ELSEVIER

Ceramics International 30 (2004) 1107–1113

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Processing and properties of the ceramic conductive multilayer device solid oxide fuel cell (SOFC)

D. Stöver*, H.P. Buchkremer, S. Uhlenbruck

Institute for Materials and Processes in Energy Systems (IWV-1), Forschungszentrum Juelich GmbH, Juelich, Germany

Received 6 December 2003; accepted 18 December 2003

Abstract

Solid oxide fuel cell (SOFC) systems are worldwide under development in the 1–1000 kW range where shifts from laboratory testing to trials for market penetration become visible. Materials systems are available allowing the processing of multilayer devices mainly out of conductive ceramic materials to fulfill the demands of a fuel cell system with sufficient power density.

A main drawback for real market introduction and maturity still is high cost, related to materials as well as processing. Alternative cheaper raw materials, as well as the replacement of expensive and complicated processing steps by cheaper and simpler techniques are being considered. In addition to that the use of new materials with enhanced electronic, ionic and catalytic activities are looked for to show the way to increased power densities, as enlarging power densities means material saving and cost reduction too.

The multilayer SOFC device consists of:

- a porous, gas permeable, electronic conductive substrate carrier (either acting as anode or cathode);
- an anode or cathode functional layer being porous with high specific surface area (three phase boundary contact);
- a gas tight ion conducting (negligible electronic conduction) electrolyte;
- a cathode or anode functional layer with a porous high specific surface area (three phase boundary contact);
- a porous cathode or anode for gas penetration;
- contact layers making the electronic joints between cells.

The overall processing of this system has to be made as simple as possible (cost effective), i.e. using as few and as cheap as possible processing methods to fulfill the property demands of the single layers and the multilayer device.

The set of multilayers used today has to be reconsidered looking for superior properties like higher ionic conductivity (electrolytes other than YSZ), increased oxygen exchange activity (other perovskites than LSM ($La_{0.65}Sr_{0.3}MnO_3$)), new redox stable and catalytic active anode materials (oxides instead of Ni in Ni/YSZ cermet) as well as new contact layers with improved long-term resistance stability. The state-of-the-art fuel cell is described, processing and properties are given and alternatives for materials and processes will be discussed.

Keywords: Solid oxide fuel cell; Oxides; Solid–solid interfaces; Fast ion conductors; Electron conductors

1. Introduction

Today electrical energy is generated via a thermal engine process, i.e. lignite, hard coal, natural gas or mineral oil fired, and a turbine is powered by the produced hot gas. The mechanical energy is then converted into electrical energy by means of an electric generator.

So the whole chain of energy conversion comprises a primary energy carrier which is mainly fossil, a combustion process to convert the chemical energy into heat (in a nuclear power plant the heat is generated by a nuclear reaction), then into mechanical and finally into electrical energy. The intermediate steps of heat production and mechanical energy are connected with losses of efficiency. Moreover, the maximum efficiency of such a heat engine is limited by the Carnot efficiency.

Therefore, the objective is to optimize the efficiency of power generation to save primary energy carriers and reduce

---

* Corresponding author. Tel.: +49-2461614010; fax: +49-2461618210.
E-mail address: d.stoever@fz-juelich.de (D. Stöver).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.12.018

the emissions of power plants. With regard to the preceding section it would be advantageous to directly convert primary energy carriers into electrical energy. This can be done by fuel cells. Solid oxide fuel cells (SOFCs) in addition offer the advantage to be powered by hydrogen as well as by hydrocarbons like methane.

The fundamental reaction in a fuel cell is: $2H_2 + O_2 \rightarrow 2H_2O$. In order to prevent a direct reaction between oxygen and hydrogen these two gases and the corresponding partial reactions, the oxidation of the hydrogen: $H_2 \rightarrow 2H^+ + 2e^-$, and the reduction of oxygen: $O_2 + 4e^- \rightarrow 2O^{2-}$, have to be separated. This is the task of the fuel cell membrane.

