600 to 800        | 1.1 ±0.1       | 1000 to 600    | 1.02 ±0.05  |
|                           | 800 to 1000       | 1.44±0.02      |                      |
| Pyramid (C)               | 600 to 1000       | 1.03±0.02      | 1000 to 600      | 0.98±0.01   |
| Bulk YSZ                  | 600 to 1000       | 0.92±0.03      | 1000 to 600      | 0.92±0.03   |
| YSZ grain interior [58]   | 200 to 500        | 1.07           |                      |
| YSZ grain boundary [58]   | 200 to 500        | 1.12           |                      |

8.3 Temperature effect on the LSCN contact interface

Increasing the temperature of an LSCN contact caused a decrease in the contact resistance as shown in figure 8.5. Only one experiment with LSCN was carried out and in
Figure 8.4. Contact resistance dependence on temperature for an as-pressed YSZ sample (type A) in air (0.08% H$_2$O). The rate of temperature change was 50°C/h for the increasing and decreasing ramp. The small bump on the lower graph is due to the formation of a fresh contact at 800°C where potential sweep and load sweep measurements were performed before continued heating of the samples. The samples were held at 1000°C for 24 hours before cooling began.

In this experiment, load sweep and potential sweep experiments were conducted at room temperature, 200, 400, 600 and 800°C. The breaks in the heating curve in figure 8.5 reflect the time where the contact interface was held at constant temperature during these experiments.

After 24 hours at 1000°C the two LSCN samples could no longer be separated in situ in the furnace. After the samples had been at 1000°C the contact resistance showed the same variation below 900°C as the bulk resistivity of the LSCN.

After the experiment, the room temperature contact resistance had dropped from 310 mΩcm$^2$ to 7 mΩcm$^2$. The contact resistance at 1000°C was 20 mΩcm$^2$.

Figure 8.5. Contact resistance dependence on temperature for a LSCN type A contact in air. The rate of temperature change was 50°C/h for the increasing and decreasing ramp. Each break in the curve represents a time period of approximately 24 hours where potential sweep and load sweep experiments were conducted.
9 Load induced resistance variations

All the interfaces without sinterable contact layers showed a significant decrease in the contact resistance when the interface load was increased.

9.1 LSM contact behaviour

Two sets of experimental data are shown in figure 9.1. These data can be fitted to a power law:

\[ ASR = kP^{-p} \]  \hspace{1cm} (9.1)

where \( p \) is the load exponent. All the data from the load experiment could be fitted with equation 9.1. The results of the load experiments are summarised in table 9.1. The load exponents were determined for loads from 100 g/cm\(^2\) to 2000 g/cm\(^2\) as the data below this range generally was noisy.

![Graph A](image1.png)  \hspace{1cm} ![Graph B](image2.png)

*Figure 9.1. Log(ASR) versus log(P) for LSM contacts. A: An as-pressed sample (type A) at 400\(^\circ\)C and B: a pyramid sample (type C) at 800\(^\circ\)C.*

All load-unload runs showed difference between loading and unloading runs, where the resistance was lower during unloading than during loading (figure 9.1).

Aged contacts had smaller load exponents than fresh contacts at all temperatures (table 9.1).

<table>
<thead>
<tr>
<th>Sample type</th>
<th>T / (^\circ)C</th>
<th>( p ) fresh</th>
<th>( p ) aged</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-pressed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A)</td>
<td>25</td>
<td>0.5 ± 0.13</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.6 ± 0.06</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.45 ± 0.05</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.7 ± 0.04</td>
<td>0.65</td>
</tr>
<tr>
<td>Polished</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B)</td>
<td>25</td>
<td>1 ± 0.14</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>1.09 ± 0.005</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>1.09 ± 0.005</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.8 ± 0.01</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyramid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C)</td>
<td>25</td>
<td>0.5 ± 0.1</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.6 ± 0.02</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.37 ± 0.025</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.75 ± 0.08</td>
<td></td>
</tr>
</tbody>
</table>

Contacts that had been heated to 1000\(^\circ\)C showed almost no change in contact resistance with changing load (\( p = 0.05 \)), and could not be separated in situ, thus no results for fresh contacts could be obtained at this temperature.
9.2 YSZ contact behaviour

The contacts were investigated at contact loads ranging from 100 to 2000 g/cm². The observed load exponents are shown in table 9.2. The uncertainties reported in table 9.2 are based on the variation of the load exponents observed between three individual load sweep experiments.

Table 9.2. Load exponents for fresh and aged YSZ contacts at different temperatures. Uncertainties are based on differences in exponents between different experiments.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>T / °C</th>
<th>$p_{\text{fresh}}$</th>
<th>$p_{\text{aged}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-pressed</td>
<td>600</td>
<td>0.85 ± 0.1</td>
<td>0.45 ± 0.02</td>
</tr>
<tr>
<td>(type A)</td>
<td>600</td>
<td>0.80 ± 0.01</td>
<td>0.56 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.99 ± 0.01</td>
<td>0.50 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>0.84 ± 0.05</td>
<td>0.59 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.8 ± 0.1</td>
<td>0.45 ± 0.02</td>
</tr>
<tr>
<td>Pyramid</td>
<td>600</td>
<td>0.44 ± 0.03</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td>(type C)</td>
<td>600</td>
<td>0.44 ± 0.03</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.54 ± 0.03</td>
<td>0.28 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.32 ± 0.03</td>
<td>0.15 ± 0.01</td>
</tr>
</tbody>
</table>

Four experimental series involving as-pressed samples (type A) and one experimental series with a pyramid sample (type C) were performed. Multiple load experiments were performed in each experimental series and the load exponents reported in table 9.2 are averages. Extreme contact resistances were observed in two of the experimental series involving as-pressed samples (type A). In these series, the contact resistance was above 1 MΩcm² at all the investigated temperatures. These results were not included in the following analysis. For the other experiments, contact resistance ranged from a few kΩ to 100 kΩ.

Figure 9.2 shows the load-unload characteristics for fresh YSZ contacts between as-pressed samples. The load exponents reported in table 9.2 for the fresh contacts are for the loading run, as the load exponent found during the unloading run was lower than during the loading run.

Figure 9.2. Contact resistance versus load for fresh contacts between as-pressed YSZ samples at 800°C.

The load exponents for the fresh YSZ contacts were always higher than the exponents observed for the aged contacts. Figure 9.3 shows a comparison between the two types of contacts for as-pressed YSZ samples (type A).
For fresh contacts, the load exponents were generally high. For the as-pressed samples (type A) the average value of the load exponents was between 0.8 and 0.85 except at 800°C where the observed load exponent was higher (table 9.2). For the pyramid samples, the load exponents for fresh contacts was below 0.6 at all temperatures.

The load exponents for the different types of contacts were largely independent of temperature (table 9.2 and figure 9.3).

At temperatures above 1050°C, the as-pressed YSZ samples (type A) sintered together, preventing in situ lifting of the upper sample. No sintering effects were observed for the pyramid YSZ sample (type C) which was not subjected to temperatures above 1000°C.

The aged YSZ contacts showed a difference in contact resistance between loading and unloading. Figure 9.4 shows a hysteresis loop for aged contacts. This was observed at all the investigated temperatures for as-pressed samples (type A). The pyramid sample (type C) also showed this hysterisis, although to a lesser extent. The first load run for aged contacts always showed a higher contact resistance than the following runs (figure 9.4). This was observed at all temperatures and for all sample types.

Figure 9.4. Contact resistance versus load for an aged contact between as-pressed YSZ samples at 800°C. Three load-unload runs were performed and a distinct hysteresis loop was observed for the second and third load run.
9.3 LSCN contact deformation

One experimental series with as-pressed LSCN samples was performed. The contact resistance for the LSCN samples could be described by equation 9.1 and the observed load exponents are shown in table 9.3.

Table 9.3. Load exponents for a contact between as-pressed LSCN samples at different temperatures. Uncertainties are based on difference between the exponents obtained from three different load sweeps.

<table>
<thead>
<tr>
<th>T / °C</th>
<th>p fresh</th>
<th>p aged</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.88 ± 0.11</td>
<td>0.56 ± 0.11</td>
</tr>
<tr>
<td>170</td>
<td>0.82 ± 0.1</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td>400</td>
<td>0.62 ± 0.03</td>
<td>0.48 ± 0.02</td>
</tr>
<tr>
<td>600</td>
<td>0.58 ± 0.05</td>
<td>0.30 ± 0.02</td>
</tr>
<tr>
<td>800</td>
<td>0.63 ± 0.08</td>
<td>0.24 ± 0.02</td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td>0.06</td>
</tr>
</tbody>
</table>

No data for fresh contacts could be obtained at 1000°C as it was not possible to lift the top sample in situ in the furnace. At this temperature, the data for the aged contacts were also different than those observed at lower temperatures (the load exponent was below 0.1).

The LSCN contact load-unload runs for aged contacts showed a hysteresis loop as shown in figure 9.5.

The fresh LSCN contacts showed a higher contact resistance during the loading runs than during the unloading runs as shown in figure 9.6.

Figure 9.5. Contact resistance dependency on load for aged LSCN contacts. The curve above the hysteresis loop is the first load run where the contact resistance was higher than for the following runs. Data are for as-pressed LSCN samples at 400°C.
Figure 9.6. Contact resistance dependency on load for fresh contacts between as-pressed LSCN contacts at 400°C.
10 Polarisation dependence of the contact resistance

The three analysed materials all showed non-linear current-voltage behaviour. The LSM and LSCN materials only showed this at low temperature, whereas the YSZ showed a small non-linearity at all temperatures.

10.1 LSM contact interfaces

The current response to linear potential sweeps was strongly non-linear at temperatures below 600°C. Above this temperature the current-voltage response was linear in the investigated potential range. This is shown in figure 10.1 where fits of the observed current-voltage behaviour with equation 4.48 are shown.

![Figure 10.1. Current response to linear potential sweeps at different temperatures (RT for room temperature) for polished surfaces (type B) of LSM. The sweep rate was 0.5 V/min and the contact load was 200 g/cm². The solid lines are the calculated response according to equation 4.48.](image)

For the experiments at room temperature, the number of barriers ($n$) for the as-pressed and polished samples (type A and B) was calculated to be between 4.2 and 4.4, whereas it was approximately 3.3 at 200°C and above. At temperatures where the current-voltage response was linear, no values for $n$ could be obtained as the non-linearity determines the number of barriers observed.

