Thermal Expansion of SOFC Materials

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Abstract. A short overview is given for the thermal expansion of solid oxide fuel cell materials. The thermomechanical compatibility of state-of-the-art materials is compared with alternative, new materials. With these alternatives a better adjustment of the thermal expansion coefficients of the various fuel cell components is possible and fuel cells based on the newly developed materials are proposed.

1. Introduction

Besides the electrical and electrocatalytic properties of electrochemical converters, thermomechanical properties i.e. thermal expansion coefficient (TEC), morphological and geometrical stability in different atmospheres, mechanical toughness etc. $-$ are important criteria for material selection and application at high temperatures. In the solid oxide fuel cell (SOFC) several functional materials (anode, electrolyte membrane, cathode, interconnect, contact layers, sealing) have to be joined. Therefore, a major challenge in SOFC research is to find materials with similar thermal expansions to avoid mechanical stresses, especially during thermal cycling.

The materials combination used for Jülich's planar anode-supported SOFC design [1] fulfils this requirement quite well. Only the electrolyte has 20 % lower thermal expansion compared to the other cell components. New composites for anode substrates, based on $Ni/Al₂O₃$ or $Ni/TiO₂$ cermets [2], and the use of advanced perovskite materials for cathodes with lower TEC led to improved membrane-electrodes assemblies (MEA). The interconnect, however, is now a matter of concern and its thermal expansion should be adjusted to the ceramic components. New interconnect developments based on titanates [3] may give a reasonable solution for a future SOFC design.

2. Experimental

The thermal expansion measurements were carried out with Netzsch push-rod dilatometers 402E or 402C. If

gases other than air were applied, the measurements were performed under flowing gas. Both dilatometers were calibrated with a sapphire single crystal and a rod of NiCr20 alloy. Corrections of the expansion data were made using an interpolation routine with the two sets of calibration measurements.

All specimens were either prepared from powder precursors by uniaxial or isostatic pressing into a rectangular shape (40 \times 5 \times 3-5 mm) and subsequent sintering or by cutting from larger components, as in the case of substrate or interconnect specimens. The terminal faces were cut and polished to give samples 25 mm in length.

3. Currently Used Materials for Anode-Supported Planar SOFC at Research Centre Jiilich

Since the early 90s Research Centre Jülich has made tremendous progress in the development of anode-supported planar SOFCs as is documented in several status reports [1,4-7]. The main improvements in materials and components development during the past five years have been the introduction of composite electrodes resulting in better cell performance, the application of ferritic steel as the interconnect and housing material, and an optimised sealing glass with high thermal expansion coefficient and high glass transition temperature. In Fig. 1 a schematic cross section through an SOFC stacking unit including interconnect plates is shown and gives an impression of how many different components have to be joined before cell operation. The thermal expansion of the ceramic materials of the MEA is given in Fig. 2 together with the

Fig. 1. Schematic cross section of a repeating unit of an SOFC stack (FZJ design); the dimensions of the layers are not true to scale,

TEC of interconnect and sealant materials. In Table 1 the linear TECs between room temperature and 800 $^{\circ}$ C as well as between room temperature and $1000 °C$ are listed for the various materials shown in Fig. 2.

4. Alternative Component Materials for SOFC with Improved Thermomechanical Properties

Numerous developments have been undertaken world-wide to improve the electrical and electrochemical properties of the MEA components by means of compositional or microstructural optimisations. In most cases where new materials have been proposed, only minor attention was paid to the thermomechanical behaviour of single or joined components. However, the deflection of SOFC components during sintering [12,13] due to different sintering activities or during thermal cycling due to thermal expansion mismatches [8,14] is of great technological importance and has to be minimised. Therefore a common

Fig. 2. Thermal expansion curves of the materials currently used for SOFC components in Jülich: cathode and cathodic contact layer $(La_{0.65}Sr_{0.3}MnO₃, \bullet)$, membrane (8YSZ, \Box), anode and anode substrate (Ni/8YSZ, O), interconnect (steel 1.4742, X10CrAl 18, \blacksquare), glass sealing (BaO-Al₂O₃-Nd₂O₃- $SiO₂, *).$

thermal expansion behaviour of all SOFC components is desired and in the following attempts at modelling an SOFC with optimised TECs are described comparing various materials for each SOFC component.