A fuel cell membrane consists of a gas tight electrolyte that is capable of conducting oxygen ions. In one gas chamber the oxidant (air) is supplied. The oxygen gas diffuses through the air electrode (cathode) to the electrolyte and takes up two electrons per oxygen atom and then migrates as an oxygen ion through the electrolyte. In the fuel gas chamber the hydrogen gas is oxidised at the fuel gas electrode (anode)–electrolyte interface. The electrons then move along an outer circuit to the cathode. In the case of hydrocarbons the fuel gas is first reformed to hydrogen by either direct reformation (directly into hydrogen and carbon dioxide) or by a shift reaction (intermediate generation of carbon monoxide).

The efficiency of a fuel cell is not limited by the Carnot efficiency.

From the Nernst equation one can calculate the open cell voltage or “electromotoric force” E_0 as:

$$E_0 = \frac{RT}{zF} \ln \frac{p(O_{2,K})}{p(O_{2,A})}$$

where R is the ideal gas constant, T is the (absolute) temperature, z the number of moving electrons, F is the Faraday constant, and $p(O_{2,K/A})$ are the oxygen partial pressure on the cathode and anode side, respectively.

For the reduction of an oxygen molecule $z = 4$ electrons are necessary. The oxygen partial pressure on the air side is 0.2 bar, while it is roughly 10^{-20} bar on the hydrogen gas side. From this an electromotoric force of $E_0 = 1.2\,\text{V}$ can be deducted. The efficiency η of a fuel cell is defined as the ratio of the change of the Gibbs' free enthalpy ΔG and enthalpy ΔH

$$\eta_{\text{BZ max}} = \frac{\Delta G}{\Delta H}$$

ΔG can be calculated from the open cell voltage E_0 as $\Delta G = nFE_0$, with n the number of moving electrons for the generation of one molecule of H_2O ($n = 2$). With $E_0 = 1.2$ V, $n = 2$, and $\Delta H = 249.5$ kJ/mole (experiment) this implies: $\eta_{\text{BZmax}} = 92\%$.

Besides the high efficiency, even under partial load conditions, the further advantages of fuel cells are (i) no moving parts having thus no wear issues, no mechanical stress and no noise, (ii) easy adaptation of the power to the demand (watt to megawatt region), (iii) the waste heat can be used to further increase the over-all efficiency (e.g. by turbines in the case of SOFCs), good specific weight (power/kg) compared to batteries and (iv) environment-friendliness (in the case of H_2 no emission, low emission when using hydrocarbons).

The requirements for an electrolyte can be summarised as follows:

- high ionic conductivity;
- no electronic conductivity;
- gas tightness;
- thermal expansion coefficient adjusted to anode and cathode (becomes important with increasing operating temperature of the fuel cell);
- no chemical reactions with the anode and the cathode;
- stable against oxidising and reducing atmospheres (air/fuel gas).

The electrodes have to fulfill the following demands:

- high electronic conductivity;
- air and fuel gas must be transported from the gas chambers to the electrolyte;
- catalytic activity (adsorption, dissociation and electrochemical reaction);
- no chemical reaction with the electrolyte or interconnect material;
- stable against air and fuel gas atmospheres, respectively;
- thermal expansion coefficient has to match to the adjacent components.

Fig. 1 shows the setup of a planar fuel cell in a metallic housing (“stack”) in a more realistic way. Here, the fuel cell consists of a porous anode substrate, a so-called anode functional layer where the electrochemical reaction takes place(which will be described in detail later), an electrolyte, a cathode functional layer where the oxygen gas is reduced in the main and a cathode that acts as a current collector. The metallic parts enable the gas supply and electrically interconnect adjacent fuel cell membranes. Contact layers are necessary in order to optimize the electrical contact between fuel cell and interconnect. For insulation and sealing of the several gas chambers a glass solder is used.