The pyramid samples (type C) required a higher number of barriers to fit the data than the as-pressed and polished samples (A and B) and when the contact load was changed, a change in the number of barriers necessary to fit the data was observed as shown in table 10.1.

After heating the current-voltage response was more linear than before. Figure 10.2 shows the room temperature current-voltage behaviour of a contact before and after the contact was heated to 800°C and 1000°C, respectively. Contacts heated to 1000°C showed linear current response in the investigated potential range after cooling to room temperature.
Table 10.1. Number of potential barriers at room temperature within LSM pyramid contacts (type C) at different loads.

<table>
<thead>
<tr>
<th>Load / g cm$^{-2}$</th>
<th>$n$</th>
<th>Load / g cm$^{-2}$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>5.9 ± 0.1</td>
<td>200</td>
<td>6.9 ± 0.1</td>
</tr>
<tr>
<td>66</td>
<td>6.4 ± 0.1</td>
<td>266</td>
<td>7.0 ± 0.1</td>
</tr>
<tr>
<td>100</td>
<td>6.5 ± 0.1</td>
<td>400</td>
<td>7.1 ± 0.1</td>
</tr>
<tr>
<td>133</td>
<td>6.7 ± 0.1</td>
<td>533</td>
<td>7.2 ± 0.1</td>
</tr>
</tbody>
</table>

Figure 10.2. Current-voltage behaviour of a contact between polished samples (type B) at room temperature for a fresh contact, after the contact has been annealed at 800°C for 24 hours and after the contact has been annealed at 1000°C for 24 hours (aged contacts). The sweep rate was 2 mA/min and the contact load was 200 g/cm$^2$.

10.2 YSZ contact interfaces

Only YSZ contact interfaces exhibited non-linearity above 600°C. The low conductivity of the YSZ prevented high current densities at high temperatures and resulted in high contact polarisations during the measurements. Figure 10.3 and 10.4 shows typical linear potential sweeps of a fresh YSZ contact and the dotted gray lines are asymptotes at a polarisation of 0 Volt.

Equation 4.48 was fitted to the observed non-linear behaviour and an $n$-value of 22 ± 1 was observed. This value was obtained at all the temperatures for all the YSZ contact experiments.

10.3 LSCN contact interfaces

As shown in figure 10.5 the LSCN contact interfaces exhibited strong non-linear current-voltage behaviour at room temperature. Analysing these data with respect to equation 4.48 showed that they could be fitted by only one barrier at the contact interface. The $n$-values found for all the room temperature data were 1.1 ± 0.1.

The high conductivity of the LSCN interface resulted in contact potentials below 0.06 V at 200°C for a current density of 0.5 A/cm$^2$. This prevented non-linear current-voltage behaviour to be observed as the potential range is close to the linear range for a single potential barrier (refer section 4.2). At temperatures above room temperature only linear current-voltage behaviour was observed in the investigated potential range as shown in figure 10.6.
Figure 10.3. Current response to linear potential sweep at 600°C for a fresh contact between two YSZ type A samples. The sweep rate was 2 V/min and the contact load was 230 g/cm². The dotted grey line is the asymptote at a polarisation of 0V.

Figure 10.4. Current response to linear potential sweep at 1000°C for a fresh contact between two YSZ type A samples. The sweep rate was 2 V/min and the contact load was 210 g/cm². The dotted grey line is the asymptote at a polarisation of 0V.
Figure 10.5. Current response to linear potential sweep at room temperature for fresh and aged contacts between two as-pressed LSCN samples. The sweep rate was 0.2 V/min and the load was 200 g/cm².

Figure 10.6. Current response to linear potential sweep at 400°C for a contact between as-pressed LSCN samples. The sweep rate was 0.05 V/min and the load was 200 g/cm².
11 Discussion

Contact resistance between ceramic components has been ascribed to both current constriction and resistive phases at the interface [6,31]. Fleig and Maier [41] have formulated a quantitative model for the constriction part of the contact resistance.

Resistive phases may result from regular bulk resistive phases formed by chemical interaction between the two materials brought into contact or from atomic monolayers of absorbed molecules at the interface. The resistive phases may behave as potential barriers. The interface part of the contact resistance between the materials in this study is interpreted as a chemical or physical change in the interface region and is described by a model based on potential barriers.

Figure 11.1. Schematic view of a ceramic contact. The total contact resistance consists of two parts: Contributions from current constriction (one from either side of the contact) and an interface resistance. The interface resistance may be due to resistive phases or potential barriers at the interface.

Figure 11.1 is a schematic representation of a ceramic contact point showing the two parts of the contact resistance. The two parts are individually dependent on the area of contact. The constriction part of the contact resistance is inversely proportional to the radius of the contact points (\( R \propto 1/r \), equation 3.2), whereas the interface contribution is inversely proportional to the square of the radius (\( R \propto 1/r^2 \), equation 3.10). The combined resistance is therefore in general not a simple function of the contact area.

11.1 Potential barrier behaviour of contact interfaces

All the investigated materials showed a non-linear current-voltage response. The LSM and LSCN showed this at low temperatures, whereas the YSZ showed non-linear behaviour at all the investigated temperatures (chapter 10). One model which can describe the observed behaviour of the contact interfaces involves potential barriers in the interfacial region.

Placing two conducting materials close to each other effectively creates a single potential barrier as in vacuum diodes [47]. This barrier may also exist if the materials touch each other and the interface has a lower conductivity than the bulk. Therefore it would be expected to observe one potential barrier in the interface between two ceramic components. If more than one barrier is observed they must be due to variations of the electrical field in the vicinity of the interface. Displacements of the cations and anions from their regular sites have been found in NaCl [49]. Creating a surface results in chemical enrichment/depletion of the surface layers. Several materials with different surface chemistries compared to the bulk are known [50]. The displacements of the ions and change in surface chemistry result in the formation of space charges and potential barriers in the surface region of the crystals [50]. Mechanical load influences the electrical field in the surface of a crystal by adding a mechanical stress field that change the position of the ions.
11.1.1 LSM contact interfaces

A model of identical consecutive potential barriers can be fitted to the observed current-voltage behaviour of the contact interfaces. Figure 11.2 shows the non-linear current-voltage behaviour of a fresh contact (type I) between as-pressed samples (type A). The number of barriers necessary to model the observed data were 4.3±0.2 and this number was typical for the as-pressed and polished LSM interfaces at room temperature.

The non-integer numbers of barriers found by fitting equation 4.48 with the observed current-voltage response may be a result of different height of the individual barriers (section 4.3.3). Another reason may be that the measured response is the average of a large number of contact points.

![Figure 11.2. Measured and calculated current response to changes in contact polarisation for fresh contacts (LSM type A) at room temperature.](image)

The temperature influenced the number of barriers. For the as-pressed and polished surfaces (type A and B), the number of barriers observed at room temperature was 4.3±0.2, whereas it was 3.3±0.2 at 200°C and 400°C. The difference may be due to desorption of oxygen, water or organic molecules from the interface. Desorption of oxygen has been reported for lanthanum manganite at temperatures around 200°C [59].

Different surface morphologies show a difference in the number of barriers necessary to model the observed current-voltage response. As-pressed and polished surfaces (type A and B) show a low number of barriers (3 to 5, section 10.1), whereas pyramid surfaces show a higher number of barriers (from 5 to 7 table 10.1).

One explanation for the high number of barriers necessary to describe the current-voltage response of the pyramid samples is the higher mechanical stress field. Cracks in the contact region of the pyramid samples (figure 6.5) suggest that the mechanical load was close to the compressive fracture strength of the LSM. This may result in changed current-voltage behaviour and the observation of more barriers. An approximately linear relation between the number of barriers and the logarithmic contact load was found as shown in figure 11.3. This may be explained by a higher compression at higher loads.

11.1.2 YSZ interfaces

The YSZ contact interfaces showed a weak non-linear current-voltage behaviour at all the investigated temperatures (figure 10.3 and 10.4). The number of barriers necessary to fit the measured current-voltage response with equation 4.48 was 22±1, which is a considerably higher number than what was observed for the LSM contact interfaces. The
activation energy across the YSZ contact interface at decreasing temperatures was equal
to that for grain boundary conductivity (table 8.3). This suggests that current constriction
dominates the contact behaviour for YSZ and that the grain boundaries in the bulk YSZ
were responsible for the weak non-linear current-voltage response.

11.1.3 LSCN interfaces

The high conductivity of the LSCN results in a low Debye length. This prevents forma-
tion of potential barriers within the crystals. Chemical enrichment/depletion might still
be present, but would not influence the current-voltage behaviour. Therefore only one
potential barrier (the interface itself) would be observed.

The current-voltage behaviour of the LSCN contact interfaces at room temperature
was similar to that of a single potential barrier (the interface itself, figure 10.5). At higher
temperatures, the potential difference across the contact interface was not high enough to
allow distinction between potential barrier behaviour and linear behaviour (figure 10.6).
It is therefore not possible to exclude an influence of a potential barrier on the contact
resistance above room temperature.

11.1.4 Correlation between potential barrier models and observed behaviour

Potential barriers may have different shapes and relative sizes. It is investigated which
types of barriers that may be responsible for the observed behaviour. In chapter 4, differ-
ent barrier models were described. The observed current-voltage behaviour for the LSCN
contacts could be fitted with equation 4.7, which describes the simple square barrier. This
model was not adequate for the LSM and YSZ contact interfaces. Figure 11.4 shows the
observed current voltage behaviour for a contact between as-pressed LSM samples at
room temperature compared to the expected behaviour for a single barrier and for multi-
ple barriers. A model of one or two barriers did not fit the data.

If the current-voltage behaviour of a model consisting of one large barrier (the inter-
face) in series with a number of small barriers (electron jump within the LSM) with equal
height (equation 4.55) was fitted to the observed behaviour, poor fits were obtained as
shown in figure 11.5. The barrier height of the small barriers was chosen to be equal to
the activation energy for charge transfer in polycrystalline LSM, and the height of the
large barrier was optimised for best fit. The poor fit observed in figure 11.5 suggests that
the current-voltage behaviour of LSM contact interfaces can not be described by one large barrier in series with a number of smaller barriers.