4.1. Electrolyte Materials. Although the anode substrate and interconnect plates are the biggest parts in a planar anode-supported SOFC (see Fig. 1), the solid electrolyte is still a key component due to co-firing with the substrate [12]. Up to now it is still not conclusively known whether the optimisation of TECs should follow the TEC of the electrolyte membrane, because it significantly influences the bending of the MEA, or the TEC of the

Table 1. Linear thermal expansion coefficients for currently used SOFC materials.

Component	Material	$\alpha_{30-800\degree C}$ $/10^{-6}$ K ⁻¹	$\alpha_{30-1000\degree C}$ $/10^{-6}$ K ⁻¹	Ref.
inter-connect	ferritic steel, X10CrAl 18	12.9	13.9	[8]
cathode	perovskite, La _{0.65} Sr _{0.3} MnO ₃	12.0	12.3	this work
electrolyte	fluorite, $8YSZ \equiv Zr_{0.85}Y_{0.15}O_{2-x}$	10.5	10.9	[9,10]
anode / substrate	cermet, 40 v/o Ni + 60 v/o $8YSZ$	12.5	12.6	[8, 11]
glass sealing	glass-ceramic, BaO-Al ₂ O ₃ -Nd ₂ O ₃ -SiO ₂	13.3	13.6	[6]

Material	Abbreviation	$a30-800^{\circ}$ C $/10^{-6}$ K ⁻¹	$a30-1000$ °C $/10^{-6}$ K ⁻¹	Ref.
$Zr_{0.85}Y_{0.15}O_{1.93}$	8YSZ	10.5	10.9	[9, 10]
$Zr_{0.82}Y_{0.18}O_{1.91}$	10YSZ	10.6	11.0	[10]
$Zr_{0.85}Sc_{0.15}O_{1.93}$	8ScSZ	10.3	10.4	$[15]$
$Zr_{0.80}Sc_{0.19}Al_{0.02}O_{1.90}$	10 _{Sc} SZ	10.5	10.9	$[10]$
$Ce0.8Gd0.2O1.90$	CGO	12.5	12.7	[10]
$Ce0.9Sr0.1O1.90$	CSO	12.8	13.1	$[10]$
$La0.8Sr0.2Ga0.9Mg0.1O3-x$	LSGM-8291	10.4	10.8	[8]
$La0.8Sr0.2Ga0.8Mg0.2O3-x$	LSGM-8282	10.5	11.3	[16]
$La0.9Sr0.1Ga0.8Mg0.2O3-x$	LSGM-9182	10.9	11.4	[8]
La _{0.9} Sr _{0.1} Ga _{0.75} Mg _{0.2} Co _{0.05} O _{3-x}	LSGM-9182Co5	12.3	13.0	this work

Table 2. Linear thermal expansion coefficients between 30 $^{\circ}$ C and 800 $^{\circ}$ C as well as between 30 $^{\circ}$ C and 1000 $^{\circ}$ C for oxide ion conductors

interconnect due to the great thickness and rigidity of the metallic plate. In any case, the choice of materials for the electrolyte is very limited and is summarised in Table 2.

The only materials with $\alpha_{30-1000^{\circ}C} > 11 \times 10^{-6} \text{ K}^{-1}$ which would be suitable for an adjustment of TECs with those of metallic interconnects are the ceria-based electrolytes and cobalt-containing lanthanum gallates. However, both classes exhibit significant disadvantages. The ceria materials swell in reducing atmospheres due to the formation of Ce^{3+} and the release of oxygen from the crystalline lattice [8,17,18] and the lanthanum gallates show several chemical instabilities, e.g. Ga evaporation during sintering [19,20], interaction with NiO during sintering [21,22] or degradation during long-term exposure in reducing environments (gallium oxide depletion) [22-24], which make them dubious candidates for further application in SOFCs.