2. Processing of the multilayer device SOFC

Firstly, the processing of anode-supported SOFCs is shown and later on generalised to other concepts (see also [1–3]).

To secure a sufficient mechanical stability of this fuel cell, with layer thickness of only few microns, a substrate is installed. This can in principle be of the same material as the anode (“anode substrate”) or any other ceramic or metallic material as far as it fulfils the requirements of chemical stability, high conductivity and open porosity.

The first method that should be described here to produce substrates is *warm-pressing*. Here, the powders are coated

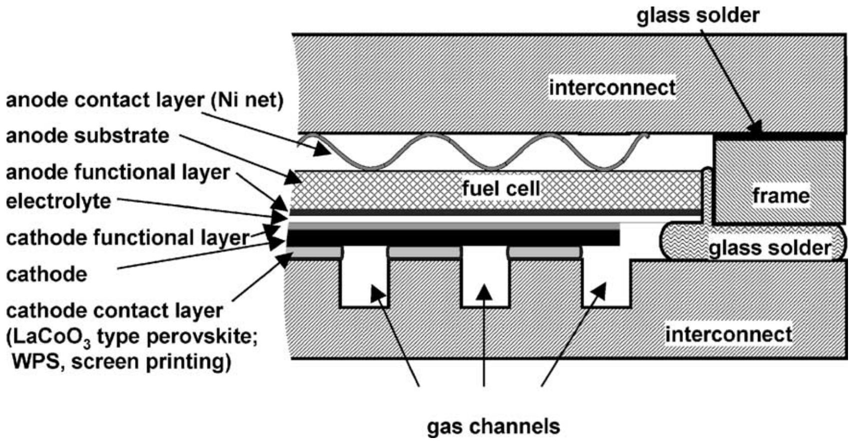

Fig. 1. Drawing of a fuel cell membrane in a metallic housing.

with a binder and then pressed. In a heating step to about 100 °C the binder becomes soft and the material can be further compacted. During the cooling phase the binder hardens again. The result is a green body of the substrate which can be easily handled and subsequently fired to burn the organic out and to sinter the powder to get a solid porous substrate.

An industrially established and cost effective alternative to produce ceramic plates is tape casting. Powders are dispersed in a solvent (e.g. ethanol), and plasticizers and binders are added. After removal of the air the slurry is cast on top of a supporting tape and controlled in height by a Doctor Blade. In sophisticated drying steps a green tape of the starting powders is formed which can then be sintered to a porous ceramic.

On top of the substrate the anode functional layer is cast. In the Vacuum-Slip-Casting® process the porous substrate is used as a filter where the solvent of a suspension of the functional layer material—nickel oxide (NiO) and yttria-stabilised zirconia (YSZ)—is sucked through while a “filter cake” of the material is remains on top of the substrate.

The features of a functional layer can be seen in Fig. 2.

To enable the anode partial reactions shown in Fig. 2 three phases have to be present: the hydrogen gas, an electron conducting phase and an ion conducting phase. In the sketch of the anode–electrolyte interface the points where theses phases meet are marked with small circles. Since these so-called three phase points mark the area where the oxidation of the hydrogen takes place and thus determines the reaction rate, the purpose of processing the functional layer is to increase the number of the electrochemical active sites. In contrast to the functional layer the substrate has only to secure a good gas transport and good conductivity.

For processing an electrolyte layer Vacuum-Slip-Casting can also be used.

A technically simple processing route of processing cathodes is “Wet Powder Spraying” (WPS). The cathode material is ground to the desired particle size and dispersed in a solvent. This suspension is subsequently sprayed on top of the electrolyte via an airbrush gun.