Figure 11.4. Current-voltage behaviour for an LSM type A contact at room temperature compared to the expected behaviour for different potential barrier models.

Figure 11.5. Current potential behaviour for multi barrier model consisting of one large barrier ($E_a = 0.4 \text{ eV}$) and 100 small barriers ($E_a = 0.11 \text{ eV}$) at 200 °C (line). The experimental data obtained at 200 °C for a contact between polished LSM surfaces (type B) are shown for comparison.

The model of multiple consecutive barriers did fit the observed behaviour as shown in figure 11.4. This model could describe all the current-voltage data observed. The only other model, which could describe the observed data was the model of a single barrier with a polarisationally dependent variable barrier height (section 4.4.1). Polarisation of a barrier may change the barrier height. If the observed current-voltage behaviour is due to a single potential barrier with variable barrier height, then the height must depend on the polarisation of the barrier as shown in figure 11.6.

The model of consecutive potential barriers and the model of one polarisationally dependent barrier described the observed current-voltage responses equally well. Of these two models the model of consecutive barriers was chosen as the most likely, as impurity gradients or in the outer portions of the crystals in the contact may create potential barriers within the materials [50].
11.2 Contact area analysis

All the contact interfaces without sinterable layers were investigated by SEM. For the YSZ and LSM as-pressed and polished samples it was not possible to locate any contact areas. The contact area morphology of the LSM and YSZ pyramid samples was different from the surrounding unaffected areas (figure 6.6 and 6.9). The LSCN as-pressed surfaces (type A) also showed a few areas with a difference in the surface morphology compared to the normal surface. The contact morphology of the pyramid LSM was characterised by the formation of an area with a smaller grain size than the unchanged areas and generally had a cracked appearance (figure 6.7 and 6.12). The reason for this change is not well understood, but may be due to the formation of small cracks due to mechanical load. It was only possible to determine the size of the contact areas on the pyramid samples.

To indicate which part of the contact resistance that dominates at any given temperature, the ratio between the measured contact resistance ($R_{\text{measured}}$) and the resistance calculated on the basis of current constriction ($R_{\text{calculated}}$) is used. ($R_{\text{calculated}}$) is the minimum resistance for a contact, as it does not include potential barriers or resistive phases. The lower the ratio is, the more dominating the current constriction is. The ratio between the measured and calculated contact resistance is influenced by the accuracy in the contact area determination as well as by the influence of resistive phases on the contact resistance.

11.2.1 Comparison of LSM contact resistance determined by different methods

The contact area for the pyramid sample was $2.4 \times 10^{-4}$ cm$^2$ distributed over 36 pyramid tips. The observation of fractures in the pyramid tips after the experiment at room temperature show that the contact load for this contact geometry was similar to the compressive fracture strength for the LSM. Based on the optically measured contact area and using equation 3.18, the fracture strength of the LSM was calculated to be 140 MPa, which is similar to the bending strength of the LSM reported by D’Souza [60].

The contact resistance ($R_{\text{calculated}}$) was calculated using equation 3.14, assuming no resistive phases at the interface. The ratio between the measured and the calculated contact resistance are shown in table 11.1. The contact areas at the pyramid tips showed a high porosity (figure 6.7). Therefore the effective contact area was probably smaller than the measured, estimated to be up to 30% less. If the measured contact area was larger than the physical contact area, then the calculated contact resistance would be lower than the real value. This would result in ratios between the measured and the calculated contact
Table 11.1. Ratios of the calculated and the measured contact resistance for different sample types at different temperatures. For the sinterable contact layers $R_{\text{calculated}}$ was found using equation 3.10

<table>
<thead>
<tr>
<th>Sample type</th>
<th>T / °C</th>
<th>$R_{\text{measured}} / R_{\text{calculated}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM pyramid (type C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>3.6</td>
</tr>
<tr>
<td>Sinterable contact (type D)</td>
<td>800</td>
<td>3.1</td>
</tr>
<tr>
<td>Sinterable contact (type E)</td>
<td>800</td>
<td>2.0</td>
</tr>
</tbody>
</table>

resistance above 1 even for a contact with current constriction only. The measured contact resistance was between 2.5 and 3.8 times the calculated at temperatures above room temperature, suggesting that current constriction was important at these temperatures. At room temperature, the ratio between the measured and the calculated contact resistance was 30, indicating that at this temperature, current constriction was not dominating. At room temperature, a non-linear current-voltage response was also observed, supporting that the interface contribution was dominating at this temperature.

11.2.2 Sinterable contact interfaces

The experiments involving sinterable contact layers initially showed high contact resistances. After heating to 900°C the layers had sintered and low contact resistances were measured (figures 7.4 and 7.5). Most of the improvement in electrical conductivity occurred at temperatures below 600°C (figures 7.4 and 7.5). This was due to the evaporation or burning of the organic binder at low temperatures. Diffusion and sintering were active above 800°C as evident by the decrease in the contact layer height above this temperature (figure 7.5).

The resistances of the sinterable layers were 5 and 15 mΩcm² compared to 150 - 500 mΩcm² observed for all the other LSM contact interfaces (table 7.2). This shows that much larger contact areas were achieved with the sinterable layers. The post-test contact area determination confirmed that the sinterable layers had been in contact with approximately 40% (type D) and 20% (type E) of the geometrical area (section 6.1.3). The sinterable layers were porous, therefore contact may not have been achieved everywhere where it was assumed. This is especially the case for the layer consisting of small cylinders (type E), where individual cylinders may have remained in place even if they had not been in contact with both samples during the experiment. The ratios between the measured and calculated contact resistance reported are therefore maximum values.

For the sinterable contact layers (type D and E) the ratios between the measured and the calculated contact resistance (equation 3.10) were 3.1 and 2.0 respectively (table 11.1). The low ratios suggests that current constriction was the dominating part in the contact resistance for these contact interfaces.

Despite the difference in layer height and contact area available for the two sinterable layers, the resistances were approximately equal. The resistance for the cylindrical layer (type E) was only 3 times larger than for the other layer even though the cylindrical layer (type E) was almost 10 times higher than the LSM tape (type D). This was counteracted by a difference in the conductivity of the two layers and by the fact that only 40% of the LSM tape (type D) had been in contact.

11.2.3 Comparison of YSZ contact resistance determined by different methods

The flat areas observed on the tips of the YSZ pyramids (figure 6.10B) were assumed to be the area of contact. The total area of contact was determined to be $8 \cdot 10^{-5}$ cm² distributed
over 14 pyramid tips. The resistance originating from constriction was calculated and compared with the measured resistance as shown in table 11.2.

Table 11.2. Ratios of the calculated and the measured contact resistance for the YSZ pyramid sample at different temperatures.

<table>
<thead>
<tr>
<th>T / °C</th>
<th>$R_{\text{measured}} / R_{\text{calculated}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>5.9</td>
</tr>
<tr>
<td>800</td>
<td>4.6</td>
</tr>
<tr>
<td>1000</td>
<td>2.5</td>
</tr>
</tbody>
</table>

At high temperatures the ratio was low and it increased as the temperature was lowered. This indicates that at high temperatures the contact resistance for the YSZ pyramid sample was dominated by current constriction, whereas at lower temperatures, the interface contribution became more and more important.

11.2.4 Fast Fourier transformation analysis

The Fourier transformation analysis of the as-pressed and polished LSM samples only showed the long range hills on the as-pressed sample (figure 6.19) and no features could be observed for the polished sample (figure 6.20). This method was therefore not suitable to correlate surface morphology with contact resistance behaviour.

11.3 Load induced resistance variations

The contact resistance of the investigated materials was dependent on the contact load. An increase in the mechanical load of a contact interface resulted in a lower contact resistance. The resistance response to variations in the contact load could be modelled by a power law function (equation 9.1). The exponent in this equation was termed the load exponent ($p$). Power law dependence of the contact resistance on the contact load was predicted by the analysis of mathematical models for contact point deformation (chapter 3) and different load exponents could be explained by different resistance and contact deformation models as shown in table 11.3.

Table 11.3. Expected load exponents for different contact models discussed in chapter 3. $n$ is the number of contact points, and $r$ is their radius.

<table>
<thead>
<tr>
<th>Load model</th>
<th>Resistance model</th>
<th>Expected load exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Hertz sphere</td>
<td>constriction</td>
<td>1/3 [29]</td>
</tr>
<tr>
<td></td>
<td>resistive phase</td>
<td>2/3 (equation 3.11)</td>
</tr>
<tr>
<td>Fracture strength equivalent area</td>
<td>constriction, constant $n$</td>
<td>1/2 (equation 3.19)</td>
</tr>
<tr>
<td></td>
<td>constriction, constant $r$</td>
<td>1 (equation 3.20)</td>
</tr>
<tr>
<td></td>
<td>resistive phase</td>
<td>1 (equation 3.10)</td>
</tr>
<tr>
<td>Plastic deformation, metals</td>
<td></td>
<td>1/2 [29, 33]</td>
</tr>
</tbody>
</table>

Two different contact types were investigated. Fresh contacts, where the samples had been brought into contact less than one hour before the measurements, and aged contacts, where the samples had been in contact under mechanical load for 1 to 5 days (section 5.3.2). The contact resistance was determined at different loads, and each load sweep (0 g/cm² - 2000 g/cm² - 0 g/cm²) was repeated three times where possible (section 5.3.2). The resistance at any given load was lower during unloading than during loading for fresh contacts. One explanation for this may be small scale brittle fracture. An increase in load...
would result in an increased contact area by brittle fracture until the contact area is able to support the mechanical load, causing an irreversible change in the contact interface.

All the investigated materials showed lower load exponents for aged contacts compared to fresh contacts and this was observed at all temperatures (table 9.1, 9.2 and 9.3). The load exponent for fresh contacts was generally twice that observed for aged contacts. The expected difference between a contact dominated by current constriction and one dominated by the interface contribution would be a 1:2 difference in the load exponent (table 11.3). If ageing of a contact results in the suppression of the interface contribution, lower contact resistance and load exponents would be observed.