Therefore, the most useful electrolyte materials are the zirconia-based materials, of which the materials with 8-11 mol% scandia or 10 mol% yttria are the most reliable because they have high and not perturbated ionic conductivity even after long periods at high temperature [15, 25,26]. Hence, the thermal expansion of the other cell components should be oriented towards the TECs of the zirconia electrolytes.

4.2. Cathode Materials. During recent years a lot of perovskites $(ABO₃)$ with lanthanum and strontium cations on the A-site and combinations of Fe/Mn [27- 29], Fe/Co [30-34] or Mn/Co [35-37] on the B-site have

been investigated by many research groups. The outcome of these investigations is that the ionic and electronic transport properties are highest for compositions containing about 50% Sr on the A-site and 50-100% Co on the B-site [33-35]. These compositions are beneficial for electrochemical performance, but on the contrary disadvantageous with respect to the TECs of these materials [33-35] and to interactions with 8YSZ (formation of $SrZO₃$ or $La₂Zr₂O₇$). A solution for reducing the TEC and maintaining good conductivities is the substitution of

Fig. 3. Linear thermal expansion coefficients between room temperature and 800 $^{\circ}$ C for various perovskite compositions with the general formula $Ln_{1-x-y}Sr_{x}Mn_{1-z}Co_{z}O_{3}$. The symbols correspond to the series with $x = 0.3$, $y =$ 0.05, $z = 0.2$ (\blacksquare); $x = 0.3$, $y = 0.05$, $z = 0$ (\square); $x = 0.2$, $y =$ $0, z = 0.2$ (\bullet) [35,39,42]; $x = 0.2$, $y = 0$ or 0.01, $z = 0$ (\circ) [35,39,42,46]; $x = 0.3$, $y = 0$ or 0.01, $z = 0$ (ϵ) [40,41,46].

Table 3. Linear thermal expansion coefficients between 30° C and 800° C as well as between 30° C and 1000° C of perovskites for SOFC cathodes

*: value for 200-800°C; $\stackrel{\#}{\sim}$ value for 25-1100 °C

lanthanum by other rare earth ions, which has been reported in a series of articles [32,38-45]. The TECs of the perovskites decrease with decreasing ionic radius of the lanthanide ion, which is shown in Fig. 3 and Table 3. Slight variations of Sr or Co content can be compensated by introducing the proper lanthanide ion. However, large amounts of Sr and/or Co always lead to high TECs not applicable to SOFCs [8,34,44]. A decrease of TEC was only observed for substutions of La with Pr or Nd. Other lanthanides did not significantly change the TEC. The TECs of the series $Ln_{0.65}Sr_{0.3}MnO_{3-x}$ and $Ln_{0.65}Sr_{0.2}$ $Mn_{0.8}Co_{0.2}O_{3-x}$ coincide with the results obtained on $Ln_{0.7}Sr_{0.3}MnO_{3-x}$ [40,41,46] (Fig. 3) and demonstrate that the variation of Sr content is the dominating parameter for tuning the TEC of these perovskites. The measured TECs of the gadolinium compounds showed the largest deviations from literature data (Fig. 3) and it is assumed that the data in the previous report [42] were not properly corrected for sample holder material or instrumental peculiarities.

4.3. Anode and Substrate Materials. Usually an SOFC with a thin electrolyte is built up on one of the electrodes as the supporting unit. In the case of the cathode, the TEC can be adjusted much more easily to that of the solid electrolyte used in the system (cf. Tables 2 and 3). So far an anode substrate had the disadvantage that the Ni (or the

Material / Company	$\alpha_{30-800\degree C}$	$\alpha_{30-1000\degree C}$	Ref.
	$/10^{-6}$ K ⁻¹	$/10^{-6}$ K ⁻¹	
Macor®/ Corning Glass Work	12.5		[51]
Photoveel [®] / Sumitomo Photon Ceramics	10.5		[51]
Al ₂ O ₃ -MgO-SiO ₂ -B ₂ O ₃ / FZJ	11.4	12.0	[6]
Al ₂ O ₃ -MgO-CaO-BaO-SiO ₂ -B ₂ O ₃ / FZJ	12.3	13.3	[6]
Al ₂ O ₃ -Nd ₂ O ₃ -BaO-SiO ₂ / FZJ	13.2	13.5	[6]