Problems of Wet Powder Spraying are the material losses due to “overspray” and its sensitivity to changes in

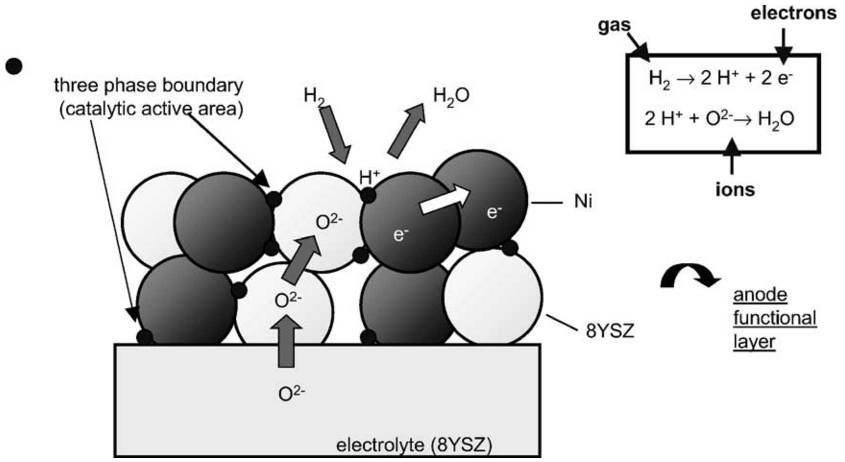

Fig. 2. Illustration of the tree phase boundary.

temperature and humidity. Both of these parameters influence the drying speed of the suspension in the spraying cone and thus the quality of the sprayed cathode layer.

An established technique which does not show the problems of Wet Powder Spraying is screen-printing. The powder is mixed with a binder, then homogenised to a paste and finally screen-printed. Nevertheless, this method is limited to planar geometries.

Besides the planar anode-supported concept other designs are also well established. Within the scope of planar SOFCs there are also electrolyte-supported designs. The latter has an electrolyte of about 250 μm in thickness. On the one hand, since the typical electrolyte material YSZ has a very high strength these cells exhibit good mechanical stability. On the other hand, the ionic conductivity of YSZ is low ($\sim 10^{-1}$ S/cm at 900 °C), and one either obtains low performance of the SOFC due to a large internal resistance, or the temperature has to be increased (thermally activated conductivity behaviour) which causes problems with regard to degradation.

A problem of all stack concepts with planar SOFC is the separation and sealing of the gas chamber to avoid the direct reaction of the fuel gas and the air. Today glass solders can be used. Nevertheless, the compound of metallic components, a ceramic fuel cell membrane and the glass suffers from a disastrous thermal cycling behaviour because of the different thermal expansion coefficients of these materials. Moreover, the interfacial reactions of these materials at high temperature leads to further stability problems [5,6].

A design that manages without sealing in the hot region is the tubular concept which has been established by Siemens–Westinghouse (Fig. 3).

The manufacturing of tubular SOFCs starts with the extrusion of the air–electrode-supported cathode tube made of lanthanum–calcium–manganite (tube dimensions: length 180 cm; active length 150 cm; diameter 22 mm; wall thickness 2 mm; power 140 W per single cell) [4]. For extrusion the starting powder is mixed with solvents and paraffins/waxes and then compacted, degassed, homogenised and subsequently moulded by means of a conveyor screw. After drying and sintering at temperatures larger than 1500 °C the ceramic interconnect (lanthanum chromite) is added via plasma spraying alongside the tube as a 10 mm broad strip. This interconnect is subsequently sintered to gas tightness. Thereafter the interconnect is masked and then the electrolyte, consisting of eight YSZs, is added via electrochemical vapor deposition (EVD) or atmospheric plasma spraying and sintering. Finally, the tube is coated with metallic nickel in a nickel bath. The nickel and the YSZ form a well-penetrated structure of numerous triple phase points.

Disadvantages of this design are the expensive processing techniques like EVD. Moreover, in the tubular concept the electrons have to pass from one tube to the next in a maximum of half the circumference of the tube (∼33 mm). This can be partially absorbed by the “high power density (HPD)” design: with the flattened HPD design this path is reduced to ∼10 mm.