11.3.1 Simulated load behaviour of LSM contact interfaces

The three-dimensional maps in figure 6.15 allowed simulation of the contact resistance dependence on the contact load. The maps were investigated by converting them to sets of two-dimensional area maps at different indentations. Figure 11.7 shows maps for relative areas of 0.1%, 0.2% and 0.5% of the geometrical area for the two surface morphologies.

Each map was analysed by the UTHSCSA Image Tool software for the number of contact points and their average size. Figure 11.8 shows how the number of contact points and their radius changed with load. The area multiplied by the fracture strength (140 MPa, section 11.2.1) determined the theoretical load corresponding to the contact area on each map.

Equation 3.14 was used to calculate the expected contact resistance behaviour at varying contact loads for each sample. The results are shown in figure 11.9.

The number of contact points for the polished sample increases almost linearly with contact load, whereas the radius of the contact points was almost constant (figure 11.8). This corresponded to a load exponent of 1.02 (figure 11.9 B) and is in agreement with equation 3.10 (table 11.3). For the as-pressed sample the number of contact points increases and at the same time the radius of the contact points increases corresponding to a load exponent of 0.83 (figure 11.9 A). If the number of contact points increases, and at the same time the radius of the contact points increases, load exponents between 0.5 and 1 is the result (table 11.3).

11.3.2 LSM contact behaviour

The load exponent for the fresh LSM contacts ranged from 0.37 to 1.09 (table 9.1). These values were compared to the models for contact point deformation and formation of contact points presented in table 11.3. The load exponents for fresh contacts between polished surfaces (type B) were close to one, which was equal to the simulated load exponent for this sample type (figure 11.9 B). This suggests that the main reason for the observed load dependence is the formation of more contact points with approximately similar size (table 11.3).

For the as-pressed and pyramid samples (type A and C) the load exponents were between 0.37 and 0.75 for fresh contacts (table 9.1). This suggests that some deformation of the individual contact points did occur when the contacts were loaded. A load exponent of 1 would only be expected if the contact deformation was dominated by the formation of more contact points. (table 11.3). The surface morphology of the pyramid and as-pressed samples (figure 6.4 and 11.8) shows that some deformation of the individual contact points was to be expected. For these samples larger indentations than for the polished surfaces are necessary for a given increase in contact area (figure 6.16). Large indentations require deformation of some of the contact points and lower load exponents will be the result (table 11.3). The simulated load exponent for the as-pressed sample was 0.83 and this was close to the experimental values, supporting that some deformation of

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2http://www.uthscsa.edu/dig/itdesc.html
Figure 11.7. Contact area-indentation maps for different surfaces. From top to bottom the images show 0.1%, 0.2% and 0.5% of the geometrical area. A – C are images from a polished sample (type B) and D – F are from an as-pressed sample (type A).

Figure 11.8. The simulated number of contact points (A) and their radius (B) as a function of contact load (P) for polished and as-pressed samples.
the individual contact points occurred.

The low load exponents found at 1000°C were influenced by sintering effects and were therefore not included in the following analysis. The lowest load exponents for fresh and aged contacts for as-pressed and pyramid samples (type A and type C) were found at 600°C. They may be explained by the presence of potential barriers at the contact interface below this temperature. Contribution from the interface resistance part of the contact resistance would dominate and this would result in high load exponents (table 11.3). At 600°C and above, the influence of the potential barriers was not observed (figure 4.48) and therefore the main contribution to the contact resistance was probably current conduction. If this was the case, it would result in lower load exponents compared to contacts with influence of the interface contribution (table 11.3). Load exponents at 800°C showed larger values than at 600°C (table 9.1). At 800°C the contact resistance decreases up to 50% over time (table 7.1) which was interpreted as a sintering effect and this sintering may influence the load exponents resulting in larger values than at 600°C.

11.3.3 YSZ contact behaviour

The YSZ contacts responded to changes in mechanical load in a similar manner as the LSM contacts and a linear dependence between log(ASR) and log(P) was found (figure 9.4 and 9.2). The resulting load exponents were between 0.8 and 1 for the fresh as-pressed surfaces (type A) and between 0.3 and 0.55 for fresh pyramid contacts (type C, table 9.2). This suggests that the as-pressed surfaces primarily respond to changes in load by creating more contact points, whereas the pyramid YSZ contacts respond by deformation of existing contact points combined with formation of new points. The plane contact area (figure 6.10) observed on the pyramid YSZ sample after the experiments shows that deformation of the YSZ had taken place.

The aged contacts showed a hysteresis after the contacts had been loaded for the first time (figure 9.4). The probable explanation for this is the ferroelastic behaviour of the YSZ [61]. Ferroelastic behaviour is the mechanical equivalent to ferroelectric behaviour where the polarisation of a crystal results in deformation. For ferroelastic materials, a reversible deformation is observed when the crystal is stressed. This deformation is not permanent, but can only be reversed by applying stress to the crystal in another direction. A similar mechanism may be responsible for some the difference between the loading and the unloading run (figure 9.2) for the fresh contacts.

The load exponents for the YSZ contact was relatively independent on the temperature (figure 9.3). This suggests that only minor change in the contact mechanism occurred in the investigated temperature range. The observation of a weak non-linear current-voltage response at all the investigated temperatures for the YSZ contacts supported that only minor changes in the contact mechanism occurred.
11.3.4 LSCN contact behaviour

The aged LSCN contacts showed a hysteresis loop (figure 9.5) similar to the YSZ contacts. The most likely explanation for this is ferroelastic behaviour of the LSCN. Ferroelastic behaviour has been reported for calcium doped lanthanum cobaltite (LCC) [62] and may explain why the first load-run for the aged contacts was different from the following runs. This can be explained by a permanent reorientation of some of the domains resulting in a non-reversible change in the sample surface. A difference in the load response between the first and subsequent deformations has been reported for stress-strain experiments on LCC where a permanent reorientation of some of the domains were assumed to be responsible [62].

Ferroelastic behaviour may also explain some of the difference between the loading and unloading runs for the fresh contacts as was the case for YSZ (figure 9.6).

The load exponents for the LSCN contacts generally decreased with increasing temperature (table 9.3). One explanation for this could be decreased influence of potential barriers at the contact interface (section 10.3). This would result in a change from a situation where the contact resistance is concentrated at the interface to a situation where current constriction dominates, resulting in a gradual decrease of the load exponent (table 11.3).

11.4 Temperature effect on the contact resistance

The bulk conductivity of the LSM and YSZ increased with increasing temperatures and this variation was described by an Arrhenius equation.

The expected resistance behaviour for contact resistance due to current constriction would be equal to the behaviour of the bulk material as the bulk conductivity determines the contact resistance (equation 3.1). The expected resistance behaviour of an interface with potential barriers is an Arrhenius type decrease of the contact resistance at increasing temperatures (section 4). The activation energy found by Arrhenius analysis is the barrier height and if the material is a semiconductor or an ionic conductor, the observed activation energy would be higher than the bulk activation energy if potential barriers influence the contact resistance.

The LSM and YSZ contact interfaces showed a temperature dependence of the contact resistance consistent with Arrhenius behaviour. The contact resistance for the LSCN contacts was influenced by a change in the oxygen stoichiometry of the bulk LSCN, which resulted a deviation from an Arrhenius behaviour.

A thermal cycle (25°C - 800°C - 25°C) lowered the room temperature contact resistance. This effect was observed for all the contact interfaces and is reflected in the higher activation energy during heating compared to the activation energy during the subsequent cooling (table 8.1 and 8.3). This behaviour may be explained by either a progressive increase in the contact area during heating, or the height of the potential barriers decrease when the contact has been at high temperatures (above 800°C). At the onset of sintering, the contact interface behaviour may approaches that of a normal grain boundary resulting in lower barrier heights.

11.4.1 Temperature effect on LSM contact interfaces

For the pyramid sample, the activation energy above 200°C was almost equal to the activation energy for the bulk LSM, suggesting that the contact resistance for the pyramid sample was dominated by current constriction above this temperature. This is in agreement with the contact area measurements (section 11.2.1) and is further supported by the observation of linear current-voltage behaviour at all temperatures above room temperature. For the other interface types, the activation energy was higher than the bulk (table 8.1). This indicates that the contact resistance was not dominated by current constriction for these interfaces. This was supported by the observation of non-linear current-voltage
behaviour up to 400°C (figure 4.48), which also showed that the interface resistance was important at these temperatures.

11.4.2 Temperature effect on YSZ contact interfaces

The activation energy of the YSZ contact interfaces was between 0.98 and 1.4 eV (table 8.3). The bulk YSZ activation energy measured in this study was 0.92 eV, which is in agreement with values found in the literature [16, 58, 63].

The activation energy for the contact resistance was higher during heating of the contact than during cooling (table 8.3). The activation energy measured for the pyramid sample (type C) was close the bulk value, whereas for the as-pressed samples the activation energy was higher indicating an influence of interface resistance. The conductivity of bulk YSZ can be divided into a grain boundary contribution and a bulk crystal contribution by impedance spectroscopy [16, 58, 63]. The activation energy for grain boundary conductivity is typically 0.1 to 0.2 eV higher than for the bulk crystal [58]. The likely explanation for the observed contact interface activation energies is that the contact interface behaves as a grain boundary and that the contact resistance is dominated by current constriction. An other indication of this was the high number of potential barriers necessary to describe the weak non-linear current-voltage response. The number of barriers could then be the number of grain boundaries influencing the current within the volume of YSZ where the current was concentrated due to the current constriction. The contact area determination in section 11.2.3 also suggested that for the pyramid YSZ sample, the contact resistance was dominated by current constriction at high temperatures.

11.4.3 Temperature effect on LSCN contact interfaces

Before the LSCN contact had been at 1000°C, increasing the temperature of the contact resulted in a decrease in the contact resistance. The resistance dropped from 0.3 Ωcm² at room temperature to 20 mΩcm² at 1000°C (figure 8.5). As opposed to the other investigated materials, the bulk conductivity of the LSCN decreases with increasing temperature.

After the contact had been at 1000°C, the contact resistance decreased during cooling due to the conductivity increase of the bulk material. The LSCN contact could not be separated in situ in the furnace at 1000°C. This indicated that the samples had sintered together, and this was supported by the small change in the contact resistance when the samples was brought back to room temperature.