Table 4. Linear thermal expansion coefficients between 30 \degree C and 800 \degree C as well as between 30 \degree C and 1000 \degree C of glasses for SOFC sealings

NiO in the oxidised state) has a higher TEC than 8YSZ and therefore also the widely used Ni/8YSZ cermet [48,49]. Alternative cermets can be used if the electrochemical and mechanical functions of the substrates are separated and if the substrate serves only as an electronically conductive support for the electrocatalytically active components. Cermets based on Ni and binary or ternary oxides, e.g. Ni/Cr₂O₃ [50], Ni/Al₂O₃ [2], Ni/TiO₂ [2], Ni/NiCr₂O₄ [50] or Ni/NiAl₂O₄ have been considered for such fuel cells. These cermets allow an exact adjustment of the TEC to that of 8YSZ because the mentioned oxides have a lower TEC than 8YSZ, which is increased by the addition of Ni (or NiO). Additional advantages of such systems have been described elsewhere in more detail [2,11].

For the anode functional layer, however, a new material with an appropriate TEC is not in sight today and the conventional Ni/8YSZ cermet remains a necessary material for the catalytic active layer. The possibility of substituting mixed-conducting ceramics instead of 8YSZ has to be explored in the future.

4.4. Glass Sealing Materials. During recent years continuous attempts have been undertaken to optimise the thermal properties of the sealing material. With regard to the TEC, progress has been achieved by increasing the thermal expansion but maintaining a high glass transition temperature and proper softening temperature. The TECs of sealing glasses with the most promising properties tested in various SOFC stack tests in Jiilich are listed in Table 4 together with some commercial examples given in the literature. Because sealants are a very sensitive issue in SOFC development, and in most cases proprietary, no detailed information is published [51,53]. A noteworthy investigation of complex glasses in the SrO- $La_2O_3-Al_2O_3-B_2O_3-SiO_2$ system was carried out by Krumpelt et al. [54]. The glasses or glass-ceramics have high TECs ranging from $8-13 \times 10^{-6}$ K⁻¹ and show softening temperatures between $600-800$ °C. Although the TECs are appropriate for SOFC application, the softening temperatures are too low for the actual SOFC systems under development and hence they are not listed in Table 4. However, if operation temperatures between 500-700 ^oC are envisaged and realised, such glasses could be attractive for assembling the SOFC stack.

4.5. Interconnect Materials. Since the SOFC development tends towards lower operating temperatures, the interconnect materials based on lanthanum chromite are substituted by metallic interconnects, either by chromium-based alloys [55] or by ferritic steels [1,5,6]. The Cr-based alloys can withstand temperatures of up to 1000 $\rm ^{\circ}C$, but they are rather expensive today and form Cr₂O₃ or spinel scales in contact with perovskite materials [56-58]. The release of Cr species into the cathode compartment [59] and scale formation lead to deterioration of the catalytic activity of the cathode [58]. Therefore protective layers are needed to minimise oxide scale growth and the degradation of the cathode [60]. Instead, ferritic steels have a limiting operation temperature of about 800 $^{\circ}C$, but they are commercially available at a low price level. They also differ significantly in their thermal expansion behaviour as shown in Table 5. The Cr-based alloy has a TEC closer to 8YSZ, whereas the ferritic steel has TECs comparable with those of the anode substrate. Apart from ferritic steels also Ni-based alloys were considered [35], but showed too large thermal expansions. Regarding a TEC adjusted to 8YSZ, it will be a difficult task to find

Material	$\alpha_{30-800\degree C}$ $/10^{-6}$ K ⁻¹	$\alpha_{30-1000^{\circ}C}$ $/10^{-6}$ K ⁻¹	Ref.
Cr Fe5 Y_2O_31		11.3	[55]
Cr Fe5 Y_2O_31	11.3	12.0	[8]
X 10 CrAl 18 (1.4742)	12.9	13.9	[8]
$La0.9Sr0.1CrO3$		10.7	[48]
$La0.79Sr0.2CrO3$		$11.1*$	[47]
$La0.7Ca0.3Cr0.5Ti0.5O3$	9.6	10.1	this work
La_{0} 7Sr ₀ 3Cr ₀ 8Ti _{0.2} O ₃	10.4	10.7	this work

Table 5. Linear thermal expansion coefficients (measured in air) between 30° C and 800° C as well as between 30 $^{\circ}$ C and 1000 $^{\circ}$ C of interconnect materials for SOFC

*: value for 350-1000 ~

an optimised ferritic alloy, although first investigations in this direction showed some perspectives for future model alloys [61].