A considerable portion of the over-all cost for ceramic high temperature fuel cells is the cost for sintering. Therefore, efforts are done to minimize the number of firing steps, i.e. a common sintering of several components (“cofiring”). One of the main problems is the different sintering rate of the components which lead to tensile stresses and

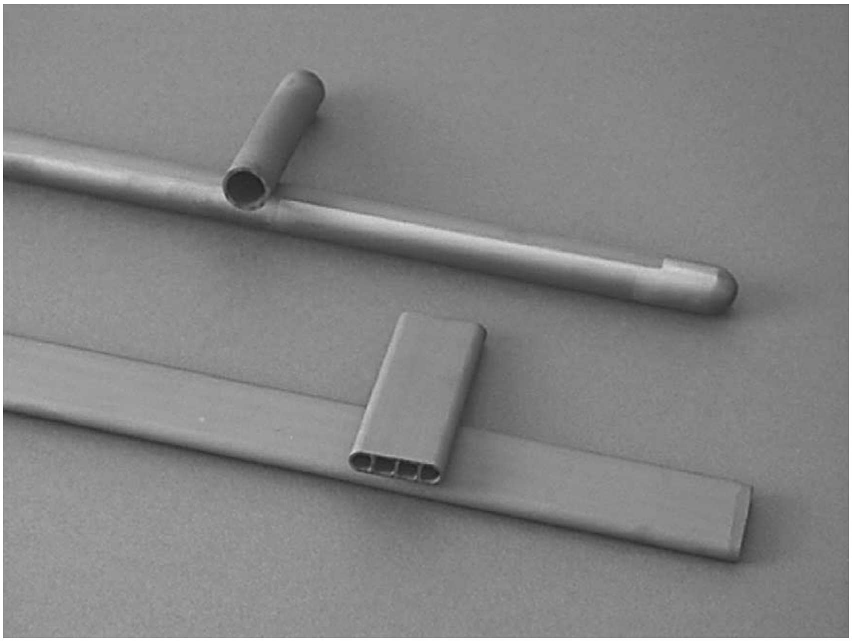

Fig. 3. Tubular (top) and novel HPD design (bottom; four channel design) (Siemens Westinghouse design).

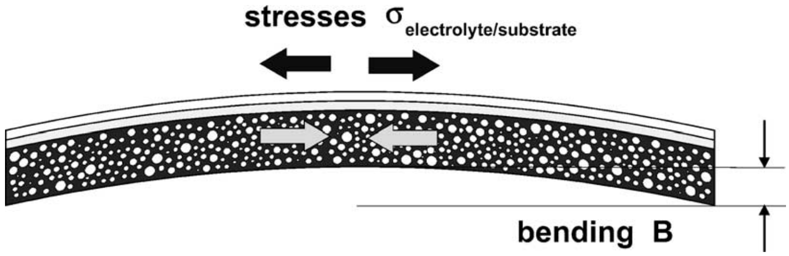

Fig. 4. Stresses and bending during sintering of components with different sintering rates.

compressive stresses, respectively, and bending. The bending B (as defined in Fig. 4) depends on the ("free") shrinkage rates $\dot{\varepsilon}^{\text{free}}_{\text{electrolyte}}$ and $\dot{\varepsilon}^{\text{free}}_{\text{electrolyte}}$, on the Poisson number $\nu_{\text{electrolyte}}$ and $\nu_{\text{substrate}}$, the thickness of the electrolyte layer (s) and the substrate (D), the width of the substrate (L) and the generalised viscosities $\eta_{\text{electrolyte}}$ and $\eta_{\text{substrate}}$.

$$B(t) \approx \frac{3sL^2}{4D^2}\int_0^t \frac{(1-\nu_{\text{substrate}}(t))\sigma_{\text{electrolyte}}(t)}{\eta_{\text{substrate}}(t)}\,\mathrm{d}t \quad \text{with}$$

$$\sigma_{\text{electrolyte}} = \frac{\dot{\varepsilon}^{\text{free}}_{\text{substrate}} - \dot{\varepsilon}^{\text{free}}_{\text{electrolyte}}}{1-\nu_{\text{substrate}}} \times \eta_{\text{electrolyte}}$$