The LSCN contact resistance did not show a typical Arrhenius type dependence on the temperature. Strontium doped lanthanum cobaltite is a non-stoichiometric compound [64–68] and the oxygen stoichiometry change with temperature [64, 68]. As the conductivity of the material depends on the oxygen stoichiometry, deviation from pure Arrhenius behaviour is expected.

11.4.4 Temperature effect on sinterable contact interfaces

After the sinterable contact interfaces had been above 800°C the temperature dependence of the contact resistance was close to that for the bulk LSM (table 8.1). This suggest that potential barriers did not influence the contact resistance for these contacts. This is supported by the contact area determination in section 11.2.2. Changing the mechanical load on the sinterable contact (type E) did not result in changes in the contact resistance. This indicates that the layer was mechanically stable. The layer (type E) was also thermally stable, as the contact resistance did not change significantly after two thermal cycles (section 7.2).
11.5 Atmospheric influence on LSM contact resistance

Changes in atmospheric composition between air and nitrogen had little effect on the current-voltage response (table 8.2). This was expected, as the bulk conductivity does not change in the investigated $p_O$ range [69–71].

After annealing at 800°C for 4 hours, the activation energy between 800°C and 200°C did not show any dependence on the atmospheric composition. The low temperature (below 200°C) activation energy and hence the potential barrier height for LSM was dependent on the oxygen partial pressure as shown in figure 8.3. A lower oxygen partial pressure resulted in slightly higher activation energy for the contact interfaces. This was not observed for the bulk material, showing a specific change in the electrical properties of the interface. This was probably due to a change in the oxygen stoichiometry of the surface. Apparently the water content did not have any influence on the contact resistance, suggesting that adsorption of water is not important for LSM surfaces. Surface chemistry may be significantly different from bulk chemistry [50]. This explains why the surface properties are different from the bulk properties.

11.6 Contact ageing

The contact resistance generally decreased over time after the formation of a new contact. Exceptions to this behaviour were LSM contacts at 200°C and 600°C (figure 7.1) and LSCN contacts at room temperature (figure 7.9).

The most likely explanation for the decrease in contact resistance at temperatures above 200°C is surface relaxation and small-scale deformation of the contact areas resulting in larger contact areas. This is supported by the large relative decrease in contact resistance observed at high temperatures (800°C for LSM, table 7.1 and 1000°C for YSZ, figure 7.8) where diffusion is faster than at lower temperatures. Most of the change in the contact resistance was observed during the first 24 hours after the contact was created (figure 7.1 and 7.6). Diffusion would also account for this, as the deformation rate is dependent on the stress [57], and the contact stress is lowered when a contact area increases.

The relatively large initial decrease in the LSM contact resistance at room temperature (table 7.1) could be due to a change in the concentration of adsorbed oxygen, water and organic species. If this is the case, it indicates that the mechanical load influences the surface energy and makes it more favorable for the surface adsorbates (water and/or organic species) to diffuse away. At 200°C the water and organic species would probably evaporate and this could account for the instability of the LSM contact resistance observed at this temperature (figure 7.1). Similar effects would not be expected at temperatures above 200°C where all volatile species have evaporated.

The large relative decrease in the contact resistance observed at high temperatures (800°C for LSM and 1000°C for YSZ) suggests that contacts with low contact resistance can only be achieved by heating the contacts. The contact interfaces have to be heated to high temperatures in order for diffusion or creep to create large contact areas and hence low contact resistances. This is also the case for the sinterable contact interfaces, where the contact resistance is high until the contact have been heated to more than 800°C.

11.6.1 LSM contact creep

The height of the pyramid sample decreased 10 $\mu$m over a time period of 2 days (figure 7.3). Primary creep (equation 7.1) is the expected deformation mechanism for a material without prior deformation at high temperatures and high stresses [57]. A fresh contact has not been subjected to prior deformation. Therefore, lifting and subsequently lowering the top sample would result in new areas in contact. The deformation of the pyramid sample at 800°C indicates that diffusion is operative at this temperature for LSM.
11.7 Summary of the different methods of discrimination between interface and current constriction resistance

The different methods of contact resistance analysis discussed earlier resulted in discrimination between contact resistance dominated by current constriction and the interface contribution. Table 11.4 summarises the contact resistance behaviour. Non-linear current-voltage behaviour indicates that the interface resistance contribution is dominating and for the current-voltage analysis (U-I), the maximum temperatures where non-linear behaviour was observed are shown. For the experiments with changing temperatures, the temperatures where the measured activation energy during heating was higher than the bulk are shown and high activation energy indicates interface resistance domination. For the load sweep analysis the discrimination are based on changes in the observed load exponents, where high exponents indicates interface resistance domination.

Generally the contact resistance of the investigated materials was dominated by the interface contribution at low temperatures. At high temperatures, the contact resistance was due to current constriction. The temperature where the shift between interface domination and constriction domination is observed depended on the method. However, current constriction generally dominated at temperatures above 600°C, whereas the interface contribution dominated below 400°C.

Table 11.4. Summary of contact resistance contributions determined by different methods. C is current constriction, I is interface resistance and RT is room temperature. Where no temperature is given, the resistance contribution was dominating at all investigated temperatures.

<table>
<thead>
<tr>
<th>Type</th>
<th>U-I</th>
<th>Load</th>
<th>Area</th>
<th>Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM A</td>
<td>RT</td>
<td>T≤400°C, I</td>
<td>T≤600°C, C</td>
<td>T&lt;800°C, I</td>
</tr>
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<td></td>
<td></td>
<td>T≥600°C, C</td>
<td></td>
<td>T=800°C, C</td>
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<tr>
<td>B</td>
<td>T≤400°C, I</td>
<td>T&lt;800°C, I</td>
<td>T&lt;800°C, C</td>
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<td>T=800°C, C</td>
</tr>
<tr>
<td>C</td>
<td>RT</td>
<td>T≤400°C, I</td>
<td>RT</td>
<td>T≥400°C, C</td>
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<td></td>
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<td>T≥600°C, C</td>
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<tr>
<td>YSZ A</td>
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<td>T&lt;1000°C, C</td>
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<td></td>
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<td>T=1000°C, C</td>
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<tr>
<td>C</td>
<td>C</td>
<td></td>
<td>T≥800°C, C</td>
<td>C</td>
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<tr>
<td>LSCN A</td>
<td>RT</td>
<td>T≤200°C, I</td>
<td>T≥600°C, C</td>
<td>T=1000°C, C</td>
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<td>T≥200°C, I</td>
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<td>T≥600°C, C</td>
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<td>T&gt;800°C, C</td>
</tr>
</tbody>
</table>
12 Conclusion

The electrical contact between identical materials was investigated in conjunction with five different surface morphologies/contact interface types. The materials were strontium doped lanthanum manganite (LSM), yttria doped zirconia (YSZ) and strontium and nickel doped lanthanum cobaltite (LSCN). The surface types investigated were: as-pressed, polished, pyramid surfaces, and sinterable contact layers between polished surfaces.

The measured resistance for a ceramic contact was a sum of two contributions. These were current constriction due to low contact area and interface resistance due to resistive phases or potential barriers at the interface.

Depending on the materials and temperature, either the current constriction or the interface resistance contribution was dominating. For the LSM and LSCN the interface resistance was generally dominating at low temperatures, whereas the current constriction resistance was dominating at high temperatures. For the YSZ, current constriction dominated at all investigated temperatures.

At low temperatures contact resistance showed highly non-linear current-voltage response. This can be explained by potential barriers at the interface.

For some contact geometries it was possible to determine the actual contact area and for these contacts good agreement between the calculated and measured contact resistance was found.

Low contact resistance was only achieved by using sinterable contact layers and the contact resistance for the sinterable layers was 10 times lower than for any of the other interface types. If low contact resistance is desired, it is necessary to include sinterable contact layers between the components.

12.1 Potential barrier behaviour of ceramic contact interfaces

- All three investigated materials showed non-linear current-voltage response in certain temperature ranges. The non-linearity observed could be explained by the existence of potential barriers at the contact interface.

- Numerous models of single and multiple potential barriers were analysed. The only model, which could fit the observed current-voltage response and had a barrier height that was independent of the contact polarisation, was a model of consecutive potential barriers.

- YSZ contact interfaces showed non-linear behaviour at all the investigated temperatures, whereas LSM and LSCN only showed this behaviour at low temperatures. For the LSM non-linear behaviour could be observed below 600 °C whereas for the LSCN non-linear behaviour was only observed at room temperature.

- For LSM and YSZ the number of potential barriers necessary to model the observed current-voltage response was higher than 1 at all temperatures where non-linear behaviour was observed.

- The LSCN contact interfaces could be described by only one potential barrier at the interface. The likely explanation for this is that the high conductivity of the LSCN prevented formation of thick charge enriched/depleted layers near the surface. This prevented formation of potential barriers inside the LSCN samples, and thus only the contact interface potential barrier was observed.

- The YSZ interfaces showed a weak non-linear current-voltage response. The number of barriers necessary to describe the observed data was 22±1 and the apparent activation energy for the YSZ contact interfaces was equal to that reported for grain
boundary conductivity. This resulted in the conclusion that the potential barrier effect observed for YSZ contact interfaces was a grain boundary effect originating from the bulk.

- The surface morphology influences the number of barriers necessary to model the observed current-voltage behaviour. This was shown by the difference between pyramidal LSM (n = 5 to 7) and plane LSM surfaces (as-pressed and polished, n = 3 to 4).

- At room temperature the as-pressed and polished LSM surfaces required 4.3±0.2 barriers at the interface to model the observed data. At higher temperatures the number of barriers was 3.3±0.2 for these interfaces. This shift may be due to desorption of organic molecules from the interface.

- The height of the potential barriers depended on the surface morphology. As-pressed surfaces showed barrier heights of 0.23±0.01 eV compared to 0.34±0.01 eV for the polished surfaces.

- Heating the LSM contact interfaces to 800°C resulted in a reduction of the measured potential barrier height. The barrier height after heating was 0.10±0.01 eV for the pyramid surface compared to 0.18±0.01 eV for the as-pressed surfaces. This may be due to sintering effects which may suppress the interface resistance contribution to the contact resistance.