As in the case of the cathodes, the interconnect materials based on lanthanum chromite are still attractive due to the possibility of simultaneous substitutions on the A and B sites of the perovskite and thereby tuning the TEC and other materials properties. A lot of compositions have been investigated in the past and, as an example, one of the materials matching the TEC of 8YSZ is

Fig. 4. Isothermal length changes in oxidising and reducing atmospheres for $La_{0.7}Ca_{0.3}Cr_{0.5}Ti_{0.5}O_3$ (top) and $La_{0.7}Sr_{0.3}Cr_{0.8}Ti_{0.2}O₃$ (bottom). For the sake of comparison, the scaling of the length changes is the same in both graphs. The time scale was set to zero for the first change from air to Ar/4% $H₂$.

 La_0 $_9$ Sr₀ $_1$ CrO₃ [48]. However, the main problem associated with lanthanum chromites is the volume expansion in reducing atmosphere [62,63]. In the past only the multiple-doped interconnect from Dornier had sufficient shape stability for advanced SOFC development [51]. Recently Mitsubishi staff have presented an interesting alternative based on $La_{1-x}EA_xCr_{1-y}Ti_vO_3$ (EA = Mg, Ca, Sr, Ba) [3]. Here the Ti substitution suppresses the swelling in reducing atmosphere, as can also be seen in Fig. 4 in the case of $La_{0.7}Ca_{0.3}Cr_{0.5}Ti_{0.5}O_3$ [64]. The length change between oxidising and reducing atmosphere is not only very small (0.005%), it is negative, too. This phenomenon has also been observed in titania-containing zirconates with fluorite structure [8] and seems to be typical of titanium-rich compounds. The TEC of this material is about 7 % smaller than that of 8YSZ and can be tuned by slightly varying the cation ratios. On the contrary, $La_{0.7}Sr_{0.3}Cr_{0.8}Ti_{0.2}O_3$ exactly fits the TEC of 8YSZ (Table 5) but shows the typical expansion in atmospheres with low $p(O_2)$ [62,63], which prevents the application of such compounds as interconnecting materials.

A general difference in both materials is observed during atmospheric cycling: the Ti-rich perovskite (and also the fluorite [8]) reaches the equilibrium length within 3-30 minutes, whereas the length change of the Cr-rich material is composed of a fast increase at the beginning and a subsequent slow increase over several hours to reach equilibrium. The reasons for the two contributions are explained here by a (fast) electronic reduction of the cations (the reduction of $(Cr, Ti)^{4+}$ to $(Cr, Ti)^{3+}$) and a (slow)

Table 6. Materials and linear thermal expansion coefficients for a high-temperature planar anode-supported SOFC operating at 1000°C selected from Tables 2-5.

diffusion-controlled release of oxygen from the lattice [63]. The whole reaction can be written in the Kröger-Vink notation for the chromite as

$$
O_0^{\ x} + 2 Cr_{Cr}^{\ x} = V_0^{\ x} + 1/2 O_2 \ (gas) + 2 Cr_{Cr}^{\prime} \tag{1}
$$

as the sum of the individual reactions of the ions in the crystalline lattice

$$
O_0^{\ x} = V_0^{\ \ \cdot \ \ \cdot} + 1/2 \ O_2 \ (gas) + 2e^t \tag{2}
$$

and

$$
2 C_{r}^{x} + 2e^{2} = 2 C_{r}^{2}
$$
 (3)

For the Ti-rich materials it is surprising that no volume increase occurs as for the chromites, since the trivalent cations have a larger ionic radius than the tetravalent cations. This means that the titanium ions remain in their original valence state, which is in agreement with the low amount of oxygen released from the lattice [8], but it is surprising that the chromium ions are not reduced as in the case of $La_{0.7}Sr_{0.3}Cr_{0.8}Ti_{0.2}O_3$.