One idea to minimize the bending is a "symmetric cell" design. While the electrolyte layer is printed on the top side, a honeycomb-like structure of the electrolyte material is screen-printed on the bottom side. Assuming a homogeneous stress distribution, a honeycomb structure covering half of the substrate area and with a thickness twice as thick as the electrolyte should lead to no bending of the whole ensemble any more.

3. Materials development

3.1. Electrolyte materials

As pointed out in the preceding paragraph the ionic conductivity of the electrolyte material YSZ proved to be a bottleneck. Therefore, a material screening to look for better ion conducting materials is necessary. In Fig. 5 the ion transport properties of some selected materials is shown. Doped ceria as well as scandium-substituted zirconia and $LaGaO_3$-based materials exhibit a higher ionic conductivity. Nevertheless, the ionic conductivity is only one criterion for a suitable electrolyte. Doped ceria for instance reacts with YSZ (e.g. in the substrate) and forms low ion conducting phases (worse than YSZ and ceria themselves).

Moreover, at low oxygen partial pressures doped ceria can change its valence ($Ce^{4+} \leftrightarrow Ce^{3+}$), which leads to enhanced electronic conductivity and lattice expansion [7,8]. $LaGaO_3$-based materials suffer from an evaporation of Gallium and from reactions with the adjacent electrodes. On the anode side lanthanum reacts with the zirconium in the

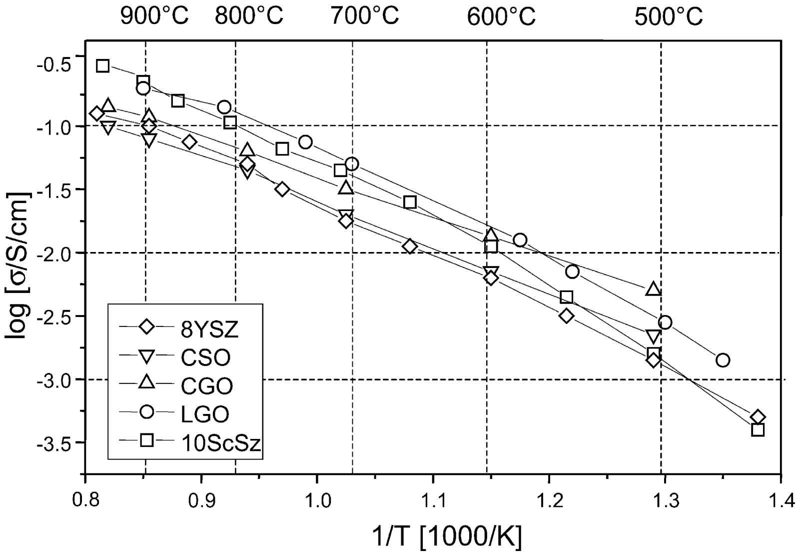

Fig. 5. Ionic conductivities of selected electrolyte materials: CSO, SrO-substituted CeO_2; CGO, Gd_2O_3-substituted CeO_2; LGO, (Sr^{2+}, Mg^{2+})-doped $LaGaO_3$; 10 ScSZ, 10 mol.% Sc_2O_3-stabilized ZrO_2 [10].