### 12.2 Contact area analysis

- Due to the geometry of the pyramid samples, it was possible to measure the maximum extent of the contact area. At high temperatures the contact resistance calculated on the basis of current constriction was less than the measured contact resistance by a factor of 2.5 for the YSZ (at 1000°C) and 3.5 for the LSM at 800°C.

- At low temperatures, the contact resistance of the pyramid samples was dominated by the interface contribution, whereas current constriction dominated at high temperatures.

- The ratio between the contact resistance measured at 800°C by electrical means and the contact resistance calculated based on optically measured contact areas was between 2 and 3 for the sinterable contact layers. This proved that after sintering current constriction was dominating for these contacts.

- The contact area achieved with sinterable LSM contact interfaces was in the order of 20 to 40% of the geometrical area. The contact area was more than 100 times larger than that found for all the other contact geometries, proving that good electrical and mechanical contact between ceramic components can be achieved only by including sinterable contact layers.

### 12.3 Load influence on contact resistance

- The contact resistance was highly dependent on the contact load. Power law dependence between the contact load and the contact resistance was observed at temperatures below 1000°C for all materials and sample types without sinterable contact layers.

- Comparison of simulated and experimentally determined contact load exponents for LSM contact interfaces showed good agreement. For the polished sample, the measured load exponent and the calculated load exponent was 1.05±0.04 and 1.02 respectively. For the as-pressed surface, the measured and calculated load exponent was 0.6±0.2 and 0.82 respectively. This proved that the contact resistance for these
contact interfaces could be described by current constriction resistance from a number of contact points.

- Polished samples respond to an increase in contact load primarily by creating more contact points resulting in load exponents of approximately 1.
- As-pressed and pyramid surfaces respond by creating more contact points and by deforming already formed contact points. This result in load exponents between 0.5 and 1 for fresh contacts.
- Aged contacts showed smaller load exponents compared to fresh contacts. This was observed for all three materials and for all sample types without sinterable contact layers.

12.4 Temperature effect on ceramic contact resistance

- Significant reduction of the contact resistance can be obtained by heating the contact interface to 800°C or above depending on the temperature where sintering effects become important for the specific materials.
- After a contact interface had been at temperatures where sintering effects were significant, the contact resistance dependence on the temperature was similar to the dependence of the bulk conductivity on the temperature indicating that current constriction was dominating the contact resistance for these interfaces.

12.5 Atmospheric influence on LSM contact interfaces

- The oxygen partial pressure of the test atmosphere had a small influence on the potential barrier height. This shows that the \( p_{O_2} \) had some influence on the outermost layers of the LSM crystals. The influence of the atmosphere on the contact resistance was only investigated for the LSM.

12.6 Ageing effects of ceramic contact resistance

- Over time the contact resistance of a newly created interface was generally reduced. This reduction was largest at temperatures where sintering effects were significant.
- Small scale diffusion and creep may also occur at lower temperatures resulting in small reductions of the contact resistance.
- An increase in the contact resistance was sometimes observed at intermediate temperatures. This was possibly due to surface energy relaxation that may reduce the area of contact.

12.7 Effect of sinterable contact layers on the contact resistance

- A sinterable contact layer consisting of LSM particles in an organic binder between compact LSM interfaces reduced the contact resistance by a factor of more than 10 compared to interfaces without sinterable layers. This was observed for both types of investigated sinterable contact layers. The low contact resistance of these interfaces were achieved after the contact interfaces had been at sintering temperatures.
- After sintering no change in the contact resistance was measured while changing the contact load for these contacts.
- Only a small increase in the contact resistance was measured after thermal cycling.
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A Modelling of resistance heating

Studies performed to determine the effect of resistance heating on ceramic contacts established that low resistance heating was to be expected in LSM contacts [46]. In order to verify this, model calculations were carried out using numerical integration software. The thermal conductivity of LSM is 2.1 W/mK [72], and the emissivity is assumed to be 0.8. An electrical resistivity of $1.25 \cdot 10^{-4}$ Ωm was chosen. This corresponds to 80 S/cm, as the conductivity of porous LSM is somewhat lower than the value for the dense material. All values are assumed to be temperature independent in the temperature range investigated (1000 to 1100°C) and, where possible, values for 1000°C have been used.

A.1 Geometric model

As a simple model of a ceramic contact the following geometry has been considered (figure A.1). At the interface between the cylinder and the cones a 'super-conducting' spherical cap has been inserted to make the calculations one-dimensional. For numerical calculations of the heat and current transfer the following conditions apply: The cone and the cylinder are divided into small sections, each $\Delta x$ long and with cross-sectional area $A(x)$. The area $A(x)$ of a cap at distance $x$ is (refer figure A.1):

$$A(x) = 2\pi (1 - \cos \theta) r_{\text{sphere},x}^2$$  \hspace{1cm} (A.1)
$$r_{\text{sphere},x} = a + x + h$$  \hspace{1cm} (A.2)
$$r_{\text{sphere},x}^2 = x^2 + 2x(a + h) + 2ah + h^2 + a^2$$  \hspace{1cm} (A.3)

Writing this in full while inserting expressions for $a$ and $h$ [73] gives a quadratic function $A(x) = C_1 x^2 + C_2 x + C_3$ where

$$C_1 = 2\pi (1 - \cos \theta)$$  \hspace{1cm} (A.4)
$$C_2 = 2r \left( \frac{1}{\sin \theta} - 1 \right) C_1$$  \hspace{1cm} (A.5)

Figure A.1. a: A contact-model based on a cylinder with radius $r$ and height $2r$ sandwiched between two cones with opening angle $\theta$. b: Geometrical constructions necessary for smooth contact between the cylinder and the cones in order to reduce the mathematical problem to a one-dimensional one. The figure is a cross-section of figure a and the 'super-conducting' spherical cap is the shaded area between the cylinder and the cone. Due to the rotational symmetry only one side of the cone and cylinder is shown.
\[ C_3 = r^2 \left( \frac{1}{\sin \theta} - 1 \right)^2 C_1 \] (A.6)

As \( C_2^2 = 4C_1C_3 \) the area can be written as:

\[ A(x) = C_1(x + \frac{C_2}{2C_1})^2 \] (A.7)

For a more comprehensive model description please refer to Koch [73].

### A.2 Electrical heating of a contact

The potential drop \( dU \) over a slab with length \( dx \) and cross-sectional area \( A(x) \) of a material obeying Ohm’s law is:

\[ dU = I \rho dx = \frac{I \rho dx}{A(x)} \] (A.8)

When this is applied to the cone sections and cylinder and the combined integral is solved, the combined contact resistance is:

\[ R = \rho \left( \frac{2}{\pi r} - \frac{2}{C_1 x_{\text{max}} + \frac{C_2}{2}} + \frac{2}{C_1 r + \frac{C_2}{2}} \right) \] (A.9)

The incremental resistance \( R_{\Delta x} \), of a section \( \Delta x \) of a cone at a distance \( x \) from the center of the contact is [73]:

\[ R_{\Delta x} = \rho \left( \frac{1}{C_1 x + \frac{C_2}{2}} - \frac{1}{C_1 (x + \Delta x) + \frac{C_2}{2}} \right) \] (A.10)

Total power dissipated in a contact of a given configuration is \( P = U_{\text{total}} \cdot I \), but it is only in the case of \( \theta = 0 \) that the power is dissipated evenly over the entire contact due to the even distribution of the resistance. Consequently the temperature profile is not a parabolic function of the distance from the centre of the contact (radiation-loss neglected) as it is for a straight rod [74]. When radiation-loss due to heat loss from the contact is included the problem is further complicated. In this model the radiation-loss from the contact is included over the entire space-angle to a heat sink with temperature \( T_{\text{ambient}} \). This is clearly an overestimation of the heat-loss due to radiation and the temperature attained by this model has to be a minimum temperature. On the other hand, excluding the radiation-loss gives a maximum temperature for a given geometry. Both temperatures were determined for the investigated geometry. The heat balance of a volume-element, \( n \), in a series of segments connected end to end along the \( x \)-axis may be written as:

\[ \Delta Q_n = Q_{\text{in},n} - Q_{\text{out},n} + I^2 R_n - Q_{\text{radiation},n} \] (A.11)

\[ Q_{\text{in},n} = k A_n \frac{T_{n-1} - T_n}{\Delta x} \] (A.12)

\[ Q_{\text{out},n} = k A_n \frac{T_n - T_{n+1}}{\Delta x} \] (A.13)

\( R_n \) is calculated using equation A.10 for the cones with \( R_n = R_{\Delta x} \). For the cylindrical elements in the center

\[ R_n = \rho \frac{\Delta x}{A_n} \] (A.14)

was used. The current \( I \) was calculated using the relation: \( U = I R_{\text{total}} \). \( R_{\text{total}} \) is given by equation A.9. The radiation-loss is defined as:

\[ Q_{\text{radiation},n} = \epsilon \sigma A_{\text{radiation},n} (T_n^4 - T_{\text{ambient}}^4) \] (A.15)

Where \( \epsilon \) is the emissivity of the material in question, \( A_{\text{radiation},n} \) is the surface-area from which radiation is allowed and \( \sigma \) is Stefan-Bolzmann’s constant. The temperature-change
over time is calculated using the following iterative method, where $C_n$ is the heat capacity of the element.

$$T_{n,t+\Delta t} = T_{n,t} + \frac{\Delta t \Delta Q_n}{C_n}$$  \hspace{1cm} (A.16)

In order to investigate the thermal evolution of LSM point contacts, a numerical iteration model was set up. The considered model used half a contact point (due to symmetry) (refer figure A.1). The resultant cone and cylinder was divided in a number of segments (from 30 to 50 depending on accuracy needed). At the start of the iteration all segments in the model are at the same temperature as the surroundings, and when the iteration starts the individual elements in the model heats up. The iterations were stopped when a steady state was observed. The ambient temperature used in the calculations is 1000°C.

### A.3 Model results

If a current is passed through an array of contact points a potential difference exist across the contact interface. For practical applications in SOFC, the potential loss due to contact resistance should be less than 0.2 V if high power densities are desired. The potential loss due to contact resistance was dependent on the size of the individual contact points and the average distance ($d$) between them (figure A.2).