To understand this phenomenon, it is necessary to investigate the electronic states and binding energies of both Ti and Cr by photoelectron spectroscopy. Also the epansion behaviour in dependence of oxygen partial pressure

has to be investigated in more detail by dilatometry and X-ray diffraction.

5. Planar Anode-Supported SOFCs with Improved Thermomechanical Properties and Materials Research for Their Realisation

Based on the materials data listed in Tables 2-5, a model SOFC for high and low operating temperatures is proposed in Table 6 and 7. In both cases the TECs of the chosen materials should be close to the TEC of the solid electrolyte. Apart from the adjusted TECs, the components of the high-temperature SOFC (HT-SOFC) have to have better chemical stability rather than maximised electrochemical performance, because the electrochemical reactions are much more accelerated at 1000 °C than at 750°C. For the low-temperature SOFC (LT-SOFC), highly catalytically reactive electrodes are needed to maintain sufficient power output, whereas diffusive interactions at the interfaces are suppressed due to the low operating temperature.

With these general guidelines in mind, the proposed HT-SOFC contains a lanthanum chromite interconnect (advantages: best chemical stability, lowest rate of chromium evaporation, sufficient electrical conductivity), a praseodymium manganite cathode (advantages: lower cathodic overpotential than lanthanum manganites [7,39, 65,66], low amount of Sr minimises reactions with the electrolyte), a 10YSZ membrane (advantages: good long-

Table 7. Materials and linear thermal expansion coefficients for a low-temperature planar anodesupported SOFC operating at 750°C selected from Tables 2-5.

term stability of ionic conductivity, commercially available, more readily available than ScSZ), a Ni/8YSZ cermet as the anode functional layer on a $Ni/Al₂O₃$ (50:50) v/o) substrate (advantages: good high-temperature stability, adjusted TEC [2], low-cost raw materials) and finally a glass-ceramic sealing, preferably based on the Dornier composition [51] due to good experience in SOFC assemblies in the past [51, 67]. The most critical point in this materials selection is the anode with a 15% higher TEC compared to the other cell components. Here a substitution of the YSZ by a different mixed conducting material should be considered.

For the LT-SOFC the materials are easily selected for the MEA, i.e. a sub-stoichiometric praseodymium manganite with higher Sr content for improved electrochemical performance, a 10YSZ electrolyte and a Ni/8YSZ anode as mentioned above and a $Ni/TiO₂$ substrate with high electrical conductivity and gas permeability as well as low sintering temperature [2,11]. Whereas the reduced TEC gives more degrees of freedom in the case of sealant development for assembling temperatures in the range of 800-900 \degree C, the interconnect material is the most critical point of concern. In principle both a ceramic or a metallic bipolar plate can be considered, but both materials have to be optimised. On the one hand, the lanthanum chromite has low electrical conductivity at low temperatures, especially in atmospheres with low oxygen partial pressures. This has to be improved significantly besides the challenging thermomechanical properties. On the other hand,

there is no ferritic steel available with TEC \approx 10-12 \times 10^{-6} K⁻¹ and much effort is needed to achieve such low thermal expansions by multi-element alloying. A rather expensive and intermediate solution to this material problem is the Cr-based alloy. Here the Cr evaporation and protection layers have to be re-evaluated with respect to the significantly lowered operating temperatures in comparison with the temperatures applied in the past.

6. Conclusions

Due to the restricted choice of electrolyte materials the other SOFC components should follow the TEC of the membrane material (YSZ or ScSZ). Based on the thermal expansion data available, two sets of materials were selected to design a high- and low-temperature SOFC. Whereas materials for the MEAs can be clearly identified, the interconnect and sealant materials are still a matter of development and optimisation. Also new anode materials based on cermets containing Ni and mixed-conducting ceramics are needed for TEC adjustment.

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