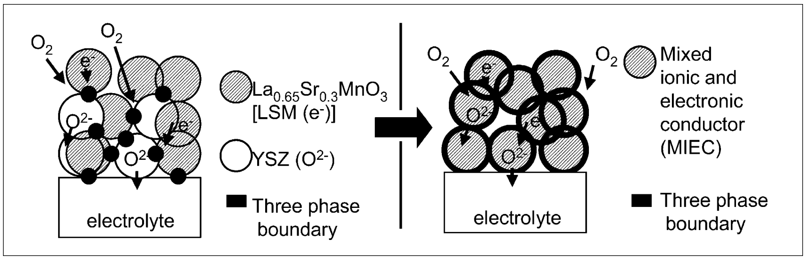

Fig. 6. Cathode functional layer made of LSM/YSZ (left) and with a mixed ion and electron conducting material (right).

anode forming insulating $LaZrO_x$ phases. Nickel and zirconium can also diffuse into the $LaGaO_3$ material. Moreover the $LaGaO_3$-based material itself tends to generate considerable amounts of impurity phase like $LaSrGaO_7$. Scandium on the other hand is a very rare and expensive element [9].

3.2. Cathode materials

To enable the partial reaction $O_2 + 4e^- \rightarrow 2O^{2-}$ oxygen gas, electrons and a medium to transport the oxygen ions are necessary (three phase boundary, similar to the anode functional layer). Since the ionic conductivity of the perovskite LSM is negligibly small, the functional layer is a mixture of LSM and the electrolyte material, YSZ. This is sketched on the left side in Fig. 6. The three phase area where oxygen gas, electrons and an ion conducting phase are present is marked with small grey circles. The number of three phase points determine the oxygen reduction rate and thus the performance of the cathode.

A different approach is shown on the right side of Fig. 6. The three phase area would be vastly increased (grey area on the surface of the balls in the sketch) when the cathode material has an intrinsic electronic *and* ionic conductivity. $(La,Sr)(Co,Fe)O_{3-\delta}$ materials (LSCF) exhibit these properties: for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ the electronic conductivity is about 280 S/cm at 800 °C while the ionic conductivity is around 2×10^{-3} S/cm. Moreover, the surface exchange kinetics are faster compared to LSM.

A disadvantage from the viewpoint of physics is the large thermal expansion coefficient α that is considerably larger than the expansion coefficient of YSZ ($\alpha = 15.1 \times 10^{-6}\,K^{-1}$ (20–800 °C) for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ versus $\alpha = 10.8 \times 10^{-6}\,K^{-1}$ for YSZ). It was pointed out by Ullmann et al. that there is a clear correlation between high ionic conductivity and high thermal expansion coefficient [11]. For that reason there always has to be a compromise between ion conductivity and unacceptable high thermal expansion.

A further disadvantage is the low chemical stability compared to LSM. On the one hand, LSCF allows the oxygen to move easily from lattice site to lattice site. On the other hand, Sr ions can diffuse too. Direct contact between LSCF and YSZ electrolyte leads to the formation of insulating SrZrO3 at the LSCF–YSZ interface when sintering the cathode at temperature above 1000 °C. An interlayer consisting of for example Gd-doped ceria (CGO) spatially separates LSCF and YSZ and thus can suppress the formation of SrZrO3.

In Fig. 7 the current–voltage curves of selected cathode materials are presented (details of the electrochemical cell tests see [12]).

A 2% A-site substoichiometry leads to significantly higher current densities which can be explained by a higher number of defects. The substoichiometric materials show a higher sintering activity, and therefore sintering temperature T_S of the cathode has been adapted to obtain similar microstructures for all cathodes. Moreover, a reduced sintering temperature implies a reduced tendency for $SrZrO_3$ formation. A 5% substoichiometry, however, seems to lead to lower performance than 2% substoichiometry.

The powder synthesis route of the cathode materials (spray-drying, Pechini) presumably has no influence on the performance (see $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$).