![Figure A.2. The potential-drop which is necessary to get the indicated current densities through an array of contact-points with different average distances. The individual contact points have a diameter of 1 µm and the contact cones have an opening angle of 30° (refer figure A.1). The temperature is assumed to be 1000°C 10 µm from the contact.](image)

As the potential available for SOFC-related contacts is below 0.2 Volts for the individual interfaces (as each cell contains more than one contact interface and on average generates less than one volt), it is observed that the average distance between individual contact points is small (less than 200 µm), or the individual contact points are large (figures A.2 and A.3).

The numerical calculations showed that in order to achieve an overall contact resistance below 0.2 Ωcm² (corresponding to a contact potential of 0.2 V at 1 A/cm²), as needed in most real SOFC contacts at elevated temperatures, the average distance between the individual contact points must be in the range of a few hundred microns. This applies for small contact points (figure A.3). When this is combined with the temperature-distance characteristics for an array of contact points (figure A.4) it is clear that temperatures above 20°C of ambient is not to be expected in properly made ceramic contacts for SOFC use.

Alternatively, if an interface exists in which the contact points have a diameter of 1 µm and an average distance of 400 µm, the overall contact resistance is 0.68 Ωcm². If
Figure A.3. Contact resistance (in $\Omega cm^2$) for an array of contact points with diameters of 1, 2, 4 and 8 $\mu$m. The individual contacts have an opening angle of 30° and an outer radius of 10 $\mu$m.

This interface is subjected to an overall current density of 1 A/cm$^2$, this would result in temperatures exceeding 60°C above the surroundings (refer figure A.3 and A.4).

Figure A.4. Temperature in array of contact-points versus distance. The diameter of the contact-points vary (1, 2, 4 and 8 $\mu$m). The opening angle is 30° and the overall current density for all the curves is 1 Acm$^{-2}$.

A.4 Conclusion

The model calculations lead to the conclusion that, for correctly made SOFC-stacks with contact point distances below 100 $\mu$m, resistance heating in the contact points should not be a problem. Resistance heating of the contact points will normally only arise when defect contact surfaces (e.g. large distance between small individual contact points) between individual SOFC-elements are present. If defects are present, they will give rise to contact resistance exceeding 0.2 $\Omega cm^2$. 

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B Derivation of equation 4.25

Equation 4.24 describes the current response to two potential barriers shown in figure 4.4. In order to obtain $x$ the following steps are used:

$$\exp\left(-\frac{x \cdot F + \Delta U F}{2 \cdot RT}\right) - \exp\left(-\frac{x \cdot F}{RT}\right) = \exp\left(\frac{x \cdot F}{RT}\right) - \exp\left(\frac{x \cdot F - \Delta U F}{2 \cdot RT}\right)$$  \hspace{1cm} (B.1)

$$\exp\left(-\frac{2 \cdot x \cdot F}{RT}\right) = \frac{1 - \exp\left(-\frac{\Delta U F}{2 \cdot RT}\right)}{\exp\left(\frac{\Delta U F}{2 \cdot RT}\right) - 1}$$  \hspace{1cm} (B.2)

$$\exp\left(\frac{2 \cdot x \cdot F}{RT}\right) = \frac{\exp\left(\frac{\Delta U F}{2 \cdot RT}\right) - 1}{1 - \exp\left(-\frac{\Delta U F}{2 \cdot RT}\right)}$$  \hspace{1cm} (B.3)

$$x = \frac{RT}{2 \cdot F} \ln \frac{\exp\left(\frac{\Delta U F}{2 \cdot RT}\right) - 1}{1 - \exp\left(-\frac{\Delta U F}{2 \cdot RT}\right)}$$  \hspace{1cm} (B.4)

$$x = \frac{RT}{2 \cdot F} \ln \left(\exp\left(\frac{\Delta U F}{2 \cdot RT}\right) \cdot \frac{1 - \exp\left(-\frac{\Delta U F}{2 \cdot RT}\right)}{1 - \exp\left(-\frac{\Delta U F}{2 \cdot RT}\right)}\right)$$

$$x = \frac{RT}{2 \cdot F} \frac{\Delta U F}{2 \cdot RT}$$  \hspace{1cm} (B.5)

$$x = \frac{\Delta U}{4}$$  \hspace{1cm} (B.6)
C Derivation of equation 4.37

The exchange currents across a barrier with a constant energy valley is:

\[ I_{1+} = N_0 K \exp \left( \frac{-E_a}{RT} \exp \frac{\alpha \Delta UF}{RT} \right) \]  \hspace{1cm} (C.1)

\[ I_{1-} = -N K \exp \left( \frac{-E_a + E}{RT} \right) = -N_0 K \exp \left( \frac{-E_a}{RT} \right) \]  \hspace{1cm} (C.2)

\[ I_1 = N_0 K \exp \left( \frac{-E_a}{RT} \right) \left( \exp \frac{\alpha \Delta UF}{RT} - 1 \right) \]  \hspace{1cm} (C.3)

\[ I_{2+} = N K \exp \left( \frac{-E_a + E}{RT} \right) = N_0 K \exp \left( \frac{-E_a}{RT} \right) \]  \hspace{1cm} (C.4)

\[ I_{2-} = N_0 K \exp \left( \frac{-E_a}{RT} \right) \exp \left( \frac{(1 - \alpha) \Delta UF}{RT} \right) \]  \hspace{1cm} (C.5)

\[ I_2 = N_0 K \exp \left( \frac{-E_a}{RT} \right) \left( 1 - \exp \left( \frac{(1 - \alpha) \Delta UF}{RT} \right) \right) \]  \hspace{1cm} (C.6)

Steady state is assumed and using \( X = \frac{\Delta UF}{RT} \) results in:

\[ I_1 = I_2 \]  \hspace{1cm} (C.7)

\[ \exp \frac{\alpha \Delta UF}{RT} - 1 = 1 - \exp \left( \frac{(1 - \alpha) \Delta UF}{RT} \right) \]  \hspace{1cm} (C.8)

\[ \exp \frac{\alpha \Delta UF}{RT} + \exp \left( \frac{(1 - \alpha) \Delta UF}{RT} \right) = 2 \]  \hspace{1cm} (C.9)

\[ \exp \alpha X + \exp -X \exp -\alpha X = 2 \]  \hspace{1cm} (C.10)

\[ \exp \alpha X (1 + \exp -X) = 2 \]  \hspace{1cm} (C.11)

\[ \exp \alpha X = \frac{2}{1 + \exp -X} \]  \hspace{1cm} (C.12)

\[ \alpha X = \ln \frac{2}{1 + \exp -X} \]  \hspace{1cm} (C.13)

\[ \alpha = \frac{RT}{\Delta UF} \ln \frac{2}{1 + \exp \frac{\Delta UF}{RT}} \]  \hspace{1cm} (C.14)

Substituting this into equation C.3 and substituting: \( X = N_0 K \exp \left( \frac{E_a}{RT} \right) \) results in:

\[ I_1 = N_0 K \exp \left( \frac{E_a}{RT} \right) \left( \exp \left( \frac{\alpha \Delta UF}{RT} \right) - 1 \right) \]  \hspace{1cm} (C.15)

\[ I_1 = X \left( \exp \left( \frac{\alpha \Delta UF}{RT} \right) - 1 \right) \]  \hspace{1cm} (C.16)

\[ I_1 = X \left( \exp \left( \frac{\frac{RT}{\Delta UF} \ln \frac{2}{1 + \exp \frac{\Delta UF}{RT}}}{RT} \right) - 1 \right) \]  \hspace{1cm} (C.17)

\[ I_1 = X \left( \exp \ln \frac{2}{1 + \exp \frac{\Delta UF}{RT}} - 1 \right) \]  \hspace{1cm} (C.18)

\[ I_1 = X \left( \frac{2}{1 + \exp \frac{\Delta UF}{RT}} - 1 \right) \]  \hspace{1cm} (C.19)

\[ I_1 = X \frac{2 - (1 + \exp \frac{\Delta UF}{RT})}{1 + \exp \frac{\Delta UF}{RT}} \]  \hspace{1cm} (C.20)
\[ I_1 = X \frac{1 - \exp \left( \frac{-\Delta U_F}{RT} \right)}{1 + \exp \left( \frac{-\Delta U_F}{RT} \right)} \]  
(C.21)

\[ I_1 = N_0 K \exp \left( \frac{-E_a}{RT} \right) \cdot \frac{1 - \exp \left( \frac{-\Delta U_F}{RT} \right)}{1 + \exp \left( \frac{-\Delta U_F}{RT} \right)} \]  
(C.22)

which is equal to equation 4.37.
Derivation of equation 4.46

The exchange-currents through two barriers with activation energy $E_a$ and $E_b$, where $\alpha$ describes how the barriers share the external potential is:

$$I_a^+ = N_0 K \exp \left( -\frac{E_a}{RT} \exp \frac{\alpha \Delta UF}{2RT} \right)$$ (D.1)

$$I_a^- = -N_0 K \exp \left( -\frac{E_a}{RT} \exp -\frac{-\alpha \Delta UF}{2RT} \right)$$ (D.2)

$$I_b^+ = N_0 K \exp \left( -\frac{E_b}{RT} \exp \frac{(1-\alpha) \Delta UF}{2RT} \right)$$ (D.3)

$$I_b^- = -N_0 K \exp \left( -\frac{E_b}{RT} \exp -\frac{1-\alpha) \Delta UF}{2RT} \right)$$ (D.4)

The current across each barrier is:

$$I_a = N_0 K \exp \left( -\frac{E_a}{RT} \left( \exp \frac{\alpha \Delta UF}{2RT} - \exp -\frac{-\alpha \Delta UF}{2RT} \right) \right)$$ (D.5)

$$I_b = N_0 K \exp \left( -\frac{E_b}{RT} \left( \exp \frac{(1-\alpha) \Delta UF}{2RT} - \exp -\frac{(1-\alpha) \Delta UF}{2RT} \right) \right)$$ (D.6)