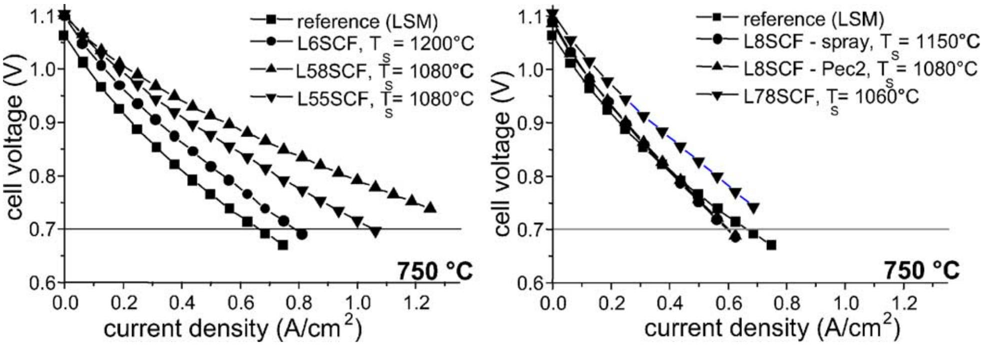

Fig. 7. Current–voltage curves of SOFCs with $(La,Sr)(Co,Fe)O_{3-\delta}$ cathodes.

Solid oxide fuel cells with $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ cathodes exhibited current densities of 1.43 A/cm^2 (i.e. 1.0 W/cm^2) at 750 °C and 0.7 V, which is more than twice high compared to LSM reference cells (0.67 A/cm^2).

4. Summary

Solid oxide fuel cells are highly efficient energy converters which can be directly powered with methane. One of the main drawbacks is the cost per kilowatt of power density. This cost can either be reduced by establishing cheaper and industry compatible manufacturing routes like tape casting or screen-printing, or to introduce novel materials that show better performance than the state-of-the-art materials. This last point is a tremendous task because the materials have to meet a whole set of requirements to be suitable for SOFCs. Many candidates have been identified in the past which surpass single properties of the current electrode and electrolyte materials, respectively (e.g. better ionic conductivity than YSZ), nevertheless, drawbacks in other necessary properties (e.g. chemical stability) vote against them.

References

[1] W.A. Meulenberg, N. H. Menzler, H.P. Buchkremer, D. Stöver, in: A. Manthiram, P.N. Kumta, S.K. Sundaram, G. Ceder (Eds.), Ceramics transaction: Materials for electrochemical energy conversion and storage, vol. 127, The American Ceramic Society, 2002, pp. 99–108.
[2] D. Simwonis, A. Naoumidis, F.J. Dias, J. Linke, A. Moropoulou, J. Mater. Res. 12 (1997) 1508–1518.
[3] A.A.E. Hassan, N.H. Menzler, G. Blass, M.E. Ali, H.P. Buchkremer, D. Stöver, Adv. Eng. Mater. 4 (2002) 125–129.
[4] K. Hassmann, SOFC power plants, the Siemens–Westinghouse approach, Fuel Cells 1 (2001) 78–84.
[5] N. Lah, K. Singh, L. Singheiser, K. Hilpert, D. Bahadur, J. Mater. Sci. 35 (2000) 3089–3096.
[6] T. Schwickert, P. Geasee, A. Janke, R. Conradt, U. Diekmann, in: Proceedings of IBSC 2000, Albuquerque, NM, USA, pp. 116–122.
[7] T. Hirota, N. Sakai, H. Yokokawa, M. Dokya, T. Kawada, J. van Herle, K. Sasaki, J. Electroceram. 1 (2) (1997) 155–164.
[8] H. Inaba, H. Tagawa, Solid State Ionics 83 (1996) 1–16.
[9] A. Ahmad-Khanlou, Ph.D. thesis, Forschungszentrum Juelich, Germany, 2000.
[10] F. Tietz, G. Stochniol, A. Naoumidis, in: EUROMAT-97 Proceedings, Maastricht, NL, April 1997, pp. 271–274.
[11] H. Ullmann, N. Trofimenko, F. Tietz, D. Stöver, A. Ahmad-Khanlou, Solid State Ionics 138 (2000) 79–90.
[12] L.G.J. de Haart, K. Mayer, U. Stimming, I.C. Vinke, J. Power Sources 71 (1998) 302–305.