As steady state is assumed, the two current $I_a^+$ and $I_b^-$ must be equal:

$$\exp \left( -\frac{E_a}{RT} \left( \exp \frac{\alpha \Delta UF}{2RT} - \exp -\frac{-\alpha \Delta UF}{2RT} \right) \right) =$$

$$\exp \left( -\frac{E_b}{RT} \left( \exp \frac{(1-\alpha) \Delta UF}{2RT} - \exp -\frac{(1-\alpha) \Delta UF}{2RT} \right) \right)$$ (D.7)

Using the following substitutions make the reduction of the equation simpler:

$$A = \exp \left( -\frac{E_a}{RT} \right)$$ (D.8)

$$B = \exp \left( -\frac{E_b}{RT} \right)$$ (D.9)

$$X = \exp \left( \frac{\alpha \Delta UF}{2RT} \right)$$ (D.10)

$$Y = \exp \left( \frac{\Delta UF}{2RT} \right)$$ (D.11)

Equation D.7 becomes:

$$AX \frac{X - 1}{X} = BY \left( \frac{Y - X}{Y} \right)$$ (D.12)

$$AX - A = BY \frac{Y}{X} - BX \frac{X}{Y}$$ (D.13)

$$AX^2 - A = BY - BX^2 \frac{Y}{Y}$$ (D.14)

$$AX^2 + BX^2 \frac{X}{Y} = BY + A$$ (D.15)

$$X^2 \left( A + \frac{B}{Y} \right) = BY + A$$ (D.16)

$$X^2 = \frac{BY + A}{A + Y}$$ (D.17)

$$X^2 = Y^2 \frac{A + BY}{AY + B}$$ (D.18)
\[ X^2 = \frac{Y \frac{A}{Y} + Y}{\frac{A}{Y} + 1} \]  
(D.19)

\[ X^2 = \frac{Y \frac{1}{Y} + \frac{1}{h} Y}{\frac{1}{Y} + \frac{1}{h}} \]  
(D.20)

\[ X = \sqrt{\frac{Y \frac{1}{Y} + \frac{1}{h} Y}{\frac{1}{Y} + \frac{1}{h}}} \]  
(D.21)

The step from equation D.20 to equation D.21 can only be made if \( X^2 \) is positive. As all the variables are exponential functions, \( A, B \) and \( Y \) are positive, this results in \( X^2 \) being positive.

Reversing the substitutions yields:

\[
\exp \frac{\alpha \Delta U F}{2RT} = \sqrt[\frac{\exp \frac{E_b}{RT} + \exp \frac{E_a}{RT} \exp \frac{\Delta U F}{2RT}}{\exp \frac{E_b}{RT} \exp \frac{\Delta U F}{2RT} + \exp \frac{E_a}{RT}}} 
\]  
(D.22)

Rearranging this results in:

\[
\frac{\alpha \Delta U F}{2RT} = \ln \sqrt[\frac{\exp \frac{E_b}{RT} + \exp \frac{E_a}{RT} \exp \frac{\Delta U F}{2RT}}{\exp \frac{E_b}{RT} \exp \frac{\Delta U F}{2RT} + \exp \frac{E_a}{RT}}} + \ln \frac{\frac{2RT}{\Delta U F} + \frac{2RT}{\Delta U F} \ln \frac{\exp \frac{E_b}{RT} + \exp \frac{E_a}{RT} \exp \frac{\Delta U F}{2RT}}{\exp \frac{E_b}{RT} \exp \frac{\Delta U F}{2RT} + \exp \frac{E_a}{RT}}}{\frac{2RT}{\Delta U F} + \frac{2RT}{\Delta U F} \ln \frac{\exp \frac{E_b}{RT} + \exp \frac{E_a}{RT} \exp \frac{\Delta U F}{2RT}}{\exp \frac{E_b}{RT} \exp \frac{\Delta U F}{2RT} + \exp \frac{E_a}{RT}}} 
\]  
(D.23)

\[
\alpha = \frac{2RT}{\Delta U F} \ln \frac{\exp \frac{E_b}{RT} + \exp \frac{E_a}{RT} \exp \frac{\Delta U F}{2RT}}{\exp \frac{E_b}{RT} \exp \frac{\Delta U F}{2RT} + \exp \frac{E_a}{RT}} 
\]  
(D.24)

or:

\[
\alpha = \frac{RT}{\Delta U F} \ln \frac{\exp \frac{E_b}{RT} \exp \frac{\Delta U F}{2RT} + \exp \frac{E_a}{RT} \exp \frac{\Delta U F}{2RT}}{\exp \frac{E_b}{RT} + \exp \frac{E_a}{RT} + \frac{1}{2}} 
\]  
(D.25)

or:

\[
\alpha = \frac{RT}{\Delta U F} \ln \frac{\exp \frac{E_b}{RT} \exp \frac{\Delta U F}{2RT} + \exp \frac{E_a}{RT} \exp \frac{\Delta U F}{2RT} + \frac{1}{2}}{\exp \frac{E_b}{RT} + \exp \frac{E_a}{RT} + \frac{1}{2}} 
\]  
(D.27)
E Derivation of equation 4.47

The exchange currents across a barrier with variable barrier height are:

\[ I_+ = N_0 K \exp \left( \frac{-E(U)}{RT} \exp \frac{\Delta U F}{2RT} \right) \]  \hspace{1cm} (E.1)

\[ I_- = -N_0 K \exp \left( \frac{-E(U)}{RT} \exp \frac{-\Delta U F}{2RT} \right) \]  \hspace{1cm} (E.2)

\[ I = N_0 K \exp \left( \frac{-E(U)}{RT} \left( \exp \frac{\Delta U F}{2RT} - \exp \frac{-\Delta U F}{2RT} \right) \right) \]  \hspace{1cm} (E.3)

\[ I = N_0 K \exp \left( \frac{-E(U)}{RT} \exp \frac{\Delta U F}{2RT} \right) \]  \hspace{1cm} (E.4)

Similarly, if the experimental data fits equation 4.48 and \( \alpha = \frac{1}{n} \), then the current-voltage dependence can be formulated as:

\[ I_{a+} = N_0 K \exp \left( \frac{-E_a}{RT} \exp \frac{\alpha \Delta U F}{2RT} \right) \]  \hspace{1cm} (E.5)

\[ I_{a-} = -N_0 K \exp \left( \frac{-E_a}{RT} \exp \frac{-\alpha \Delta U F}{2RT} \right) \]  \hspace{1cm} (E.6)

\[ I_a = N_0 K \exp \left( \frac{-E_a}{RT} \left( \exp \frac{\alpha \Delta U F}{2RT} - \exp \frac{-\alpha \Delta U F}{2RT} \right) \right) \]  \hspace{1cm} (E.7)

\[ I_a = N_0 K \exp \left( \frac{-E_a}{RT} \exp \frac{\alpha \Delta U F}{2RT} \right) \]  \hspace{1cm} (E.8)

The current from equation E.4 have to fit the observed data:

\[ I = I_a \]  \hspace{1cm} (E.9)

\[ \exp \left( \frac{-E(U)}{RT} \exp \frac{\Delta U F}{2RT} \right) = \exp \left( \frac{-E_a}{RT} \exp \frac{\alpha \Delta U F}{2RT} \right) \]  \hspace{1cm} (E.10)

\[ \exp \left( \frac{-E(U)}{RT} \right) = \exp \left( \frac{-E_a}{RT} \exp \frac{\alpha \Delta U F}{2RT} \right) \]  \hspace{1cm} (E.11)

\[ \frac{-E(U)}{RT} = \frac{-E_a}{RT} + \ln \left( \frac{\sinh \frac{\alpha \Delta U F}{2RT}}{\sinh \frac{\Delta U F}{2RT}} \right) \]  \hspace{1cm} (E.12)

\[ E(U) = E_a - RT \ln \left( \frac{\sinh \frac{\alpha \Delta U F}{2RT}}{\sinh \frac{\Delta U F}{2RT}} \right) \]  \hspace{1cm} (E.13)

Equation E.13 is the same as equation 4.47.
F List of publications by the author


In preparation: Søren Koch and Peter Vang Hendriksen: *Contact resistance at ceramic interfaces and its dependence on mechanical load*, Solid State Ionics

References


[22] Y. Larring and T. Norby, Spinel and perovskite functional layers between Plansee metallic interconnect (Cr-5 wt % Fe-1 wt % Y$_2$O$_3$) and ceramic (La$_{0.85}$Sr$_{0.15}$)$_{0.91}$MnO$_3$ cathode materials for solid oxide fuel cells, Journal of the Electrochemical Society, 147, 3251–3256 (2000).


The contact resistance can be divided into two main contributions. The small area of contact between ceramic components results in resistance due to current constriction. Resistive phases or potential barriers at the interface result in an interface contribution to the contact resistance, which may be smaller or larger than the constriction resistance. The contact resistance between pairs of three different materials were analysed (strontium doped lanthanum manganite, yttria stabilised zirconia and strontium and nickel doped lanthanum cobaltite), and the effects of temperature, atmosphere, polarisation and mechanical load on the contact resistance were investigated. The investigations revealed that the mechanical load of a ceramic contact has a high influence on the contact resistance, and generally power law dependence between the contact resistance and the mechanical load was found. The influence of the mechanical load on the contact resistance was ascribed to an area effect. The contact resistance of the investigated materials was dominated by current constriction at high temperatures. The measured contact resistance was comparable to the resistance calculated on basis of the contact areas found by optical and electron microscopy. At low temperatures, the interface contribution to the contact resistance was dominating. The cobaltite interface could be described by one potential barrier at the contact interface, whereas the manganite interfaces required several consecutive potential barriers to model the observed behaviour. The current-voltage behaviour of the YSZ contact interfaces was only weakly non-linear, and could be described by $22 \pm 1$ barriers in series. Contact interfaces with sinterable contact layers were also investigated, and the measured contact resistance for these interfaces were more than 10 times less than for the other interfaces.

Descriptors INIS/EDB
AGING; CERAMICS; COBALT COMPOUNDS; DOPED MATERIALS; ELECTRIC CONDUCTIVITY; INTERFACES; LANTHANUM COMPOUNDS; MANGANESE COMPOUNDS; MECHANICAL PROPERTIES; POLARIZATION; SOLID OXIDE FUEL CELLS; STRESSES; STRONTIUM COMPOUNDS; TEMPERATURE DEPENDENCE; YTTRIUM OXIDES; ZIRCONIUM OXIDES